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SOME NOVEL ORGANOSILANE REACTIONS CATALYZED BY TITANOCENES

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by

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Montreal

A thesis submitted to the

Faculty of Graduate Studies and Research

in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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SOME NOVEL ORGANOSILANE REACTIONS CATALYZED BY TITANOCENES

Ph.D.

Ronghua Shu

Chemistry

Abstract

This thesis presents some novel organosilane reactions catalyzed by titanocenes.

Heterodehydrocoupling between silanes and phosphines has been accomplished with titanocenes as catalysts. The reaction has the characteristics of high yield and high selectivity and can be carried out under mild conditions. Monophosphinosilanes and diphosphinosilanes can be selectively obtained from the reactions of secondary phosphines and silanes. Primary phosphines react with primary silanes to produce 1,3,5-triphospha-2,4,6-trisilacyclohexanes. A two-catalytic-cycled mechanism is proposed with titanocene hydride as the key catalytic species.

Hydrosilation/hydrogenation of some aromatic N-heterocycles (namely pyridine, 3picoline, 4-picoline, 3,5-lutidine, and quinoline) has been achieved with titanocene derivatives as catalysts. A variety of hydrosilated/hydrogenated products, either fully or partially saturated, may be produced depending on conditions. A reaction mechanism is proposed based on isolated and structurally characterized pyridine titanocene complexes, on the effects of substituent on the rates, and on H/D exchange studies. It is suggested that a key step in the hydrogenation/hydrosilation reaction is the formation of a mono- $\eta^1(N)$ complex between the pyridine ring and the titanocene silyl complex. It is proposed that the rate determining step is an intramolecular insertion of -N=C- into the Ti-Si bond. If the strong coordination or the intramolecular insertion is prohibited by either steric effects or electronic effects, or if the complex is of too high stability, no hydrogenation/hydrosilation product is obtained. Extensive H/D exchange at the 2- and 6- positions of the pyridine is attributed to a reversible ortho-metallation of pyridine in a Ti-H complex.

Cp₂TiMe₂ catalyzed hydrosilation/hydrogenation reactions of nicotinates, ethyl benzoate, and lactones have been studied. With ethyl nicotinate as the substrate, the hydrosilation occurs on the ring to give ethyl N-(methylphenylsilyl)-1,6-dihydronicotinate as the only product. No reaction at the ester group is observed. However, when the substrate is ethyl isonicotinate, ethyl 2-methylnicotinate or ethyl 6-methylnicotinate, the hydrosilation/hydrogenation only occurs at the ester groups and the carboalkoxy group is tranformed into either a silyl ether group or an alkyl group.

Copolymers can be produced from the titanocene catalyzed ring opening hydrosilation/hydrogenation reactions of lactones and PhMeSiH₂. A key intermediate in these reactions, $Cp[\mu-(\eta^1:\eta^5-C_5H_4)](THF)Ti(\mu-H)TiCp_2$, is isolated and well characterized by x-ray crystallography. The successful isolation and characterization of this product provides the first direct evidence to support the involvement of Cp_2Ti in numerous Cp_2TiMe_2 catalyzed reactions in addition to correcting an earlier incorrect assignment of the structure of this frequently cited compound.

DE NOUVELLES RÉACTIONS D'ORGANOSILANES CATALYSÉES PAR LE TITANOCÈNE.

Doctorat

Ronghua Shu

Chimie

Résumé

Dans cette thèse, nous présentons de nouvelles voies de synthèses d'organosilanes catalysés par des titanocènes.

L'hétérocouplage entre silanes et phosphines ayant été effectué avec des titanocènes utilisés comme catalyseurs. La réaction est caractérisée par un rendement élevé, une haute sélectivité et peut être réalisée dans des conditions douces. Les monophosphinosilanes et les diphosphinosilanes peuvent être obtenus sélectivement à partir de réactions secondaires avec les silanes. Les phosphines primaires réagissent avec les silanes primaires pour donner les 1,3,5-triphospha-2,4,6-trisilacyclohexanes. Deux mécanismes catalytiques cycliques sont proposés avec l'hydrure de silane comme l'éspece catalytique clée.

L'hydrosilation/hydrogénation de certains N-hétérocycliques aromatiques (pyridine, 3-picoline, 4-picoline, 3,5-lutidine et quinoline) a été obtenu avec des dérivés de titanocène comme catalyseurs. Une varieté de produits hydrosililés/hydrogénés aussi bien totalement que partiellement saturés peuvent être obtenus dépendement des conditions. Un mécanisme réactionnel est proposé, basé sur des complexes pyridine de titanocène qui ont été isolés et dont la structure a été déterminée, sur les effets des substituants, les vitesses de réactions ainsi que les études d'échange H/D. Il est suggéré que l'étape clée de la réaction d'hydrosilation/hydrogénation est la formation d'un complex mono-h¹-(N) entre le cycle de la pyridine et le complex du titanocène sililé. Il est proposé que l'étape déterminante de la vitesse est une insertion intramoléculaire de

-N=C- dans la laison Ti-Si-Si. Si la coordination est solide ou l'insertion intramoléculaire est bloquée, soit par l'effet stérique ou par l'effet éléctronique ou encore si le complexe est de haute stabilité, aucun produit d'hydrogénation ou d'hydrosililation n'est obtenu. Un échange excessif H/D aux positions 2- et 6- de la pyridine est attribué à l'orthométallation reversible de la pyridine dans le complex Ti-H.

Cp₂TiMe₂ catalyse les réactions d'hydrosilation/hydrogénation des nicotinates, les benzoates d'ethyl, et les lactones ont été étudiés. Avec le nicotinate d'ethyle comme substrat, l'hydrosilation a lieu sur le cycle pour donner l'ethyl N-(methylphenylsilil)-1,6dihydronicotinate comme unique produit. Aucune réaction au niveau du groupe ester n'est observée. Cependant quand le substrat est l'isonicotinate d'ethyle, 2-methylnicotinate d'ethyle ou 6-methylnicotinate d'ethyle, l'hydrosilation/ hydrogénation a lieu au niveau des groupes esters et le groupement carboalkoxy est transformé soit en ether de silyle soit en groupement alkyle.

Les copolymers peuvent être produit à partir du titanocène catalysant les réactions d'hydrosilation/hydrogénation par ouverture de cycle des lactones et PhMeSiH₂. L'intermédiaire clée pour ces réactions, $Cp[\mu-(\eta^1:\eta^5-C_5H_4)](THF)Ti(\mu-H)TiCp_2$, est isolé et bien caractérisé par diffraction aux rayons X. Le succès dans l'isolation et la caractérisation de ce produit fournit la première évidence directe qui soutient l'implication de Cp₂Ti dans d'innombrables réactions catalytiques par Cp₂TiMe₂ en plus de corriger de précédentes attributions de structure de ce composé fréquement cité.

V

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List of Abbreviations

Å	Angstrom (1 Å = 10^{-10} m)
b.p.	boiling point
BTHIE	bis-(1,2-tetrahydroindenyl)ethane
<i>n-</i> Bu	normal-butyl
<i>i-</i> Bu	iso-butyl
t-Bu	tert-butyl
cat.	catalyst
COSY	(homonuclear chemical shift) correlation spectroscopy
Ср	η^{5} -cyclopentadienyl (η^{5} -C ₅ H ₅)
Cp*	η^5 -pentamethylcyclopentadienyl
Су	cyclohexyl
DEPA	distortionless enhancement by polarization transfer
DEZ	diethylzirconocene
DIBAH	diisobutylaluminum hydride
EPR	electron paramagnetic resonance
Et	ethyl, CH ₃ CH ₂
FAB	fast atom bombardment
FT-IR	Fourier transform infrared
GPC	gel permeation chromatography
HDN	hydrodenitrogenation
HMQC	heteronuclear multiple quantum coherence
IR	infrared
Me	methyl, CH ₃
Mn	number-average molecular weight
MOCVD	metallorganic chemical vapor deposition

m.p.	melting point
MS	mass spectrometry
Mw	weight-average weight
NCO	no coupling observed
NMR	nuclear magnetic resonance
NOESY	(two-dimentional) nuclear overhauser effect spectroscopy
ORTEP	Oak Ridge Thermal Ellipsoid Plot
Ph	phenyl
PMHS	poly(methylhydrosiloxane)
ppm	parts per million
psi	pound per square inch
Ру	pyridine
TBAF	tetrabutylammonium fluoride
THF	tetrahydrofuran
TMS	Tetramethylsilane

Abbreviations used to describe NMR peaks

br	broad
d	doublet
dd	doublet of doublet
dt	doublet of triplet
m	multiplet
q	quartet
S	singlet

Abbreviations used to describe IR peaks

m medium

S	strong
vs	very strong
vw	very weak
w	weak

List of Compounds





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CHAPTER 1

A BRIEF REVIEW OF TITANOCENE CHEMISTRY

1.1 General introduction

Organotitanium compounds have attracted considerable and growing interest in several areas of chemistry since their first introduction in the early 1950's. The ability of titanium to form σ - or π - bonds with a large variety of ligands has led to the synthesis and characterization of numerous organotitanium derivatives. Some of the earliest examples attracted attention for their application in Ziegler-Natta polymerization of olefins. Unlike many other transition metals, the use of titanium is not limited to catalytic systems, but it is often used in stoichiometric quantities, due to the high abundance, low cost and low intrinsic toxicity of this element. In recent years organotitanium compounds with one or two cyclopentadienyl substituents have found increasing use for a variety of reactions.¹ In the chemical reactions with silanes, phosphines, olefins, hydrogen, carbon monoxide, and dinitrogen, etc., titanocene or bis(η^5 -cyclopentadienyl)titanium (η^5 -cyclopentadienyl will be abbreviated throughout this thesis as Cp), Cp₂Ti, has often been implicated as a highly reactive intermediate, though it has never actually been isolated as a discrete chemical compound.

The remarkable reactivity of titanocene has received tremendous attention of both inorganic and organic chemists. An important aspect of titanocene chemistry, has been the isolation and characterization of titanocene derivatives. While titanocene itself remains elusive, many derivatives of titanocene have been successfully isolated and wellcharacterized. They are normally either trapped from reactions in which titanocene is believed to be involved or synthesized through conventional synthetic methods. These derivatives are helpful for understanding reaction mechanisms, but do not generally provide

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prima facie evidence that titanocene is present. The search for titanocene continues to form an important part of this research area.

Another indispensable part of titanocene chemistry is the discovery and exploration of novel reactions. The rich chemistry of titanocene is evident from the large number of well-known catalytic and stochiometric reactions, including reduction and oxidation of unsaturated organic compounds, formation of C-C and C=C bonds,²⁻⁴ ring formation reactions,⁵ and polymerization reactions,⁶⁻⁹ etc.. The remarkable versatility of titanocene is also manifested by the frequent appearance of reports about novel reactions with titanocene either as a catalyst or a reagent. More than 300 papers have been published on titanocene within the last three years. The pursuit of unprecedented reactions with titanocene has been for decades, and will remain, one of the challenges of great interest to both inorganic and organic chemists.

Metallocenes of Group 4 present a lot of similarities in one way or another. This review only covers parts of titanocene chemistry of relevence to the thesis.

1.2 Background of titanocene

1.2.1 History of titanocene

Organometallic compounds of the group 4 metals could not be isolated until good inert atmosphere techniques were developed in the early 1950's, due to their high sensitivity to air, moisture and other hydroxylic species. The first organotitanium compound, TiPh(O-i-Pr)₃, was isolated in 1952.¹⁰ Since then the organometallic chernistry of Group 4 metals has developed rapidly, due in large part to the discovery of the catalytic role played by titanium halides with aluminum alkyls in the polymerization of ethene.¹¹ The discovery of ferrocene^{12,13} and its sandwich structure^{14,15} stimulated research interest into this kind of sandwich transition metal compound. As a result many

bis(cyclopentadienyl) complexes of the first row transition metals have been prepared. The first bis(cyclopentadienyl) compound of titanium, Cp_2TiBr_2 , was reported in 1953 by Wilkinson et al.¹⁶ By far the majority of the organometallic compounds of titanium contain the cyclopentadienyl ligand bonded in the pentahapto fashion (η^5 -C₅H₅). The unique stabilizing influence of this ligand allows the isolation of many organometallic compounds. However, the ferrocene analog, titanocene has never been obtained. Though many groups claimed the success preparing titanocene, none has survived closer scrutiny.

While "titanocene" seemed to be easy to synthesize, full characterization could never be achieved. The difficult journey of searching for titanocene has been extensively reviewed by Pez and Armor¹⁷ from its start in the early 1950's till the beginning of 1980's. Several routes have been explored.¹⁸⁻²⁰ The major reaction employed for synthesis of titanocene was through reduction of titanocene halides or alkyls.²¹⁻²³ Although various "titanocene" materials have been reported by different groups, most likely the major components of these "titanocenes" are μ -(η^5 : η^5 -C₁₀H₈)- μ (H)₂-(η^5 -C₅H₅)₂Ti₂ (1), μ -(η^1 : η^5 -C₅H₄)(η^5 -C₅H₅)₃Ti₂ (2), and μ (H)₂-(η^5 -C₅H₅)₄Ti₂ (3).



Figure. 1.1 Postulated rearrangement of $(\eta^5-Cp)_2Ti$ to $(\eta^5-Cp)(\eta^1-Cp)Ti$ hydride^{24a}

Compound 1 was found by Brintzinger and Bercaw²⁴ as the main product in the various reactions of $(\eta^5-C_5H_5)_2$ TiCl₂ with Na, Na/Hg. and sodium naphthalene. The formation of 1 was explained by the highly coordinatively unsaturated titanium(II) center in the bent $(\eta^5-C_5H_5)_2$ Ti intermediate abstracting hydrogen from the C₅H₅ ligand to yield a titanafulvene-hydride structure (**Fig. 1.1**). Further dimerization yields 1. Brintzinger and co-workers also found that while hydrogenolysis of $(\eta^5-C_5H_5)_2$ TiMe₂ solution at room temperature yields mainly 1, reaction of solid $(\eta^5-C_5H_5)_2$ TiMe₂ with hydrogen produces 3, and treatment of a saturated hexane solution of $(\eta^5-C_5H_5)_2$ TiMe₂ with H₂ at 0 °C gave a gray-green, presumably polymeric hydride.²⁵ It seems that when external H is accessible the titanocene (Cp₂Ti) produced in the synthetic reactions tends to gain H from the external H source under suitable conditions and 3 is formed, however when no external H is available, Cp₂Ti tends to abstract internal H (H on C₅H₅ ligand) and 1 is formed. In both cases, it is certain that Cp₂Ti is produced.

Compound 2 was synthesized by Pez^{26} by the reduction of $(\eta^5-C_5H_5)_2TiCl_2$ with 2 equivalents of potassium naphthalene. The structure was deduced from the x-ray structure of a crystalline derivative, obtained by slow diffusion of isopentane into solutions of 2 in tetrahydrofuran. However, the proposed structure is enigmatic in that it contains one hydrogen less than is expected for a dimer of titanocene and it is hard to account for the formation of 2 in relation to 1 or 3. Given the similarity of the reagents used to make 1 and 2, it might be expected that 2 is a precursor to 1. A plausible interpretation would be that 2 results from dimerization of 4 with a molecule of titanocene, while 1 results from dimerization of two molecules of 4. The resolution of this enigma is the subject of **Chapter 5** of the present thesis.

The unsuccessful attempts to obtain Cp₂Ti in discrete form is in sharp contrast to the related case of Cp*₂Ti (Cp* = η^5 -pentamethylpentadienyl). Unlike Cp₂Ti, Cp*₂Ti has

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no α -hydrogen available to shift, while at the same time it has a has higher electron density on the Ti center. On the other hand, the bulkier Cp* group makes the dimerization of Cp*Ti species less possible than in the case of Cp₂Ti. Thus Cp*₂Ti was predicted to be more stable than Cp₂Ti. Bercaw and Brintzinger²⁷ successfully prepared Cp*₂Ti by the following reaction sequence (**Eq. 1.1—1.3**).

$$[C_5(CH_3)_5]_2TiCl_2 + 2LiCH_3 \longrightarrow [C_5(CH_3)_5]_2Ti(CH_3)_2 + 2LiCl Eq.1.1$$

$$[C_{5}(CH_{3})_{5}]_{2}Ti(CH_{3})_{2} \xrightarrow{100^{\circ}} C_{10}(CH_{3})_{10}CH_{2}Ti + CH_{4}$$
 Eq.1.2

$$C_{10}(CH_3)_{10}CH_2Ti + H_2$$
 Hexane $[C_5(CH_3)_5]_2Ti + CH_4$ Eq.1.3

Cp*2TiH was also easily made according to Eq.1.4 by Teuben and co-workers.²⁸

$$Cp_{2}^{*}TiR + H_{2} \xrightarrow{25^{\circ}C. \ 1 \text{ atm}} Cp_{2}^{*}TiH + RH$$
 Eq. 1.4

The easier access to $Cp*_2Ti$ and $Cp*_2TiH$ strongly implies that the elusiveness of the Cp_2Ti counterparts is due their high activity towards hydrogen abstraction and high tendency to dimerize.

It can be concluded that titanocene was produced in the various reactions designed for its synthesis by reduction of titanocene halides or alkyl titanocenes by chemical or photochemical methods. The main product in those synthetic reactions is **1** or **3** depending on the reaction conditions. By introducing PMe₃ or CO into these synthetic reduction reactions, $Cp_2Ti(PMe_3)_2]^{29}$ and $[Cp_2Ti(CO)_2]^{18b.30.31}$ have been obtained. Both $[Cp_2Ti(PMe_3)_2]$ and $[Cp_2Ti(CO)_2]$ can be considered as titanocene stabilized by PMe₃ and CO respectively.

Titanocene catalyzed reactions have been extensively studied and have found wide applications.³²⁻³⁵ However, the mechanisms involved are not yet well-understood. Part of

the difficulty may due to the lack of a direct method for detection and to the high reactivity of titanocene. Nevertheless, titanocene has been proposed as a key intermediate in numerous reactions catalyzed by titanocene derivatives. Efforts to find evidence to support the essential role of titanocene in these reactions have led to the isolation and characterization of several titanocene derivatives. Among these derivatives are $5-10.^{36-40}$ The formation of all these compounds has been explained by reactions involving titanocene as a precursor. However, they can only be regarded as indirect evidence for the involvement of titanocene in the corresponding reactions.



In summary, from the earliest studies to the present time, the pursuit of titanocene has produced many interesting and useful results, yet the identity of titanocene remains elusive. The structural characterization of titanocene remains an important goal since the theoretical predictions of its electronic and molecular structures still require experimental confirmation.

1.2.2 Theoretical background

Although there are many similarities between the chemistries of the group 4 metallocenes, titanocene derivatives exhibit a particularly distinctive and rich chemistry involving all of the common oxidation states (II, III, and IV). All of the oxidation states are represented by an important number of isolated and well-characterized compounds. The most common oxidation state for group 4 metallocene derivatives is +4. This is the maximum valence state that can be observed for the group, giving a d⁰ configuration. A major difference between the first member Ti and the subsequent members Zr and Hf of this group is the relative accessibility of lower oxidation states, the Ti(IV)/Ti(III) reduction potential being relatively low.⁴¹

bis(η^{5} -Despite the easy access to the low oxidation states. cyclopentadienyl)titanium, Cp₂Ti, has never been obtained as a discrete compound while the other elements of the first transition series from vanadium to nickel form stable $bis(\eta^{5})$ cyclopentadienyl) complexes which are easily prepared using standard methods of organometallic synthesis. Both experimental and theoretical research has led to the conclusion that these metallocenes have the normal π -sandwich structure typical of ferrocene. The elusiveness of titanocene is believed to be due to its unique electronic structure.

A theoretical description of first row metallocenes was first presented by Lauher and Hoffmann.⁴² Their general conclusions have since been confirmed by more rigorous theoretical methods.^{43,44} Normal bis(cyclopentadienyl) transition metal complexes, Cp₂M, such as ferrocene are highly symmetric molecules with parallel cyclopentadiene rings (11). Their symmetry is D_{5h} if the two rings are eclipsed, or D_{5d} if the rings are staggered. A

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bent Cp₂M fragment with tilted Cp rings (12) has $C_{2\nu}$ symmetry if the Cp ligands have an eclipsed geometry, and only Cs symmetry if the rings are staggered.



In D_{5d} geometry the π orbitals of the $C_5H_5^-$ ligands yield three sets of approximately degenerate orbitals: a low-lying filled pair of a_{1g} and a_{2u} symmetry, a set of filled orbitals, e_{1g} and e_{1u} , and a high-lying empty set of antibonding orbitals of symmetry e_{2g} and e_{2u} . These interact with the orbitals of the metal as shown in the correlated diagram in **Figure 1.2**. This ordering of energy levels is characteristic of a normal Cp₂M complex. There is a strong interaction with the metal s and p orbitals and also a strong bonding interaction with the $e_{1g}(d_{xz}, d_{yz})$ set. The remaining three d orbitals of the metal, $a_{1g}(d_z^2)$ and the $e_{2g}(d_x^2-y^2, d_{xy})$ set, remain essentially nonbonding. Thus the d-level splitting is e_{2g} $\leq a_{1g} < e_{1g}^*$ or $(d_x^2-y^2) \leq (d_z^2) < (d_{xz}, d_{yz})$.



Figure 1.2 Interaction diagram for a D_{5d} metallocene, The frontier orbitals are in the box.⁴²

Ferrocene has an ideal 18-electron configuration making it the most stable of the metallocenes. Cobaltocene (a d⁷—19 electron complex) and nickelocene (d⁸—20 electron complex) both have excess electrons which occupy the higher lying $e_{1g}*(d_{xz}, d_{yz})$ orbitals. This explains their easy oxidization.⁴⁵ Vanadocene is a d³—15 electron complex and chromocene is a d⁴—16 electron complex. Both are electron deficient, having fewer than 6 d electrons, and the three nonbonding orbitals are only partially filled. However, none of the three orbitals is empty. On the other hand titanocene is a d²—14 electron complex. With only two available electrons, one of the nonbonding orbitals must be empty and some sort of distortion is probable.

Titanocene is dramatically different from the other metallocenes.^{1,46-48} Extended Hückel calculations^{42,49} of the variation in the total energy of Cp₂Ti with respect to ω , the angle between the planes of the C₅H₅ rings, indicate that titanocene is most stable in the bent configuration with $\omega = 30-40^{\circ}$, while vanadocene, Cp₂V, on the other hand is most stable with $\omega = 0^{\circ}$, i.e. in the normal π -sandwich configuration with cyclopentadienyl rings parallel (Fig.1.3).⁴⁹



Figure 1.3 Total energy as a function of angle ω between the planes of the two aromatic ring ligands for Cp₂V and Cp₂Ti⁴⁹

However, Harrod et al.⁴³ found that the optimized structure of both the ground state and the first excited state of Cp₂Ti have the ω value of 0°. This theoretical discrepancy may only be resolved by concrete experimental evidence.

It has been proposed⁵⁰ that a transition metal complex having at least one available electron pair and one unfilled orbital in the valence shell should possess chemical characteristics akin to those of carbenes. By the above criteria, Cp_2Ti can be considered to be such a "carbenoid," and it was expected that it should undergo facile bond addition and bond insertion reactions, by analogy with the chemistry of carbenes. From a molecular orbital point of view, the analogy between Cp_2Ti and a carbene has been illustrated in **Fig.** 1.4.⁴⁹



Figure 1.4 Schematic representation of the essentially nonbonding molecular orbitals in a bent $(\pi - C_5H_5)_2$ Ti molecule ($\omega = 30^\circ$). For comparison, the corresponding orbitals of a carbene and their interactions with bonding and antibonding orbitals of a substrate are traced at the right (hatched orbitals are doubly occupied).⁴⁹

The most striking modes of reaction of a carbene are its facile insertion into σ bonds, addition to π bonds,⁵¹ and its formation of complexes with π acceptors like CO or

N₂.^{52,53} The simultaneous σ interaction (its empty p orbital with a bonding orbital of the substrate) and π interaction (its filled σ orbital overlaps with the corresponding antibonding orbital of the substrate) result in the smoothness of these reactions. As shown in **Fig.1.4**, with orbitals 33 (a₁) and 32 (b₂) assuming the roles of the σ and p orbitals of carbene R₂C respectively, it is obvious that similar interactions can be pictured for the species of Cp₂Ti in its bent conformation. An important feature is that the two orbitals not only have an appropriate symmetry, but also a spatial extension favorable for extensive σ and π overlap. The presence of a third low-lying orbital (31 (a₁)) in the bent Cp₂Ti offers it the option of binding two ligands as in Cp₂Ti(CO)₂ and Cp₂Ti(PMe₃)₂, an option not available to carbenes.

The carbene-type structure of titanocene provides the basic reason for its elusive character and for having such a rich chemistry. The anticipated high reactivity of titanocene supports the expectation that its isolation and characterization will remain a considerable challenge. It is also not surprising that titanocene and its derivatives often present unpredictable reactivities and provide a wide variety of novel compounds for the study of electronic and magnetic properties.⁵⁴

1.3 Titanocene chemistry

Titanocene chemistry has enjoyed a colorful history, from an early interest in N_2 fixation and olefin polymerization to the present broad activity in organic and inorganic syntheses. The extensive studies on titanocene chemistry have been reviewed by several authors.^{17,32,44} In this introduction only chemistry appropriate to the main stream of the present thesis, namely hydrosilation, hydrogenation, and dehydrocoupling reactions, will
be reviewed in detail. Other reactions, such as redistribution reactions, will be briefly discussed as relevant to the chemistry of the thesis.

1.3.1 Hydrosilation reactions

Hydrosilation is a reaction in which a silicon hydride bond adds across a multiple bond of an unsaturated molecule (Eq. 1.5). Catalytic hydrosilation is one of the

> Si-H + U <u>Catalyst</u> Si-U-H Eq.1.5 U = unsaturated molecule, such as ketones, esters, imines, olefins

fundamental methods for the synthesis of organosilicon compounds and organosilyl derivatives, and is now of considerable industrial significance.^{55,56}

Three classes of catalytic hydrosilation reactions have been documented in the literature: (1) Free-radical chain hydrosilation in which the Si-H bond is homolytically cleaved into radicals in the presence of an initiator, or under irradiation conditions, (2) Nucleophilic-electrophilic catalytic hydrosilation in which the Si-H bond is activated by an organic base (e.g. amines, phosphines, etc.), or metal salts, (3) Transition metal and organometallic compound catalyzed hydrosilation. The last class is of scientific and commercial importance, and reactions catalyzed by later transition metals were extensively reviewed by Ojima⁵⁵ in 1989. A recent review has been published covering the applications of cyclopentadienyl titanium derivatives in organic synthesis.³² Due to its relevance to this thesis, this section will mainly focus on titanocene catalyzed hydrosilations.

The origin of transition metal complex catalyzed hydrosilation reactions can be traced to $1957.^{57}$ In the following few decades the area was well-explored^{58.59} with the development of Chalk-Harrod mechanism (Fig. 1.5)⁶⁰ and its variants.⁶¹⁻⁶³ However,

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this period was dominated by late transition metal catalysts due to their exceptionally high catalytic activity.⁵⁵ During the past decade, early transition metal complexes have been found to be active for the hydrosilation of a variety of substrates and an increasing amount of attention has been diverted to them.



Figure 1.5 Tolman catalytic cycle for the Chalk-Harrod mechanism of alkene hydrosilation

1.3.1.1 Hydrosilation of olefins

Hydrosilation of olefins, catalyzed by a group 4 metallocene was first reported by Harrod and Yun in 1987.⁶⁴ In the dehydrocoupling polymerization of phenylsilane and cohydrogenation of olefin catalyzed by Cp_2TiMe_2 , it was found that some olefins underwent hydrogenation, double bond isomerization, and hydrosilation reactions. In one particular case hydrosilation products dominated at low catalyst concentration. Deuterium labeling studies confirmed that the co-hydrogenation of norbornene gave exclusively the *cis* -exo product. Presumably the hydrosilation reaction also proceeded by *cis* addition. All observations in this experiment are reminiscent of those for late transition metal catalyzed hydrosilation. Following Harrod and Yun's report, several groups showed that group 4 metallocenes are active catalysts for the hydrosilation of olefinic substrates.

Takahashi and co-workers reported the hydrosilation of 1-olefins by the use of diethylzirconocene (DEZ),⁶⁵ generated *in situ* by mixing of Cp₂ZrCl₂ and EtMgBr, as the catalyst precursor. Moderate to good yields and >99% regioselectivity for the 1-silyl product were obtained. In comparison, the Ti(IV) and Nb(IV) analogues gave low yields of product (less than 10%).

Corey and Zhu⁶⁶ extended Harrod and Yun's experiment to Cp₂MCl₂/n-BuLi (M = Ti, Zr, Hf) catalyzed reactions of phenylmethylsilane in the presence of olefins. A range of reactions were demonstrated, including hydrosilation of the olefins, isomerization/hydrosilation of internal olefins, dehydrocoupling of the silane to silicon oligomers, and dehydrocoupling of the silanes with the olefins to form vinylsilanes (Scheme 1.1). A mechanism, involving the insertion of an olefin into the M-Si bond followed by σ -bond metathesis with free silane, was proposed to explain the observed products.



Waymouth and Kesti⁶⁷ reported that a Cp_2MCl_2/n -BuLi (M=Ti, Zr, Hf) system catalyzes the hydrosilation of olefins with diphenylsilane. It is not surprising that this work, which closely parallels that of Corey's, provided almost identical results except that diphenylsilane gave a lower reaction rate due to the bulky substituents on silicon. Generally, higher temperature favors both the dehydrogenative oligomerization of silane and the dehydrosilation of olefin reactions.

Lee and Han^{68} recently reported that activated titanocene (Cp₂Ti) prepared by the reduction of titanocene dichloride with excess lithium in dimethoxymethane effectively catalyses the hydrosilation of alkenes by alkyl- or phenylsilanes (Eq. 1.6).

$$R'-SiH_3 + R$$
 [Activated Cp_2Ti] R SiH₂R' Eq. 1.6

1.3.1.2 Hydrosilation of carbonyl compounds

While the titanocene catalyzed hydrogenation of carbonyl compounds was reported more than a decade $ago,^{69}$ the use of titanocene catalysts for hydrosilation of carbonyl compounds is relatively new, though the reaction takes place readily with various catalytic systems. An early example involved the use of diphenyl titanocene as a catalyst for the hydrosilation of ketones at elevated temperature (**Eq. 1.7**).⁷⁰ A titanocene hydride was proposed as an important intermediate. The product was obtained in good to quantitative conversion with both primary and secondary silanes.



The catalytic, asymmetric hydrosilation of ketones using chiral titanocene compounds to give optically active alcohols has been the subject of several recent reports. Halterman et al.⁷¹ studied the hydrosilation of prochiral aromatic ketones with several titanium complexes, but only low to moderate enantioselectivities were observed.

Buchwald et al.⁷² reported the application of a system to the hydrosilation of aromatic ketones using poly(methylhydrosiloxane) (PMHS) as the source of Si-H and 14 activated with butyllithium as the catalyst. Work-up of he reaction affords alcohols with excellent enantioselectivity and is general for aromatic ketones with a moderate degree of functional group compatibility. The active species was also proposed to be a titanium hydride.



Xin and Harrod⁷³ reported the hydrosilation of a wide variety of dialkyl ketones with enantioselectivities of up to 70% using PhMeSiH₂ or Ph₂SiH₂ as the hydrosilating agent and **13**, activated with methyllithium, as the catalyst. The selectivity was found to be very sensitive to the steric qualities of the alkyl groups. Further study⁷⁴ revealed that with (EtO)₃SiH. Me(EtO)₂SiH, [MeSi(H)O]₄, Me₃SiO[MeSi(H)O]_nSiMe₃ or MeSiH₃ as the hydrosilating agent, the reaction rates are one to two orders of magnitude faster than with MePhSiH₂ or Ph₂SiH₂. Me(EtO)₂SiH, [MeSi(H)O]₄, and Me₃SiO[MeSi(H)O]_nSiMe₃ undergo rapid redistribution in the presence of the catalyst yielding MeSiH₃ which is believed to be the actual hydrosilating agent. The ee's for the hydrosilation product of acetophenone are consistently much higher (ca. 99%) for the n-BuLi based catalyst than for the MeLi based catalyst (ca. 40-50%). Titanium hydrides are proposed as the key intermediate in these catalytic hydrosilation reactions.

Titanocene catalyzed hydrosilation of esters was achieved a decade later than the first report of their titanocene-catalyzed hydrogenation.^{75,76} Buchwald and co-workers⁷⁷⁻

⁸⁰ developed several procedures for the overall reduction of esters to primary alcohols via titanocene catalyzed hydrosilation. The air stable system of the combination of Ti(O-i-Pr)4 with (EtO)₃SiH converts esters to alcohols in excellent yield and with a high level of functional group compatibility.^{78,80} Another system for the conversion of esters to primary alcohols was also developed with a titanocene-based catalytic system employing (EtO)₃SiH as the stoichiometric reductant.^{77,79} Catalyst generation was effected by the addition of n-BuLi to Cp₂TiCl₂ (Eq. 1.8). The system was found to be relatively insensitive to the presence of adventitious moisture or small amounts of oxygen, and was effective for the reduction of a great variety of ester substrates. A high degree of selectivity was reported. For example, ethyl 6-bromohexanoate is cleanly converted to 6-bromo-1-hexanol. Likewise, α,β -unsaturated esters and esters containing phenolic, amino, or cyclopropyl groups, as well as di- and trisubstituted olefins, are efficiently transformed into the corresponding primary alcohols. A methyl ester can even be selectively reduced in the presence of a tert-butyl ester. However, a more hindered titanocene dichloride species. ethylene-1,2-bis(η^{5} -4,5,6,7-tetrahydro-1-indenyl)titanium dichloride (14) (X=Cl), is required for the selective hydrosilation of an ester in the presence of a ketone, or a terminal olefin, or an epoxide.



It is known that $(EtO)_3SiH$ undergoes rapid redistribution to yield SiH₄ in the presence of titanocene catalysts.⁷³ To avoid the danger of SiH₄ and reduce the cost, two modifications have been introduced to the Cp₂TiCl₂/n-BuLi/(EtO)₃SiH system:⁷⁹ (a) the

use of PMHS instead of $(EtO)_3SiH$ to eliminate the generation of SiH_4 ; (b) the use of EtMgBr instead of n-BuLi to generate an active catalyst system. The conversion of esters to the corresponding alcohols was accomplished in good to excellent yield using this system.

The catalytic reduction of five- and six-membered ring lactones to the corresponding lactols can also be accomplished using titanocene-based catalytic systems. Buchwald et al.^{81,82} reported a convenient method for the conversion of lactones to lactols via hydrosilation (**Eq. 1.9**). The hydrosilation to lactols was carried out via air-stable titanocene difluoride or a titanocene diphenoxide precatalyst using PMHS as the stoichiometric reductant. The activation of the catalyst can be achieved by reacting with phenylsilane or using tetrabutylammonium fluoride (TBAF). The amount of titanocene catalyst can be as low as 0.5% relative to lactone substrate without any decrease in yield. Aromatic halides and α -substituted lactones can also be reduced to the corresponding lactols without any epimerization.



1.3.1.3 Hydrosilation of imines

Hydrosilation of imines has also been achieved with a titanocene-based catalyst.⁸³ Treatment of (S,S)-ethylenebis(η^5 -tetrahydroindenyl)titanium difluoride (15) with phenylsilane generates a catalytically active titanocene hydride species. The formation of a strong Si-F bond may provide the driving force for the formation of the Ti-H bond. The system was found to be very effective for conversion of imines to amines in very high yield and high enantioselectivity under mild conditions (Eq. 1.10).



As has been demonstrated by numerous reports, there is a variety of titanocenebased catalysts which are effective for the hydrosilation of unsaturated organic compounds. The key intermediates in these different systems are proposed to be the corresponding Ti(III) hydrides.⁶⁴⁻⁸³ The synthesis, isolation and characterization of **7**, **8**, **9** and rac-[(BTHIE)TiH]₂ (**16**) [BTHIE = bis-(1,2-tetrahydroindenyl)ethane]¹⁰¹ are commonly regarded as the evidence for the essential role Ti(III) hydride in titanocene catalyzed silane reactions.



1.3.2 Hydrogenation reactions

Hydrogenation of unsaturated organic compounds is of great importance in organic synthesis. Many metals and metal complexes have been found to catalyze such hydrogenation reactions. The use of titanium compounds as homogeneous catalysts for alkene and alkyne reduction was first reported by Breslow et al.⁸⁴ They showed that Ziegler/Natta catalysts had high activity in such reactions. Some titanocene derivatives have since been used as well.

Compound 2 was found by Pez^{26} to be a very effective catalyst for hydrogenation of C₂H₄ and cyclohexene. More active catalysts can also be prepared by reaction of 1methyl-η-allylbiscyclopentadienyltitanium with H₂.⁸⁵ The dicarbonyl complex, Cp₂Ti(CO)₂ has been shown to be a catalyst for the hydrogenation of acetylene at 50 atm of H₂.⁸⁶ (Ph₂C₂)(CO)TiCp₂, obtained from the treatment of Cp₂Ti(CO)₂ with diphenylacetylene, is also a very effective hydrogenation catalyst for acetylene as well as for olefins.⁸⁷ Brubacker and co-workers⁸⁸ have prepared polymer-attached Cp₂TiCl₂ When activated with butyllithium in hexane, the supported titanium complex was much more reactive with respect to the catalytic hydrogenation of cyclohexene as compared with the reduced, nonattached titanocene dichloride.

Samuel⁸⁹ reported that dialkyltitanocene compounds, Cp_2TiR_2 (R = CH₃; $CH_2C_6H_6$; C_6H_5), when photolyzed under hydrogen are efficient catalyst precursors for the hydrogenation of linear and cyclic olefins under mild conditions.

The active catalytic species for these hydrogenation reactions is believed to be a $Cp_2Ti(III)$ hydride compound which can be produced by reduction of the corresponding dichlorides⁹⁰ or dialkyl compounds.^{25c,64a,91}. The hydride species adds readily to alkenes to form titanocene alkides which can undergo hydrogenolysis to yield the alkanes and regenerate the catalyst (**Fig. 1.6**). The hydrogenation of alkynes proceeds similarly.



Figure 1.6 A possible mechanism for the hydrogenation of alkenes with $Cp_2Ti(III)$ hydride

The titanacyclopropene **17** was reported as an effective homogeneous hydrogenation catalyst for a variety of olefins and alkynes.⁹² Harrod and Yun^{64a} found that dimethyl titanocene activated by a silane is effective for the hydrogenation as well as for the isomerization and hydrosilation of olefins. Some substituted titanocene derivatives have also been activated and used for the hydrogenation of olefins.^{93,94}



Catalytic enantioselective hydrogenation of prochiral alkenes can be achieved with chiral titanocene catalysts.⁹⁵ Kagan⁹⁶ reported low %ee's with complexes such as **18**. The use of other more symmetrical titanocenes such as **19**^{97,98} and **20**⁹⁹ bearing novel annulated Cp ligands led to improved enatioselectivities only in certain cases.



Buchwald et al.¹⁰⁰ developed a very effective chiral titanocene catalyst by activating **13** and **14** with butyllithium. They obtained the corresponding Ti(III) hydride species¹⁰¹ which proved to be a highly enantioselective hydrogenation catalyst for unfunctionalized trisubstituted olefins, including acyclic and cyclic derivatives. With the same catalyst, high enantioselectivities were also obtained in the asymmetric hydrogenation of 1,1-disubstituted enamines to give the corresponding tertiary amines (**Eq. 1.11**). This reaction proceeded under milder condition than were necessary for trisubstituted olefins.¹⁰²



1.3.3 Homodehydrocoupling polymerizations

Homodehydrocoupling provides a versatile and clean route to the synthesis of homopolymers and oligomers via the formation of E-E (element - element) bonds. The generalized homodehydrocoupling reaction is shown in Eq. 1.12. This reaction has been used for the formation of a number of different element-element bonds.^{33,103,104}

$$2 R_{n}EH \longrightarrow R_{n}E-ER_{n} + H_{2} \qquad Eq. 1.12$$

$$(R = organyl or H)$$

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1.3.3.1 Dehydropolymerizations of silanes

Polysilanes have received particular attention as SiC ceramic precursors, 105 materials.106 photoresistors,¹⁰⁷ luminescent deep-UV eletroconductor¹⁰⁸ and photoinitiators.^{109,110} There are several excellent reviews on the preparation, structure, properties, photochemistry, and redistribution of polysilanes.^{103,111a,112-117} The most common methods for the preparation of polysilanes are Wurtz-type coupling of halosilanes using alkali metals, and coupling of halosilanes with organoalkali metals or Grignard reagents, as shown in Eq. 1.13. These conventional methods have some drawbacks¹¹¹ in the control of the polymer structures and molecular-weight distributions, the introduction of functional groups, and/or the creation of new polymer frameworks. Some other synthetic methods have also been developed, such as anionic polymerization of masked disilenes,¹¹⁸ ring-opening polymerization of cyclic oligosilanes,¹¹⁹ electroreductive polymerization of organodichlorosilanes,¹²⁰ sonochemical polymerization of organodichlorosilanes,¹²¹ electrochemical polymerization of hydrosilanes,¹²² catalytic dehydropolymerization of hydrosilanes by activated transition metals,123 and redistributive polymerization of hydrodisilanes catalyzed by potassium hydride.¹²⁴

$$R_{2}SiCl_{2} \xrightarrow{Na, -NaCl} (SiR_{2})_{n}$$
Eq. 1.13
$$Eq. 1.13$$

Dehydropolymerization is among the attractive methods for synthesis of polysilanes. It only involves the elimination of H₂ and formation of Si-Si bonds and no other objectionable side product is produced (**Eq. 1.14**). Titanocene was among the first transition metal compounds identified as catalysts for silane dehydropolymerization.¹⁰³ Harrod and co-workers¹²⁵⁻¹²⁷ pioneered this chemistry using dimethyl titanocene. Nakano

and co-workers¹²⁸ used diphenyltitanocene in the same manner. The combination of titanocene dichloride and butylithium was studied extensively by Corey.¹²⁹ This group also explored the use of bimetallic titanium and zirconium complexes as catalysts in the presence of butyllithium for the dehydrocoupling of PhSiH₃ to polysilane.¹³⁰ Dioumaev and Harrod¹³¹ recently reported that cation-like catalysts give polymers with higher molecular weights. The reactivity of hydrosilanes towards dehydrocoupling follows the order: primary > secondary > tertiary,^{129a} which most probably reflects steric constrains in the condensation reaction. Corriu and coworkers¹³² developed a system using diphenoxytitanocene for silane polymerization.

$$H - Si - H \xrightarrow{cat.} H \left[\begin{array}{c} R^{1} \\ I \\ Si - H \\ R^{2} \end{array} \right] H + H_{2} \qquad Eq. 1.14$$

Some cyclic pentamers and hexamers are found as minor products in the silane polymerization catalyzed by titanocene.¹³³ These cyclic products may be produced either via direct cyclization of the corresponding linear oligomers or via redistribution of longer linear polymers. The formation of cyclic oligomers is irreversible and competes with the formation of longer polymers. However, it provides a route to some interesting cyclic silane oligomers. All-trans hexabenzylcyclohexasilane was obtained in a good yield with Cp_2TiMe_2 as catalyst¹³⁴ and some of its spectroscopic properties have been studied.^{134a,135}

The titanocene catalyzed dehydrocoupling provides a new approach to silane polymers. However, as with the other methods, there are still serious problems to overcome. The major drawback of this method so far is the relatively low molecular weights of the polysilane produced and its limited applicability to secondary silanes.¹³⁶⁻¹³⁸

The optimal mechanical and optical properties would be hard to achieve without a methodology to synthesize polysilanes of higher molecular weight.

