SILYLTITANOCENE AND SILYLZIRCONOCENE COMPLEXES. INTERMEDIATES IN CATALYTIC COUPLING OF ORGANOSILANES

by

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SILYL-TITANOCENE/ZIRCONOCENE COMPLEXES IN COUPLING OF ORGANOSILANES

ABSTRACT

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SILYLTITANOCENE AND SILYLZIRCONOCENE COMPLEXES. INTERMEDIATES IN CATALYTIC COUPLING OF ORGANOSILANES

Primary silanes of the type $RSiH_3$, where R = phenyl (Ph), benzyl (Bz) and n-hexyl, undergo catalytic dehydrogenative polymerisation in the presence of catalytic amounts of Cp_2TiMe_2 (Cp = η^5-C_5H_5) to give linear oligomers consisting of about 10 silicon atoms, regardless of the reaction conditions. When the amount of Cp_2TiMe_2 was increased, novel organometallic complexes of the type $\{(Cp_2Ti)_2(\mu\text{-}H)(\mu\text{-}HSiRH)\}$ and $\{Cp_2Ti(\mu\text{-}HSiRH)\}_2$ were isolated and characterised. X-ray crystal structural characterisation has confirmed the first Ti-H-Si-Ti bridged systems. Other titanocenes (Cp'_2TiMe_2(Cp' = η^5-C_5H_4Me), $[Cp_2TiH]_n$, $[Cp_2Ti]_2$ and $Cp_2Ti(CO)_2$) also polymerised $PhSiH_3$, and in addition gave analogous complexes under the appropriate conditions. Furthermore $PhSiH_3$ undergoes polymerisation in the presence of $CpCp^*TiMe_2$ (Cp^* = η^5-C_5Me_5), but not $Cp^*_2TiMe_2$. Polymerisation of $RSiH_3$ (R = phenyl and benzyl) also occurs in the presence of Cp_2ZrMe_2

and complexes of the type $\{Cp_2(SiHMeR)Zr(\mu-H)_2Zr(SiH_2R)Cp_2\}$ have been identified, and isolated (R = phenyl). $[Cp_2ZrH_2]_n$ also polymerises $PhSiH_3$, with the associated production of $\{Cp_2Zr(\mu-H)(SiH_2Ph)\}_2$. The analogous complex was also observed during the reaction of Cp_2ZrMe_2 with $BzSiH_3$. The reactions have been followed by ^1H and ^{29}Si NMR, and possible reaction paths are discussed.

RÉSUMÉ

Chimie Clare AITKEN PhD

LES COMPLEXES DU SILYLTITANOCÈNE ET DU SILYLZIRCONOCÈNE. INTERMEDIAIRES DANS LE COUPLAGE CATALYTIQUE DES ORGANOSILANES

Les silanes du type $RSiH_3$, (où R = phényl (Ph), benzyl (Bz) et n-hexyl), ont été polymérisés par déshydrogenation catalytique en présence du catalyseur Cp_2TiMe_2 (Cp = η^5-C_5H_5). Cette réaction donne des oligomères linéaires contenant environ dix atomes de silicium, quelles que soient les conditions de réactions. Lorsque le rapport Cp_2TiMe_2:Silane a été augmenté, de nouveaux composés du type $\{(Cp_2Ti)_2(\mu\text{-H})(\mu\text{-HSiRH})\}$ et $\{Cp_2Ti(\mu\text{-HSiRH})\}_2$ furent isolés et caractérisés. Les structures obtenues par diffractions de rayon-X prouvent l'existence des premiers systèmes contenant les ponts Ti-H-Si-Ti. D'autres titanocènes (Cp'_2TiMe_2(où Cp' = η^5-C_5H_4Me), $[Cp_2TiH]_n$, $[Cp_2Ti]_2$ and $Cp_2Ti(CO)_2$) ont donné des résultats similaires: polymérisation du $PhSiH_3$ et complexes pontés comme ci-haut. Par contre, $CpCp^*TiMe_2$ (Cp^* = η^5-C_5Me_5), mais non $Cp^*_2TiMe_2$ a polymérisé le $PhSiH_3$ sans donner de complexes pontés. La polymérisation a aussi lieu en présence du Cp_2ZrMe_2 et des composés du type $\{Cp_2(SiHMeR)Zr(\mu\text{-}H)_2Zr(SiH_2R)Cp_2\}$ ont été isolés et identifiés (lorsque R = Ph). De plus $[Cp_2ZrH_2]_n$ polymérise le phénylsilane avec production de $\{Cp_2Zr(\mu\text{-}H)(SiH_2Ph)\}_2$. Toutes ces réactions ont été suivies par RMN de ^{1}H et de ^{29}Si. Différents mécanismes de réaction sont examinés.

To Alan

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LIST OF ABBREVIATIONS

Å	angstrom (1 angstrom = 10^{-10} m)
i-Bu	*iso*-butyl
n-Bu	*normal*-butyl
t-Bu	*ter*-butyl
Bz	benzyl
Cp	η^5-cyclopentadienyl (η^5-C_5H_5)
Cp'	η^5-methylcyclopentadienyl (η^5-$C_5H_4CH_3$)
Cp*	η^5-pentamethylcyclopentadienyl (η^5-$C_5(CH_3)_5$)
D	Dalton (1 D = 1 atomic mass unit)
ESR	electron spin resonance
Et	ethyl
GPC	gel permeation chromatography
HOMO	Highest occupied molecular orbital
Hx	*normal*-hexyl
IR	infra-red
LUMO	lowest unoccupied molecular orbital
Me	methyl
Mes	mesityl
NMR	nuclear magnetic resonance
O.A.	oxidative addition
Ph	phenyl
ppm	parts per million
i-Pr	*iso*-propyl
n-Pr	*normal*-propyl

R.E.	reductive elimination
TCNE	tetracyanoethylene
THF	tetrahydrofuran
TMS	tetramethylsilane
$\nu_{\frac{1}{2}}$	linewidth at half-height

Abbreviations used to describe NMR peaks

ABq	AB quartet
bb	broad band
bm	broadened multiplet
d	doublet
dbm	doublet of broadened multiplets
ddd	doubled of doublets of doublets
m	multiplet
obb	overlapping broad band
q	quartet
s	singlet
t	triplet
td	triplet of doublets

CHAPTER I

INTRODUCTION

I.1 A BRIEF INTRODUCTION TO SOME ASPECTS OF ORGANOSILICON CHEMISTRY

Organosilicon compounds today form a large class of organometallic compounds. They are usually defined as those compounds containing at least one Si-C bond. Although the bond dissociation energies for Si-C bonds are less than those of comparable C-C bonds, they are still quite high, being of the order of 250 - 335 kJ mol^{-1} (1). The first organosilicon compound prepared was tetraethylsilane, obtained from silicon tetrachloride and diethylzinc in 1863 by Charles Friedel and James Crafts (2). Subsequent to this, the discovery of Grignard reagents and their application to organosilicon chemistry independantly by Kipping and Dilthey in 1904, led to the development of a facile, selective way to produce Si-C bonds (3,4). The general equation for the Grignard alkylation reaction is as follows:

$$RMgX + \equiv Si-X \longrightarrow \equiv Si-R + MgX_2 \qquad I.1$$

Although silicon lies in the same group of the periodic table as carbon, many differences are apparent in their chemistries. The presence of accessible 3d orbitals in the case of silicon can enable expansion of the coordination sphere to occur. In addition, electronegativities are quite different, being of the order of 1.8 for silicon and 2.5 for carbon (on the Pauling scale) (5). Thus a Si-C bond is quite polar and may react in one of two ways, either by nucleophilic attack at silicon or electrophilic attack at carbon, examples of which are given in equations I.2 and I.3 (6,7):

$$Me_3SiOSiMe_3 + H_2O \xrightarrow{OH^-} Me_3SiOSiMe_2(OH) + CH_4 \qquad I.2$$

$$Me_4Si + HCl \xrightarrow{AlCl_3} Me_3SiCl + CH_4 \qquad I.3$$

In the example given by equation I.2, nucleophilic substitution is facilitated by the presence of an electron-withdrawing group on each silicon. This results in the silicon atom being made more positive and thus more susceptible to nucleophilic attack. Equation I.3 is an example of the electrophilic substitution of tetramethylsilane, involving electrophilic attack at a negatively charged carbon atom.

Organosilicon hydrides are an important class of organosilicon compounds. A wide range of hydrido derivatives exists, including those of both mono and polysilanes. The usual way of obtaining monosilanes in the laboratory is via a reduction of the corresponding organohalogenosilane with a reagent such as lithium aluminium hydride, usually in an ethereal solvent. An average Si-H bond at 293 kJ/mol* is weaker than the analogous C-H bond at 410 kJ/mol* (8), and this is reflected in the increased reactivity of the Si-H bond. In addition to this, the bonds are generally polarised in opposite directions, ie: $Si^{\delta+}-H^{\delta-}$ and $C^{\delta-}-H^{\delta+}$, although an exception to this rule may occur if highly electronegative atoms are attached to silicon, in which case the polarity may be reversed. Reaction products from comparable silicon and carbon hydrides are frequently different however, and reflect the differences in electronegativities of silicon and carbon. Equations I.4 and I.5 give examples of reactions that show this trend (9):

$$\underline{n}\text{-BuLi} + Ph_3SiH \longrightarrow Ph_3Si\text{-}\underline{n}\text{-Bu} + LiH \qquad I.4$$

$$\underline{n}\text{-BuLi} + Ph_3CH \longrightarrow Ph_3CLi + \underline{n}\text{-BuH} \qquad I.5$$

As in the case of Si-C, the Si-H bond may undergo nucleophilic substitution at silicon, or electrophilic substitution at hydrogen. Homolytic fission of the Si-H bond may also occur, one example being the thermal decomposition of alkylsilanes.

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*Converted to SI units by the author.

Within the series $R_{4-n}SiH_n$ (R = alkyl/aryl, n = 0-4), oxidation of the silane becomes easier the more Si-H bonds there are. Hence SiH_4 tends to explode in air whilst $PhSiH_3$ is usually purified by distillation at 120°C in air. Secondary and tertiary silanes are even more stable.

Within the last few years, an important new area of organosilicon chemistry has emerged. This includes the isolation of stable compounds containing multiple bonds to silicon. The first synthesis of a silene (Si=C) was reported in 1981 by Brook et al. (10). The compound obtained was 2-adamantyl-2-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-silaethene, $\{(Me_3Si)_2Si=C(OSiMe_3)(C_{10}H_{15})\}$. The stability of the compound is high, and is attributed in part to steric effects of the bulky substituents. In addition to this, the nature of the substituents is thought to inhibit dimerisation ~~(11).~~ At about the same time, the synthesis of the first stable disilene (Si=Si) was reported by West et al. (12). The compound obtained was tetramesityldisilene, and was prepared by photolysis of 2,2-bis(mesityl)hexamethyltrisilane. The mechanism was found to involve formation of a divalent silylene species $Mes_2Si:$, and its subsequent dimerisation. The presence of this species was confirmed by trapping experiments with Et_3SiH, in which the formation of $Et_3Si-Si(Mes)_2H$ was observed. As in the case of the silaethene discussed earlier, the presence of bulky groups was again found to impart stability, and help prevent polymerisation.

A large number of silylenes have now been obtained by photolysis either as the divalent silicon species in hydrocarbon or argon matrices, or as the dimerisation product, the disilene (13). In the case where non-bulky groups such as methyl are attached to silicon, although the silylene is stable in a hydrocarbon matrix at 77°K, it converts to the polysilane polymer $(RR'Si)_n$ upon warming in the absence of a suitable trapping agent (14). Insertion of silylenes into Si-H or Si-Si bonds provides a route for progressive catenation, and it seems likely that they may well be involved in silane polymerisation reactions.

I.2 INTRODUCTION TO ORGANOSILICON POLYMERS

To date, virtually all polymer chemistry has revolved around one element in the periodic table, carbon. There are, however, a number of other elements that can undergo catenation. The most significant obstacle to a rapid expansion of this field seems to be a lack of good preparative methods. Most inorganic oligomers or polymers contain phosphorus, sulphur or silicon as at least one of the backbone components. Some examples of these include polymeric sulphur, poly(sulphur nitride), polysilazanes and polyphosphazanes (15). Polysilanes and polysiloxanes, two of the most important inorganic polymers will be discussed in more detail later.

Research on inorganic macromolecules seems to have begun with the preparation of potassium fluorosilicate by Berzelius in 1824 (16). The silicates are ionic salts consisting of alternating sequences of silicon and oxygen, and are components of glass and ceramics. Their organic analogues, polysiloxanes, consist of long chains or rings containing the $(RR'Si{-}O{-})_n$ unit. Occasionally some of the silicon atoms in the siloxane chain may be replaced by other atoms. In this case they are known as heterosiloxanes. One example of this is a boron-silicon polymer known as "bouncing putty" (17). A number of heteroatoms may be incorporated into the siloxane backbone. These include B, Al, Ga, Ti, Ge, Sn, Pb, P, As, Sb, V, Nb, Ta, Cr and W (18).

I.2.1 - Organopolysiloxanes (Silicones)

Polysiloxanes are inorganic based polymers containing as a backbone the Si-O-Si link. The name silicone was introduced by Wöhler in 1857 and was subsequently used to describe compounds thought to be analogous to ketones i.e.: R_2SiO. These were later formulated as siloxanes although the name silicone remained. The name silicone is now more of an industrial term for organopolysiloxanes, usually those of higher molecular weight (19).

Preparation of silicones usually involves the hydrolysis of organochlorosilanes. Thus it was not until the development of a good, relatively cheap method of synthesizing the latter that silicones could grow in industrial importance. A commercially viable route to organochlorosilanes was developed by E.G. Rochow at General Electric and was published in 1945. This process, known as the "Direct Process", involves the passage of an organic halide over heated silicon metal in the presence of a catalyst - usually copper although other metals may also be used (20). In the case of methyl chloride, the process is usually run in the temperature range 250-350°C and at a pressure of from 1 to 5 atmos. The major equation for this reaction is as follows (21):

$$2MeCl + Si \xrightarrow{M} Me_2SiCl_2 + heat \qquad I.6$$

M = metal catalyst

The reaction is exothermic and gives rise to a number of additional products. In order of abundance, Me_2SiCl_2, $MeSiCl_3$ and Me_3SiCl are all produced. Small quantities of other compounds are also obtained including Me_4Si, disilanes, alkanes and alkenes. Thus conditions such as temperature, pressure and catalyst are optimised to maximise the yield of Me_2SiCl_2 which may be subsequently hydrolysed to give polydimethylsiloxane.

I.2.2 Organopolysilanes

Organopolysilanes are defined as those organosilicon compounds which possess linear chains or rings of silicon atoms with at least one Si-C bond, and structures analogous to those of saturated alkanes. The first compound obtained containing a Si-Si bond was hexaethyldisilane in 1869 (22). It was however nearly a century before detailed investigation was undertaken into the properties and chemistry of oligo- or polysilanes (23). The ability of carbon atoms to form chains of C-C bonds of various types has been known for a long time. Chains thousands of atoms long are known, together with crosslinking, branching and cyclisation. This ability of carbon is arguably its most important feature and gives rise to the immense field of organic chemistry.

On descending group 14 of the periodic table, silicon is found directly beneath carbon. Hence some similar chemistry between the two is to be expected. Although compounds containing the Si-Si link have been known for a long time, study on molecules of this type has been limited by the lower stability of the Si-Si bond (222 kJ/mol*) relative to that of the C-C bond (347 kJ/mol*) (24). This is probably due in part to to the larger size of the silicon atom, resulting in poorer orbital overlap. An additional problem is the high stability of the Si-O bond (452 kJ/mol*) compared to that of the C-O bond (360 kJ/mol*) (25). Thus there is a constant drive towards the thermodynamically stable siloxane link.

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*Converted to SI units by the author.

The last ten years have seen a tremendous growth in the area of polysilane chemistry. This has stemmed in part from the discovery in 1975 by Yajima et al., that silicon carbide fibres possessing high tensile strength and good oxidation resistance could be obtained from polydimethylsilane (26). Although permethylpolysilane had been obtained by Burkhard as early as 1949 (27), Yajima et al. found that upon heating it to 400 or 500°C, the silicon atom backbone could be converted to one containing alternating Si and C atoms ie: polycarbosilane or $(-HSiCH_3-CH_2-)_n$ (n = 1500). Subsequent melt spinning was found to produce polycarbosilane fibres which could then be cured in air and crosslinked. Finally, upon heating the cured fibres to 1250°C slowly in the absence of oxygen, hydrogen and some carbon was removed as CH_4. Eventually fibres consisting of a skeletal backbone of alternating Si and C atoms were obtained, ranging in diameter from 10 to 15 μm (28). The discovery of ceramic fibres such as these has led to the growing interest in the development of polysilanes as a whole.

The most common method employed today for the synthesis of both linear and cyclic organopolysilanes is the condensation of halosilanes, usually chlorosilanes, by active metals such as sodium. Methylchlorosilanes are commonly used because of their ready availability in large quantities from ~~the~~ silicone industry. Consequently, methylpolysilanes are the most widely studied polysilanes, particularly in view of their role as precursors to silicon carbide fibres. In addition, considering the low stability of the Si-H bond compared to the C-H bond, and its susceptibility to attack by bases, acids and even oxygen, most workers in the field have focused on the peralkyl and peraryl derivatives.

In a typical condensation reaction, a mixture of products, both linear and cyclic is usually obtained. Different conditions and chlorosilanes may be employed to optimise the yield of the desired product. Conditions have been optimised in the cocondensation reaction of Me_2SiCl_2 and $MePhSiCl_2$, with Na, to obtain high molecular weight linear polysilanes (29):

$$Me_2SiCl_2 + MePhSiCl_2 \xrightarrow[90\text{-}100^\circ C]{Na/Tol} -\left[(Me_2Si)_x\ (MePhSi)_y\right]- + NaCl \qquad I.7$$

In this case the product obtained was found to consist of 30% soluble low molecular weight oligomers including cyclics, together with approximately 5% insoluble material. After these were removed, Gel Permeation Chromatography indicated that chain lengths of greater than 3000 silicon atoms were present. In addition, it was shown that the phenylmethylsilane copolymer could undergo conversion to the silicon carbide at high temperatures without initial conversion to a carbosilane polymer.

The first cyclosilanes were made by F.S. Kipping et al. in the early 1920's (30,31). They were a number of perphenylcyclosilanes and were obtained from the condensation of diphenyldichlorosilane with alkali metals, although the structures were not elucidated. It was not until the 1960's that Gilman et al. were able to show that Kipping had in fact obtained $(Ph_2Si)_n$ where n = 4, 5 and 6 (32,33). It is now known that reaction conditions may be varied to control the relative amounts of each ring formed. For example, if Ph_2SiCl_2 is reacted with two equivalents of Li in THF, the cyclotetrasilane $(Ph_2Si)_4$ is produced in up to 75% yield. Excess Li and longer reaction times lead to the formation of the thermodynamically stable cyclopentasilane $(Ph_2Si)_5$. In both these cases, and many other syntheses of diphenylcyclosilanes, the six-membered ring is usually obtained as a by-product (23).

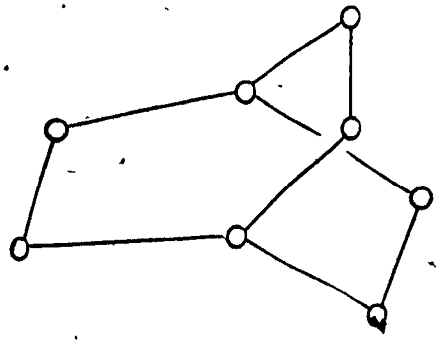
The most widely studied alkylcyclopolysilanes have been the small ring permethylcyclopolysilanes containing 4,5,6 and 7 Si atoms (34). For these permethylcyclosilanes, unlike the perphenyl ones mentioned above, the hexamer has been found to be the thermodynamically most stable product. It was first obtained by Burkhard in 1949 in small yield along with the permethylsilane linear polymer $(Me_2Si)_n$ (27). Although he reacted neat dimethyldichlorosilane with metallic sodium in a steel autoclave, the most standard synthesis today utilises Na/K alloy in refluxing THF for a much higher yield of 85%

(35). Equilibration of $(Me_2Si)_6$ at 46°C in the presence of Na/K alloy has been shown to yield 90% $(Me_2Si)_6$ together with 9% $(Me_2Si)_5$ and 1% $(Me_2Si)_7$ (36). The latter two compounds are preferentially made using a non-equilibrium process. For example, slow addition of Me_2SiCl_2 to Na/K alloy in refluxing THF, gives rise to a partially kinetic controlled reaction in which greater amounts of the pentamer and heptamer are produced (23). Photolysis of permethylcyclohexasilane in cyclohexane for 20 hours has been shown to give predominantly the pentamer in 70% yield along with the tetramer in 17% yield (37). Crystal structures for a number of these cyclosilanes have now been determined, the first of which was the molecular structure of dodecamethylcyclohexasilane in 1972 (38). The structure of $(Me_2Si)_6$ showed it to have a strain free chair conformation exactly like cyclohexane. A conformational equilibrium of the type observed for cyclohexane must therefore exist to account for only 1 NMR signal observed down to -90°C (39). Subsequently, octamethylcyclotetrasilane, $(Me_2Si)_4$, has had an X-ray crystal structure determined, showing it to possess a planar Si_4 ring (40). Most recently, the structure of tetradecamethylcycloheptasilane, $(Me_2Si)_7$, has been determined to consist of a twist chair conformation similar to cycloheptane (41).

Much larger permethylcyclosilanes have now been made, and rings containing up to 35 Si atoms now exist (42,43). The methylcyclopolysilanes are usually obtained from the condensation of Me_2SiCl_2 with Na/K in THF as mentioned earlier. Although this procedure tends to yield mainly $(Me_2Si)_6$ under standard reaction conditions, medium and large rings may be obtained by slow addition of the chlorosilane to the metal alloy in refluxing THF.

Within the last few years, a number of cyclic polysilanes containing groups other than methyl have been obtained. These include Et, n-Pr, n-Bu, i-Pr and i-Bu (44-46). In addition, a series of polyspirocyclopolysilanes $[(CH_2)_4Si]_n$ where n = 5-12, and $[(CH_2)_5Si]_n$ where n = 4-6 have been prepared and characterised (47,48). In the case of $[(CH_2)_4Si]_5$ and $[(CH_2)_5Si]_5$, X-ray crystal structures were obtained. The cyclotetramethylene rotane that was found to be the thermodynamically stable one, was the six-membered ring whilst the greater steric bulk of the cyclopentamethylene group gave the cyclopentasilane as the thermodynamically favoured ring.

A third type of organopolysilane is a type of cyclosilane possessing a three dimensional and polycyclic structure. These are known as cage polysilanes and although little work has been done to date, it seems likely that condensation of halosilanes will once again be the major preparative route employed. In fact Indriksons and West obtained the first cage polysilane from the cocondensation of $MeSiCl_3$ and Me_2SiCl_2 (molar ratio 1:1) with Na/K alloy in the presence of naphthalene (49). After a work-up involving preparative gas chromatography, tetradecamethylbicyclo [2.2.2] octasilane, $Me_{14}Si_8$ was obtained in 0.5% yield, together with a residue which consisted primarily of siloxanes resulting from reaction of $MeSiCl_3$ with THF. The molecular formula of $Me_{14}Si_8$ was established by mass spectroscopy and the structure postulated was deduced largely from its simple ^1H NMR spectrum which gave two peaks in an intensity ratio of 6:1. In addition, ^{13}C data was also obtained and the following bicyclo structure proposed:

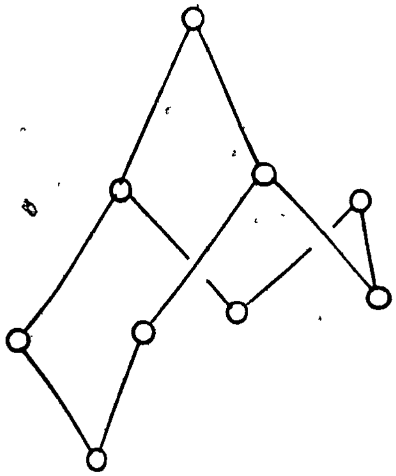


O = Si atom

I

Subsequent improvement to the synthetic procedure outlined above, led to the isolation of five more cage polysilanes (50). The use of naphthalene and Na/K alloy was found to be essential in preventing the formation of high polymers. In addition, it was shown that THF was the most suitable solvent, but that the yield of $Me_{14}Si_8$ could be increased tenfold to 5% by changing the ratio of chlorosilanes

$MeSiCl_3$:Me_2SiCl_2 to 1:3. The other cage compounds which were eventually obtained after a long and difficult purification process had their molecular formulae established by high resolution mass spectroscopy as $Me_{16}Si_9$, $Me_{16}Si_{10}$, $Me_{18}Si_{10}$, $Me_{18}Si_{11}$ and $Me_{22}Si_{13}$. All were obtained in yields of less than 5% with the bulk of the residue said to be "polymer". Various speculations were offered as to the actual structures, once more primarily based on their NMR spectra, but it was not until 1975 that a crystal structure was determined by Stallings and Donohue (51). Single crystals of hexadecamethylbicyclo [3.3.1] nonasilane, $Me_{16}Si_9$ were obtained and the definitive structure shown to be:



II

In considering all polysilanes, both linear and cyclic, there has been no progress made in their preparation using catalytic methods. In fact, prior to the work presented in this thesis, the only example known is of the use of Wilkinson's catalyst, $(Ph_3P)_3RhCl$. This was reacted with a number of silanes to give a variety of simple di- and trisilanes together with some "higher polysilanes" (52). Phenylsilane, $PhSiH_3$, was reported to yield 1,2-diphenyldisilane, 1,1,2-triphenyldisilane and 1,2,3-triphenyltrisilane as well as some disproportionation products and some higher polymers. Although the latter were not identified, the authors were able to trap the silylene, $Ph_2Si:$, by using Et_3SiH, and obtain $Et_3SiSiPh_2H$.

There are a number of interesting properties associated with polysilanes. Although they are structurally analogous to alkanes, many of their physical and chemical properties are similar to those of unsaturated hydrocarbons. For example, it has been known for a long time that the Si-Si bond in linear polysilanes acts as a chromophore in much the same way as a conjugated polyene, with the UV absorption bands shifting to longer wavelengths as the polysilane chain length increases. This property seems to have first been noticed for those polysilanes possessing attached phenyl groups. It was initially suggested that the absorption band observed for Ph_6Si_2 was due to an interaction between the phenyl groups through a type of conjugation involving the vacant Si 3d orbitals (53). Eventually, however, it was shown that the polysilane chain itself was absorbing radiation, and a series of linear permethylpolysilane derivatives $Me(Me_2Si)_nMe$ where

n_c = 2 to 8, had their UV spectra measured (54). In fact the peralkylpolysilanes were the first compounds with no π, d or lone-pair electrons to show long wavelength absorptions (23). The value for λ_{max} in these compounds was found to increase as the chain lengthened, with a value of approximately 300 nm for an infinite chain length (55). It has been suggested that polysilane transitions involve either electron promotion from a σ_{Si-Si} HOMO, delocalised over the silicon backbone, to a delocalised orbital which could be either σ^* or 3d (56,57). In addition to establishing that the intense UV absorptions observed for polysilanes were due to the chromophoric nature of the Si-Si bond, Gilman et al. also showed that phenyl substitution further increased the value for λ_{max} (54). This was thought to be a result of lengthening the conjugated system.

The cyclic polysilanes are similar to the linear polysilanes in that they also show electronic absorptions at relatively long wavelengths. However, the bands of the small ring cyclosilanes ($n \geqq 5$) undergo a hypsochromic shift (change to shorter wavelength) with increasing catenation. It has been suggested that this hypsochromic shift is dependant on a deviation from planarity as the ring gets larger, perhaps leading to less overlap between adjacent Si 3d orbitals, giving rise to wider spaced molecular energy levels (39). Such an argument is plausible only if the transitions are of the type $\sigma \rightarrow \pi$, with actual involvement of the d orbitals.

As the number of silicon atoms in the ring becomes large, the trend reverses and bathochromic shifts (to longer wavelength) analogous to those of linear polysilanes, are seen. This trend reversal occurs at $n = 7$ for the permethylcyclosilanes (43).

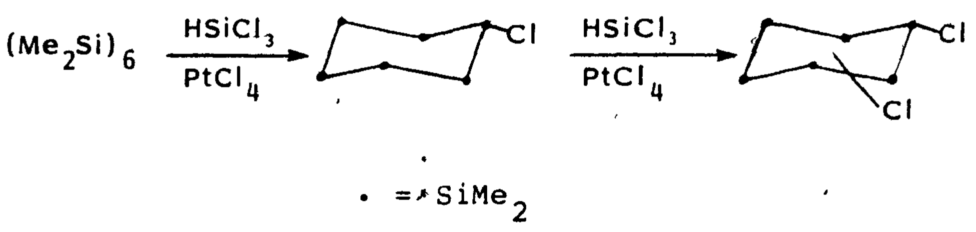
A number of potential applications of polysilanes utilises their photoactivity under UV radiation. Alkylpolysilanes undergo photoscission processes to give both silyl and silylene derived products whilst arylpolysilanes undergo both photoscission and photo-cross-linking upon irradiation with UV light (58). Furthermore Trefonas et al. have suggested that the reported action of polysilanes as photoinitiators for alkene polymerisation, is likely a result of the production of silyl radicals, produced photolytically. In addition there is much current interest in the role of polysilanes as self-developing photoresists in the manufacture of silicon chips (59).

A number of comparisons have been made between aromatic compounds and cyclosilanes. One example of this is the apparent ease with which the latter may be reduced, either chemically or electrochemically, to produce anion radicals (34,60). Usually anion radicals contain unpaired electrons in low lying π^* molecular orbitals. ESR spectroscopy has shown that in cyclopolysilane anion radicals, the unpaired electron is completely delocalised over the ring (60). In addition, it is thought that it exists in an orbital of essentially π

character, presumably made up of 3d or 4p combinations from the silicon atoms (39,60). It seems likely then that the cyclopolysilanes possess delocalised Si-Si σ-bonding orbitals analogous to the filled π orbitals of benzene. Likewise it has been suggested that the delocalised π-orbital (from 3d + 4p atomic orbitals on silicon) in polysilanes is analogous to the unfilled π* LUMO of benzene (34).

Both linear and cyclic polysilanes have been found to form charge transfer complexes with a number of acceptors, an example of the latter being tetracyanoethylene, TCNE, in much the same way as aromatic hydrocarbons or lone pair donors (61). The low ionisation potentials observed for polysilanes enables charge to be donated from the delocalised sigma electrons of the Si-Si bonds.

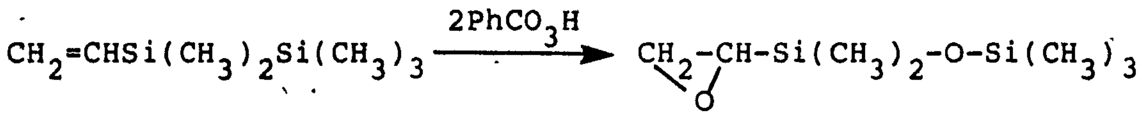
Finally, cyclosilanes resemble aromatic compounds in some of their substitution reactions. An example of this involves chlorodemethylation of $(Me_2Si)_6$, followed by the introduction of a second chlorine as shown in equation I.8 (60):



I.8

Only four of the seven possible isomers for the dichloro species were observed by NMR, in a ratio of 4:2:2:1. It has been suggested that the 1,4-trans compound is probably the most abundant product. The reaction suggests that the first chlorine atom is able to effect the position of subsequent substituents in much the same way as occurs in the electrophilic substitution of benzene.

In a similar way, linear silanes may be thought analogous to alkenes. Sakurai et al. have shown that peroxybenzoic acid reacts with organodisilanes to insert an oxygen atom into the Si-Si bond in much the same way as epoxidation of alkenes occurs (62). In fact, in the case of vinyldisilane, both the vinyl group and the Si-Si link were oxidised as shown in equation I.9:



$$CH_2{=}CHSi(CH_3)_2Si(CH_3)_3 \xrightarrow{2PhCO_3H} \underset{O}{CH_2-CH}-Si(CH_3)_2-O-Si(CH_3)_3$$

I.9

In conclusion, it seems likely that organopolysilanes will form an important class of macromolecules, possessing properties pertinent to inorganic chemistry, polymer chemistry and ceramics. Their applicability to the ceramics industry is causing an increasing amount of interest from both academic and industrial institutions.