Considerable effort has been dedicated to elucidating the dehydropolymerization mechanisms, to finding the most efficient catalysts, to increasing the polymer molecular weights, to preparing polysilanes stereoselectively, and to dehydropolymerizing various types of hydrosilanes to functional polysilanes. Four mechanistic schemes have been proposed to rationalize silane polymerization catalyzed by group 4 metallocenes. Among them the Tilley σ -bond metathesis mechanism^{115,116,136,137,139,140} has proven to have the widest applicability¹⁴¹⁻¹⁴³ although it was developed mainly from the study of zirconocene and hafnocene catalysts. The mechanism involves a sequence of σ -bond metatheses among Si-H, M-H, and M-Si bonds (**Fig.1.7**).



Figure 1.7 The Tilley s-bond metathesis mechanism

1.3.3.2 Dehydropolymerizations of germanes

Polyorganogermanes and polystannanes have also attracted considerable attention in recent years due to their electronic conductivity, photoconductivity, and thermochromic properties.¹⁴⁴ Generally, polygermanes are prepared by the Wurtz-type coupling of halogermanes.¹⁴⁵⁻¹⁴⁷ More recently polygermanes have been made by dehydrocoupling of organogermanes. Some late transition metal-based complexes are effective catalysts for the coupling of germanes.¹⁴⁸ The application of titanocene for catalyzing germane dehydropolymerization was first reported in 1988.¹⁴⁹ Both PhGeH₃ and Ph₂GeH₂ were found to undergo dehydrocoupling reactions in the presence of Cp₂TiMe₂. In contrast to the case of PhSiH₃ where linear polymers and oligomers are the major products, PhGeH₃ is readily converted to insoluble gel presumably due to cross-linking.¹⁴⁹ However, the catalyst chemistry is the same for Ge and Si, as all of the observable Ti species in the functioning systems are in the form of Ti(III). In the case of Ph₂GeH₂, two parallel reactions are observed. One, which involves Ti(IV), selectively yields tetraphenyldigermane. The other, which occurs as the Ti spontaneously reduces to Ti(III), rapidly produces a mixture of oligomers.¹⁴⁹

The mechanism for germane dehydropolymerization catalyzed by titanocenes is expected to be similar to that for the organosilane polymerization. The results with Ph₂GeH₂ and Cp_2TiMe_2 imply that other mechanisms may also be applicable to germane dehydropolymerizations. When Ti remains in oxidation state IV, the results point to a slow σ bond metathesis mechanism (**Fig. 1.7**). The much faster dehydrocoupling reaction after the reduction of Ti(IV) to Ti(III) can be rationalized either by σ -bond metathesis at Ti(III), or by a one-electron redox mechanism proposed by Dioumaev and Harrod.^{131d}

1.3.3.3 Dehydropolymerizations of phosphines

It is reasonable to expect that phosphines would undergo dehydrocoupling reactions similar to those of silanes since they are isoelectronic. Some dehydrooligomerization reactions leading to phosphine oligomers have been reported by Stephan using zirconocene derivatives.¹⁵⁰⁻¹⁵³ However, attempts to polymerize primary or secondary phosphines with Cp₂TiMe₂ were unsuccessful. The negative results were explained in terms of the particular properties of phosphines.¹⁵⁴ Subsequently, **16** was found to be an effective catalyst at room temperature for the oligomerization of PhPH₂ affording a mixture of cyclic and linear oligophosphines with (PhP)₆ the most abundant of the rings.^{40,155} The mechanisms of these reactions were interpreted in terms of the oxidative addition of phosphines to Cp₂Ti(II), conproportionation of Cp₂Ti(II) and Cp₂Ti(IV) to Cp₂Ti(III), and σ -bond metathesis reactions of P-H, Ti-H, and Ti-P compounds.⁴⁰

1.3.4 Heterodehydrocoupling reactions

Heterodehydrocoupling reactions, in which E-E' bonds are formed, are less well developed. However, They have been used for the syntheses of some main group compounds.¹⁵⁶ The heterodehydrocouplings of Si-H/H-O, Si-H/H-N, Si-H/H-C and some heavier elements have been achieved with titanocene as the catalyst.^{35,103}

1.3.4.1 Si-H/H-O dehydrocoupling

Si-H/H-O dehydrocoupling can be an effective alternative approach for the formation of silyl ethers. Silyl ethers have been employed by both organic and inorganic chemists in a variety of applications, from protecting groups in organic synthesis to sol-gel preparations. The most common methods for formation of silyl ethers are the reactions of chlorosilanes either with an alcohol in the presence of an HCl acceptor or with an alkoxide.¹⁵⁷ The conversion of a hydrosilane to a silyl ether in the presence of an alcohol can also be accomplished under the catalytic influence of some metal compounds.^{103,157,158}

The first example using titanocene for the formation of silyl ethers was reported by Nakano and Nagai.¹⁵⁹ They reported using Cp₂TiPh₂ to promote the alcoholysis of monosilanes. A detailed survey of the dehydrocoupling of a range of organosilanes and alcohols was carried out by Corey and Bedard¹⁶⁰ using Cp₂TiCl₂/nBuLi as the catalytic system. The results showed that the catalyst is effective under mild conditions. With primary alcohols, the corresponding alkoxysilanes can be obtained in near quantitative yields, while with secondary and tertiary alcohols, more forcing conditions are required. Increasing the steric bulk of the substituents on the silane also leads to longer reaction periods and/or a need for higher temperature. Partial substitution is not achievable with the less hindered silanes, even using a substoichiometric amount of the alcohol and low temperature. This behavior was explained by the rapid redistribution of the hydroalkoxysilane intermediates. This suggestion is in conformity with the observation that steric encumbrance on the silicon has a significant effect on the rates of dimethyltitanocenecatalyzed silane redistribution reactions.¹⁶¹

As intramolecular hydrosilation has extensive applications in controlling regio- and enantioselectivity.¹⁶² Xin and Harrod¹⁶³ carried out dehydrocoupling reactions of diorganosilanes and unsaturated alcohols using titanocene based catalyst. However, the titanocene-based catalysts are not promising in synthetic applications due to several other side reactions such as hydrogenation and redistribution reactions.

1.3.4.2 Si-H/H-N dehydrocoupling

Dehydrocoupling makes hydrosilazanes accessible with relative ease. The heterogeneous catalyzed coupling of hydrosilanes and amines has long been recognized as a useful route to silazanes.¹⁶⁴ Several transition-metal-based homogeneous catalysts have also been explored.¹⁶⁵ However, Cp₂TiMe₂ is the only homogeneous catalyst which has been systematically studied for the reaction of silanes and ammonia.¹⁶⁶ It was found that

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this catalyst is effective for primary, secondary, and tertiary organosilanes, but the products from primary and secondary organosilanes are quite complicated and vary with reaction conditions. In the cases of PhMe₂SiH and PhMeSiH₂, the initial products observed are disilazanes (**Eq. 1.15**) but not monosilazanes under all the conditions explored. The second Si-H bond of PhMeSiH₂ undergoes further reaction affording products of greater complexity than the disilazane. Interestingly the third N-H bond is inert towards further reaction under the conditions used.¹⁶⁷

$$PhMeSiH_2 + NH_3 \longrightarrow (PhMeSiH)_2NH$$
 Eq. 1.15

The reactions of phenylsilane with substituted hydrazines are also effectively catalyzed to give polymers.¹⁶⁶⁻¹⁶⁸ Compared with NH₃ and amines, N₂H₄ and substituted hydrazines have higher reactivity with silanes. N₂H₄ can spontaneously react with PhSiH₃ to give soluble polymers in which most of the Si-H have reacted. In the presence of Cp₂TiMe₂ the reaction is violent and the product is insoluble due to high cross-linking.¹⁶⁷ However, the reactions between methyl substituted hydrazines and silanes are much slower. With Cp₂TiMe₂ as the catalyst, the dehydrocoupling reactions proceed more slowly as the degree of methyl substitution increases.

1.3.4.3 Dehydrocoupling of tributylstannane and tellurium

Fisher and Piers¹⁵⁶ succeeded in synthesizing $[Bu_3Sn]_2(\mu-Te)$ through dehydrogenative cross coupling using titanocene based catalyst (Eq. 1.16). This kind of compound can be used as MOCVD (metallorganic chemical vapor deposition) precursors for main group metal tellurides.¹⁵⁶



The overall reaction of Eq. 1.16 is not strictly speaking a dehydrocoupling since it does not involve a Te-H bond. A complex catalytic cycle was proposed (Fig. 1.8).



Figure. 1.8 Proposed mechanism for Cp*₂TiH catalyzed coupling of Bu₃SnH and Ph₃P=Te (In the scheme Ti = Cp*₂Ti)

1.4 Scope of this thesis

This thesis presents several novel reactions catalyzed by titanocenes. The heterodehydrocoupling reactions of silanes (primary and secondary) and phosphines (primary and secondary) with Cp_2TiMe_2 and $CpCp*TiMe_2$ as the catalysts are presented in Chapter 2. In Chapter 3, the results of hydrosilation/hydrogenation reactions of pyridine and its derivatives, including pyridine, 3-picoline, 4-picoline, 3,5-lutidine and quinoline are described. Hydrosilation/hydrogenation of nicotinates and esters is the subject of Chapter 4. Chapter 5 presents the crystal structure of a titanocene intermediate in these reactions and discusses its essential role in the titanocene catalytic cycle.

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CHAPTER 2

HETERODEHYDROCOUPLING OF PHOSPHINES AND SILANES CATALYZED BY TITANOCENE: A NOVEL ROUTE TO THE FORMATION OF SI-P BONDS

2.1 Introduction

Titanocene has attracted the attention of organic and inorganic chemists for decades particularly in relation to Ziegler/Natta catalysis.^{1,2} Since Harrod et al.'s first report of the dehydrocoupling of silanes catalyzed by group 4 metallocenes³, a new chapter in the story of titanocene chemistry has been revealed based on its ability to activate Si-H bonds. Polymerization of primary silanes, hydrogenation and hydrosilation of unsaturated organic compounds,⁴ and catalytic redistribution reactions of hydrosilanes,⁵ have been reported. While a great effort has been devoted to developing systems of synthetic interest, understanding the catalytic properties of titanocenes has also been an interesting challenge.

It is commonly proposed that Ti(III) and Ti(II) species are active intermediates in the various catalytic reactions. Because of their high reactivity, instability and sensitivity to oxygen, these species are difficult to isolate and characterize. In certain cases they may be trapped and identified by reaction with ligands such as phosphines and pyridines,⁶⁻⁹ e.g. $Cp_2Ti(SiHRR')PMe_3$ (R, R'=H, Me, Ph),^{6.7} and $Cp_2Ti(SiHPh_2)(Py).^8$

Attempts to synthesize novel phosphido complexes from phosphines showed that P-P bonds can result from activation by the metallocenes of group 4 elements.¹⁰ Harrod and coworkers found the reaction of Cp₂TiMe₂ with PhSiH₃ in the presence of Cy₂PH (Cy = cyclohexyl) is photoinitiated to give paramagnetic solutions of Cp₂Ti(SiH₂Ph)(PHCy₂).⁶ Under the same conditions, a reaction with Ph₂SiH₂ gave crystalline (Cp₂Ti)₂(μ -H)(μ -PCy₂). Under continuous photolysis Cp₂TiMe₂ reacts with CyPH₂, in the presence of either PhSiH₃ or Ph₂SiH₂, to give [Cp₂Ti(μ -PHCy)]₂. Rac-[(EBTHI)Ti(μ -H)]₂ (EBTHI =

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ethylene-1,2-bis(η^{5} -4,5,6,7-tetrahydro-1-indenyl)) reacts with PhPH₂ to give the complex (EBTHI)Ti(P₂Ph₂), **21**.



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More interestingly, in this reaction, excess $PhPH_2$ is polymerized by dehydrocoupling to give a mixture of linear and cyclic oligophosphanes. These results showed that the reactions of titanocene with secondary and primary phosphines resemble in many aspects those of the isoelectronic silanes.

While the metallocene catalyzed dehydrocoupling of silanes remains the most active area,¹¹ dehydrocoupling polymerization of germanes¹² and stannanes¹³ is also attracting attention. Group 4 metallocenes have also been successfully applied to other *hetero*dehydrocoupling reactions, including the formation of Sn-Te,¹⁴ Si-N,^{15,16} Si-C,¹⁷ Si-O,¹⁸ and B-N¹⁹ bonds. However, a survey of the literature revealed no report of Si-P bond formation by dehydrocoupling.

Compounds containing Si-P bonds are well known. The first such compounds were hydrides prepared in 1953 by two groups.²⁰ While Aylett, Emeleus, and Maddock prepared the compounds SiH₃PI₂, (SiH₃)₂PI, and (SiH₃)₃P by the reaction of SiH₃I with white phosphorus,^{20a} Friz obtained SiH₃PH₂ by the pyrochemical reaction of SiH₄ and PH₃ at 450 °C.^{20b} Four years later, Kuchen and Buchwald obtained Me₃SiPPh₂ by reaction of trimethylchlorosilane with the sodium cleavage product of

tetraphenyldiphosphine.²¹ Subsequently, Parshall and Lindsey²² developed a general synthesis of alkylsilylphosphines using the metathesis of alkylchlorosilanes with alkyllithium compounds and phosphines. More recently, many Si-P containing compounds have been prepared. Some examples of the more commonly used methods are the following (Eq. 2.1 - 2.4):²³

(1) Reaction of a chlorosilane with an alkali metal phosphide. e.g.

$$PhPK_2 + 2 (CH_3)_3SiCl \longrightarrow PhP[Si(CH_3)_3]_2$$
 Eq. 2.1

(2) Wurtz/Grignard type reactions of alkylphosphorus chloride, or arylphosphorus chloride, with chlorosilane in the presence of sodium or magnesium, e.g.

$$(CH_3)_3 CPCl_2 + 2 (CH_3)_3 SiCl \xrightarrow{Mg/THF} (CH_3)_3 CP[Si(CH_3)_3]_2$$
 Eq. 2.2

(3) Reaction of a silyltriflate with an organic phosphine. e.g.

$$3 R^{1}R^{2}Si(OSO_{2}CF_{3})_{2} + 3 PhPH_{2} \xrightarrow{6 NEt_{3}} (R^{1}R^{2}Si-PPh)_{3}$$
 Eq. 2.3

(4) Reaction of a disilene with white phosphorus, e.g., 24



Compounds containing Si-P bonds are of interest both because of the reactivity of the Si-P bond and the donor properties of the lone pair on the phosphorus.²⁵ Due to the

highly reactive Si-P bond, organosilvlphosphines offer considerable potential for synthesis. Some novel organophosphorous and organophophorus-metal compounds have been prepared using organosilylphosphines as synthons e.g. $[Co_4(\mu^3-PPh_3)_4](PPh_3)_4]$ was prepared from the reaction of CoCl₂·2PPh₃ with (Me₃Si)₂PPh.²⁶ On the other hand, phosphorus-containing compounds play an important role as ligands. Cyclic multidentate ligands are especially interesting for the synthesis of complexes with a rigid stereochemistry and with defined redox and magnetic properties, as shown by numerous investigations of macrocycles with nitrogen and sulfur atoms as hard and soft donor centers, respectively.²⁷ Although they are considered stereochemically superior to analogous acvelic phosphane ligands and the need for such ligands is great,²⁸ only a few cyclic phosphorus ligands, such as phospha crown ethers, have been reported due to the difficulties in preparation. Among such cyclic compounds, six-membered siliconphosphorus heterocycles have been proposed as catalyst ligands owing to the steric accessibility of the transition metal. Schumann and Benda prepared and studied nonaphenylcyclotrisilatriphosphane.²⁹ Driess and co-workers have reported several studies of phospha crown ethers, and other compouds containing Si-P bonds by the reaction of chlorosilanes and lithium phosphides.³⁰ 1.3.5-triphospha-2,4.6-trisilacyclohexanes were successfully prepared by this group using chlorosilanes and lithium phosphides as the starting materials. For example, 1,3,5-Tricvclohexyl-2.4,6-tris(o-methylphenyl)-1.3,5triphospha-2,4,6-trisilacyclohexane was obtained from the reaction shown in Eq. 2.5. Recently, template syntheses of such compounds have also been reported.³¹

$$3 \xrightarrow{R} Si \xrightarrow{Cl} + 3 Cy - P \xrightarrow{Li}_{H} \xrightarrow{3 BuLi}_{-6 LiCl} \xrightarrow{R} Si \xrightarrow{H} \xrightarrow{Cy}_{R} Si \xrightarrow{R} Eq. 2.5$$

$$(R = -)$$

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The near absence of transition metal complex catalyzed reactions of P-H compounds is in striking contrast to the catalytic chemistry of Si-H. An early study of reactions of phenylsilane and CpCp*TiMe₂, or Cp₂TiMe₂, in the presence of phosphines afforded needle-shaped crystalline products which were initially thought to be all-trans hexaphenylcyclohexasilane.³² In the present work attempts were made to use this method to synthesize the all-trans cyclohexamers of other primary arylsilanes. Several 4alkoxyphenylsilanes were tried with CpCp*TiMe₂ and Cp₂TiMe₂ along with phenyl- and cyclohexylphosphines. In none of these reactions were cyclohexasilanes produced. However, isolation of di(4-alkoxyphenyl)silanes in 35% yield showed that silane redistribution is a major competitive reaction along with polymerization of these palkoxyphenylsilanes. When 4-tolylsilane was used, a white crystalline product was obtained. Contrary to expectation, it was found that this product was not a cyclohexasilane. but a 1,3,5-triphospha-2,4,6-trisila-cyclohexane. Further study revealed that titanocene catalysed cross-coupling reactions between silanes and phosphines is facile especially with secondary phosphines. This provides a convenient access to a class of silvlphosphine compounds which are moisture and oxygen sensitive. This chapter presents the results of a more detailed examination of this chemistry.

2.2 Results and Discussion

2.2.1 Reactions of silanes and secondary phosphines catalyzed by Cp2TiMe2

The reactions between primary or secondary silanes and Cp_2TiMe_2 are very facile. Without the presence of phosphines, silane oligomers and polymers are the expected products from a reaction of silane and Cp_2TiMe_2 . However, the reaction course is totally altered by the addition of phosphines. In a typical reaction of a silane with Cp_2TiMe_2 , after an induction period ranging from a few seconds to dozens of minutes, the solution turns to dark blue accompanied by gas (H₂ and CH₄) evolution. On addition of a primary or secondary phosphine, the solution turns dark purple, the characteristic color of a titanocene phosphine/phosphido complex. If the phosphine is added before the silane, or together with the silane, the color changes from orange to dark purple progressively in a much longer period with slow gas evolution. Light and heat can speed up the initiation reaction. Although titanocenes, as well as zirconocenes,¹⁰ have been shown to oligomerize and polymerize organosilanes and organophosphines, the reactions of R_nSiH_{4-n} (n = 1 or 2)

Phosphine	Silane	Reaction	Product	Yield (%) ^b
		time [h]		
Ph ₂ PH	p-TolSiH ₃	2	<i>p</i> -TolH ₂ SiPPh ₂	84
			p-TolHSi(PPh ₂) ₂	16
		9	p-TolHSi(PPh ₂) ₂	100 ^d
11	PhSiH ₃	2	PhH ₂ SiPPh ₂	81
			PhHSi(PPh ₂) ₂	19
н	CySiH ₃	2	CyH ₂ SiPPh ₂	100
11	Ph_2SiH_2	2	Ph ₂ HSiPPh ₂	100
"	PhMeSiH ₂	2	PhMeHSiPPh ₂	100
Cy ₂ PH	<i>p</i> -TolSiH ₃	24	<i>p</i> -TolH ₂ SiPCy ₂	24
"	PhSiH ₃	24	PhH ₂ SiPCy ₂	21
"	CySiH ₃	24	CyH ₂ SiPCy ₂	100
"	Ph ₂ SiH ₂	24	Ph ₂ HSiPCy ₂	43
"		24	Ph ₂ HSiPCy ₂	88c
"	PhMeSiH ₂	24	PhMeHSiPCy ₂	100

Table 2.1 Heterodehydrocoupling of secondary phosphines and silanes withCp2TiMe2 as the catalyst^a

a. all the reactions were run at room temperature with ratios of silane to phosphine between 1.1 : 1 to 1.3 : 1, no solvent was used unless otherwise noted, . b. based on integration of ³¹P NMR. c. reaction was run at 55 °C. d. ratio of phosphine to silane was 2 : 1.

and phosphines R_mPH_{3-m} (m = 1 or 2) in the presence of Cp_2TiMe_2 , silylphosphines are the major products instead of silane oligomers/polymers and/or phosphine oligomers. In
other words, heterodehydrocoupling of phosphines and silanes takes place preferentially over homodehydrocoupling of silanes and phosphines respectively. The products from the reactions between some secondary phosphines and primary or secondary silanes catalyzed by Cp_2TiMe_2 are listed in **Table 2.1**. It is evident that the heterodehydrocoupling of secondary phosphines and silanes is very facile in certain cases. The yields are excellent and the selectivity for the formation of monophosphinosilanes is very high. In the cases of *p*-TolSiH₃ and PhSiH₃, diphosphinosilanes can be selectively obtained by increasing the ratios of phosphine to silane.

2.2.1.1 Reactions of primary silanes and Ph₂PH

There are two kinds of major products obtained from the Cp_2TiMe_2 catalyzed reactions between primary silanes and Ph_2PH , namely RH_2SiPPh_2 and $RHSi(PPh_2)_2$. Although there are three H's available on Si, only two of them are active for heterodehydrocoupling under the reaction conditions used.

p-TolSiH₃ (*p*-Tol = *p*-CH₃C₆H₄) reacted with Ph₂PH in the presence of Cp₂TiMe₂ producing two major products, *p*-TolH₂SiPPh₂ and *p*-TolHSi(PPh₂)₂. *p*-TolHSi(PPh₂)₂ was produced from the further reaction between *p*-TolH₂SiPPh₂ and Ph₂PH. The ratio between the two products depends on the ratio of the silane to the phosphine. If the ratio is higher than 1:1 in favor of silane, *p*-TolH₂SiPPh₂ is the major product along with a minor amount of *p*-TolHSi(PPh₂)₂ as shown in **Table 2.1**. However, when more Ph₂PH is present than silane, *p*-TolH₂SiPPh₂ is readily converted to *p*-TolHSi(PPh₂)₂. A reaction with a ratio of 2:1 (Ph₂PH : *p*-TolSiH₃) showed that all *p*-TolH₂SiPPh₂ was converted to *p*-TolHSi(PPh₂)₂. In the final reaction mixture, *p*-TolHSi(PPh₂)₂ was found as the only heterodehydrocoupling product and no *p*-TolH₂SiPPh₂ was detected. *p*-TolHSi(PPh₂)₂ was separated from the reaction mixture as a white solid in 75% isolated yield. ¹H NMR, ²⁹Si NMR and ³¹P NMR spectra and MS

confirmed the assignment for this compound (Fig. 2.1). As can be seen, the triplet resonance at 5.54 ppm in Fig. 2.1C, which is assignable to Si-H, collapsed into a singlet with ^{31}P decoupled (Fig. 2.1D). The ^{29}Si spectrum showed a triplet at -11.6 ppm with ¹H decoupled (Fig. 2.1A) while with ¹H coupled a doublet of triplets is observed (Fig. 2.1B). All these results support a structure in which two phosphorus atoms are present and one H is attached to the Si.

The stepwise conversion from silane to monophosphinosilane then to diphosphinosilane was explicitly shown by an NMR experiment. Fig. 2.2 shows an arrayed ³¹P NMR experiment. The reaction was run with a ratio (Ph₂PH to *p*-TolSiH₃) of 2 : 1 and 3% Cp₂TiMe₂ per silane, and C₆D₆ was employed as solvent. The slower reaction rate compared with the ones listed in **Table 2.1** is due to the lower concentration with the use of C₆D₆. As can be seen from Fig. 2.2, *p*-TolH₂SiPPh₂ was produced first (indicated by the resonance at -72 ppm), then *p*-TolHSi(PPh₂)₂ (resonance at -64 ppm) appeared as the result of further dehydrocoupling between *p*-TolH₂SiPPh₂ and Ph₂PH (Eq. 2.6). The conversion from *p*-TolSiH₃ to *p*-TolHSi(PPh₂)₂ was not complete even after the 10.5 hours. This observation indicates that *p*-TolSiH₃ has higher activity toward heterocoupling than *p*-TolH₂SiPPh₂, due either to higher steric encumbrance or lower complexing ability of the latter and also suggests the reactivity of Si-H follows the order:

$RH_2Si-H > P-RHSi-H > P_2RSi-H$

$$\begin{array}{c} H \\ R-Si-H + H-PPh_2 \xrightarrow{Cp_2TiMe_2} -H_2 \xrightarrow{H} R-Si-PPh_2 \xrightarrow{+Ph_2PH} R-Si-PPh_2 \xrightarrow{H} R-Ph_2 \xrightarrow{H} R-Ph_2 \xrightarrow{H} R-Ph_2 \xrightarrow{H}$$



Figure 2.1 ¹H and ²⁹Si NMR spectra of $(p-Tol)HSi(PPh_2)_2$ (in C_6D_6)A. ²⁹Si NMR spectrum with ¹H decoupledB. ²⁹Si NMR spectrum with ¹H couplingC. ¹H NMR spectrum with ³¹P couplingD. ¹H NMR spectrum with ³¹P decoupled





It is interesting that the signals corresponding to Ph_2PH (-40 ppm) and *p*-TolH₂SiPPh₂ (-72 ppm) are broad while the one from *p*-TolHSi(PPh₂)₂ (-64 ppm) is sharp. Evidently, the broadening is not simply due to a large scale paramagnetic relaxation, since all peaks are not equally broadened. It is most likely due to a rapid on and off complexing between Ph₂PH or *p*-TolH₂SiPPh₂ and the small amount of paramagnetic catalytic titanocene species. The sharp resonance of *p*-TolHSi(PPh₂)₂ shows its complexing/decomplexing rate is slower than those of Ph₂PH and *p*-TolH₂SiPPh₂.

Similarly, PhSiH₃ reacted with Ph₂PH under the catalytic influence of Cp₂TiMe₂ to yield Ph₂PSiH₂Ph and PhHSi(PPh₂)₂. At room temperature, a hundred percent conversion was obtained within two hours (based on phosphine) when excess silane was used. As in the case of *p*-tolylsilane, PhHSi(PPh₂)₂ was produced via the further coupling reaction between Ph₂PSiH₂Ph and Ph₂PH. Thus, PhHSi(PPh₂)₂ is favored by excess phosphine while Ph₂PSiH₂Ph is favored by excess silane.

CySiH₃ reacted quantitatively with Ph₂PH in the presence of Cp₂TiMe₂ to give CyH₂SiPPh₂ in 100% yield in 2 hours at room temperature when the silane was in excess. In contrast to *p*-TolSiH₃ and PhSiH₃, only a small amount of CyHSi(PPh₂)₂ was detected when phosphine was in excess. The higher selectivity for the formation of monophosphinosilane, compared to *p*-TolSiH₃ and PhSiH₃, is attributable to the larger steric effect of Cy relative to Ph and *p*-Tol. Under the same conditions, the induction period for the reaction of CySiH₃ with Cp₂TiMe₂ is also longer than that for PhSiH₃ and *p*-TolSiH₃.

It is well known that, under the catalytic effect of Cp_2TiMe_2 , primary silanes are apt to undergo dehydrocoupling to afford silane oligomers and polymers. However, in the above reactions, no such products were detectable upon the completion of the heterodehydrocoupling.

2.2.1.2 Reactions of secondary silanes with Ph2PH

 Ph_2SiH_2 was reacted with diphenylphosphine in the presence of Cp_2TiMe_2 (Eq. 2.7). The reaction went to completion within 2 hours at room temperature and the heterocoupling product, $Ph_2HSiPPh_2$, was obtained as the only product in 100% yield (NMR). No further coupling between $Ph_2HSiPPh_2$ and Ph_2PH was observed. This observation is in conformity with results from primary silanes that the last Si-H bond is inert toward further coupling reaction.

Essentially the same result was obtained with PhMeSiH₂.

(100%, NMR yield)

2.2.1.3 Reactions of primary silanes and Cy2PH

In contrast to the reactions with Ph_2PH , only one major product. RH_2SiPCy_2 , was obtained from the Cp₂TiMe₂ catalyzed reaction between primary silanes and Cy₂PH (**Table 2.1**). The reactions were repeated with various ratios of silane to phosphine with no change in the outcome.

The reaction of *p*-tolylsilane and Cy₂PH catalyzed by Cp₂TiMe₂ was much slower than the reaction with Ph₂PH. Only 24 % of Cy₂PH was converted to *p*-TolH₂SiPCy₂ after 24 hours. No *p*-TolHSi(PCy₂)₂ was found even with excess Cy₂PH. This difference is undoubtedly due to the steric hindrance of the bulkier Cy group which makes the further activation of the second Si-H too difficult to undergo any further crosscoupling. At higher temperature, the reaction is faster, but homocoupling of *p*-TolSiH₃ competes with the heterodehydrocoupling reaction. When the reaction was run at 55 °C, after 24 hours, the yield of *p*-TolH₂SiPCy₂ was 27% (based on ³¹P NMR integration) while the p-TolSiH₃ was totally consumed. The observed broad ¹H NMR peaks can be assigned to Si-H and Ar-H suggesting that silane polymers and oligomers were formed. Several singlet ³¹P resonances were found between -60 and -46 ppm, which were tentatively assigned to the heterodehydrocoupling products of Cy_2PH and the silane oligomers and polymers.

Similarly, the reaction of PhSiH₃ and Cy₂PH catalyzed by Cp₂TiMe₂ was much slower than the reaction with Ph₂PH. After 24 hours, only 21 % Cy₂PH was converted to PhH₂SiPCy₂, and no PhHSi(PCy₂)₂ was found even with excess phosphine.

As in the cases of phenylsilane and p-tolylsilane, no $CyHSi(PCy_2)_2$ was found from the reaction of $CySiH_3$ and Cy_2PH . However the reaction rate for the formation of CyH_2SiPCy_2 is much faster than in the cases of PhSiH_3 and p-TolSiH_3. CyH_2SiPCy_2 was obtained from the reaction in 100% yield within 24 hours at room temperature when silane was in excess. This reaction rate difference may result from the difference of electronic effect between Cy group and Ph or p-Tol group. Further work with acyclic nalkyl silanes should be helpful to elucidate the reaction in more detail.

2.2.1.4 Reactions of secondary silanes with Cy2PH

From the reaction of Ph_2SiH_2 and Cy_2PH catalyzed by Cp_2TiMe_2 at room temperature, $Ph_2HSiPCy_2$ was obtained as the only product in 43% yield (by NMR) within 24 hours. No further coupling between $Ph_2HSiPCy_2$ and Cy_2PH was observed. This observation is in conformity with previous results that the last Si-H bond is inert toward further coupling reaction. At higher temperature(55 °C), the reaction goes faster, and 88% conversion of Cy_2PH to $Ph_2HSiPCy_2$ was obtained in 24 hours.

PhMeSiH₂ reacted with Cy₂PH in the presence of Cp₂TiMe₂ affording PhMeHSiPCy₂ in 100% yield (by NMR) within 24 hours at room temperature. As in the case of Ph₂SiH₂, no further heterocoupling reaction leading to PhMeSi(PCy₂)₂ was observed, implying that the Si-H in PhMeHSiPCy₂ is also inactive for heterocoupling reactions.

The difference in the results between Ph_2SiH_2 and $PhMeSiH_2$ is probably due to different electronic and steric effects of Ph and Me groups, but to distinguish between the contributions of electronic and steric effects would require much more detailed experiments.

2.2.2 Reactions of silanes and secondary phosphines catalyzed by CpCp*TiMe₂

It is well known that CpCp*TiMe₂ is also an active precatalyst for the polymerization of silanes but the reaction is much slower than with Cp₂TiMe₂.^{32d} The present study showed that CpCp*TiMe₂ is also active for some silane-phosphine heterodehydrocoupling reactions (**Table 2.2**). However, some differences have been observed compared with the cases of Cp₂TiMe₂. With CpCp*TiMe₂ as the precatalyst, the heterocoupling reactions between *p*-TolSiH₃ or PhSiH₃ and Ph₂PH were faster than with Cp₂TiMe₂ under the same conditions. On the other hand the heterodehydrocoupling reaction of Ph₂PH and CySiH₃ was much slower than with Cp₂TiMe₂. In the cases of Ph₂SiH₂, and PhMeSiH₂, no cross-coupling was observed with a CpCp*TiMe₂ catalyst after several days at room temperature. However, when the reactions were run at 55 °C, Ph₂HSiPPh₂ or PhMeHSiPPh₂ was obtained in 100% yield within 12 hours. These patterns again reflect the delicate balance of steric effects influencing the rates of metallocene catalyzed dehydrocoupling reactions.

With Cy₂PH, slow reactions were observed with primary silanes. In the cases of p-TolSiH₃ and CySiH₃, the yields for corresponding products, p-TolH₂SiPCy₂ and CyH₂SiPCy₂, were only 20% and 1.3% respectively after 4 days. Both are slower than with Cp₂TiMe₂ as the catalyst. At 55 °C, p-TolSiH₃ homocoupling became a competitive

reaction, while in the case of the CySiH₃ heterocoupling was still the dominant reaction and CyH_2SiPCy_2 was obtained in a 76% yield after 24 hours.

With CpCp*TiMe₂ as catalyst, no cross-coupling reactions were observed between Ph_2SiH_2 , or $PhMeSiH_2$ and Ph_2PH when the reactions were run at room temperature. At 55 °C, $Ph_2HSiPCy_2$ and $PhMeHSiPCy_2$ were obtained in a yield of 75% and 72% respectively after 24 hours.

Phosphine	Silane	Reaction time [h]	Product	Yield (%) ^b
Ph ₂ PH	p-TolSiH ₃	2	p-TolH ₂ SiPPh ₂	100
	PhSiH ₃	2	PhH ₂ SiPPh ₂	100
	CySiH ₃	4 days	CyH ₂ SiPPh ₂	68
	Ph_2SiH_2	<u>3 days</u>	No coupling observed	
		12	Ph2HSiPPh2	100°
	PhMeSiH ₂	3 days	No coupling observed	
		12	PhMeHSiPPh ₂	100c
Cy ₂ PH	<i>p</i> -TolSiH ₃	4 days	p-TolH2SiPCy2	20
	CySiH ₃	24	CyH ₂ SiPCy ₂	1.3
		24.	CyH ₂ SiPCy ₂	76 ^c
	Ph_2SiH_2	24	No coupling observed	
		24	Ph ₂ HSiPCy ₂	75°
	PhMeSiH ₂	24	No coupling observed	
		24	PhMeHSiPCy ₂	72°

Table 2.2 Heterodehydrocoupling of secondary phosphines and silanes with CpCp*TiMe₂ as the catalyst ^a

a. all reactions were run at room temperature using 3-5 mol% CpCp*TiMe₂(based on silane); the ratios of silane to phosphine were between 1.1 : 1 to 1.3 : 1. b. based on integration of ³¹P NMR. c. reactions were run at 55 °C.

With $CpCp*TiMe_2$ as the precatalyst, the initiation time is longer than with Cp_2TiMe_2 . In some cases, illumination with a 100 W tungsten lamp was used to accelerate

the initiation of the reaction. The solution turned from orange to purple instead of dark blue as in the cases where Cp_2TiMe_2 was used. Mild gas evolution was observed accompanying the color change.

Unlike the case of Cp₂TiMe₂ as the catalyst, CpCp*TiMe₂ catalyzed the reaction of equimolar *p*-TolSiH₃ and Ph₂PH to yield *p*-TolH₂SiPPh₂ as the only product (**Eq. 2.8**). When the ratio of Ph₂PH to silane was 2:1, *p*-TolH₂Si(PPh₂)₂ was found only in 5% yield. This is in contrast to the reaction with Cp₂TiMe₂ where *p*-TolHSi(PPh₂)₂ can be obtained as the only product through further heterodehydrocoupling of *p*-TolH₂SiPPh₂ and Ph₂PH by employing more Ph₂PH. Thus with CpCp*TiMe₂ as the catalyst monophosphinosilanes can be selectively obtained as the only product from the cross-coupling reactions of secondary phosphines and silanes.

RSiH₃ + Ph₂PH
$$\xrightarrow{CpCp*TiMe_2}_{-H_2}$$
 RH₂SiPPh₂ Eq. 2.8
(R = Ph or *p*-Tol)

2.2.3 Reactions of silanes and primary phosphines catalyzed by Cp₂TiMe₂

A notable feature of the above silane-phosphine heterodehydrocoupling reactions is that all the products obtained have a Si-H moiety. Therefore, only two kinds of possible product can be obtained from the reactions of primary silanes and secondary phosphines. The reactions of primary phosphines and silanes gave some unexpected results.

Although it was expected that the lower steric hindrance of the primary phosphines would make the heterodehydrocoupling easier, the results (**Table 2.3**) showed that, with Cp_2TiMe_2 as the catalyst, no heterodehydrocoupling reactions of phenylphosphine (PhPH₂) and silanes could be detected, while some slow but interesting

heterodehydrocoupling reactions were noticed with the bulkier cyclohexylphosphine $(CyPH_2)$.

The heterocoupling reactions of CyPH₂ and CySiH₃, Ph₂SiH₂ or PhMeSiH₂ lead only to monophosphinosilanes over a period of days. The reaction rates are too slow to be of any practical interest. However, with *p*-TolSiH₃ and PhSiH₃, the reactions are faster. Unlike the silanes, the two P-H bonds of CyPH₂ are both active, and this provides a route to longer chains with alternating Si and P. In the reaction of CyPH₂ and p-tolylsilane in the presence of Cp₂TiMe₂, *p*-TolH₂SiPHCy was observed first, then (*p*-TolH₂Si)₂PCy appeared. This stepwise chain-growth was explicitly observed by NMR. The ³¹P NMR of the reaction mixture shows a resonance at -143 ppm. With ¹H coupling the resonance is a doublet, which suggests one H is attached to the P. The resonance of the corresponding H was found at 4.8 ppm. This species can be assigned as *p*-TolH₂SiPHCy. The next species to appear is (*p*-TolH₂Si)₂PCy. Its ³¹P resonance was found as a singlet at -182 ppm and showed no P-H coupling. The Si-H was found as a doublet at 4.9 ppm in the ¹H spectrum. Decoupling the ³¹P resonance at -182 ppm collapsed the ¹H doublet at 4.9 ppm to a singlet.

The cross-coupling reaction continued to form p-TolHSi(PHCy)₂ and some other longer chains with alternating Si and P. The resonances found at -168 to -170 ppm can be assigned to the P's in the middle of the chains while the resonances at -130 to -135 ppm are assignable to the P's at the ends. Two days later, 1,3,5-tri(cyclohexylphospha)-2,4,6-tri(ptolylsila)cyclohexane appeared as a white crystalline precipitate. The isolated yield reached 30% after four weeks. Eventually, all the other ³¹P NMR resonances assignable to CyPH₂ and acyclic chain species were no longer detectable.

1,3,5-tri(cyclohexylphospha)-2,4,6-tri(*p*-tolylsila)cyclohexane was characterized by NMR, IR, mass spectrum and elemental analysis. Its ¹H NMR spectrum (**Fig. 2.3A**) shows a multiplet at 5.94 ppm which can be assigned to the H on Si. Compared with the chemical shifts of primary silane oligomers and polymers,³³ this chemical shift is at a lower





field suggesting that the Si might be attached to P. The ²⁹Si resonance was found at -15 ppm which is also at an unusually low field for silane oligomers and polymers. Once again, an attachment of P can be the explanation for the low field chemical shift. The presence of the phosphine segment in the compound is confirmed by the multiplet resonances at 0.7-2.3 ppm in the ¹H NMR spectrum, assignable to Cy from the phosphine. The ³¹P resonance was found at -162 ppm which is also hard to assign to phosphine oligomers and polymers.⁶ When the ³¹P resonance at -162 ppm was decoupled, the multiplet ¹H resonance at 5.95 ppm collapsed into a singlet (**Fig. 2.3B**) implying the multiplet is due to the P coupling. However, the absence of an H on P suggests that there is no P-H residue in this compound, otherwise it should be easily recognized by the large P-H coupling.



tolylsila)cyclohexane (KBr)

The IR spectrum (Fig. 2.4) shows only one sharp peak at 2104 cm⁻¹ confirming the existence of only Si-H or P-H in this compound. Mass analysis showed a molecular weight of 702 which matches the formula of $(C_{13}H_{19}SiP)_3$. Elemental analysis is also in conformity with the assignment. Based on these results, this compound is assigned as 1,3,5-tri(cyclohexylphospha)-2,4,6-tri(p-tolylsila)cyclohexane. It is believed that this compound has an all-trans structure with all the p-Tol and Cy groups at the equatorial positions by comparing with the compounds reported by Driess.³⁰

The same sequence of reactions was observed with *p*-propylphenylsilane and phenylsilane. Similar 1,3,5-triphospha-2,4,6-trisila cyclic hexamers were observed. In the case of phenylsilane, 1,3,5-tri(cyclohexylphospha)-2,4,6-tri(phenylsila)cyclohexane³⁰ was obtained as nice crystals in 53% isolated yield within two weeks. Its solubility is lower than 1,3,5-tri(cyclohexylphospha)-2,4,6-tri(*p*-tolylsila)cyclohexane.

Phosphine	Silane	Reaction time [h]	Product	Yield(%)(NMR, based on phosphine)
PhPH ₂	p-TolSiH3	24	No coupling observed	
	PhSiH ₃	24	No coupling observed	
	CySiH ₃	24	No coupling observed	
	Ph_2SiH_2	24	No coupling observed	
	PhMeSiH ₂	24	No coupling observed	
СуРН ₂	p-TolSiH3	3	<i>p</i> -TolH ₂ SiPHCy	3.3
			<i>p</i> -TolHSi(PHCy) ₂	0.3
		4 weeks	c-[p-TolHSiPCy]3	(30)#
	PhSiH ₃	3	PhH ₂ SiPHCy	8.5
			PhHSi(PHCy) ₂	1.2
		4 weeks	c-(CyPSiHPh)3	(53)#
	CySiH ₃	3	No coupling observed	
		24	CyH ₂ SiPHCy	3
	Ph_2SiH_2	24	Ph ₂ HSiPHCy	2
	PhMeSiH ₂	3	No coupling observed	
		24	PhMeHSiPHCy	<1

Table 2.3 Dehydrogenative cross-coupling between primaryphosphines and silanes in the presence of Cp2TiMe2*

*Reactions were run at room temperature using 3-5 mol% Cp_2TiMe_2 as of silane. The ratio of silane to phosphine was between 1.1 to 1.3. # isolated yield.

2.2.4 Reactions of silanes and primary phosphines catalyzed by CpCp*TiMe2

2.2.4.1 Reactions of secondary silanes and primary phosphines catalyzed by CpCp*TiMe2

 $CpCp*TiMe_2$ is less active than Cp_2TiMe_2 in catalyzing the cross-coupling between secondary phosphines and secondary silanes. However, it catalyzes the heterodehydrocoupling reactions of both PhPH₂ and CyPH₂ with silanes while Cp_2TiMe_2 catalyzes only CyPH₂ cross-coupling. The CpCp*TiMe₂ catalyzed reactions and products with secondary silanes and primary phosphines are listed in **Table 2.4**.

Table 2.4 Dehydrogenative cross-coupling between primary phosphines and secondary silanes in the presence of CpCp*TiMe₂

Phosphine	Silane	Reaction time [h]	Product	Yield (%) (NMR, based on phosphine)
PhPH ₂	Ph_2SiH_2	12	Ph ₂ HSiPHPh	50
	PhMeSiH ₂	6	PhMeHSiPHPh	100
CyPH ₂	Ph_2SiH_2	24	Ph ₂ HSiPHCy	100
	PhMeSiH ₂	2	PhMeHSiPHCy	100

The CpCp*TiMe₂ catalyzed reaction of Ph_2SiH_2 and CyPH₂ went to completion within 24 hours at room temperature to give $Ph_2HSiPCyH$ as the only product in 100% yield (by NMR). No further coupling between $Ph_2HSiPCyH$ and $CyPH_2$ or Ph_2SiH_2 was observed, suggesting that the Si-H and P-H bonds are inert for further heterocoupling under these conditions.

PhMeSiH₂ reacted with CyPH₂ in the presence of CpCp*TiMe₂ affording CyHP-SiHPhMe in 100% yield (by NMR) within 2 hours at room temperature. As in the case of Ph₂SiH₂, no further heterocoupling reaction leading to PhMeSi(PHCy)₂ or CyP(SiHPhMe)₂ was observed, implying that the Si-H and P-H in CyHP-SiHPhMe are also inactive for further heterocoupling reactions with CpCp*TiMe₂ as the precatalyst.

The low activity of Si-H in CyHPSiHPhMe and Ph₂HSiPCyH is expected compared with cases using Cp₂TiMe₂ as catalyst. The unexpected low activity of P-H in the products may due to the larger steric hindrance.

The difference in the results between Ph_2SiH_2 and $PhMeSiH_2$ is probably due to different electronic and steric effects of Ph and Me groups

2.2.4.2 Reactions of primary silanes and primary phosphines catalyzed by CpCp*TiMe2

CpCp*TiMe₂ behaves similarly to Cp₂TiMe₂ for coupling CyPH₂ with *p*-tolylsilane. An NMR experiment showed a reaction sequence similar to that of Cp₂TiMe₂. *p*-TolH₂SiPHCy was the initial product followed by CyP[SiH(*p*-Tol)]₂. Then, uncharacterized longer chains appeared. The cyclic 1,3,5-triphospha-2,4,6-trisila hexamer was the final product. However, its formation was slower compared to the reaction with Cp₂TiMe₂ as the catalyst. This may be attributable to the bulkier Cp* group hindering the cyclization of Si-P chain.

White needle-shaped crystals of the cyclic product were obtained from the reaction of PhSiH₃ and PhPH₂ catalyzed by CpCp*TiMe₂. This compound is sparingly soluble in benzene and toluene. Its ¹H NMR spectrum showed multiplet resonances at 6.18 ppm (Si-H), 6.7-7.0 and 7.5-7.8 ppm (Ph-H). Its IR (KBr) spectrum showed a band at 2106 cm⁻¹ for v_{Si-H} . A broad resonance was found at -162 ppm in its ³¹P NMR spectrum. Based on these results, which are comparable to those of 1,3,5-tri(cyclohexylphospha)-2,4,6-tri(*p*tolylsila)cyclohexane, this compound was assigned as a 1,3,5-tri(phenylphospha)-2,4,6tri(phenylsila)cyclohexane ((PhP-SiHPh)₃).³⁰ 1,3,5-tri(phenylphospha)-2,4,6-tri(*p*-Tolsila)cyclohexane was obtained when *p*-tolylsilane was used instead of phenylsilane. The ¹H NMR spectrum of this compound showed multiplet resonances at 6.18 (Si-H), 6.6-6.9, 7.4-7.8 ppm (Ph-H and *p*-Tol-H) and a singlet at 1.80 ppm (CH₃). The ³¹P NMR spectrum showed a broad resonance at - 162 ppm. The v_{Si-H} was found at 2104 cm⁻¹ (IR).

2.2.5 Discussion of Mechanism

2.2.5.1 Mechanism with Cp₂TiMe₂ and CpCp*TiMe₂ as the catalysts.

In the course of attempts to elucidate the involvement of titanocene in catalytic reactions, great effort has been made to capture the possible intermediates. Both $Cp_2Ti(II)$ and $Cp_2Ti(III)$ have been proposed as the intermediates. While the existence of $Cp_2Ti(III)$ species in titanocene catalyzed reactions has been unambiguously proven by the isolation of several $Cp_2Ti(III)$ intermediates,³ no $Cp_2Ti(II)$ species has been obtained as a discrete compound.

Based on the available information and our present results, a mechanism is proposed (Scheme 2.1) to rationalize the heterodehydrocoupling of silanes and phosphines.

The initiation reactions between Cp_2TiMe_2 and silane could be as follows (Eq. 2.9):

Si-Me +
$$Cp_2Ti$$
 H Cp_2TiMe_2 + Si-H Cp_2Ti Me + CH₄ Eq. 2.9

Reductive elimination from either Cp₂TiH(Me) (**Eq. 2.10**) or Cp₂Ti(Si)(Me) (**Eq. 2.11**), or both yields Cp₂Ti(II):



Scheme 2.1



With the isolation of several Cp₂Ti(III) species from the Cp₂TiMe₂ catalyzed reactions, it is believed that Cp₂Ti(III) plays a more important role in the catalytic cycle.^{3,34} The probable route for the formation of Cp₂Ti(III) is through the conproportionation of Cp₂Ti(II) and Cp₂Ti(IV) (Eq. 2.12).

$$Cp_2TiMe_2 + Cp_2Ti \longrightarrow 2 Cp_2Ti-Me$$
 Eq. 2.12

Cp₂Ti-Me can further react with Si-H as shown in Eq. 2.13

Si-Me +
$$Cp_2Ti$$
-H $\leftarrow Cp_2Ti$ -Me + Si-H $\leftarrow Cp_2Ti$ -Si + CH₄ Eq. 2.13

Si-Me is always detected in silane/Cp₂TiMe₂ reactions and the existence of Cp₂Ti-Si is supported by the isolation and the characterization of its dimer by X-ray crystallography and NMR.^{3c} Cp_2Ti -Me can also react with P-H in a similar way as shown in **Eq. 2.14.** However, the strong complexing ability of phosphines makes it predictable that the reaction towards the right should dominate. The low tendency of the reaction moving leftwards explains the absence of P-Me from the reaction mixture.

$$Cp_2Ti-H + P-Me - Cp_2Ti-Me + P-H - Cp_2Ti-P + CH_4$$
 Eq. 2.14

Cp₂Ti-H can either react with P-H or Si-H through σ -bond metathesis to form Cp₂Ti-P and Cp₂Ti-Si respectively (**Eq. 2.15, Eq. 2.16**).

$$Cp_{2}Ti-H + P-H \longrightarrow Cp_{2}Ti-P + H_{2} \qquad Eq. 2.15$$

$$Cp_{2}Ti-H + Si-H \longrightarrow Cp_{2}Ti-Si + H_{2} \qquad Eq. 2.16$$

In principle, homocoupling and heterocoupling are both possible, *i.e.* Cp_2Ti-P reacts with P-H for P-P coupling or reacts with Si-H for Si-P coupling, and Cp_2Ti-Si reacts with Si-H for Si-Si coupling, or reacts with P-H for Si-P coupling. The preference for heterocoupling over homocoupling may be attributable to the difference of electronegativities (P - 2.2, Si - 1.9) which may favor hetero- over homocoupling.

The gas evolution observed upon the addition of phosphines was much faster than that from the initiation reaction of Cp₂TiMe₂ and silanes. This suggests that the reactions shown in **Eq. 2.14** and **Eq. 2.15** are faster than the ones in **Eq. 2.13** and **Eq. 2.16**. A remarkable feature of these reactions is the much lower reactivity of the less sterically encumbered phosphines. The reactions with primary phosphines were much slower than with secondary phosphines when Cp₂TiMe₂ was used. No appreciable reaction was observed with PhPH₂ while slow reaction was the case with CyPH₂. Such behavior is counter to that expected for σ -bond metathesis chemistry where the larger groups should hinder the formation of the transition state.³⁵ The observed different reaction rates for primary phosphines and secondary phosphines could be due to the effect of Cp_2Ti-P stability on the reaction rates via formation of a phosphorus-containing titanocene complex that is too stable to sustain the catalytic cycle of the cross-coupling, or homocoupling reactions.

On the other hand, Cp_2Ti -P can form dimers (Eq. 2.17). Compound 10 has been isolated and characterized by X-ray crystallography (Fig. 2.5).⁶



Figure 2.5 Structure of $[Cp_2Ti(\mu-PHCy)]_2$ (10)

The dimerization of Cp₂Ti-P surely does not favor the heterodehydrocoupling, especially since some dimers, such as $[Cp_2Ti(\mu-PHCy)]_2$, are only sparingly soluble in hydrocarbon solvents. The bulkier phosphines, such as secondary phosphines favor the left side of the equilibrium (Eq. 2.17) while the primary phosphines favor the right side. This also is in conformity with the observation that the reaction rates with primary phosphines are much slower than with the secondary phosphines.

While the steric effects of the organophosphines are evident in comparing the products obtained with Ph_2PH and Cy_2PH , the steric effects of the catalysts are also

evident. The bulkier CpCp*TiMe₂ (Cp* = η^5 -pentamethylcyclopentadienyl) catalyzes the cross-coupling of phenylphosphine or cyclohexylphosphine and silanes, whereas Cp₂TiMe₂ shows little activity in doing so. The explanation for this may lie in an unusually stable phosphide-, or hydride-bridged dimer when Cp₂TiMe₂ is the catalyst.⁶ With CpCp*TiMe₂, the dimerization is less favourable due to the greater bulk of the Cp* ligand. This makes the catalytically active monomer more available to the substrates. The Cp* ligand is known to reduce the tendency of CpCp'MX complexes to dimerize. Reactions of diphenylphosphine produced silanes with monophosphinosilane primary and diphosphinosilane when the catalyst was Cp2TiMe2, but only monophosphinosilane could be obtained with CpCp*TiMe2. In this case the bulkier Cp* group hinders the approach of the monophosphinosilane to the catalyst center to undergo further reaction. Apparently, with secondary phosphines, the stability of the Cp₂Ti-P dimer is not high enough to prevent catalysis.

The intermediate roles of Cp₂Ti-Si and Cp₂Ti-P were both tested using $[Cp_2Ti(\mu-HSi(p-Tol)H)]_2$ and $[Cp_2Ti(\mu-PHCy)]_2$ and the corresponding phosphine or silane as the starting materials. Essentially the same heterodehydrocoupling products were obtained as using Cp₂TiMe₂ as a precatalyst. With $[Cp_2Ti(\mu-HSi(p-Tol)H)]_2$ as the catalyst, the reaction occured without an induction period, while with $[Cp_2Ti(\mu-PHCy)]_2$ as catalyst a long induction period was observed. This observation is in conformity with the slow reactions with CyPH₂.

2.2.5.2 Mechanism study with $Cp_2Ti(PMe_3)_2$ as the precatalyst.

Keeping in mind the fact that low valent titanocene species play important roles in the catalytic reactions, and based on the observation that the same results were obtained with $Cp_2Ti(PMe_3)_2$ instead of Cp_2TiMe_2 as the precatalyst for the reaction of *p*-tolylsilane and $CyPH_2$, a parallel study was carried out by Dr. L. Hao in this laboratory to investigate

the heterodehydrocoupling reactions of silanes and phosphines using $Cp_2Ti(PMe_3)_2$ as the precatalyst.³⁶ The results and conclusions of that study are summarized below.

Both catalytic and stoichiometric reactions of $Cp_2Ti(PMe_3)_2$ (22) with RR'PH (R = Ph, R' = Ph or H; R = Cy, R' = H) were carried out. Although the presence of excess PMe₃ reduces the activity of 22 relative to Cp_2TiMe_2 as a heterodehydrocoupling catalyst, it greatly facilitates the observation of intermediate titanocene(III) species by EPR spectroscopy.

$$\frac{Cp_2 Ti(PMe_3)_2}{PhSiH_3 + Ph_2 PH \frac{3-10 \mod \%}{Toluene, 25 \degree C}} PhH_2 SiPPh_2 + (Ph_2P)_2 SiHPh + H_2 \qquad Eq. 2.18$$

In a typical catalytic experiment, depicted in Eq. 2.18, reaction of equimolar amounts of PhSiH₃ and Ph₂PH in the presence of 5 mol % of 22 gave the products PhH₂SiPPh₂ and (Ph₂P)₂SiHPh at ambient temperature.

Scheme 2.2



A series of experiments were performed which demonstrated the occurrence of the reactions shown in Scheme 2.2. A reaction of equimolar amounts of 22 and Ph_2PH at room temperature gave the known phosphido compound 23a cleanly as dark green crystals

in 86% isolated yield.⁹ With a 2:1 molar ratio of 22 to Ph₂PH, 23a and the hydride 24 were formed in a 1:1 ratio, as shown by EPR spectroscopy (Fig. 2.6, 2.7).³⁷ These compounds could result from the oxidative addition of a P-H bond to 22 (or, more likely,



2.051 1.992 1.937

Figure 2.7 EPR spectrum of Cp₂TiPPh₂(PMe₃)(23a)

one of its phosphine dissociation products) to give the intermediate 25. This intermediate then conproportionates with a second molecule of 22 to give an equal mixture of 23a and 24. Compound 25 was not observed, even at low temperatures, presumably due to its rapid reaction with 22. A similar sequence to that shown in Scheme 2.2 occurred in the reactions of 22 with primary phosphines RPH_2 (R = Ph, Cy), to yield the phosphido

compounds $Cp_2Ti(PHR)(PMe_3)$ (23b, R = Ph; 23c, R = Cy), as shown by the EPR spectroscopy (Fig. 2.8). Compound 23b and 23c lose PMe_3 easily to form the



Figure 2.8 EPR spectrum of Cp₂TiPHPh(PMe₃) (23b)

phosphido bridged dimers $[Cp_2Ti(\mu-PHR)]_2$ (26a, R = Ph; 26b, R = Cy). The poor solubility of these dimers pulls the PMe₃ dissociation equilibrium in the direction of 26 by precipitation of the dark purple crystals in high yield (82% for 26a and 81% for 26b) (see Eq. 2.19). On the other hand, 23a can be isolated, either as a consequence of tighter binding of the PMe₃, or due to its more sterically demanding phosphido ligand destabilizing the dimer.⁹ Addition of PMe₃ to a toluene solution of 26a or 26b regenerated 23b and 23c, respectively, proving the reversibility of Eq. 2.19.⁶ No



reaction occurred between 22 and Cy₂PH, presumably because of steric hindrance. The rates of the reactions of 22 with phosphines to give 23 follow the order PhPH₂ > Ph₂PH \sim CyPH₂.

Treatment of a toluene solution of 23a with PhSiH₃ (2 eq.) led to its complete conversion to $Cp_2Ti(PhSiH_2)(PMe_3)$, 27 (Fig. 2.9),³⁶ with the production of Ph₂PSiH₂Ph and a minor amount of (Ph₂P)₂SiHPh. At ambient temperature this reaction took about 2 h and produced a color change from turquoise/green to purple. Addition of Ph₂PH (2 eq.) to this purple solution regenerated 23a fully in 1 h, showing that the conversion of 27 to 23a is about twice as fast as that of 23a to 27. A sample of 27, prepared from Cp₂TiMe₂ and PhSiH₃ in the presence of PMe₃,³⁶ also reacted with Ph₂PH to give 23a and PhH₂SiPPh₂. These results indicate that the reaction most likely proceeds via 24 (Scheme 2.3), even though 24 was not observed in the course of the reaction by EPR spectroscopy.



Figure. 2.9 EPR spectrum of Cp₂TiSiH₂Ph(PMe₃) (27)

A sample of **24**, generated from the reaction of the "grey-green" form of titanocene hydride and PMe₃.^{37b,c} was converted cleanly to **23a** or **27** by adding Ph₂PH or PhSiH₃, respectively. The reactions of **24** with PhSiH₃ or Ph₂PH are complete immediately following mixing at room temperature as shown by the EPR spectra, in contrast to the much slower reactions of **23a** with PhSiH₃, or **27** with phosphine which took place in the

order of hours. Consequently, it is not surprising that the extremely low steady state concentration of 24 makes it difficult to detect by EPR, even at temperatures down to -50 $^{\circ}$ C.

The simplest interpretation of the foregoing experimental results is that the catalytic heterodehydrocoupling reaction involves a sequence of σ -bond metatheses occurring between substrates and Ti(III)-X species, where X = silyl, phosphide or H. Such a cycle is shown in Scheme 2.3.

Given the reactivity patterns of phosphines and silanes determined before, it is surprising that no heterodehydrocoupling reaction occurred between PhSiH₃ and PhPH₂. Compound **23b** does react with PhSiH₃ (2 equiv.) to give **27** at a similar rate to **23a**, and **23b** is regenerated by treating **27** with PhPH₂ (2 equiv.). However, under catalytic conditions, the phosphine reactant is present at a much higher concentration than PMe₃





introduced with the catalyst. Independent EPR measurements clearly show phosphine ligand exchange in 23b in the presence of excess reactant phosphine to give 28 (Scheme 2.4). Among the phosphines studied in these reactions, PhPH₂ is the least basic, but also the least sterically demanding ligand. If the steric factor predominates, then the formation constant for 28 could be high compared to its analogs $Cp_2TiPh_2(PHPh_2)$ and $Cp_2TiPHCy(PHCy_2)$. This in turn could lead to depletion of the reactive intermediates in

the catalytic cycle, as shown in Scheme 2.4. This interpretation is supported by the fact that 28 is the only EPR active species observed for PhPH₂ under catalytic conditions, while a mixture of paramagnetic species is observed with Ph₂PH or CyPH₂.

Based on this reasoning, a reaction of PhSiH₃ and PhPH₂ in a molar ratio of 6:1, in the presence of 10 mol % of 22, was carried out. The heterodehydrocoupling reaction did take place slowly under these conditions with 80% conversion (based on integration of ³¹P NMR spectra) of PhPH₂ to PhHPSiH₂Ph, PhP(SiH₂Ph)₂ and a small amount of higher oligomers in a period of 3 weeks.

It should be noted that no homodehydrocoupling of PhSiH₃ or of RR'PH occurred in any of the reactions described above. Reaction of 22 with excess PhSiH₃ gave first the η^2 -Si-H complex, Cp₂Ti(η^2 -HSiH₂Ph)PMe₃,³⁹ which slowly decomposed to give 27 with evolution of H₂.⁶ No Si-Si coupling products were detected over a period of weeks. It is evident that the presence of excess phosphine suppresses the homodehydrocoupling reactions, either through formation of 27 (silane coupling), or 23 (phosphine coupling). This also leads to the conclusion that all of the σ -bond metatheses of the catalytic cycle shown in Scheme 2.3 require predissociation of the phosphine ligand (Scheme 2.4).

Scheme 2.4



Most of the key intermediates in the $Cp_2Ti(PMe_3)_2$ catalysed reactions are thus easily detected by EPR spectroscopy. The finding that $Cp_2TiH(PMe_3)$ is an intermediate in these reactions supports the proposal that the hydride Cp_2TiH is a key intermediate in the silane and phosphine heterodehydrocoupling reaction.

2.3 Summary

Titanocene has been found to be an effective catalyst for heterodehydrocoupling between silanes and phosphines. This reaction has some generality. Both secondary silanes and primary silanes can be used to couple with phosphines. The reactions with secondary phosphines are much faster than with primary phosphines. Monophosphinosilane and diphosphinosilane can be selectively obtained from the reactions of secondary phosphines and primary silanes. Bulkier phosphines or silanes favor the formation of monophosphinosilane. Primary phosphines slowly react in a stepwise fashion with primary silanes to produce longer chains. All-trans 1,3,5-trisila-2,4,6-triphosphacyclohexanes are obtained in crystal form in some cases. The formation of these products may occur through cyclization of a six membered chain, or through redistribution of some longer chains. The high selectivity towards formation of this kind of product can be attributed to its low solubility and probably to thermodynamic stability of the ring.

This discovery provides a new approach for the synthesis of Si-P containing compounds which are of potential application in synthetic as well as in coordination chemistry. The method has some advantages: (1) The reaction can be carried out under mild conditions. The titanocene catalyzed cross-coupling occurs smoothly at ambient temperature. Dimethyltitanocene and hydrosilanes can be routinely handled and many are commercially available. Most of the other methods^{23c} depend on chlorosilanes and alkali metal phosphides as starting materials. Special care is needed for the handling of these extremely air and moisture sensitive materials, and reactions are carried out at low temperature (e.g. -70 °C) to avoid dangerously violent reactions. (2) The titanocene catalyzed heterodehydrocoupling reaction has the characteristic of high yield and high

selectivity. In the cases using secondary silanes and secondary phosphines, monophosphinosilanes are obtained in excellent yield. While in the cases of primary arylsilanes, both monophosphinosilanes and diphosphinosilanes can be selectively obtained by choosing a suitable catalyst and ratio of silane to phosphine. No side products were found in an appreciable amount. (3) Another feature of this method is that a Si-H bond can be preserved. This active site may be used for the synthesis of other novel compounds.

2.4 Experimental Section

2.4.1 General manipulations

2.4.1.1 Reaction set-up

All manipulations were performed under an atmosphere of argon using Schlenk techniques. Dry, oxygen free solvents were employed throughout. Glassware was flamedried or oven-dried before use. In a typical reaction, the required amount of Cp₂TiMe₂ or CpCp*TiMe₂ was first added to a Schlenk flask and connected to vacuum to remove the air carried by the sample and then the flask was filled with Ar. The procedure was repeated several times. The relevant phosphine and silane were added with micro syringe. Samples for NMR analysis were prepared under Ar.

2.4.1.2 Purification strategy

 $(p-TolHSiPCy)_3$, $(p-TolHSiPPh)_3$, $(PhHSiPPh)_3$ were crystallized from the corresponding reaction solutions by using n-hexane as the solvent. $(PhHSiPCy)_3$ was crystallized from the reaction solution by using benzene as the solvent.

 $Ph_2HSiPPh_2$ can be produced and separated from the reaction of Ph_2PH and Ph_2SiH_2 catalyzed by Cp_2TiMe_2 at room temperature or by $CpCp*TiMe_2$ at about 55 °C. With $CpCp*TiMe_2$ the purification can be accomplished by washing the reaction product with hexane till the washings are colorless and then drying the product *in vacuo*. The low solubility of $Ph_2HSiPPh_2$ and higher solubility of the titanocene species with Cp* (compared with the ones carrying two Cp groups) ensured the convenient separation of this product. With Cp_2TiMe_2 as the catalyst, the purification can be carried out according to the strategy described below.

The monophosphinosilanes and diphosphinosilanes were separated using following procedure. The catalyst was removed first by passing through a short silica gel column. The silica gel was predried in the oven (120 °C), evacuated for one hour while it was hot and then loaded in the column. Benzene was used as the eluent and was removed under vacuum along with the residual substrates, to yield the product.

2.4.2 Materials and Analyses

2.4.2.1 Materials

Cp₂TiMe₂ and CpCp*TiMe₂ were synthesized according to literature procedures.⁴⁰ Silanes were prepared by a standard procedure via the reaction of the corresponding chlorosilanes with LiAlH₄.⁴¹ Phosphines were bought from Strem Chemicals and used as received, or purified by distillation as required.

2.4.2.2 Analyses

Mass spectroscopic analyses were performed by the Mass Spectroscopy Laboratory of the Chemistry Department. A small amount of the purified reaction product was loaded in a melting tube using benzene or hexane as solvent. Then the solvent, along with any other residual volatiles was removed *in vacuo*. The tube was flame sealed to avoid contact with air before analysis.

¹H NMR spectra were recorded on Varian XL-200, and Unity-500 spectrometers using using internal solvent references. ¹H{³¹P} NMR experiments were carried out on the Unity-500. ²⁹Si NMR spectra were recorded on a Varian XL-300 operating at 59.9 MHz using C₆D₆ as solvent and tetramethylsilane as a reference at 0.00 ppm. ³¹P NMR spectra were recorded on a Varian XL-300 operating at 121 MHz, or on Unity-500 at 202.3 MHz and were referenced with 85% H₃PO₄ at 0.00 ppm.

Complete NMR data for all new products are listed in Appendix I and II.

2.4.3 Reactions of phosphines and silanes catalyzed by Cp₂TiMe₂

2.4.3.1 Reactions of secondary phosphines with silanes

The following is a typical procedure used in screening reactions by NMR. All other reactions were carried out in the same way to give the results shown in **Table 2.1**.

p-TolSiH₃ (0.20 mL, 1.42 mmol) was added to Cp₂TiMe₂ (10 mg, 0.05 mmol; 3.5 mol% catalyst per silane). After a while, the solution color changed to dark blue accompanied by gas evolution. Then Ph₂PH (0.20 ml, 1.13 mmol) was added. The solution turned to dark purple along with more rapid gas evolution. The mixture was stirred at room temperature for two hours. ³¹P, ²⁹Si, and ¹H NMR (benzene-d₆, 22°C) showed two products were produced, (*p*-Tol)H₂SiPPh₂ and (*p*-Tol)HSi(PPh₂)₂, with yields of 84% and 16% respectively. (see **Appendix I** for NMR data).

2.4.3.2 Synthesis and isolation of (p-Tol)HSi(PPh₂)₂

p-TolSiH₃ (0.50 mL, 3.6 mmol) was added to Cp₂TiMe₂ (30 mg, 0.15 mmol; 4.2

mol% catalyst per silane). After a while, the solution color changed to dark blue accompanied by gas evolution. Then Ph₂PH (1.20 ml, 6.8 mmol) was added to the mixture. The solution turned to dark purple along with more rapid gas evolution. The mixture was stirred at room temperature for 9 hours. ³¹P NMR (benzene-d₆, 22°C, 121 MHz), and ¹H NMR (benzene-d₆, 22°C, 200 MHz) showed *p*-TolHSi(PPh₂)₂ was the only product. Benzene (1 ml) was added to the sticky mixture. The catalyst was removed by passing the mixture through a short silica gel column using 60 ml benzene as the eluent. The silica gel was predried in a 120 °C oven, pumped under vacuum for one hour and then loaded on the column. A viscous slightly brownish liquid was obtained after the benzene was removed under vacuum... Hexane (2 ml) was added to the liquid and the mixture was put in the refrigerator at 5°C. A white precipitate was obtained in half an hour. The precipitate was washed with cold hexane (0 °C) three times and dried in vacuo. 1.3 g of (*p*-Tol)HSi(PPh₂)₂ (mp. 75-77°C) was obtained (75% isolated yield). MS (CI): m/z (%): 491 (59) [M⁺ + H], 305 (12) [M - PC₁2H₁₀]

2.4.3.3 Reaction of Ph₂PH with p-TolSiH₃ (NMR tube experiment)

p-TolSiH₃ (0.05 mL, 0.35 mmol) was added to a Cp₂TiMe₂ solution (3 mg, 0.01 mmol. in 0.40 ml C₆D₆). After a while, the solution color changed to blue accompanied by gas evolution. Then Ph₂PH (0.15 ml, 0.85 mmol) was added to the mixture. The solution turned to dark purple along with more rapid gas evolution. The reaction was followed with arrayed ³¹P NMR (22 °C, 121 MHz). (p-Tol)H₂SiPPh₂ appeared within 5 minutes and the highest resonance intensity was observed in 6 hours when (p-Tol)HSi(PPh₂)₂ was formed. As more and more (p-Tol)HSi(PPh₂)₂ was produced, the intensity of the (p-Tol)H₂SiPPh₂ resonance decreased. Some residual (p-Tol)H₂SiPPh₂ was still found after 10.5 hours. No signal was observed in the ²⁹Si spectrum due to the triphosphosilane.

2.4.3.4 Reactions of PhPH₂ with silanes

The reaction mixtures were prepared by adding *p*-TolSiH₃ (0.20 mL, 1.42 mmol), PhSiH₃ (0.20 mL, 1.62 mmol), CySiH₃ (0.20 mL, 1.54 mmol), Ph₂SiH₂ (0.30 mL, 1.38 mmol) and PhMeSiH₂ (0.20 mL, 1.45 mmol) respectively to Cp₂TiMe₂ (10 mg, 0.05 mmol). After the solution color changed to dark blue accompanied by gas evolution, PhPH₂ (0.12 ml, 1.13 mmol) was added to the mixture. The solution turned to dark purple. The mixture was stirred at room temperature for 24 hours, no heterodehydrogenative coupling was observed by ³¹P ²⁹Si, or ¹H NMR (benzene-d₆, 22°C).

2.4.3.5 Reactions of CyPH₂ with *p*-TolSiH₃ in the presence of Cp₂TiMe₂ — synthesis of [CyPSiH(*p*-Tol)]₃

p-TolSiH₃ (0.60 ml, 4.26 mmol) and CyPH₂ (0.50 ml, 3.65 mmol) were added to a solution of Cp₂TiMe₂ (10 mg, 0.05 mmol: 1.2 mol% catalyst per silane) in 3 ml of hexane. After thorough mixing, the solution was left to stand unperturbed. The solution turned dark purple with formation of white crystals in a week. The crystals were separated from the solution. washed with hexane and dried in vacuo. More crystals were formed and separated after a further three weeks. The cumulative yield was 0.25 g (30% isolated yield). The product was assigned as (*p*-TolHSiPCy)₃ on the basis of NMR spectra (see **Appendix II**. IR (KBr): v_{Si-H} [cm⁻¹] = 2104: MS (FAB): m/z (%): 703 (3) [M + H], 619 (9) [M - C₆H₁₁]. Anal. Calcd. for (*p*-TolHSiPCy)₃: C 66.7, H 8.1, P 13.2; found: C 66.38. H 8.40, P, 13.02.

2.4.3.6 Reaction of CyPH₂ with PhSiH₃ in the presence of Cp₂TiMe₂ synthesis of (PhHSiPCy)₃

PhSiH₃ (0.35 mL, 2.84 mmol) and CyPH₂ (0.35 ml, 2.56 mmol) were added to a solution of Cp₂TiMe₂ (5 mg, 0.02 mmol; 1 mol% catalyst per silane) in 10 ml of toluene. After thoroughly mixed, the solution was left to stand unperturbed. The solution turned dark purple with formation of white crystals in a week. White crystals were separated from the solution (0.30 g, 53% isolated yield). The product was assigned as (PhHSiPCy)₃ on the basis of NMR data (see **Appendix II**) IR (KBr): v_{SiH} [cm⁻¹] = 2106; FAB MS(*m*-nitrobenzyl alcohol matrix): m/z (%): 661 (4.4) [M+H], 577 (13.3) [M-C₆H₁₁]. Anal. Calcd. for (PhSiH-PCy)₃: C, 65.42; H, 7.78; P, 14.06. Found: C, 65.52; H, 8.10; P, 14.17.]

2.4.3.7 Reactions of CyPH₂ with secondary silanes and CySiH₃

The reaction mixtures were prepared by adding CySiH₃ (0.20 mL, 1.54 mmol), Ph₂SiH₂ (0.30 mL, 1.38 mmol) and PhMeSiH₂ (0.20 mL, 1.45 mmol) respectively to Cp₂TiMe₂ (10 mg, 0.05 mmol). After the solution color changed to dark blue accompanied by gas evolution, CyPH₂ (0.15 ml, 1.13 mmol) was added to the mixture. The solution turned to dark purple. The mixture was stirred at room temperature for 24 hours and periodically checked by ³¹P, ²⁹Si, and ¹H NMR (benzene-d₆, 22°C).

Parallel reactions at 55°C were carried out using the same method except that the temperature was controlled using a silicon oil bath.

2.4.4 Reactions of phosphines and silanes catalyzed by CpCp*TiMe2

2.4.4.1 Reactions of Ph₂PH with *p*-TolSiH₃ and PhSiH₃

p-TolSiH₃ (0.05 mL, 0.35 mmol) was added to CpCp*TiMe₂ (3.9 mg, 0.01 . mmol, 2.8 mol% catalyst per silane). After a while, the solution color changed to brown

accompanied by gas evolution. Then, Ph₂PH (0.05 ml, 0.28 mmol) was added to the mixture. The solution turned to dark purple along with more rapid gas evolution. The reaction was followed with ³¹P NMR (22°C, 121 MHz). (*p*-Tol)H₂SiPPh₂ was found in 100% yield based on phosphine. The reaction was complete in 1.5 hours.

A reaction with PhSiH₃ was run under the identical conditions. Essentially the same result was obtained.

All other reactions with CpCp*TiMe₂ as catalyst were carried out using the same method (see **Table 2.2**).

2.4.4.2 Reaction of Ph₂PH with Ph₂SiH₂

Ph₂SiH₂ (0.30 mL, 1.38 mmol) was added to CpCp*TiMe₂ (13 mg, 0.05 mmol; 3.6 mol% catalyst per silane). After a while, the solution color changed to dark brown accompanied by gas evolution. Then, Ph₂PH (0.20 ml, 1.13 mmol) was added to the mixture. The solution turned to dark purple along with more gas evolution. The mixture was stirred at room temperature for 24 hours. No heterodehydrocoupling was observed by ^{31}P , ^{29}Si , or ¹H NMR (benzene-d₆, 22 °C).

A parallel reaction was run under identical conditions except the temperature was 55 °C. $Ph_2PSiHPh_2$ was produced in a 100% conversion in 12 hours. 0.26 g of product was separated as a white solid (m.p. 104 - 107°C) by washing the solid product several times with hexane (5 ml) till the washings were colorless. The product was dried *in vacuo* (63% isolated yield).

2.4.4.3 Reaction of Ph₂PH with PhMeSiH₂

PhMeSiH₂ (0.20 mL, 1.45 mmol) was added to CpCp*TiMe₂ (13 mg, 0.05 mmol; 3.4 mol% catalyst per silane). After a while, the solution color changed to dark brown

accompanied by gas evolution. Then, Ph_2PH (0.20 ml, 1.13 mmol) was added to the mixture. The solution turned to dark purple along with more gas evolution. The mixture was stirred at room temperature for 24 hours. No heterodehydrocoupling was observed by NMR.

A parallel reaction was run under identical conditions except the temperature was 55 °C. Ph₂HSiPPh₂ was produced in a 100% NMR yield in 12 hours.

2.4.4.4 Reaction of PhPH₂ with Ph₂SiH₂ or PhMeSiH₂

Ph₂SiH₂ (0.28 mL, 1.30 mmol) was added to CpCp*TiMe₂ (13 mg, 0.05 mmol; 3.8 mol% catalyst per silane). After a while, the solution color changed to dark brown accompanied by gas evolution. Then, PhPH₂ (0.11 ml, 1.0 mmol) was added to the mixture. The solution turned to dark purple along with more gas evolution. The mixture was stirred at room temperature for 12 hours. PhHPSiHPh₂ was obtained in 50% yield by NMR analysis.

A reaction of PhPH₂ and PhMeSiH₂ was carried out under the same conditions, 100% NMR yield was achieved in six hours.

2.4.4.5 Reaction of CyPH₂ with Ph₂SiH₂ or PhMeSiH₂

Ph₂SiH₂ (0.28 mL, 1.30 mmol) was added to CpCp*TiMe₂ (13 mg, 0.05 mmol; 3.8 mol% catalyst per silane). After a while, the solution color changed to dark brown accompanied by gas evolution. Then PhPH₂ (0.15 ml, 1.0 mmol) was added to the mixture. The solution turned to dark purple along with more gas evolution. The mixture was stirred at room temperature for 24 hours. CyHPSiHPh₂ was obtained in 100% yield according to NMR analysis.
A reaction of $CyPH_2$ and $PhMeSiH_2$ was carried out under the same conditions, 100% NMR yield was achieved in two hours.

2.4.4.6 Reaction of PhPH₂ with p-TolSiH₃

p-TolSiH₃ (0.50 ml, 3.55 mmol) and PhPH₂ (0.50 ml, 4.54 mmol) were added to a solution of CpCp*TiMe₂ (20 mg, 0.07 mmol; 2 mol% catalyst per silane) in 5.0 ml hexane. After thoroughly mixed, the solution was left unperturbed. The solution turned dark purple progressively with formation of white crystals in three days. In the following days some more white solid was formed. 0.24 g of white solid was separated from the solution after washed with hexane and dried *in vacuo*. (30% isolated yield). The product was assigned as $[(p-Tol)HSiPPh]_3$ on the basis of NMR data (see **Appedix II**). IR (KBr): $v_{Si-H}[cm^{-1}] = 2106$; FAB MS (*m*-nitrobenzyl alcohol matrix): m/z (%): 685 (10) [M⁺ + H].

2.4.5 Reactions of Ph₂PH with *p*-TolSiH₃ in the presence of $\{Cp_2Ti[\mu - HSiH(p - Tol)]\}_2$

 $50 \ \mu\text{I} (0.35 \ \text{mmol}) \text{ of } p\text{-TolSiH3} \text{ and } 50 \ \mu\text{I} (0.28 \ \text{mmol}) \text{ of } Ph_2PH \text{ were added to a} {Cp_2Ti[\mu-HSiH(p-Tol)]}_2 \text{ solution (4.0 mg, 0.007 mmol in 0.40 ml toluene-d_8) in an NMR tube kept in dry ice. The original solution was dark blue. The reaction was followed with an arrayed ³¹P NMR experiment at room temperature. After 12 hours, (p-Tol)H_2SiPPh_2 and (p-Tol)HSi(PPh_2)_2, were found as the major products with yields of 83% and 17% respectively.$

2.4.6 Reactions of Ph₂PH with *p*-TolSiH₃ in the presence of [Cp₂Ti(μ-PCyH)]₂ (NMR experiment)

 $50 \ \mu\text{I} (0.35 \ \text{mmol}) \text{ of } p\text{-TolSiH3} \text{ and } 50 \ \mu\text{I} (0.28 \ \text{mmol}) \text{ of } \text{Cy}_2\text{PH} \text{ were added to a} [Cp_2\text{Ti}(\mu\text{-PCyH})]_2 \text{ solution } (3.0 \ \text{mg}, \text{ in } 0.40 \ \text{ml toluene-d}_8) \text{ in an NMR tube kept in dry} ice. The original solution was dark purple. Some [Cp_2\text{Ti}(\mu\text{-PCyH})]_2 was not dissolved. The reaction was followed by ³¹P NMR at room temperature. Heterodehydrocoupling was observed after 24 hours. After 3 days, (p-Tol)H_2SiPPh_2 and (p-Tol)HSi(PPh_2)_2, were found as the major products with yields of 96% and 4% respectively.$

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CHAPTER 3

HOMOGENEOUS HYDROSILATION/HYDROGENATION REACTIONS OF PYRIDINES AND QUINOLINE WITH PHENYLMETHYLSILANE CATALYZED BY TITANOCENES

3.1 Introduction

Pyridine is an aromatic molecule with a resonance stabilization energy (35 kcal/mol) similar to that of benzene. It contains a delocalized 6π -electron system, and its molecular dimensions (C-C, 1.397 Å; C-H, 1.084 Å) are extremely close to those of benzene. However, pyridine differs from benzene in its basicity and polarity (dipole moment, 2.26 D). It has a lone pair of electrons on the nitrogen atom.¹ This supplies the basis for the chemistry of pyridine which is quite different from benzene. The N atom in a pyridine ring is able to form a dative bond with a proton or a metal atom center and other Lewis acids by donating its lone pair of electrons. This property of pyridine makes it more susceptible to activation than benzene, through the formation of complexes at the N site.

Completely or partially hydrogenated pyridine rings occur widely in many synthetic and naturally occurring compounds such as the alkaloids. One of the strategies for synthesis of alkaloids is based on selective reduction of a pyridine precursor by hydride addition or catalytic hydrogenation.² Pyridines and quinolines are also some of the more common heterocyclic compounds in petroleum and coal-derived liquids. Hydrogenation of these compounds is an essential part of catalytic hydrodenitrogenation(HDN) of these liquid fuels reducing the emissions of NO_x upon their combustion. Thus, reduction of pyridines through hydride addition and hydrogenation has attracted much attention, and been extensively studied.³ Electrocatalytic hydrogenation of pyridine was also reported by Kirilyus.⁴ Lithium aluminum hydride has been widely used in reducing organic compounds,⁵ but, it only reacts very slowly with pyridine. Pyridine can even be used as a solvent in the reduction of ketones with lithium aluminum hydride.⁶ However, lithium triethylborohydride (a superhydride) was reported as an effective agent for the reduction of pyridines.⁷ Pyridine rings can be completely and easily reduced in high yields by lithium triethylborohydride.

Reduction of pyridines through catalytic hydrogenation is another important way to obtain reduced pyridine ring products, and an important step in fuel processing as well. Most of the existing methods use heterogeneous catalysts based on platinum-group metals. The high resonance energy of the pyridine ring makes it quite difficult to hydrogenate. In most cases harsh conditions (high temperature, high pressure) are required to carry out such hydrogenation. A systematic study by Ryashentseva⁸ showed that selective hydrogenation of aryl-substituted pyridines, isoquinolines, etc., can be achieved by using rhenium heptasulfide as the catalyst. However, high hydrogen pressure (130-200 atm) and high temperature (200-280 °C) are essential for success. In an HDN process, 300-450 °C and ≥ 2000 psi H₂ are claimed as the standard conditions.⁹

Fish's group at Berkeley did some elegant research on the homogeneous catalytic hydrogenation of pyridines, and quinolines with rhodium and ruthenium complexes.¹⁰ Some regioselectively hydrogenated products were obtained with quinolines, but with pyridines the rings were completely hydrogenated. The usual conditions used were 40-80°C and 500 psi of H₂. Other homogeneous systems of Fe, Mn, Rh, Os, Ru, and Ir complexes have been studied by other groups.¹¹

Although hydrogenation of pyridines has been extensively studied, the hydrosilation of pyridines remains underdeveloped. The synthesis of pyridine complexes of titanocene by reactions of hydrosilane with Cp_2TiMe_2 in the presence of pyridine was studied by Mu^{12} and Xin.¹³ Mu Prepared crystalline complexes of the type:

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The complex 29, and analogs with different silyl ligands, were characterized in solution by EPR spectroscopy, but no crystal structures were obtained. On the other hand, the structure of 30 was confirmed by single crystal X-ray analysis, but neither NMR, or EPR spectroscopy gave any clue to its structure.

Subsequently, a preliminary study by Woo and Harrod showed that Cp_2TiMe_2 and $CpCp*TiMe_2$ were catalytically active for the hydrosilation of pyridine.¹⁴

Although hydrosilation of ketones, esters, olefins, and alkynes has been extensively studied,¹⁵ to our knowledge, there is no report of hydrosilation of aromatic nuclei under homogeneous catalytic conditions. Cook and Lyons reported the first example of hydrosilation of pyridines in the 1960's using palladium and other heterogeneous catalysts.¹⁶ Product yields were modest and there appears to have been no further exploitation of this reaction. Since pyridine rings are widely found in pharmaceutical and natural compounds, and pyridine chemistry is of great interest to synthetic chemists, it was decided to investigate the hydrogenation/hydrosilation of pyridines, catalyzed by titanocenes in more detail. The present chapter presents the results of such a study.

3.2 Results

3.2.1 Hydrosilation/hydrogenation of pyridine with PhMeSiH2 and Cp2TiMe2

The reaction between Cp_2TiMe_2 and PhMeSiH₂ is strongly affected by the presence of pyridine. In the absence of pyridine, Cp₂TiMe₂ catalyses the dehydrogenative coupling of the silane to low molecular weight oligosilanes. As the reaction occurs, the solution changes from orange to dark blue. In the presence of pyridine, the reaction mixture changes color from orange to violet and eventually to dark purple. The reaction was monitored by ¹H NMR spectroscopy, which showed that the pyridine nucleus was undergoing reduction. After nearly complete reaction of pyridine, a single product was isolated from the mixture by fractional distillation. Based on ¹H NMR (Fig. 3.1) along with decoupling, COSY, and ¹³C NMR experiments, and its mass spectrum, this product was identified as N-(phenylmethylsilyl)-1,2,3,4-tetrahydropyridine. All the CH_2 hydrogen pairs are expected to be diastereotopic due to the existence of the chiral Si in the molecule. Selective decoupling experiments and simulation showed that the ¹H NMR spectrum of this product is a complicated second order spectrum rather than a simple first order one. The complexity arises from the three sets of AB protons at C-2, C-3, and C-4, and the couplings between these protons. The remote couplings between the protons at C-2 and C-4 were also observed with a decoupling experiment and confirmed by simulation.