1.3 A BRIEF INTRODUCTION TO THE ORGANOMETALLIC CHEMISTRY OF TITANIUM AND ZIRCONIUM

The existence of organometallic compounds of the group 4 metals was suspected as early as the middle of the last century (63). In the early 1860's, reaction was reported between $TiCl_4$ and a number of alkylating agents such as Et_2Zn (64,65), Et_4Sn (66) and Et_2Hg (67). Subsequently, the discovery of Grignard reagants, as in the case of organosilicon chemistry, led to a resurgence of interest in organometallic compounds of many kinds. Due to the high oxophilic nature of the group 4 metals, it was not until good inert atmosphere techniques were developed that the first organotitanium compound, $TiPh(O\text{-}\underline{i}\text{-}Pr)_3$, could be isolated. This occurred in 1952 (68). One of the first organozirconium compounds, Cp_2ZrBr_2, was also isolated in the early 1950's by Wilkinson *et al.* (69). The discovery of the catalytic role played by titanium halides with aluminium alkyls in the polymerisation of ethene (70), together with the discovery of ferrocene (71), provided a strong impetus for the development of organotitanium chemistry as a whole. The organometallic chemistry of zirconium and hafnium has not developed as fast, perhaps due to their greater sensitivity to moisture and other hydroxylic species, rendering their preparation and isolation more difficult.

Organometallic compounds of the group 4 metals may contain organic groups bonded in a σ- and/or π-fashion. An example of a σ-bonded ligand is an alkyl group, whilst the cyclopentadienyl anion, (Cp^-), provides an example of a ligand bound to the metal through a π-type bond. In fact, cyclopentadienyl compounds formed some of the earliest group 4 compounds, with the first being made shortly after the discovery of ferrocene (69). It was subsequently found that the presence of cyclopentadienyl groups on the metal imparted stability, probably by blocking coordination sites that might otherwise be available for use in a number of decomposition pathways (63).

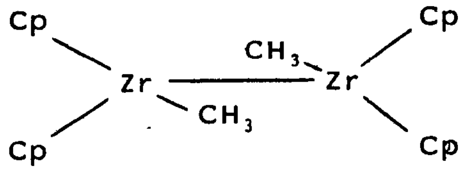
The most common oxidation state for group 4 organometallic compounds is +4. This is the maximum that may be observed for the group, giving a $3d^0$ configuration. A major difference between the first member of the group, Ti, and subsequent members Zr and Hf, is the relative accessibility of lower oxidation states (72). Thus Ti(IV) reduces much more easily than Zr(IV) or Hf(IV). In addition, Zr(III) complexes tend to be more kinetically labile than their Ti(III) analogues. As a consequence, Zr(III) organometallics are not common, and Hf(III) organometallics even less so. As the oxidation state becomes lower, it is increasingly important to have π-acceptor ligands present in the coordination sphere, and virtually all low valent complexes of the group 4 metals contain at least one cyclopentadienyl ligand.

1.3.1 Introduction to bis(cyclopentadienyl)titanium(IV) and zirconium(IV) alkyl complexes

Bis(cyclopentadienyl)titanium and -zirconium alkyl complexes contain both the π-bonding cyclopentadienyl ligand and the σ-bonding alkyl group. They usually possess the general formula Cp_2MR_2 where M = Ti/Zr and R = alkyl, with the metal being in the +4 oxidation state. However, lower oxidation state Cp_2TiR derivatives are known although they have only been isolated with large sterically hindered alkyl groups. Examples of complexes isolated include Cp_2TiBz (Bz = benzyl) (73), and $Cp_2TiCH_2C(CH_3)_3$ (74). The large size of the alkyl groups was found to preclude dimerisation. To date, it seems that there are no neutral complexes of the type Cp_2ZrR free from a supporting N_2 ligand. Thus Na amalgam reduction of Cp_2ZrClR (R = $CH(SiMe_3)_2$) was found to yield a Zr(III) dinitrogen complex according to the following equation (75):

$$Cp_2ZrClR + Na + N_2 \longrightarrow Cp_2Zr(\eta^2\text{-}N_2)R + NaCl \qquad I.10$$

It has recently been reported that the complex $\{Cp_2ZrCl\}_2$ reacts with MeLi to yield a diamagnetic solid which was characterised as $\{Cp_2ZrMe\}_2$ (76). The only evidence in support of the postulated structure was a ^1H NMR spectrum together with some chemical tests. The dimer suggested is necessary to account for the diamagnetic nature of the species observed. The complex was not isolated as such, but only obtained as a red oil on which the NMR and reactions were performed. The structure postulated by Cuenca and Royo is as follows:



III

The first complex of the type Cp_2MR_2 (M=Ti, Zr or Hf) to be prepared appears to have been Cp_2TiMe_2 in 1956 (77). Initially it was obtained in low yield from the reaction of MeMgI with Cp_2TiCl_2 in THF. Subsequent workers obtained higher yields using MeLi as the alkylating agent and this method is now preferred (78). It was however 15 years or so before the analogous complex Cp_2ZrMe_2 was first isolated, from the reaction of MeLi with Cp_2ZrCl_2 (79,80). This is likely to be a result of the the extreme sensitivity of dimethylzirconocene toward moisture and other hydroxylic compounds, although its thermal stability was reported higher than that of Cp_2TiMe_2.

A number of other complexes of the type Cp_2MR_2 have been isolated for both titanium and zirconium. The general preparative routes are as outlined above for the dimethyl complexes; they are obtained from the action of either a Grignard or an alkyl lithium reagent on the appropriate dichlorometallocene. Bulky alkyl groups with no β-hydrogen atoms were found to impart the highest degree of thermal stability. Examples of some preparative reactions are given in equations I.11 and I.12 (81,82):

$$Cp_2TiCl_2 + 2Li(CH_2SiMe_3) \xrightarrow{Et_2O} Cp_2Ti(CH_2SiMe_3)_2 \qquad I.11$$

$$Cp_2ZrCl_2 + 2BzMgX \xrightarrow{Et_2O} Cp_2ZrBz_2 + MgX_2 + MgCl_2 \qquad I.12$$

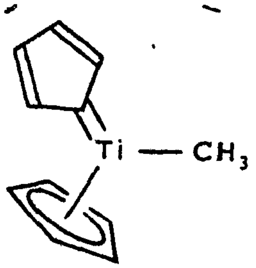
The most widely studied compounds to date however, remain dimethyltitanocene and -zirconocene. A number of thermolysis and photolysis studies have been undertaken, primarily to determine the decomposition pathways of these two complexes. In particular, Cp_2TiMe_2 is very heat and light sensitive, decomposing in a spectacular autocatalytic manner, unless stored at low temperature, under air and in the dark. The thermal decomposition of Cp_2TiMe_2 has been studied in both the solid state and in a number of solvents (83,84). In all cases methane was the predominant product, together with only trace amounts of ethane. Deuterium labelling studies have shown that the methane produced resulted from hydrogen abstraction from either the cyclopentadienyl rings or from the methyl groups themselves, and from the solvent only in the case of diethyl ether. At temperatures greater than 100°C solid state decomposition was found to give rise to ethene, cyclopentadiene and methylcyclopentadiene, in addition to methane and ethane (83). Labelling studies showed that the ethene arose exclusively from decomposition of the cyclopentadienyl ligands and formed approximately 10% of the volatiles. Thermolysis of Cp_2TiMe_2-d_6 showed that the methylcyclopentadiene formed (3%) was produced by a simple combination of methyl and cyclopentadienyl substituents. Precisely where the ethane came from is not clear. Thermolysis of Cp_2TiMe_2-d_6 produced no C_2D_6, and so it was thought unlikely that coupling of methyl radicals from homolytic Ti-C bond cleavage was occurring in a straightforward manner.

As already mentioned, Cp_2ZrMe_2 is more thermally stable than Cp_2TiMe_2 and does not decompose in an autocatalytic manner. In the solid state, thermal decomposition of dimethylzirconocene has been shown to produce methane and cyclopentadiene together with very small amounts of methylcyclopentadiene, all explicable by direct fragmentation of Cp_2ZrMe_2 (83). Razuvaev _et al_. have shown that the thermolysis of Cp_2ZrMe_2-d_{10} at 230°C gives rise to a major decomposition product, methane, which consists of predominantly CH_3D (56%), together with CH_4 (17%) and CH_2D_2 (16%) (85). CD_4 comprised only 3% of the decomposition products. The formation of such an isotopic distribution was thought to be due to D/H exchange reactions between the cyclopentadienyl rings and the methyl groups, after initial transfer of D/H to the metal from both ligands. Such exchange reactions seemed to be less important for the analogous titanium compound Cp_2TiMe_2-d_{10}. Upon thermolysis at 90°C for 30 minutes, the latter was found to produce CH_4(54%), CH_3D (41%) and only small amounts of CH_2D_2 and CHD_3. No CD_4 was observed. At about the same time, Erskine _et_ _al_. reported the observation of hydrogen exchange between cyclopentadienyl rings and methyl groups during the thermolysis of dimethyltitanocene, and various deuterated analogues (86). At 310°K Cp_2TiMe_2-d_{10} was found to produce CH_4 predominantly for the first 100 hours, with a gradually increasing proportion of the various deuterated methanes observed as a function of time.

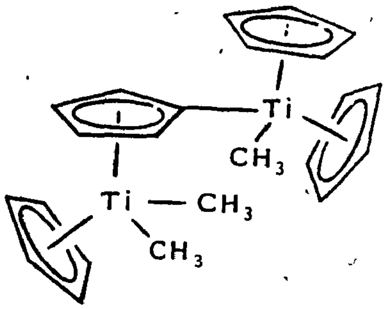
The reported light sensitivity of Cp_2TiMe_2 has resulted in a number of photolysis studies of both dimethyltitanocene and -zirconocene. Alt and Rausch studied the photolysis of Cp_2MMe_2 (M = Ti, Zr and Hf), and postulated that initially a facile homolytic cleavage of the methyl-metal bond occurred, according to the following equation (87):

$$Cp_2MMe_2 \xrightarrow[\text{solvent}]{h\nu} Cp_2M + 2\cdot Me \qquad \text{I.13}$$

In pentane solution, the final products obtained were methane and the appropriate metallocene. The organometallic residue was said to possess only π-cyclopentadienyl groups with no evidence of metal hydrides. Subsequent studies involving selective deuterium labelling on the cyclopentadienyl groups and the methyl groups of Cp_2TiMe_2, showed that the methane obtained (99% of the volatiles), never derived its hydrogen atoms from the solvent (88). These results are the same as those obtained in the thermolysis studies discussed earlier. Rausch *et al*. postulated that photolysis could give rise to a carbene complex of the type $Cp_2Ti{=}CH_2$, produced after intramolecular abstraction of a hydrogen atom from one methyl group by the other (88). When the cyclopentadienyl ring is the source of hydrogen for methane formation, they suggested two possible intermediates depending on whether hydrogen abstraction took place in an intramolecular or intermolecular manner:



Intramolecular
Intermediate



Intermolecular
Intermediate

Bamford et al. have also studied the photolysis of Cp_2TiMe_2 and reported that Cp_2TiMe_2-d_6 in toluene-d_8 gave only CD_3H with no CD_4 (89). This suggests that hydrogen abstraction occurs exclusively from the cyclopentadienyl rings, contrary to what was observed by Rausch et al. (88). The fact that no CD_4 was observed precludes involvement by both the solvent and the other methyl group. Free methyl radicals were not thought to exist.

Photodecomposition studies on Cp_2ZrMe_2, including labelled analogues, have shown the products to be methane and zirconocene, the former being produced from the abstraction of H atoms from the cyclopentadienyl rings (90). An ESR study undertaken by Atkinson et al. detected the presence of an unidentified zirconium(III) hydride during the photolysis of Cp_2ZrMe_2 in toluene solution (91). The only organic fragment detected by them was the methyl radical.

It has recently been reported that dialkyltitanocene compounds including Cp_2TiMe_2 may be photolysed under hydrogen to give efficient catalysts for the hydrogenation of linear and cyclic alkenes (92). It was thought likely that homolytic cleavage of Ti-C bonds was induced by the action of light, leading to the formation of Ti^{3+} species, detected by ESR.

The extreme reactivity of dimethyltitanocene under certain circumstances, leading to its ready loss of methyl ligands as methane, coupled with its ease of preparation, give it potential as an in situ source of titanocene. Examples of photochemically induced reactions of Cp_2TiMe_2 are given in equations I.14 and I.15 (93,94):

$$Cp_2TiMe_2 \xrightarrow[\text{pentane}]{h\nu/CO} Cp_2Ti(CO)_2 \qquad \text{I.14}$$

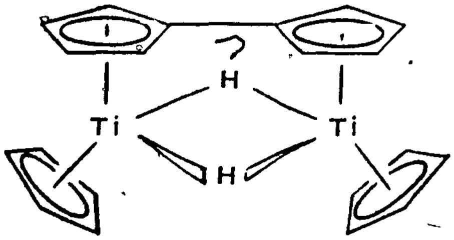
$$Cp_2TiMe_2 \xrightarrow[\text{benzene}]{h\nu/\text{sulphur}} Cp_2TiS_5 + MeS_nMe \qquad \text{I.15}$$

It seems likely that the analogous compound Cp_2ZrMe_2 is capable of acting in a similar manner, and photolysis experiments have already shown methane is lost to produce in situ "zirconocene". No true species Cp_2Zr has been isolated although it is possible, as in the case of titanium, that such a species plays a role in the chemical reactivity of Cp_2ZrMe_2.

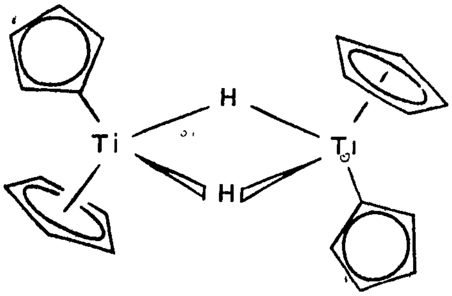
I.3.2 Introduction to some aspects of the chemistry of bis(cyclopentadienyl)titanium/zirconium and their hydride derivatives

Within the last few years, two important reviews have appeared, one focussing on the chemistry of titanocene and zirconocene, and the other on the hydrides of the titanium and vanadium group elements (95,96). It is readily apparent from these articles that the topics of early transition metallocenes and their hydrides are closely tied. Historically, more work has been done on the titanium derivatives and these have been given prominence in the literature.

The earliest report of a species formulated as titanocene was in 1956, soon after the isolation of ferrocene (97). Subsequent to this, Watt and Baye could not duplicate the synthesis and despite trying other ways, were unable to obtain titanocene (98). It eventually became evident after numerous attempts to isolate the species Cp_2Ti by many workers, that in situ titanocene could readily abstract hydrogens from the coordinated cyclopentadienyl ligands (99). In fact Brintzinger and Bercaw eventually proposed that a bridging hydride must be present in the structure of the green dimer which was obtained from a number of reactions including the reduction of dichlorotitanocene with either sodium naphthalenide or sodium sand, and reaction of dimethyltitanocene solutions with hydrogen at 20°C (100). The evidence for the structure of this dimer came predominantly from IR spectroscopy, the strong band at 1230 cm^{-1} being assigned to a bridging hydride. In fact two possible structures were postulated, dependant on the mode of bonding of the C_5H_4 units. The structures proposed for this titanocene were as follows:

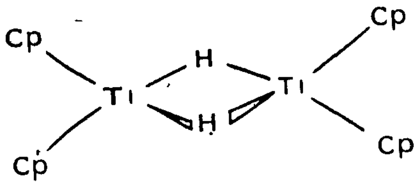


IV



V

Although crystals suitable for X-ray diffraction have never been obtained, eventually an X-ray crystal structure of the related hydroxyl compound was obtained (101). The structure determined was analagous to that of IV and was taken as evidence for the π-bonded fulvalene ligand in the proposed structure of titanocene. It has been suggested that the tendency of Cp_2Ti to abstract hydrogens is a reflection of its carbene-like reactivity (100). Carbenes are known to rearrange by an α-hydrogen abstraction process to yield an alkene. Similarly it is reasonable to assume that for a species such as Cp_2Ti, the unsaturated Ti(II) centre could abstract a hydrogen atom from a cyclopentadienyl ring to give a titanafulvene hydride which could then dimerise to yield IV (95). Hydrogen abstraction to yield a fulvene followed by dimerisation was not found to occur when the "titanocene" was prepared directly from solid Cp_2TiMe_2 and hydrogen at 0°C, with no solvent present (102). In this case Bercaw et al. obtained a violet bridging dihydride dimer with four π-bonded cyclopentadienyl ligands. The IR spectrum showed no evidence of σ-bonded rings, expected in a fulvalene type of complex. The structure suggested by them was as follows:



VI

Upon heating to 150°C in vacuo, VI was found to convert to IV via the loss of hydrogen. It was also found that species VI slowly converted to a polymeric form, a grey-green complex formulated as $[Cp_2TiH]_n$ at RT. Both dimer and polymer were shown to have identical chemical reactivity, with the polymeric nature of the grey-green form being proposed as a result of its relative lack of solubility (103). It was also realised that the grey-green hydride could be obtained from the reaction of Cp_2TiMe_2 with H_2 in solution, but at 0°C rather than the 20°C necessary to obtain the fulvalene species IV.

The polymeric hydride has been found to be a good source of a reactive form of titanocene. Bercaw et al. were able to show that suspension of $[Cp_2TiH]_n$ in solvents such as toluene or ether at RT led to loss of H_2, giving rise to a species with the composition $[Cp_2Ti]_n$ (103). A simple metallocene type of IR spectrum was reported, characteristic of π-bonded cyclopentadienyl groups, and molecular weight studies showed $[Cp_2Ti]_n$ to be dimeric in solution. Chemical tests were used to substantiate the structure, and reaction of $[Cp_2Ti]_2$ solutions with CO and HCl to yield the dicarbonyl and dichloride respectively, was said to be indicative of the existence of a Ti(II) species.

As a consequence of the apparent close relationship between "titanocene" and its hydride derivatives, Bercaw et al. attempted the preparation of decamethyltitanocene, Cp^*_2Ti ($Cp^* = \eta^5-C_5Me_5$), (103). It was thought that the latter would be far more stable than its unsubstituted analogue, due to the lack of available hydrogen atoms on the cyclopentadienyl rings. The lower reactivity of $Cp^*_2TiMe_2$ compared to Cp_2TiMe_2 necessitated the development of a long preparative route for Cp^*_2Ti via three intermediates (104). Eventually, pure material was obtained by reaction of decamethyltitanocene dihydride with N_2 to form a dinuclear dinitrogen complex. Subsequent loss of nitrogen gave rise to orange crystalline Cp^*_2Ti. In solution at RT, it was found that decamethyltitanocene exists in equilibrium with a tautomer, formed by a carbene-like insertion into the C-H bond of a pentamethylcyclopentadienyl ligand. Bercaw was able to show that for solutions of Cp_2^*Ti, stirring under D_2 caused all ring methyl protons to be substituted by deuterons (104). Although this process was reversible, upon heating decomposition was noted, with loss of hydrogen.

Zirconium is analogous to titanium in that no stable monomer Cp_2Zr has ever been isolated. In fact it is likely that any such species, perhaps formed in situ, would even more readily form complex hydrides than the corresponding titanium species. Heats of formation for the dihydrides TiH_2 and ZrH_2 have been given as -123 kJ/mol** and -159 kJ/mol** respectively (105). Many attempts to obtain zirconocene by various methods, usually involving a reduction of Cp_2ZrCl_2, have resulted in failure. Watt and Drummond were the first to report a synthesis and characterisation of a species they called zirconocene (106). Although the correct stoichiometry was obtained and IR spectroscopy showed that there was no apparent evidence of Zr-H bonds, subsequently other workers were able to prepare the same material and show that metal hydrides were in fact present (107).

Preparation of the substituted zirconocene, decamethylzirconocene, Cp_2^*Zr, was achieved by reduction of $Cp_2^*ZrCl_2$ with excess Na amalgam in toluene under N_2 (108). Initially the dinitrogen complex $\{Cp_4^*Zr_2(N_2)_3\}$ was obtained,

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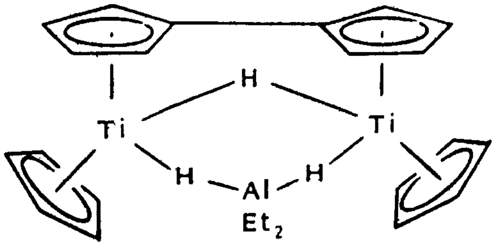
** Converted to SI units by the author.

which was then found to slowly release its coordinated nitrogen in vacuo. It is interesting to note that the remaining solution seemed to consist mainly of $Cp^*(C_5Me_4CH_2)ZrH$ based on NMR results. It was suggested that formation of this could arise from its tautomer Cp^*_2Zr via a reversible ring methyl hydrogen abstraction by the Zr centre, in the same way as was observed for titanium (104). Thus tautomerism was found to exist, although the predominant species in solution was the hydride. This probably reflects the greater stability of the Zr-C and Zr-H bonds.

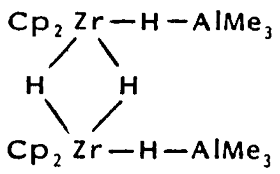
Until as recently as 1970, there were only three hydrides of the group 4 elements that had been characterised. $Cp_2ZrH(BH_4)$ and $[Cp_2ZrH_2]_n$ had been obtained by James et al. by the action of 1 and 2 moles respectively of trialkylamines on $Cp_2Zr(BH_4)_2$ (109). The only other hydride characterised to any degree was that discussed above i.e., complex VI (102). The action of $LiAlH_4$ on various cyclopentadienyl halides subsequently enabled Wailes and Weigold to obtain a number of hydrides including Cp_2ZrHCl, $Cp_2ZrH(AlH_4)$, $Cp_2ZrH(CH_3)$ and $\{[Cp_2ZrH]_2O\cdot Cp_2ZrH_2\}$ (110). In addition to this, they obtained $[Cp_2ZrH_2]_n$ by the action of $LiAlH_4$ on $[Cp_2ZrCl]_2O$. Although $Cp_2ZrH(CH_3)$ was reported by Wailes and Weigold to be polymeric, other hydrides of the formula Cp_2ZrHR all appear to be dimeric in benzene solution. Examples of these include those complexes where R = ethyl, cyclohexyl, neopentyl and noctyl (111). Recently $[Cp_2ZrH_2]_n$ has also been reported dimeric in both benzene and toluene solution (112).

A particularly interesting class of hydride derivatives of titanocene and zirconocene are those complexes with a hydride bridging the group 4 metal to another metal, often a main group metal such as either boron or aluminium. One example of such a bridging hydride is Cp_2TiBH_4, best prepared by the reaction of Cp_2TiCl_2 with $NaBH_4$ (113). In this case the BH_4 group is attached to the titanium atom through a double hydrogen bridge (96). An analogous reaction with the corresponding zirconium compound did not result in reduction, and the bis(tetrahydroborate) was obtained (114). A number of Ti-H-Al compounds have also been reported, one of which includes the mixed aluminotitanium hydride, $\{(CpTi)_2(\mu\text{-}H)(\mu\text{-}H_2AlEt_2)(\mu\text{-}C_{10}H_8)\}$ (115). This was obtained by the reaction, at 25°C, of Et_3Al on the "titanocene" formulated as the fulvalene dimer, IV. X-ray crystallography showed that the fulvalene ligand remained intact and the structure of $\{(CpTi)_2(\mu\text{-}H)(\mu\text{-}H_2AlEt_2)(\mu\text{-}C_{10}H_8)\}$ was found to be:



VII

The structure of this complex is particularly interesting for a number of reasons. In addition to the fulvalene ligand, there is a bridging Ti-H-Ti bond and two bridging Ti-H-Al bonds. A reaction has also been reported between the polymeric hydride of zirconium, $[Cp_2ZrH_2]_n$, and Me_3Al (116). In this case a complex was reported, formulated as $\{Cp_2ZrH_2 \cdot AlMe_3\}_2$, which was assigned the following structure based on spectroscopic evidence:



VIII

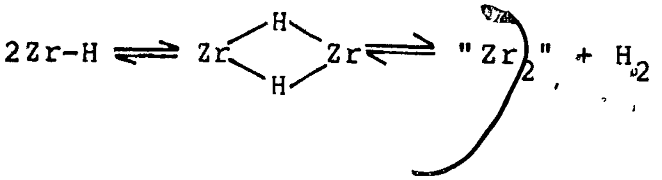
The first report of structural evidence for a binuclear hydride of zirconium with bridging hydride ligands has only appeared recently (117). In fact the characteristic insolubility of complexes such as $[Cp_2ZrH_2]_n$ has prevented their complete structural characterisation. Jones and Petersen have used the methylcyclopentadienyl ligand, Cp', and exploited the favourable properties of increased solubility and crystallisability it imparts on the complex of which it forms part. Thus by reacting $LiAlH(O\text{-}\underline{t}\text{-}Bu)_3$ with Cp'_2ZrCl_2 (2:1) in THF, they were able to isolate $\{Cp'_2ZrH(\mu\text{-}H)\}_2$ in high yield and subsequently confirm the structure by X-ray diffraction. The molecular structure was shown to consist of two Cp'_2ZrH units, bridged by two 2-electron, 3-centre Zr-H-Zr bonds. Subsequently they were able to show that both thermolysis and photolysis of benzene solutions of $\{Cp'_2ZrH(\mu\text{-}H)\}_2$ proceed with the initial formation of a paramagnetic zirconocene hydride together with an associated loss of 1 mole of H_2 as given by the following equations (118,119):

$$\{Cp'_2ZrH(\mu\text{-}H)\}_2 \xrightarrow{h\nu \text{ or } \Delta} 2\text{"}Cp'_2ZrH\text{"} + H_2 \qquad 1.16$$

Thermolysis studies showed that hydrogen was lost from the methylcyclopentadienyl rings as well as arising from reductive elimination of two of the hydride ligands. Thus, 3 moles of H_2 were eventually collected per mole of $\{Cp'_2ZrH(\mu\text{-}H)\}_2$. Joining the two rings with a dialkylsilyl bridge to form complexes of the type $\{[SiR_2(C_5H_4)_2]ZrH(\mu\text{-}H)\}_2$ was found to restrict their chemical participation, and upon thermolysis only 2 moles of H_2 were evolved per mole of complex. Thus the associated paramagnetic zirconocene hydride was found to be more stable than that formed in the decomposition of $\{Cp'_2ZrH(\mu\text{-}H)\}_2$. The first mole of H_2 obtained from the decompositon of dialkylsilyl bridged species was again thought to occur via a reductive elimination of two hydride ligands as H_2 (119):

$$\{[SiR_2(C_5H_4)_2]ZrH(\mu\text{-}H)\}_2 \xrightarrow{h\nu \text{ or } \Delta} 2\text{"}[SiR_2(C_5H_4)_2]ZrH\text{"} + H_2 \qquad \text{I.17}$$

Bajgur *et al*. also suggested that subsequent hydrogen loss might occur via the formation of a dinuclear hydride intermediate:



$$2Zr\text{-}H \rightleftharpoons Zr(\mu\text{-}H)_2Zr \rightleftharpoons \text{"}Zr_2\text{"} + H_2 \qquad \text{I.18}$$

Such a reaction would however not occur to any significant extent under the reaction conditions used (i.e., sealed tube). In the case of $\{Cp'_2ZrH(\mu\text{-}H)\}_2$ the methylcyclopentadienyl rings must be involved in hydrogen elimination to account for the observed 3 moles of H_2. It has already been shown that ring methyl-to-metal hydride transfer can occur in pentamethylcyclopentadienylzirconium complexes (108), and hydride abstractions from cyclopentadienyl ligands are well known, accounting for the high reactivity of titanocene (100). These alternative pathways for loss of hydrogen are not available in the complexes $\{[SiR_2(C_5H_4)_2]ZrH(\mu\text{-}H)\}_2$, and so upon thermolysis only 2 moles of H per mole of complex is evolved.

In conclusion, it is only recently that the chemistry of the organometallic hydrides of the group 4 elements has started to be explored. This is due in part to their low solubility and high oxophilic nature, together with difficulties associated with the detection of metal hydrides. Early work relied on chemical tests to detect their presence. Hydrogen atoms coordinated to group 4 metals always act in a hydridic manner and so will readily react with proton sources such as acids to generate H_2. Reaction with CCl_4 or $CHCl_3$ will yield $CHCl_3$ and CH_2Cl_2 respectively which may be detected by ^1H NMR. Spectroscopic evidence for group 4 metal-hydride bonds is not easy to obtain. As already mentioned,the usual lack of solubility makes the obtaining of NMR spectra difficult. Often paramagnetic species are involved, necessitating the use of ESR, rather than NMR techniques. Although IR spectroscopy has been widely used, the intensity of M-H stretching frequencies is often low, causing some confusion in early attempts to isolate titanocene. Few X-ray diffraction studies have been done, indicative of the difficulty associated with the obtaining of suitable crystals. In addition there are other problems associated with X-ray location of H atoms attached to the much larger transition metal. The positional accuracy of the hydride is often low for two reasons. Firstly the intensity of the X-rays scattered from H is low, and secondly, H atoms possess a high thermal motion, causing scattering of X-rays to become more diffuse (120).

Thus it may be seen that in addition to difficulties in the synthesis of group 4 M-H complexes, characterisation is often complicated as well. Modification of ligands, as in the work of Jones and Petersen, is likely to be one way of removing some of the obstacles.

I.3.3 Introduction to some aspects of titanium/zirconium silyl chemistry

The first example of a compound containing a silicon transition metal bond was $Me_3SiFe(CO)_2Cp$, prepared by Piper et al. in 1956 (121). It was not however until 1968 that the first complex containing a Si-Ti bond was reported (122). The method of preparation was salt elimination using a group 4 anion. Thus the complexes $(Ph_3Si)_4Ti$ and $Cp_2Ti(SiPh_3)_2$ were prepared according to the following equations:

$$TiCl_4 + 4Ph_3SiK \xrightarrow[0°C]{Ether} (Ph_3Si)_4Ti + 4KCl \qquad I.19$$

$$Cp_2TiCl_2 + 2Ph_3SiK \xrightarrow[0°C]{Diglyme} Cp_2Ti(SiPh_3)_2 + 2KCl \qquad I.20$$

These two complexes ostensibly containing Si-Ti bonds were however prepared in air, and it was later suggested by Kingston and Lappert that instead of $(Ph_3Si)_4Ti$, $(Ph_3SiO)_4Ti$ had been obtained (123).

Prior to the work of Hengge and Zimmerman on the above mentioned titanium complexes, a communication had appeared 1 year earlier on the preparation of $Cp_2ZrCl(SiPh_3)$ (124). This was in fact the first group 4-14 complex to be obtained. It was prepared by a salt elimination method, by the reaction of Ph_3SiLi with Cp_2ZrCl_2 at -50°C in THF. In addition to being the first group 4 silyl complex, it was also the first example of a stable metal silyl complex with the metal in as high an oxidation state as +4. It is interesting to note that only the monosilyl complex was obtained, attempts to obtain the bis(silyl) complex failed and only afforded tarry residues. A X-ray crystal structure showed $Cp_2ZrCl(SiPh_3)$ to possess essentially a tetrahedral environment about both zirconium and silicon (125). A long bond length was reported for Zr-Si, relative to other second row M-Si bond lengths, presumably indicative of the absence of any $d\pi$-$p\pi$ backbonding onto silicon.