N-(phenylmethylsilyl)-1,2,3,4-tetrahydropyridine remained as the major product when the reaction was repeated with excess H to saturate the pyridine ring, e.g., 1 atm of hydrogen gas or a higher ratio of silane to pyridine. This implies that the failure of the last double bond to react may be due to some stabilizing effects rather than deficiency of hydrogen.

Varying the temperature from 25°C to 80°C only affected the reaction rate and no difference in the product composition was observed. At 25 °C, the reaction needs 36 hours to complete. While at 80 °C, the reaction is complete in 12 hours.

N-(phenylmethylsilyl)-1,2,3,4-tetrahydropyridine is stable at 100-150 °C under argon. No disproportion to give pyridine and piperidine was observed in the study.





The last double bond in the product can be hydrogenated under more severe conditions. When the reaction was run under H₂ (250 psi) at 80°C, N-(phenylmethylsilyl)-piperidine (**Fig. 3.2**) was obtained (80% yield by NMR). This product presumably results from the formation of N-(phenylmethylsilyl)-1,2,3,4-tetrahydropyridine followed by further hydrogenation.



The reactions of Cp_2TiMe_2 with PhSiH₃ or 4-CH₃OPhSiH₃ in the presence of pyridine gave polysilanes but no hydrosilated/hydrogenated product. This is presumably due to the higher activity of the primary silanes toward dehydrocoupling polymerization than PhMeSiH₂

Experiments using pyridine-d₅ or PhMeSiD₂ showed that there was hydrogen scrambling between silane and pyridine. C-5 was the least active position for exchange. The distribution of protons and deuterons in the main products of several reactions using deuterated reactants are shown in **Table 3.1**.

When PhMeSiD₂ was reacted with normal pyridine, PhMeSiD_nH_{2-n} and PhMe₂SiH were detected in the product mixture, proving that H/D exchange between the silane and pyridine was occurring. Based on the ¹H NMR spectrum of pyridine recovered from the reaction mixture, there is more exchange at positions 2 and 6 than at positions 3



Reaction	Integrals of ¹ H NMR Signals of the Isolated product
Pyridine/PhMeSiH ₂ /Cp ₂ TiMe ₂	12.2(2), 13.2(3), 12.9(4), 6.4(5), 6.1(6), 12.7 and 20.8(C_6H_5), 5.8(Si-H), 17.5(Si-CH ₃)
Pyridine-d5/PhMeSiH2/Cp2TiMe2	3.9(2), 3.7(3), 4.5(4), 0.6(5), 1.7(6), 11.6 and 22.8(C_6H_5), 2.4(Si-H), 13.9(Si-CH ₃)
	D NMR: 4.0(2), 5.9(3), 3.1(4), 1.8(5), 0.9(6), 0.7(Si-D). [Si-CD ₃ and C ₆ D ₅ not detected].
Pyridine/PhMeSiD ₂ /Cp ₂ TiMe ₂	9.1(2), 14.4(3), 11.9(4), 8.0(5), 4.3(6), 25.1 and 50.6(C_6H_5), 6.6(Si-H), 27.2(Si- CH ₃)

Table 3.1	$^{1}\mathrm{H}$	NMR	signal	integrals	of the	isolated	major	products	from
	va	rious	pyridi	ne/PhMeS	iH ₂ /Cp	2TiMe2	reactio	ons*	

* Numbers in parenthesis identify locations of ring protons.

and 5 on the pyridine molecule. Although no Si-H signal was detectable in the original PhMeSiD₂, it appeared in the product with good resolution and comparable intensity to the H signal from pyridine. The well resolved quartet of Si-H showed that no significant amounts of Si-CH₂D, Si-CHD₂, or Si-CD₃ were formed during the reaction. The slightly deformed doublet of SiCH₃ shows that some Si-D is retained in the product. This was confirmed by ²H NMR. The ²H-NMR spectra showed all the corresponding signals except for the methyl group and the phenyl ring. On the other hand, the signals due to the hetero-ring changed their original patterns compared with Fig. 3.1, in a manner consistent with the production of CHD rather than CH₂ groups. Although peaks 5 and 6 should both correspond to a single H, the intensity of 5 is nearly double the intensity of 6. This is an indication that more H/D exchange occurred at 6 than at 5. Positions 2, 4, and 6 appear to have the same extent of H/D exchange while position 3 has less.

When pyridine-d₅ was reacted with PhMeSiH₂, the intensity of the Si-H signal of the product was only half of that expected with normal pyridine, relative to the Ph protons (Fig. 3.3). In the crude reaction mixture, protons on residual pyridine were detected by



Figure 3.3 ¹H NMR spectrum of the product isolated from the reaction of pyridine-d₅, PhMeSiH₂ and Cp₂TiMe₂

¹H NMR, proving that H/D exchange between silane and pyridine had occurred during the reaction. Once again it can be seen that there is more H/D exchange at positions 2 and 6 than at positions 3 and 5 in the isolated product. In the ¹H NMR spectrum of pyridine recovered from the reaction mixture, the signal intensities of H-2 and H-6 are much higher than those of H-3 and H-5. In the product the lower intensity of H-5 than H-6 also means more D/H exchange occurred at position 6. A ²H NMR spectrum showed no signals attributable to CH₃ and Ph-H which means little or no H/D exchange has occurred between CH₃, Ph-H and pyridine-d₅.

3.2.2 Hydrosilation/hydrogenation of substituted pyridines with PhMeSiH₂ and Cp₂TiMe₂

3.2.2.1 3-Picoline

While no hydrogenation/hydrosilation product was obtained with 2-picoline or 2,6dimethoxypyridine, 3-picoline was hydrosilylated/hydrogenated by Cp₂TiMe₂/PhMeSiH₂. With 3-picoline, the same color changes were observed as in the case of pyridine, though the rate of change was slower. From a reaction run at 80 °C, two major products were obtained. According to the ¹H NMR spectrum these products accounted for 90% of the reacted 3-picoline. They were identified by ¹H NMR and MS as N-(phenylmethylsilyl)-1,4,5,6-tetrahydro-3-picoline (**31**) and N-(phenylmethylsilyl)-1,2,3,4-tetrahydro-3picoline (**32**). A small amount of N-(phenylmethylsilyl)-1,4-dihydro-3-picoline (**33**) was also detected. At 0°C the reaction afforded **33** as the major product along with **31** as a minor product. When the reaction mixture was warmed up to room temperature, the amount of **31** increased.

Table 3.2 shows the percentages of these compounds obtained at different temperatures after 36 hours. According to the results, the percentage of 33 decreased as

the temperature increased. Compound 32 was not detected when the reaction was run at room temperature or below, and its percentage went up when the temperature increased, while the percentage of 31 reached maximum about 50°C and then decreased as the temperature further increased.



Table 3.2. Percentage of the pro-	ducts in the	mixture(%)*
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Temperature (°C)	(phenylmethylsilyl)- 1,4-dihydro-3- picoline (33)	N- (phenylmethylsilyl)- 1,2,3,4-tetrahydro- 3-picoline (32)	N- (phenylmethylsilyl)- 1,4,5,6-tetrahydro- 3-picoline (31)
0	88	N.D.**	12
24	85	N.D.	15
50	27	17.2	56
60	19	27	49
80	3	57	39
80#	N.D.	N.D.	30

* According to NMR ** N.D. not detected # under 200 psi H₂, isolated yield

These results show that 33 can be obtained as the dominant product at room temperature or below. At higher temperatures both 32 and 31 can be obtained with higher yields than 33. While 31 is favored at lower temperatures. the thermodynamically less stable compound, 32, is favoured at higher temperature.

¹H NMR showed two distinctive protons at C-2 in **32**. By means of NOESY experiment, the resonances at 2.6 ppm and 2.98 ppm were assigned to the *cis* and *trans* to CH₃ protons respectively. A similar pattern for the C-4 protons was also confirmed by COSY and NOESY experiments, the chemical shifts were found to be 1.70 ppm and 2.04 ppm. The complexity of these NMR resonances is attributable to the existence of the two nearby chiral centers (C-3 and Si).

An attempt to obtain pure 33 was unsuccessful. The product was obtained as a major one at low temperature (0 °C). However, a mixture of 32, 31 and 33 was obtained in a 2:2:1 ratio after vacuum distillation. When the reaction mixture was reacted with fresh PhMeSiH₂ and Cp₂TiMe₂, 31 was obtained as the major product. It is likely that 33 was converted to 31 by PhMeSiH₂ and Cp₂TiMe₂, and that 33 is an intermediate for the formation of 31.

When the reaction was run at 80 °C under 200 psi of hydrogen, 31 (Fig. 3.4) was obtained as the major product. 3-Methylpiperidine was also detected as one of the products in the reaction mixture although it was not obtained in pure form due to the closeness of its boiling point to those of residual starting materials. This product was probably produced through further hydrogenation of 32 under the severe hydrogenation reaction conditions. It is reasonable to attribute the higher stability of the last double bond in 31, compared to 32, to the electronic and steric effects of the methyl group.

When deuterated phenylmethylsilane (PhMeSiD₂) was used in the reaction, an Si-H resonance appeared which indicated that hydrogen exchange between PhMeSiD₂ and 3-





picoline occurred. It was also evident from the ¹H NMR spectrum of the product that one of the H's on the double bond was retained more than the other in 32. The intensity of H-5 is much higher than H-6. These results parallel those obtained with pyridine and again show the high reactivity of the 2,6-positions of the pyridine nucleus to H/D exchange.

3.2.2.2 3-Ethylpyridine

Compared to Me, the Et group has a higher electron donating ability and a larger steric effect. Both the larger electron donating ability and the steric effect should favour the product with the double bond on the same side as ethyl group. When 3-ethylpyridine was reacted with PhMeSiH₂ in the presence of Cp₂TiMe₂ at 80°C, N-(phenylmethylsilyl)-1,4,5,6-tetrahydro-3-ethylpyridine and N-(phenylmethylsilyl)-1,2,3,4-tetrahydro-3-ethylpyridine were obtained as the two major products in a 1:1 ratio. This compares to the case of 3-picoline where the corresponding ratio was 1:1.5. These results are in agreement with the expected trend.

3.2.2.3 4-Picoline

A reaction of 4-picoline with PhMeSiH₂ in the presence of Cp₂TiMe₂ gave N-(phenylmethylsilyl)-1,2,3,4-tetrahydro-4-picoline as the major product (Eq. 3.3). The reaction rate was slower than 3-picoline under the same conditions while the color change was the same. When deuterated PhMeSiD₂ was used instead of PhMeSiH₂, the same product was obtained with H/D scrambling between the ring protons and PhMeSiD₂. The ¹H NMR signal integrals are shown in **Table 3.3**. It is also clear that H-6 is the position having most H/D exchange, as in the case with pyridine or 3-picoline.

¹H NMR (**Fig. 3.5**) shows two distinct protons at C-3. This diastereotopy is a reflection of the presence of two chiral centers: Si and C-4. A NOESY experiment showed





that the H cis to the CH_3 group is at the higher field and the trans one at the lower field. The difference between the two protons at C-2 can be observed by their mutual NOE effect. But the difference is much smaller than in N-(phenylmethylsilyl)-1,2,3,4-tetrahydro-3picoline.

Reaction	¹ H NMR integrals of the isolated N- (phenylmethylsilyl)-1,2,3,4-tetrahydro-4- picoline
4-picoline/PhMeSiH ₂ /Cp ₂ TiMe ₂	8.8(2), 7.0 and 7.2(3), 4.4(4), 4.9(5), 4.1(6), 12.9(CH ₃), 3.9(Si-H), 11.9(Si- CH ₃), 12.5 and 23.3(Ph-H)
4-picoline/PhMeSiD ₂ /Cp ₂ TiMe ₂	4.37(2), 6.86 and 4.98(3), 2.08(4), 4.97(5), 1.40(6), 14.45(CH ₃), 1.76(Si- H), 18.54(Si-CH ₃), 8.77 and 17.65(Ph- H)

 Table 3.3 ¹H NMR signal intensities of the isolated major products from the various 4-picoline/PhMeSiH₂/Cp₂TiMe₂ reactions*

* Numbers in parenthesis identify locations of ring protons



3.2.2.4 3,5-Lutidine

Reaction of 3,5-lutidine with PhMeSiH₂ in the presence of Cp₂TiMe₂ gave N-(phenylmethylsilyl)-1,4-dihydro-3,5-lutidine as the major product (**Eq. 3.4**). Only a trace amount of 3,4-lutidine was hydrogenated/hydrosilylated under these conditions. The reaction rate was much slower than in the cases of pyridine, 3-picoline, and 4-picoline. When this reaction was carried out under 250 psi H₂, a mixture of N-(phenylmethylsilyl)-1,4-dihydro-3,5-lutidine and N-(phenylmethylsilyl)-1,4,5,6-tetrahydro-3,5-lutidine was obtained in a ratio of 1:2 (**Fig. 3.6**). A reaction with PhMeSiD₂ resulted in extensive H/D



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scrambling, but none of the H's on the ring was observed with more H/D exchange than the others.



3.2.2.5 Relative reaction rates of the pyridines

It was noticed that hydrosilation/hydrogenation reaction rates were different from

Substrate	Reaction time,(hour)	Conversion, %		
Ethyl nicotinate*	3	100		
pyridine	8	90		
3-picoline	8	34		
4-picoline	8	13		
3,5-lutidine	24	15		

Table 3.4 Relative reaction rate of pyridines/PhMeSiH2/Cp2TiMe2(10% Catalyst, 80°C)

* See Chapter 4.

substrate to substrate when pyridine, 3-picoline, 4-picoline and 3,5-lutidine respectively were reacted with phenylmethylsilane and Cp_2TiMe_2 . When these reactions were carried out under the same conditions, 100% conversion was found with ethyl nicotinate (see **Chapter 4**), while only 15% conversion with 3,5-lutidine. The rates of these pyridines are shown in **Table 3.4**.

3.2.2.6 Quinoline

The hydrogenation of quinoline has received a lot of attention.^{3,9,10} There is, however, no report of its hydrosilation.



Reaction of quinoline with PhMeSiH₂ in the presence of Cp₂TiMe₂ at room temperature yielded N-phenyImethylsilyl-1.2.3,4-tetrahydroquinoline and NphenyImethylsilyl-1,4-dihydroquinoline in 3:1 ratio. Conjugation between the double bond and the lone electron pair on the N should make the double bond resistant to further hydrogenation. If the reaction is carried out under 250 psi of H₂ at 80°C, only NphenyImethylsilyl-1,2.3,4-tetrahydroquinoline is obtained.

3.2.2.7 H/D exchange between C_5D_5N and H_2 in the presence of $(Cp_2TiH)_2$

Since the pyridine ring can be hydrosilated/hydrogenated in the presence of Cp_2TiMe_2 and PhMeSiH₂, it was expected that a titanocene based catalyst might catalyse hydrogenation. However, only a small amount of pyridine (ca. 5%) was hydrogenated when a mixture of C_5D_5N and $(Cp_2TiH)_2^{17}$ was kept under 400 psi H₂ and at 80 °C for 24 hours. On the other hand, extensive H/D exchange was observed at positions 2 and 6 on the pyridine ring. This observation implies that the presence of silane is essential for the titanocene catalyzed reduction of pyridines.

3.3 Discussion

3.3.1 The double bond in the products

It is interesting to find that most of the hydrosilated/hydrogenated products tend to retain one or two double bonds. Experiments have shown that this may be due to higher stability of these compounds rather than hydrogen deficiency. A similar resistance of the last double bond to hydrogenation was observed by Brown et al.^{7a} They reported the reduction of pyridine to 1,2,3,4-tetrahydropyridine with two equivalents of lithium triethylborohydride. However, the addition of one more equivalent of lithium triethylborohydride was quite slow and incomplete. Subsequently, Caroll and Blough^{7b} reported that the complete reduction of pyridine to piperidine was rapid with the same reagents. Gambarotta¹⁸ reported an example of regioselective hydrogenation of pyridine when studying complexes of vanadium. The failure of the last double bond to react was attributed to the conjugation of the C=C π -bond with the vanadium center through the trigonal-planar coordination geometry of the nitrogen atom.

Theoretical studies, ¹⁹⁻²² carried out on cyclic allylamine/enamine systems, showed that vinyl amines like 1,2,3,4-tetrahydropyridine are stabilized by significant conjugation between the nitrogen lone pair and the π -bond. The conjugation can be maximized by the presence of a substituent at the N equatorial position as in the case of N-methyl-1,2,3,4-tetrahydropyridine (34). The constrained configuration of dehydroquinuclidine (35) prohibits a π interaction between the nitrogen lone pair and C=C bond. In contrast, compound 34 has a conformation which favors a π interaction between the nitrogen lone pair and the carbon-carbon double bond. The existence of the last double bond in our product can be rationalized by this theory. It is reasonable to believe that the bulky phenylmethylsilyl group, PhMe(H)Si, would be at the equatorial position on the nitrogen which enhances the conjugation of the C=C with the nitrogen lone pair. This conjugation may be accounted for by the remaining double bond in the hydrosilated/hydrogenated products. From the above, it appears that electronic factors play a more important role in stability of the remaining double bond and steric factors only enhance this effect.



3.3.2 H/D exchange

Experiments with deuterated reagents have demonstrated that positions 2 and 6 are more active for H/D exchange. A possible mechanism for the exchange at positions 2 and 6 is shown in **Scheme 3.1**. Cyclometallation reactions of complexes of pyridines with zirconocene or titanocene have been reported by Jordan's and Teuben's groups

respectively.^{23,24} This type of ortho-metallation of pyridine by other early transition metals has also been reported.²⁵

In a reaction of Ph_2SiH_2 with Cp_2TiMe_2 in the presence pyridine, crystalline $Cp_2Ti(SiHPh_2)(Py)$, **36**, was obtained. In the solid state 15 is present as two conforms (**Fig.3.7**).²⁶ Although some slight differences were found between the structures of the two conforms, both showed that there is a close contact between Si and ortho-hydrogen H(2) (2.83 Å; molecule 1) or H(56) (2.82 Å; molecule 2). These distances are much shorter than the calculated contact radius (3.3 Å) and probably represent a minimum approach that can be tolerated without some distortion of the molecule. This close approach of the Si to the proximal pyridine C-H hydrogen revealed in structure of **36** strongly supports the mechanism shown in **Scheme 3.1**.





Figure 3.7 Crystal structure of Cp₂Ti(SiHPh₂)(Py) (36)

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Further reaction following the exchange would lead to the products with more exchange at positions 2 and 6. The pyridine dissociated from the complex would also show the phenomenon which is in conformity with what was observed.

Metal hydride addition to the heteroaromatic rings is one of the proposed mechanisms for the hydrogenation of these aromatic nuclei.²⁷ As Ti-H is known to be present in Cp₂TiMe₂/silane reaction products, another plausible explanation for the observed H/D exchange is reversible addition of Ti-H(D) to the pyridine ring followed by hydrosilation and hydrogenation to yield the final product. If this is one of the actual mechanisms, Ti-H would be an effective catalyst for hydrogenation of pyridine, since the hydrogenation of the resulting diene is expected to be facile. However the study of the reaction of pyridine-d₅ and H₂ with (Cp₂Ti-H)₂ as catalyst showed only a small amount of piperidine, but extensive H/D exchange at the 2 and 6 positions. Therefore the mechanism shown in Scheme 3.2 is more plausible. (Cp₂Ti-H)₂ is an effective catalyst for H/D exchange but not an effective catalyst for the hydrogenation of pyridines.



A reaction of 2,3-lutidine, PhMeSiD₂ and Cp₂TiMe₂ yielded no hydrogenated/hydrosilated product, but showed extensive H/D exchange at C-6. No H/D exchange occurred at the methyl groups in positions 2 and 3. This result implies that a complex between titanocene species and 2,3-lutidine was formed. The failure to afford any hydrogenated/hydrosilated product may result from the steric effect of the methyl group at C-2. A similar result was also reported by Teuben and Klei²⁸ in the study of cyclometallation of alkyl titanocene with pyridines where a reaction resulting in deuteriopyridines was used to demonstrate the existence of a Ti-C bond at the 6-position in the pyridine complex as shown below:

$$Cp_{2}Ti = N = \frac{D_{2}O/DCl}{R} + Cp_{2}TiCl_{2}$$
(3.6)

The enhanced H/D exchange at positions 2 and 6 may also result from a rapid reversible hydrosilation exchange under the catalytic influence of Cp_2TiMe_2 . Such a reaction mechanism with deuterated pyridine is shown in Scheme 3.3.

Scheme 3.3



The addition of an Si-H bond to the ring would make the ring easier to hydrogenate by destroying its aromatic properties. However, due to the need to overcome the aromatic stabilization energy, the forward reaction should be very slow, while the reverse reaction is expected to be very facile (re-aromatization). Thus the reversibility from a hydrosilated ring back to an aromatic ring would be very high. The experiments with 2,3-lutidine, Cp₂Ti-H and deuterated reagents suggest that Schemes 3.1 and 3.2 represent the two main paths for H/D exchange.

3.3.3 Hydrosilation/hydrogenation

Pyridines do not react with either PhMeSiH₂ or Cp₂TiMe₂ separately. Although $[Cp_2Ti-H]_2$ can be produced via the reaction of Cp₂TiMe₂ and H₂, no reaction was observed when Cp₂TiMe₂ was put under 250 psi H₂ in the presence of pyridine and the mixture retained its original orange color. Even with preprepared $[Cp_2Ti-H]_2$, only a small amount of pyridine was hydrogenated under 400 psi H₂ at 80 °C in the absence of silane. Thus Cp₂TiMe₂ cannot effectively catalyze the hydrogenation of pyridine alone, and silane cannot hydrosilate pyridine without Cp₂TiMe₂.





The active catalyst results from reactions between Cp₂TiMe₂ and the silane. Some reactions that have been proposed for the reduction of Cp₂TiMe₂ by silanes are summarized in Scheme 3.4.29 The active catalyst is first produced through the reaction of Cp₂TiMe₂ and silane. As is indicated in Scheme 3.4, silanes can reduce Cp₂Ti(IV) to Cp₂Ti(II) and $Cp_2Ti(III)$ species. Compounds of both of the lower oxidation states may be catalytically active 30-32 In reactions of Cp₂TiMe₂ with silanes, the color change is always accompanied by gas evolution and it is known that CH₄ and H₂ are the two major components of the evolved gas.²⁹ In the present research, as in earlier studies, R₂MeSiH was always detected in the reaction mixture. Recent success in the synthesis and characterization of the titanocene(III) pyridine complexes. 29. 30. and (BTHIE)Ti(Me)(Py)¹³ permits some speculation on the mechanism(s) of pyridine hydrosilation/hydrogenation.

In the absence of added H_2 , silane is the only source of the H's added to the pyridine. The H could be added to the pyridines in the form of either H₂, Si-H, or Ti-H. H_2 may be produced through the dehydrocoupling polymerization of silanes and then added to the diene produced by the initial hydrosilation step. Such dehydrocoupling/hydrogenation is well established.³³ However, the polymerization activity of silanes follows the order:

primary silane > secondary silane >> tertiary silane

This explains why with phenylsilane and 4-methoxyphenylsilane, only oligosilanes and other silane products were obtained but little hydrogenated/hydrosilated products. The high polymerization activity of primary silanes suppressed the hydrosilation/hydrogenation reactions. When PhMeSiH₂ reacted with Cp₂TiMe₂ in the absence of pyridine at room temperature, although the solution color changed from orange to dark blue immediately,

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only a small amount of PhMeHSiSiHMePh was found in 24 hours. If pyridine was added to the catalyst before PhMeSiH₂, no color change or reaction was observed at room temperature in 24 hours. The low activity toward dehydrocoupling of PhMeSiH₂ strongly suggests that free H₂ is not the only hydrogen source for hydrogenation. Catalyst mediated H transfer from Si-H to the substrate must play a more important role. The involvement of Ti-H intermediates is plausible in view of the isolation of **30** and other Ti-H species in $Cp_2TiMe_2/organosilane$ reactions.

It is reasonable to believe that Ti(II) and Ti(III) are key species for the catalytic hydrosilation/hydrogenation of the pyridines. Low valent titanocenes can be very effective catalysts for the hydrogenation of some olefins.³⁰ However, they failed to hydrogenate benzene. The high resonance energy and low coordinating power of benzene explains the resistance of benzene to hydrogenation under the catalytic influence of these titanocenes. On the other hand, pyridine, which has a resonance energy close to that of benzene but is strongly coordinating, also showed resistance to hydrogenation. No substantial hydrogenation was observed under one atmosphere of H₂ in the presence of a catalytic amount of Cp₂TiMe₂ and PhMeSiH₂(1:1) or (Cp₂TiH)_n prepared following the reference procedure.¹⁷

The fact that pyridines are hydrogenated/hydrosilated while benzene is not, suggests that the N atom in the pyridines is a key factor for the success of the hydrosilation/hydrogenation reactions, and hydrosilation necessarily precedes hydrogenation under the conditions applied. Since the hydrogenation of olefins, and particularly 1,3-dienes, with Cp₂TiMe₂ and silanes is a facile reaction,³³ the hydrogenation reaction of the dienes produced by initial hydrosilation is not unexpected.

Heterocyclic compounds such as pyridines and quinolines are generally regarded as good ligands due to the presence of at least one nitrogen atom with a localized pair of electrons. A lot of research has been carried out to understand the hydrogenation mechanism of indoles, pyridines, and quinolines.³⁴ Pyridines in their transition metal

complexes can coordinate as $\eta^1(N)$, $\eta^2(C, C)$,³⁵ $\eta^2(N, C)$,³⁶ or η^6 ligands^{37,38} (Fig. 3.8).

Although pyridines can act as $\eta^2(C, C)$, $\eta^2(N, C)$, η^6 , and even as a bridging ligand,³⁹ by far the most common coordination mode is $\eta^1(N)$,⁴⁰ in which the lone



electron pair on the nitrogen donates to a Lewis acidic metal center. A careful search of the literature showed that in the limited number of $\eta^2(C, C)$, and $\eta^2(N, C)$ examples, the pyridines involved had substituents at the 2 and 6 positions. Probably in these cases the steric hindrance makes the η^2 coordination preferred over η^1 coordination. Fish et al.³⁸ demonstrated that several important criteria have profound effects on the bonding mode of nitrogen heterocyclic ligands to the metal center, i.e., steric and electronic effects, which control the availability of lone-pair electrons on the nitrogen atom and affect the lability of the metal-N bond. These workers concluded that several parallel reaction routes are involved leading to the same final products. A possible reaction cycle which conforms to the results obtained in earlier and the present work is shown in **Scheme 3.5**.⁴¹ Cp₂Ti-H produced by the reaction of Cp₂TiMe₂ with a silane is widely believed to be the active catalyst in the reactions of silanes. The titanocene hydrides made through conventional methods all showed activities in catalyzing various reactions.³⁰ Although the simple form

compound due to its high activity and sensitivity, several Ti(III)-H compounds have been isolated from dimethyltitanocene/silane reactions. The successful preparation and characterization of 9,⁴² and 37 through the reaction of Cp₂TiMe₂ and silanes point to the participation of Cp₂Ti-H in these reactions. This possibility is also supported by the report of the preparation and characterization of rac-{[C₂H₄(η^5 -tetrahydroindenyl)₂]Ti^{III}(μ -H)}₂⁴³ where the bulkier, more strongly electron-donating tetrahydroindenyl groups stabilize the titanocene hydride dimer. Moreover, Cp₂Ti(H)(PRR'₂) (R = Ph, R' = Me or R = Me, R' = Ph), which are complexes of Cp₂Ti-H with a phosphine, have been detected by EPR.⁴⁴



Metathesis of PhMeSiH₂ with Cp_2TiH gives $Cp_2TiSiHPhMe$ and H_2 . Once again, no Cp_2Ti -Si has been isolated as a discrete chemical compound. However, its existence is

reasonable given the earlier isolation of 7 and 8, and the interconversions among 7, 8, and 9.^{29a} This species has also been trapped with phosphines. The coordinatively unsaturated structure of Cp₂Ti-Si makes it ready to accept ligands carrying lone pair electrons, e.g. pyridines and quinoline to form Cp₂Ti(Si)(Py) complexes. η^6 (Py) coordination should be difficult to form due to steric hindrance and the 18-electron rule. η^1 (N)(Py) complexes, Cp₂Ti(SiHRR')(Py), have been identified¹³ in the reaction mixture of Cp₂TiMe₂ and silanes in the presence of pyridines, by EPR spectroscopy and elemental analysis.





In the crystal structure of 36,²⁶ the pyridine ring is almost co-planar with the bisector plane of the Cp-Ti-Cp angle. A shift of the pyridine ring on the bisector plane should encounter little steric barrier. A reasonable first step for hydrosilation is the insertion of the -N=C- group into a Ti-Si bond (Scheme 3.6). The driving force for this reaction is the


sacrifice of a weak Ti-Si bond and the gain of a strong Si-N bond. The product of this insertion **38** would then undergo σ -bond metathesis of Ti-C with Si-H to give hydrosilation product and regenerate Ti-Si. Depending on the substrate, the hydrosilation product may either undergo further hydrogenation, as in the cases of pyridine, 3-picoline and 4-picoline, or isomerization as in the case of 3,5-lutidine.

The formation of a titanocene(III)- $\eta^1(N)$ pyridine complex activates the pyridine towards subsequent hydrosilation/hydrogenation reactions. If reasonably strong coordination of the pyridine to Ti cannot occur, because of steric effects or electronic effects. no hydrogenation/hydrosilation product will be obtained. This is the case for 2-picoline. 2.3-lutidine, and 2.6-dimethoxypyridine and some nicotinates (see **Chapter 4**). Another possible cause for the inhibition of hydrosilation/hydrogenation reactions in the cases with substituents at positions 2 and 6 may be hindrance by these substituents to the attack of the Si on N or the shifting of the titanium center to C. This is reasonable considering the two Cp groups on the Ti and the Ph group on the Si. In the first two cases, the observed H/D exchange between pyridine and silane indicates the formation of a weak complex which is in conformity with the observation of the color change during the reaction, but no hydrosilated/hydrogenated product was obtained.

The initial hydrosilation involves the rupture of the dative bond between Ti and N. The strength of the bond parallels the relative rates of reaction (**Table 3.4**).

The larger the electron density on N, the higher the basicity and the stronger the Ti-N bond should be. Considering the electron-density distribution on the unsubstituted pyridine ring (N-5.92, positions 2 and 6 - 3.63, positions 3 and 5 - 4.05, and position 4 -3.89)⁴⁵ and the available pK_a values (pyridine, 5.58: 3-picoline, 5.70; 4-picoline, 5.99).⁴⁶ it can be deduced that the electron densities on N are in the reverse order of the reactivities shown in (**Eq. 3.7**).

It appears that (in the absence of major steric effects) the stronger the Ti-N bond, the lower the reaction rate. A methyl group at the 4 position donates more electron density



than at the 3 position. Thus a stronger Ti-N bond is expected in the complex of 4-picoline than in that of 3-picoline, resulting in a lower reaction rate. In **Scheme 3.6** the formation of the Si-N bond proceeds simultaneously with the breaking of the Ti-N dative bond. Due to the high resonance energy of the aromatic ring, a high activation energy is expected for this step, which would probably make it the rate determining step. The effect of Ti \leftarrow N bond strength suggests that considerable Ti \leftarrow N bond breaking has occurred in the 4-center transition state. If the $\eta^1(N)$ -bonded complex is too stable, the hydrosilation reaction could be completely inhibited. This might be the case with 3,4-lutidine, where only a trace of hydrosilated/hydrogenated product was detected by NMR.

In the case of 3-picoline, there are two possibilities for the Si to approach the N. One is from the same side as the methyl group to form 39 leading to 31, the other is from the opposite side to form 40 leading to 32 (Scheme 3.7).

Scheme 3.7



Obviously attack from the same side as the methyl group is stericaly favored while the other way will result in the methyl group approaching the two Cp groups. As the activation energy for formation of 40 is higher than that for 39, the rate of formation of 40 (and hence 32) will increase relative to that of 39 with increasing temperature. Such a change in relative rates is evident in the results of **Table 3.2**.

3.4 Summary

The homogeneous catalytic hydrosilation/hydrogenation of some aromatic Nheterocycles. (namely pyridine, 3-picoline, 4-picoline, 3.5-lutidine, and quinoline) has been achieved using titanocene derivatives as catalysts. A variety of hydrosilated/hydrogenated products, either fully or partially saturated, may be produced depending on conditions. A reaction mechanism is proposed based on isolated and structurally characterized pyridine titanocene complexes, on the effects of substituent on the rates, and on H/D exchange studies. It is suggested that a key step in the hydrogenation/hydrosilation reaction is the formation of a mono- $\eta^{1}(N)$ complex between the pyridine ring and the titanocene species. It is proposed that the rate determining step is an intramolecular insertion of -N=C- into the Ti-Si bond. If strong coordination between the titanocene species and the substrates is prohibited either by steric effects or electronic effects. or if the complex is of too high stability, no hydrogenation/hydrosilation product is obtained. Extensive H/D exchange at the 2- and 6- positions of the pyridine is attributed to a reverse ortho-metallation of pyridine in a Ti-H complex.

3.5 Experimental Section

3.5.1 General manipulations

All manipulations were performed under an atmosphere of nitrogen or argon using

Schlenk techniques. Dry, oxygen free solvents were employed throughout. Glassware was flame-dried or oven-dried before use. In a typical reaction, the required amount of Cp₂TiMe₂ was first added to a Schlenk flask and connected to vacuum to remove the air carried by the sample. The flask was then filled with Ar and the procedure was repeated several times. The required amounts of pyridine and silane were added with a micro-syringe. NMR samples were prepared under Ar.

3.5.2 Materials and Analyses

Mass analyses were performed by the Chemistry Department MS service. Proton NMR spectra were recorded on Varian XL-200, XL-300, Gemini-200, and Unity-500 spectrometers using internal solvent references. HMQC, COSY, and NOESY spectra were recorded on the Unity-500 spectrometer. Carbon-13 NMR spectra were recorded on the Unity-500 spectrometer using $C_6D_6(128.0 \text{ ppm})$ as reference. Silicon-29 NMR spectra were recorded on a Varian XL-300 operating at 59.9 MHz in C_6D_6 . An external standard of tetramethylsilane (0.00 ppm) was used. The NMR data for all products are listed in **Appendix III**.

Pyridine and its derivatives were all from Aldrich Chemical Co. and were purified by distillation over calcium hydride before use. Pyridine-d₅ (from Aldrich) was dried over 4 Å molecular sieves. Dimethyltitanocene was prepared by a literature procedure and recrystallized from pentane.⁴⁷ Phenylmethylsilane was prepared by a standard procedure via the reaction of the corresponding phenylmethylsilane dichloride with LiAlH₄.⁴⁸ Deuterated PhMeSiH₂ was prepared following the same procedure with LiAlD₄ instead of LiAlH₄. CpCp*TiMe₂ was synthesized according to a literature procedure.⁴⁹

3.5.3 Synthesis of N-(phenylmethylsilyl)-1,2,3,4-tetrahydropyridine

In a Schlenk tube, PhMeSiH₂ (3.5 mL, 25.6 mmol) and pyridine (1.0 mL, 12.5 mmol) were added to Cp₂TiMe₂ (0.13 g, 0.7 mmol; 6 mol% catalyst based on pyridine). After a while, the solution color changed to dark blue, then purple, accompanied by gas evolution. The mixture was stirred at 80°C. After 12 hours, the dark-brown-purple reaction mixture was distilled under vacuum. 1.29 g (50% isolated yield) N-(phenylmethylsilyl)-1.2.3.4-tetrahydropyridine was separated as a colorless liquid (b.p. 57° C/0.12 mmHg). MS (EI). m/z(%): 203 (100) [M⁺], 188 (18.5) [M⁺ – CH₃], 121 (76.6) [M⁺ – C₅H₈N]).

COSY and decoupling NMR experiments were in conformity with the structure assignment.

3.5.4 Reaction of pyridine, Cp₂TiMe₂ and PhMeSiD₂

In a Schlenk tube, PhMeSiD₂ (0.44 mL, 3.2 mmol) and pyridine (0.09 mL. 1.0 mmol) were added to Cp_2TiMe_2 (23 mg, 0.11 mmol; 10 mol% catalyst per pyridine). After a while, the solution color changed to dark blue then purple accompanied by gas evolution. The mixture was stirred under 80°C. After 12 hours, N-(phenylmethylsilyl)-1.2.3.4-tetrahydropyridine(H/D) was afforded in 94% yield according to NMR.

3.5.5 Reaction of pyridine-d5, Cp2TiMe2 and PhMeSiH2

In a Schlenk tube. PhMeSiH₂ (0.89 mL, 6.5 mmol) and pyridine-d₅ (0.35 mL, 4.32 mmol) were added to Cp₂TiMe₂ (45 mg, 0.22 mmol; 5 mol%). After a while, the solution color changed to dark blue then purple accompanied by gas evolution. The mixture was stirred at 80°C. After 8 hours, the dark-brown-purple reaction mixture was distilled under vacuum. 0.19 g (20% isolated yield) N-(phenylmethylsilyl)-1.2,3,4-tetrahydropyridine(H/D) was separated as a colorless liquid (b.p. $57^{\circ}C/0.12 \text{ mmHg}$)

3.5.6 Synthesis of N-(phenylmethylsilyl)-piperidine

PhMeSiH₂ (5.0 mL, 36.5 mmol), pyridine (2.0 mL, 24.7 mmol) and Cp₂TiMe₂ (0.36 g, 1.72 mmol) were added to a glass-liner. The reaction mixture was thoroughly mixed, sealed in the autoclave and refluxed under H₂. The reaction conditions were set at 80 °C and 250 psi(H₂). After 24 hours, 2.0 g of N-(phenylmethylsilyl)-piperidine (40% isolated yield based on pyridine) was isolated as a yellow liquid (b.p. 54-56°C/0.01mmHg) by vacuum distillation.

COSY, and HMQC NMR experiments were in conformity with the structure assignment.

3.5.7 Reaction of Cp₂TiMe₂, pyridine-d₅ and PhMeSiD₂ under argon

PhMeSiD₂ (0.30 mL, 2.2 mmol), and pyridine-d₅ (0.12 mL, 1.4 mmol) were added to Cp_2TiMe_2 (0.15 g, 0.36 mmol). The reaction mixture was stirred at room temperature. After three days, the dark-brown solution was subject to fractional distillation. 0.2 g N-(phenylmethylsilyl)-1,2,3,4-tetradeuteropyridine was collected as colorless liquid. No appreciable H/D exchange was detected.

3.5.8 Reaction of Cp₂TiMe₂, pyridine-d₅ and PhMeSiD₂ under hydrogen.

PhMeSiD₂ (0.30 mL, 2.2 mmol), and pyridine-d₅ (0.12 mL, 1.4 mmol) were added to Cp_2TiMe_2 (0.15 g, 0.36 mmol). The reaction mixture was stirred at room temperature under hydrogen (1 atm). After three days, the dark-brown solution was subject to fractional distillation. 0.18 g N-(phenylmethylsilyl)-1,2,3,4-tetrahydropyridine (H/D) was collected as colorless liquid.

3.5.9 Reaction of 3-picoline, Cp₂TiMe₂ and PhMeSiH₂

PhMeSiH₂ (3.56 mL, 26 mmol), 3-picoline (1.8 mL, 18.4 mmol) and Cp₂TiMe₂ (0.40 g, 1.8 mmol; 10 mol%) were added to a Schlenk tube. The mixture was stirred at 80°C. After six days, the dark-brown-purple reaction mixture was subject to vacuum distillation. 1.3 g of a colorless liquid was obtained (b.p. 84-86°C/0.02 mmHg). NMR showed it to be a mixture of N-(phenylmethylsilyl)-1,4,5,6-tetrahydro-3-picoline and N-(phenylmethylsilyl)-1,2,3,4-tetrahydro-3-picoline (with a ratio of 2:1). MS (EI): m/z (%): 217 (100) [M⁺], 202 (50) [M⁺ – C₇H₉Si], 121 (26) [M⁺ – C₉H₁₀N].

3.5.10 Reaction of 3-picoline, Cp₂TiMe₂ and PhMeSiH₂ under H₂

PhMeSiH₂ (3.56 mL, 26 mmol), 3-picoline (1.8 mL, 18.4 mmol) and Cp₂TiMe₂ (0.40 g, 1.8 mmol; 10 mol%) were added to a Parr Reactor, The mixture was heated at 80°C under hydrogen (200 psi). After four days, the dark-brown-purple reaction mixture was distilled under vacuum. 1.0 g N-(phenylmethylsilyl)-1,4,5,6-tetrahydro-3-picoline was obtained as colorless liquid (b.p. 84-86°C/0.02 mmHg).

3.5.11 Reaction of 3-picoline, Cp2TiMe2 and PhMeSiD2

PhMeSiD₂ (3.56 mL, 26 mmol), 3-picoline (1.8 mL, 18.4 mmol) and Cp₂TiMe₂ (0.40 g, 1.8 mmol; 10 mol%) were added to a Schlenk tube. The mixture was stirred at 80°C. After six days stirring, the dark-brown-purple reaction mixture was subject to vacuum distillation. 1.4 g of a colorless liquid was obtained (b.p. 84-86°C/0.02 mmHg). NMR showed a mixture of N-(phenylmethylsilyl)-1,4,5,6-tetrahydro-3-picoline (H/D) and

N-(phenylmethylsilyl)-1,2,3,4-tetrahydro-3-picoline (H/D).

3.5.12 Reaction of 3-ethylpyridine, Cp₂TiMe₂ and PhMeSiH₂

PhMeSiH₂ (1.78 mL, 13 mmol), 3-ethylpyridine (1.11 mL, 9.16 mmol) and Cp₂TiMe₂ (0.2 g, 0.90 mmol; 10 mol%) were added to a Schlenk tube. The mixture was stirred at 80°C for ten days. The resulting dark-brown-purple reaction mixture was distilled under vacuum to give 1.0g of a colorless liquid (88-92°C/0.02 mmHg). According to NMR the product was a mixture of N-(phenylmethylsilyl)-1,4,5,6-tetrahydro-3-ethylpyridine, and N-(phenylmethylsilyl)-1,2,3,4-tetrahydro-3-ethylpyridine (in a ratio of 1:1). MS (EI): m/z (%): 231 (52.3) [M⁺], 216 (63.8) [M⁺ – CH₃], 202 (60.0) [M⁺ – CH₂CH₃], 121 (100) [M⁺ – C₇H₁₂N], 111 (18.7) [M⁺ – C₇H₈Si]].

3.5.13 Synthesis of N-(phenylmethylsilyl)-1,2,3,4-tetrahydro-4-picoline

PhMeSiH₂ (3.56 mL, 26 mmol), 4-picoline (1.8 mL, 18.4 mmol) and Cp₂TiMe₂ (0.40 g, 1.8 mmol; 10 mol%) were added to a Schlenk tube. The mixture was stirred at 80°C for six days. The dark-brown-purple reaction mixture was distilled under vacuum to give N-(phenylmethylsilyl)-1,2,3,4-tetrahydro-4-picoline as colorless liquid (2.1g, 53% isolated yield based on 4-picoline, b.p 85-87°C/0.15 mmHg). MS (EI): m/z (%): 217 (37) [M⁺], 202 (100) [M⁺ – CH₃], 121 (37) [M⁺ – C₅H₈N].

3.5.14 Reaction of 4-picoline, Cp₂TiMe₂ and PhMeSiD₂

PhMeSiD₂ (3.56 mL, 26 mmol), 4-picoline(1.8 mL, 18.4 mmol) and Cp₂TiMe₂ (0.40 g, 1.8 mmol; 10 mol%) were added to a Schlenk tube. The mixture was stirred at 80°C for six days. The dark-brown-purple reaction mixture was distilled under vacuum to

give N-(phenylmethylsilyl)-1,2,3,4-tetrahydro-4-picoline as a colorless liquid (2.2g, 53% isolated yield based on 4-picoline, b.p 85-87°C/0.15 mmHg)

3.5.15 Preparation of N-(phenylmethylsilyl)-1,2,3,4-tetrahydroquinoline

PhMeSiH₂ (6.0 mL, 43.2 mmol) and quinoline (3.3 mL, 28.8 mmol) were added to Cp_2TiMe_2 (0.60 g, 2.88 mmol; 10 mol%) in an autoclave. The temperature and H₂ pressure were set at 80 °C and 200 psi respectively. After 48 hours, N-(phenylmethylsilyl)-1,2,3,4-tetrahydroquinoline was separated by vacuum distillation as a yellowish liquid (4.0g, 54% isolated yield, b.p 160°C/0.02 mmHg). MS (EI): m/z (%): 253 (100) [M⁺], 132 (38.3) [M⁺ - C₇H₉Si], 121 (42.1) [M⁺ - C₉H₁₀N]

3.5.16 Reaction of quinoline, Cp2TiMe2, and PhMeSiH2

PhMeSiH₂ (2.0 mL, 14.4 mmol) and quinoline (1.1 mL, 9.6 mmol) were added to Cp₂TiMe₂ (0.20 g, 0.96 mmol; 10 mol%). The reaction mixture was stirred at 80°C for 3 days. N-(phenylmethylsilyl)-1,2,3,4-tetrahydroquinoline and N-(phenylmethylsilyl)-1,4-dihydroquinoline were formed in a ratio of 3:1. A small amount of 1,2,3,4-tetrahydroquinoline [¹H NMR (benzene-*d*₆, 22 °C, 500 MHz): 1.57 (m, 2H, NCH₂CH₂ CH₂), 2.51 (t, J = 6.3 Hz, 2H, NCH₂CH₂CH₂), 2.76 (t, J = 5.54 Hz, 2H, NCH₂), 3.0 (b, 1H, NH), 6.22 (d, J = 8.0 Hz, 1H), 6.62 (t, J = 7.0 Hz, 1H), 6.85 (d, J = 7.0 Hz, 1H), 6.95 (t, J = 7.0 Hz, 1H)] was also detected in the mixture.

3.5.17 Reaction of 3,5-lutidine, Cp₂TiMe₂ and PhMeSiH₂

PhMeSiH₂ (3.56 mL, 26 mmol), 3,5-lutidine(2.1 mL, 18.4 mmol) and Cp₂TiMe₂ (0.31 g, 1.41 mmol; 8 mol%) were added to a Schlenk tube. After a while the

solution turned dark blue, then violet, progressively accompanied by gas evolution. The violet solution was stirred at 80°C in an oil-bath for 8 days. The greenish reaction mixture was distilled under vacuum. N-(phenylmethylsilyl)-1,4-dihydro-3,5-lutidine was the main product (2.5 g, 60% yield, b.p. 80-90 °C/0.02 mmHg). MS (FAB, NBA), m/z: 229 $[M^+]$.

3.5.18 Reaction of 3,5-lutidine, Cp₂TiMe₂ and PhMeSiD₂

PhMeSiD₂ (3.56 mL, 26 mmol), 3,5-lutidine(2.1 mL, 18.4 mmol) and Cp₂TiMe₂ (0.31 g, 1.41 mmol; 8 mol%) were added to a Schlenk tube. After a while the solution turned dark blue, then violet, progressively accompanied by gas evolution. The violet solution was heated to 80°C in an oil-bath for 8 days. The reaction mixture was distilled under vacuum. N-(phenyImethylsilyl)-1,4-dihydro-3,5-lutidine (H/D) (2.4 g, 70% yield) was isolated as a colorless liquid (b.p. 80-90 °C/0.02 mmHg).

3.5.19 Reaction of 3,5-lutidine, Cp₂TiMe₂ and PhMeSiH₂ under H₂

PhMeSiH₂ (3.60 mL, 26.4 mmol), 3,5-lutidine (2.1 mL, 18.4 mmol) and Cp₂TiMe₂ (0.41 g, 1.80 mmol; 10 mol%) were added to a Parr reactor which was then charged with H₂ (250 psi) and kept at 80°C for three days. 60% of the 3,5-lutidine was converted to N-(phenylmethylsilyl)-1,4-dihydro-3,5-lutidine and N-(phenylmethylsilyl)-1,2,3,4-tetrahydro-3,5-lutidine (ratio 1:2 by NMR).

3.5.20 Reaction of 3,4-lutidine, Cp2TiMe2 and PhMeSiH2 under H2

PhMeSiH₂ (3.2 mL, 26.0 mmol), 3,4-lutidine (1.8 mL, 17.3 mmol) and Cp₂TiMe₂ (0.36 g, 1.73 mmol; 10 mol%) were added to a Parr reactor which was then charged with

 H_2 (250 psi) and heated at 80°C for three days. No hydrosilated/hydrogenated products were detected.

A similar reaction was run under Ar instead of H_2 with the same results.

3.5.21 Reactions of pyridine, 3-picoline, 4-picoline and 3,5-lutidine with Cp₂TiMe₂ and PhMeSiH₂ rate Comparison

In separate Schlenk reactors, pyridine (0.35 ml, 4.6 mmol), 3-picoline (0.45 ml, 4.6 mmol), 4-picoline (0.45 ml, 4.6 mmol), and 3,5-lutidine (0.48 ml, 4.6 mmol) were added to the mixture of Cp_2TiMe_2 (0.09 g, 0.43 mmol) and PhMeSiH₂ (0.89 ml, 6.5 mmol) together with 50 µl of Si(Et)₄ (in the case of pyridine 0.13 ml of C₆D₆ was also added). The mixtures were stirred at room temperature. NMR samples were extracted periodically by syringe. The conversions were calculated based on the comparison of integrals.

3.5.23 Reaction of pyridine-d5 and H2 catalyzed by Cp2Ti-H

Pyridine-d₅ (0.30 ml, 3.94 mmol) was added to a solution of Cp₂Ti-H [50 mg (0.28 mmol) in 1 ml toluene-d₈]. The mixture was kept under 400 psi H₂ and 80 °C for ten hours. ¹H NMR spectra showed less than 10% of the pyridine was hydrogenated, but most of the D at positions 2 and 6 was exchanged with H.

3.5.24 Reaction of 2,3-lutidine with PhMeSiD₂ in the presence of Cp₂TiMe₂

2,3-lutidine (0.30 ml, 2.87 mmol) was added to the mixture of Cp_2TiMe_2 (0.03 g, 0.14 mmol) and PhMeSiD₂ (0.60 ml, 4.4 mmol). The mixture was stirred at 80 °C for 24

hours. ¹H NMR spectra showed no hydrosilation/hydrogenation product, but most of the H at position 6 was exchanged with D.

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CHAPTER 4

HYDROSILATION/HYDROGENATION REACTIONS OF NICOTINATES AND ETHYL BENZOATE WITH PhMeSiH₂ CATALYZED BY TITANOCENES

4.1 Introduction

Functional group manipulation is the foundation of organic synthesis. Therefore it attracts great attention. Transformations of aldehydes and ketones to alcohols (or even hydrocarbons) and transformations of esters to alcohols or aldehydes have all been explored and well established. These transformations can be achieved by two major routes: (1) reaction with metal hydrides, (2) hydrogenation and hydrosilation catalyzed by metals or metal complexes.

Lithium aluminum hydride (lithium alanate), sodium aluminum hydride, and aluminum hydride, for example, are well known reducing agents in organic chemistry. They are traditionally used for the reduction of various carbonyl and other functionalities. However, their strong reducing power makes it hard to control the reactions especially when partial reduction is needed as in some cases with esters. This disadvantage of these agents prompted some modifications. Alkoxy, or amino substituents and alkyl groups have been introduced, and several modified aluminum hydrides have become the current choices to accomplish the partial reduction of carbonyl compounds,¹ e.g., **Eq. 4.1**.

However, the mandatory use of low temperature (usually -78 °C) is regarded as a disadvantage for using these reagents.

Since the discovery in 1972 that Wilkinson's complex, RhCl(PPh₃)₃, is an extremely effective catalyst for the hydrosilation of carbonyl compounds,² hydrosilation has been developed as an important method for the reduction of carbonyl compounds since the resultant Si-O bond can very easily undergo hydrolysis. It has been found that the hydrosilation of carbonyl compounds can be effected by various catalytic systems.³ Transition metal complexes other than Wilkinson's complex, including platinum,⁴ ruthenium^{5.6} and rhodium^{7.9} have also been shown to have a good catalytic activity. Some selective and asymmetric hydrosilations of carbonyl compounds have been achieved using these transition metal complexes as catalysts.¹⁰ Corriu's and Fujita's groups reported that some alkali metal salts and ammonium fluorides are also effective for hydrosilation reactions (**Eq. 4.2**).^{11,12}

$$\frac{R}{R'}C=O + HSiX_3 - \frac{cat.}{R'}CH-OSiX_3$$
 Eq. 4.2

Recently, titanocene derivatives were added to the list of catalysts for the hydrosilation of carbonyl compounds.^{3b} They have found wide applicability in organic chemistry including hydrogenation and hydrosilation of carbonyl compounds. Hydrosilation of both ketones,¹³ and lactones¹⁴ has been reported. Buchwald and co-workers¹⁵ developed several procedures for the overall reduction of esters to primary alcohols *via* titanium-catalyzed hydrosilation reactions. A variety of esters, including those containing bromo-, phenoxy-, amino-, alkenyl or cyclopropyl- groups, as well as α , β -unsaturated esters, can be reduced with triethoxysilane and catalytic amounts of titanocene dichloride, preactivated with butyllithium.^{15a} This procedure can be used for the selective reduction of methyl esters in the presence of *t*butyl esters. For substrates containing a terminal olefin or an epoxide a more hindered titanocene dichloride species, such as bis(tetrahydroindenyl)titanium dichloride ([EBTHI]TiCl₂), is required. Other procedures

involving safer and cheaper reagents, such as PMHS and EtMgBr in the place of (EtO)₃SiH and *n*BuLi were also reported.^{15c}

In the study of hydrosilation/hydrogenation of pyridines employing Cp₂TiMe₂ as the catalyst (see **Chapter 3**), it was found that electronwithdrawing groups on the pyridine ring exert a different influence on the reaction from electron donating groups. In the case of carboalkoxy substituted pyridines the reactions occured at the ester group instead of the pyridine ring, except for the case of ethyl nicotinate. More interestingly, an unprecendented example of the one-pot transformation from an ester group to an alkyl group was observed. This chapter presents the results of hydrosilation/hydrogenation reactions of some nicotinates, ethyl benzoate and lactones.

4.2 Results and Discussion

4.2.1 Hydrosilation/hydrogenation of nicotinates

4.2.1.1 Hydrosilation/hydrogenation of ethyl nicotinate

Reaction of ethyl nicotinate and PhMeSiH₂ in the presence of Cp_2TiMe_2 produce ethyl N-phenylmethylsilyl-1.6-dihydronicotinate (41) (Eq. 4.3). The pyridine ring was



hydrosilated as in the cases of pyridine, 3-picoline, 4-picoline, and 3.5-lutidine described in Chapter 3. The same color change, from dark blue to brown, was observed. However, the reaction went to completion much faster than those of pyridine and its alkyl substituted derivatives (complete reactions within three hours as opposed to more than 8 hours at 80 °C). Evidently the higher reaction rate is attributable to the electron-withdrawing effect of the ester group. As discussed in **Chapter 3**, the formation of a complex between the substrate and the titanocene species is a crucial step in the reaction. The higher the electron density on the N atom the stronger the N \rightarrow Ti bond would be expected. The reverse order of the reaction rate relative to the basicity suggests the N \rightarrow Ti bond breaking step is possibly the rate controlling step in the hydrosilation/hydrogenation reaction.

The reaction product was identified from its ¹H NMR spectrum which gave resonances of H-2, H-4, H-5 and H-6 at 7.48 (s), 5.95 (dd), 4.60 (dt) and 3.32 (m) ppm respectively. This assignment was confirmed by decoupling, COSY and HMQC NMR experiments.

In contrast to the cases of pyridine and the alkyl substituted pyridines, the final product has a hydrogen added at the 6 position. Although with 3-picoline and 3,5-lutidine, the monohydro products, 1-(phenylmethylsilyl)-1,4-dihydro-3-picoline and 1- (phenylmethylsilyl)-1,4-dihydro-3,5-lutidine, were obtained, the hydrogen added at the 4 position rather than the position 2 or 6. This observation is attributable to the conjugation between the C=O double bond of the ester group and the remaining double bonds on the pyridine ring. With the hydrogen added at the 6 position, C=O conjugates with two double bonds; if the hydrogen adds at the 4 position C=O only conjugates with one double bond. Evidently the former product is favored.

4.2.1.2 Hydrosilation/hydrogenation of ethyl isonicotinate

Reaction of ethyl isonicotinate with PhMeSiH₂ in the presence of Cp_2TiMe_2 gives totally different results from the ethyl nicotinate. As described above, in the case of ethyl nicotinate the ring was reduced, but not the ester group. However, with the ester group at the 4-position, instead of the 3-position, the ester group was reduced producing 4-picoline and 42 (Eq. 4.4). This dramatic change undoubtedly originates from the stronger electron-withdrawing effect of the ester group at the 4-position than at the 3-position. Obviously there are two potential reaction sites: the ring and the ester group. For the reaction to take place on the ring, the key step is the formation of a complex through the coordination of N to the Ti on the titanocene species as discussed in the previous chapter. If the coordination is very weak or can't be formed, no hydrogenation/hydrosilation would be expected on the ring whereas the ester group would competitively undergo hydrogenation/hydrosilation reactions. This hypothesis is strongly supported by the different behaviors exhibited by ethyl nicotinate and ethyl isonicotinate. In the former case, with the ester group at the 3 position, the coordination between N and Ti is still strong enough to sustain the hydrosilation/hydrogenation on the ring, while in the latter case, a stronger electron-withdrawing effect weakens the coordination ability of N which disfavors the hydrosilation on the ring and hence favors the hydrosilation/hydrogenation on the ester group.



Although hydrosilation of esters has been well-documented with various systems ranging from salt initiated reactions to early and late transition metal complex catalyzed ones, in all these numerous examples, the products were without exception the silyl ethers. To our knowledge, no example has been reported of a one-pot transformation of an ester group to an alkyl group though this transformation can be achieved through several steps with ease.

4.2.1.3 Hydrosilation/hydrogenation of ethyl 2-methylnicotinate and methyl 6-methylnicotinate

Cp₂TiMe₂ catalyzed reaction of ethyl 2-methylnicotinate and PhMeSiH₂ yields 2,3lutidine and 43 (Eq. 4.5). With a methyl group at position 2, higher electron density on the N would be expected compared with ethyl nicotinate which would favor the complexing between Ti and N. However, a methyl group at position 2 also introduces higher steric hindrance to the formation of the complex. By the comparison with the case of 2-picoline where no hydrosilation/hydrogenation was observed (although H/D exchange occurred at position 6), it is to be expected that reduction would occur at the ester group rather than the ring.



Similarly, reaction of methyl 6-methylnicotinate and PhMeSiH₂ in the presence of Cp_2TiMe_2 produces 2,5-lutidine and 44 (Eq. 4.6). The presence of a methyl group at the 6 position favors the hydrosilation/hydrogenation reactions at the ester group rather than on the ring, as in the case of ethyl 2-methylnicotinate.



4.2.2 Hydrosilation/hydrogenation of ethyl benzoate

The hydrosilation/hydrogenation of ethyl isonicotinate, ethyl 2-methyl nicotinate and methyl 6-methylnicotinate showed two kinds of transformations: (1) from an ester group to a silyl ether group; (2) from an ester group to an alkyl group. In order to test whether the transformation of the ester group to alkane is peculiar to these nicotinates or is more general, ethyl benzoate was reacted with Cp₂TiMe₂ and PhMeSiH₂. Once again, the same transformations were detected, giving toluene and **45** (Eq. 4.7). However, the reaction was much faster and much more violent than in the cases of nicotinates. The complexing between N in nicotinates and Ti in the catalytic species may partly account for the different reaction rates. In the reaction of ethyl benzoate with PhMeSiH₂ in the presence of Cp₂TiMe₂, dramatic gas (CH₄ and H₂) evolution was observed after the initiation reaction, and 100% conversion was achieved when the gas evolution ceased.



(100% conversion)

Entry	Ratio of Cp ₂ TiMe ₂ to ethyl benzoate (%)	Temperature (°C)	Yield of toluene (based on ¹ H NMR
			integration) (%)
1	5	20	5
2	10	20	10
3	20	20	19
4	20	20	47
5	30	20	11
6	40	20	13
7	10	0	1.7
8a	20	20	4
9b	20	20	3
10	20	40	40
110	20	40	100

Table 4.1 Reaction of ethyl benzoate with PhMeSiH₂ and Cp₂TiMe₂ under various conditions

a) ethyl benzoate was added dropwise after the initiation reaction of PhMeSiH₂ and Cp₂TiMe₂. b) 0.10 ml PhMeSiH₂ was added to the mixture of Cp₂TiMe₂ (0.088 g, 0.43 mmol) and ethyl benzoate (0.30 ml, 2.13 mmol), after the solution color changed from orange to dark violet blue, 0.50 ml more PhMeSiH₂ was added to the mixture drop-wise. c) the reaction was run under 40 psi H₂.

Several methods were tried to boost the yield of toluene including varying temperature, ratio of Cp_2TiMe_2 to ethyl benzoate, and sequence of addition of starting materials (**Table 4.1**). When the reaction was performed at room temperature with different ratios of Cp_2TiMe_2 to ethyl benzoate ranging between 5% and 40% (entries 1 to 6), the results showed that when the ratio was not higher than 20%, toluene yield increased as the ratio increased (entries 1 to 4). However, lower yields of toluene were obtained, when the ratio was higher than 20% (entries 5 and 6).

When the reaction was run at 0 °C, the yield of toluene was about 2% while 10% catalyst was used (entry 7). Dropwise addition of ethyl benzoate, or silane after the initiation reaction of PhMeSiH₂ and Cp₂TiMe₂ also led to a low yield of toluene (entries 8, and 9).

On the other hand, as high as 40% yield of toluene was obtained when the reaction was run under argon at 40 °C (entry 10). If the reaction was run under 40 psi H₂ at 40 °C, the toluene yield was 100% (entry 11).

However, despite the general trends observed, in some trials, unexpectedly high toluene yields were obtained as in Entry 4. This implies that some uncontrolled factors play important roles in determining the selectivity.

When compound **45** was reacted with PhMeSiH₂, in the presence of Cp_2TiMe_2 , no toluene was produced. This result suggests that compound **45** is not an intermediate on the way to toluene.

In an effort to capture a possible catalyst intermediate, a stoichiometric reaction of Cp_2TiMe_2 , PhMeSiH₂ and ethyl benzoate was carried out. The green crystalline product of this reaction proved to be the ethoxo-bridged titanocene dimer. $[Cp_2Ti(\mu-OCH_2CH_3)]_2$ (46) (Fig. 4.1) reported by Samuel and co-workers and synthesized through the reaction of Cp_2TiMe_2 and triethoxysilane.¹⁶ Compound 46 was first briefly mentioned along with $[Cp_2Ti(\mu-OPh)]_2$ by Lappert in 1971.¹⁷

While no reaction was observed between **46** and ethyl benzoate. **46** reacted with PhMeSiH₂ at room temperature producing a small amount of dimer of PhMeSiH₂ in 24 hours. Interestingly no transfer of ethoxy group to silane was positively detected. When ethyl benzoate was added to the mixture of **46** and PhMeSiH₂, **45** was produced as the major product. This suggests that **46** is also an effective precatalyst for the activation of the Si-H bond. It is not supprising that **46** is also active for the polymerization of primary silanes. Corriu¹⁸ has shown that [Cp₂Ti(OPh)₂ is active for similar reactions. It is not supprising that a Ti(III) compound such as **46** is also active for polymerization of silanes.



Figure. 4.1 Crystal structure of [Cp₂Ti(µ-OCH₂CH₃)]₂ (46)^{16a}

4.2.3 Reaction of lactones with PhMeSiH₂ catalyzed by Cp₂TiMe₂

The transformation of the carbethoxyl group of ethyl benzoate into an alkyl group prompted us to study the reaction with lactones, which can be considered as aliphatic esters. When γ -butyrolactone was reacted with PhMeSiH₂ and Cp₂TiMe₂ as the catalyst at 80 °C, a viscous mixture was obtained in 24 hours. The mixture was soluble in THF. When the THF solution was dropped into methanol, a white precipitate was obtained. Based on ¹H and ¹³C{¹H} NMR spectra, the white solid was assigned as copolymer **47** (Eq. **4.8**). GPC analysis indicates $M_{\rm w} = 4.9 \times 10^3$ with $M_{\rm w}/M_{\rm n} = 1.3$.

Similar results were obtained with (±)- β -butyrolactone. When (±)- β -butyrolactone was reacted with PhMeSiH₂ with Cp₂TiMe₂ as the catalyst (**Eq. 4.9**), **48** was produced $(M_{\rm w} = 1.8 \times 10^3 \text{ with } M_{\rm w}/M_{\rm n} = 1.2).$





4.3 Discussion of mechanism

Formation of a complex with the substrate is considered a prerequisite for an organometallic compound to act as a catalyst. In the cases of nicotinates, there are two major possible reaction sites, the O atom in the carbonyl group and N atom in the ring. Both the O and N are able to donate lone pair electrons to enable the substrate to form a complex with the catalytic titanocene species. Which site is favored in the reaction is determined by steric and electronic factors.

Interestingly, in the case of ethyl nicotinate, the reaction mainly occurred on the ring, and no significant hydrosilation/hydrogenation on the ester group was observed. As discussed in Chapter 3, while both Cp₂Ti-Si and Cp₂Ti-H are available in the system, only Cp₂Ti-Si is effective for the hydrosilation/hydrogenation of the pyridine ring. A possible route is similar to the one shown in Scheme 3.5. The first step is the formation of complex 49 between Cp₂Ti-Si and ethyl nicotinate with the N on the ring donating the lone pair of electrons to Ti center (Eq. 4.10).



Complex 49 undergoes further reaction with the addition of the Ti-Si bond to the C=N. For an unsymmetric substrate such as ethyl nicotinate, there are two possible ways to add the Ti-Si bond to the ring: (1) Si attacks the N atom from the same side of the carbethoxy group; (2) Si attacks the N from the opposite side of the carbethoxy group. With Si attacking from the same side of the carboethoxy group and the Cp₂Ti moiety shifting to the position 6 (Scheme 4.1), 50 would be the expected compound which undergoes σ -bond metathesis with Si-H to give the final product 41. While attack from the other side would lead to the formation of 51, and 52 would be the expected final product from further σ -bond metathesis of 51 with Si-H (Scheme 4.2). However, 52 was not detected as a final product. This may be attributable to the steric hindrance of the carboethoxy group which makes the shift of the Cp₂Ti moiety to the position 2 hard to proceed. This is in conformity with the observation in the case of 3-picoline where the similar addition of Si-Ti is not favored and the crystal structure of compound 36 is also in support of the steric hindrance explanation (see Chapter 3).







When there is a substituent at position 2 or 6, i.e. ethyl 2-ethylnicotinate or methyl 6-methylnicotinate, the hydrosilation/hydrogenation reactions occurred on the ester group instead of the ring. This is attributed to the steric effect of the substituents at position 2 or 6. It is reasonable to believe that a complex of Cp_2Ti -Si with ethyl 2-methylnicotinate or methyl 6-methylnicotinate would be too difficult to form. Even if the complex can be formed, the further addition of the Ti-Si bond to the ring would be inhibited by the presence of the methyl group at position 2 or 6.

The formation of a complex between the substrate and Cp_2Ti -H has been demonstrated by H/D exchange experiments (see **Chapter 3**). While no hydrogenation/hydrosilation on the ring occurred, significant H/D exchange was observed at the 6 position. The formation of a complex is also suggested by the different reaction rates of ethyl 2-methylnicotinate (or methyl 6-methylnicotinate) and ethyl benzoate. Undoubtedly, formation of a complex between Ti and the ring N would disfavor reaction of the carbalkoxy group by lowering the number of catalyst sites available to it. While the reactions were performed under the same conditions, in the case of ethyl 2-methylnicotinate or methyl 6-methylnicotinate a much longer time (more than 24 hours) is needed for 100% conversion.

The apparent sensitivity of reaction mechanism to the strength of the $N\rightarrow$ Ti coordination is evident from the results obtained with ethyl nicotinate and ethyl isonicotinate. Although in these two cases the only difference is the position of the carbalkoxy group, two different types of product resulted: with ethyl nicotinate the ring was hydrosilated, whereas with ethyl isonicotinate the ester group was hydrosilated. A difference of steric effect is unlikely to be the reason since an ester group at position 3 should be even more a hindrance for the reaction on the ring than an ester at position 4. The most likely reason for this difference is that the carbalkoxy group at position 4 exerts a stronger electron withdrawing effect on the N than at position 3, hence reducing the basicity of the N on the ring to the point that hydrosilation occured on the carbalkoxy group rather than the ring.

Hydrosilation of esters has previously been reported by Buchwald et al.¹⁵ A mechanism was proposed on the basis of relatively little experimental evidence. A similar reaction route is shown in **Scheme 4.3** on the basis of some convincing evidence from the present study. The initially formed catalyst Cp₂Ti-H adds to the carbonyl group of the ester substrate leading to intermediate **53**. Further stabilization of **53** could derive from coordination of the ethoxy group to the titanium center. Decomposition of **53** to an aldehyde then occurs with formation of a titanocene alkoxide. The successful isolation and characterization of the ethoxo-bridged titanocene dimer **46** from the stoichiometric reaction strongly supports this mode of decomposition of **53**. Addition of Cp₂Ti-H to the aldehyde followed by σ -bond metathesis with Si-H, transforms it into either a silyl ether or an alkyl group with regeneration of the titanocene hydride. The titanocene ethoxide may rejoin the catalytic cycle as titanocene hydride through σ -bond metathesis with Si-H as shown in **Eq. 4.11**.



Both toluene and silvl ether were obtained from a reaction of benzaldehyde with $PhMeSiH_2$ using Cp_2TiMe_2 as the catalyst, thus indicating that benzaldehyde is a plausible intermediate in the overall ester reduction.



Scheme 4.3

In the cases of lactones, the reaction may also follow the route shown in Scheme 4.3. Decomposition of 53 leads to the opening of the ring. A plausible mechanism for the formation of a longer chain is shown in Scheme 4.4. The Si-H bond in a silane is more active when there is an alkoxy substituent, thus the formation of the copolymer is reasonable.¹¹

In the case of ethyl benzoate, the transformation from a carbalkoxy group to an alkyl group is favored at higher temperature and in a H₂ atmosphere as was shown. A competitive reaction shown in Eq. 4.12 with the one shown in Eq. 4.11 accounts for the formation of the alkyl group. The activation energy for the reaction shown Eq. 4.12 could be higher than that for Eq. 4.11, which in turn makes Eq. 4.12 preferred at higher temperature. Cp₂Ti-O-Si would then react with Si-H as in Eq. 4.13 to reproduce the Cp₂Ti-H.

$$Cp_{2}Ti-OR + Si-H \longrightarrow Cp_{2}Ti-O-Si + H-R \qquad Eq. 4.12$$

$$Cp_{2}Ti-O-Si + Si-H \longrightarrow Cp_{2}Ti-H + Si-O-Si \qquad Eq. 4.13$$

Another plausible pathway is that **53** reacts with the silane through a σ -bond metathesis to regenerate the catalyst and the alkoxysilane **54** (Eq. 4.14). Compound **54** then undergoes further reaction with the silane to produce the ether or the alkoxysilane as shown in Eq. 4.15 and Eq. 4.16 respectively.¹¹ Since some uncontrolled factors play important roles in the production of toluene, further work is needed to examine the mechanism in depth.

The ether produced reacts with Cp_2Ti-H to produce the alkyl group and the titanocene alkoxide (Eq. 4.17). In a reaction of benzyl methyl ether and PhMeSiH₂ in the presence of Cp_2TiMe_2 , only toluene but no silyl ether was observed. On the other hand, a similar reaction with silyl ether as the starting material produced no toluene.



The high toluene yield under a H_2 atmosphere may imply that titanocene hydride plays an important role in the transformation of the carboalkoxy group to an alkyl group.

The titanocene(III) alkoxide (46), can also act as a catalyst for the hydrosilation of esters and the polymerization of phenylsilane. Further work is needed to clarify whether it works in the same way as Cp_2TiMe_2 does, *i.e.*, through the formation of $Cp_2Ti(III)$ hydride or in a different way, without transferring the alkoxy group to the substrate. Several pieces of evidence point to the latter pathway. As described earlier, no alkoxy group transfer to the silane was positively detected in the reaction of PhMeSiH₂ and 46 while the silane dimer was observed.

 $Cp_2Ti(III)$ hydride is extremely air sensitive while large crystals of 46 can be handled in air for a few minutes as indicated by Samuel et al.^{16a} Buchwald et al.^{15a} found that the reduction of esters with HSi(OEt)₃ using Cp₂TiCl₂/n-BuLi as the catalyst is relatively insensitive to the presence of adventitious moisture or small amounts of oxygen. A system for the hydrosilation of esters with Ti(O-i-Pr)₄ as catalyst was also shown to be

air-stable.^{15b} All these observations imply that the alkoxy group may stay on the catalytic species throughout the catalytic cycle and its existence makes the catalytic system less moisture and oxygen sensitive.

4.4 Summary

Cp₂TiMe₂ catalyzed hydrosilation/hydrogenation reactions of nicotinates and ethyl benzoate have been studied. With ethyl nicotinate as the substrate, the hydrosilation reaction occurred on the ring and ethyl N-(methylphenylsilyl)-1,6-dihydronicotinate was obtained as the only product. No reaction was observed at the ester group. However, with the substrates ethyl isonicotinate, ethyl 2-methylnicotinate or ethyl 6-methylnicotinate, the hydrosilation/hydrogenation occurred only at the ester groups and two types of transformation were found:

(1) carbalkoxy into alkoxysilane:



(2) carbalkoxy group into an alkyl group:



In the case of ethyl isonicotinate, alkoxysilane **42** was produced. The difference of the reaction site between ethyl nicotinate and ethyl isonicotinate is attributed to the different electronic effects of position 3 and position 4 on the pyridine ring.

In the case of ethyl 2-methylnicotinate, a mixture of alkoxysilane 43 and 2,3lutidine was obtained. In the case of methyl 6-methylnicotinate, compound 44 and 2,5lutidine were obtained. Benzyl ethoxymethylphenylsilyl ether and toluene were produced in the reaction of ethyl benzoate and PhMeSiH₂ catalyzed by Cp₂TiMe₂. The production of toluene can be suppressed by using mild conditions such as low temperature and slow addition of ethyl benzoate or silane after the initiation reaction of Cp₂TiMe₂ with PhMeSiH₂. On the other hand, high toluene yield can be obtained at high temperature(about 40 °C) and under H₂ (40 psi).

Copolymers were obtained from the reactions of lactones with $PhMeSiH_2$ catalyzed by Cp_2TiMe_2 .

4.5 Experimental section

4.5.1 General manipulations

All manipulations were performed under an atmosphere of nitrogen or argon using Schlenk techniques. Dry, oxygen free solvents were employed throughout. Glassware was flame-dried or oven-dried before use.

4.5.2 Analyses and materials

4.5.2.1 Analyses

Proton NMR spectra were recorded on Varian XL-200, XL-300, Gemini-200, and Unity-500 spectrometers using internal solvent reference. Carbon-13 NMR spectra were recorded on a Unity-500 NMR spectrometer using C_6D_6 (128.0 ppm) as reference.

GPC analyses were run with THF as solvent and calibrated relative to polystyrene standard.

4.5.2.2 Materials

Ethyl nicotinate, ethyl isonicotinate, ethyl 2-methylnicotinate, methyl 6methylnicotinate, ethyl benzoate, benzaldehyde, and benzyl alcohol were purchased from Aldrich Chemical Co. and purified by distillation over calcium hydride before use. γ -Butyrolactone and (±)- β -butyrolactone were purchased from Aldrich and distilled prior to use.

Benzylmethyl ether was prepared using the following procedure: sodium was added to benzyl alcohol in a molar ratio of 1:1. After the sodium had dissolved, CH_3I was added dropwise using a syringe. A white solid appeared upon the addition of CH_3I . After stirring the suspension for one hour, dilute HCl solution (5ml concentrated HCl in 30 ml H₂O) was added dropwise to the mixture. The organic phase was washed three times with distilled water and then dried with MgSO₄. Pure benzylmethyl ether was obtained by distillation in 80% isolated yield.

Dimethyltitanocene and phenylmethylsilane were prepared following the same procedure described in 2.4.2.1 (Chapter 2).

4.5.3 Reaction of ethyl nicotinate and PhMeSiH₂ in the presence of Cp₂TiMe₂

PhMeSiH₂ (0.45 mL, 3.3 mmol) and ethyl nicotinate (0.3 mL, 2.2 mmol) were added to Cp₂TiMe₂ (40 mg, 0.20 mmol). After a ten minutes, the solution color changed from orange to dark blue, then purple, accompanied by gas (CH₄, and H₂) evolution. The mixture was stirred at 80°C. Quantitative conversion was obtained in 3 hours. Ethyl N-(phenylmethylsilyl)-1,6-dihydronicotinate was obtained in 90% yield according to NMR. ¹H NMR (δ ppm): 0.06 (d, J = 3.5 Hz, 3H, SiCH₃), 0.97 (t, J = 7.2 Hz, 3H, OCH₂CH₃), 3.32 (m, 2H, NCHC(OEt)CHCHCH₂), 4.06 (t, J = 7.2 Hz, 2H,
OCH₂CH₃), 4.60 (dt, J = 8.0 Hz, J' = 3.4 Hz, 1H, NCHC(OEt)CHCHCH₂), 4.72 (q, J = 3.5 Hz, 1H, Si-H), 5.58 (dm, J = 8.0 Hz, 1H, NCHC(OEt)CHCHCH₂), 7.48 (s, 1H, NCHC(OEt)CHCHCH₂). MS (EI) m/e (%): 274 (M⁺ + 1) (3.6), 196 (M⁺ - C₆H₅) (4.4).

4.5.4 Reaction of ethyl isonicotinate and PhMeSiH₂ in the presence of Cp₂TiMe₂

PhMeSiH₂ (0.26 mL, 1.91 mmol) and ethyl isonicotinate (0.13 mL, 0.95 mmol) were added to Cp₂TiMe₂ (10 mg, 0.05 mmol) in a Schlenk tube. The color of the solution became dark blue then brown over the course of three hours. The solution was stirred at 80 °C for a further36 hours. 4-picoline and the silylether, 42, were observed in the reaction mixture.(1:5). ¹H NMR data (δ , ppm) for 42: 0.35 (s, 3H, Si-CH₃), 1.15 (t, 3H, OCH₂CH₃), 3.7 (q, 2H, OCH₂CH₃), 4.61 (m, 2H, -CH₂O-), 6.8 - 8.5 (m, 9H, Ph-H and the H on the pyridine ring).

4.5.5 Reaction of ethyl 2-methylnicotinate and PhMeSiH₂ in the presence of Cp₂TiMe₂

PhMeSiH₂ (0.30 mL, 2.1 mmol) and ethyl 2-methylnicotinate (0.2 mL, 1.3 mmol) were added to Cp₂TiMe₂ (24 mg, 0.11 mmol). After a while, the solution color changed to dark blue then brown accompanied by gas evolution. The mixture was stirred at room temperature for 24 hours. Quantitative conversion was obtained in 5 hours. 2,3-Lutidine and compound **43** were detected in a 2:3 ratio by ¹H NMR (in benzene - d_6 , 20 °C). ¹H NMR data (δ , ppm) for compound **43**: 0.35 (s, 3H, Si-CH₃), 1.15 (t, 3H, OCH₂CH₃), 2.40 (s, 3H, Me on the ring), 3.7 (q, 2H, OCH₂CH₃), 4.60 (m, 2H, -CH₂-O), 6.7 -8.6 (m, 8H, Ph-H and H's on the pyridine ring).

4.5.6 Reaction of methyl 6-methylnicotinate and PhMeSiH₂ in the presence of Cp₂TiMe₂

PhMeSiH₂ (0.15 mL, 1.1 mmol) and methyl 6-methylnicotinate (0.07 g, 0.46 mmol) were added to Cp₂TiMe₂ (10 mg, 0.05 mmol). After a while, the solution color changed to dark brown accompanied by gas evolution. The mixture was stirred at room temperature for 24 hours. Quantitative conversion was obtained. 2,6-lutidine and compound 44 were detected in a ratio of 1:4 by ¹H NMR (in benzene - d_6 , 20 °C). ¹H NMR data (δ , ppm) for compound 44: 0.37 (s, 3H, Si-CH₃), 2.50 (s, 3H, Me on the ring), 3.40 (s, 3H, OCH₃), 4.65 (m, 2H, -OCH₂-O), 6.6 - 8.0 (m, 8H, Ph-H and H's on the pyridine ring).

4.5.7 Reaction of ethyl benzoate and PhMeSiH₂ in the presence of Cp₂TiMe₂

PhMeSiH₂ (0.20 mL, 1.4 mmol) and ethyl nicotinate (0.10 mL, 0.70 mmol) were added to Cp₂TiMe₂ (14 mg, 0.07 mmol). After a while, the solution color changed to dark blue then brown accompanied by violent gas evolution. The mixture was stirred at room temperature. Quantitative conversion was obtained within one hour. Toluene was found in 10% yield along with compound 45. ¹H NMR data for compound 45: 0.34 (s, 3H, Si-CH₃). 1.15 (t, 3H, -OCH₂CH₃), 3.70 (q, 2H, OCH₂CH₃), 4.78 (m, 2H, -CH₂-O-), 6.9 - 8.0 (m, Ph-H and the H's on the pyridine ring).

The experiments for exploring the effects of various reaction conditions, such as percentage of catalyst, temperature, the order of adding the reactants, were carried out following the above general procedures.

4.5.8 Preparation of [Cp₂Ti(µ-OEt)]₂

PhMeSiH₂ (0.70 mL, 4.9 mmol) and ethyl benzoate (0.40 mL, 2.5 mmol) were added to a solution of Cp₂TiMe₂ (0.50 g, 2.4 mmol in 40 ml toluene and 10 ml benzene). The solution changed to dark green with precipitation of green crystals of $[Cp_2Ti(\mu-OEt)]_2$. $[Cp_2Ti(\mu-OEt)]_2$ was separated from the solution, washed with hexane and dried in *vacuo* (0.40 g; 75% isolated yield).

4.5.9 Reaction of ethyl benzoate and PhMeSiH₂ in the presence of $[Cp_2Ti(\mu-OEt)]_2$

PhMeSiH₂ (0.34 ml, 2.60 mmol) was added to $[Cp_2Ti(\mu-OEt)]_2$ (50 mg, 0.11 mmol). The mixture was stirred at room temperature for 24 hours. The formation of 1,2-dimethyl-1.2-diphenyldisilane was observed by ¹H NMR. Ethyl benzoate (0.17 ml, 1.06 mmol) was then added. Gas evolution was observed in 5 minutes while the solution changed color from green to yellow/green. A conversion of 86% was obtained in 12 hours. No toluene was detected by ¹H NMR.

4.5.10 Reaction of benzaldehyde and PhMeSiH₂ in the presence of Cp₂TiMe₂

PhMeSiH₂ (0.40 mL, 3.06 mmol) and benzaldehyde (0.20 mL, 1.97 mmol) were added to Cp_2TiMe_2 (55 mg, 0.28 mmol). After a while, the solution color changed to purple then dark blue accompanied by gas evolution. Toluene was found in a 50% yield (by ¹H NMR).

4.5.11 Reaction of benzylmethyl ether and PhMeSiH₂ in the presence of Cp₂TiMe₂

PhMeSiH₂ (0.60 ml, 4.20 mmol) and benzyl methyl ether (0.30 ml, 2.46 mmol) were added to Cp_2TiMe_2 (0.10 g, 0.48 mmol). After a while, the solution color changed to

dark blue accompanied by gas evolution. Toluene was detected in 0.5% yield by ¹H NMR. After stirring at 60 °C for 4 hours, the toluene yield increased to 10% by ¹H NMR.

In the absence of Cp_2TiMe_2 , reaction of benzylmethyl ether with PhMeSiH₂, and benzylmethyl ether with (EtO)Me₂SiH at 60 °C yielded no toluene in 12 hours.

4.5.12 Reaction of γ-butyrolactone and PhMeSiH₂ in the presence of Cp₂TiMe₂

γ-Butyrolactone (0.30 ml, 3.9 mmol) and PhMeSiH₂(0.60 ml, 4.2 mmol) were added to a solution of Cp₂TiMe₂ (0.05 g, 0.24 mmol in 1 ml THF). After thorough mixing, the mixture was stirred for 10 hours at 80 °C. Then the reaction mixture was added dropwise to 10 ml of well-stirred methanol; 0.3 g of a white precipitate was obtained. The compound was assigned as -[OSiPhMeO(CH₂)₄]_n- based on ¹H and ¹³C NMR. GPC analysis indicated a $M_w = 4.9 \times 10^3$, $M_w/M_n = 1.3$. ¹H NMR data (δ , ppm): 0.40 (s, 3H, Si-CH₃). 1.7 (b, 4H, CH₂(CH₂)₂CH₂), 3.75 (b, 4H, CH₂(CH₂)₂CH₂), 7.0 - 8.0 (m, 5H, Ph-H). ¹³C {¹H} NMR data (δ , ppm): -5 (1C, SiCH₃), 29 (2C, CH₂(CH₂)₂CH₂), 62 (2C, CH₂(CH₂)₂CH₂), 130, 134 (6C, C₆H₅).

4.5.13 Reaction of (\pm) - β -butyrolactone and PhMeSiH₂ in the presence of Cp₂TiMe₂

(±)-β-Butyrolactone (0.30 ml, 3.7 mmol) and PhMeSiH₂ (0.55 ml, 3.8 mmol) were added to a solution of Cp₂TiMe₂ (0.05 g, 0.24 mmol, in 1 ml THF). After thorough mixing, the mixture was stirred for 8 hours at 80 °C. The reaction mixture was added drop-wise to 10 ml of well stirred methanol. 0.28 g of a white precipitate was obtained. The compound was assigned as -[OSiPhMeO(CH₂)₂CH(CH₃)]_n- based on ¹H NMR. GPC analysis indicates $M_w = 1.8 \times 10^3$ with $M_w/M_n = 1.2$. ¹H NMR data (δ , ppm): 0.40 (s,

3H, Si-CH₃), 1.1 (m, 3H, CH₂CH₂CH(CH₃)), 1.4 (m, 2H, CH₂CH₂CH(CH₃)), 3.6 (m, 2H, CH₂CH₂CH(CH₃)), 3.9 (m, 1H, CH₂CH₂CH(CH₃)), 7.1 - 7.9 (m, 5H, Ph-H).