Most of the reported complexes containing a Ti/Zr-Si bond appear to possess phenyl groups on the silicon. There are however exceptions, and the second most common substituent is the methyl group. The preparation and characterisation of $Cp_2TiCl(SiMe_3)$ has recently been reported by Rösch <u>et al</u>. (126). This was obtained according to the following reaction:

$$Cp_2TiCl_2 + Al(SiMe_3)_3 \cdot Et_2O \xrightarrow{\text{Pentane}} Cp_2TiCl(SiMe_3) + ? \qquad \text{I.21}$$

Exactly what happened to the aluminium in the rection was not elucidated. It has been suggested in a recent review that disubstitution is the norm for titanium in these types of complex i.e., $Cp_2Ti(SiR_3)_2$ is usually expected (127). Rösch et al. however reported that even with 2 moles of $Al(SiMe_3)_3 \cdot Et_2O$ no disubstituted product, $Cp_2Ti(SiMe_3)_2$ was observed. At about the same time, the analogous zirconium compound, $Cp_2ZrCl(SiMe_3)$ was prepared according to the following reaction (128):

$$Cp_2ZrCl_2 + 3Hg[SiMe_3]_2 \xrightarrow[\text{9 days}]{\text{Benzene}} Cp_2ZrCl(SiMe_3) + ? \qquad \text{I.22}$$

It was reported that the product was obtained in 33% yield. Despite using an excess of $Hg[SiMe_3]_2$, it was thought only the monosubstituted derivative was obtained. When the reaction time was increased to 15 days, although the yield of monosubstituted product was increased to 58%, the disubstituted product $Cp_2Zr(SiMe_3)_2$, was also said to have been obtained in 11% yield. Both compounds were obtained by sublimation and were reported to be white. The complex $Cp_2ZrCl(SiMe_3)$ has recently been remade by Tilley using the same preparative method as was discussed earlier for the analogous titanium complex (129). The colour of the material isolated in this case was red, similar to that of $Cp_2ZrCl(SiPh_3)$, and it now seems likely that the earlier work of Blakeney and Gladysz was wrong. It now appears that as discussed earlier when $(Ph_3SiO)_4Ti$ was isolated instead of $(Ph_3Si)_4Ti$, the siloxide $Cp_2ZrCl(OSiMe_3)$ was most likely obtained by Blakeney and Gladysz in their attempts to obtain $Cp_2ZrCl(SiMe_3)$. Although their reactions were done under N_2, oxygen must somehow have been incorporated. Tilley was able to isolate $Cp_2ZrCl(OSiMe_3)$ from Me_3SiK and Cp_2ZrCl_2, and show that it did indeed possess similar properties to the "$Cp_2ZrCl(SiMe_3)$" obtained by Blakeney and Gladysz (129). In view of Tilley's work, it now appears questionable also if $Cp_2Zr(SiMe_3)_2$ was obtained, and not $Cp_2Zr(OSiMe_3)_2$.

Tilley has prepared and characterised a number of trimethylsilyl derivatives of bis(cyclopentadienyl)zirconium and hafnium (129). The zirconium complexes are of interest in relation to the work to be presented here, and so it is upon these that we shall focus. Development of the chemistry of trimethylsilyl derivatives of zirconium, involving a Zr-Si bond, was dependant on the development of suitable starting materials. The species $Cp_2MCl(SiMe_3)$ (M = Zr/Hf) were ideal for this, the zirconium one having been discussed earlier. Studies of these starting materials have also been undertaken, in addition to their preparation and characterisation.

Thermal decomposition of $Cp_2ZrCl(SiMe_3)$ in C_6D_6 at 97°C was reported to yield Me_3SiH together with a major zirconium-containing product. It was thought that the zirconium species was most likely $\{Cp(C_5H_4)ZrCl\}_n$, based on the similarity of its ^1H NMR spectrum to that of $\{Cp(C_5H_4)ZrI\}_n$, reported by Gell et al. (130). It is likely that to produce such a zirconium species, as well as to account for the formation of Me_3SiH, silyl abstraction of protons from the cyclopentadienyl groups occurs. Reaction of $Cp_2ZrCl(SiMe_3)$ with a number of nucleophilic reagants NaS_2CNEt_2, $LiBH_4$ and $LiOCMe_3$ has resulted in new zirconium silyl complexes. The reactions are as follows (129):

$$Cp_2ZrCl(SiMe_3) + NaS_2CNEt_2 \xrightarrow[Et_2O]{-NaCl} Cp_2Zr(SiMe_3)(S_2CNEt_2) \qquad I.23$$

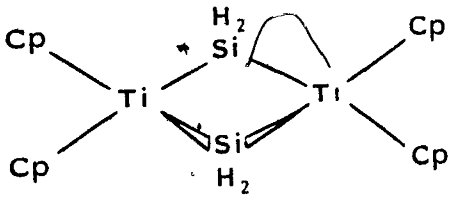
$$Cp_2ZrCl(SiMe_3) + LiBH_4 \xrightarrow[Et_2O/-78^\circ C]{-LiCl} Cp_2Zr(SiMe_3)(BH_4) \qquad I.24$$

$$Cp_2ZrCl(SiMe_3) + LiOCMe_3 \xrightarrow[Et_2O]{-LiCl} Cp_2Zr(SiMe_3)(Me_3CO) \qquad I.25$$

The product obtained in reaction I.23 had its structure determined by X-ray crystallography, and the presence of a

Zr-Si bond was confirmed. It was subsequently shown that the Zr-Si bond in $Cp_2ZrCl(SiMe_3)$ could react reversibly with CO to yield a CO insertion product (131). The X-ray crystal structure reported for $Cp_2ZrCl(OCSiMe_3)$ showed that the silaacyl ligand existed in an η^2-form. This complex is of considerable interest because it is the first report of a direct insertion product of this type.

Two complexes of particular interest involving Ti-Si bonds have yet to be mentioned. The first of these was obtained in 1973 by Hencken and Weiss (132). They obtained the complex $\{Cp_2Ti(\mu\text{-}SiH_2)_2TiCp_2\}$ from the reaction of $KSiH_3$ with Cp_2TiCl_2. A crystal structure revealed the presence of a dimer with a ~~planar~~ Si_2Ti_2 ring. The structure was only refined to an R value of 9% and in view of the product characterised in this work, $\{(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}HSiPhH)\}_2$, the true structure might conceivably be $\{(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}HSiH_2)\}_2$. The structure obtained by Hencken and Weiss is as follows:



IX

A second complex also of interest is the complex $\{Ph_2Si(Ph_2Si)_3TiCp_2\}$ prepared by Holtman and Schram in 1980 from the reaction of Cp_2TiCl_2 with $Li_2(Ph_2Si)_4$ in THF (133). Although it was poorly characterised and obtained only as an oil, the titanium atom was reportedly attached to a catenated silicon ring. Thus the example provides some precedance for titanium attached to an oligosilyl fragment.

It is rather surprising that few lower valent titanium silyl complexes exist. As discussed previously, oxidation states of less than +4 are not readily accessible for Zr complexes, and so the fact that to date no Zr(III) or Zr(II) silyl complexes exist is hardly surprising. Lower oxidation states for titanium such as Ti(III) might well provide increased stability to a Ti-Si bond by $d\pi-p\pi$ backbonding into the empty orbitals on silicon. There appear to be no examples of a Ti(III)-Si bond, although Ti has been reported to form bonds of this type to other group 14 metals (127). There has however been a report of a Ti(II) complex containing Ti-Si bonds. Razuvaev <u>et al</u>. claim to have isolated $\{(Me_3Si)_2Ti\cdot 2THF\}$ from $TiCl_4$ and Me_3SiLi (134).

In conclusion, it is evident that there are only a few examples of compounds where Ti or Zr is directly bound to Si. It is very likely that this is a result of a lack of preparative methods together with difficult purification procedures. In addition, the oxygen sensitivity of titanium and zirconium organometallic compounds has already been shown to be a problem, with metal siloxy species being often isolated instead of the expected metal silyl complexes.

I.4 STATEMENT OF THE RESEARCH

As already mentioned, there has been only one report of a catalytic polymerisation of silanes to polysilanes prior to the work presented in this thesis. Wilkinson's catalyst was found to give a number of small oligosilanes, consisting of at most three silicon atoms (52). Subsequent to this Samuel and Harrod reported a reaction between a number of silanes and Cp_2TiR_2, where R = Me/Bz, to form a unique bis-(cyclopentadienyl)titanium hydride complex (characterised by ESR) according to the following equation, given for the case where R = Me (135):

$$\begin{aligned} 4Cp_2TiMe_2 + 8R_3SiH \longrightarrow 2\{[Cp_2TiH]_2(\mu\text{-}H)\} &+ 6R_3SiMe \\ &+ R_6Si_2 + 2MeH \qquad \text{I.26} \end{aligned}$$

In fact, it became evident that the reaction was very interesting, and not as straightforward as it initially appeared. It was noted that in the presence of excess $PhSiH_3$, gas evolution continued long after the completion of reaction I.26. The solution became noticeably more viscous, most likely due to build-up of polysilane. The original aim of the work presented in this thesis, therefore, was the further study of the reaction shown in equation I.26, with possible isolation of the titanium hydride, as well as the isolation and characterisation of the polysilanes produced in the presence of excess silane. By modification of the reaction conditions, it was hoped that a control of the polymer molecular weights could be achieved. In addition to the isolation of polysilane from the reaction of $PhSiH_3$ with Cp_2TiMe_2, two new organometallic complexes containing Ti-H-Si-Ti bridges were obtained, and their full X-ray structural characterisation is presented in this thesis. Further studies on the reaction between a number of other primary silanes ($PhSiD_3$, $BzSiH_3$, $BzSiD_3$ and $HxSiH_3$) and a number of titanocenes (Cp_2TiMe_2, Cp'_2TiMe_2, $CpCp^*TiMe_2$, $Cp^*_2TiMe_2$, $[Cp_2TiH]_n$ and $[Cp_2Ti]_2$) will also be discussed. As an extension of this work, the results of the reaction between $PhSiH_3$, $PhSiD_3$, $BzSiH_3$ and $BzSiD_3$, and Cp_2ZrMe_2 as well as between $[Cp_2ZrH_2]_n$ and $PhSiH_3$ will also be presented. It is interesting to note that reaction has already been reported between Cp_2TiMe_2 and Et_3GeH/Et_3SnH, and between Cp_2ZrMe_2 and Et_3GeH (136). The authors were trying to obtain $Cp_2M(Sn/GeEt_3)_2$. In fact no stable products were isolated, the reaction mixture was found to contain either hexaethyldigermane or -stannane, said to arise from decomposition of an intermediate organometallic species. In all cases methane was evolved and Cp_2M was said to be present, evidence for which came from the observation of dichlorotitanocene and H_2 upon addition of HCl to the reaction mixture.

CHAPTER II

EXPERIMENTAL

II.1 INSTRUMENTATION

Infrared spectra (4000-400 cm^{-1}) were recorded for either neat samples or pentane films, between KBr plates on a Perkin Elmer 297 spectrometer. All spectra were calibrated using the peak at 1601 cm^{-1} of a polystyrene film. The resolution is 4 cm^{-1} for all spectra.

^1H NMR spectra were recorded on a Varian XL-200 spectrometer operating in the pulsed FT mode. All chemical shifts (± 0.05) are reported in ppm relative to tetramethylsilane, TMS. At no time was TMS added to the sample. Negative chemical shift values indicate upfield shifts from the reference. When C_6D_6 was the solvent, referencing was achieved via the use of the "SETREF" command. In the cases where either toluene-d_8 or THF-d_8 was the solvent, referencing was achieved by the use of a residual solvent peak. The details of a typical set of ^1H coupled and decoupled instrumental parameters for a sample run in toluene-d_8 are given in TABLE II.1.

^{29}Si NMR spectra were measured on a Varian XL-300 spectrometer at 59.59 MHz, using a 5 mm broad band probe, with the external lock turned to off. The chemical shifts (± 1) are reported in ppm relative to external TMS/$CDCl_3$ (1:1 v/v at ambient temperature). Polarisation transfer pulse sequences were used in order to optimise the observation of the nuclei. Prior to each measurement, the proton pulse width, PP, was calibrated using dioxane. Since no ^{29}Si satellites were

TABLE II.1: ^{1}H NMR INSTRUMENT PARAMETERS

PARAMETER	^{1}H COUPLED	^{1}H DECOUPLED
TRANSMITTER NUCLEUS, TN	1.200	1.200
SWEEP WIDTH, SW	14992.5	14992.5
TRANSMITTER OFFSET, TO (Hz)	0	0
ACQUISITION TIME, AT (sec)	0.534	0.534
NUMBER OF POINTS, NP	16000	16000
PULSE WIDTH, PW (μ sec)	4.0	4.0
EQUILIBRIUM DELAY, D_1	2.000	2.000
DECOUPLER NUCLEUS, DN	-	1.200
DECOUPLER POWER LEVEL, DLP	-	LOW (0-60 dB)
DECOUPLER MODE	-	YYY
DIGITAL RESOLUTION (Hz)	1.87	1.87

observed in any of the ^{1}H NMR spectra, the $^{1}J_{Si-H}$ value for the parent silane was initially used (200 Hz for $PhSiH_3$) together with a large sweep width, SW, to locate the peaks in the decoupled spectra. In the case of the organometallic complexes, coupled spectra were subsequently obtained using the same conditions to obtain a more accurate $^{1}J_{Si-H}$ value for the particular complex under study, and the parameters were then modified to optimise the coupled spectra. Both INEPT

(Insensitive Nucleus Enhancement through Polarisation Transfer) and DEPT (Distortionless Enhancement by Polarisation Transfer) pulse sequences were used and are as follows for the ^1H decoupled case (137,138):

90° (H,X) - $\tau/2$ - 180° (H,X), 180° (Si,X) - $\tau/2$ - 90° (H,Y),
90° (Si,X) - $\Delta/2$ - 180° (H,X), 180° (Si, X) - $\Delta/2$ - decouple,
acquire

INEPT PULSE SEQUENCE
FOR ^1H DECOUPLED SPECTRA

90° (H,Y) - τ - 180° (H,X), 90° (Si,X) - τ - σ(H,X),
180° (Si,X) - τ - decouple, acquire

DEPT PULSE SEQUENCE
FOR ^1H DECOUPLED SPECTRA

In the case of the decoupled spectrum obtained using the INEPT pulse sequence, a total excitation transfer delay, τ (D_3 in the instrument parameter list), of 2.5×10^{-3}s was used. The refocussing delay used, Δ (D_2 in the instrument parameter list), was 1.67×10^{-3}s. After the parameters had been optimised for the coupled spectrum, an excitation transfer delay of 3.33×10^{-3}s was used. A full set of typical parameters for a ^1H decoupled INEPT spectrum (before optimisation), taken in THF-d_8, together with those for the corresponding coupled spectrum (after optimisation) is given in TABLE II.2. In the case of the decoupled spectrum obtained using the DEPT pulse sequence, an excitation transfer delay of 3.23×10^{-3}s was used together with a pulse flip angle, θ, of 45°. This ensured enhancement of all silicon atoms with attached protons. A set of typical optimised parameters for both a ^1H decoupled DEPT spectrum measured in THF-d_8, together with that for the corresponding coupled spectrum is given in TABLE II.2. Variation of the θ pulse by use of an array was employed in the measurement of ^{29}Si DEPT NMR spectra of some oligosilanes, enabling the silicons to be differentiated according to their number of attached protons. Thus ^1H decoupled DEPT spectra of oligohexylsilane and oligophenylsilane were run, with an excitation transfer delay of 2.5×10^{-3}s (based on $^1J_{Si-H} = 200$ Hz for the parent silane), and using an array for θ of 45°, 90° and 135°.

All NMR spectra, both ^1H and ^{29}Si, were measured at ambient temperature unless otherwise indicated (20°C ± 3), and on saturated solutions. Peaks are described as given in the list of abbreviations.

Molecular weight measurements were obtained on a Corona/Wescan model 232A molecular weight apparatus using the principle of vapour pressure osmometry. All measurements were made in toluene at 50°C. The instrument was calibrated immediately before use with either sucrose octaacetate or with

TABLE II.2: ^{29}Si NMR INSTRUMENT PARAMETERS

PARAMETER	INEPT		DEPT	
	DECOUPLED	COUPLED	DECOUPLED	COUPLED
TRANSMITTER NUCLEUS, TN	29.000	29.000	29.000	29.000
SWEEP WIDTH, SW	50,000	7142.9	14992.5	14992.5
TRANSMITTER OFFSET, TO	6,000	5,800	0	0
ACQUISITION TIME, AQ	0.300	2.240	1.142	1.142
DIGITAL RESOLUTION (Hz)	3.33	0.45	0.88	0.88
NUMBER OF POINTS, NP	30,016	32,000	34,240	34,240
PULSE WIDTH, (μ sec)	21.5	21.5	21.5	21.5
EQUILIBRIUM DELAY, D1	2.000	1.000	2.000	2.000
EXCITATION TRANSFER, DELAY D3 (sec)	2.5×10^{-3}	3.33×10^{-3}	3.23×10^{-3}	3.23×10^{-3}
REFOCUSSING DELAY, D2 (sec)	1.67×10^{-3}	-	-	-
PULSE FLIP ANGLE, θ (°)	-	-	45	45
COUPLING CONSTANT $^1J_{Si-H}$ (Hz)	200	150	155	155
MULTIPLICITY	4	2	-	-
PROTON 90° PULSE, PP (μ sec)	41.1	41.1	48.2	48.2
DECOUPLER NUCLEUS	1.750	-	1.750	-
DECOUPLER POWER	HIGH	-	HIGH	-
DECOUPLER MODE	NY	-	NNY	-

a Waters Associates calibration standard #41994. The calibration was always checked with a compound of known molecular weight. The molecular weights are reported in Daltons (D).

The X-ray crystal structure determinations were done by the Laboratoire des Structures aux Rayons-X, Université de Montréal. Experimental details are given in APPENDIX I.

Elemental analyses for C, H and Si were performed by Spang Microanalytical Laboratory, Eagle Harbour, Michigan.

II.2 GENERAL PROCEDURES

All manipulations were carried out using standard inert atmosphere techniques under argon (U.H.P., Linde). All glassware used in the manipulation of zirconium compounds was dried at 115°C overnight and cooled under vacuum. C_6D_6 and toluene-d_8 were obtained from Merck, Sharpe and Dohme, and THF-d_8 was obtained from Aldrich. All deuterated solvents were generally used as received after degassing and purging with argon. Degassing was generally accomplished by the use of 3 freeze-pump-thaw cycles, and the solvents were stored in Schlenk tubes over 5A molecular sieves. For the zirconium compounds, deuterated solvents were trap-to-trap distilled before use, from sodium/benzophenone. Toluene, hexanes and THF were freshly distilled from sodium/benzophenone, and collected under N_2. Subsequent freeze-thaw degassing under vacuum was followed by purging with argon. Diethylether (anhydrous) was obtained from Fisher Scientific, and used from the freshly opened can after degassing as described above. Dichloromethane was refluxed over P_2O_5 and collected under N_2. Carbon monoxide and hydrogen were both obtained as prepurified gases from Linde.

Florisil (60-100 mesh) and silica gel (70-230 mesh) were obtained from the Fisher Scientific Co., and Merck, respectively, and used as received. Cp_2TiCl_2 and Cp_2ZrCl_2 (Alfa Ventron) together with $TiCl_4$ (J.T. Baker Co.), were all used as received. Cp'_2TiCl_2, where Cp' = $C_5H_4CH_3$, was obtained as a gift from Dr. J.M. McCall, and Cp*MgCl·THF, where Cp* = $C_5(CH_3)_5$, was kindly supplied by Mr. J.P. Barry. $Cp_2Ti(CO)_2$ was obtained from Mr. S. Morris. $CpTiCl_3$ was obtained from Strem Chemicals and recrystallised from toluene/hexanes before use $(Cp_2ZrCl)_2O$ was prepared according to a standard literature procedure (110 and refs. therein).

The literature methods for the preparation of $Cp^*_2TiCl_2$ give relatively low yields (31-65%), due to the production of Cp^*TiCl_3 as a side product (103,104). Fagan <u>et al</u>. have reported high yields of $Cp^*_2MCl_2$ (M = Th, U) were obtained by reaction of MCl_4 with Cp*MgCl·THF (slight excess) in toluene at 100°C (139). Thus Fagan's method was used to obtain $Cp^*_2TiCl_2$ with the following modifications. Work up of the product mixture was done in air and after the initial filtration, all the toluene was removed to give a red-brown solid which contained Cp^*TiCl_3. Soxhlet extraction, according to the method of Bercaw et al. (103), was not completely successful in removing the contaminant. Chromatography of the residue on a silica gel column, using CH_2Cl_2 as the eluant gave pure $Cp^*_2TiCl_2$ (~ 40%).

The compound $CpCp^*TiCl_2$ was obtained by the reaction of $Cp^*MgCl \cdot THF$ with $CpTiCl_3$ (1:1 molar ratio) in toluene at 90°C under argon. After 2 days, filtration through celite gave a clear red solution which was evaporated to yield a solid residue. A mixture of $CpCp^*TiCl_2$ and Cp_2TiCl_2 was obtained. The former was isolated (30%) after chromatography on a silica gel column using CH_2Cl_2 as the eluant.

$PhSiCl_3$ and $BzSiCl_3$ ($Bz = C_6H_5CH_2$) together with $HxSiH_3$ ($Hx = n\text{-}C_6H_{13}$) and $PhSiH_3$ were obtained from either Petrarch Systems Inc. or Silar Laboratories Inc. $LiAlH_4$ and $LiAlD_4$ were purchased from Aldrich. $BzSiH_3$, $BzSiD_3$ and $PhSiD_3$ were prepared by the action of a small excess (10%) of $LiAlH_4$/$LiAlD_4$ on the appropriate chlorosilane in diethyl ether as described in the literature (140). Methyllithium was purchased from Aldrich as an ethereal solution and used as received.

The complexes Cp_2TiMe_2, Cp'_2TiMe_2, $Cp^*_2TiMe_2$ and $CpCp^*TiMe_2$ were prepared by the action of MeLi on the appropriate dichlorometallocene (stoichiometric ratio) in Et_2O. The procedure followed for the preparation of Cp_2TiMe_2 was largely that used by Klaus and Bestian (78). The reaction was however done in air with no special precaution against exposure of it to light. After recrystallisation from hexanes, the orange crystalline product (90%) was stored in its mother liquor at -20°C in the dark. The compound was recrystallised before use upon any sign of decomposition. The compound Cp'_2TiMe_2 was prepared in the same way although the yields were much lower (~ 30%). The compounds $Cp^*_2TiMe_2$ and $CpCp^*TiMe_2$ were prepared (80%) according to the method reported for $Cp^*_2TiMe_2$ (103). All compounds were stored in their mother liquor at -20°C in the dark. The compounds $[Cp_2TiH]_n$ (46%) and $[Cp_2Ti]_2$ were prepared from Cp_2TiMe_2 according to the method of Bercaw *et al*. (103). The solvent used to prepare $[Cp_2Ti]_2$ was toluene.

Cp_2ZrMe_2 was prepared from Cp_2ZrCl_2 and MeLi in diethylether according to literature procedures (79,80) at -20°C as suggested by Samuel and Rausch (79). Purification of the material was accomplished by two sublimations under high vacuum (10^{-4} torr at 90°C). The extreme moisture sensitivity of Cp_2ZrMe_2 necessitated storage under argon. Generally, the compound was used right after preparation or resublimed immediately before use. Yields were generally low, of the order of 45%. It was found to be light sensitive and thus stored in the dark. $[Cp_2ZrH_2]_n$ was prepared according to the method of Wailes and Weigold (110).

II.3 REACTIONS BETWEEN $PhSiH_3$ AND SOME BIS(η^5-CYCLOPENTADIENYL) DERIVATIVES OF TITANIUM

II.3.1 Reaction of $PhSiH_3$ with Cp_2TiMe_2 (1:1 molar ratio); isolation of μ-hydrido-1(H)1'(Si)-μ-phenylsilyl-tetrakis(η^5-cyclopentadienyl)-dititanium(III), $\{[(\eta^5-C_5H_5)_2Ti]_2(\mu-H)(\mu-HSi(C_6H_5)H)\}$, X

In a typical reaction, $PhSiH_3$ (0.15 mL, 1.21 mmol) was added to a solution of freshly recrystallised Cp_2TiMe_2 (0.247 g, 1.18 mmol) in Et_2O (3 mL). After an induction period, generally lasting only a few seconds, a spectacular colour change from orange to blue/black occurred. This was accompanied by a sudden, rapid evolution of gas. After about 2 hours, the supernatant liquid was decanted to leave a residual blue/black crystalline solid. This was washed with cold Et_2O (3 x 5 mL) and vacuum dried to give pure $\{[\eta^5-C_5H_5)_2Ti]_2-(\mu-H)(\mu-HSiPhH)\}$, (X) (0.165 g, 60% yield). Larger single crystals suitable for X-ray diffraction were obtained in lower yield (23%) by reacting $PhSiH_3$ (0.21 mL, 1.68 mmol) with Cp_2TiMe_2(0.353 g, 1.70 mmol) in a mixture of Et_2O (4 mL) and toluene (1 mL). The crystals obtained were again washed with cold Et_2O in the manner described above, and vacuum dried.

^1H NMR (C_6D_6): δ 7.87-7.01 (m, Ph); δ 5.61 (20H, bb, Cp, $\nu_{\frac{1}{2}}$ = 31 Hz); δ 4.54 (1H, bb, Si-H, $\nu_{\frac{1}{2}}$ = 53 Hz); δ -12.17 (1H, bb, Si-H-Ti, $\nu_{\frac{1}{2}}$ = 61 Hz). Although a range is given for the phenyl protons, the relative insolubility of complex X in

C_6D_6 made it impossible to quote an accurate range, or integral, due to overlap with the band from the residual protons of C_6D_6.

^{1}H NMR (THF-d_8): δ 8.24-6.83 (5H, m, Ph); δ 5.82 (20 H, bb, Cp, $\nu_{\frac{1}{2}}$ = 29 Hz); δ 4.15 (1H, bb, Si-H, $\nu_{\frac{1}{2}}$ = 67 Hz); δ -12.36 (1H, bb, Si-H-Ti, $\nu_{\frac{1}{2}}$ = 93 Hz).

^{1}H NMR (THF-d_8, -50°C): δ 8.24-6.83 (5H, m, Ph); δ 5.86 (5H, s, Cp), δ 5.77 (5H, s, Cp), δ 5.69 (5H, s, Cp), δ 5.64 (5H, s, Cp); δ 4.15 (1H, s, Si-H, $\nu_{\frac{1}{2}}$ = 11 Hz); δ -12.21 (1H, S, Si-H-Ti, $\nu_{\frac{1}{2}}$ = 12 Hz); δ -19.51 (1H, s, Ti-H-Ti, $\nu_{\frac{1}{2}}$ = 62 Hz).

The ^{1}H NMR data given here is for characterisation purposes only. Other data will be reported later when the temperature dependance of the ^{1}H NMR is discussed.

^{29}Si NMR (INEPT, THF-d_8, -80°C): δ 87 (ddd, $^1J_{Si-H}$ = 148 Hz, $^1J_{Si-H(Ti)}$ = 58 Hz, $^2J_{Si-(Ti)-H}$ = 14 Hz).

ANALYSIS: Calcd for $C_{26}H_{28}SiTi_2$: C, 67.24; H, 6.09; Si, 6.05. Found: C, 67.08; H, 6.18; Si, 6.00.

II.3.2 Reaction of $PhSiH_3$ with Cp_2TiMe_2 (~ 3:1 molar ratio); isolation of bis(1(H)1'(Si)1(Si')1'(H')-μ-phenylsilyl)-tetrakis(η^5-cyclopentadienyl)-dititanium(III), $\{(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}HSi(C_6H_5)H)\}_2$, XI

In a typical reaction, $PhSiH_3$ (0.50 mL, 4.02 mmol) was added to a solution of freshly recrystallised Cp_2TiMe_2

(0.302 g, 1.45 mmol) in toluene (5 mL). The solution rapidly changed colour from orange to blue/black, with evolution of gas. Slow gas evolution continued for 24 hours, after which time a solid crystalline material had deposited. The supernatant liquid was decanted and the blue/black crystals were washed with cold Et_2O (3 x 5 mL). Subsequent vacuum drying gave well formed crystals of $\{(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}HSiPhH)\}_2$ (<u>XI</u>) (0.31 g, 75% yield) suitable for X-ray diffraction.

^1H NMR (C_6D_6): δ 7.92-7.28 (10H, m, Ph); δ 5.12 (1H, s, Si-<u>H</u>); δ 4.86 (10H, s, Cp), 4.65 (10H, s, Cp); δ -8.73 (1H, s, Si-<u>H</u>-Ti).

^1H NMR (THF-d_8): δ 7.88-6.77 (m, Ph); δ 5.07 (10H, s, Cp), δ 4.82 (10H, s, Cp); δ 4.89 (1H, s, Si-<u>H</u>); δ -8.81 (1H, s, Si-<u>H</u>-Ti).

The conversion of complex <u>XI</u> to complex <u>X</u> in solution complicates the assignment of an accurate chemical shift range and integral to the phenyl groups. This conversion occurs even more readily in THF.

ANALYSIS: Calcd for $C_{32}H_{34}Si_2Ti_2$: C, 67.35; H, 6.02; Si, 9.85. Found: C, 67.42; H, 6.10; Si, 9.77.

II.3.3 Reaction of $PhSiH_3$ with a metastable form of titanocene $[Cp_2Ti]_2$ and its precursor, $[Cp_2TiH]_n$

$[Cp_2TiH]_n$ (0.02 g, 0.28 mmol) was placed in an NMR tube together with C_6D_6 (0.5 mL) and $PhSiH_3$ (0.04 mL, 0.32

mmol). The $PhSiH_3$ was added immediately after the C_6D_6 before decomposition to $[Cp_2Ti]_2$ could occur. The solution became blue immediately upon additon of $PhSiH_3$, and gas evolution commenced. After approximately 20 minutes, the ^1H NMR spectrum was measured. The spectrum observed showed the presence of both complexes <u>X</u> and <u>XI</u>, the ^1H NMR details of which were reported above.

$[Cp_2Ti]_2$ was obtained by stirring $[Cp_2TiH]_n$ (~ 0.18 g, 1.0 mmol) in toluene (10 mL) for 2 hours. The colour changed from greyish/green to black. The solution was reduced to half volume, 2 mL of which was transferred to a Schlenk tube. $PhSiH_3$ (0.05 mL, 0.4 mmol) was then added, whereupon the black solution immediately became dark blue in colour and gas evolution commenced. The solution was left overnight, and the next day a crystalline solid had formed. The supernatant was removed and the solid washed with cold Et_2O (3 x 2 mL) and vacuum dried. The solid was shown to be <u>XI</u> from its ^1H NMR spectrum measured in C_6D_6. The supernatant was pumped dry and ^1H NMR in C_6D_6 showed it to consist of both complexes <u>X</u> and <u>XI</u>, together with some $(HPhSi)_n$ oligomer (the details of the ^1H NMR spectrum of oligophenylsilane will be discussed later).

II.3.4 <u>Reaction of $PhSiH_3$ with $Cp_2Ti(CO)_2$ (16:1 molar ratio)</u>

$PhSiH_3$ (1 mL, 8 mmol) was added to $Cp_2Ti(CO)_2$ (0.119 g, 0.51 mmol) in C_6D_6 (1 mL). Although initially no colour change was noted, very slow gas evolution was observed. The reaction mixture was left for 2 months during which time it gradually darkened in colour through blue to green. A very viscous solution resulted. Removal of a portion to observe the ^1H NMR spectrum indicated complete polymerisation of the $PhSiH_3$. In fact only oligosilane was observed, the ^1H NMR details of which will be given later.

II.3.5 Reaction of $PhSiH_3$ with Cp'_2TiMe_2 (1:1 molar ratio); isolation of μ-hydrido-1(H)1'(Si)-μ-phenylsilyl-tetrakis(η^5-methylcyclopentadienyl)-dititanium(III), $\{[(\eta^5\text{-}C_5H_4CH_3)_2Ti]_2(\mu\text{-}H)(\mu\text{-}HSi(C_6H_5)H)\}$, XII

$PhSiH_3$ (0.11 mL, 0.88 mmol) was added to a solution of freshly recrystallised Cp'_2TiMe_2 (0.21 g, 0.89 mmol) in Et_2O (3 mL). Within a few minutes a rapid colour change from orange to blue/black occurred together with considerable gas evolution lasting a few seconds. The solution was left 16 hours after which time a crystalline solid had formed. The supernatant was decanted and the crystals were vacuum dried to give pure $\{[(\eta^5\text{-}C_5H_4Me)_2Ti]_2(\mu\text{-}H)(\mu\text{-}HSiPhH)\}$ (XII) (0.07 g, 30%). It was found to be extremely air sensitive and pyrophoric.