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CHAPTER 5

ONE STEP CLOSER TO TITANOCENE —THE STRUCTURE OF TITANOCENE DIMER REVISITED

5.1 Introduction

Titanocene, Cp₂Ti, has long been proposed as an important intermediate in numerous titanocene catalyzed reactions of organosilanes. However, it has proven to be the most elusive of all the simple metallocenes of the first transition period.¹⁻⁴ Several groups claimed success in preparing titanocene at first, but none has proven to be authentic. Some substituted derivatives.⁵⁻⁸ such as **2**, **3**, **7**, **8**, **9**, and even Cp*₂Ti,⁹ have been reported, but the parent molecule has yet to be detected.⁵ Its existence remains an assumption based on the characterized derivatives. Part of the difficulty in obtaining titanocene is its high reactivity. This is compounded by the ease with which hydride decoys, whose elemental composition is very close to that of titanocene, result from synthetic reactions designed to produce titanocene. While designing synthetic reactions to yield titanocene still has a long way to go, its isolation from, or detection in a real catalytic reaction is a much tougher challenge. A further difficulty in pursuing titanocene is the absence of a sensitive spectroscopic probe for its detection, which theoretical calculations predict will have a triplet electronic ground state.⁶

A particularly interesting molecule, $(\eta^5 - C_5H_5)_3(\mu - \eta^5 - \eta^1 - C_5H_4)Ti_2(C_4H_8O)$, **2**, whose structure corresponded closely to that of a dimer of titanocene with only one less hydrogen, was reported many years ago by Pez.⁷ **2** was prepared through the reaction of Cp₂TiCl₂ with potassium naphthalene at -80 °C followed by recrystallization from THF solution. Considerable effort was expended to establish the presence of a hydride in the

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structure, but the physical evidence (including a crystal structure) did not support such a conclusion. The crystal structure of **2**, shown in **Fig.5.1**, formally consists of an $(\eta^{5}-C_{p})(\eta^{5}-C_{5}H_{4})(Ti(II)(THF))$ moiety coupled through a C atom of one of its Cp rings to an $(\eta^{5}-C_{p})_{2}(\eta^{1}-C_{5}H_{4})Ti(III)$ moiety. The molecule should therefore be paramagnetic, most likely with one unpaired electron. Temperature dependent shifts of the single broad ¹H-NMR peak followed a trend expected for a paramagnetic compound, but neither magnetochemical nor epr data were reported.

Figure 5.1. Structure of dimeric titanocene (2) from Ref. 7.



As part of the study of Cp₂TiMe₂ catalyzed ester reduction (see **Chapter 4**) the behavior of some lactones was investigated. A stoichiometric reaction of Cp₂TiMe₂, with γ -butyrolactone, or (±)- β -butyrolactone, yielded a dark-gray crystalline product which turned out to be a real dimer of the long pursued titanocene. This is not only the first direct evidence for the participation of titanocene in Cp₂TiMe₂ catalyzed silane reactions, but also the closest approach to titanocene. This chapter presents a description of the synthesis and x-ray analysis of the titanocene dimer, and its intermediate role in Cp₂TiMe₂ catalyzed silane reactions.

5.2 Results and discussion

5.2.1 Synthesis of $Cp[\mu \cdot (\eta^1: \eta^5 \cdot C_5H_4)](THF)Ti(\mu \cdot H)TiCp_2 \cdot 1/2THF$ (37)

A stoichiometric reaction of Cp₂TiMe₂, PhMeSiH₂ and γ -butyrolactone, or (±)- β butyrolactone (1 : 2 : 1, molar ratio), in a mixture of hexane and tetrahydrofuran (15:2) yielded well formed, gray plates of Cp[μ -(η^1 : η^5 -C₅H₄)](THF)Ti(μ -H)TiCp₂·1/2THF (Eq. 5.1).

$$Cp_2TiMe_2 + PhMeSiH_2 \xrightarrow{hexane/THF, lactone}$$
 Crystalline product Eq. 5.1

The product turned brown immediately when it was exposed to dry-oxygen or air. Probably due to its extreme air-sensitivity and instability, no reproducible IR spectrum was obtained despite many attempts. A ¹H NMR spectrum showed only broad peaks which were hard to assign. An EPR spectrum showed a featureless broad singlet. Although these spectroscopic results give no concrete evidence for an unambiguous assignment, they clearly point to a paramagnetic compound, or the presence of strongly paramagnetic impurities.

5.2.2 Crystal structure of Cp[μ -(η^1 : η^5 -C₅H₄)](THF)Ti(μ -H)TiCp₂ ·1/2THF (37)

Although the structure of **37** could not be assigned by spectroscopic methods, this is not unexpected since no convincing analytic evidence has been shown to confirm titanocene's existence since the pursuit began in the early 1950's. Fortunately, due to the high quality of the crystal, it was successfully characterized by single-crystal x-ray crystallography. The crystals were found to be monoclinic, space group C2/c, and in each unit cell, there are eight molecules of $C_{24}H_{28}OTi_2$ and four THF molecules occupying diffuse positions in the crystal lattice.

The crystal arrangement and molecular structure of **37** are shown in **Fig. 5.2**, **5.3**, and **5.4** respectively. The full structure report of **37** is presented in **Appendix IV**. The molecule is seen to consist of an assembly of three planar η^5 - bound C₅H₅, cyclopentadienyl rings and one η^1 and η^5 bound, planar, C₅H₄, cyclopentadienyl ligand that serves to bridge the two titanium atoms. One hydrogen also serves to bridge the titanium atoms. A molecule of THF is coordinated to the (η^5 -C₅H₅- η^5 -C₅H₄)Ti moiety. The two titanium atoms can be assigned either as Ti(II) and Ti(IV) or both as Ti(III). In either assignment, the compound could be paramagnetic.

The mean distance between the titanium and the carbon atoms of the $(\eta-C_5H_5)$ rings is 2.388Å. The distance between C1 and Ti2 is 2.207(5)Å. All are in conformity with the assignment that three of the Cp's are coordinating to Ti1 and Ti2 in η^5 -mode while the fourth one is coordinating in η^1 - and η^5 - modes, serving to bridge Ti1 and Ti2. These values are essentially the same as reported by Pez within the error range.⁷ It can be concluded that **37** and **2** are the same compound by comparing the molecular bond distances, bond angles, and related data of **37** in **Appendix IV** and those of **2** (see **Appendix V**).



Figure 5.2 Stereoscopic view of crystal structure of (C₅H₅)₃(C₅H₄)HTi₂(C₄H₈O)·1/2C₄H₈O



Figure 5.3 Molecular structure of (C₅H₅)₃(C₅H₄)HTi₂(C₄H₈O)·1/2C₄H₈O (Front view)
Ellipsoids drawn at 40% probability level. Hydrogen represented by sphere of arbitrary size. Bond length (Å): Ti(1)-Ti(2) 3.329 (2); Ti(2)-C(1) 2.207 (5);
Ti(2)-H(1) 1.82 (2); Ti(1)-H(1) 1.83 (2). Bond Angle (in degree): C(1)-Ti(2)-Ti(1) 44.12 (12); C(1)-Ti(2)-H(1) 68.3 (14); Ti(1)-Ti(2)-H(1) 24.2 (14).

However, as shown in **Figure 5.1** and **Figure 5.3**, there are two striking differences in the assigned structures: 2 has a Ti-Ti bond while **37** has none. and **37** has a bridging H while **2** has none. In the present work, the quality of the crystals, and data collection using Cu Ka radiation permitted the refinement of a bridging hydride ligand between the two Ti atoms. The Ti-H bonds were constrained to be similar (see experimental section). It is known that Cu K α radiation is more sensitive to light atoms than Mo K α radiation used for the analysis of **2**.⁷

The major revisions (one bridging hydrogen is located; no Ti-Ti bond is regarded present) make the structure more reasonable even with respect to the synthetic reaction used in Ref. 7, as the author noted that 2 "contains one less hydrogen atom than might be

expected for a product obtained by the reduction of $(C_5H_5)_2TiCl_2$ with 2 mol of potassium naphthalene." Moreover the author did try to locate the possible hydrogen. However, only the positions near the C1 (**Fig. 5.3**) ((numbered as C5 in reference 7 shown in **Fig. 5.1**) were tried. In view of the revised structure (**Fig.5.3**), the failure to locate the hydrogen is not surprising. C1 and the bridging H are actually on the diagonal positions of the tetragon formed by Ti1, Ti2, C1 and H1 as can be seen in **Fig.5.4**. This can also be shown by the related bond angles. The angle of C1-Ti1-H1 is 65.3 (14), Ti2-Ti1-H1 is 24.0 (14). and C1-Ti1-Ti2 is 41.37 (12); while C1-Ti2-H1 is 68.3 (14), Ti1-Ti2-H1 is 24.2 (14) and C1-Ti2-Ti1 is 44.12 (12). This can explain why the structure can't be well refined when a hydrogen is placed at the positions near C1. The successful location of the bridging hydrogen provides a satisfying revision to the structure of **2** which puzzled concerned chemists for years.



Figure 5.4 Molecular structure of (C₅H₅)₃(C₅H₄)HTi₂(C₄H₈O)·1/2C₄H₈O (Side view)

Given the presence of the bridging hydrogen and the distance between the two Ti atoms, the previously proposed Ti-Ti bond is unlikely. The atomic radius of Ti is 1.47Å, and the Ti-Ti bond distance is 2.8956 Å in titanium metal (α -form).¹⁰ The Ti-Ti distance of 3.329 Å is too long to be described as a metal-metal bond with the valencies of the Ti atoms considered. The bridging H helps hold the two Ti centers together and makes the invocation of a Ti-Ti bond unnecessary for the observed conformation of the Cp rings as claimed by Ref. 7.

5.3 Compound 37 and titanocene

Although titanocene has yet to be detected by physicochemical means. it has played a long and interesting role in catalysis, organic synthesis and the general development of the organometallic chemistry of the transition elements. In the two decades following the establishment of the structure of ferrocene, many attempts were made to prepare titanocene and a rather complicated and confusing body of literature accumulated.¹ Most of the putative titanocenes turned out to be hydrides of various kinds. The inclusion of the hydride bridge in the structure of **37** makes it a true dimer of titanocene. in which the Ti(II) of one titanocene inserts into a C-H bond of a second titanocene (**Eq. 5.2**). The



coordination of a THF molecule may help to stabilize the dimer in solution and then precipitate under suitable conditions. The unsuccessful attempts to obtain NMR and EPR

spectra to assign the structure of **37** may imply it is paramagnetic and that **Eq. 5.2** is a fast equilibrium. In the solution the EPR spectrum showed a broad singlet.

The intermediacy of $Cp_2Ti(II)$ has been postulated in a number of stoichiometric and catalytic reactions involving Cp_2TiMe_2 as the precatalyst, but hitherto the evidence has been indirect. The synthesis and characterization of **37** not only provides a revision to the structure of **2**, but also provides more direct evidence for the postulate that titanocene is a key intermediate in numerous Cp_2TiMe_2 catalyzed reactions. The formation of titanocene in reactions of Cp_2TiMe_2 and silanes has been eaplained as shown in **Eq.5.3**.or Eq.5.4.¹⁴

$$Cp_2Ti < CH_3 \xrightarrow{Si-H} Cp_2Ti < CH_3 \xrightarrow{Si-H} Cp_2Ti < CH_3 \xrightarrow{Si-H} Cp_2Ti$$
 Eq. 5.3

or

$$Cp_2Ti < CH_3 \xrightarrow{CH_3} Cp_2Ti < H_3 \xrightarrow{CH_3} Cp_2Ti < H_4 \xrightarrow{CH_3} Cp_2Ti$$
 Eq. 5.4

The so called "carbenoid" Cp₂Ti is very active.¹¹ Depending on the reaction conditions, it can: (1) dimerise; (2) react with a silane to produce the isolated 7 and 8;⁸ (3) undergo conproportionation reactions with Ti(IV) species and σ -bond metatheses to produce the key catalytic species, of Cp₂Ti-H, as described in previous chapters. The first two routes are favored in stoichiometric reactions where only stoichiometric amounts, or a slight excess of silane is available. Evidently the reactivity of the silane has some effect on the reaction with Cp₂Ti. For primary silanes, the second route is preferred over the first route while in the cases of secondary silanes the first route is the choice due to the lower activity of the secondary silanes. This can be the reason why in the primary silanes only 7 and 8 have been isolated, whereas in the present study titanocene dimer has been obtained. The presence of THF may inhibit further C-H addition to the second Ti leading to the formation of 1.5 The third route is applicable in catalytic reactions where a large excess of silane is present.

The synthetic reaction described above provides a very simple synthesis for **37**. Although a reaction occurs in the absence of the butyrolactone, we have not been able to obtain the titanocene dimer from it. The coordination ability of butyrolactone may help to lower the titanocene reactivity and steer the reaction towards the formation of **37**, rather than in the direction of a titanocene silyl complex. Maybe the very rapid tranfer of silyl and hydride to the lactone depletes hydride and silyl complex concentrations and raise the steady state concentration of titanocene. The product that crystallises out may be the least soluble, the most concentrated, or both.

5.4 Summary

In summary, $Cp[\mu-(\eta^1:\eta^5-C_5H_4)](THF)Ti(\mu-H)TiCp_2$, (**37**) which can be viewed as a dimer of titanocene (Cp_2Ti) has been isolated for the first time from a Cp_2TiMe_2 catalyzed reaction. The preparation of the crystalline product provided a first direct evidence to support the involvement of Cp_2Ti in numerous Cp_2TiMe_2 reactions and paved a possible way for elucidating the mechanisms of these reactions.

Based on the analysis results, this compound was first synthesized by Pez in 1972 through the conventional method of reducing titanocene dichloride with potassium naphthalene. However, the bridging H was not located. The higher quality of the crystal and modern technique enables us to correct the misunderstanding of the old assignment.

5.5 Experimental section

5.5.1 General manipulation and materials

All manipulations were performed under an atmosphere of nitrogen or argon using Schlenk techniques. Dry, oxygen free solvents were employed throughout. Glassware was flame-dried or oven-dried before use. In a typical reaction, the required amount of Cp_2TiMe_2 was first added to a Schlenk flask and connected to vacuum to remove the air carried by the sample. The flask was then filled with Ar. The procedure was repeated several times. The required reagents were added with a micro syringe.

 γ -butyrolactone was purchased from Aldrich and distilled prior to use.

Dimethyltitanocene, and phenylmethylsilane was prepared by the procedures described in 2.4.2.1 (Chapter 2).

5.5.2 Sythesis of crystalline $C_{26}H_{32}O_{1.5}Ti_2$ (37)

 γ -Butyrolactone (0.02 ml, 0.26 mmol) and PhMeSiH₂(0.07 ml, 0.49 mmol) were added to a Cp₂TiMe₂ in hexane/THF solution (50 mg, 0.24 mmol, in 15 ml hexane and 2 ml THF). After thorough mixing, the flask was left undisturbed for 24 h. 33 mg of dark gray plates was separated from the solution (65% isolated yield).

5.5.3 Collection of x-ray data and structure determination

The data were collected and refined by Dr. Anne-Marie Lebuis of the McGill University Crystallography Laboratory.

For the x-ray work, a crystal of **37** of dimensions of $0.52 \times 0.29 \times 0.01$ mm was mounted in a glass capillary under argon. The refinement of Pez was in the I2/a space group. We used the conventional C2/c orientation in our refinement. *Crystal data*: Formula: $C_{24}H_{28}O_1Ti_2 \cdot 1/2C_4H_8O_1$; FW = 456.299; monoclinic, C2/c; a = 31.232 (13), b = 7.998 (3), c = 19.603 (9), β = 116.78 (3); Z = 8, Z' = 1; Dc = 1.387 g/cm³. Data were collected on a CAD4 diffractometer using Cu K α radiation. In all. 29561 reflections were measured of which 4145 unique (Rint 14.9%) were used for structure solution and refinement. Data corrected for absorption (μ = 63.48 cm-1, transmission range: 0.2708 to 0.9287). Final agreement factors: R1: (obs/all) 0.059/0.094, wR2: 0.143/0.157. Structure was solved by SHELXLS-96¹² and refined in SHELXL-96.¹³ All non-hydrogen atoms are anisotropic, hydrogen atoms are calculated except the bridging hydride which was located in the difference map and refined isotropically with the restraint that both Ti-H distances be similar.

The full x-ray crystallography analysis report is listed in Appendix IV.

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CHAPTER 6 CONCLUDING REMARKS

6.1 Conclusions

Titanocene chemistry has been explored for nearly half a century with catalytic chemistry as a major part. Owing to its unique structure, the formation of complexes with some electron donating ligands is an essential part of the chemistry. The study of titanocene chemistry demonstrates the indispensable relation between coordination chemistry and reaction/catalytic chemistry of titanocene: investigating catalysis leads to new complexes; making new complexes leads to new catalysis.

Our initial interest in using phosphine ligands to study the catalyst intermediates and enhance the selectivity for the formation of cyclohexasilanes led to the discovery of heterodehydrocoupling of silanes with phosphines. Monophosphinosilanes, diphosphinosilanes, and all-trans 1,3,5-triphospha-2,4,6-trisilacyclohexanes can be obtained from the titanocene catalyzed heterodehydrocoupling of phosphines with silanes. This unprecedented reaction is featured with high yield and selectivity, and provides a novel route for the synthesis of P-Si bond containing compounds.

The investigating of the mechanism of the heterodehydrocoupling reaction of phosphine with silane resulted in the observation of some new titanocene complexes, such as Cp₂Ti(PMe₃)PHPh, Cp₂Ti(PMe₃)PHCy, Cp₂Ti(PH₂Ph)PHPh. These observations not only are helpful for the understanding of the titanocene catalyzed heterodehydrocoupling reactions, but also reveal some new aspects of titanocene coordination chemistry.

Our interest in synthesizing some titanocene-pyridine complexes led to the first example of hydrosilation/hydrogenation of pyridines. Some hydrosilated/hydrogenated products were obtained from the reactions of pyridines and methylphenylsilane in the presence of titanocene as catalyst. Either fully or partially saturated products with a silyl group on the N atom can be produced depending on conditions. Substituents on the pyridine rings have some effects on the reactivity and selectivity.

The study of Cp_2TiMe_2 catalyzed hydrosilation/hydrogenation reactions of nicotinates, ethyl benzoate following the study of hydrosilation/hydrogenation of alkyl substituted pyridines led to the isolation of ethoxo-bridged titanocene dimer, a known compound made through synthetic reaction. The isolation of this compound enabled us to address a convincing mechanism for the hydrosilation of carboalkoxy compounds.

The study of the mechanism of titanocene catalyzed hydrosilation/hydrogenation of lactones led to the isolation of a titanocene dimer, $Cp[\mu-(\eta^1:\eta^5-C_5H_4)](THF)Ti(\mu-H)TiCp_2$. This compound was obtained through a different synthetic reaction a long time ago the original structural assignment proved to be incorrect. The isolation and x-ray crystallography characterization of this compound not only reveals the real titanocene dimer identity of this compound but also showed the first direct and concrete evidence for the involvement of Cp_2Ti in numerous Cp_2TiMe_2 catalyzed reactions. This knowledge is helpful for elucidating the mechanisms of these reactions.

The present thesis clearly shows that new catalysis is often heralded by studies of coordination chemistry, while a better understanding of coordination chemistry often results from catalysis studies.

6.2 Contributions to original knowledge

1. Heterodehydrocoupling reactions of organosilanes and phosphines have been observed for the first time and afford a novel route for the synthesis of Si-P containing compounds. Monophosphino- and diphosphinosilanes were synthesized using silanes (primary and secondary) and phosphines (primary and secondary) as starting materials and Cp_2TiMe_2 or $CpCp*TiMe_2$ as catalyst.

2. CpCp*TiMe₂ catalyzed heterodehydrocoupling reactions of phenylphosphines and primary silanes were used for the synthesis of some triphenylphosphatrisilacyclohexanes. The new compounds 1,3,5-triphenylphospha-2,4,6-triphenylsilacyclohexane and 1,3,5-triphenylphospha-2,4,6-tri(*p*-Tolyl)silacyclohexane were obtained from heterodehydrocoupling reactions of phenylphosphines with phenylsilane and *p*-tolylsilane respectively. The previously reported 1,3,5-tricyclohexylphospha-2,4,6triphenylsilacyclohexane and the new compound 1,3,5-tricyclohexylphospha-2,4,6-tri-(*p*-Tol)silacyclohexane were obtained from the Cp₂TiMe₂ catalyzed heterodehydrocoupling of cyclohexylphosphine with phenylsilane and *p*-tolylsilane respectively.

3. Hydrosilation/hydrogenation of pyridine, 3-picoline, 4-picoline, 3,5-lutidine, and quinoline, has been achieved using titanocene derivatives as precatalysts. Some regioselectively hydrosilated/hydrogenated products were obtained. Either fully or partially saturated products may be produced depending on conditions. The important role of titanocene hydride in the reactions has been implicated by using isotope labelling experiments and titanocene hydride as catalyst.

4. Cp_2TiMe_2 catalyzed hydrosilation/hydrogenation reactions of nicotinates and ethyl benzoate have been studied. Two types of transformation of the ester group, i.e., ester group to alkoxysilane and ester group to an alkyl group have been observed. The former transformation is dominant under mild conditions. The latter one is dominant at higher temperature and under a H₂ atmosphere.

5. Copolymerization of PhMeSiH₂ with γ -butyrolactone or (±)- β -butyrolactone has been achieved with Cp₂TiMe₂ as the precatalyst.

6. Titanocene dimer has been isolated in the form of $Cp[\mu-(\eta^1:\eta^5-C_5H_4)](THF)Ti(\mu-H)TiCp_2$ from a Cp_2TiMe_2 catalyzed silane reaction for the first time and characterized by single crystal x-ray crystallography.

6.3 Suggestions for further work

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1. It was found that the formation of triphospha-trisilacyclohexanes is very slow in the heterodehydrocoupling reactions of primary silanes and primary phosphines. The strong complexing between the Ti center and the primary phosphine may be the major cause. It would be worthwhile to develop an efficient system for the synthesis of triphospha-trisilacyclohexanes by adjusting the complexing abilities of the phosphine and the titanocene catalysts, e.g. introducing electron withdrawing groups on the phosphines and electron releasing groups on the titanocene.

2. Titanocene catalyzed heterodehydrocoupling reactions of primary phosphines and silanes yield cyclic heterohexamers. It would be interesting to explore various combinations of phosphines and silanes as starting materials for some macromolecules, such as primary phosphines with primary disilanes, primary silanes with primary diphosphines.

3. Some reaction rate differences were observed between alkylsilanes and arylsilanes in heterocoupling reactions. The differences may originate either from difference of electronic effect or steric effect. Some further work with a variety of alkylsilanes and phosphines would be helpful to clarify these delicate effects.

4. The discrepancy between the long-proposed, essential intermediate titanocene and the few isolated titanocene derivatives in titanocene catalyzed reactions has not been clearly addressed due to the inaccessibility of the true titanocene. It would be worthwhile to find out whether the titanocene derivatives, such as 7, 8, 9, 10, 29, and 30, can be directly derived from the titanocene dimer as proposed under some conditions. The results would be helpful to the understanding of titanocene catalytic chemistry.

5. Some electronic and steric effect on the outcome of the hydrosilation/hydrogenation of pyridines have been observed and a mechanism has been proposed based on these observations. Some further work would be worthwhile to clarify

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this mechanism, e.g. using pyridine derivatives with various substituents at different positions, and titanocenes with one or two Cp* groups.

6. The hydrosilation/hydrogenation of pyridines has been achieved. It would interesting to see whether other aromatic heterocyclic compounds, such as thiophene and pyrhole, can be hydrosilated/hydrogenated in a similar way by adjusting the substrates and catalyst based on the proposed mechanism.

7. It was found that the transformation from a carboalkoxy group to an alkyl group is favored under H_2 atmosphere. Some further study would be worthwhile to find out the optimum conditions for quantitative conversion of a carboalkoxy group to an alkyl group.

APPENDIX I

¹H NMR, ³¹P NMR, and ²⁹Si NMR data of products from the reactions of

secondary phosphines and silanes

Product	¹ H NMR (δ ppm; J Hz)	³¹ P NMR and ²⁸ Si NMR	
Ph ₂ P-SiH ₂ (p-Tol)	2.00 (s, 3H, PhCH ₃); 5.00 (d, 2H,	³¹ P NMR: -71 (s)	
	Si- H , $J_{\text{HP}} = 20$; 6.7-7.7 (m, 14H, ϕ - H , Ph- H)		
Ph ₂ P-SiH(p- Tol)PPh ₂	2.06 (s, 3H, ϕ -CH ₃); 5.54 (t, J_{HP} = 15.2, J_{HSi} = 203.9, 1H Si-H); 6.7-7.7 (m, 24 H, ϕ -H, Ph-H)	³¹ P NMR: -64 (s) ²⁹ Si NMR: -11.6 (t, J_{SiP} =49.2 Hz)	
Ph ₂ P-SiH ₂ Ph	4.95 (d, J_{HP} = 19.5, 2H, Si-H); 6.9- 7.7 (m, 15H, Ph-H)	³¹ P NMR: -71 (s) ²⁹ Si NMR: -32 (b)	
Ph ₂ P-SiHPh-PPh ₂	5.51 (t, J_{HP} = 14.8, 1H, Si-H), 6.9- 7.7 (m, 25H, Ph-H)	³¹ P NMR: -64 (s) ²⁹ Si NMR: -11.2 (t, J _{Si} P = 50.8 Hz)	
Ph ₂ P-SiH ₂ Cy	0.89-1.89 (m, 11H, Cy-H); 4.30 (dm, J _{HP} =16.2, 2H, Si-H); 6.93-7.7 (m, 10H, Ph-H)	³¹ P NMR: -64.5 (s) ²⁹ Si NMR: -22 (b)	
Ph ₂ P-SiHPh ₂	5.56 (d, J _{HP} = 14.3, 1H, Si- H); 6.8- 7.6 (m, 20H, Ph- H)	³¹ P NMR: -66.7 (s) ²⁹ Si NMR: -13.8 (d, $J_{SiP} = 27.8 \text{ Hz}$)	
Ph ₂ P-SiHPhMe	0.30 (m, ${}^{3}J_{HH} = 4.0$, ${}^{3}J_{PH} = 4.30$, 3H, Si-CH ₃); 5.02(dq, ${}^{2}J_{HP} = 17.6$, ${}^{3}J_{HH} = 4.0$, 1H, Si-H); 6.8-7.5(m, 15H, Ph-H)	³¹ P NMR: -65.1(s) ²⁹ Si NMR: -13.5(b)	
Cy ₂ P-SiH ₂ (<i>p</i> -Tol)	1.0-1.83 (m, 22H, Cy-H); 2.05 (s, 3H, ϕ -CH ₃); 4.83 (d, $J_{HP} = 15.9$, 1H, Si-H); 6.93-6.98, 7.61-7.67 (m, 4H, f-H)	³¹ P NMR: -64.3 (s) ²⁹ Si NMR: -39.4 (d, $J_{SiP} = 41.2 \text{ Hz}$)	

Cy ₂ P-SiH ₂ Ph	0.98-1.98 (m, 22H, Cy- H); 4.80 (d, $J_{PH} = 15.6$, 2H, Si- H); 6.93-7.74 (m, 5H, Ph- H)	³¹ P NMR: -64.2 (s) ²⁹ Si NMR: -39 (d, J_{SiP} = 43.7 Hz)
Cy ₂ P-SiH ₂ Cy	0.95-2.08 (m, 33H, Cy-H); 4.11 (dd, $J_{\text{HP}} = 9.8$, $J_{\text{HH}} = 3.4$, 2H, Si-H)	³¹ P NMR: -68.2 (s) ²⁹ Si NMR: -29.2 (d, $J_{SiP} = 45.3 \text{ Hz}$)
Cy ₂ P-SiHPh ₂	0.95-2.04 (m, Cy- H); 5.50 (d, J _{HP} = 10.6, Si- H); 6.96-7.84 (Ph- H)	³¹ P NMR: -61.3 (s) ²⁹ Si NMR: -15.9 (d, $J_{SiP} = 36.9 \text{ Hz}$)
Cy ₂ P-SiHMePh	0.56 (m, ${}^{3}J_{HH} = 4.0$, ${}^{3}J_{PH} = 3.4$, 1H, Si-CH ₃); 0.97-2.00 (m, 22H, Cy-H); 4.94 (dq, ${}^{2}J_{HP} = 15.6$, ${}^{3}J_{HH} = 4.0$, 1H, Si-H); 7.06-7.7 (m, 5H, Ph-H)	³¹ P NMR: -58.0 (s) ²⁹ Si NMR: -18.9 (d, J_{SiP} = 38.9 Hz)
CyHP-SiH ₂ (p-Tol)	0.86-1.99, 2.0 (m, s,15H, Cy-H, ϕ - CH ₃), 2.37 (dm, J_{HP} = 193.6, 1H, P-H); 4.70-4.81 (m, 2H, Si-H), 6.90-6.97, 7.42-7.50 (m, m, 4H, ϕ - H)	³¹ P NMR: -143 (s) ²⁹ Si NMR: -39.4 (d, $J_{SiP} = 32.2 \text{ Hz}$)
CyP[SiH ₂ (p-Tol)] ₂	0.66-2.20, 2.0 (m, s, 17H, Cy-H, ϕ -H); 4.87(d, J_{HP} = 17.1, 4H, Si- H), 6.90-6.97, 7.42-7.50 (m, m, 8H, ϕ -H)	³¹ P: -182 (s) ²⁹ Si NMR: -36.6 (d, J_{SiP} = 39.6 Hz, J_{SiH} = 201.1 Hz)
(CyPSiH(p-tolyl))3	0.7-2.2, 2.0 (m, s, 42H, Cy-H, φ- H); 6.0 (m, 3H, Si-H), 7.0-7.1, 7.9-8.0 (m,m, 12H, Ph-H)	³¹ P: -160 (b) ²⁹ Si NMR: -15 (b)
CyHP-SiH ₂ Ph	0.86-1.99 (m, 11H, Cy-H); 2.35 (dm, $J_{\text{HP}} = 192.2$, 1H, P-H); 4.73-4.83 (m, 2H, Si-H), 6.98-7.80 (m, 5H, Ph-H)	$^{31}P: -143.8 (s)$ $^{29}Si NMR: -36.2 (d, J_{SiP} = 39.5 Hz)$

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CvP-(SiH2Ph)2		31P182(S)
·) - (<u>-</u> / <u>-</u>	0.86-1.99 (m, 11H, Cy-H); 4.80 (d,	295: NNAD: 14.0(d La:D
	$J_{\rm HP} = 17.2, 4$ H, Si- H), 6.98-7.80	$-50.9 H_7$
	(m, 10H, Ph-H)	= 50.7 112,
(CyPSiHPh)3	0.80-2.2 (m, 33 H, Cy-H); 5.9 (m,	³¹ P: -158 (m)
	3 H, Si-H), 7.0-7.3, 7.9-8.1 (m, m,	
	15 H, Ph-H)	
Ph ₂ HSi-PHCy	0.9-1.8 (m, 11H, Cy-H); 2.49 (dt,	³¹ P NMR: -138.6 (s)
	$^{2}J_{\text{HP}} = 193.4, \ ^{3}J_{\text{HH}} = 2.49, \ 1\text{H}, \ P$ -	²⁹ Si NMR: -15.8 (d, $I_{0:0} = 30.1 \text{ Hz}$)
	H); 5.54 (dd, ${}^{3}J_{\text{HP}} = 13.8$, ${}^{3}J_{\text{HH}} =$	$J_{SIP} = J_{0.1} I_{IZ}$
	4.1, 1H, Si-H), 6.9-7.8 (m, 10H,	
	Ph-H)	
CyHP-SiHPhMe	0.40 (m, 3H, CH ₃); 0.92-1.90(m,	³¹ P NMR: -133 (s)
	11H, Cy-H); 2.31 (dm, 1H, P-H);	²⁹ Si NMR:
	4.95(m, 1H, Si-H),7.08-7.2, 7.48-	
	7.6(m, m, 5H, Ph-H)	
PhHP-SiHPh ₂	3.68 (dd, $J_{\rm PH}$ = 204 Hz, ${}^{3}J_{\rm HH}$ = 4.0	³¹ P NMR: -134 (s),
	Hz, 1 H, P-H); 5.43(dd, ${}^{3}J_{PH} =$	29 Si NMR: -12.9 (d, $I_{5:D} = 27.4 \text{ Hz}$)
	17.2 Hz, ${}^{3}J_{\text{HH}}$ = 4.0 Hz, 1H, Si-H),	551r - 27.4 112)
	6.8-7.6 (m, 15H, Ph- H)	

b broad; d doublet; t triplet; q quartet; m multiplet; s singlet.

Appendix II

the reaction of primary phosphines and silanes						
Product	¹ H NMR (δ ppm)	³¹ P NMR and ²⁹ Si NMR(δ ppm)	IR(KBr) ,			
			$v(SiH)(cm^{-1})$			
	0.70-2.30 (m, 33H, Cy-H);	³¹ P: -160 (b)	2104			
$(p-101S1H-PCy)_3$	2.05 (s, 9H, φ-CH ₃); 6.0	29 Si: -15 (b)	2104			
	(m, 3H, Si-H), 7.04, 7.95					
	(m, m, 12H, φ- H)					
(PhSiH-PCy) ₃	0.80-2.20 (m, 33H, Cy-H),	³¹ P: -157 (b)	2106			
	7.3, 7.9-8.1 (m, m, 15H,		2100			
	Ph- H)					
(p-C ₃ H ₇ ϕ SiH-PCy) ₃	0.70-2.50 (m, 53 H, Cy-H,	³¹ P: -160 (b)				
	ϕ -C ₃ H ₇); 6.0 (m, 3H, Si-					
	H); 7.1, 8.0 (m, m, 12H, ϕ -		-			
	H)					
(p-TolSiH-PPh)3	1.86 (s, 9H, φ-CH ₃); 6.24	³¹ P: -160 (b)	2106			
	(m, 3H, Si- H); 6.7-7.0, 7.5		<i>4</i> 100			
	-7.9 (m, m, 27H, \$\$-H , Ph-					
	H)					

¹H NMR, ³¹P NMR, and ²⁹Si NMR data of products from the reaction of primary phosphines and silanes

b broad; d doublet; t triplet; q quartet; m multiplet; s singlet.

Appendix III

Selected NMR data for the products from the hydrosilation/hydrogenation of pyridines

Substrate	Products	¹ H NMR (δ ppm, C ₆ D ₆ , 22 °C, TMS internal reference)
pyridine		7.2-7.7 (m, Ph, 5 H); 6.28 (dt, ${}^{3}J$ = 7.8 Hz, ${}^{4}J$ = 3.0 Hz,
		1H, NCH ₂ CH ₂ CH ₂ CH=CH); 5.01 (q, $J = 3.3$ Hz, 1H,
		SiH); 4.62 (m, 1 H, NCH ₂ CH ₂ CH ₂ CH ₂ CH); 2.99 (m,
		2H, $NCH_2CH_2CH_2CH=CH$, 2.00 (m, 2H,
	Si-H	NCH ₂ CH ₂ CH ₂ CH=CH); 1.57 (m, $2H$,
	Pn Me	NCH ₂ CH ₂ CH ₂ CH ₂ CH=CH); 0.28 (d, $J = 3.3$ Hz, 3H,
		SiC H ₃);
		$^{29}Si\{^{1}H\}:-9.1$
		7.2-7.7 (m, Ph, 5H); 5.02 (q, $J = 3.0$ Hz, 1H, SiH); 2.79
	\sim	(m, 4H, NC H_2 CH ₂ CH ₂ CH ₂ CH ₂ CH ₂), 1.40 (quint, ${}^{3}J = 5.5$
		Hz, 2H, $NCH_2CH_2CH_2CH_2CH_2$; 1.27 (m, 4H,
	Sit ^H	$NCH_2CH_2CH_2CH_2CH_2$; 0.29 (d, $J = 3.0$ Hz, 3H,
	Ph Me	SiCH ₃)
		29 Si{ 1 H}: -10.5
3-picoline		7.2 - 7.7 (m, 5H, Ph); 6.22 (m, 1H,
		NCH ₂ CH(CH ₃)CH ₂ CH=CH); 4.99 (q, $J = 3.3$ Hz, 1H,
	CH,	Si H); 4.57 (m, 1H, NCH ₂ CH(CH ₃)CH ₂ CH=CH); 2.98,
		2.60 (m, m, 2H, NCH ₂ CH(CH ₃)CH ₂ CH=CH), 1.70, 2.04
	Si-H	(m, m, 2H, NCH ₂ CH(CH ₃)C H_2 CH=CH); 1.75 (m, 1H,
	Ph Me	NCH ₂ C H (CH ₃)CH ₂ CH=CH); 0.72 (m, 3H,
		$NCH_2CH(CH_3)CH_2CH=CH) 0.30 (d, J = 3.3 Hz, 3H,$
		SiCH ₃)
		7.1-7.6 (m, Ph , 5H); 6.08 (m, 1H,
	СН3	NC $H=C(CH_3)CH_2CH_2CH_2$; 5.02 (q, $J = 3.3$ Hz, 1H,
		Si H); 2.91 (m, 2H, NCH=C(CH ₃)CH ₂ CH ₂ CH ₂), 1.85 (t,
	, si.H	J = 6.25 Hz, 2H, NCH=C(CH ₃)CH ₂ CH ₂ CH ₂); 1.61 (m,
	Ph Me	3H, NCH=C(CH ₃)CH ₂ CH ₂ CH ₂); 1.55 (m, 2H,
		NCH=C(CH ₃)CH ₂ CH ₂ CH ₂); 0.28 (d, $J = 3.3$ Hz, 3H,
		SiCH ₃)

3-picoline		7.2-7.7 (m, Ph , 5H); 5.95 (d, $J = 8.1$, 1H,
		NCHC(CH ₃)CH ₂ CHCH); 5.78 (s, 1H,
	CH3 CH3	NCHC(CH ₃)CH ₂ CHCH); 4.92 (q, $J = 3.8$, 1H, SiH); 4.54
	N N	$dt, ^{3}J = 8.1 Hz, ^{3}J' = 3.0 Hz, 2H,$
	Bi-H Si-H	NCHC(CH ₃)CH ₂ CHCH); 2.86 (m, $2H$,
		NCHC(CH ₃)C H_2 CHCH); 1.37 (s, 3H,
		NCHC(C H_3)CH ₂ CHCH),
4-picoline		7.2-7.7 (m. Ph. 5H); 6.26 (dt. ${}^{3}J = 7.8$ Hz, ${}^{4}J = 1.8$ Hz,
		1H, NCH ₂ CH ₂ CH(CH ₃)CH=CH); 5.04 (q, $J = 3.3$ Hz,
	СН	1H. SiH): 4.56 (m. 1H. NCH2CH2CH(CH3)CH=CH);
		$3.02 \text{ (m. 2H. NCH_2CH_2CH(CH_3)CH=CH)}, 2.28 \text{ (m. 2H. })$
		NCH ₂ CH ₂ CH ₂ CH ₃ CH=CH): 1.6. 1.3 (m. 2H.
	Ph Me	$NCH_2CH_2CH(CH_3)CH=CH); 1.0 (d. 3H.)$
		NCH ₂ CH ₂ CH(CH ₂)CH=CH) 0.30 (d $I = 3.3$ Hz 3H
		$SiCH_2$
3 5-		71-75 (m Ph 5H): 587 (s 2H
lutidine		$NCH=C(CH_2)CH_2(CH_2)C=CH$): 4.99 (a) $I = 3.4$ Hz
indumo	H ₃ C CH ₃	$1H \text{ Si}H$: 2.69 (m 2H NCH-C(CH_2)CH_2(CH_2)C=CH)
	N.	1.44 (s 6H NCH=C(CH_2)CH_2(CH_2)C=CH_2(0.13)C=CH_2(
	Ph Me	-34 Hz 3H SiCH ₂)
		295: (111), 20
		(1.1-1.5) (m, <i>Ph</i> , 5H); 6.05 (m, 1H, 1H)
		$NCH=C(CH_3)CH_2(CH_3)CHCH_2$; 5.03 (m, 1H, SIH);
	H ₃ C CH ₃	2.94, 2.53 (m, m, 2H, NCH=C(CH ₃)CH ₂ (CH ₃)CHCH ₂);
		1.65-1.88 (m, 2H, NCH=C(CH ₃)C H_2 (CH ₃)CHCH ₂),
	Si-H	1.60 (s, 3H, NCH=C(CH ₃)CH ₂ (CH ₃)CHCH ₂); 1.55 (m,
	Ph Me	1H, NCH=C(CH ₃)CH ₂ (CH ₃)CHCH ₂); 0.73 (m, 3H,
		NCH=C(CH ₃)CH ₂ (CH ₃)CHCH ₂); 0.25 (d, $J = 3.4$ Hz,
		3H, SiC H ₃)

quinoline		7.1 - 7.5 (m, 4H, ϕ -H); 6.22 (dt, ² J = 7.7 Hz, 1H, NCH=CHCH ₂); 4.71 (m, 1H, NCH=CHCH ₂); 3.48 (m, 2H, NCH=CHCH ₂); 5.0 (q, J = 3.3 Hz, 1H, Si-H); 0.38 (d, J = 3.3 Hz, 3H, SiCH ₃) ²⁹ Si{ ¹ H}: -10.6
	PhH Me	6.7-7.7 (m, 4H, C ₆ H ₄); 5.39 (q, $J = 3.5$ Hz, 1H, Si H); 3.1 (m, m, 2H, NCH ₂ CH ₂ CH ₂); 2.60 (t, $J = 6.6$ Hz, 2H, NCH ₂ CH ₂ CH ₂), 1.55 (m, 2H, NCH ₂ CH ₂ CH ₂), 0.43 (d, $J = 3.5$ Hz, 3H, SiCH ₃) ²⁹ Si{ ¹ H}: -12.6

Appendix IV

Full report of crystal and molecular structure of

 $C_{26}H_{32}O_{1.5}Ti_2$ (37)

Table AIV.1 Crystal data and structure refinement for $C_{26}H_{32}O_{1.5}Ti_2$

Crystal data				
Chemical formula, sum		$C_{26}H_{32}O_{1.5}Ti_2$		
Chemical formula, moiety		$C_{26}H_{28}OTi_2 \cdot 1/2OC_4H_8$		
Chemical formula weight, Mr	464.32	2		
Cell setting		Monoclinic		
Space group		C 2/c		
Unit cell dimensions (Å, deg)		a = 31.232 (13)	alpha = 90	
		b = 7.998 (3)	beta = 116.78 (3)	
		c = 19.603(9)	gamma = 90	
Volume of unit cell, V (Å ³)		4371 (3)		
Formula units cell per cell, Z		8		
Density calculated from formula and cell, Dx (Mg/m ³)	1.387			
F (000)		1952		
Radiation type	CuK\a			
Wavelength, lambda (Å)		1.54056		
No. of reflections for cell measurement		25		
Theta range (deg)		40 to 50		
Linear absorption coefficient, mu (mm ⁻¹)		6.348		

Measurement temperature (K) 293 (2)Crystal shapeplateColourdarkSize (mm) $0.52 \times 0.29 \times 0.01$

Data collection

Diffractometer type	Nonius CAD4
Data-collection method	omega/2theta scans
Absorption corretion type	Analytical
Maxmum and minimum transmission	L
values, Tmax and Tmin	0.93 and 0.27
No. of reflections measured	29561
No. of independent reflections	4145
No. of observed reflections	2439
Criteron for observed	
reflections	> 2\s(I)
Rint	0.149
Minimum and maximum values	
of theta (deg)	3.17 to 69.96
Ranges of h, k, l	-38<= h <=38, -9<= k <=9, -23<= l <=23
No. of standard reflections	5
Interval, time (min)	60
Intensity decay (%)	7.41

Refinment

Refinment method	Full-matrix on F ²
Final R indices, I>2sigma (I)	R1 = 0.0594, $wR2 = 0.1426$

R indices, all data R1 = 0.0944, wR2 = 0.1574Goodness-of-fit on F², S 0.841 $R1 = \sum (||F_0| - |F_c||) / \sum (|F_0|),$ $wR2 = [\sum [w (F_0^2 - F_c^2)^2] / \sum [w (F_0^2)^2]]^{1/2}$ and $GoF = [\sum w(F_0^2 - F_c^2)^2]/(No. of refins - No. of params.)]^{1/2}$ No. of reflections used in refinement 4145 No. of parameters refined 272 No. of restraints 1 Method of refining and locating H atoms constr Weighting scheme based on measured e. s. d's $\sum w(F_0^2 - F_c^2)$ Function minimized calc Maximum shift/sigma 0.044 Delta rho max (eA⁻³) 0.744 DELTA rho min (eA^{-3}) -1.028 Extinction correction method SHELXL-93 (1995) Secondary extinction value 0.0028 (5)

Table AIV.2 Atomic coordinates and equivalent isotropic displacement

parameters ($A^2 \times 10^2$) for 37

$Ueq = 1/3\sum_{i}\sum_{j}U_{ij}a^{*}_{i}a^{*}_{j}a_{i}a_{j}$				
	×	У	Z	U _{eq}
Ti(1)	0.18117(3)	0.57458(10)	0.32101(5)	2.66(2)
Ti(2)	0.10890(3)	0.68627(10)	0.14188(5)	2.81(2)
0(1)	0.14769(12)	0.7424(4)	0.3750(2)	3.46(8)
C(1)	0.1845(2)	0.7320(6)	0.2238(3)	2.97(10)
č(2)	0.2211(2)	0.6046(6)	0.2473(3)	3.32(11)
C(3)	0.2558(2)	0.6305(7)	0.3223(3)	3.78(12)
C(4)	0.2425(2)	0.7751(6)	0.3495(3)	3.79(12)
C(5)	0.2003(2)	0.8358(6)	0.2893(3)	3.34(11)
C(6)	0.1479(2)	0.3581(7)	0.3653(4)	4.8(2)
C(7)	0.1577(2)	0.2885(6)	0.3098(3)	4.7(2)
C(3)	0.2072(2)	0.2907(6)	0.3352(4)	5.1(2)
C(9)	0.2274(2)	0.3624(7)	0.4075(4)	5.4(2)
C(10)	0.1913(2)	0.4035(7)	0.4268(3)	5.2(2)
C(12)	0.1749(2)	0.8588(7)	0.4358(3)	4.61(14)
C(13)	0.1416(2)	0.9150(9)	0.4684(4)	5.2(2)
C(14)	0.0929(2)	0.8702(9)	0.4084(4)	6.5(2)
C(15)	0.1009(2)	0.7193(8)	0.3727(3)	4.9(2)
C(16)	0.0884(2)	0.9094(6)	0.2009(3)	3.93(12)
C(17)	0.1015(2)	0.9816(5)	0.1483(3)	4.55(14)
C(18)	0.0572(2)	0.9319(7)	0.0755(3)	5.3(2)
C(19)	0.0332(2)	0.8333(7)	0.0843(3)	5.0(2)
C(20)	0.0454(2)	0.8173(7)	0.1508(3)	4.21(13)
C(21)	0.1458(2)	0.5442(7)	0.0759(3)	3.87(12)
C(22)	0.1330(2)	0.4223(5)	0.1132(3)	3.77(12)
C(23)	0.0825(2)	0.4219(6)	0.0811(3)	4.15(13)
C(24)	0.0655(2)	0.5402(7)	0.0225(3)	4.28(13)
C(25)	0.1048(2)	0.6180(7)	0.0205(3)	4.00(13)
0(2)	0.0000	0.4887(10)	0.2500	9.4(3)
C(25)	0.0074(3)	0.3963(13)	0.1998(5)	10.0(3)
C(27)	0.0027(5)	0.2217(13)	0.2142(9)	19.1(9)

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Table AIV.3 Bond length (Å) and angles (deg) for 37

TI(1)-0(1)	2.239(3)	Ti(1) - C(2)	2.307(5)	
Ti(1) - C(1)	2.325(5)	Ti(1)-C(5)	2.333(5)	
Ti(1) - C(3)	2,363(5)	Ti(1) - C(4)	2.365(5)	
$T_1(1) = C(9)$	2.373(5)	Ti(1) - C(6)	2,375(5)	
$r_{1}(1) = r_{1}(7)$	2 382(5)	$T_{1}(1) = C(10)$	2 383(5)	
11(1) = C(7)	2.302(3)	$m_{i}(1) = m_{i}(2)$	2.202(2)	
	2.323(3)		3.349(2)	
	1.63(2)		2.207(3)	
Ti(2) - C(16)	2.305(5)	T1(2) - C(23)	2.383(5)	
Ti(2) - C(17)	2.384(5)	Ti(2) - C(20)	2.386(5)	
Ti(2)+C(25)	2.388(5)	Ti(2) - C(18)	2.391(5)	
Ti(2)-C(22)	2.392(5)	Ti(2) - C(21)	2.397(5)	
Ti(2)-C(24)	2.412(5)	Ti(2)-C(19)	2.417(5)	
Ti(2)-E(1)	1.82(2)	0(1)-C(12)	1.448(6)	
0(1)-C(15)	1.455(6)	C(1)-C(5)	1.418(5)	
C(1) - C(2)	1.443(6)	C(2) - C(3)	1.395(7)	
C(2) - H(2)	0.9300	C(3) - C(4)	1,412(7)	
C(3) = F(3)	0 6300	C(4) - C(5)	1 402 (7)	
C(4) = E(4)	0.5300	C(5) - F(5)	0 9300	
C(4) = B(4)	0.3300		1 307(9)	
	1.3/4(/)		1.397(8)	
$C(b) \neq \pi(b)$	0.9300	C(7) - C(B)	1.394(8)	
C(7) - E(7)	0.9300	C(B) - C(9)	1.389(8)	
C(B)-H(B)	0.9300	C(9) - C(10)	1.379(8)	
C(9)-H(7)	0.9300	C(10) - H(10)	0.9300	
C(12) - C(13)	1.514(7)	C(12)-H(12A)	0.9700	
C(12)-H(12B)	0.9700	C(13) - C(14)	1.486(8)	
C(13)-E(13A)	0.9700	C(13)-H(13B)	0.9700	
C(14)-C(15)	1.470(8)	C(14)-H(14A)	0.9700	
C(14)-H(14B)	0.9790	C(15)-H(15A)	0.9700	
C(15)-H(15B)	0.9700	C(16) - C(17)	1.386(7)	
C(15) - C(20)	1 398(7)	C(36) - H(36)	0 9300	
C(17) - C(18)	1 406(R)	C(17) = F(17)	0.9300	
C(28) - C(28)	1 394(2)		0.5300	
C(28) = C(22)	1.334(3)		0.5300	
	1.3/0(/)		0.5300	
C(20)-H(25)	0.9300	C(21) = C(22)	1.395(/)	
C(21) - C(25)	1.402(7)	C(21) - H(21)	0.9300	
C(22) - C(23)	1.407(7)	C(22) - H(22)	0.9300	
C(23)-C(24)	1.395(7)	C(23)-H(23)	0.9300	
C(24)-C(25)	1.392(7)	C(24) - H(24)	0.9300	
C(25)-H(25)	0.9300	O(2) - C(26)	1.331(9)	
0(2)-C(25)#1	1.331(9)	C(26)-C(27)	1.444(13)	
C(26)-H(25A)	0.9700	C(26)-H(26B)	0.9700	
C(27)-C(27)#1	1.49(2)	C(27)-H(27A)	0.9700	
C(27)-H(27E)	0.9700			
O(1) - Ti(1) - C(2)	137.1(2)	0(1) - Ti	(1) - C(1)	105.4(2)
C(2) = Ti(1) = C(1)	36 3(2)	0(1)-Ti	(1) - C(5)	79 6(2)
$C(2) = m^2 (1) = C(2)$	57 6121		(1) - C(5)	35 4(2)
$O(2) = T^{2}(2) = O(3)$	101.0(2)		(1)-0(3)	32.2(2)
C(1) = 12(1) = C(3)	123.4(2) 50.0/2)			57 5(2)
	23.9(2)			57.5(2)
	67.J(2)	C(2)-T1		57.9(2)
U(1) - 11(1) - C(4)	59.7(2)	C(5)-Ti	$(\perp) - C(4)$	34.7(2)
$C(3) - T_2(1) - C(4)$	34.3(2)	0(1)-Ti	(l)-C(9)	110.8(2)
C(2) - Ti(1) - C(9)	101.3(2)	C(1)-Ti	(l)-C(9)	137.3(2)
C(5) - Ti(1) - C(9)	133.2(2)	C(3)-Ti	(l)-C(9)	81.2(2)
C(4) - Ti(1) - C(9)	98.5(2)	0(1)-Ti((1)-C(5)	83.7(2)
C(2) - Ti(1) - C(6)	138.9(2)	C(1)-T1(1)-C(6)	151.9(2)

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			336 E(2)
C(5) - Ti(1) - C(6)	163.1(2)		55 3(2)
C(4) - Ti(1) - C(6)	148.1(2)	C(9) - Ti(1) - C(0)	38.2(2)
0(1) - Ti(1) - C(7)	115.5(2)	c(2) - Ti(1) - c(7)	103.8(2)
c(1) - Ti(1) - C(7)	124.B(2)	C(5) - Ti(1) - C(7)	160.1(2)
$c(3) - \pi i(1) - c(7)$	116.3(2)	C(4) - Ti(1) - C(7)	148.8(2)
C(9) = Ti(1) = C(7)	56.1(2)	C(6) - Ti(1) - C(7)	33.6(2)
$O(1) = T_1(1) = O(10)$	80.8(2)	c(2) - Ti(1) - c(10)	135.0(2)
O(1) = 12(1) = O(10)	170 5/2)	C(5) - Ti(1) - C(10)	142.8(2)
C(1) = C(1) = C(10)	110 8(2)	C(4) - Ti(1) - C(10)	114.1(2)
C(3) = 11(1) = C(10)	33 7(7)	C(6) - Ti(1) - C(10)	34.1(2)
$C(9) = T_1(1) = C(10)$	55.7(2)	$O(1) = T_1(1) = C(8)$	135.3(2)
C(7) - Ti(1) - C(10)	50.2(2)	$C(1) = T_{1}(1) = C(B)$	118.2(2)
C(2) - Ti(1) - C(B)	85.4(2)	C(1) = 1 + (1) = C(0)	84 0(2)
C(5) - Ti(1) - C(8)	140.2(2)		33 6/2)
C(4) - Ti(1) - C(8)	114.9(2)	C(9) - TT(1) - C(8)	33-3(2)
C(6) - Ti(1) - C(8)	56.4(2)	$C(7) - T_1(1) - C(8)$	34.0(2)
C(10) - Ti(1) - C(8)	56.4(2)	O(1) - Ti(1) - Ti(2)	95.65(10)
c(2) - Ti(1) - Ti(2)	67.19(13)	C(1) - Ti(1) - Ti(2)	41.37(12)
C(5) - Ti(1) - Ti(2)	67.16(12)	C(3) - Ti(1) - Ti(2)	99.06(13)
C(4) - Ti(1) - Ti(2)	99.18(13)	C(9) - Ti(1) - Ti(2)	148.3(2)
c(5) = mi(1) = mi(2)	112.4(2)	C(7) - Ti(1) - Ti(2)	97.25(14)
c(0) = mi(1) = mi(2)	146.4(2)	C(B) - Ti(1) - Ti(2)	114.3(2)
$(10)^{-12}(2)^{-12}(0)$	87 6(15)	c(2) - Ti(1) - H(1)	88.3(14)
O(1) = 12(1) = 2(1)	65 3(1Z)	C(5) - Ti(1) - H(1)	68(2)
		$C(4) = m_{1}(1) = H(1)$	122(2)
		$C(5) = m_1(2) = E(3)$	29(2)
C(3) - Ti(1) - H(1)	. 130(2)	c(0) = 12(1) + c(1)	123(2)
C(7) - Ti(1) - H(1)	50(2)	$m_{1}(2) - m_{1}(2) - m_{1}(2)$	24 0(14)
C(8) - Ti(1) - I(1)	107(2)		121 7(2)
C(1) - Ti(2) - C(16)	67.4(2)	C(1) = T1(2) = C(23)	
c(16)-Ti(2)-C(23)	143.6(2)	C(1) - T1(2) - C(17)	53.3(2)
C(16) - Ti(2) - C(17)	33.9(2)	C(23) - Ti(2) - C(17)	152.5(2)
C(1) - Ti(2) - C(20)	119.7(2)	C(16) - Ti(2) - C(20)	36.2(2)
C(23) - Ti(2) - C(20)	110.2(2)	2(17) - Ti(2) - C(20)	56.6(2)
c(1) - mi(2) - c(25)	108.5(2)	c(16)-Ti(2)-C(25)	139.0(2)
c(23) - Ti(2) - C(25)	55.5(2)	C(17) - Ti(2) - C(25)	108.7(2)
C(20) - Ti(2) - C(25)	125.1(2)	C(1) - Ti(2) - C(18)	113.7(2)
C(16) - Ti(2) - C(18)	56.3(2)	C(23) - Ti(2) - C(15)	118.5(2)
C(17) - Ti(2) - C(18)	34.2(2)	C(20) - Ti(2) - C(13)	35.0(2)
$C(25) = m^{\frac{1}{2}}(2) = C(18)$	E2.E(2)	C(1) - Ti(2) - C(22)	28.3(2)
c(15) = m(2) = c(22)	154.5(2)	C(23)-Ti(2)-C(22)	34.3(2)
c(17) = m(2) = c(27)	159.6(2)	C(20) - Ti(2) - C(22)	142.2(2)
c(27) = c(2) - c(22)	56 3 (2)	C(18) - Ti(2) - C(22)	138.5(2)
C(23) = 11(2) = C(22)	81 7 (2)	C(16) - Ti(2) - C(21)	158.3(2)
	55 8/21	C(17) - Ci(2) - C(21)	125.8(2)
C(23) = PE(2) = C(21)	159 7 (2)	C(25) = Ti(2) = C(21)	34.1(2)
C(20) = TE(2) = C(21)		C(22) = mi(2) = C(21)	34.0(2)
C(18) - Ti(2) - C(21)		c(22) = 22(2) - c(22)	133.0(2)
C(1) - TI(2) - C(24)	13/-6(2)	C(23) = 22(2) = C(24)	120 6(2)
$C(23) - T_{1}(2) - C(24)$	33.8(2)	C(27) = 2(27) = C(24)	33 7(2)
C(20) - Ti(2) - C(24)	102.8(2)	C(23) = P1(2) = C(24)	55 7 (7)
C(15) - Ti(2) - C(24)	86.6(2)	C(22) = T1(2) = C(24)	139 5(2)
C(21) - Ti(2) - C(24)	55.3(2)	C(1) - T1(2) - C(19)	233.3(2)
C(16) - Ti(2) - C(19)	55.9(2)	C(23) - T1(2) - C(19)	70.8(2) 22 2/2)
C(17) - Ti(2) - C(19)	56.3(2)	C(20) - Ti(2) - C(19)	33.2(2)
C(25)-Ti(2)-C(19)	92.5(2)	C(18) - Ti(2) - C(19)	33.7(2)
C(22)-Ti(2)-C(19)	131.7(2)	C(21) - Ti(2) - C(19)	. 126.5(2)
C(24)-Ti(2)-C(19)	77.2(2)	C(1) - Ti(2) - Ti(1)	44.12(12)
C(16)-Ti(2)-Ti(1)	83.71(13)	C(23)-Ti(2)-Ti(1)	101.90(14)
C(17) - Ti(2) - Ti(1)	104.1(2)	C(20)-Ti(2)-Ti(1)	99.63(14)
C(25)-Ti(2)-Ti(1)	134.15(14)	C(18)-Ti(2)-Ti(1)	137.6(2)
C(22) - Ti(2) - Ti(1)	E2.E5(13)	C(21)-Ti(2)-Ti(1)	100.21(14)
C(24)-Ti(2)-Ti(1)	135.29(14)	C(19) - Ti(2) - Ti(1)	132.76(14)
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C(1) - Ti(2) - H(1)	68.3(14)	C(16) - Ti(2) - H(1)	82(2)
C(23) - Ti(2) - H(1)	E9 (2)	C(17)-Ti(2)-H(1)	112(2)
C(20) - Ti(2) - H(1)	85(2)	C(25) - Ti(2) - H(1)	139(2)
C(18) - Ti(2) - H(1)	138(2)	C(22)-Ti(2)-H(1)	82(2)
C(21) - Ti(2) - H(1)	110(2)	C(24) - Ti(2) - H(1)	122 (2)
C(19) = Ti(2) = H(1)	116.7(14)	Ti(1) - Ti(2) - H(1)	24 2(14)
C(12) = O(1) = C(15)	708 4(4)	$C(12) = O(1) = T_1(1)$	123 3/3)
C(15) = O(1) = T(1)	175 9/71	C(21) = O(2) + 12(2)	
	122.3(3)		102.8(4)
C(3) = C(1) = T1(2)	123.3(4)	C(2) = C(1) = TI(2)	123.3(3)
C(5) - C(1) - T1(1)	/2.0(3)	C(2) - C(1) - TI(1)	71.2(3)
Ti(2) - C(1) - Ti(1)	94.5(2)	C(3) - C(2) - C(1)	111.1(4)
C(3)-C(2)-Ti(1)	74.8(3)	C(1) - C(2) - Ti(1)	72.5(3)
C(3)-C(2)-H(2)	124.5	C(1)-C(2)-H(2)	124.5
Ti(1)-C(2)-H(2)	119.8	C(2) - C(3) - C(4)	107.4(4)
C(2) - C(3) - Ti(1)	70.4(3)	C(4) - C(3) - Ti(1)	72.7(3)
C(2) - C(3) - H(3)	126.3	C(4)-C(3)-H(3)	126.3
Ti(1) - C(3) - H(3)	122.3	C(5) - C(4) - C(3)	106.9(5)
C(5) - C(4) - Ti(1)	71.4(3)	C(3) - C(4) - Ti(1)	72.6(3)
C(5) = C(4) = H(4)	126.6	C(3) = C(4) = H(4)	126.6
$T_{1}^{(1)} = C(A) = T(A)$	121.3	C(4) = C(5) = C(1)	111 8/51
	73 9/31		72 0 (2)
	1010(0)		12.0(3)
	121.1	C(1) = C(5) = R(5)	100 1/5)
	22.02		
	/3.3(3)		/3.2(3)
	140.9		125.9
	119-2		108.5(5)
C(e) - C(7) - 22(1)	72.9(3)	C(B) - C(7) - T1(1)	73.1(3)
C(6) - C(7) - H(7)	125.7	C(5) - C(7) - H(7)	125.7
Ti(1) - C(7) - H(7)	120.0	C(9) - C(8) - C(7)	106.9(5)
C(9) - C(8) - Ti(1)	72.6(3)	C(7) - C(8) - Ti(1)	72.9(3)
C(5)-C(8)-H(8)	125.5	C(7)-C(8)-H(8)	126.6
Ti(1)-C(8)-H(8)	119.9	C(10) - C(9) - C(8)	109.0(6)
C(10)-C(9)-Ti(1)	73.5(3)	C(E) - C(9) - Ti(1)	73.5(3)
C(10)-C(9)-H(9)	125.5	C(8)-C(9)-H(9)	125.5
Ti(1)-C(9)-H(9)	119.3	C(9) - C(10) - C(5)	107.3(5)
C(9) - C(10) - Ti(1)	· 72.8(3)	C(6) - C(10) - Ti(1)	72.5(3)
C(9)-C(10)-H(10)	126.3	C(6)-C(10)-H(10)	126.3
Ti(1) - C(10) - H(10)	120.1	O(1) - C(12) - C(13)	106.1(4)
0(1)-C(12)-H(12A)	110.5	C(13) - C(12) - H(12A)	110.5
O(1) - C(12) - H(12B)	110.5	C(13) - C(12) - H(123)	110.5
H(12A) - C(12) - H(12B)	198.7	C(14) - C(13) - C(12)	104 3 (5)
C(14) = C(13) = H(132)	110 9	C(32) = C(33) = H(132)	110 8
C(14) = C(13) = H(13R)	1-0.9	C(12) = C(23) = H(132)	110 9
H(131)_C(13)_H(13P)	108 9		104 3/51
C(15) = C(14) = B(145)	10 9		104.1(3)
C(15) = C(14) = R(14R)	110.9		110.9
	100.9		105 3757
n(14A)-C(14)-R(14B)	109.0		105.3(5)
	110.7	C(14) - C(15) - H(15A)	110.7
O(1) - O(15) - H(15B)	110.7	C(14) - C(15) - H(15B)	110.7
H(15A) - C(15) - H(15B)	108.8	C(17) - C(16) - C(20)	108.5(5)
C(17) - C(16) - T1(2)	73.7(3)	C(20) - C(16) - Ti(2)	73.7(3)
C(17) - C(16) - H(16)	125.7	C(20)-C(16)-H(16)	125.7
Ti(2) - C(16) - H(16)	118.7	C(15)-C(17)-C(18)	107.1(5)
C(16)-C(17)-Ti(2)	72.3(3)	c(18)-c(17)-Ti(2)	73.2(3)
C(15)-C(17)-H(17)	126.5	C(18)-C(17)-H(17)	126.5
Ti(2)-C(17)-H(17)	119.9	C(19) - C(18) - C(17)	107_9(5)
C(19) - C(18) - Ti(2)	74.2(3)	C(17)-C(18)-Ti(2)	72.6(3)
C(19)-C(18)-H(18)	126.1	C(17)-C(18)-H(18)	126.1
Ti(2)-C(18)-H(18)	119.1	C(20)-C(19)-C(18)	108.4(5)
C(20)-C(19)-Ti(2)	72.2(3)	C(1B) - C(19) - Ti(2)	72.1(3)

C(20)-C(19)-H(19)	125.8	C(18)-C(19)-H(19)	125.8
Ti(2) - C(19) - H(19)	121.6	C(19)-C(20)-C(16)	108.1(5)
C(19) - C(20) - Ti(2)	74.7(3)	C(16) - C(20) - Ti(2)	72.1(3)
C(19)-C(20)-H(20)	126.0	C(16)-C(20)-H(20)	125.0
Ti(2) - C(20) - H(20)	119.1	C(22) - C(21) - C(25)	107.3(5)
C(22) - C(21) - Ti(2)	72.8(3)	C(25) - C(21) - Ti(2)	72.6(3)
C(22)-C(21)-H(21)	126.3	C(25)-C(21)-H(21)	126.3
Ti(2)-C(21)-H(21)	120.1	C(21)-C(22)-C(23)	108.3(5)
C(21) - C(22) - Ti(2)	73.2(3)	C(23) - C(22) - Ti(2)	72.5(3)
C(21)-C(22)-H(22)	125.8	C(23)-C(22)-H(22)	125.8
Ti(2)-C(22)-H(22)	120.2	C(24)-C(23)-C(22)	107.6(5)
C(24) - C(23) - Ti(2)	74.2(3)	C(22) - C(23) - Ti(2)	73.2(3)
C(24) - C(23) - H(23)	126.2	C(22)-C(23)-H(23)	126.2
Ti(2) - C(23) - H(23)	118.4	C(25)-C(24)-C(23)	108.2(5)
C(25) - C(24) - Ti(2)	72.2(3)	C(23) - C(24) - Ti(2)	72.0(3)
C(25)-C(24)-H(24)	125.9	C(23)~C(24)-H(24)	125.9
Ti(2) - C(24) - H(24)	121.6	C(24) - C(25) - C(21)	108.5(5)
C(24) - C(25) - Ti(2)	74.1(3)	C(21) - C(25) - Ti(2)	73.3(3)
C(24)-C(25)-H(25)	125.7	C(21)-C(25)-H(25)	125.7
Ti(2) - C(25) - H(25)	118.8	C(26)-O(2)-C(26)#1	112.5(10)
0(2)-C(25)-C(27)	109.0(8)	0(2)-C(25)-H(25A)	109.9
C(27)-C(26)-H(26A)	109.9	0(2)-C(25)-H(26B)	109.9
C(27)-C(26)-H(253)	109.9	H(26A) - C(26) - H(25B)	108.3
C(26)-C(27)-C(27)#1	104.4(6)	C(26)-C(27)-H(27A)	110.9
C(27)#1-C(27)-H(27A)	110.9	C(26)-C(27)-H(27B)	110.9
C(27) # 1 - C(27) - H(27B)	110.9	H(27A) - C(27) - H(27B)	108.9

Symmetry transformations used to generate equivalent atoms: #1 -x,y,-z+1/2

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	106.9(2)	C(2) - Ti(1) - Ti(2) - C(1)	-32.3(2)
O(1) - U1(1) - U1(2) - O(1)	30.7(2)	C(3) - Ti(1) - Ti(2) - C(1)	-19.2(2)
$C(5) - T_1(1) - T_1(2) - C(1)$	17 0(2)	C(9) - Ti(1) - Ti(2) - C(1)	-106.2(4)
$C(4) - T_1(1) - T_1(2) - C(1)$	-157 6(2)	C(7) - Ti(1) - Ti(2) - C(1)	-136.4(2)
C(5) - Ti(1) - Ti(2) - C(1)		C(B) - Ti(1) - Ti(2) - C(1)	-105.7(2)
C(10) - Ti(1) - Ti(2) - C(1)		C(2) = Ti(1) = Ti(2) = C(16)	-125.1(2)
O(1) - Ti(1) - Ti(2) - C(16)	14.1(2)	C(5) - Ti(1) - Ti(2) - C(16)	-62.1(2)
C(1) - Ti(1) - Ti(2) - C(16)	-92.5(2)	C(J) = Ti(I) = Ti(J) = C(If)	-75.8(2)
C(3) - Ti(1) - Ti(2) - C(15)	-111.0(2)	$\Box_{(2)} = \pm (2) = \pm (2) = \Box_{(2)} = \Box_{(2)}$	99.6(2)
C(9) - Ti(1) - Ti(2) - C(16)	151.0(3)	C(0) = II(1) = II(1) = C(1)	96.1(3)
C(7) - Ti(1) - Ti(2) - C(16)	130.8(2)	C(10) - C(1) - C(2) - C(2)	-129.4(2)
C(B) - Ti(1) - Ti(2) - C(15)	151.5(2)	O(1) = 11(1) = 11(2) = C(23)	123 5(2)
C(2) - Ti(1) - Ti(2) - C(23)	91.3(2)	C(1) = T1(1) = T1(2) = C(23)	105 4(2)
C(5) - Ti(1) - Ti(2) - C(23)	154.4(2)	C(3) - Ti(1) - Ti(2) - C(23)	17 4/3)
C(4) - Ti(1) - Ti(2) - C(23)	140.6(2)	C(9) - Ti(1) - Ti(2) - C(23)	17.10(2)
C(6) - Ti(1) - Ti(2) - C(23)	-43.9(2)	C(7) - Ti(1) - Ti(2) - C(23)	-12.5(2)
c(10)-Ti(1)-Ti(2)-C(23)	-47.5(3)	C(8) - Ti(1) - Ti(2) - C(23)	17.3(2)
O(1) - Ti(1) - Ti(2) - C(17)	41.5(2)	C(2) - Ti(1) - Ti(2) - C(1)	-97.7(2)
C(1) = mi(1) = mi(2) = C(17)	-65.5(2)	C(5) - Ti(1) - Ti(2) - C(17)	-34.7(2)
c(1) = m(1) = m(2) = c(17)	-83.7(2)	C(4) - Ti(1) - Ti(2) - C(17)	-48.4(2)
C(2) = m(1) - m(2) - C(17)	-171.6(3)	c(5)-Ti(1)-Ti(2)-C(17)	127.0(2)
C(3) = T(2) = T(2) = C(17)	158.1(2)	c(10)-Ti(1)-Ti(2)-C(17)	123.4(3)
C(7) = 1(1) = 1(2) = C(17)	-171.2(2)	0(1)-Ti(1)-Ti(2)-C(20)	-16.2(2)
C(2) = C(2) = C(2)	-155.5(2)	C(1) - Ti(1) - Ti(2) - C(20)	-123.2(2)
C(2) = 11(1) = 11(2) = C(20)	-92.4(2)	c(3)-Ti(1)-Ti(2)-C(20)	-141.4(2)
C(3) = C(2)	-106.2(2)	c(9) - Ti(1) - Ti(2) - c(20)	130.6(3)
C(4) = 21(2) - 21(2) - C(20)	£9.2(2)	C(7) - Ti(1) - Ti(2) - C(20)	100.4(2)
C(0) = C(1) = C(1) = C(1)	55.7(3)	C(8) - Ti(1) - Ti(2) - C(20)	131.1(2)
O(1) = Ti(1) = Ti(2) = C(25)	175.2(2)	C(2) - Ti(1) - Ti(2) - C(25)	36.9(2)
O(1) = II(1) = II(2) = O(25)	£9.2(3)	C(5) - Ti(1) - Ti(2) - C(25)	100.0(2)
C(2) = 12(2) = 12(2) = 0(25)	51.0(2)	C(4) - Ti(1) - Ti(2) - C(25)	86.2(2)
C(3) = 12(2) = 0(2)	-37.0(4)	C(5) - Ti(1) - Ti(2) - C(25)	-98.4(2)
C(2) = C(2) $C(2)$ $C(2)$	-67.2(2)	C(10) - Ti(1) - Ti(2) - C(25)	-101.9(3)
C(7) = 12(2) + 12(2) + C(25)	-36.5(2)	O(1) - Ti(1) - Ti(2) - C(1B)	32.8(3)
C(3) = C(2) + C(2) C(3) = C(2) + C(2)	-106.4(3)	c(1)-Ti(1)-Ti(2)-C(18)	-74.1(3)
C(2) = 12(2) = 12(2) = 0(10)	-43.4(3)	C(3) - Ti(1) - Ti(2) - C(18)	-92.3(3)
C(3) = 12(2) = 0(20)	-57.1(3)	C(9) - Ti(1) - Ti(2) - C(18)	179.7(4)
C(2) = 12(2) = C(20)	118.3(3)	C(7) - Ti(1) - Ti(2) - C(1B)	149.4(3)
C(0) = 22(2) = 22(2) = C(20)	114 B(4)	C(8) - Ti(1) - Ti(2) - C(18)	-179.8(3)
C(10) = 11(1) = 11(2) = 0(10)	-158 1(2)	C(2) - Ti(1) - Ti(2) - C(22)	62.7(2)
O(1) = O(2) = O(2)	95 0(2)	C(5) - Ti(1) - Ti(2) - C(22)	125.7(2)
C(1) = m(1) = m(2) = C(22)	75.8(2)	C(4) - Ti(1) - Ti(2) - C(22)	112.0(2)
C(3) = C(1) = C(2) = C(22)	-11 2 (3)	C(5) - Ti(1) - Ti(2) - C(22)	-72.5(2)
$C(9) = T_2(1) = T_1(2) = C(22)$	-47 5(7)	C(10) - Ti(1) - Ti(2) - C(22)	-76.1(3)
$C(7) - T_1(1) - T_1(2) - C(22)$		O(1) - Ti(1) - Ti(2) - C(21)	172.5(2)
$C(2) = T_1(1) = T_1(2) = C(22)$	-10.7(2)	C(1) - Ti(1) - Ti(2) - C(21)	65.7(2)
$C(2) - T_1(1) - T_1(2) - C(21)$	53.4(2)	C(3) = Ti(1) = Ti(2) = C(21)	47.5(2)
$C(5) - T_2(1) - T_1(2) - C(21)$	50.4(2)	C(9) = Ti(1) = Ti(2) = C(21)	-40.5(3)
C(4) - 21(1) - 21(2) - 0(21)		C(7) = Ti(1) = Ti(2) = C(21)	-70.8(2)
C(6) - Ti(1) - Ti(2) - C(21)	-101.7(2)	C(R) = mi(1) = mi(2) = C(21)	-40-0(2)
C(10) - Ti(1) - Ti(2) - C(21)	-103.4(2)	C(2) = Ti(2) = Ti(2) = C(24)	25.1(2)
O(1) - Ti(1) - Ti(2) - C(24)	-153./(4)	$C(2) = T_{2}(2) = T_{2}(2) = C(24)$	148.1(2)
C(1) - Ti(1) - Ti(2) - C(24)	11/.6(3)	(3) = (2) = (2) = (2) (3) = (3) = (2) = (22)	134.4(2)
C(3) - Ti(1) - Ti(2) - C(24)	99.2(2)	u(4/=++++=/=+++/=+++/=+++/ n(5)_m;(1)_m;(2)_0(22)	-50.2(2)
C(9) - Ti(1) - Ti(2) - C(24)	11.2(4)	G(0)-++(+)-++(+)-G(++) G(1))-mi(1)-mi(2)-C(24)	-53.7(3)
C(7) - Ti(1) - Ti(2) - C(24)	-19.0(3)	(1) = 1 + (1) = 1 + (2) = 0 + (2)	_15 3/01
C(8) - Ti(1) - Ti(2) - C(24)	11.7(3)		-177 7/21
c(2)-Ti(1)-Ti(2)-C(19)	-154.5(2)	C(1) - C(1) - C(2) - C(2)	-142.213)

Table AIV.4 Torsion angles (deg) for 37

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	69 E /31	c(3) = mi(1) = mi(2) = c(19)	-140.4(2)
C(5) - Ti(1) - Ti(2) - C(19)	-31.3(3)	c(3) = mi(1) = mi(2) = c(19)	131.6(4)
C(4) - Ti(1) - Ti(2) - C(19)	-103.2(3)	$(3)^{-1}(1)^{-1}(2)^{-1}(19)$	101.3(3)
C(6) - Ti(1) - Ti(2) - C(19)	70.2(3)	C(7) = 11(1) = 12(1) = C(19)	132.1(3)
C(10) - Ti(1) - Ti(2) - C(19)	66.7(3)	C(8) = 11(1) = 11(2) = C(12)	-85 B(4)
c(2) - Ti(1) - O(1) - C(12)	-65.5(4)	C(1) - T1(1) - O(1) - C(12)	-23.0(4)
C(5) - Ti(1) - O(1) - C(12)	-62.3(4)	C(3) - T1(1) - O(1) - C(12)	
C(4) - Ti(1) - O(1) - C(12)	-28.6(4)	C(9) - Ti(1) - O(1) - C(12)	
C(6) - Ti(1) - O(1) - C(12)	120.3(4)	C(7) - Ti(1) - O(1) - C(12)	131.6(4)
C(10) - Ti(1) - O(1) - C(12)	E5.9(4)	C(3) - Ti(1) - O(1) - C(12)	97.0(4)
$\pi i(2) - \pi i(1) - O(1) - C(12)$	-127.8(4)	C(2) - Ti(1) - O(1) - C(15)	134.1(4)
C(1) - Ti(1) - O(1) - C(15)	112.9(4)	C(5) - Ti(1) - O(1) - C(15)	137.4(4)
C(3) - Ti(1) - O(1) - C(15)	175.7(4)	C(4) - Ti(1) - O(1) - C(15)	171.0(4)
C(9) = Ti(1) = O(1) = C(15)	-90.2(4)	C(6) - Ti(1) - O(1) - C(15)	-40.0(4)
C(7) = C(1) = O(1) = C(13)	-28.9(4)	C(10) - Ti(1) - O(1) - C(15)	-74.4(4)
$C(8) = m^{2}(1) = O(1) = C(15)$	-62.7(5)	Ti(2) - Ti(1) - O(1) - C(15)	71.9(4)
C(15) = m(2) = C(1) = C(5)	11.8(4)	C(23) - Ti(2) - C(1) - C(5)	-145.1(4)
c(17) = c(1) = c(1) = c(5)	45.6(4)	C(20) - Ti(2) - C(1) - C(5)	0.0(5)
C(1) = 12(1) = C(1) = C(5)	153.3(4)	C(18) - Ti(2) - C(1) - C(5)	63.0(4)
C(23) = 12(2) = C(1) = C(3)	-153.3(4)	C(21) - Ti(2) - C(1) - C(5)	173.4(4)
C(22) = 11(2) = C(1) = C(5)	175 4(4)	C(19) - Ti(2) - C(1) - C(5)	25.3(5)
$C(24) = T_2(2) = C(1) = C(3)$	-71 8(4)	C(15) - Ti(2) - C(1) - C(2)	154.0(4)
Ti(1) - Ti(2) - C(1) - C(3)	-/1.0(4)	C(17) = m(2) = C(1) = C(2)	-172.1(4)
C(23) - Ti(2) - C(1) - C(2)	-2.8(3)	C(25) = mi(2) = C(2) = C(2)	-54.5(4)
C(20) - Ti(2) - C(1) - C(2)	142-2(4)	C(23) = T(2) = C(2) = C(2)	-11.1(4)
C(18) - Ti(2) - C(1) - C(2)	-154.7(4)	C(22) = C(2) = C(2) = C(2)	-42.4(5)
C(21) - Ti(2) - C(1) - C(2)	-44.4(4)	C(2k) = 22(2) = C(2) = C(2)	70 4 (4)
C(19) - Ti(2) - C(1) - C(2)	1/7.5(4)	$2 \leq (1) = 1 \leq (2) = C(1) = C(2)$	-73 2(2)
C(16) - Ti(2) - C(1) - Ti(1)	83.5(2)	C(23) = PI(2) = C(1) = I(1)	71 8(2)
C(17) - Ti(2) - C(1) - Ti(1)	117.5(2)	C(20) = C(2) = C(2) = C(2)	134 9(2)
C(25) - Ti(2) - C(1) - Ti(1)	-134.9(2)	C(1B) = C1(2) = C(1) = 1 = (1)	-114 8(2)
C(22) - Ti(2) - C(1) - Ti(1)	-81.5(2)	C(21) - TI(2) - C(1) - I(1)	
C(24) - Ti(2) - C(1) - Ti(1)	-112.8(2)	C(19) - T1(2) - C(1) - C(1)	-130 5(4)
O(1) - Ti(1) - C(1) - C(5)	44.8(3)	C(2) - Ti(1) - C(1) - C(5)	-110.0(%)
c(3)-Ti(1)-C(1)-C(5)	-75.2(3)	C(4) - Ti(1) - C(1) - C(5)	
C(9) - Ti(1) - C(1) - C(5)	-102.5(4)	C(5) - Ti(1) - C(1) - C(5)	150.7(4)
c(7) - Ti(1) - c(1) - c(5)	-178.0(3)	C(10) - Ti(1) - C(1) - C(5)	
C(8) - Ti(1) - C(1) - C(5)	-138.7(3)	Ti(2) - Ti(1) - C(1) - C(3)	123.7(3)
O(1) - Ti(1) - C(1) - C(2)	155.4(3)	C(5) - Ti(1) - C(1) - C(2)	TT010(4)
C(3) - Ti(1) - C(1) - C(2)	35.4(3)	C(4) - Ti(1) - C(1) - C(2)	/5.8(3)
C(9) - Ti(1) - C(1) - C(2)	B.1(4)	C(5) - Ti(1) - C(1) - C(2)	-98.7(4)
C(7) - Ci(1) - C(1) - C(2)	-57.4(3)	C(10) - Ti(1) - C(1) - C(2)	25.0(13)
C(B) - Ti(1) - C(1) - C(2)	-28.0(4)	Ti(2) - Ti(1) - C(1) - C(2)	-123.7(3)
O(1) - Ti(1) - C(1) - Ti(2)	-80.9(2)	C(2) - Ti(1) - C(1) - Ti(2)	123.7(3)
C(5) - Ti(1) - C(1) - Ti(2)	-125.7(3)	C(3) - Ti(1) - C(1) - Ti(2)	159.1(3)
C(4) - Ti(1) - C(1) - Ti(2)	-150.5(3)	C(9) - Ti(1) - C(1) - Ti(2)	131.B(3)
C(6) - Ti(1) - C(1) - Ti(2)	25.0(5)	C(7) - Ti(1) - C(1) - Ti(2)	55.3(3)
c(10) = mi(1) = c(1) = mi(2)	148.7(11)	C(B) - Ti(1) - C(1) - Ti(2)	95.7(2)
C(5) = C(2) = C(2) = C(3)	0.9(5)	Ti(2) - C(1) - C(2) - C(3)	-148.3(3)
mi(1) = C(1) = C(2) = C(3)	-65.5(4)	C(5)-C(1)-C(2)-Ti(1)	66.3(3)
mi(2) = C(2) = C(2) = C(2)	-82.8(3)	O(1) - Ti(1) - C(2) - C(3)	82.3(3)
c(1) = c(2) = c(2) = c(2)	118.4(4)	C(5) - Ti(1) - C(2) - C(3)	78.4(3)
C(1) = 11(1) = C(2) = C(3)	37 7 (3)	C(9) - Ti(1) - C(2) - C(3)	-56.0(3)
	-106 6(4)	C(7) - Ti(1) - C(2) - C(3)	-113.5(3)
C(0) + 12(1) - C(2) - C(3)	-100.0(4)	C(B) - Ti(1) - C(2) - C(3)	-B6.1(3)
c(10) = 22(1) = c(2) = c(3)	-33.9(4/ 125 A/2)	O(1) = Ti(1) = C(2) = C(1)	-36.2(4)
$T_1(2) = T_2(1) = C(2) = C(3)$	-40 0(3)	C(3) = Ti(1) = C(2) = C(1)	-118.4(4)
C(5) - T1(1) - C(2) - C(1)	-40.0(3)	C(P) = mi(1) = C(2) = C(1)	-174.4(3)
$C(4) - T_1(1) - C(2) - C(1)$	-81.3(3)		128 0(3)
C(6) - T1(1) - C(2) - C(1)	133.U(3)		155 4(3)
$C(10) - T_2(1) - C(2) - C(1)$	-14.4(3)		0 2/21
T1(2) - Ti(1) - C(2) - C(1)	36.6(2)		54 D(3)
Ti(1) - C(2) - C(3) - C(4)	-63.8(3)	C(1) - C(2) - C(3) - T1(1)	04.0(3)