^1H NMR (toluene-d_8): δ 7.80-6.87 (m, Ph); δ 6.67-4.80 (16H, bm, Cp-H); δ 4.45 (1H, bb, Si-H, $\nu_{\frac{1}{2}}$ = 27 Hz); δ 1.95-1.17 (12H, bm, Cp-CH_3); δ -12.26 (1H, bb, Si-H-Ti, $\nu_{\frac{1}{2}}$ = 53 Hz).

^{1}H NMR (toluene-d_8, −48°C): δ 7.80-6.84 (m, Ph); δ 6.67-4.62 (16H, m, Cp-$\underline{H}$); δ 4.45 (1H, s, Si-$\underline{H}$, $\nu_{\frac{1}{2}}$ = 10 Hz); δ 1.46 (3H, s, Cp-C$\underline{H}_3$), δ 1.42 (3H, s, Cp-C$\underline{H}_3$), δ 1.19 (3H, s, Cp-C$\underline{H}_3$), δ 1.04 (3H, s, Cp-C$\underline{H}_3$); δ −12.09 (1H, s, Si-$\underline{H}$-Ti, $\nu_{\frac{1}{2}}$ = 19 Hz); δ −18.96 (1H, bb, Ti-$\underline{H}$-Ti, $\nu_{\frac{1}{2}}$ = 76 Hz). These NMR results are given for characterisation purposes only. Additional data will be reported later when the variable temperature dependance of the ^{1}H NMR is discussed. Overlap of the phenyl protons with the residual protons of the deuterated solvent prevented accurate peak assignments.

ANALYSIS: Calcd for $C_{30}H_{36}SiTi_2$: C, 69.22; H, 6.97. Found: C, 66.79; H, 7.00.

II.3.6 Reaction of $PhSiH_3$ with Cp'_2TiMe_2 (3:1 molar ratio); attempted isolation of bis(1(H)1'(Si)1(Si')1'(H')-μ-phenylsilyl)-tetrakis(η^5-methylcyclopentadienyl)-dititanium(III), $\{(\eta^5\text{-}C_5H_4CH_3)_2Ti(\mu\text{-}HSi(C_6H_5)H)\}_2$, XIII

$PhSiH_3$ (0.49 mL, 3.9 mmol) was added to a solution of freshly recrystallised Cp'_2TiMe_2 (0.312 g, 1.32 mmol) in toluene (1.5 mL). Within a few minutes a rapid colour change from orange to blue/black occurred together with considerable gas evolution. The latter continued for several hours. The solution was left for 16 hours. No solids had formed after this time and so the solution was cooled in ice. After one day a precipitate had deposited and the supernatant was removed.

The blue-black crystalline solid was washed with cold Et_2O (2 x 5 mL) and pumped dry to give 0.05 g solid material.

^1H NMR (C_6D_6): In addition to peaks assigned to complex XII, the following, assigned to $\{(\eta^5\text{-}C_5H_4Me)_2Ti\text{-}(\mu\text{-}HSiPhH)\}_2$ (XIII), were observed: δ 1.91 (s, Cp-$C\underline{H}_3$), δ 1.51 (s, Cp-$C\underline{H}_3$); δ -8.50 (s, Si-$\underline{H}$-Ti). Accurate integrals were not obtained because of overlap with peaks assigned to XII.

II.3.7 Reaction of $PhSiH_3$ with $Cp^*_2TiMe_2$ (7:1 molar ratio)

A number of reactions were tried and no clear results obtained. The reaction that gave the most information is reported as follows: $PhSiH_3$ (0.05 mL, 0.4 mmol) was added to a solution of $Cp^*_2TiMe_2$ (0.013 g, 0.06 mmol) in C_6D_6/toluene-d_8 0.4 mL). The solution was left for 1 day during which time a very slow gas evolution occurred. The solution slowly darkened in colour from orange to red/orange. After 1 day the ^1H NMR spectrum was measured. A series of variable temperature ^1H NMR spectra were also obtained, the results of which will be discussed later. The spectrum was rerun after several days, and despite such an excess of $PhSiH_3$, little, if any oligophenylsilane was observed.

II.3.8 Reaction of $PhSiH_3$ with $CpCp^*TiMe_2$ (1:1 molar ratio)

$PhSiH_3$ (0.2 mL, 1.60 mmol) was added to a solution of $CpCp^*TiMe_2$ (0.435 g, 1.56 mmol) in Et_2O (7 mL). Within 5 minutes gas evolution had started, and the solution darkened in colour, becoming, after approximately 1 hour, red/brown. The reaction solution was cooled with an ice bath for 5 hours whereupon a brown solid was deposited. The solid was washed with cold Et_2O (2 x 5 mL), however due to its solubility the washings were combined with the original supernatant solution, and the total evaporated to half volume and cooled at -20°C for 16 hours. Removal of the supernatant gave 0.12 g of a brown solid. This was washed with cold Et_2O (1 x 2 mL) and dried under vacuum.

^1H NMR (C_6D_6) δ 2.49-0.86 (bb, Cp-C$\underline{H}_3$, $\nu_{\frac{1}{2}}$ = 62 Hz). The residual proton peak from C_6D_6 overlaps a very broad band, due to protons from Ph and Cp-$\underline{H}$ groups. The broad band is barely noticeable above the baseline. Details of some variable temperature ^1H NMR experiments conducted on this solid will be given later.

ANALYSIS: C, 67.74; H, 7.01.

II.4 REACTION BETWEEN $HxSiH_3$ (Hx = $\underline{n}$-C_6H_{13}) AND Cp_2TiMe_2 (2:1 MOLAR RATIO)

Hexylsilane (0.27 mL, 1.67 mmol) was added to a solution of freshly recrystallised Cp_2TiMe_2 (0.172 g, 0.83 mmol) in Et_2O (3 mL). An immediate, spectacular colour change from orange to blue/black occurred, accompanied by considerable gas evolution which lasted a few minutes. The solution was left at -12°C for a number of hours but no change occurred. The solvent was removed *in vacuo* and the residue dried under vacuum. A portion was dissolved in toluene-d_8 and a ^1H NMR spectrum measured.

^1H NMR (toluene-d_8): μ-hydrido-1(H)1'(Si)-μ-hexylsilyltetrakis(η^5-cyclopentadienyl)-dititanium(III), $\{[(\eta^5\text{-}C_5H_5)_2Ti]_2(\mu\text{-}H)(\mu\text{-}HSiHxH)\}$, *XIV*, δ 5.69, 5.64 (10H, 2 obb, Cp); δ 5.44 (10H, bb, Cp, $\nu_{\frac{1}{2}}$ = 17 Hz); δ 3.75 (1H, bb, Si-$\underline{H}$, $\nu_{\frac{1}{2}}$ = 21 Hz); δ -13.33 (1H, bb, Si-$\underline{H}$-Ti, $\nu_{\frac{1}{2}}$ = 50 Hz). Bis(1(H)1'(Si)1-(Si')1'(H')-μ-hexylsilyl)-tetrakis(η^5-cyclopentadienyl)-dititanium (III), $\{(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}HSiHxH)\}_2$, *XV*, *isomer a*, δ 4.66 (10H, s, Cp), δ 4.57 (10H, s, Cp); δ -10.08 (1H, s, Si-$\underline{H}$-Ti). *Isomer b*, δ 4.64 (10H, s, Cp), δ 4.58 (10H, s, Cp); δ -10.20 (1H, s, Si-$\underline{H}$-Ti). The terminal Si-$\underline{H}$ resonances for the two isomers overlapped and were observed as a complex multiplet at 3.91 ppm. Although this spectrum and the temperature dependance of the ^1H NMR will be discussed later, for full characterisation of complex *XIV*, the following is given.

^1H NMR (toluene-d_8 -58°C): *XIV*, δ 5.64 (5H, s, Cp), δ 5.57 (5H, s, Cp), δ 5.36 (10H, s, Cp); δ 3.87 (1H, bb, Si-$\underline{H}$, $\nu_{\frac{1}{2}}$ = 16 Hz); δ -13.13 (1H, bb, Si-$\underline{H}$-Ti, $\nu_{\frac{1}{2}}$ = 13 Hz); δ -19.52 (1H, bb, Ti-$\underline{H}$-Ti, $\nu_{\frac{1}{2}}$ = 40 Hz). A multiplet assigned to the protons of the *n*-C_6H_{13} groups appears at δ 2.17-0.83. This range does not change with temperature, and consists of protons from both complexes *XIV* and *XV*.

II.5 REACTION BETWEEN BzSiH$_3$ (Bz = $C_6H_5CH_2$) AND Cp_2TiMe_2 (1:1 MOLAR RATIO)

Benzylsilane (0.27 mL, 1.97 mmol) was added to a solution of Cp_2TiMe_2 (0.4 g, 1.92 mmol) in Et_2O (5 mL). An immediate colour change from orange to blue/black occurred with considerable gas evolution for a few seconds. After 10 hours solid material had formed which was washed with cold Et_2O (3 x 3 mL) and vacuum dried to give 0.22 g.

^1H NMR (C_6D_6): μ-hydrido-1(H)1'(Si)-μ-benzylsilyl-tetrakis(η^5-cyclopentadienyl)-dititanium(III), $\{[(\eta^5-C_5H_5)_2-Ti]_2(\mu-H)(\mu-HSiBzH)\}$, XVI, δ 5.65, 5.45 (20H, 2 bb, Cp); δ -12.85 (1H, bb, Si-H-Ti, $\nu_{\frac{1}{2}}$ = 64 Hz). Bis(1(H)1'(Si)1(Si')1'-(H')-μ-benzylsilyl)-tetrakis(η^5-cyclopentadienyl)-dititanium-(III), $\{(\eta^5-C_5H_5)_2Ti(\mu-HSiBzH)\}_2$, XVII, isomer a, δ 4.61 (10H, s, Cp), δ 4.46 (10H, s, Cp); δ 2.64, 2.44 (4H, ABq, Si-CH$_2$, $^2J_{H-H}$ = 13 Hz); δ -10.02 (2H, s, Si-H-Ti). Isomer b, δ 4.58 (10H, s, Cp), δ 4.54 (10H, s, Cp); δ 2.73, 2.52 (4H, ABq, Si-CH$_2$, $^2J_{H-H}$ = 12 Hz); δ -9.73 (2H, s, Si-H-Ti). A multiplet assigned to the protons of the C_6H_5 groups appears at δ 7.60-6.93. This range includes phenyl protons for complexes XVI, XVII and the solvent. For full characterisation of complex XVI, the following is given:

^1H NMR (THF-d_8): XVI, δ 5.76 (20H, bb, Cp, $\nu_{\frac{1}{2}}$ = 21 Hz); δ -13.01 (1H, bb, Si-H-Ti, $\nu_{\frac{1}{2}}$ = 54 Hz).

^1H NMR (THF-d_8 -50°C): XVI, δ 5.69 (5H, s, Cp), δ 5.58 (10H, s, Cp), δ 5.43 (5H, s, Cp); δ -12.92 (1H, bb, Si-$\underline{H}$-Ti, $\nu_{\frac{1}{2}}$ = 14 Hz); δ -19.46 (1H, bb, Ti-$\underline{H}$-Ti, $\nu_{\frac{1}{2}}$ = 53 Hz). The range for C_6H_5 protons in this solvent is δ 7.69-6.72, and includes those from complexes XVI and XVII.

II.6 REACTIONS BETWEEN $PhSiH_3$ AND SOME BIS(η^5-CYCLOPENTADIENYL) DERIVATIVES OF ZIRCONIUM

II.6.1 Reaction of $PhSiH_3$ with Cp_2ZrMe_2 (3:1 molar ratio); isolation of di-μ-hydrido-1-methylphenylsilyl-1'-phenylsilyl-tetrakis(η^5-cyclopentadienyl)-dizirconium (IV), $\{(\eta^5\text{-}C_5H_5)_2[SiH(CH_3)(C_6H_5)]Zr(\mu\text{-}H)_2Zr[SiH_2\text{-}(C_6H_5)](\eta^5\text{-}C_5H_5)_2\}$, XVIII

In a typical reaction, $PhSiH_3$ (1 mL, 8 mmol) was added to a solution of freshly sublimed Cp_2ZrMe_2 (0.66 g, 2.6 mmol), in toluene (5 mL). The solution rapidly changed colour from colourless through yellow to dark orange. The colour change was gradual, in contrast to the analogous titanium reaction. Vigorous gas evolution also occurred. The solution was left 16 hours whereupon orange crystals suitable for X-ray analysis had deposited. These were washed with cold Et_2O (3 x 5 mL) and vacuum dried to give pure $\{(\eta^5\text{-}C_5H_5)_2(SiHMePh)Zr\text{-}(\mu\text{-}H)_2Zr(SiH_2Ph)(\eta^5\text{-}C_5H_5)_2\}$, XVIII (0.33 g, 38%).

^{1}H NMR (C_6D_6): δ 7.69-7.11 (m, Ph); δ 5.50 (5H, s, Cp), δ 5.42 (5H, s, Cp), δ 5.36 (5H, s, Cp), δ 5.27 (5H, s, Cp); δ 4.89 (1H, bm, Si(CH_3)-$\underline{H}$); δ 4.78 (2H, s, Si-$\underline{H}_2$); δ

0.58 (3H, d, Si(H)-C$\underline{H}_3$, $^3J_{H-H}$ = 4 Hz); δ -4.96, -5.09 (2H, ABq, Zr-$\underline{H}_2$-Zr, $^2J_{H-H}$ = 11 Hz).

The range given for the protons of the phenyl groups is not particularly accurate, and no integral is given, due to the overlap of these protons with the residual ^{1}H signal from C_6D_6 which was large due to the low solubility of the complex.

^{1}H NMR (THF-d_8): δ 7.58-7.03 (10H, m, Ph); δ 5.78 (5H, s, Cp), δ 5.70 (5H, s, Cp), δ 5.63 (5H, s, Cp), δ 5.53 (5H, s, Cp); δ 4.57 (1H, bm, Si(CH$_3$)-$\underline{H}$); δ 4.34 (2H, s, Si-$\underline{H}_2$); δ 0.43 (3H, d, Si(H)-C$\underline{H}_3$, $^3J_{H-H}$ = 4 Hz); δ -4.98, -5.03 (2H, ABq, Zr-$\underline{H}_2$-Zr, $^2J_{H-H}$= 11 Hz).

^{29}Si NMR (DEPT, THF-d_8): δ 16 (dbm, $\underline{Si}$(H)(CH$_3$), $^1J_{Si-H}$ = 168 Hz); δ -8 (td, $\underline{Si}$-H$_2$, $^1J_{Si-H}$ = 158.1 Hz, $^2J_{Si-(Zr)-H}$ = 4.4 Hz).

ANALYSIS: Calcd for $C_{33}H_{38}Si_2Zr_2$: C, 58.87; H, 5.69; Si, 8.34. Found: C, 58.41; H, 5.86; Si, 8.73.

II.6.2 Reaction of PhSiH$_3$ with [Cp$_2$ZrH$_2$]$_n$ (4.5:1 molar ratio); attempted isolation of di-μ-hydrido-1,1'-bis-(phenylsilyl)-tetrakis(η^5-cyclopentadienyl)-dizirconium(IV), {(η^5-C$_5$H$_5$)$_2$Zr(μ-H)[$\dot{S}$iH$_2$(C$_6$H$_5$)]}$_2$, XIX

In a typical reaction, PhSiH$_3$ (1 mL, 8 mmol) was added to [Cp$_2$ZrH$_2$]$_n$ (0.4 g, 1.79 mmol) in THF (5 mL). Upon addition of silane, the reaction mixture became pale yellow. In addition, slow gas evolution was observed. After approximately 16 hours, all the hydride had dissolved and the solution was a dark orange/brown in colour. No solid was obtained upon cooling the solution. Addition of less polar solvents and cooling did not give a precipitate. The volatiles were removed from the reaction mixture to give an oily gum. This was dissolved in C_6D_6 and a ^1H NMR spectrum was obtained.

^1H NMR residue (C_6D_6): δ 8.22-6.58 (bm, Ph); δ 6.39-4.41 (bm, Si-H/Cp); δ 5.40 (s, Cp); δ -4.93 (s, Zr-H_2-Zr).

II.7 REACTION BETWEEN $BzSiH_3$ AND Cp_2ZrMe_2 (3:1 MOLAR RATIO)

Benzylsilane (0.56 mL, 4.1 mmol) was added to a solution of freshly sublimed Cp_2ZrMe_2 (0.347 g, 1.4 mmol) in Et_2O (5 mL) which had been filtered through celite. The solution was left overnight during which time it steadily became a darker orange/brown colour. Steady gas evolution occurred during this time. After completion of the reaction, an orange/brown cyrstalline solid had deposited. This was washed with cold Et_2O (3 x 2 mL) and dried *in vacuo* to give 0.2 g of product.

^1H NMR (THF-d_8): Di-μ-hydrido-1-methylbenzylsilyl-1'-benzylsilyl-tetrakis(η^5-cyclopentadienyl)-dizirconium(IV), $\{(\eta^5\text{-}C_5H_5)_2(SiHMeBz)Zr(\mu\text{-}H)_2Zr(SiH_2Bz)(\eta^5\text{-}C_5H_5)_2\}$, XX, δ 4.09 (1H, bm, Si(CH_3)-H); δ 3.83 (2H, t, Si-H_2, $^3J_{H-H}$ = 6 Hz); δ 2.22 (4H, t, Si-CH_2-, $^3J_{H-H}$ = 6 Hz); δ 0.07 (3H, d, Si(H)CH_3,

$^{3}J_{H-H}$ = 4 Hz); δ -5.28, -5.11 (2H, ABq, Zr-$\underline{H}_2$-Zr, ^{2}J = 11 Hz). Di-μ-hydrido-1,1'-bis(benzylsilyl)-tetrakis(η^5-cyclopentadienyl)-dizirconium(IV), $\{(\eta^5-C_5H_5)_2Zr(\mu-H)(SiH_2Bz)\}_2$, XXI, δ 3.83 (4H, t, Si-$\underline{H}_2$, $^{3}J_{H-H}$ = 6 Hz); δ 2.22 (4H, t, Si-C$\underline{H}_2$-, $^{3}J_{H-H}$ = 6 Hz); δ -5.13 (2H, s, Zr-$\underline{H}_2$-Zr). Peaks attributed to the cyclopentadienyl groups of XX and XXI are present as a multiplet occurring at δ 5.79-5.73. Although these peaks are not distinguishable in THF-d_8, they are clearly visible as a set of 4 singlets together with an overlapping larger singlet in C_6D_6. Peak positions for the cyclopentadienyl groups in this solvent are as follows, XX: δ 5.420, δ 5.413, δ 5.405 and δ 5.392. XXI: δ 5.400. These are given to three decimal places because 5 peaks were clearly visible and if rounded off to two decimal points (± 0.05 ppm), they would not be distinguishable. Phenyl protons are present as a multiplet at δ 7.29-6.85 but due to overlap of those from both complexes XX and XXI, no assignment is possible.

II.8 ^{1}H NMR STUDIES OF THE Cp_2TiMe_2 CATALYSED POLYMERISATIONS OF $RSiH_3$, WHERE R = Ph, Hx AND Bz AND OF $RSiD_3$, WHERE R = Ph AND Bz

A number of reactions were performed, and studied in situ by ^{1}H NMR spectroscopy. All measurements were done on a Varian-XL-200 spectrometer. In a typical experiment a relatively large excess of silane (~ 0.38-1.7 mmol) was added to a solution of freshly recrystallised Cp_2TiMe_2, (0.04-0.12 mmol) in deuterated solvent (~ 0.4 mL - usually C_6D_6) in a 5 mm NMR tube. Typically 4 transients were collected, and the sample was removed from the probe between acquisitions. The NMR tube was sealed with a rubber septum which facilitated periodic release of pressure built up by the gas evolution simply by piercing it with a steel needle. The initial violent nature of the gas evolution necessitated great care and rapid removal of the sample from the probe after the spectrum had been accumulated. Generally, spectra were run every 2 or 3 minutes for the first 10 minutes and then at longer intervals as the reaction slowed. As polymerisation to oligosilane occurs over several days, the continuing slow gas evolution required periodic release of excess gas, and storage of the whole NMR tube under argon. The experimental details are given in TABLE II.3. A discussion of the reaction is given in APPENDIX I.

II.9 ^{1}H NMR STUDIES OF THE Cp_2ZrMe_2 CATALYSED POLYMERISATIONS OF $RSiH_3$, WHERE R = Ph AND Bz, AND OF $PhSiD_3$

The general experimental procedure used was the same as that given above for Cp_2TiMe_2. The experimental conditions for the $CpZrMe_2$ reactions are given in TABLE II:4. A discussion of the reaction is given in APPENDIX II.

TABLE II.3: EXPERIMENTAL DETAILS FOR REACTIONS OF PRIMARY SILANES WITH Cp_2TiMe_2 AS FOLLOWED BY ^1H NMR[a,b]

SILANE	Cp_2TiMe_2 (MOLES)	SILANE/Cp_2TiMe_2 (MOLAR RATIO)
$PhSiH_3$	12×10^{-5}	20
$PhSiH_3$[c]	4.2×10^{-5}	9
$PhSiD_3$	12×10^{-5}	20
$BzSiH_3$	3.8×10^{-5}	44
$BzSiD_3$	3.8×10^{-5}	45
$HxSiH_3$	12×10^{-5}	15

[a] at ambient temperature [b] in C_6D_6 [c] in THF-d_8

TABLE II.4: EXPERIMENTAL DETAILS FOR REACTIONS OF PRIMARY SILANES WITH Cp_2ZrMe_2 AS FOLLOWED BY ^1H NMR[a,b]

SILANE	Cp_2ZrMe_2 (MOLES)	SILANE/Cp_2ZrMe_2 (MOLAR RATIO)
$PhSiH_3$	12×10^{-5}	21
$PhSiD_3$	12×10^{-5}	19
$BzSiH_3$	20×10^{-5}	2

[a] at ambient temperature [b] in C_6D_6

II.10 CHARACTERISATION OF SOME OLIGOSILANES PREPARED FROM PRIMARY SILANES BY REACTION WITH Cp_2TiMe_2/Cp_2ZrMe_2

II.10.1 Preparation of oligomers

Two oligomers were prepared and characterised by ^1H and ^{29}Si DEPT NMR, IR and molecular weight measurements. These were the oligosilanes resulting from the polymerisation of $PhSiH_3$ using Cp_2TiMe_2 or Cp_2ZrMe_2 and $HxSiH_3$ using Cp_2TiMe_2. Typically oligomers were prepared by adding the silane (usually 50-100 mole excess) to a solution of the dimethyl metallocene (usually 25-50 mg) in toluene (5 mL). Gas evolution and the same colour changes as described earlier occurred. The solution was stirred at ambient temperature unless otherwise indicated, for 2 days. After this time the volatiles were removed and collected. Their ^1H NMR spectrum, taken on either a Varian T60 or T60A instrument, showed complete absence of the parent silane. Removal of the metal-containing species from the oligomers proved difficult, but passage of the reaction mixture dissolved in toluene through a florisil column in air removed most of them.

$(HPHSi)_n$: IR (pentane film): ν(Si-H) 2085 cm^{-1}, "q" (Whiffen's notation (141)) 1100 cm^{-1}, δ(Si-H) 910 cm^{-1}. ^1H NMR (C_6D_6): δ 8.00-6.72 (5H, bm, Ph); δ 5.43-4.29 (1H, bm, Si-$\underline{H}$). ^{29}Si NMR (DEPT, C_6D_6): δ-55 to -59 (m, $\underline{Si}$-H_2); δ-59 to -66 (m, $\underline{Si}$-H).

$(HHxSi)_n$: IR (neat): ν(Si-H) 2080 cm^{-1}, δ(Si-H) 940 cm^{-1}. ^1H NMR (C_6D_6): δ 4.13-3.81 (1H, bb, Si-<u>H</u>); δ 1.81-0.68 (13H, m, Hx). ^{29}Si NMR (DEPT, C_6D_6): δ-54 to -57 (m, <u>Si</u>-H_2); δ-57 to -68 (m, <u>Si</u>-H).

II.10.2 Oligomer molecular weight studies.

In the case of $(HPhSi)_n$, a number of reaction conditions were used in its preparation in order to examine the effect of these on its molecular weight. This study was by no means exhaustive. Prior to the molecular weight measurement, the samples were checked for oxidation by recording the infrared spectrum (a large band at 1100 cm^{-1} appears if oxidation has occurred). This was repeated after the measurement. Experimental conditions of the reactions used to prepare the polymers for the molecular weight studies are given in TABLE II.5.

TABLE II.5: EXPERIMENTAL CONDITIONS FOR THE PREPARATION OF OLIGOMERS USED IN MOLECULAR WEIGHT STUDIES[a]

OLIGOMER	CATALYST PRECURSOR
A) $(HPhSi)_n$	Cp_2TiMe_2 (2 mol %)
B) $(HPhSi)_n$[b]	Cp_2TiMe_2 (2 mol %)
C) $(HPhSi)_n$	Cp_2TiMe_2 (10 mol %)
D) $(HPhSi)_n$	Cp_2ZrMe_2 (1 mol %)
E) $(HHxSi)_n$	Cp_2TiMe_2 (2 mol %)

[a] ambient temperature/2days

[b] 60°C/40 mins followed by ambient temperature/2 days

CHAPTER III

RESULTS AND DISCUSSION

III.1 THE CHARACTERISATION OF $\{[(\eta^5\text{-}C_5H_5)_2Ti]_2(\mu\text{-}H)\text{-}(\mu\text{-}HSi(C_6H_5)H)\}$, $\underline{X}$

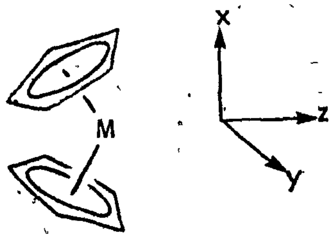
III.1.1 Reaction of $PhSiH_3$ with Cp_2TiMe_2 (1:1 molar ratio); isolation of complex $\underline{X}$

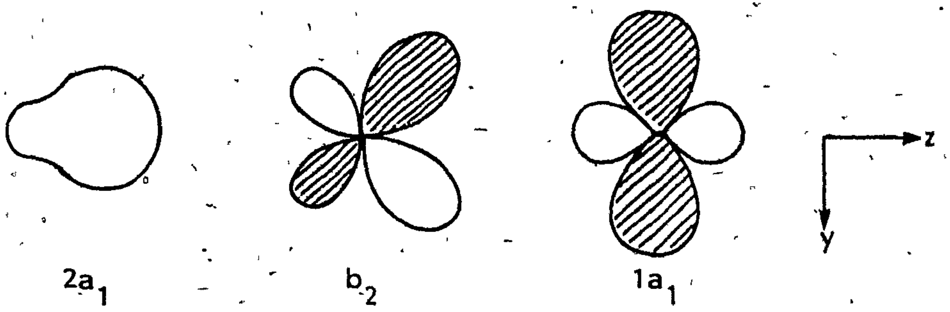
Pure $\underline{X}$ may be isolated by the reaction (1:1 stoichiometric ratio) of $PhSiH_3$ with Cp_2TiMe_2. When diethylether is the reaction solvent, the organosilane products remain in solution. Based on those products observed in the ^1H NMR spectrum (C_6D_6), the reaction equation is given below:

$$2Cp_2TiMe_2 + 3PhSiH_3 \xrightarrow{Et_2O} 2MeH + 2MePhSiH_2 + \underset{\underline{X}}{\{(Cp_2Ti)_2(\mu\text{-}H)(\mu\text{-}HSiPhH)\}} \qquad \text{III.1}$$

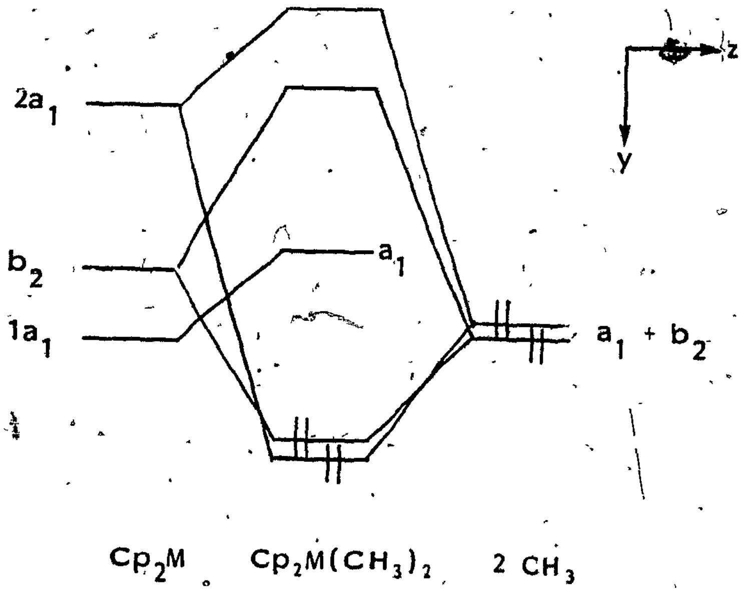
Based on this equation, an excess of dimethyltitanocene was present. When the ratio of Cp_2TiMe_2 to $PhSiH_3$ was greater than 1:1, a black oil was obtained. The ^1H NMR spectrum (C_6D_6) showed that it contained traces of $\underline{X}$ as well as a mixture of other cyclopentadienyl compounds. In addition to this, a singlet was observed at -7.6 ppm in C_6D_6, possibly due to a bridging Si-H-Ti species. It is possible that given the propensity of low valent titanocene species to rearrange to $\eta^5{:}\eta^5$-fulvalene ($C_{10}H_8$)-containing complexes (100), this could account for the complicated cyclopentadienyl region observed. In the case where the stoichiometry of Cp_2TiMe_2 to $PhSiH_3$ was 1:1, the fate of the excess titanium was not determined. When the ratio of Cp_2TiMe_2 to $PhSiH_3$ was less than 1:1, complex XI was formed in addition to complex X. In this case H_2 evolution was also observed together with the buildup of oligophenylsilane.

One interesting aspect of the reaction is the source of the hydrogen in the methane which is produced (equation III.1). When $PhSiD_3$ was reacted with Cp_2TiMe_2, the characteristic triplet at 0.17 ppm for CH_3D was observed in the ^1H NMR spectrum (C_6D_6), consistent with the conclusion that the evolved methane obtained its proton from the silane. This result is important as it shows that the cyclopentadienyl protons and the protons of the other methyl group are not involved in the production of methane. It was observed that methane evolution began before the intense blue colour of X was observed, and before the formation of methylphenylsilane, $MePhSiH_2$. A number of possibilities exist to account for this. However, since Cp_2TiMe_2 is a Ti(IV) d^0 complex, initial oxidative addition of $PhSiH_3$ seems unlikely. A theoretical study of the electronic structure of Cp_2ML_n molecules ($n =$ 1-3) has shown that bent Cp_2M fragments possess three low-lying frontier orbitals, the shapes of which, together with the associated coordinate system are shown below (142):



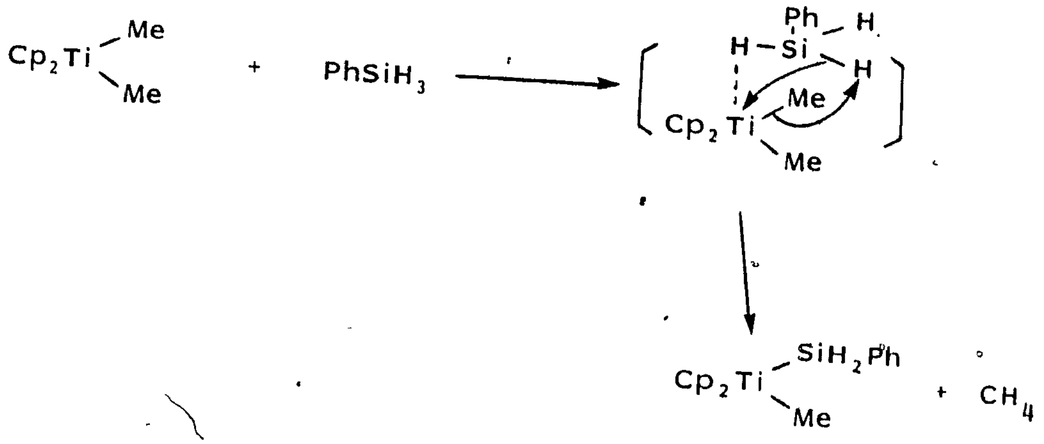


The interaction of the frontier molecular orbitals of a Cp_2M unit with two σ-donor ligands such as CH_3 is shown below:

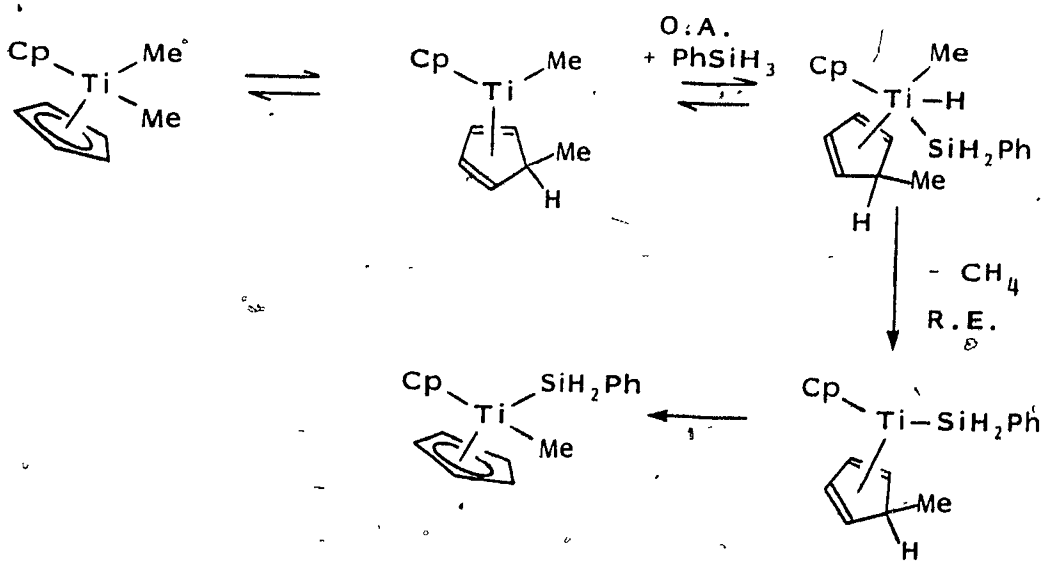


Thus dialkyl complexes such as Cp_2TiMe_2 possess one low-lying empty orbital, the $1a_1$. This is a laterally extending orbital, and represents the lowest lying acceptor orbital for the electron pair of an incoming ligand. Thus, initial interaction between $PhSiH_3$ and Cp_2TiMe_2 leading to the evolution of methane, may occur via the utilisation of this orbital. Two possible ways in which this might occur are shown in SCHEMES III.1 and III.2.

Both SCHEMES III.1 and III.2 have no precedant in silane chemistry, although they have been postulated to account for some reactions of alkylhydride zirconocene derivatives with H_2. SCHEME III.1 is proposed in analogy to the heterolytic separation of a coordinated molecule of H_2 into a hydride and a proton, proposed by Gell and Schwartz to account for the H_2 dependant alkane elimination from Cp_2ZrHR (111), which was in turn proposed in analogy to the reaction between $[Cp_2ZrH_2]_n$ and $HAlR_2$ (143). SCHEME III.2 is proposed in analogy with the mechanism suggested by McAlister <u>et al</u>. to account for the fact that $Cp^*_2ZrH(CH_2CHMe_2)$ does not undergo simple reductive elimination of alkane upon pyrolysis (144). Instead, the alkyl group was found to abstract a hydrogen atom from one of the cyclopentadienyl methyl groups or from molecular hydrogen when available, leading to the production of isobutane. In considering the reaction of $PhSiH_3$ with Cp_2TiMe_2, SCHEME III.1 seems perhaps the most plausible. The production of a 5-coordinate intermediate with electrophilic attack on a coordinated methyl group could give rise to methane. SCHEME



SCHEME III.1



SCHEME III.2

III.2 seems less likely. Reduction of Ti(IV) to Ti(II) by metal-to-ring methyl transfer, followed by oxidative addition of $PhSiH_3$ seems conceivable as does the subsequent reductive elimination of methane. However, one might also expect ring-to-metal hydrogen transfer. This would lead to H/D exchange of the ring protons in the presence of $PhSiD_3$ which does not occur. Both SCHEMES III.1 and III.2 give rise to an identical titanium silyl species which can undergo reductive elimination to generate methylphenylsilane and "Cp_2Ti" according to the following equation:

$$Cp_2TiMe(SiH_2Ph) \underset{}{\overset{R.E}{\rightleftharpoons}} "Cp_2Ti" + MePhSiH_2 \qquad III.2$$

The precise structure of titanocene has not been determined due in part to its high reactivity, and so it is represented as "Cp_2Ti".

The initial observation of methane from the reaction may also be accounted for in terms of free radical production. Samuel et al. have studied the photolysis of Cp_2TiMe_2 using ESR spectroscopy, and have suggested that the primary process is the loss of a methyl radical to produce $Cp_2Ti^{III}Me$ as shown in SCHEME III.3 (145).

$$Cp_2TiMe_2 \xrightarrow{h\nu} Cp_2Ti^{III}Me + \cdot Me$$

$$2Cp_2Ti^{III}Me \xrightarrow{\Delta} [Cp_2Ti^{III}Me]_2$$

$$[Cp_2Ti^{III}Me]_2 \xrightarrow{h\nu} Cp_2Ti + \cdot Me$$

$$Cp_2Ti + Cp_2TiMe_2 \xrightarrow{\Delta} 2Cp_2Ti^{III}Me$$

$$2Cp_2Ti^{III}Me \xrightarrow{\Delta} [Cp_2Ti^{III}Me]_2$$

SCHEME III.3

Experiments suggest that the reaction between silanes and Cp_2TiMe_2 may be photoinitiated. Methyl radicals produced via SCHEME III.3 could abstract a hydrogen atom from phenylsilane to produce methane and phenylsilyl radicals. The fact that neither ethane nor disilane is observed in any of the reactions studied could be indicative of the reactivity of the parent radicals. A possible reaction of $PhSiH_3$ with methyl radicals produced in SCHEME III.3, and a subsequent reaction of SiH_2Ph radicals with Cp_2TiMe_2 is shown in equations III.3 and III.4, respectively.

$$\cdot Me + PhSiH_3 \longrightarrow MeH + \cdot SiH_2Ph \qquad III.3$$

$$\cdot SiH_2Ph + Cp_2TiMe_2 \longrightarrow MePhSiH_2 + Cp_2Ti^{III}Me \qquad III.4$$

The species $Cp_2Ti^{III}Me$ could then reenter the cycle given in SCHEME III.3.

In order to account for the production of complex X, formed during the reaction of $PhSiH_3$ with Cp_2TiMe_2, the titanocene moiety, Cp_2Ti, must remain intact. The production of a "Cp_2Ti" species can be inferred from the production of $Cp_2Ti(CO)_2$ when the reaction is carried out under CO gas. Purging of the reaction solution with argon leads to production of complex X. It seems likely therefore that the CO intercepts "Cp_2Ti". Such species are highly reactive (100), and would likely react immediately with either dimethyltitanocene as shown in SCHEME III.3, or with $PhSiH_3$ according to equations III.5 and III.6, to give X:

$$\text{"}Cp_2Ti\text{"} + PhSiH_3 \xrightleftharpoons{O.A.} Cp_2TiH(SiH_2Ph) \qquad \text{III.5}$$

$$Cp_2TiH(SiH_2Ph) + \text{"}Cp_2Ti\text{"} \rightleftharpoons \underset{\underline{X}}{\{(Cp_2Ti)_2(\mu\text{-}H)(\mu\text{-}HSiPhH)\}} \qquad \text{III.6}$$

Reaction of "Cp_2Ti" must occur rapidly, before rearrangement to fulvalene containing dimers such as $\{[(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}H)]_2\text{-}(\mu\text{-}C_{10}H_8)\}$ can occur. Further evidence for the involvement of "Cp_2Ti" was obtained from the reaction of metastable titanocene, $[Cp_2Ti]_2$ (103), and its precursor $[Cp_2TiH]_n$ (103) with $PhSiH_3$. In both cases, complex X was produced together with complex XI and oligophenylsilane. Thus it is reasonable to propose that "Cp_2Ti" is an important intermediate in these reactions. Cp_2TiMe_2 acts as a precursor, generating "Cp_2Ti" due to its propensity to generate methyl radicals.

In addition, $Cp_2Ti(CO)_2$ was found to react very slowly with $PhSiH_3$ to produce X and XI as well as oligophenylsilane. In this case a very slow gas evolution was observed along with a gradual colour change. This further suggests that it is "Cp_2Ti" that is important in the formation of complexes X and XI, as well as in the polymerisation of primary silanes, which will be discussed later.

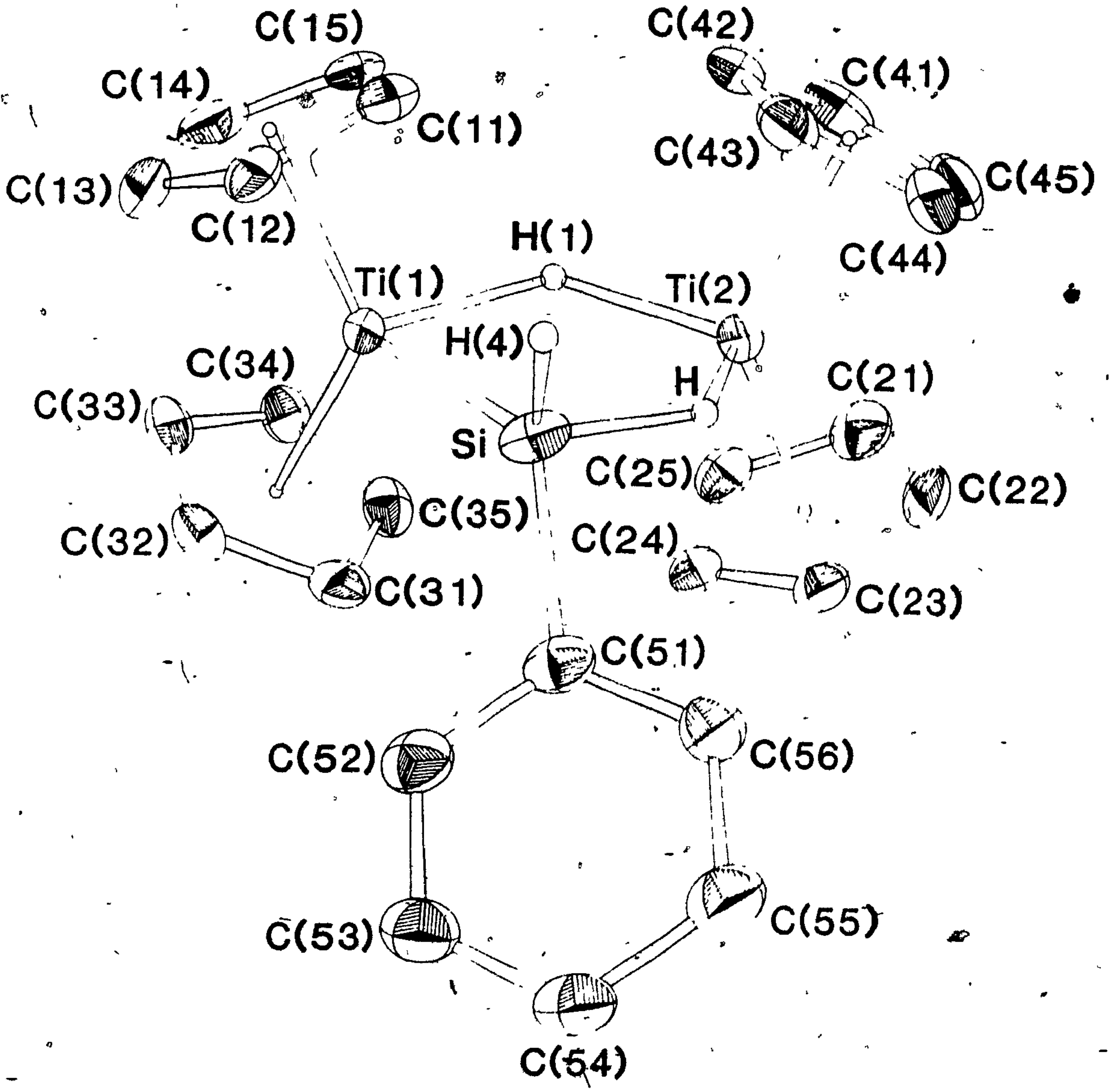
III.1.2 The molecular structure

The X-ray structural analysis of X has provided the detailed molecular configuration of this unique titanium silyl complex. The experimental details for the X-ray crystal structure determination, as performed by Dr. M. Simard, Université de Montréal, are given in APPENDIX III. APPENDIX IV, TABLES AIV-A to J, lists all crystal structure data, positional parameters, anisotropic thermal parameters, structure factor amplitudes (calculated and observed), interatomic angles and distances and some selected least squares planes as obtained from the Université de Montréal. Complex X exists as two enantiomers which co-crystallised in the crystal lattice, leading to disorder. A perspective view of one enantiomer is shown in FIGURE III.1. FIGURE AIV-A, APPENDIX IV gives a diagrammatic representation of X plus the full numbering scheme, taking into account the disorder, in order to correspond to the tables in APPENDIX IV.

Initial attempts at refinement gave an R value of 6.1% for a molecule containing two Cp_2Ti units bridged by a H atom and a $PhSiH_3$ molecule (ie, a 6-membered Ti_2SiH_3 ring). This was however, completely incompatible with the ^1H NMR results. Moreover, the silicon atom had an unusually large anisotropy. Two silicon and two hydrogen atom positions Si(1)H(2) and Si(2)H(3) were introduced (FIGURE AII-A), and refined with half occupancy in each. This gave a final R value of 4.6%.

In the tables in APPENDIX IV the two silicons Si(I) and Si(2), and the two bridging hydrides Ti-H-Si, H(2) and H(3), are listed. There is, however, only one set of coordinates for all other atoms in the molecule, including the phenyl group and hydride (H(4)) bound to the silicon. A brief explanation of the disorder present in this molecule is relevant at this point. FIGURE III.1 represents an idealised enantiomer, wherein all bond lengths and angles relevant to the central bridging part of the molecule (TABLE III.1) are given as averages of the two enantiomers. It is interesting to note that the distance between Si(1) and Si(2) is so small

FIGURE III.1: A PERSPECTIVE VIEW OF ONE ENANTIOMER OF $\{[(\eta^5\text{-}C_5H_5)_2Ti]_2(\mu\text{-}H)(\mu\text{-}HSiPhH)\}^{a,b}$



[a] phenyl and Cp hydrogen atoms omitted for clarity

[b] ellipsoids correspond to 50% probability level

TABLE III.1: SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR $\{[(\eta^5\text{-}C_5H_5)_2Ti]_2(\mu\text{-}H)(\mu\text{-}HSiPhH)\}^{a,b}$

LENGTHS	
Ti(1)-Ti(2)	3.461(1)
Ti(1)-Si	2.61 (3)
Ti(1)-H(1)	1.97 (4)
Ti(2)-H(1)	1.97 (3)
Ti(2)-H	1.58 (8)
Ti(2)-Si	2.79 (3)
Si-C(51)	1.94 (3)
Si-H	1.55 (9)
Si-H(4)	1.49 (4)

ANGLES		
H(1)-Ti(2)-H	102	(4)
H(1)-Ti(1)-Si	80	(1)
Ti(1)-Si-C(51)	128.7	(13)
Ti(1)-Si-H	106	(4)
Ti(1)-Si-H(4)	117	(3)
Ti(1)-H(1)-Ti(2)	123	(2)
Ti(2)-H-Si	126	(6)
C(51)-Si-H	98	(4)
C(51)-Si-H(4)	101	(3)
H-Si-H(4)	99	(4)
C(1G)-Ti(1)-C(3G)	130.6	(1)
C(2G)-Ti(2)-C(4G)	131.1	(1)

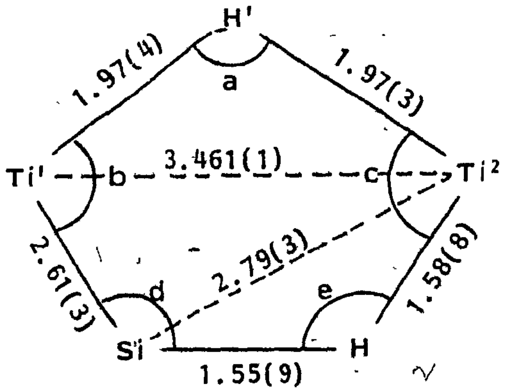
[a] the molecule appears to be disordered in the lattice with the Si-H-Ti group adopting one of two orientations. Bond lengths and angles involving atoms not numbered are averages of the lengths and angles obtained for the two enantiomers (see FIGURE AIV-A and TABLES AIV-F and AIV-G in APPENDIX IV)

[b] C(1G) = centroid of ring containing carbons C(11) to C(15)
C(2G) = centroid of ring containing carbons C(21) to C(25)
C(3G) = centroid of ring containing carbons C(31) to C(35)
C(4G) = centroid of ring containing carbons C(41) to C(45)

(~ 0.3 Å) that the phenyl group and H(4) show no disorder. The bond distances Ti(1)-H(1) and Ti(2)-H(1) were constrained to be equal as this was the only way in which they could be refined. It is possible that this is a reflection of the disorder present in the molecule.

The molecular structure of complex X consists of two Cp_2Ti units bridged by one hydrogen atom and a HSiPhH moiety to give an essentially planar, 5-membered ring. This planar central unit (FIGURE III.2) contains two 2-electron, 3-centre, bonds Ti-H-Ti and Ti-H-Si, in addition to a Ti-Si bond.

FIGURE III.2: THE CENTRAL BRIDGING UNIT OF COMPLEX X, Ti_2SiH_2 [a,b]



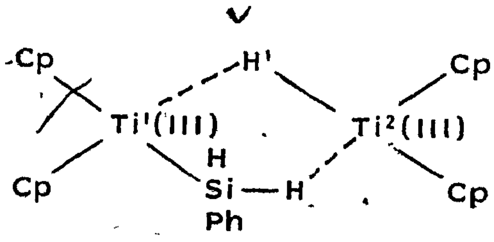
a = 123(2)°
b = 80(1)°
c = 102(4)°
d = 106(4)°
e = 126(6)°

[a] non-bonded distances are represented by dashed (---) lines

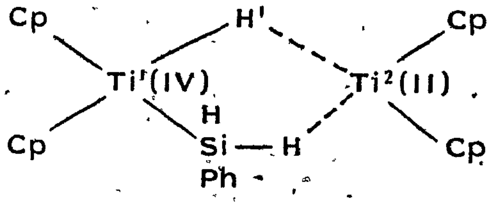
[b] bond lengths are given in Angstroms (Å) and bond angles in degrees (°)

To our knowledge, there are only two other compounds which contain a Ti-Si bond, namely, $\{Cp_2TiSiH_2\}_2$ (132) and $Cp_2TiCl(SiMe_3)$ (126). Complex X, therefore, is the first compound containing a Ti(III)-Si bond. In addition, the Ti-H-Si-Ti bridge in X is unprecedented.

The Ti-Si bond distance of 2.61 Å in X is very similar to that reported for $Cp_2TiCl(SiMe_3)$ (2.67 Å) by Rösch et al. (126). Thus although a number of valence structures are possible, in the solid state, structures XA and XB seem equally plausible:

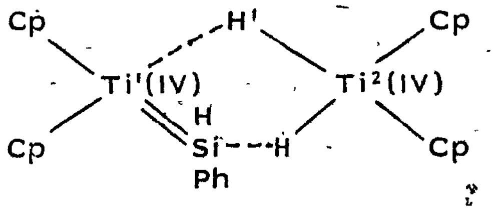


XA



XB

^1H NMR solution studies, however, indicated the presence of a paramagnetic species in low concentration, suggestive of XA, wherein the titanium atoms are in the +3 oxidation state. In such a case, backbonding into the vacant Si 3d orbitals can occur, which would tend to strengthen and shorten the observed bond. For X, either this effect is negligible, or is counteracted by an increase in bond length, expected for a bond involving Ti(III) (compared to one involving Ti(IV)). A third possible valence structure, XC, may be reasonably eliminated solely on the basis of the Ti-Si bond length, which is that expected for a Ti-Si single bond and not shortened as might be expected.



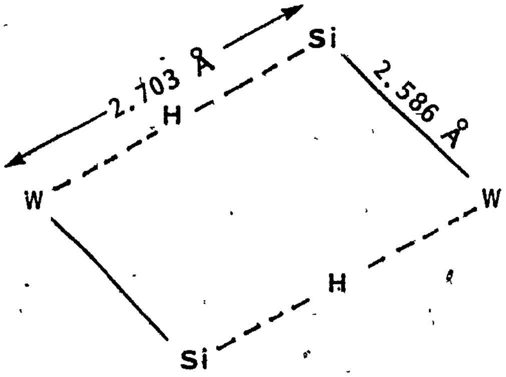
XC

XC is also not consistent with the paramagnetism detected in the ^1H NMR solution studies of X.

The bond distances Ti(1)-H(1) and Ti(2)-H(1) (1.97 Å, see FIGURE III.2), although constrained to be equal in the refinement, are comparable to the Ti-H bond distance obtained for the bridging hydride Ti-H-Ti in $\{[(\eta^5-C_5H_5)Ti]_2(\mu-H)-(\mu-H_2AlEt_2)(\mu-C_{10}H_8)\}$ (1.80 Å) (115). It has been suggested that significant distortion of a 2-electron, 3-centre bond from a symmetric configuration cannot occur (146). This was supported by the neutron diffraction study of {$HW_2(CO)_8(NO)$-$(P(OCH_3)_3)$} where the two W-H bond lengths were found to be the same.

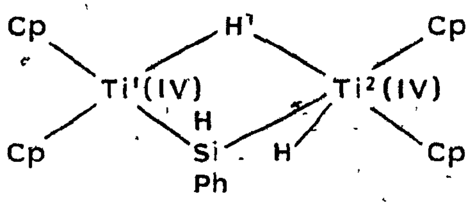
Complex X provides the first example where X-ray diffraction has confirmed the interaction of a silicon hydrogen group with a transition metal centre. Such 2-electron, 3-centre bonds have been suggested before. Although the true nature of the bonding was not unequivocally established, {$W_2(CO)_8H_2[Si(C_2H_5)_2]_2$} was thought to possess two Si-H-W bridges on the basis of the two different W-Si distances (147). The central bridge system of this complex is shown in Figure III.3.

FIGURE III.3: THE PLANAR BRIDGING UNIT OF {$W_2(CO)_8H_2$-$[Si(C_2H_5)_2]_2$}



Precedance for a similar type of bond has also been shown for the C-H moiety where the hydrogen atom may bridge the carbon and a transition metal atom, forming so-called "agostic" interactions (148,149). Evidence for agostic C-H-M interactions was initially obtained from X-ray crystal structure determinations where short M-C distances were observed. Subsequent neutron diffraction studies showed that the C-H bridging bond distances were 5-10% longer than for analogous terminal C-H bonds (148). Although the bridging silyl of <u>X</u> possesses an Si-H bond distance of 1.55 Å, comparable to a normal Si-H terminal bond length (1.49 Å) (150), the Ti(2)-H distance of 1.58 Å is clearly a bonding distance.

A fourth valence structure for <u>X</u> is possible, <u>XD</u>. The non-bonded Ti(2)-Si distance at 2.79 Å is however longer than the bonded Ti(1)-Si distance at 2.61 Å. As discussed earlier, two different M-Si distances within the same molecule have been used to infer the presence of a bridging hydride in the longer distance (147). In addition, such a structure as <u>XD</u> is not compatible with the ^{1}H NMR solution studies.



<u>XD</u>

The Ti(1)-Ti(2) distance for X is 3.46 Å which is longer than the analogous distances in $\{[(\eta^5-C_5H_5)Ti]_2(\mu-H)(\mu-H_2AlEt_2)(\mu-C_{10}H_8)\}$ (3.37 Å) (115) and $\{[(\eta^5-C_5H_5)Ti(\mu-OH)]_2(\mu-C_{10}H_8)\}$ (3.19 Å) (101) which are proposed to be non-bonding. It seems unlikely that Ti-Ti single bonds are present in these molecules although it has been suggested that in bridged systems, M-M distances may not be good criteria for the presence of bonds (151). Interestingly however, interaction between the titanium centres is observed in both cases. Magnetic susceptibility measurements have shown that $\{[(\eta^5-C_5H_5)Ti]_2(\mu-H)(\mu-H_2AlEt_2)(\mu-C_{10}H_8)\}$, VII, is diamagnetic in the solid state possibly as a result of superexchange via the bridging H atom (115). In addition, $\{[(\eta^5-C_5H_5)Ti(\mu-OH)]_2(\mu-C_{10}H_8)\}$ has been described as only weakly paramagnetic due to superexchange taking place through the bridges. Despite the large Ti-Ti separation, direct overlap of the metal centres was not entirely ruled out (101). Although a study of the magnetic properties of complex X has not been carried out, ^1H NMR solution studies suggest that it is only weakly paramagnetic. Thus despite the Ti(1)-Ti(2) separation, some degree of interaction between the two metal centres seems likely. It is possible that this interaction occurs via superexchange through the bridging hydride in the Ti-H-Ti moiety. This may help to explain why the bonded Ti(1)-Si distance is close to that observed in a terminal silyl complex. If superexchange occurred in valence structure XA, the electrons on the Ti(III) atoms would be unavailable for backbonding into the empty Si 3d orbitals.

It has already been mentioned that the Ti-H-Ti and Ti-H-Si bridges in X are electron deficient, 2-electron, 3-centre bonds. The positional accuracy of the hydrogen atom, obtained by X-ray diffraction in such bonds is often low due to the low X-ray scattering power of the hydrogen atom. It is only recently that the extent of these errors has been realised, from comparison of X-ray and neutron diffraction data for a number of complexes (152,153). It has been found that X-ray methods usually give shorter M-H distances and larger M-H-M bond angles than neutron diffraction. This is due to the covalency present in the M-H bond. Thus the X-ray determined position of the hydrogen atom in the M-H-M species tends to reflect the location of the electron density. Neutron diffraction studies however give the internuclear separations since neutrons are scattered with similar efficiency by hydrogen as by other atoms. Thus the two techniques are complementary and studies have shown that the region of maximum orbital overlap in M-H-M bonds is displaced toward the M-M internuclear vector (152,153). This suggests a significant amount of metal-metal interaction must be present in bridging hydrides of the type M-H-M, consistent with a "closed" representation for the M-H-M bond (152). In this case, the two metal hybrid orbitals and the hydrogen 1s orbital overlap in a common region of space. The Ti(1)-H(1)-Ti(2) bond angle for X

(123°) is similar to that obtained for the Th-H-Th bond angle (122°) in $\{Cp^*_2ThH(\mu\text{-}H)\}_2$ (154) and for the Zr-H-Zr bond angle (120°) in $\{Cp'_2ZrH(\mu\text{-}H)\}_2$ (117). The aluminium complex VII, however, has a Ti-H-Ti bridgehead angle of 138° (115). The Ti(2)-H-Si angle for X (126°) is comparable in magnitude to the analogous Ti-H-Al angle (135°) obtained for VII.

In conclusion, $\{[\eta^5\text{-}C_5H_5)_2Ti]_2(\mu\text{-}H)(\mu\text{-}HSiPhH)\}$ is the first example of a complex containing a hydrogen atom bridging a silyl group to an early transition metal. The X-ray crystal structure determination along with that for complex XI provides the first conclusive structural evidence for hydrogen bridging silicon to any transition metal, although such bridges are well known in aluminium and boron chemistry.

III.1.3 Variable temperature ^1H NMR studies

The ^1H NMR spectrum of X was initially obtained at ambient temperature in C_6D_6. In addition to peaks observed from the phenyl protons, a broad band at 5.61 ppm was assigned to the cyclopentadienyl protons. Single peaks at 4.54 ppm due to the terminal Si-H and at -12.12 ppm, due to the bridging hydride, Si-H-Ti, were also observed. The same spectrum in toluene-d_8 sharpened considerably (with the exception of the phenyl peaks) upon cooling, with the band assigned to the cyclopentadienyl protons splitting into 4 singlets of equal intensity. The broad bands due to the hydrides were also found to sharpen, and a third hydride peak due to Ti-H-Ti, eventually became visible at -20.17 ppm. This peak continued to sharpen with decreasing temperature. Data obtained for selected temperatures is given in TABLE III.2. Remeasurement of the ^1H NMR spectrum of X in THF-d_8 confirmed its temperature dependance. In fact, the increased solubility in this solvent gave superior spectra, particularly at low temperatures. The results were the same as in toluene-d_8, with the broad band due to the cyclopentadienyl protons suddenly splitting into 4 singlets at -5°C. Data obtained for selected temperatures is presented in TABLE III.2. The ^1H NMR spectrum of complex X in THF-d_8 at several temperatures is shown in FIGURE III.4.

In analogy with the data reported for $\{[(\eta^5-C_5H_5)-Ti]_2(\mu-H)(\mu-H_2AlEt_2)(\mu-C_{10}H_8)\}$ (δ Ti-H-Ti = -21.80 ppm), the peak observed in the region of -20 ppm for X was assigned to the bridging hydride Ti-H-Ti (115). Similarly, the position of the peaks due to the hydrides Al-H-Ti (-11.62 ppm) was used to assign the peak at -12.28 ppm to the hydride Si-H-Ti.

The observation of a paramagnetic broadening effect on the ^1H NMR spectra of Ti(III) dimers has been noted. The ^1H NMR spectrum of the aluminium complex above was reported at -48°C possibly because of paramagnetism above this temperature, although this was not stated (115). In addition, $\{[(\eta^5-C_5H_5)-Ti(\mu-OH)]_2(\mu-C_{10}H_8)\}$ was reported to give an "atypical" spectrum which may refer to paramagnetic broadening (101).