-(1) = -(1) = -(1) = -(1)	-126.2(3)	c(1) - Ti(1) - c(3) - c(2)	-37.0(3)
O(1) - 21(1) - O(3) - O(2)	-78.5(3)	C(4) - Ti(1) - C(3) - C(2)	-116.3(4)
C(3) = 11(1) = C(3) = C(2)	74 7 (3)	C(6) - Ti(1) - C(3) - C(2)	113.6(4)
$C(9) - T_{1}(1) - C(3) - C(2)$	79 5(3)	C(10) - Ti(1) - C(3) - C(2)	141.2(3)
C(7) - T(1) - C(3) - C(2)	75.5(2) 00.5(3)	$m_{1}(2) = m_{1}(1) = C(3) = C(2)$	-23.2(3)
C(8) - Ti(1) - C(3) - C(2)	50.5(3)	c(7) = m(1) = c(3) = c(4)	116.3(4)
O(1) - Ti(1) - C(3) - C(4)	-3.3(4)	C(2) = 1 (2) = C(3) = C(4)	37.6(3)
$C(1) - T_1(1) - C(3) - C(4)$	/9.3(3)	c(s) = c(s) = c(s) = c(s)	-130.1(3)
C(9) - Ti(1) - C(3) - C(4)	-119.0(3)	C(0) = II(1) = C(0) = C(4)	-102.6(3)
C(7) - Ti(1) - C(3) - C(4)	-156.1(3)	C(10) = 11(1) - C(3) - C(4)	63 1 (3)
C(B) - Ti(1) - C(3) - C(4)	-153.2(3)	$T_1(2) = T_1(1) = C(3) = C(4)$	-63 6 (3)
C(2)-C(3)-C(4)-C(5)	-1.3(5)	21(1) = C(3) = C(4) = C(5)	-73 0(3)
C(2) - C(3) - C(4) - Ti(1)	62.3(3)	$O(1) = f_1(1) = C(4) = C(5)$	75.5(2)
C(2) - Ti(1) - C(4) - C(5)	78.2(3)	C(1) = T1(1) = C(2) = C(3)	75 7(3)
C(3) - Ti(1) - C(4) - C(5)	115.3(4)	$C(9) - T_1(1) - C(4) - C(5)$	143 5/4
C(5) - Ti(1) - C(4) - C(5)	-149.4(4)	C(7) - Ti(1) - C(6) - C(5)	143.0(4)
c(10) - Ti(1) - C(4) - C(5)	-152.5(3)	C(B) - Ti(1) - C(4) - C(5)	199.3(3)
Ti(2) - Ti(1) - C(4) - C(5)	22.6(3)	O(1) - T1(1) - C(4) - C(3)	1/1./(3)
C(2) - Ti(1) - C(4) - C(3)	-37.1(3)	C(1) - Ti(1) - C(4) - C(3)	+/9.8(3)
c(5) - Ti(1) - C(4) - C(3)	-115.3(4)	C(9) - Ti(1) - C(4) - C(3)	50.9(3)
c(6) - Ti(1) - C(4) - C(3)	95.4(4)	C(7) - Ti(1) - C(4) - C(3)	28.3(5)
c(10)-Ti(1)-C(4)-C(3)	92.2(3)	C(3) - Ti(1) - C(4) - C(3)	29.6(4)
ri(2) - ri(1) - c(4) - c(3)	+92.7(3)	C(3) - C(4) - C(5) - C(1)	2.0(5)
ri(1) - C(4) - C(5) - C(1)	-52.4(3)	C(3) - C(4) - C(5) - Ti(1)	64.4(3)
c(2)-c(1)-c(5)-c(4)	-1.7(5)	Ti(2)-C(1)-C(5)-C(4)	145.5(4)
Ti(1) - C(1) - C(5) - C(4)	63.6(4)	C(2) - C(1) - C(5) - Ti(1)	-65.3(3)
Ti(2) - C(1) - C(5) - Ti(1)	E3.1(3)	O(1) - Ti(1) - C(5) - C(4)	103.5(3)
C(2) - Ti(1) - C(5) - C(4)	-79.1(3)	C(1) - Ti(1) - C(5) - C(4)	-120.1(4)
C(3) - Ti(1) - C(5) - C(4)	-37.7(3)	C(9) - Ti(1) - C(5) - C(4)	-5.2(4)
C(5) - Ti(1) - C(5) - C(4)	112.3(7)	C(7) - Ti(1) - C(5) - C(4)	-115.3(6)
c(10) - Ti(1) - C(5) - C(4)	44.2(5)	C(S) - Ti(1) - C(S) - C(4)	-54.6(5)
ri(2) - ri(1) - c(5) - c(4)	-155.7(3)	0(1) - Ti(1) - C(5) - C(1)	-136.3(3)
C(2) - Ti(1) - C(5) - C(1)	41.0(3)	C(3) - Ti(1) - C(5) - C(1)	82.4(3)
C(4) - Ti(1) - C(5) - C(1)	120.1(4)	C(9) - Ti(1) - C(5) - C(1)	114.9(4)
C(6) - Ti(1) - C(5) - C(1)	-127.5(7)	C(7) - Ti(1) - C(5) - C(1)	4.7(7)
C(10) - Ti(1) - C(5) - C(1)	164.3(3)	C(B) - Ti(1) - C(5) - C(1)	65.5(4)
$p_i(2) - p_i(1) - C(5) - C(1)$	-35.6(2)	O(1) - Ti(1) - C(5) - C(7)	151.6(4)
C(2) - Ti(1) - C(6) - C(7)	-12.3(5)	C(1) - Ti(1) - C(5) - C(7)	50.5(6)
C(5) - Ti(1) - C(6) - C(7)	- 153.0(6)	C(3) - Ti(1) - C(6) - C(7)	-64.9(5)
C(4) = m(1) = C(5) = C(7)	-120.5(4)	c(9) - c(1) - c(6) - c(7)	-78.1(4)
C(10) = mi(1) = C(6) = C(7)	-115.4(5)	C(B) - Ti(1) - C(6) - C(7)	-37.0(4)
mi(2) = mi(1) = C(6) = C(7)	6E.1(4)	0(1) - Ti(1) - C(6) - C(10)	-E3.0(4)
C(2) = mi(1) = C(6) = C(10)	103.0(4)	c(1) - Ti(1) - c(6) - c(10)	165.9(4)
C(5) = Ti(1) = C(6) = C(10)	-91.5(7)	C(3) - Ti(1) - C(6) - C(10)	50.5(5)
$C(4) = T^{2}(1) + C(6) + C(10)$	-5.1(6)	C(5) - Ti(1) - C(5) - C(10)	37.2(3)
C(7) = m(1) = C(6) = C(10)	115.4(5)	C(3) - Ti(1) - C(6) - C(10)	73.3(4)
$m_{1}(2) = m_{1}(1) = m_{1}(2) = m_{1}(1) $	-176.5(3)	C(10) - C(5) - C(7) - C(E)	-0.5(5)
$m_{1}(2) = 22(2) = 0(0)^{-1} = 0(0)^{-1}$	54.9(4)	c(10)-c(6)-c(7)-Ti(1)	-65.5(4)
21(1) = C(0) = C(0) = C(0)	-20.3(4)	C(2) - Ti(1) - C(7) - C(5)	171.5(4)
O(1) = 12(1) = C(7) = C(6)	_753 8(3)	C(5) - Ti(1) - C(7) - C(6)	-157.1(5)
C(1) = 12(1) = C(7) = C(6)	136 0(4)	C(4) - Ti(1) - C(7) - C(6)	118.4(5)
C(3) = 12(1) = C(7) = C(5)	78 5 (4)	C(10) - Ti(1) - C(7) - C(6)	37.6(4)
C(g) = 11(1) - C(7) - C(6)	115 3(5)	Ti(2) - Ti(1) - C(7) - C(6)	-120.1(4)
C(E) = 22(2) = C(7) = C(0)	-136 6(3)	C(2) - Ti(1) - C(7) - C(8)	55.3(4)
O(1) = mi(1) = O(7) = O(8)	SO 0741	C(5) - Ti(1) - C(7) - C(B)	86.6(6)
C(1) = C(1) = C(1) = C(0)	19 7/21	C(4) - Ti(1) - C(7) - C(B)	2.2(6)
C(3) = C(2) = C(2) = C(2)	_37 2(4)	C(6) - Ti(1) - C(7) - C(2)	-116.3(5)
C(3)-T2(1)-C(7)-C(5) C(10)-T(1)-C(7)-C(8)	-31.3(4)	ri(2) - ri(1) - c(7) - c(8)	123.6(3)
	-10.0(4/ D 2/2)	$r_{1}(1) = c_{1}(1) = c_{1}(1) = c_{1}(1)$	65.1(4)
C(2) = C(7) = C(3) = C(3)	-54 6/4)	O(1) = Ti(1) = C(R) = C(R)	-50.5(5)
$C(0) + C(1) + C(3) + T_{1}(1)$	-08.014/	C(1) = mi(1) = C(0) = C(0)	134 3 (4)
C(2) = TL(1) = C(8) = C(9)	1 - C - U (C)		-27.2(4)

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	C(5) = Ti(1) = C(8) = C(9)	97.5(4)	C(3) - Ti(1) - C(8) - C(9)	83.2(4)
	C(3) = 12(2) = C(0) = C(0)	66.7(4)	C(6) - Ti(1) - C(8) - C(9)	-78.0(4)
	C(4) = 12(2) = C(0) = C(0)	-114.5(5)	C(10) - Ti(1) - C(8) - C(9)	-36.7(4)
	$r_{i}(2) - r_{i}(1) - C(B) - C(9)$	-179.5(3)	0(1)-Ti(1)-C(8)-C(7)	64.0(5)
	C(2) = mi(1) = C(8) = C(7)	-127.4(4)	C(1) - Ti(1) - C(8) - C(7)	-111.2(4)
	c(2) = 12(2) - c(0) - c(7)	-148.0(3)	C(3)-T1(1)-C(8)-C(7)	-162.3(4)
	C(3) = 12(1) + C(0) = (1)	-178.8(3)	C(9)-Ti(1)-C(8)-C(7)	114.5(5)
	C(5) = Ti(1) = C(8) = C(7)	36.6(3)	C(10) - Ti(1) - C(B) - C(7)	77.8(4)
	$m_{1}(2) - m_{1}(1) - C(8) - C(7)$	-65.0(4)	C(7) - C(8) - C(9) - C(10)	0.2(6)
	$m_{1}(1) = C(R) = C(9) = C(10)$	65.5(4)	C(7) - C(8) - C(9) - Ti(1)	-65.3(4)
	O(1) = mi(1) = C(9) = C(10)	29.0(4)	C(2) - Ti(1) - C(9) - C(10)	180.0(4)
	C(1) = mi(1) = C(9) = C(10)	175.1(3)	C(5) - Ti(1) - C(9) - C(10)	124.2(4)
	C(3) = Ti(1) = C(9) = C(10)	151.4(4)	C(4) - Ti(1) - C(9) - C(10)	121.2(4)
	$C(5) = T_{1}(1) = C(9) = C(10)$	-37.7(3)	C(7) - Ti(1) - C(9) - C(10)	-78.4(4)
	C(8) - Ti(1) - C(9) - C(10)	-116.3(5)	Ti(2) - Ti(1) - C(9) - C(10)	-115.5(4)
	O(1) = Ti(1) = C(9) = C(8)	145.2(3)	C(2) - Ti(1) - C(9) - C(8)	-63.8(4)
	C(1) = Ti(1) = C(9) = C(8)	-58.7(5)	C(5) - Ti(1) - C(9) - C(8)	-119.6(4)
	C(3) = mi(1) = C(9) = C(8)	-92.3(4)	C(4) - Ti(1) - C(9) - C(8)	-122.E(4)
	C(5) - Ti(1) - C(9) - C(8)	78.5(4)	C(7) - Ti(1) - C(9) - C(8)	37.8(3)
	C(10) - Ti(1) - C(9) - C(8)	116.3(5)	Ti(2) - Ti(1) - C(9) - C(8)	0.8(6)
	C(3) - C(9) - C(10) - C(6)	-0.5(6)	Ti(1)-C(9)-C(10)-C(6)	54.9(4)
	C(8) - C(9) - C(10) - Ti(1)	-65.5(4)	C(7) - C(6) - C(10) - C(9)	0.7(6)
	Ti(1) - C(5) - C(10) - C(9)	-65.0(4)	C(7) - C(6) - C(10) - Ti(1)	65.7(4)
	O(1) - Ti(1) - C(10) - C(9)	-152.7(4)	C(2) - Ti(1) - C(10) - C(9)	0.0(5)
	C(1) - C(1) - C(10) - C(9)	-20.7(13)	C(5) - Ti(1) - C(10) - C(9)	-93.7(4)
	C(3) - Ti(1) - C(10) - C(9)	-30.4(4)	C(4) - Ti(1) - C(10) - C(9)	-67.9(4)
	C(5) - Ti(1) - C(10) - C(9)	115.1(5)	C(7) - Ti(1) - C(10) - C(9)	78.1(4)
	C(8) - Ti(1) - C(10) - C(9)	35.9(4)	Ti(2) - Ti(1) - C(10) - C(9)	120.9(4)
	O(1) - Ti(1) - C(10) - C(5)	92.2(4)	C(2) - Ti(1) - C(10) - C(5)	-115.1(4)
	C(1) - Ti(1) - C(10) - C(6)	-135.8(11)	C(5) - Ti(1) - C(10) - C(6)	151.3(3)
	C(3) - Ti(1) - C(10) - C(5)	-145.4(3)	C(4) - Ti(1) - C(10) - C(6)	17.0(3)
	C(9) - Ti(1) - C(10) - C(6)	-115.1(5)	C(7) - Ti(1) - C(10) - C(6)	= 37.0(37
	C(8) - Ti(1) - C(10) - C(6)	-78.1(4)		-166 5(4)
	C(15)-O(1)-C(12)-C(13)	-3.2(6)		-10010(4)
	O(1) - C(12) - C(13) - C(14)	-17.8(7)	C(12) = C(13) = C(14) = C(14)	-173 9(4)
	C(12) - O(1) - C(15) - C(14)	23.4(5)	$\alpha_1(1) = 0(1) = 0(15) = 0(17)$	82.9(3)
	C(13) - C(14) - C(15) - O(1)		C(20) = mi(2) = C(16) = C(17)	-115.5(5)
	C(23) - Ti(2) - C(16) - C(17)		C(1R) = mi(2) = C(16) = C(17)	-37.9(3)
	C(25) - Ti(2) - C(16) - C(17)	-33.2(3)	C(23) = C(2) - C(25) - C(17)	25.2(7)
	C(22) - Ti(2) - C(16) - C(17)	157.1(0)	C(19) = mi(2) = C(16) = C(17)	-78.8(4)
	$C(24) - T_1(2) - C(16) - C(17)$	-E1.3(4/	C(1) - T(2) - C(16) - C(20)	-161.6(3)
	$\pi_1(1) - \pi_1(2) - C(16) - C(17)$	-15 9/5)	C(17) - Ti(2) - C(16) - C(20)	115.5(5)
	C(23) = 21(2) = C(16) = C(20)	$F_{2,3}(4)$	C(18) - Ti(2) - C(16) - C(20)	77.6(4)
	C(23) = ff(2) = C(20) = C(20)	-27.4(7)	C(21) - Ti(2) - C(15) - C(20)	140.7(5)
	C(22) = 11(2) = C(10) = C(20)	33.6(4)	C(19) - Ti(2) - C(15) - C(20)	35.7(3)
	$m_{1}(1) = m_{1}(2) = c(16) = c(20)$	-117.5(3)	C(20) - C(16) - C(17) - C(18)	-0.6(6)
	m(2) = C(15) = C(17) = C(18)	65.5(3)	C(20)-C(15)-C(17)-Ti(2)	-65.0(3)
	$C(1) = m^{2}(2) = C(17) = C(16)$	-94.4(3)	C(23)-Ti(2)-C(17)-C(15)	105.6(5)
-	C(20) = Ti(2) = C(17) = C(16)	37.5(3)	C(25)-Ti(2)-C(17)-C(16)	157.7(3)
	C(12) - Ti(2) - C(17) - C(16)	114.7(5)	C(22) - Ti(2) - C(17) - C(15)	-162.7(5)
	C(21) - Ti(2) - C(17) - C(15)	-158.8(3)	C(24) - Ti(2) - C(17) - C(16)	122.8(3)
	C(19) - Ti(2) - C(17) - C(16)	77.5(4)	Ti(1) - Ti(2) - C(17) - C(16)	-54.9(3)
	C(1)-T1(2)-C(17)-C(18)	150.9(4)	C(16)-Ti(2)-C(17)-C(18)	-114.7(5)
	C(23) - Ti(2) - C(17) - C(18)	-9.1(6)	C(20) - Ti(2) - C(17) - C(18)	-77.2(4)
	C(25)-Ti(2)-C(17)-C(18)	43.0(4)	C(22) - Ti(2) - C(17) - C(18)	52.5(5)
	c(21) -Ti(2) -c(17) -c(18)	75.5(4)	C(24) - Ti(2) - C(17) - C(18)	8.1(4)
	C(19)-Ti(2)-C(17)-C(1B)	-37.2(3)	Ti(1) - Ti(2) - C(17) - C(18)	-169.5(3)
	C(16) - C(17) - C(18) - C(19)	1.4(6)	Ti(2) - C(17) - C(18) - C(19)	66.3(4)
	C(16) - C(17) - C(18) - Ti(2)	-64.9(3)	C(1)-Ti(2)-C(18)-C(19)	-147.0(3)

	C(16) - Ti(2) - C(18) - C(19)	-77.5(4)	C(23)-Ti(2)-C(18)-C(19)	60.2(4)
	C(17) = Ti(2) = C(18) = C(19)	-115.1(5)	C(20) - Ti(2) - C(18) - C(19)	-36.0(3)
	C(25) - Ti(2) - C(18) - C(19)	105.6(4)	C(22) - Ti(2) - C(18) - C(19)	96.5(4)
	c(23) = c(2) = c(2) = c(2) = c(2)	123 3 (3)	C(24) = mi(2) = C(18) = C(19)	71 9(4)
	C(22) = 12(2) = C(20) = C(10)		$C(1) - \pi i (2) - C(1R) - C(17)$	-37 9(4)
		-100.0(4)	C(1) = 22(1) = C(10) = C(17)	
	C(16) - T1(2) - C(18) - C(17)	37.5(3)	C(23) = T1(2) = C(13) = C(17)	1/5.2(3)
	C(20) - T1(2) - C(18) - C(17)	79.0(4)	C(25) - T1(2) - C(18) - C(17)	-139.4(4)
	C(22) - Ti(2) - C(1B) - C(17)	-148.5(3)	C(21) - Ti(2) - C(18) - C(17)	-121.6(3)
	C(24) - Ti(2) - C(18) - C(17)	-173.0(4)	C(19)-Ti(2)-C(18)-C(17)	115.1(5)
	Ti(1) - Ti(2) - C(18) - C(17)	15.1(5)	C(17) - C(18) - C(19) - C(20)	-1.7(5)
	Ti(2)-C(18)-C(19)-C(20)	63.5(4)	C(17)-C(18)-C(19)-Ti(2)	-65.3(4)
	C(1) - Ti(2) - C(19) - C(20)	-66.7(5)	C(16) - Ti(2) - C(19) - C(20)	-37.9(3)
	C(23) - Ti(2) - C(19) - C(20)	113.6(4)	C(17) - Ti(2) - C(19) - C(20)	-79.1(4)
	C(25) - Ti(2) - C(19) - C(20)	170.1(4)	C(18) - Ti(2) - C(19) - C(20)	-115.9(5)
	C(22) - Ti(2) - C(19) - C(20)	124.8(4)	C(21) - Ti(2) - C(19) - C(20)	168.6(3)
	C(24) - Ti(2) - C(19) - C(20)	139.8(4)	Ti(1) - Ti(2) - C(19) - C(20)	-1.7(5)
	$C(1) = m_1(2) = C(18) = C(18)$	50 2(5)	C(15) = m(2) = C(19) = C(18)	79 0 (4)
	C(23) = T(2) = C(23) = C(23)	-128 5(4)	$C(27) = T_{1}(2) = C(19) = C(19)$	
		-129.5(4)	(17) = 11(2) = 0(19) = 0(19)	77 0(4)
	C(20) = T(2) = C(13) = C(12)			-73.0(4)
	C(22) = T1(2) = C(19) = C(18)	-118.3(4)	C(21) - T1(2) - C(19) - C(18)	-/4.5(4)
	C(24) - T1(2) - C(19) - C(18)	-103.3(4)	Ti(1) - Ti(2) - C(19) - C(18)	115.2(3)
	C(18) - C(19) - C(20) - C(16)	1.4(5)	Ti(2) - C(15) - C(20) - C(15)	64.9(3)
	C(18) - C(19) - C(20) - Ti(2)	-63.5(4)	C(17) - C(16) - C(20) - C(19)	-0.5(5)
•	Ti(2) - C(16) - C(20) - C(19)	-65.5(4)	C(17) - C(16) - C(20) - Ti(2)	66.0(3)
	C(1) - Ti(2) - C(20) - C(19)	136.5(4)	C(16) - Ti(2) - C(20) - C(19)	115.3(5)
	C(23) - Ti(2) - C(20) - C(19)	-74.7(4)	C(17) - Ti(2) - C(20) - C(19)	78.1(4)
	C(25) - Ti(2) - C(20) - C(19)	-12.2(4)	C(18) - Ti(2) - C(20) - C(19)	36.7(3)
	C(22) - Ti(2) - C(20) - C(19)	-90.6(4)	C(21) - Ti(2) - C(20) - C(19)	-25.5(7)
	C(24) - Ti(2) - C(20) - C(19)	-40.2(4)	Ti(1) - Ti(2) - C(20) - C(19)	178.7(3)
	C(1)-Ti(2)-C(20)-C(15)	21.3(4)	C(23) - Ti(2) - C(20) - C(16)	170.0(3)
	C(17)-T1(2)-C(20)-C(16)	-37.1(3)	C(25)-Ti(2)-C(20)-C(16)	-127.4(3)
	C(1B) - Ti(2) - C(20) - C(16)	-78.5(4)	C(22) - Ti(2) - C(20) - C(16)	154.2(3)
	C(21) - Ti(2) - C(20) - C(15)	-140.8(5)	C(24) - Ti(2) - C(20) - C(16)	-155.5(3)
	C(19) - Ti(2) - C(20) - C(15)	-115.3(5)	Ti(1) - Ti(2) - C(20) - C(15)	63.4(3)
	C(1) - Ti(2) - C(21) - C(22)	100.4(3)	C(16) - Ti(2) - C(21) - C(22)	159.1(4)
	C(23) - Ti(2) - C(21) - C(22)	-37.2(3)	C(17) - Ti(2) - C(21) - C(22)	176.2(3)
	C(20) - Ti(2) - C(21) - C(22)	-95.3(6)	C(25) - Ti(2) - C(21) - C(22)	-115.0(4)
	C(18) = Ti(2) = C(21) = C(22)	-147 5(3)	C(24) = Ti(2) = C(21) = C(22)	-78.0(3)
	C(12), T=(2), C(21), C(22),	-112 (13)	$m_{1}(1) = m_{1}(2) = m_{1}(2) = m_{1}(2)$	60 4 (3)
	C(1) = m(2) = C(21) = C(25)	-1/4 = (3)	C(16) = mi(2) = C(21) = C(25)	-55 8(5)
	C(23) = E(2) + C(23) + C(25)	77 8(3)	C(17) - mi(2) - C(21) - C(25)	
	C(23) = 12(2) = C(22) = C(23)	11.0(3)	C(17) = C(21) = C(21) = C(25)	
	C(20) = 12(2) = C(21) = C(23)		C(21) = C(21) = C(21) = C(25)	-32.0(4)
	C(22) = 11(2) = C(21) = C(23)	223.0(4)	C(24) = 12(2) = C(21) = C(23) mi(3) = mi(3) = C(23) = C(25)	
	C(19) = 11(2) = C(21) = C(23)	2 - 7 (%)	$\pi_1(1) - \pi_1(2) - C(21) - C(23)$	1,3,4(3)
	C(25) = C(21) = C(22) = C(23)	-0.4(5)	$T_1(2) = C(21) = C(22) = C(23)$	54.5(3)
	C(25) - C(21) - C(22) - T1(2)	-64.9(3)	C(1) - T1(2) - C(22) - C(21)	-76.5(3)
	C(15) - T1(2) - C(22) - C(21)	-150.5(5)	C(23) - Ti(2) - C(22) - C(21)	115.0(5)
	C(17) - Ti(2) - C(22) - C(21)	-8.9(7)	C(20) - Ti(2) - C(22) - C(21)	143.1(3)
	C(25) - Ti(2) - C(22) - C(21)	37.6(3)	C(18) - Ti(2) - C(22) - C(21)	48.5(4)
	C(24) - Ti(2) - C(22) - C(21)	73.4(3)	C(19) - Ti(2) - C(22) - C(21)	95.0(4)
	Ti(1) - Ti(2) - C(22) - C(21)	-120.4(3)	C(1) - Ti(2) - C(22) - C(23)	157.5(3)
	C(16) - Ti(2) - C(22) - C(23)	53.4(7)	C(17) - Ti(2) - C(22) - C(23)	-125.0(5)
	C(20) - Ti(2) - C(22) - C(23)	27.1(5)	C(25)-Ti(2)-C(22)-C(23)	-78.4(3)
	C(18)-Ti(2)-C(22)-C(23)	-67.5(4)	C(21) - Ti(2) - C(22) - C(23)	-116.0(5)
	C(24) - Ti(2) - C(22) - C(23)	-37.6(3)	C(19)-Ti(2)-C(22)-C(23)	-20.0(4)
	Ti(1)-Ti(2)-C(22)-C(23)	123.6(3)	C(21)-C(22)-C(23)-C(24)	1.8(6)
	Ti(2) - C(22) - C(23) - C(24)	55.8(4)	C(21) - C(22) - C(23) - Ti(2)	-65.0(3)
	C(1) - Ti(2) - C(23) - C(24)	-129.2(3)	C(16) - Ti(2) - C(23) - C(24)	92.3(4)
	C(17)-T1(2)-C(23)-C(24)	27.3(6)	C(20) - Ti(2) - C(23) - C(24)	22.8(4)
	C(25)-Ti(2)-C(23)-C(24)	-36.5(3)	C(18) - Ti(2) - C(23) - C(24)	21.4(4)
			· · · · · · · · · · · · · · · · · · ·	

C(22) - Ti(2) - C(23) - C(24)	-114.4(5)	C(21) - Ti(2) - C(23) - C(24)	-77.6(3)
C(19) - Ci(2) - C(23) - C(24)	50.6(4)	Ti(1) - Ti(2) - C(23) - C(24)	-172.1(3)
C(1) - Ti(2) - C(23) - C(22)	-14.7(4)	C(16)-Ti(2)-C(23)-C(22)	-153.3(3)
C(17) - Ti(2) - C(23) - C(22)	141.7(4)	C(20) - Ti(2) - C(23) - C(22)	-162.7(3)
c(25) - Ti(2) - C(23) - C(22)	77.9(3)	C(18)-Ti(2)-C(23)-C(22)	135.9(3)
C(21)-Ti(2)-C(23)-C(22)	36.8(3)	C(24) - Ti(2) - C(23) - C(22)	- 114.4(5)
c(19)-Ti(2)-C(23)-C(22)	165.0(3)	Ti(1)-Ti(2)-C(23)-C(22)	-57.7(3)
C(22)-C(23)-C(24)-C(25)	-2.5(6)	Ti(2) - C(23) - C(24) - C(25)	63.6(4)
C(22) - C(23) - C(24) - Ti(2)	-66.1(3)	C(1) - Ti(2) - C(24) - C(25)	-39.8(4)
C(16) - Ti(2) - C(24) - C(25)	117.5(4)	C(23) - Ti(2) - C(24) - C(25)	-115.7(5)
C(17) - Ti(2) - C(24) - C(25)	77.6(4)	c(20) - Ti(2) - c(24) - c(25)	136.1(3)
C(18) - Ti(2) - C(24) - C(25)	82.1(3)	c(22) - Ti(2) - c(24) - c(25)	-78.5(3)
C(21)-Ti(2)-C(24)-C(25)	-37.4(3)	C(19)-Ti(2)-C(24)-C(25)	114.9(4)
Ti(1)-Ti(2)-C(24)-C(25)	-105.7(3)	C(1) - Ti(2) - C(24) - C(23)	76.9(4)
C(16) - Ti(2) - C(24) - C(23)	-125.9(3)	C(17) - Ti(2) - C(24) - C(23)	-165.8(3)
C(20) - Ti(2) - C(24) - C(23)	-107.2(3)	C(25) - Ti(2) - C(24) - C(23)	116.7(5)
C(18) - Ti(2) - C(24) - C(23)	-161.2(4)	C(22) - Ti(2) - C(24) - C(23)	38.1(3)
C(21)-Ti(2)-C(24)-C(23)	79.2(3)	C(19) - Ti(2) - C(24) - C(23)	-128.5(4)
Ti(1)-Ti(2)-C(24)-C(23)	11.0(4)	C(23) - C(24) - C(25) - C(21)	2.3(6)
Ti(2)-C(24)-C(25)-C(21)	65.7(4)	C(23) - C(24) - C(25) - Ti(2)	-63.4(4)
C(22)-C(21)-C(25)-C(24)	-1.2(6)	Ti(2) - C(21) - C(25) - C(24)	-65.2(4)
C(22)-C(21)-C(25)-Ti(2)	65.1(3)	C(1) - ti(2) - C(25) - C(24)	152.7(3)
C(16)-Ti(2)-C(25)-C(24)	-98.6(4)	C(23)-Ti(2)-C(25)-C(24)	36.6(3)
C(17)-Ti(2)-C(25)-C(24)	-117.4(3)	C(20) - Ti(2) - C(25) - C(24)	-55.7(4)
C(18)-Ti(2)-C(25)-C(24)	-94.7(4)	C(22) - Ti(2) - C(25) - C(24)	78.1(3)
C(21) - Ti(2) - C(25) - C(24)	115.5(5)	C(19) - Ti(2) - C(25) - C(24)	-62.3(3)
Ti(1)-Ti(2)-C(25)-C(24)	109.3(3)	C(1) - Ti(2) - C(25) - C(21)	37.2(3)
C(15)-Ti(2)-C(25)-C(21)	145.9(3)	C(23) - Ti(2) - C(25) - C(21)	-78.9(3)
C(17) - Ti(2) - C(25) - C(21)	127.0(3)	C(20) - Ti(2) - C(25) - C(21)	-171.2(3)
C(18)-Ti(2)-C(25)-C(21)	149.8(3)	C(22) - Ti(2) - C(25) - C(21)	-37.5(3)
C(24)-Ti(2)-C(25)-C(21)	-115.5(5)	C(19) - Ti(2) - C(25) - C(21)	-177.9(3)
Ti(1) - Ti(2) - C(25) - C(21)	-5.3(4)	C(26) #1-O(2)-C(26)-C(27)	2.7(7)
O(2)-C(25)-C(27)-C(27)#1	-7(2)		

Symmetry transformations used to generate equivalent atoms: #1 -x,y,-z+1/2

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	×	У	2	U _{iso}
(1)	0.1247(14)	0.585(6)	0.2332(11)	5(2)
(2)	0.2214	0.5167	0.2165	4.0
(3)	0.2828	0.5647	0.3494	4.5
(4)	0.2587	0.8212	0.3981	4.6
5)	0.1845	0.9325	0.2920	4.0
5)	0.1176	0.3726	0.3624	5.8
(7)	0.1351	0.2458	0.2631	5.7
(8)	0.2236	0.2516	0.3088	6.1
(9)	0.2600	0.3799	0.4380	6.5
(10)	0.1952	0.4523	0.4723	6.2
(12A)	0.1852	0.9537	0.4160	5.5
(123)	0.2031	0.8046	0.4749	5.5
(13A)	0.1488	0.8572	0.5158	7.5
(133)	0.1442	1.0345	0.4777	7.5
(14A)	0.0715	0.8471	0.4307	7.8
(143)	0.0795	0.9595	0.3714	7.8
15A)	0.1005	0.5201	0.4010	5.9
153)	0.0762	0.7083	0.3204	5.9
(16)	0.1049	0.9203	0.2538	4.7
17)	0.1279	1.0501	0.1600	5.5
(18)	0.0673	0.9598	0.0296	6.3
(19)	0.0051	0.7863	0.0449	5.0
20)	0.0303	0.7558	0.1823	5.1
(21)	0.1780	0.5712	0.0859	4.6
(22)	0.1536	0.3533	0.1525	4.5
(23)	0.0541	0.3550	0.0963	5.0
24)	0.0334	0.5631	-0.0095	5.1
25)	0.1034	0.7044	-0.0122	4.8
26A)	0.0393	0.4176	0.2048	12.0
26B)	-0.0158	0.4252	0.1483	12.0
27A)	0.0310	0.1595	0.2209	23.0
273)	-0.0252	0.1728	0.1723	23.0

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Table AIV. 5 Hydrogen coordinates and isotropic displacement

parameters $(A^2 \times 10^2)$ for 37

Table AIV.6 Anistropic parameters $(A^2 \times 10^2)$ for 37

The anisotropic displacement factor exponent takes the form:

 $-2\pi^{2}[h^{2}a^{*2}U11 + \dots + 2hka^{*}b^{*}U12]$

	U11	U22	U 33	U 23	U13	U12
	<u></u>					
Ti(1)	2.94(4)	1.83(4)	3.17(5)	0.08(4)	1.34(4)	-0.19(4)
Ti(2)	3.18(4)	1.95(4)	3.12(5)	0.11(4)	1.27(4)	0.21(4)
0(1)	3.7(2)	2.8(2)	3.8(2)	-0.9(2)	1.7(2)	-0.4(2)
C(1)	3.8(3)	2.3(2)	3.3(3)	0.4(2)	2.1(2)	-0.6(2) .
C(2)	3.3(2)	2.9(3)	4.2(3)	0.1(2)	2.1(2)	0.1(2)
C(3)	2.7(2)	3.9(3)	4.4(3)	0.7(2)	1.4(2)	0.0(2)
C(4)	3.8(3)	3.4(3)	4.1(3)	-0.3(2)	1.7(2)	-1.4(2)
C(5)	3.3(2)	2.5(2)	4.3(3)	0.4(2)	1.8(2)	-0.5(2)
C(б)	6.1(4)	2.7(3)	7.2(4)	0.9(3)	4.5(4)	0.0(3)
C(7)	6.6(4)	1.3(2)	5.1(3)	-0.4(2)	1.6(3)	-1.0(2)
C(8)	7.4(4)	1.8(3)	8.1(5)	1.3(3)	5.3(4)	1.3(3)
C(9)	4.7(3)	3.6(3)	5.7(4)	2.1(3)	0.5(3)	0.4(3)
C(10)	8.7(5)	3.2(3)	4.0(3)	1.0(3)	3.1(3)	0.5(3)
C(12)	4.4(3)	4.4(3)	4.5(3)	-1.9(3)	1.5(3)	0.1(3)
C(13)	5.1(4)	5.4(4)	6.4(4)	-2.8(4)	3.0(4)	0.3(4)
C(14)	5.3(4)	7.8(5)	7.1(4)	-2.9(4)	3.3(3)	1.0(4)
C(15)	4.0(3)	5.3(4)	5.9(4)	-1.0(3)	2.7(3)	-0.4(3)
C(16)	4.3(3)	2.8(3)	4.3(3)	-0.4(2)	1.6(3)	0.9(2)
C(17)	5.1(4)	0.9(2)	6.5(4)	0.1(2)	2.8(3)	0.4(2)
C(18)	7.5(4)	3.2(3)	5.1(4)	2.2(3)	2.9(3)	3.1(3)
C(19)	4.2(3)	4.4(3)	4.8(3)	-0.2(3)	0.6(3)	1.7(3)
C(20)	4.2(3)	3.4(3)	5.0(3)	0.1(3)	2.1(3)	1.0(3)
C(21)	4.5(3)	3.6(3)	4.2(3)	-0.9(2)	2.6(3)	-0.5(2)
C(22)	4.6(3)	2.6(3)	3.9(3)	-0.7(2)	1.8(2)	0.4(2)
C(23)	4.8(3)	2.8(3)	4.7(3)	-1.1(2)	2.0(3)	-1.0(2)
C(24)	4.1(3)	4.3(3)	3.4(3)	-0.7(2)	0.7(2)	-0.1(3)
C(25)	5.3(3)	3.3(3)	3.4(3)	-0.2(2)	2.6(3)	0.1(3)
0(2) -	14.5(7)	6.3(5)	11.1(6)	0.0	9.1(6)	0.0
C(25)	8.7(5)	14.1(9)	7.6(6)	-2.7(6)	4.1(5)	-1.2(5)
C(27)	17.2(11)	9.8(8)	36(3)	-12.6(12)	17(2)	-5.2(9)

Table AIV.7 Distances to the weighted least-squares planes for 37

Least-squares planes (x,y,z in crystal coordinates) and deviations from them (* indicates atom used to define plane) 23.799 (0.050) x + 4.450 (0.016) y - 12.529 (0.036) z = 4.852 (0.018) -0.008 (0.003) C1 * 0.002 (0.003) C2 0.004 (0.003) C3 -0.009 (0.003) C4 0.011 (0.003) C5 Rms deviation of fitted atoms = 0.008 3.975 (0.084) x + 7.231 (0.010) y - 8.261 (0.046) z = 0.156 (0.020) Angle to previous plane (with approximate esd) = 42.68 (0.24) 0.004 (0.003) C6 -0.003 (0.003) C7 0.000 (0.003) C8 0.002 (0.003) C9 * -0.004 (0.003) C10 Rms deviation of fitted atoms = 0.003 -13.220 (0.067) x + 6.485 (0.013) y + 4.321 (0.050) z = 5.154 (0.015) Angle to previous plane (with approximate esd) = 47.29 (0.19) * 0.000 (0.003) C15 0.005 (0.003) C17 -0.009 (0.003) C18 × 0.009 (0.003) C19 * -0.005 (0.003) C20 Rms deviation of fitted atoms = 0.007 . -9.484 (0.077) x + 5.478 (0.015) y + 14.273 (0.034) z = 2.674 (0.011) Angle to previous plane (with approximate esd) = 45.49 (0.23) -0.002 (0.003) C21 -0.006 (0.003) C22 0.012 (0.003) C23 -0.014 (0.003) C24 * 0.010 (0.003) C25 Rms deviation of fitted atoms = 0.010

Appendix V

Molecular bond distances, bond angles, and related data for $(\eta^5-C_5H_5)_3(\mu-\eta^5-\eta^1-C_5H_4)Ti_2(C_4H_8O) \cdot C_4H_8O$ (2) from Ref. 6 (atom numbers see Fig. 5.1)

Til-Ti2	3.363(4)	Ti2-C5	2.19(2)
Til-Ol	2.26(1)	Ti2-C15	2.39(2)
Til-Cl	2.34(2)	Ti2-C16	2.40(2)
Til-C2	2.37(2)	Ti2-C17	2.41(2)
Til-C3	2.37(2)	Ti2-C18	2.39(2)
Til-C4	2.32(2)	Ti2-C19	2.38(2)
Til-C5	2.32(2)	Ti2-C20	2.37(2)
Til-C10	2.38(2)	Ti2-C21	2.39(2)
Til-Cl1	2.38(2)	Ti2-C22	2.42(2)
Til-Cl2	2.37(2)	Ti2-C23	2.40(2)
Til-C13	2.40(2)	Ti2-C24	2.39(2)
Til-Cl4	2.39(2)	C1-C2	1.41(2)
O1-C6	1.46(2)	C2-C3	1.39(3)
O1-C9	1.45(2)	C3-C4	1.41(2)
C6-C7	1.48(4)	C4-C5	1.44(2)
C7-C8	1.46(4)	C5-C1	1.43(2)
C8-C9	1.47(3)	C15-C16	1.39(3)
C10-C11	1.36(3)	C16-C17	1.41(3)
C11-C12	1.36(3)	C17-C18	1.39(3)
C12-C13	1.34(3)	C18-C19	1.40(3)
C13-C14	1.373)	C19-C15	1.37(3)
C14-C10	1.39(3)	O2-C25	1.35(3)
C20-C21	1.40(3)	C25-C26	1.39(5)
C21-C22	1.39(3)	C26-C26'	1.65(9)
C22-C23	1.39(3)		
C23-C24	1.40(3)		

Table AV.1. Table of bond distances (Å) for (2)

(Table AV.1 CC				
C24-C20	1.40(3)	C11-H11	0.79(18)	
CI-HI	1.10(19)	C12-H12	0.88(20)	
C2-H2	0.84(18)	C13-H13	0.81(19)	
C3-H3	0.92(17)	C14-H14	0.85(18)	
C4-H4	0.87(17)	C15-H15	0.75(17)	
C6-H6,1	0.96(19)	C16-H16	1.00(18)	
C6-H6,2	0.92(18)	C17-H17	0.91(18)	
C7-H7.1	1.36(21)	C18-H18	0.77(19)	
C7-H7,2	1.05(20)	C19-H19	0.84(17)	
H8-H8,1	1.03(19)	C20-H20	0.94(17)	
C8-H8,2	1.04(18)	C21-H21	1.05(18)	
C9-H9,1	0.77(18)	C22-H22	0.93(18)	
C9-h9,2	0.85(18)	C23-H23	0.94(18)	
C10-H10	0.83(18)	C24-H24	0.96(18)	

(Table AV.1 continue)

Til-Ti2-C5	43.8(4)	C14-C10-C11	106.7(20)
Ti2-Ti1-C5	40.9(4)	C10-C11-C12	109.0(21)
Ti2-Ti1-O1	96.1(30	C11-C12-C13	108.3(22)
Ti1-O1-C6	125.4(11)	C12-C13-C14	108.5(21)
Til-01-C9	124.5(11)	C13-C14-C10	107.4(21)
Til-C5-Ti2	95.3(6)	C19-C15-C16	108.5(17)
Ti2-C5-C1	125.6(12)	C15-C16-C17	107.8(18)
Ti2-C5-C4	124.2(13)	C16-C17-C18	107.5(18)
C6-01-C9	108.2(14)	C17-C18-C19	107.5(17)
O1-C6-C7	105.1(19)	C18-C19-C15	108.7(17)
C6-C7-C8	106.3(22)	C24-C20-C21	107.8(19)
C7-C8-C9	105.7(20)	C20-C21-C22	108.0(19)
C8-C9-O1	107.7(18)	C21-C22-C23	108.1(20)
C5-C1-C2	110.9(17)	C22-C23-C24	108.6(19)
C1-C2-C3	107.9(16)	C23-C24-C20	107.4(19)
C2-C3-C4	107.6(17)	C25-O2-C25'	114.4(41)
C3-C4-C5	110.7(16)	O2-C25-C26	109.7(34)
C4-C5-C1	102.9(14)	C25-C26-C26'	102.6(24)
C2-C1-H1	127(8)	C14-C10-H10	124(14)
C5-C1-H1	122(8)	C11-C10-H10	128(14)
C1-C2-H2	133(14)	C10-C11-H11	129(15)
C3-C2-H2	119(13)	C12-C11-H11	121(16)
С2-С3-Н3	124(12)	C11-C12-H12	128(12)
C4-C3-H3	128(12)	C13-C12-H12	124(12)
C3-C4-H4	127(12)	C12-C13-H13	124(15)
C5-C4-H4	122(12)	C14-C13-H13	127(15)
O1-C6-H6,1	112(11)	C13-C14-H14	125(14)
O1-C6-H6,2	108(13)	C10-C14-H14	127(14)
C7 - C6-H6,1	114(11)	C19-C15-H15	119(17)
С7-С6-Н6,2	106(13)	C16-C15-H15	132(17)
H6,1-C6-H6,2	111(17)	C15-C16-H16	130(10)
C6-C7-H7,1	68(28)	C17-C16-H16	122(10)
С6-С7-Н7,2	127(11)	C16-C17-H17	127(12)
<u>C8-C7-H7,1</u>	134(27)	C18-C17-H17	126(12)

 Table AV.2. Table of bond angles for 2 in degrees



(Table AV.2 continue) 111(9) C8-C7-H7,2 C17-C18-H18 122(15) H7,1-C7-H7,2 129(16) 106(28) C19-C18-H18 C7-C8-H8,1 127(11) C18-C19-H19 125(14) C7-C8-H8,2 104(10) C15-C19-H19 126(14) C9-C8-H8,1 106(11) C24-C20-H20 123(11)123(11) C9-C8-H8,2 C21-C20-H20 129(11) 122(10) H8,1-C8-H8,2 93(14) C20-C21-H21 C8-C9-H9,1 111(17) C22-C21-H21 130(10) C8-C9-H9,2 119(13) C21-C22-H22 122(11) O1-C9-H9,1 108(17) C23-C22-H22 130(11) O1-C9-H9,2 115(14) C22-C23-H23 121(11) 130(11) H9,1-C9-H9,2 C24-C23-H23 95(20) C23-C24-H24 129(11) C20-C24-H24 123(11)

Plane	Atoms in plane	Equation of plane				
I	01, C6, C7, C8, C9	$0.372\mathbf{x} + 0.724\mathbf{y} - 0.581\mathbf{z} = -2.125$				
П	C1, C2, C3, C4, C5	-0.388x + 0.563y - 0.730z = -2.181				
ш	C1, C2, C3, C4	-0.399x + 0.562y - 0.725z = -2.145				
IV	C10, C11, C12, C13, C14	0.145x + 0.911y - 0.385z = -2.510				
V	C15, C16, C17, C18, C19	0.166x - 0.687y - 0.707z = -3.721				
VI	C20, C21, C22, C23, C24	-0.497x - 0.804y - 0.327z = -8.169				

Table AV.3. Weighted least-squares planes for (2)

Distances of atoms from plane (Å)

Pl	ane I	Pla	ine II	Pla	ne III	Plar	ne IV	Pla	ne V	Plar	ne VI
01	0.04	C1	0.01	Cl	0.00	C10	0.00	C15	0.00	C20	0.00
C6	-0.14	C2	-0.01	C2	0.00	C1 1	-0.01	C16	-0.01	C21	0.00
C7	0.18	C3	0.00	C3	0.00	C12	0.01	C17	0.01	C22	0.00
C8	-0.11	C4	0.01	C 4	0.00	C13	-0.01	C18	0.00	C23	0.01
C9	0.01	C5	-0.01	C5	-0.03	C14	0.00	C19	0.00	C24	0.00
Til	-0.16	Ti2	-0.96	Ti2	-1.00	Ti1	2.08	Ti2	-2.08	Ti2	2.08