TABLE III.2: ^1H NMR DATA FOR $\{[(\eta^5\text{-}C_5H_5)_2Ti]_2(\mu\text{-}H)\text{-}(\mu\text{-}HSiPhH)\}^{a,b}$

TEMPERATURE[c]	$C_5\underline{H}_5$	Si-$\underline{H}$	Si-$\underline{H}$-Ti	Ti-$\underline{H}$-Ti
Ambient[d]	5.54 (25)	4.47	-12.18	e
-20[d]	5.68, 5.49, 5.43, 5.39	4.47 (15)	-12.18 (16)	e
-50[d]	5.49, 5.31, 5.20, 5.16	4.47 (13)	-12.28 (13)	-20.17 (64)
-80[d]	5.50, 5.30, 5.18[f]	4.47 (13)	-12.26 (13)	-19.63 (19)
Ambient[g]	5.82 (29)	4.15 (67)	-12.36 (93)	e
6[g]	5.75 (43)	4.14 (22)	-12.33 (35)	e
-5[g]	5.85, 5.77, 5.69, 5.64	4.12 (12)	-12.27 (21)	e
-20[g]	5.86, 5.78, 5.70, 5.64	4.15 (10)	-12.22 (19)	-19.90 (167)
-50[g]	5.86, 5.77, 5.69, 5.64	4.15 (11)	-12.21 (12)	-19.51 (62)
-80[g]	5.86, 5.77, 5.69, 5.64	4.15 (19)	-12.22 (14)	-19.42 (18)

[a] measured in ppm

[b] numbers in brackets refer to the line width at half-height, $\nu_{\frac{1}{2}}$, in Hz

[c] measured in °C

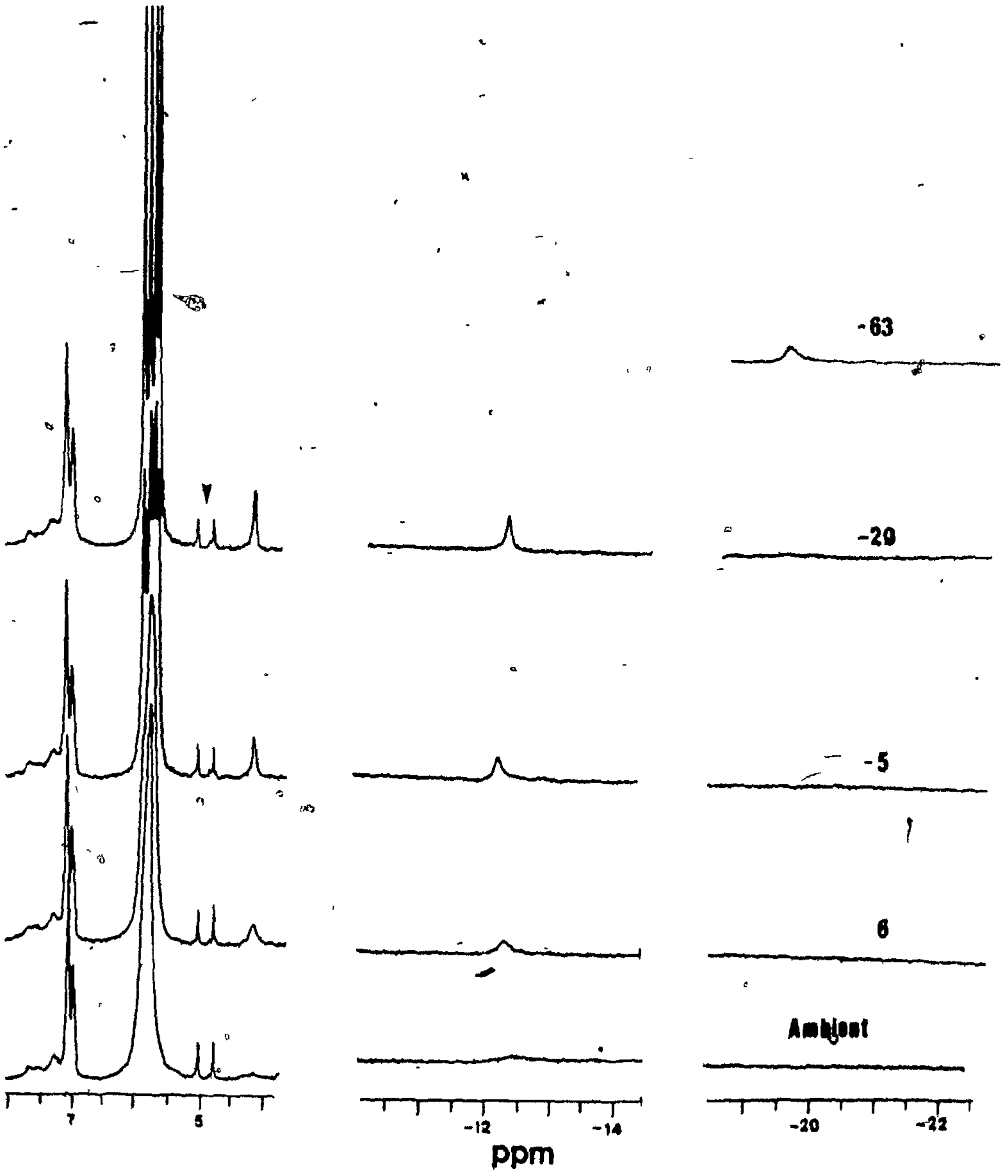
[d] in toluene-d_8

[e] peak not observed

[f] 2 overlapping singlets

[g] in THF-d_8

FIGURE III.4: ^{1}H NMR SPECTRUM OF $\{[(\eta^5\text{-}C_5H_5)_2Ti]_2(\mu\text{-}H)\text{-}(\mu\text{-}HSiPhH)\}$ AT SELECTED TEMPERATURES[a,b]



▼= trace of **XI**

[a] in THF-d_8

[b] probe temperature given in °C

Recently the temperature dependance (-60 to 25°C) of the ^1H NMR spectrum of $\{[(\eta^5-C_5H_5)Ti(\mu-H)]_2(\mu-C_{10}H_8)\}$, IV, established that a paramagnetic effect exists in solution for the complex even though it is diamagnetic in the solid state (155). IV is diamagnetic in solution at low temperatures. As in the case of X, the signal due to the bridging hydrides Ti-H-Ti was not observed at room temperature, only becoming visible at low temperature (-60°C). The peaks due to the cyclopentadienyl protons in IV were reported to move upfield as the temperature was lowered, in addition to sharpening. This trend was also noted for X in toluene-d_8 although the peak positions of the cyclopentadienyl protons remained in essentially the same positions in THF-d_8.

The line-width at half height reported for the peak due to the bridging hydride Ti-H-Ti in IV was 300 Hz at -60°C, the temperature at which it was said to appear (155). Lack of solubility prevented further cooling and the obtaining of a high resolution spectrum. The analogous value for X was 64 Hz at -50°C in toluene-d_8, and in fact the peak was visible at -20°C in THF-d_8. Although spectra for X could be obtained in both toluene-d_8 and THF-d_8 at temperatures as low as -80°C, the resolution obtained was poor. In order to account for the temperature dependance of IV, a thermal equilibrium between the singlet ground state and its excited triplet state was postulated (155). The population of the triplet state at room temperature was said to be negligible but sufficient to account for the broadening of the ^{1}H NMR spectra. It is likely that such a thermal equilibrium also exists for X, where antiferromagnetic coupling gives rise to a singlet ground state. As in the case of IV, it is probable that the population of the excited triplet state is insignificant at room temperature. The fact that the ground state of IV and X appears to be a diamagnetic singlet state, leads one to conclude that antiferromagentic rather than ferromagnetic exchange is operating. The exchange energy for two atoms i and j with spin angular momentum $\mathbf{S}_i\, h/2\pi$ and $\mathbf{S}_j\, h/2\pi$ respectively, is given by equation III.7 (156):

$$E_{ex} = -2\, J_{ex}\mathbf{S}_i\mathbf{S}_j = -2\, J_{ex}S_iS_j\cos\phi \qquad \text{III.7}$$

J_{ex} = exchange integral

ϕ = angle between spins

For the case of an antiferromagnetic interaction, J_{ex} is negative with the lowest energy state resulting from antiparallel spins ($\cos\phi = -1$).

The exchange interactions present in X may involve direct overlap of metal atomic orbitals, or a superexchange pathway through the bridge atoms. It has been suggested that the magnitude of the magnetic exchange interaction in binuclear titanium(III) dimers depends on three main criteria (157):

1) the distance of the Ti(III) atoms from the atoms of the bridge, 2) the ability of the orbitals containing the unpaired electrons on the Ti(III) centres to interact with the bridge molecular orbitals of the appropriate symmetry and 3) the bond angle between the Ti(III) atoms and the bridge atoms. McGregor _et al_. have shown that the magnetic properties are very sensitive to a change in the bridgehead angle for a number of hydroxo-bridged copper(II) complexes (158). As the angle became larger than 99°, the exchange interaction was found to switch from ferromagnetic to antiferromagnetic in nature. In addition, a superexchange mechanism with magnetic exchange interactions occurring via the bridges, was thought to be dominant in these complexes. This was supported by the fact that as the distance between the copper atoms became less, the magnitude of the antiferromagnetic coupling decreased. This was said to indicate that the through-space interaction (antiferromagnetic) contributes little to the exchange coupling for these complexes.

Direct titanium orbital overlap cannot be entirely discounted for _X_. Jungst _et al_. have shown that for $\{(\eta^5-C_5H_5)_2TiCl\}_2$, $\{(C_5H_4Me)_2TiCl\}_2$ and $\{(C_5H_4Me)_2TiBr\}_2$ direct overlap of metal orbitals is possible although the Ti-Ti separations were 3.943, 3.926 and 4.125 Å respectively (159). If a superexchange mechanism is operating for _X_, this would account for the observation of singlet and triplet states. Such an interaction would most likely occur through the Ti-H-Ti bridge rather than over the more extended Ti-H-Si-Ti bridge. The bridgehead angle of 123° observed in complex X, suggests that the electron interaction through metal-bridge bonds is antiferromagnetic in nature according to the theory of superexchange (159).

In conclusion, the population of the triplet state for complex X, although negligible at room temperature, is sufficient to broaden the ^{1}H NMR spectrum. It is interesting to note that the peaks in the ^{1}H NMR spectrum of X do not all sharpen at the same temperature. In fact, the peak due to the bridging hydride Ti-H-Ti is not present at room temperature unlike all the other peaks. This is reasonable since the hydride atom is situated between the two paramagnetic centres. The peak observed due to the hydride Ti-H-Si is also broad at room temperature ($\nu_{\frac{1}{2}}$ = 93 Hz in THF-d_8) although it is visible. It is attached to only one paramagnetic centre. The hydride attached in a terminal fashion to the silicon atom is even sharper at room temperature ($\nu_{\frac{1}{2}}$ = 67 Hz). The group furthest from the paramagnetic centres, the phenyl group, does not appear to be affected by paramagnetic broadening at all, even at room temperature.

III.1.4 Further characterisation of complex X

Reaction of X with simple molecules such as CH_2Cl_2 and CO gave Cp_2TiCl_2 and $Cp_2Ti(CO)_2$, respectively. The reaction with CO gave complete conversion to $Cp_2Ti(CO)_2$ and $PhSiH_3$ as determined by IR and ^1H NMR spectroscopy. It is possible that this reaction proceeds via titanocene according to SCHEME III.4:

$$\underset{\underline{X}}{\{(Cp_2Ti)_2(\mu\text{-}H)(\mu\text{-}HSiPhH)\}} \rightleftharpoons Cp_2TiH(SiH_2Ph) + \text{"}Cp_2Ti\text{"}$$

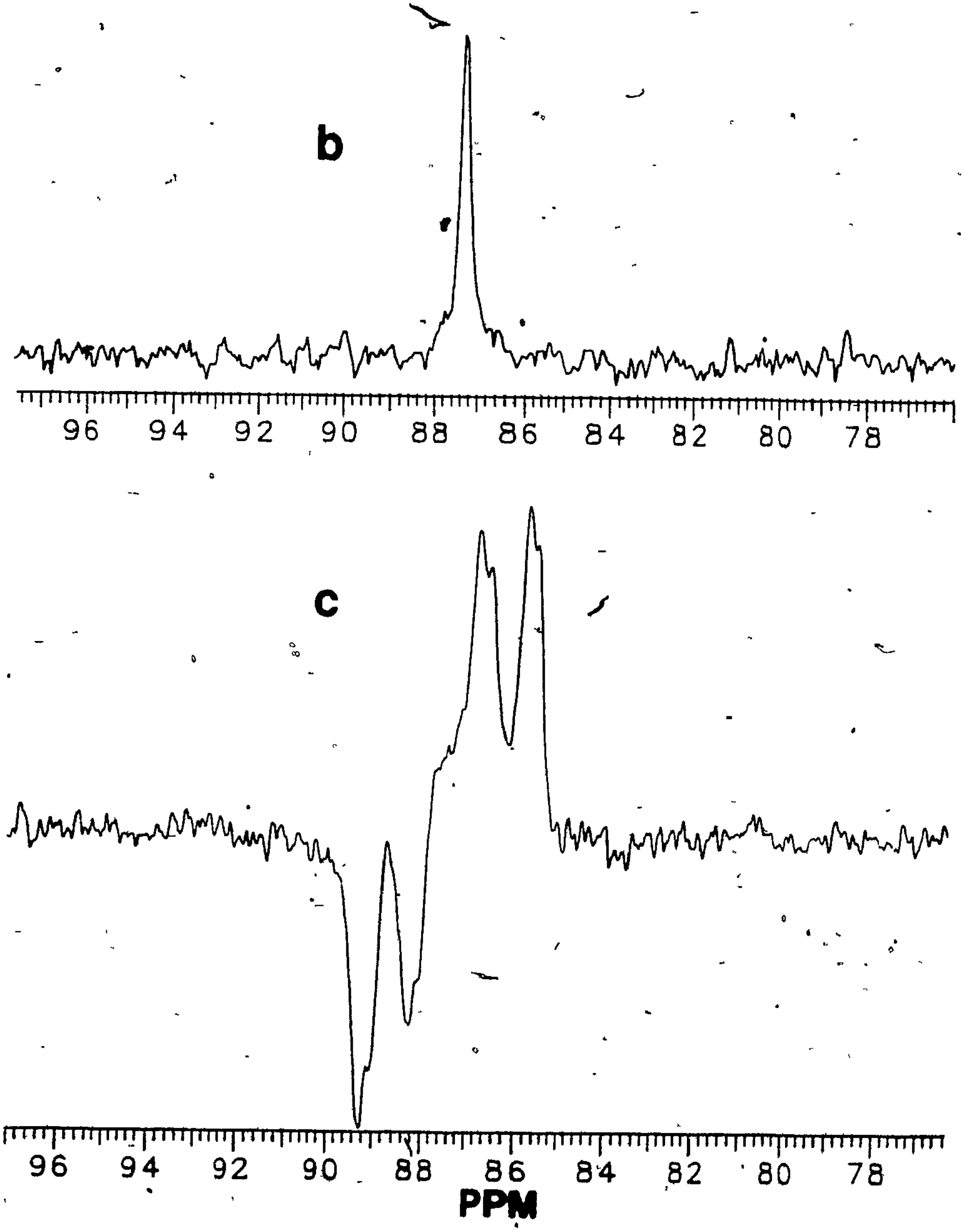
$$Cp_2TiH(SiH_2Ph) \rightleftharpoons \text{"}Cp_2Ti\text{"} + PhSiH_3$$

$$\text{"}Cp_2Ti\text{"} + 2CO \longrightarrow Cp_2Ti(CO)_2$$

SCHEME III.4

Both proton decoupled and coupled ^{29}Si NMR spectra in THF-d_8 at -80°C were obtained (FIGURE III.5). The ^{29}Si chemical shift (+ 87 ppm), is to low field of most organosilicon compounds (160). Silicon atoms attached to transition metals usually show extreme deshielding. One of the lowest field chemical shifts reported is + 173 ppm for $\{Me_2Si[Fe(CO)_4]_2\}$ where the silicon atom is attached to two transition metal centres (161). Most of the ^{29}Si NMR data reported for transition metal silyl complexes involve late transition metals. In these cases $d\pi$-$d\pi$ bonding is sometimes proposed. The fact that the ^{29}Si chemical shift for $\underline{X}$, where

FIGURE III.5: ^{29}Si INEPT NMR SPECTRUM OF $\{[\eta^5-(C_5H_5)_2Ti]_2-(\mu-H)(\mu-HSiPhH)\}^a$



^{a}in THF-d_8 at -80°C

^{b}decoupled, before optimisation of parameters

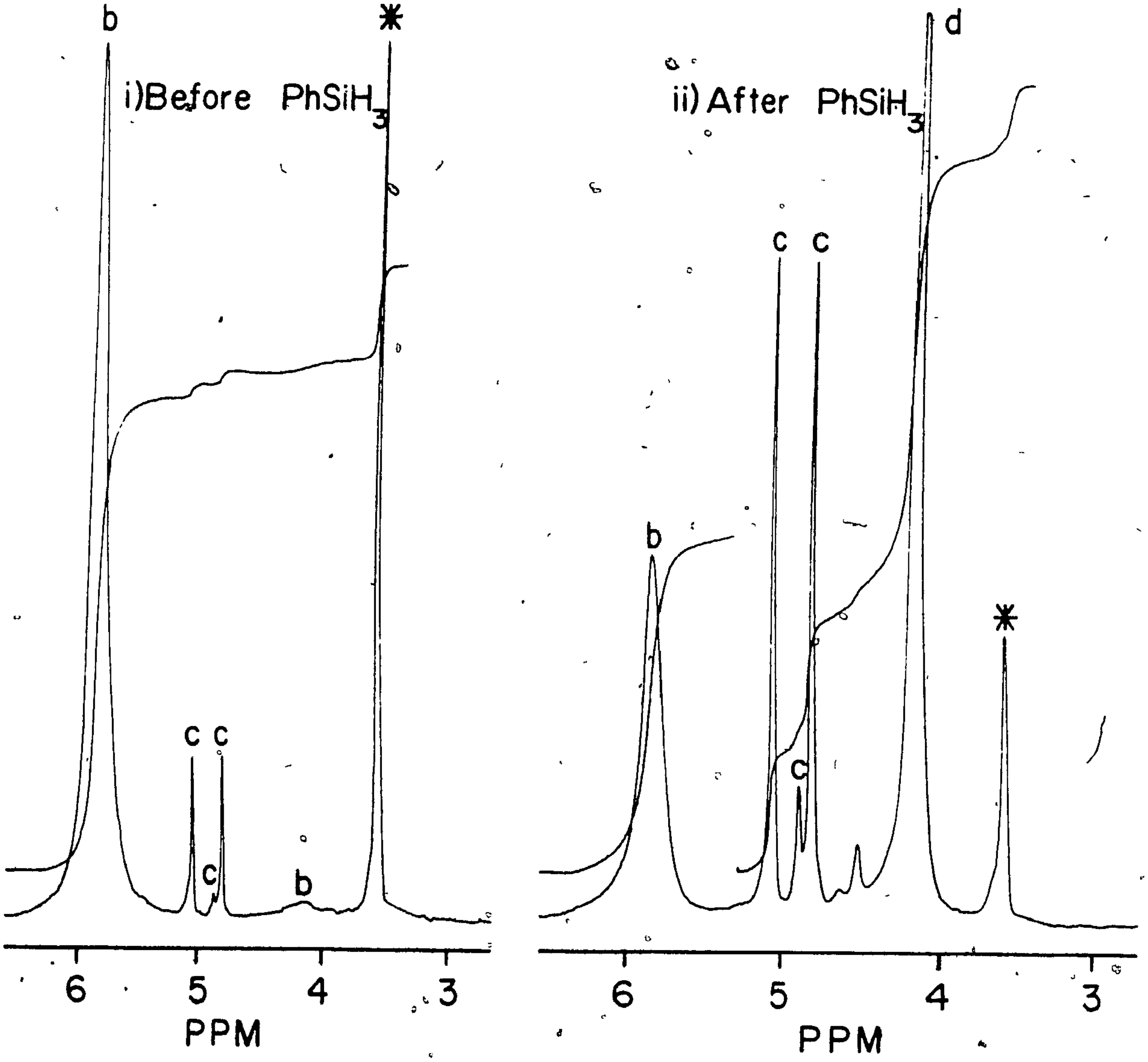
^{c}coupled, after optimisation of parameters the silicon is attached to a formal d^1 metal centre, is to low field of many other transition metal silyls, suggests d electrons to have little involvement in its determination. A number of d^6 Fe(II) complexes of the type $\{(\eta^5-C_5H_5)FeL_2R\}$, where L = neutral ligand and R = silyl group, all have ^{29}Si chemical shifts to high field of + 43 ppm (162). Thus it is generally impossible to say what, if any, effect the d electrons have on the ^{29}Si chemical shift in transition metal silyls. The hydridisation of the silicon atom in these complexes is presumably quite different from that of the parent silane, and this may influence the value also.

The ^{29}Si nucleus is coupled to all three hydrides. The values obtained for the coupling constant to the terminal hydride ($^1J_{Si-H}$ = 148 Hz), is considerably less than that observed for the parent silane (200 Hz) (163). This may be due to lower 's' character in the Si-H bond when the silicon is attached to titanium. Assuming the titanium atom is more electropositive than the silicon atom, Bent's rule could well apply. This states "atomic 's' character concentrates in orbitals directed toward electropositive substituents" (164). This rule has been applied to coupling constants involving a number of different nuclei, including silicon (165). It is likely that the value obtained for the coupling constant $^1J_{Si-H(Ti)}$, 58 Hz, also reflects the decreased 's' character in this Si-H bond, relative to that of the parent silane. In fact, it has been noted that for complexes containing agostic interactions of the type C-H-M, the value $^{1}J_{C-H}$ is often lower than might be expected as a result of the reduced bond order in the 2-electron, 3-centre bond. The value for $^{2}J_{Si-(Ti)-H}$ (14 Hz), is comparable in magnitude to that for $^{2}J_{Si-(C)-H}$ (6 Hz) (160b).

It is interesting to note that X converts to $\{(\eta^{5}-C_{5}H_{5})_{2}Ti(\mu-HSiPhH)\}_{2}$, XI, in the presence of excess $PhSiH_{3}$, in addition to initiating the polymerisation reaction. This will be discussed later. However, on the basis of ^{1}H NMR studies, it seems likely that X is produced first in the reaction of $Cp_{2}TiMe_{2}$ with $PhSiH_{3}$, and that it can be subsequently converted to XI depending on the stoichiometry of the reaction. FIGURE III.6 shows the ^{1}H NMR spectrum of X in THF-d_{8} after the addition of a few drops of $PhSiH_{3}$. As can be seen, the spectrum of pure X contains a trace of XI (2 sharp cyclopentadienyl resonances at 5.07 and 4.82 ppm, with an associated Si-H peak at 4.89 ppm). It is difficult to obtain X entirely free of XI. After addition of a few drops of $PhSiH_{3}$, the ratio of XI to X may be seen to have increased. The broad band at 5.82 ppm due to the cyclopentadienyl protons of X has decreased in intensity. It is likely that both species are involved in the polymerisation reaction. Complete conversion to XI is never observed which may indicate that both complexes are involved in some common cycle.

X, if kept in solution, slowly decomposes to give unidentified paramagnetic products, observed in the ^{1}H NMR as

FIGURE III.6: Cp/Si-H REGION OF THE ^{1}H NMR SPECTRUM OF $\{[(\eta^5\text{-}C_5H_5)_2Ti]_2(\mu\text{-}H)(\mu\text{-}HSiPhH)\}$ BEFORE AND AFTER THE ADDITION OF A FEW DROPS OF $PhSiH_3$[a]



[a] in THF-d_8. Peaks due to the solvent are marked with an asterisk (*)

[b] peaks due to X

[c] peaks due to XI

[d] peak due to the Si-H of $PhSiH_3$

broad bands at 40 and 50 ppm. ESR evidence suggests that after several days, significant conversion of the triplet state of X to $\{[(\eta^5\text{-}C_5H_5)_2TiH]_2(\mu\text{-}H)\}$ had occurred, since only the doublet of triplets, characteristic of this complex was observed (166).

III.2 THE CHARACTERISATION OF $\{(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}HSi\text{-}(C_6H_5)H)\}_2$, XI

III.2.1 Reaction of $PhSiH_3$ with Cp_2TiMe_2 (~ 3:1 molar ratio); isolation of complex XI

Pure XI was isolated by the reaction of $PhSiH_3$ with Cp_2TiMe_2 (3:1 stoichiometric ratio) in toluene, from which XI slowly crystallised. The choice of solvent is important, since the organosilane products, and any X produced, remain in solution. Based on the products observed in the ^1H NMR spectrum (C_6D_6), a possible reaction equation is suggested below:

$$\begin{aligned} 4Cp_2TiMe_2 + 8PhSiH_3 &\xrightarrow{\text{toluene}} 3MeH + 2H_2 + 5MePhSiH_2 \\ &\quad + \underset{\underline{X}}{\{(Cp_2Ti)_2(\mu\text{-}H)(\mu\text{-}HSiPhH)\}} \qquad \text{III.8} \\ &\quad + \underset{\underline{XI}}{\{Cp_2Ti(\mu\text{-}HSiPhH)\}_2} \end{aligned}$$

The excess $PhSiH_3$ present was converted eventually to oligophenylsilane with associated loss of hydrogen. The reaction is complicated by the tendancy of <u>XI</u> to convert to <u>X</u> in solution, presumably by the loss of "HPhSi" which eventually forms oligophenylsilane ("HPhSi" is represented as such because of its uncertain nature). It is thus difficult to obtain pure <u>XI</u>, and depending on the solvent used, cocrystallisation with <u>X</u> is often observed. ^1H NMR studies have shown that in the reaction of Cp_2TiMe_2 with excess $PhSiH_3$, <u>X</u> is produced first. Subsequent to this, <u>XI</u> is observed together with the formation of oligophenylsilane and hydrogen evolution. It has already been shown that <u>X</u> converts to <u>XI</u> in the presence of excess $PhSiH_3$. It is possible therefore that <u>XI</u> may be produced from <u>X</u> according to SCHEME III.5:

$$\underset{\underline{X}}{\{(Cp_2Ti)_2(\mu\text{-}H)(\mu\text{-}HSiPhH)\}} \rightleftharpoons \text{"}Cp_2Ti\text{"} + Cp_2TiH(SiH_2Ph)$$

$$\text{"}Cp_2Ti\text{"} \xrightleftharpoons{\text{xs } PhSiH_3} Cp_2TiH(SiH_2Ph)$$

$$Cp_2TiH(SiH_2Ph) \xrightarrow{-H_2} Cp_2Ti = SiHPh$$

$$Cp_2Ti = SiHPh + Cp_2TiH(SiH_2Ph) \longrightarrow \underset{\underline{XI}}{\{Cp_2Ti(\mu\text{-}HSiPhH)\}_2}$$

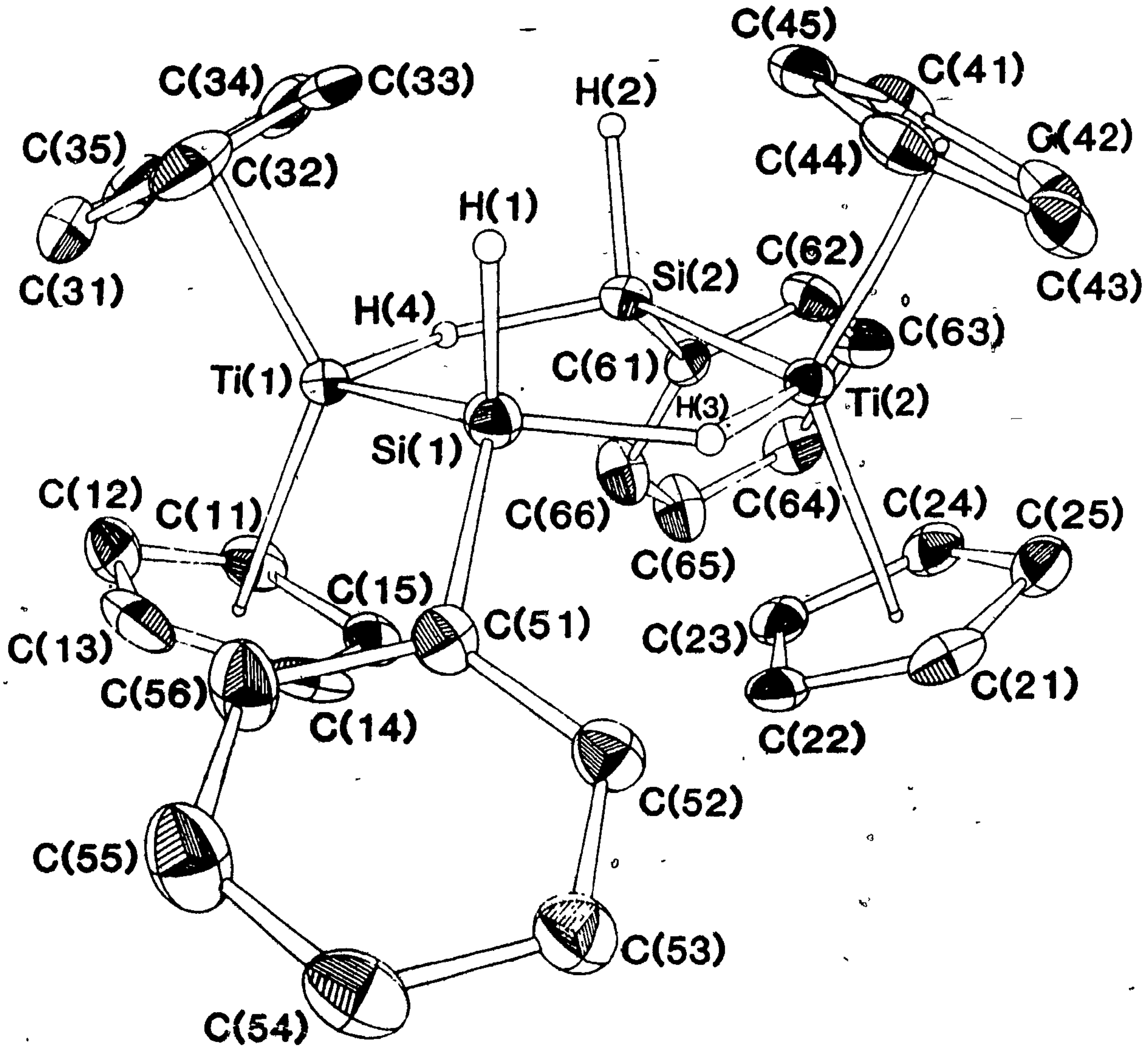
<u>SCHEME III.5</u>

Alternatively, since $Cp_2TiH(SiH_2Ph)$ has been postulated as a precursor to X (equation III.6), it seems plausible that in the presence of excess $PhSiH_3$, α-H elimination could occur at this stage, followed by dimerisation with another molecule of $Cp_2TiH(SiH_2Ph)$, to yield XI. Although complexes containing a M=Si bond have not been isolated as such, metal silene intermediates have been postulated to exist during the photochemical deoligomerisation of some polysilane iron derivatives (167). In addition, metal carbene analogues of the type $Cp_2Ti{=}CH_2$ may be generated in situ from aluminium alkyl adducts, and have been shown to react with unsaturated (e.g. olefinic) groups (168).

III.2.2 The molecular structure

The experimental details for the X-ray crystal structure determination, as performed by Dr. M. Simard, Université de Montréal, are given in APPENDIX III. The crystal structure data, positional parameters, anisotropic thermal parameters, structure factor amplitudes (calculated and observed), interatomic angles and distances and some selected least squares planes as obtained from the Université de Montréal are given in TABLES AV-A to J, APPENDIX V. A perspective drawing of XI is given in FIGURE III.7. The molecule possesses C_2 symmetry with two Cp_2Ti units bridged by two HSiPhH moieties. Thus XI contains an essentially planar

FIGURE III.7: A PERSPECTIVE VIEW OF $\{[(\eta^5-C_5H_5)_2Ti]-(\mu-HSiPhH)\}_2^{a,b}$



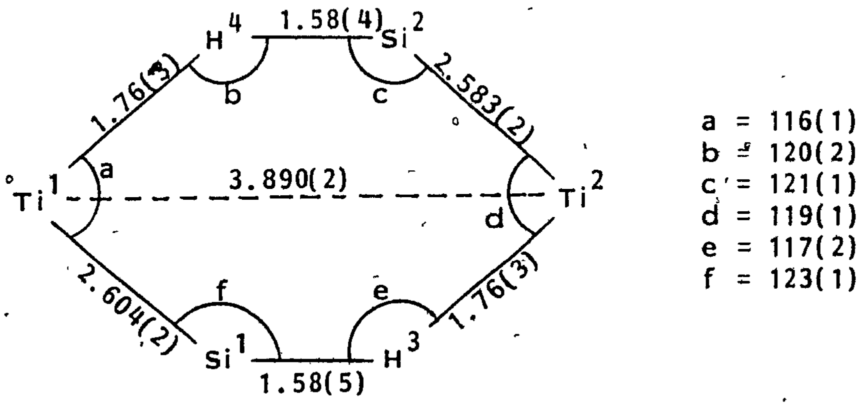
[a] phenyl and Cp hydrogen atoms omitted for clarity

[b] the ellipsoids correspond to 30% probability level

(slightly puckered) 6-membered ring with two 2-electron, 3-centre Ti-H-Si bonds. In addition, two Ti-Si bonds are present. The central 6-membered ring of the molecule is shown in FIGURE III.8, and selected interatomic distances and angles are given in TABLE III.3.

The bond distances obtained for the two Ti-Si bonds (2.60 and 2.58 Å) are very similar to that observed for complex X (2.61 Å) and for $Cp_2TiCl(SiMe_3)$ (2.67 Å) (126).

FIGURE III.8: THE CENTRAL BRIDGING UNIT OF COMPLEX XI, $Ti_2Si_2H_2$[a,b]



[a] non-bonded distances are represented by dashed (--- lines)

[b] bond lengths are given in Angstroms (Å) and bond angles in degrees (°)

TABLE III.3: SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR $\{[(\eta^5\text{-}C_5H_5)_2Ti]_2(\mu\text{-}HSiPhH)\}_2$[a]

LENGTHS	
Ti(1)-Ti(2)	3.890(2)
Ti(1)-Si(1)	2.604(2)
Ti(1)-Si(2)	2.891(2)
Ti(1)-H(4)	1.76 (3)
Ti(2)-Si(2)	2.583(2)
Ti(2)-Si(1)	2.851(2)
Ti(2)-H(3)	1.76 (3)
Si(1)-C(51)	1.943(4)
Si(1)-H(1)	1.47 (3)
Si(1)-H(3)	1.58 (5)
Si(2)-C(61)	1.935(4)
Si(2)-H(2)	1.47 (3)
Si(2)-H(4)	1.58 (4)

ANGLES	
Si(1)-Ti(1)-H(4)	116 (1)
Si(1)-Ti(1)-Si(2)	87.91(6)
Si(2)-Ti(2)-H(3)	119 (1)
Si(2)-Ti(2)-Si(1)	89.18(6)
Ti(1)-Si(1)-H(3)	123 (1)
Ti(1)-Si(1)-C(51)	123.3 (1)
Ti(1)-Si(1)-H(1)	114 (2)
Ti(1)-H(4)-Si(2)	120 (2)
Ti(2)-H(3)-Si(1)	117 (2)
Ti(2)-Si(2)-H(4)	121 (1)
Ti(2)-Si(2)-C(61)	117.7 (1)
Ti(2)-Si(2)-H(2)	114 (1)
C(1G)-Ti(1)-C(3G)	130.5 (2)
C(2G)-Ti(2)-C(4G)	132.0 (2)

[a] C(1G) = centroid of ring containing carbons C(11) to C(15)
C(2G) = centroid of ring containing carbons C(21) to C(25)
C(3G) = centroid of ring containing carbons C(31) to C(35)
C(4G) = centroid of ring containing carbons C(41) to C(45)

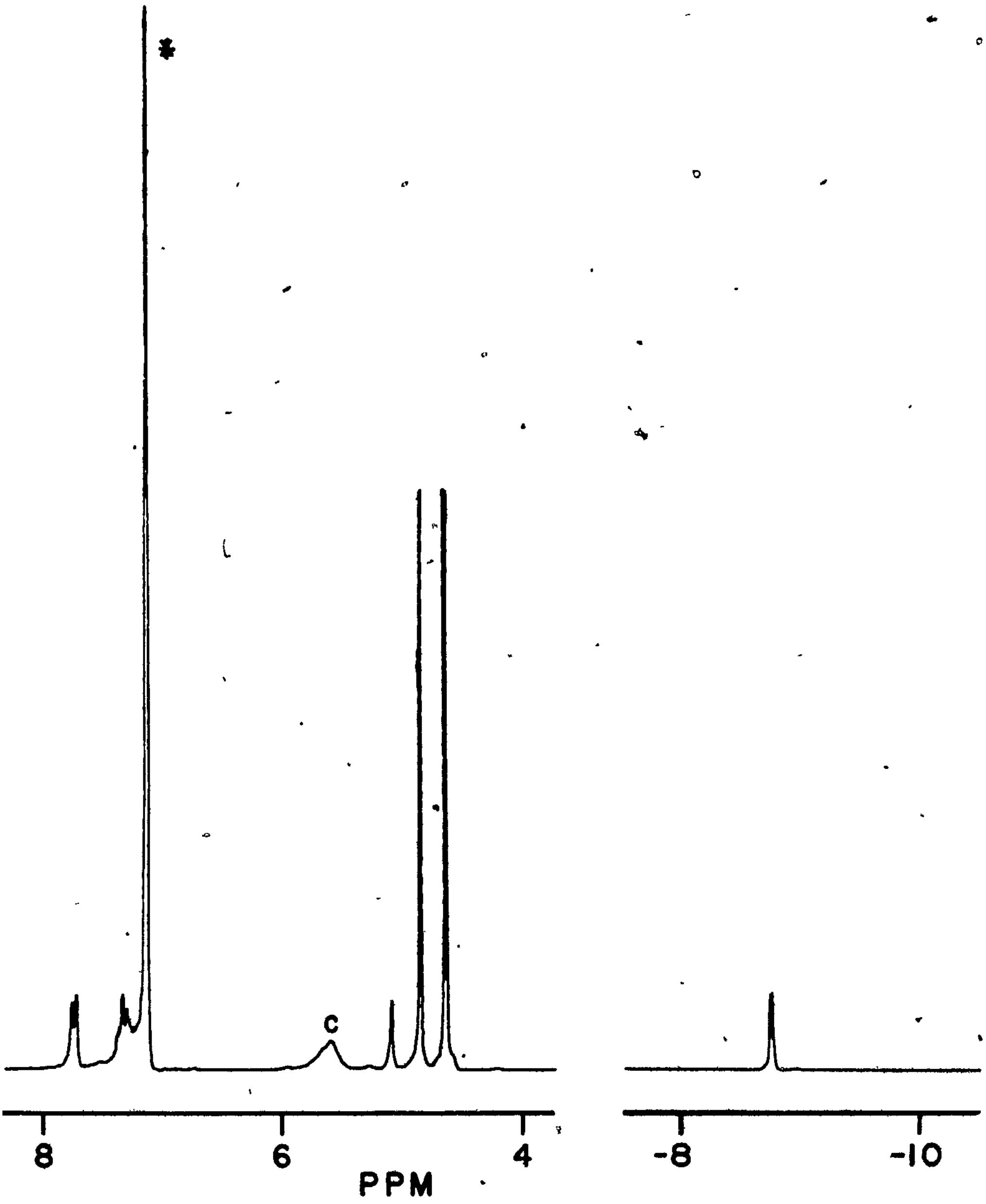
The two non-bonded Ti-Si distances across the bridging hydrides (2.85 and 2.89 Å), are longer and may be used, as in the case of X, to infer the presence of bridging hydrides (147). It is interesting to note that in XI, the phenyl groups present on the two silicon atoms are arranged in a cis configuration with respect to the 6-membered $Ti_2Si_2H_2$ ring. ^1H NMR results indicated that only one isomer was present in solution. By using molecular models, it may be seen that the cis isomer directs the two phenyl groups away from their nearest neighbours, most notably the bulky cyclopentadienyl groups.

The Ti-Ti separation (3.89 Å) suggests that a bond between them is unlikely. This separation is approximately 0.43 Å longer than the analogous one observed in X. The two Ti-H(Si) bonds (1.76 Å) are longer than that observed in X (1.58 Å) although shorter than the Ti-H distance observed in the Ti-H-Ti bridge of X (1.97 Å). However they correspond to the value obtained for Ti-H(Al) in $\{[\eta^5-C_5H_5)Ti]_2(\mu-H)-(\mu-H_2AlEt_2)(\mu-C_{10}H_8)\}$ (1.69 Å) (115).

III.2.3 General discussion

The tendency of XI to convert to X in solution, resulted in limited opportunity to study its chemistry. It reacts with CH_2Cl_2 and CO to give Cp_2TiCl_2 and $Cp_2Ti(CO)_2$, respectively, although it is possible that such reactivity is a result of initial conversion to X. The complex is very insoluble in most organic solvents (more so than X) which complicated NMR measurements. Nevertheless a ^1H NMR spectrum in C_6D_6 was obtained (FIGURE III.9). Although XI is more soluble in THF than benzene, its conversion to X is faster in this solvent. Some X can still, however, be seen in FIGURE III.9. XI is diamagnetic in solution, with no paramagnetic broadening observed at room temperature. Furthermore the ^1H NMR spectrum of XI is not temperature dependant, unlike that of X. Both titanium atoms present in XI are formally Ti(III), d^1 centres. The large Ti-Ti separation in XI probably reduces the possibility of direct metal orbital overlap relative to X. In addition superexchange, as discussed for complex X, would be less likely to occur due to the more extended Ti-H-Si-Ti bridges relative to the Ti-H-Ti bridge of X. It seems likely that the triplet state is not populated at ambient temperature in XI, and that the molecule exists solely in a diamagnetic, singlet state. As discussed previously, superexchange between binuclear Ti(III) dimers depends on a number of criteria. The angles between the titanium atoms and the bridges as well as the overall geometry of the molecule are important in determining the magnetic exchange present within the molecule. Francesconi et al. suggest that it is unusual for a ferromagnetic exchange interaction to exist in a binuclear bridged complex wherein the bridge(s) consists of more than one atom (157). Thus, in XI, where only extended

FIGURE III.9: ^{1}H NMR SPECTRUM OF $[(\eta^5-C_5H_5)_2Ti(\mu-HSiPhH)]_2$[a,b]



[a] at ambient temperature

[b] in C_6D_6. The peak due to the solvent is marked with an asterisk (*)

[c] cyclopentadienyl peak of X

bridges occur, antiferromagnetic coupling may become more important, leading to a diamagnetic singlet ground state. For XI, the excited triplet state is, therefore, not thermally accessible at ambient temperature.

Upon dissolution of XI in THF, gas evolution was observed. The ^{1}H NMR spectrum in this solvent, however, showed no obvious anomalies except a higher conversion to X than was noted in benzene. ESR evidence however showed that at ambient temperature, a sharp triplet was present, due to a single electron coupled to a pair of equivalent protons (166). This may be due to the conversion of XI to a THF solvated monomer, produced by bridge splitting of the dimer by the coordinating solvent (equation III.9):

$$\underset{\underline{XI}}{\{Cp_2Ti(\mu\text{-}HSiPhH)\}_2} \xrightleftharpoons{THF} 2\{Cp_2Ti(SiH_2Ph)(THF)\} \qquad III.9$$

Such an equilibrium accounts for the observation of the intact dimer as seen in the ^{1}H NMR spectrum of XI. The reason why conversion to X seems to occur faster in this solvent is not clear.

ESR evidence has suggested that as for X, eventual conversion of solutions of XI to $\{[(\eta^5\text{-}C_5H_5)_2TiH]_2(\mu\text{-}H)\}$ occurs after several days (166).

III.3 THE CHARACTERISATION OF $\{[(\eta^5-C_5H_4CH_3)_2Ti]_2(\mu-H)-(\mu-HSi(C_6H_5)H)\}$, XII AND $\{(\eta^5-C_5H_4CH_3)_2Ti(\mu-HSi-(C_6H_5)H)\}_2$, XIII

III.3.1 Reaction of $PhSiH_3$ with $Cp'_2TiMe'_2$ (1:1 molar ratio); isolation of complex XII

Pure XII was isolated by the reaction (1:1 stoichiometric ratio) of $PhSiH_3$ with Cp'_2TiMe_2 in diethylether. As in the analogous reaction to produce X, a spectacular colour change from orange to blue/black was noted together with an initial vigorous evolution of gas. Although the reaction was not followed in detail by ^1H NMR studies, it seems likely that the reaction is analogous to that which produced X (equation III.1). Methylcyclopentadienyl compounds are generally more soluble than the analogous cyclopentadienyl compounds, and so lower yields were obtained for XII relative to X. Rather surprisingly, solid XII was pyrophoric which complicated the obtaining of an accurate chemical analysis.

^1H NMR studies on XII showed it to be analogous to X, with paramagnetic broadening evident at ambient temperature for all protons except those of the phenyl group (FIGURE III.10). Upon lowering of the temperature, the broad peaks sharpened. Data obtained for selected temperatures is given in TABLE III.4. As observed for X, the high field hydride (-19 ppm) became clearly visible at approximately -50°C,

TABLE III.4: ^{1}H NMR DATA FOR $\{[(\eta^5\text{-}C_5H_4Me)_2Ti]_2(\mu\text{-}H)\text{-}(\mu\text{-}HSiPhH)\}^{a,b}$

TEMPERATURE[c]	$C_5\underline{H}_4$	Si-$\underline{H}$[d]	$C_5H_4C\underline{H}_3$	Si-$\underline{H}$-Ti[d]	Ti-$\underline{H}$-Ti[d]
Ambient	6.67 - 4.80	4.45 (27)	1.19 - 1.17	-12.26 (53)	e
-25	6.67 - 4.80	4.45 (7)	1.53[f], 1.27 1.13	-12.26 (27)	e
-48	6.67 - 4.62	4.45 (8)	1.46, 1.42, 1.19, 1.04	-12.09 (18)	-18.96 (76)
-68	6.69 - 4.51	4.45 (13)	1.42, 1.34, 1.12[g], 0.96	-12.07 (13)	-18.74 (57)

[a] measured in ppm

[b] in toluene-d_8

[c] measured in °C

[d] numbers in brackets refer to the line width at half height, $\nu_{\frac{1}{2}}$, in Hz

[e] peak not observed

[f] 2 overlapping singlets

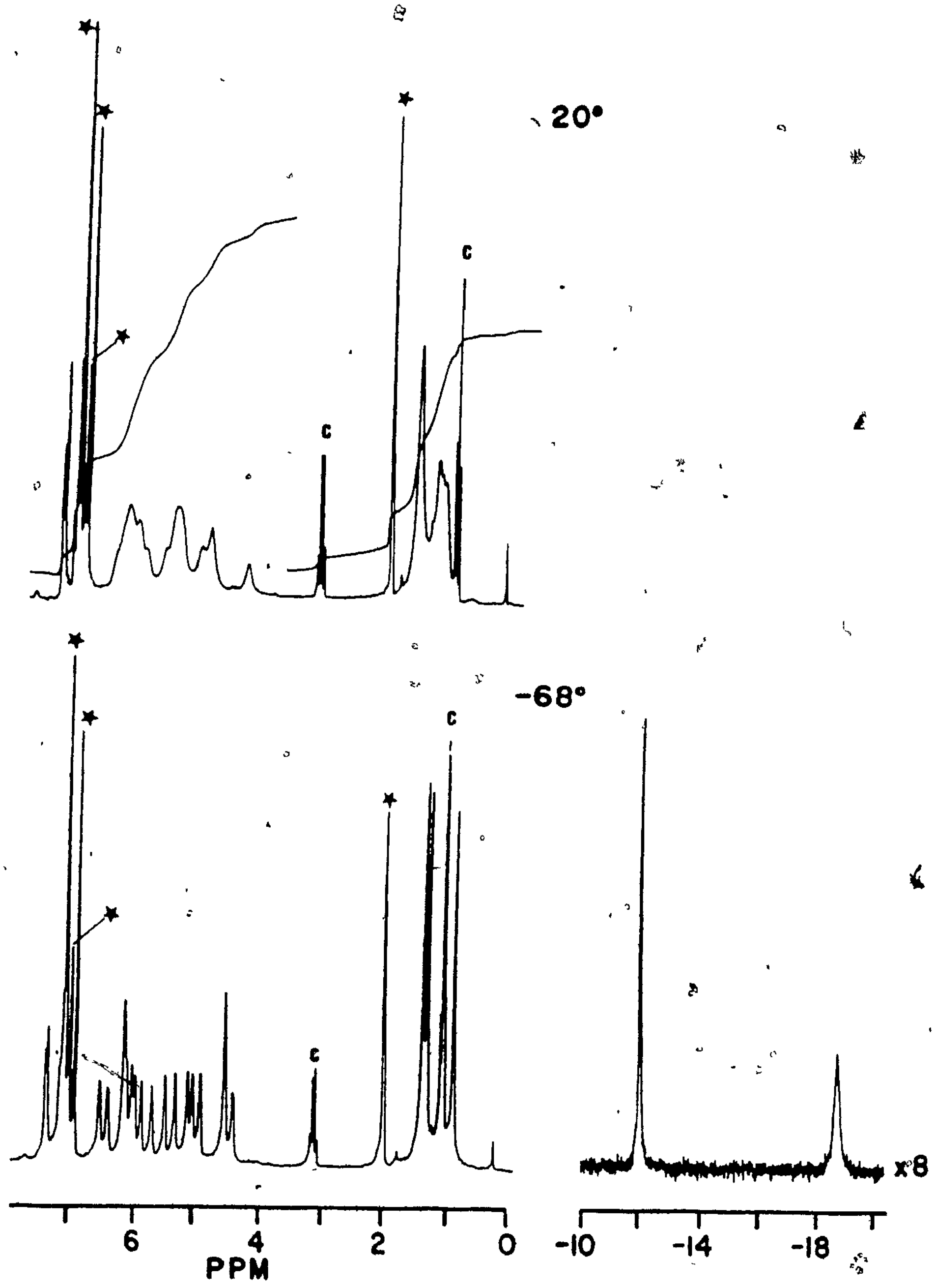
[g] peak overlaps with Et_2O

although it was observed as a broad hump in the baseline at -20°C. The ^1H NMR spectrum of XII, measured at -68°C (FIGURE III.10), illustrates the complexity of the cyclopentadienyl region. The 4 singlets due to the 4 methyl groups on the Cp's are clearly visible, however, at approximately 1 ppm, and they reflect the 4 distinct environments of the cyclopentadienyl rings. As for X, the proton resonances of XII sharpen at different temperatures. Even as low as -68°C, the hydride at -19 ppm assigned to Ti-H-Ti, is still relatively broad (57 Hz). Based on ^1H NMR studies, assuming XII is analogous to X, the structure of XII (and that of similar compounds to be discussed later) is shown in FIGURE III.11.

III.3.2 Reaction of $PhSiH_3$ with Cp'_2TiMe_2 (3:1 molar ratio); attempted isolation of complex XIII

Reaction of $PhSiH_3$ with Cp'_2TiMe_2 (3:1 stoichiometric ratio) in toluene was found to give a mixture of XII and XIII. Pure XIII could not be obtained, due to its more rapid conversion to XII in solution, relative to the conversion of XI to X. This is perhaps a result of the increased solubility of the methylcyclopentadienyl compounds. Thus the ^1H NMR spectrum (C_6D_6) showed peaks mainly due to XII in the phenyl, Si-H and Cp regions. The peaks due to Cp-CH_3 (two singlets at 1.91 and 1.51 ppm) and Si-H-Ti (one singlet at -8.5 ppm) of XIII were however discernible. They were found to increase in

FIGURE III.10: ^{1}H NMR SPECTRUM OF $\{[(\eta^5\text{-}C_5H_4Me)_2Ti]_2(\mu\text{-}H)\text{-}(\mu\text{-}HSiPhH)\}$[a,b]

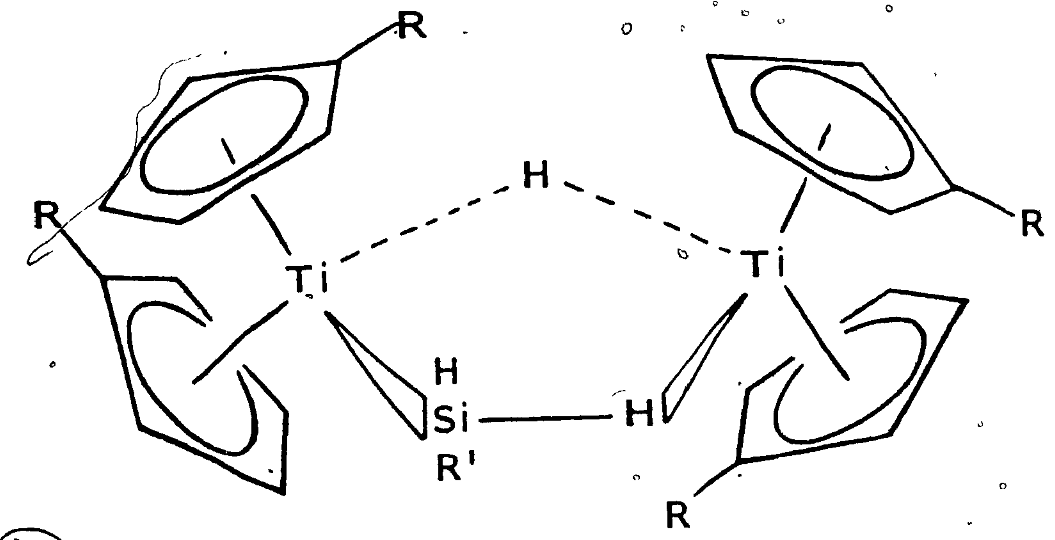


[a] in toluene-d_8. Peaks due to the solvent are marked with an asterisk (*)

[b] probe temperature given in °C

[c] peaks due to diethylether

FIGURE III.11: DIAGRAM TO SHOW THE STRUCTURE OF $\{[(\eta^5\text{-}C_5H_4R)\text{-}Ti]_2(\mu\text{-}H)(\mu\text{-}HSiR'H)\}$



X R = H R' = Ph

XII R = Me R' = Ph

XIV R = H R' = Hx

XVI R = H R' = Bz

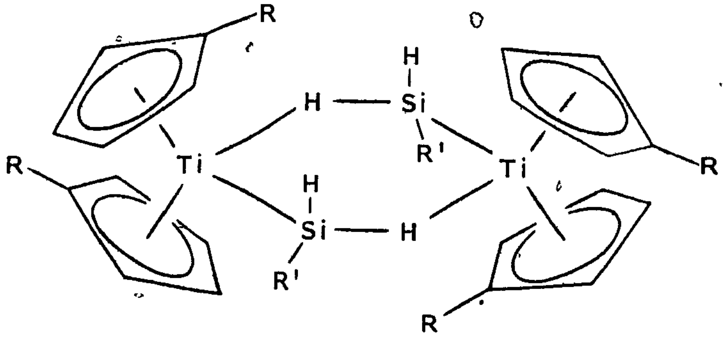
intensity relative to the peaks due to XII, upon the addition of a few drops of $PhSiH_3$ to the NMR tube. This is expected since X is known to convert to XI in the presence of excess $PhSiH_3$. Presumably a similar situation (SCHEME III.5) could account for the conversion of XII to XIII. It is reasonable that the structure of XIII is analogous to that of XI, and once more only one isomer (presumably the cis form) was observed. A representation of the structure of XIII (and similar compounds to be discussed later) is shown in FIGURE III.12. It is interesting to note that when $PhSiH_3$ was added to the NMR tube containing the mixture of XII and XIII, peaks due to $MePhSiH_2$ were observed. An explanation is not readily apparent, however, the presence of reactive paramagnetic species, invisible in the ^1H NMR spectrum, cannot be ruled out. No evidence for the involvement of the methylcyclopentadienyl groups was detected in the ^1H NMR spectra.

III.4 THE REACTION OF $PhSiH_3$ WITH SOME OTHER TITANOCENES

III.4.1 Reaction of $PhSiH_3$ with $Cp_2^*TiMe_2$ (7:1 molar ratio)

Despite a number of attempts using varied reaction conditions, no solid material was isolated. The reaction was studied by following its ^1H NMR spectrum (C_6D_6 and toluene-d_8) with time. Initially the reaction (0.013 g $Cp_2^*TiMe_2$ with 0.05 mL $PhSiH_3$ in ~ 0.4 mL solvent) was studied in C_6D_6. There

FIGURE III.12: DIAGRAM TO SHOW THE TWO ISOMERIC FORMS OF $\{(\eta^5\text{-}C_5H_4R)_2Ti(\mu\text{-}HSiR'H)\}_2$



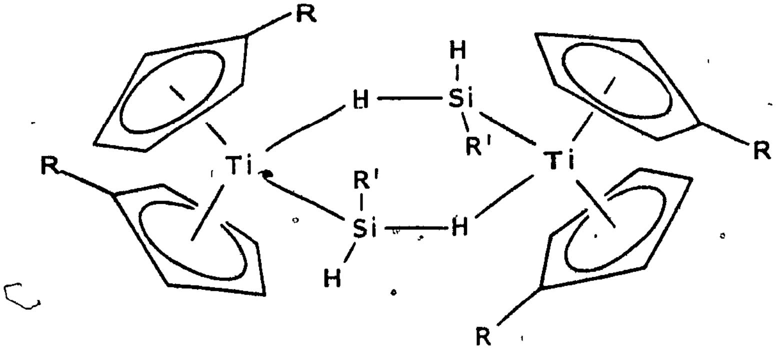
<u>XI</u> R = H R' = Ph

<u>XIII</u> R = Me R' = Ph

<u>XVa</u> R = H R' = Hx

<u>XVIIa</u> R = H R' = Bz

Isomer a (<u>cis</u>)



<u>XVb</u> R = H R' = Hx

<u>XVIIb</u> R = H R' = Bz

Isomer b (<u>trans</u>)

was no obvious immediate reaction, and no change to the spectrum was observed after several hours, however, the solution was found to slowly darken in colour. After a period of 1 day, no peaks other than those due to $PhSiH_3$ and $Cp^*_2TiMe_2$ were observed. However, the peak due to the Si-H resonances had collapsed from a sharp singlet (4.24 ppm) to a broad band ($\nu_{\frac{1}{2}}$ = 213 Hz, 4.06 ppm). All other peaks remained sharp. The solution was left for another 4 days during which time it darkened in colour to brown. In addition, gas evolution slowly occurred, necessitating its periodic removal. After this time, the ^1H NMR spectrum showed the complete absence of $Cp^*_2TiMe_2$, although a number of peaks and broad bands were now present from 2.14-0.65 ppm. The peaks due to the phenyl protons were still sharp. A small peak was observed at 0.17 ppm, and this is probably due to methane. In addition, a broad band was present at 23 ppm ($\nu_{\frac{1}{2}} \cong 700$ Hz).

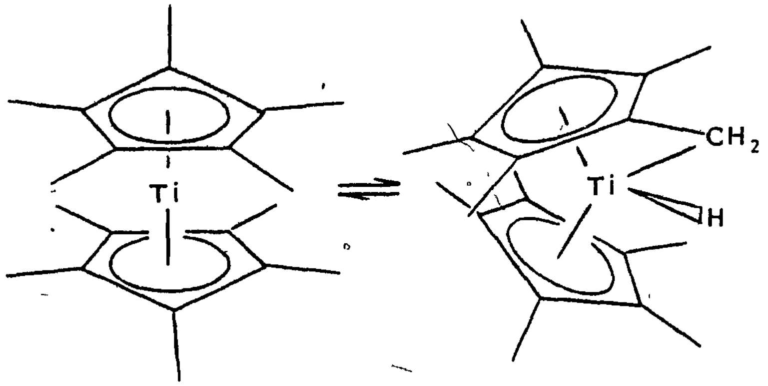
An identical study was subsequently done in toluene-d_8 so that the effect of temperature on the ^1H NMR spectrum could be examined. The solution was left for 1 day, after which time, as in C_6D_6, the Si-H peak was considerably broadened. Otherwise the spectrum showed only the peaks resulting from $PhSiH_3$ and $Cp^*_2TiMe_2$. Upon cooling the solution, the broad band due to the Si-H resonances gradually sharpened. At -78°C ($\nu_{\frac{1}{2}}$ = 24 Hz) the ^{29}Si satellites were visible. Nothing else was observed except the peaks due to the starting materials. At -93°C, the Si-H peak had sharpened further ($\nu_{\frac{1}{2}}$ = 12 Hz) although the rest of the spectrum had started to broaden. Warming the solution to room temperature caused the peak resulting from the Si-H resonances to broaden once more. The solution was left for one week before the spectrum was remeasured. At this time the spectrum was analogous to that observed in C_6D_6 after 4 days. The peaks due to $Cp^*_2TiMe_2$ had disappeared and a number of bands from 2.21-0.63 ppm were now evident. A small peak assigned to methane was present at 0.17 ppm. As in the case of the reaction done in C_6D_6, excess gas was periodically removed.

Despite the presence of a large excess of $PhSiH_3$, no oligophenylsilane was observed. Only small amounts of gas were liberated over several days, and it seems likely that this was predominantly methane. The broadening associated with the Si-H resonances of $PhSiH_3$, observed after approximately one day, might be accounted for by the equilibrium shown in equation III.10:

$$Cp^*_2Ti + PhSiH_3 \rightleftharpoons Cp^*_2TiH(SiH_2Ph) \qquad \text{III.10}$$

Such an equilibrium might well be fast on the NMR time scale at room temperature. In such a case, traces of Cp^*_2Ti might be sufficient to broaden the Si-H resonances as observed. An analogous equilibrium between Cp^*_2Ti and H_2 has been reported (104).

It has been suggested that Cp^*_2Ti exists in solution with a tautomeric form (104):



III.11

Decomposition eventually occurs by the subsequent loss of hydrogen, to yield {$Cp^*(C_5Me_4CH_2)Ti$}. Although Cp^*_2Ti was not detected in the NMR spectra during the reaction, the broad band at 23 ppm is similar to the one observed at 24 ppm, assigned to {$Cp^*(C_5Me_4CH_2)Ti$} (toluene-d_8) (104). However, the other two bands reported for the latter (12.6 and -10.9 ppm) were not observed. It has been suggested that {Cp^*-$(C_5Me_4CH_2)TiH$} is analogous in structure to {$Cp^*(C_5Me_4CH_2)$-$TiCH_3$} since it has a similar ^1H NMR spectrum, consisting of a number of signals at about 2 ppm. It has also been shown that the thermal decomposition of $Cp^*_2TiMe_2$ leads to the formation of {$Cp^*(C_5Me_4CH_2)TiCH_3$} (103, 169). In conclusion it is possible that a number of Cp^*_2Ti derivatives are present in solution.

III.4.2 Reaction of $PhSiH_3$ with $CpCp^*TiMe_2$ (1:1 molar ratio)

Upon addition of $PhSiH_3$ to an ethereal solution of $CpCp^*TiMe_2$, gas evolution was observed together with a rapid darkening in colour of the solution to red/brown. ^1H NMR studies showed that the gas evolved was methane, and that no methylphenylsilane was produced. A brown solid was isolated and studied by ^1H NMR (C_6D_6, toluene-d_8 and THF-d_8). Upon dissolution in C_6D_6, gas evolution was observed. The only clear feature in the spectrum was a broad band, assigned to Cp-C$\underline{H}_3$ resonances, at 2.49-0.86 ppm ($\nu_{\frac{1}{2}}$ = 62 Hz). In addition, a much broader band, barely above the baseline, was observed at approximately 7 ppm, possibly due to phenyl and/or cyclopentadienyl protons. No high field hydride peaks were observed. When the solution was left for 8 days, decomposition had occurred, and peaks assigned to cyclopentadienyl resonances had appeared at 6.46 and 5.58 ppm. Additional peaks due to Cp-C$\underline{H}_3$ resonances had also appeared. A small peak was also observed at approximately −18 ppm which might have been due to a Ti-$\underline{H}$-Ti species. The ^1H NMR spectrum of the brown solid was subsequently remeasured in toluene-d_8 in order that a variable temperature study could be undertaken. The spectrum was essentially the same at ambient temperature, as had been observed in C_6D_6. Lowering the temperature caused the peak due to Cp-C$\underline{H}_3$ resonances to broaden still further. One other peak appeared at 1.46 ppm, but no peaks due to either cyclopentadienyl or hydride resonances were evident. The ^1H NMR spectrum was studied from -85°C to +50°C but no sharpening of the Cp-C$\underline{H}_3$ resonances was observed. In addition, no other peaks (from 40 to -50 ppm) were observed. The variable temperature study was subsequently repeated in THF-d_8. Upon dissolution in this solvent, considerable gas evolution occurred. The Cp-C$\underline{H}_3$ region now consisted of a complex multiplet of sharp peaks (2.23-1.30 ppm), which overlapped with one of the solvent peaks. Two broad bands assigned to phenyl protons (7.75 -7.00 ppm) as well as a complex multiplet due to cyclopentadienyl protons (6.58-5.62 ppm) were present in a ratio of approximately 2:1. A singlet which may be due to a terminal Si-$\underline{H}$ resonance was observed at 4.6 ppm. When the temperature was lowered to 3°C and the spectrum remeasured, the Si-$\underline{H}$ resonance was absent and the cyclopentadienyl resonances had become much smaller. In addition, with the exception of a peak which had appeared at approximately 1.5 ppm, the multiplet assigned to Cp-C$\underline{H}_3$ resonances had become broader. The phenyl proton peaks remained the same. Further lowering of the temperature seemed to cause further broadening.

In conclusion, it seems likely that paramagnetic broadening is present in the ^1H NMR spectrum of the brown solid isolated from the reaction of $PhSiH_3$ with CpCp*$TiMe_2$. It is possible that the steric bulk associated with the pentamethylcyclopentadienyl ligand prevents the formation of dimers of the type isolated from the reaction of Cp_2TiMe_2 with

$PhSiH_3$. At present ESR measurements have shed no further light on the possible presence of paramagnetic monomers although studies are continuing (166). If the reaction of $PhSiH_3$ with $CpCp^*TiMe_2$ is carried out in the presence of a large excess of $PhSiH_3$, oligophenylsilane is produced. Thus $CpCp^*TiMe_2$ acts as a catalyst (or catalyst precursor) in the polymerisation reaction of $PhSiH_3$.

III.5 THE REACTIONS OF SOME OTHER PRIMARY SILANES WITH Cp_2TiMe_2

III.5.1 Reaction of $HxSiH_3$ with Cp_2TiMe_2 (2:1 molar ratio)

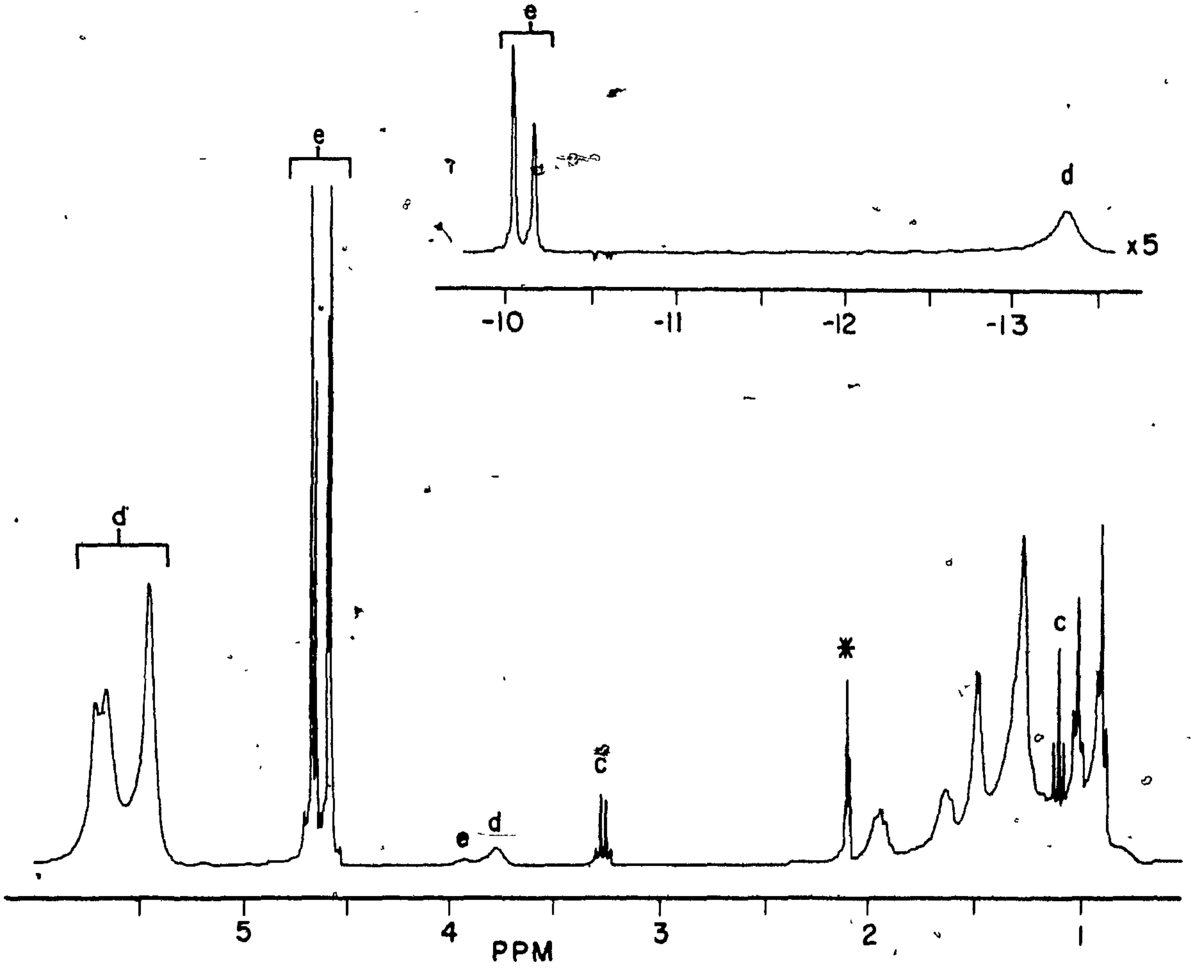
Solid material was not isolated from the reaction of hexylsilane with Cp_2TiMe_2 despite many attempts. The results suggest that for a stoichiometric ratio of 2:1 (silane to titanocene), the reaction equation is analogous to that given for the reaction of $PhSiH_3$ with Cp_2TiMe_2 (equation III.8). ^1H NMR studies of the reaction confirmed the evolution of methane, as well as the formation of methylhexylsilane, $MeHxSiH_2$ (when the reaction was done with a larger excess of $HxSiH_3$, oligohexylsilane was also observed). After the reaction was complete, and gas evolution had ceased, the volatiles were removed in vacuo. The residue was dissolved in toluene-d_8 and its ^1H NMR spectrum measured. Two complexes were identified, $\{[(\eta^5-C_5H_5)_2Ti]_2(\mu-H)(\mu-HSiHxH)\}$, XIV and

$\{(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}HSiHxH)\}_2$, XV, in a ratio of 2:1. Neither complex was isolated pure despite a number of attempts using different reaction conditions. It is likely that this is due to the high solubility of the hexyl complexes relative to their phenyl analogues X and XI, and the ideal reaction solvent mixtures not having been obtained. With the exception of the protons of the hexyl groups which were found to overlap, all other peaks due to complexes XIV and XV were assigned (see EXPERIMENTAL).

There are a number of interesting aspects to the ^1H NMR spectrum obtained for the mixture of XIV and XV (FIGURE III.13). Firstly, all the peaks attributed to XIV show paramagnetic broadening characteristic of complexes of this type. Hence a variable temperature ^1H NMR study was performed (FIGURE III.14), the results of which are summarised in TABLE III.5. One may conclude from these studies that the structure of XIV is analogous to that of X (FIGURE III.11).

Secondly, complex XV was found to be present as two isomeric forms, unlike the analogous phenyl complex where only the cis isomer was observed. The two isomers have been shown in FIGURE III.12. As may be seen in FIGURE III.13, the Cp and Si-H-Ti resonances were clearly visible for both isomers: XVa, Cp: δ 4.66, 4.57; Si-H-Ti: δ -10.08. XVb, Cp: δ 4.64, 4.58; Si-H-Ti: δ -10.20. The hexyl protons of the two isomers could not be assigned due to overlapping in this region. The terminal Si-H resonances could not be distinguished for the

FIGURE III.13: ^{1}H NMR SPECTRUM OF COMPLEXES $\{[(\eta^5\text{-}C_5H_5)_2Ti]_2\text{-}(\mu\text{-}H)(\mu\text{-}HSiHxH)\}$, XIV and $\{(\eta^5\text{-}C_5H_5)_2Ti\text{-}(\mu\text{-}HSiHxH)\}_2$, XV[a,b]



[a] at ambient temperature

[b] in toluene-d_8. Peaks due to the solvent are marked with an asterisk (*)

[c] peaks due to diethyl ether

[d] peaks due to complex XIV

[e] peaks due to complex XV

TABLE III.5: ^{1}H NMR DATA FOR $\{[(\eta^{5}-C_{5}H_{5})_{2}Ti]_{2}(\mu-H)(\mu-HSiHxH)\}$[a,b]

TEMPERATURE[c]	$C_5\underline{H}_5$[d]	Si-$\underline{H}$[d]	Si-$\underline{H}$-Ti[d]	Ti-$\underline{H}$-Ti[d]
Ambient[d]	(5.69, 5.64)[e] 5.44 (17)[f]	3.75 (21)	-13.33 (50)	g
-23	5.64, 5.57, 5.37 (5)[f]	3.75 (19)	-13.18 (17)	-19.88 (140)
-58	5.64, 5.57, 5.36[f]	3.87 (16)	-13.13 (13)	-19.52 (40)
-79	5.65, 5.58, 5.35[f]	3.93 (27)	-13.12 (23)	-19.49 (23)

[a] measured in ppm

[b] in toluene-d_8

[c] measured in °C

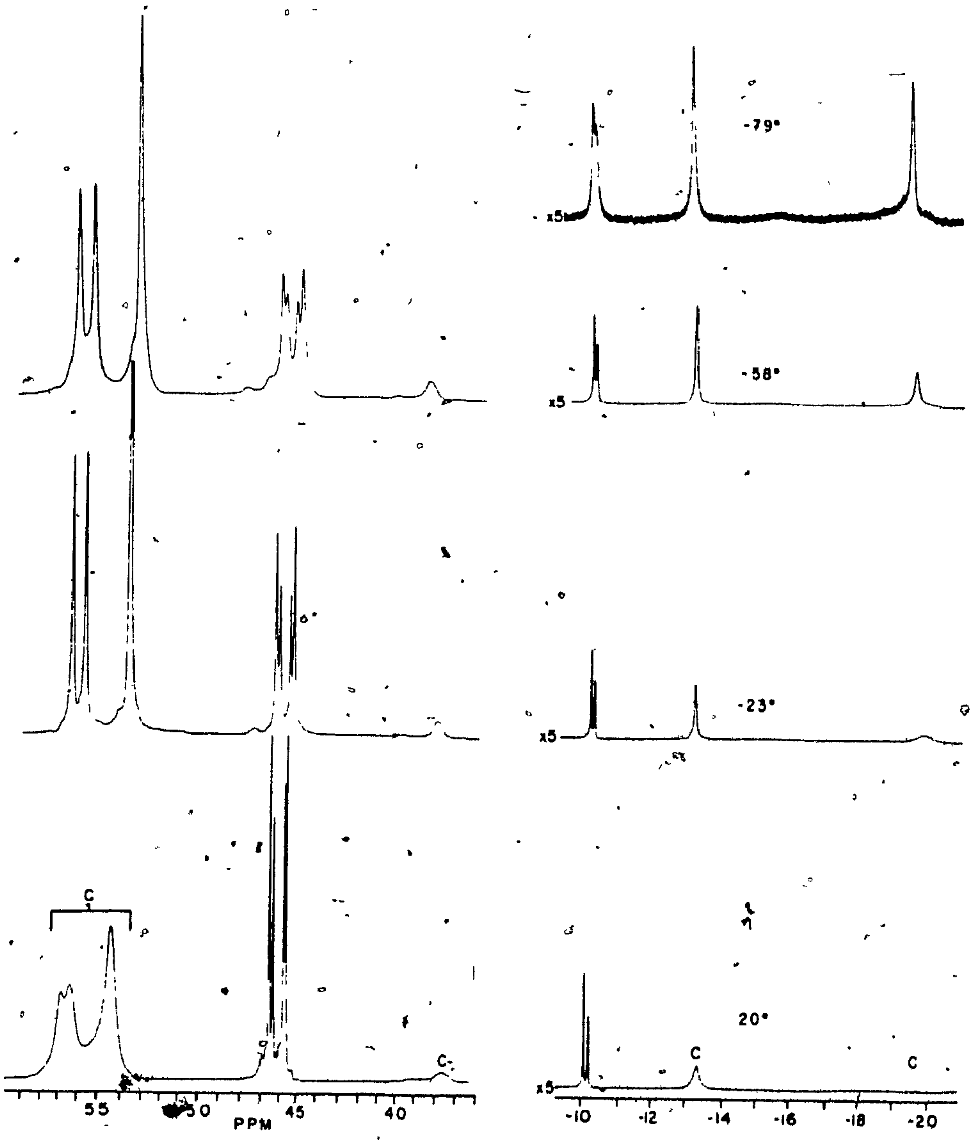
[d] numbers in brackets refer to the linewidth at half height, $\nu_{\frac{1}{2}}$, in Hz

[e] 2 overlapping broad bands

[f] 1 broad band (2 overlapping singlets)

[g] peak not observed

<u>FIGURE III.14</u>: ^{1}H NMR SPECTRUM OF COMPLEXES $\{[(\eta^5\text{-}C_5H_5)_2Ti]_2\text{-}(\mu\text{-}H)(\mu\text{-}HSiHxH)\}$, <u>XIV</u> and $\{(\eta^5\text{-}C_5H_5)_2Ti\text{-}(\mu\text{-}HSiHxH)\}_2$, <u>XV</u> AT SELECTED TEMPERATURES[a,b]



[a] in toluene-d_8

[b] probe temperature given in °C

[c] peaks due to complex <u>XIV</u>

two isomers, and were observed as a complex multiplet at 3.91 ppm. Based solely on the ^1H NMR integrals, the ratio of XVa (cis) to XVb (trans) was 1.5:1 which remained constant with time. The assignment of the isomers is based on two considerations. Firstly, in analogy with the corresponding phenyl complex XI, the cis isomer was thought to be the predominant one, present in the largest amount. More importantly however, the chemical shift separation of the two cyclopentadienyl resonances in the two isomers was different. Based merely on steric grounds, a greater chemical shift difference might reasonably be expected between the two different sets of cyclopentadienyl resonances in the cis isomer (XVa) than between those in the trans isomer (XVb).

Finally, as noted for the analogous phenyl complexes, conversion of XV to XIV occurred in solution. After 7 days, the ^1H NMR spectrum of the mixture of XIV and XV showed only peaks due to XIV. No other decomposition was evident.

III.5.2 Reaction of $BzSiH_3$ with Cp_2TiMe_2 (1:1 molar ratio)

Solid material was isolated from the reaction (1:1 stoichiometric ratio) of benzylsilane with Cp_2TiMe_2 in diethylether. Rather surprisingly, considering the stoichiometry, the ^1H NMR spectrum (C_6D_6) showed that a mixture of $\{[(\eta^5\text{-}C_5H_5)_2Ti]_2(\mu\text{-}H)(\mu HSiBzH)\}$, XVI and

$\{(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}HSiBzH)\}_2$, XVII (in the ratio of 1:3.5) had been obtained. Additional ^1H NMR studies of the reaction showed that methane and methylbenzylsilane, $MeBzSiH_2$, were also produced (in the presence of an excess of $BzSiH_3$, polymerisation to oligobenzylsilane was also noted). The reaction seems analogous to that postulated for the phenyl complex, XI (equation III.8) despite a ratio for silane to titanocene of only 1:1. The fact that XVII was observed in excess of XVI may be due to the increased solubility (ether) of the benzyl complex XVI relative to the phenyl analogue X, which allows for more facile conversion to XVII under the reaction conditions used. No other cyclopentadienyl-titanium species appeared in the ^1H NMR spectrum when a mixture of XVI and XVII was left in C_6D_6 for 4 days. However, conversion of XVII to XVI had occurred. This conversion, like that of XI to X, was more rapid in THF-d_8.

The peaks in the ^1H NMR spectrum of XVI and XVII due to XVI showed paramagnetic broadening similar to that observed for complexes X, XII and XIV. Thus the spectrum was remeasured in THF-d_8 and a variable temperature ^1H NMR study was performed, the results of which are given in TABLE III.6. The phenyl proton region was not temperature dependant, and the peaks overlapped with those from complex XVII and with those from the benzyl aromatic groups. The benzyl CH_2 and terminal Si-H protons were not detected due to overlapping

TABLE III.6: ^1H NMR DATA FOR $\{[(\eta^5-C_5H_5)_2Ti]_2(\mu-H)(\mu-HSiBzH)\}^{a,b}$

TEMPERATURE[c]	$C_5\underline{H}_5$[d]	Si-$\underline{H}$-Ti[d]	Ti-$\underline{H}$-Ti[d]
Ambient	5.76 (21)	-13.01 (54)	e
0	5.69[f], 5.49	-12.92 (24)	e
-25	5.69[f], 5.49	-12.92 (17)	-19.74 (107)
-50	5.69, 5.58[g], 5.43	-12.92 (14)	-19.46 (53)
-75	5.71[f], 5.53	-12.93 (14)	-19.43 (14)

[a] measured in ppm

[b] in THF-d_8

[c] measured in °C

[d] numbers in brackets refer to the linewidth at half height, $\nu_{\frac{1}{2}}$, in Hz

[e] peak not observed

[f] 3 overlapping singlets

[g] 2 overlapping singlets

with other peaks in these regions. The likely structure of XVI, in analogy with X, has been shown in FIGURE III.11.

As observed for the corresponding hexyl complex XV, the ^{1}H NMR spectra showed that XVII was present as two isomers (cis:trans = 1:2). The two isomers have been shown in FIGURE III:12. The cyclopentadienyl, $-CH_2$ and Si-H-Ti resonances were visible for both isomers: XVIIa, Cp: δ 4.61, 4.46; $-CH_2-$: δ 2.64, 2.44 ($^2J_{H-H}$ = 13 Hz); Si-H-Ti: δ -10.02. XVIIb, Cp: δ 4.58, 4.54; $-CH_2-$: δ 2.73, 2.52 ($^2J_{H-H}$ = 12 Hz); Si-H-Ti: δ -9.73. The assignment of the isomers was analogous to that discussed for the hexyl isomers. Peaks due to other terminal Si-H resonances were not observed. Conversion of one isomer to the other was not observed and the ratio remained constant with time.

III.6 THE CHARACTERISATION OF $\{(\eta^5-C_5H_5)_2[SiH(CH_3)(C_6H_5)]-Zr(\mu-H)_2Zr[SiH_2(C_6H_5)](\eta^5-C_5H_5)_2\}$, XVIII

III.6.1 Reaction of $PhSiH_3$ with Cp_2ZrMe_2 (3:1 molar ratio); isolation of complex XVIII

Pure XVIII was isolated by the reaction (3:1 molar ratio) of $PhSiH_3$ with Cp_2ZrMe_2. Diethylether was the preferred reaction solvent, as the organosilane products remained in solution whilst XVIII readily crystallised from it. Based on those products observed in the ^1H NMR spectrum (C_6D_6), a possible reaction equation is given below:

$$2Cp_2ZrMe_2 + 3PhSiH_3 \xrightarrow{Et_2O} 3MeH + \frac{1}{n}(HPhSi)_n + \{Cp_2(SiHMePh)Zr(\mu\text{-}H)_2Zr(SiH_2Ph)Cp_2\} \qquad III.12$$

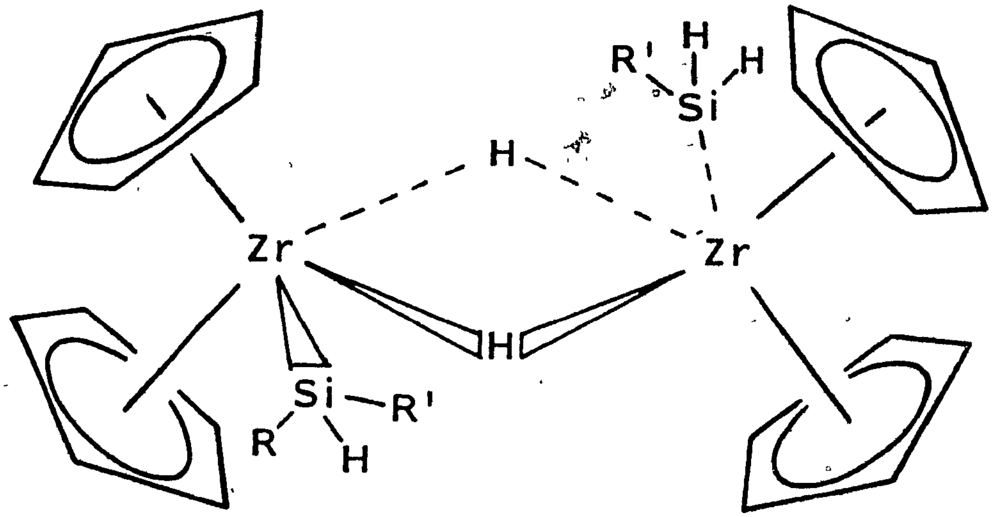
<u>XVIII</u>

The excess $PhSiH_3$ present in the reaction mixture was slowly converted to oligophenylsilane with the associated loss of H_2. ^1H NMR studies of the reaction using $PhSiD_3$, detected CH_3D (triplet at 0.17 ppm), indicative of abstraction of a deuteron from the silane. The spectacular sudden colour change observed in the titanium reactions did not occur, rather a slow change from colourless to dark orange occurred over a period of hours together with slow evolution of gas.

Complex <u>XVIII</u> is composed of the units $Cp_2ZrH(SiH_2Ph)$ and $CpZrH(SiHMePh)$, and a diagram of it is shown in FIGURE III.15.

One possible mechanism to account for the initial reaction between $PhSiH_3$ and Cp_2ZrMe_2 has already been shown in SCHEME III.1 for the analogous titanium reaction. Such a mechanism would lead to the formation of $Cp_2ZrMe(SiH_2Ph)$ which could subsequently react as shown in SCHEME III.6.

FIGURE III.15: DIAGRAM TO SHOW THE PROPOSED STRUCTURE OF $\{(\eta^5-C_5H_5)_2(SiHRR')Zr(\mu-H)_2Zr(SiH_2R')-(\eta^5-C_5H_5)_2\}$

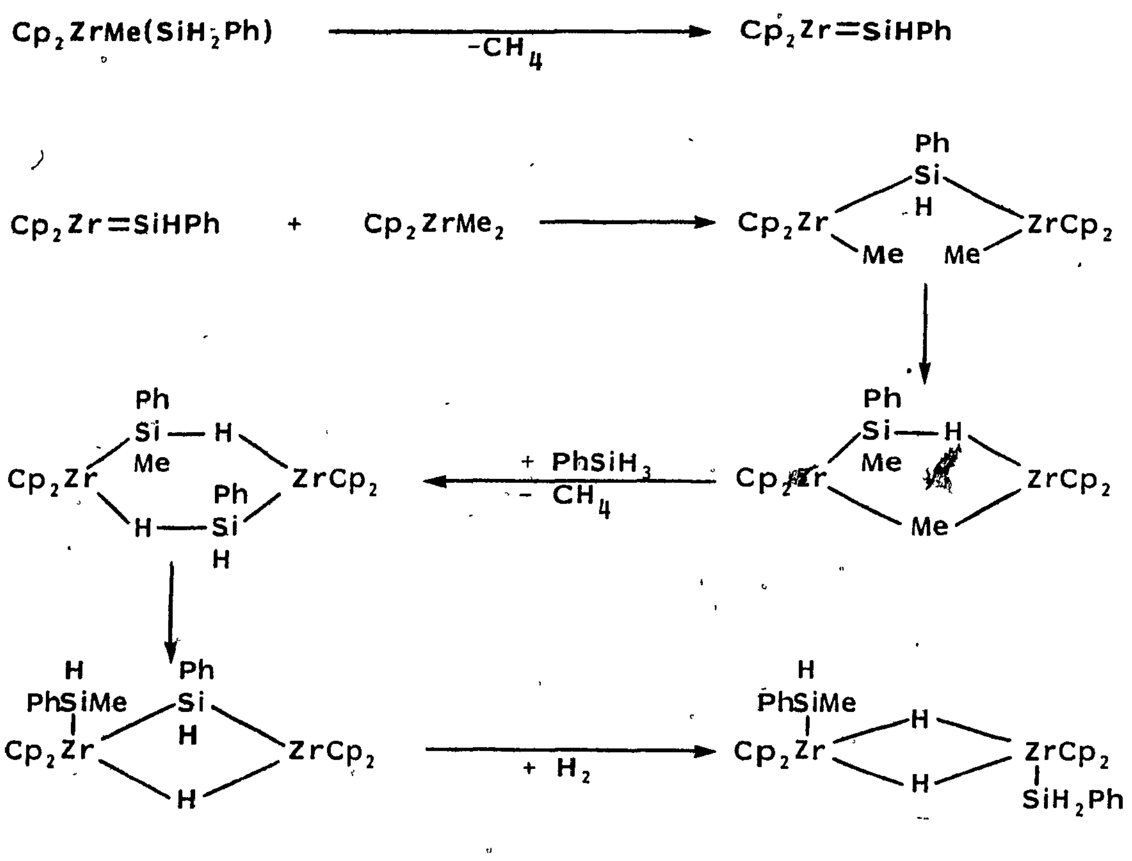


XVIII R = Me R' = Ph

XIX R = H R' = Ph

XX R = Me R' = Bz

XXI R = H R' = Bz



XVIII

SCHEME III.6

The precursor to XVIII may also react with $PhSiH_3$ to produce polysilyl metal species, a possible mechanism for which will be discussed later. Reaction with H_2 to produce XVIII removes the metal from the catalytic cycle. If XVIII is added to $PhSiH_3$, polymerisation of the latter occurs, albeit slowly, possibly by the regeneration of the active species from XVIII via loss of H_2.

The second mechanism as shown in SCHEME III.2 for the analogous titanium reaction seems unlikely here since it involves a spontaneous M(IV) to M(II) oxidation state change. McAlister et al. originally proposed the mechanism to account for the elimination of alkane from $Cp^*_2ZrH(CH_2CHMe_2)$, as already discussed (144). Subsequently however, Brintzinger has suggested that such a mechanism is unlikely because of the strong tendancy for Zr(II) species to oxidise to Zr(IV) species (170). In the case of titanium however, the lower oxidation states are more accessible and SCHEME III.2 feasible.

Equation III.12 may also involve free radicals. Samuel et al. have studied the photolysis of Cp_2ZrMe_2 using ESR spectroscopy, and have suggested that it may occur initially as shown in SCHEME III.7 (145):

$$Cp_2ZrMe_2 \xrightarrow{h\nu} Cp_2Zr^{III}Me + \cdot Me$$

$$Cp_2Zr^{III}Me \xrightleftharpoons{\Delta} [Cp_2Zr^{III}Me]_2$$

$$[Cp_2Zr^{III}Me]_2 \xrightleftharpoons[h\nu]{\Delta} Cp_2Zr + Cp_2ZrMe_2$$

SCHEME III.7

The hydride $Cp(C_5H_4)Zr^{III}H$, observed in the ESR spectrum, was thought to result from the thermal rearrangement of Cp_2Zr. The formation of an analogous hydride was not observed during the photolysis of Cp_2TiMe_2. This difference in behavior may be due, as already discussed, to the stronger Zr-H bond (95) relative to titanium. It is possible that the reaction of $PhSiH_3$ with Cp_2ZrMe_2 involves the formation of methyl radicals as shown in SCHEME III.7. Subsequently, reaction with $PhSiH_3$ (equation III.3), followed by reaction of the silyl radicals so produced (equation III.13).

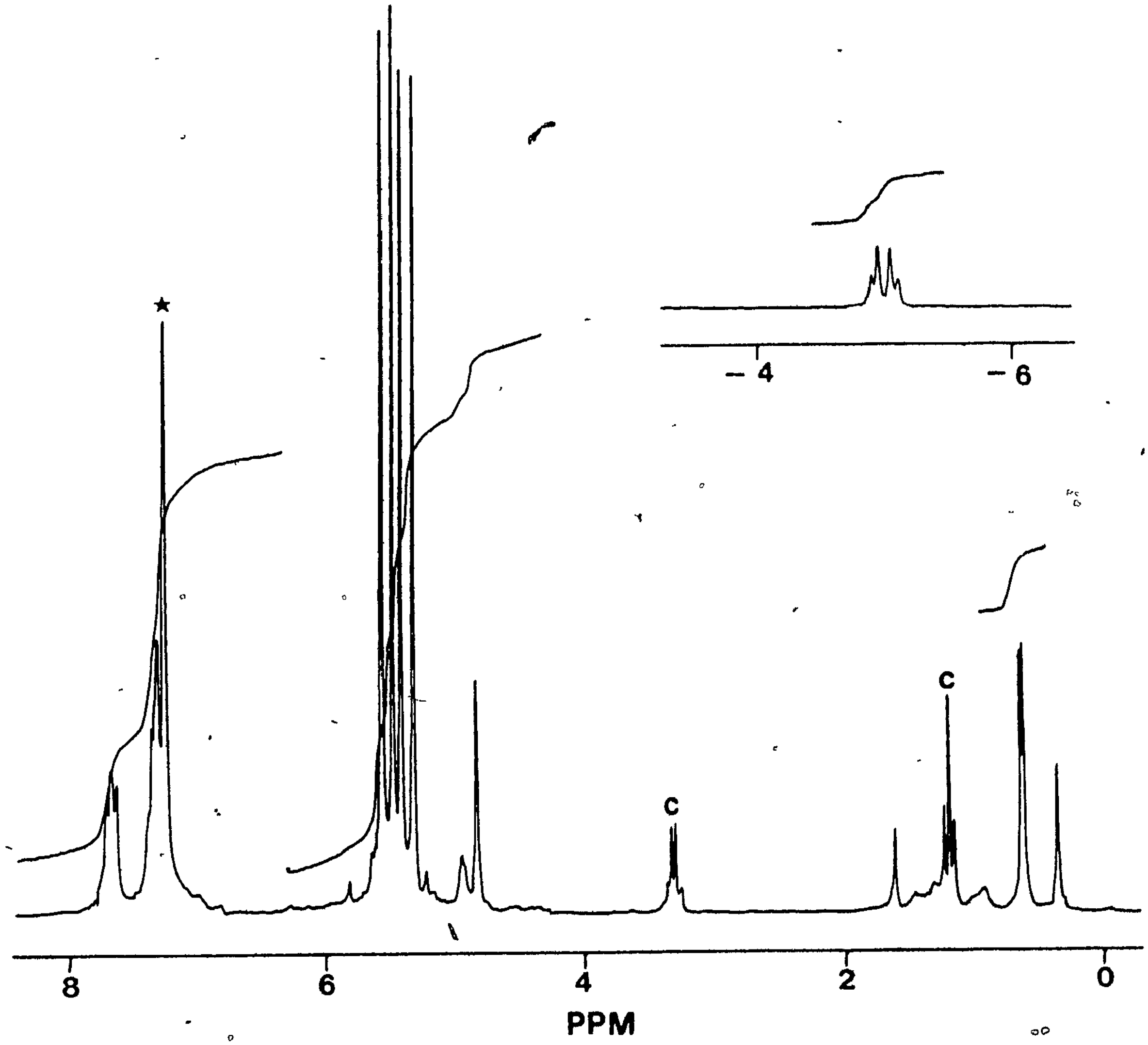
$$\cdot SiH_2Ph + Cp_2ZrMe_2 \longrightarrow Cp_2ZrMe(SiH_2Ph) + \cdot Me \qquad III.13$$

$Cp_2ZrMe(SiH_2Ph)$ so produced could subsequently react as shown in SCHEME III.6, ultimately to produce XVIII.

XVIII is sparingly soluble in most organic solvents. A ^1H NMR spectrum (C_6D_6) is however shown in FIGURE III.16. The presence of 4 cyclopentadienyl resonances of equivalent intensity, and particularly the observation of the zirconium hydrides as an AB quartet at ~ -5 ppm (characteristic of bridging zirconium hydrides) is consistent with the proposed structure (FIGURE III.15).

Structurally, XVIII is similar to $\{(\eta^5\text{-}C_5H_4Me)_2ZrH\text{-}(\mu\text{-}H)\}_2$, prepared by Jones et al. (117). The study of this

FIGURE III.16: ^{1}H NMR SPECTRUM OF $\{(\eta^5\text{-}C_5H_5)_2(SiHMePh)Zr(\mu\text{-}H)_2Zr(SiH_2Ph)(\eta^5\text{-}C_5H_5)_2\}$[a,b]



[a] at ambient temperature

[b] in C_6D_6. The peak due to the solvent is marked with an asterisk (*)

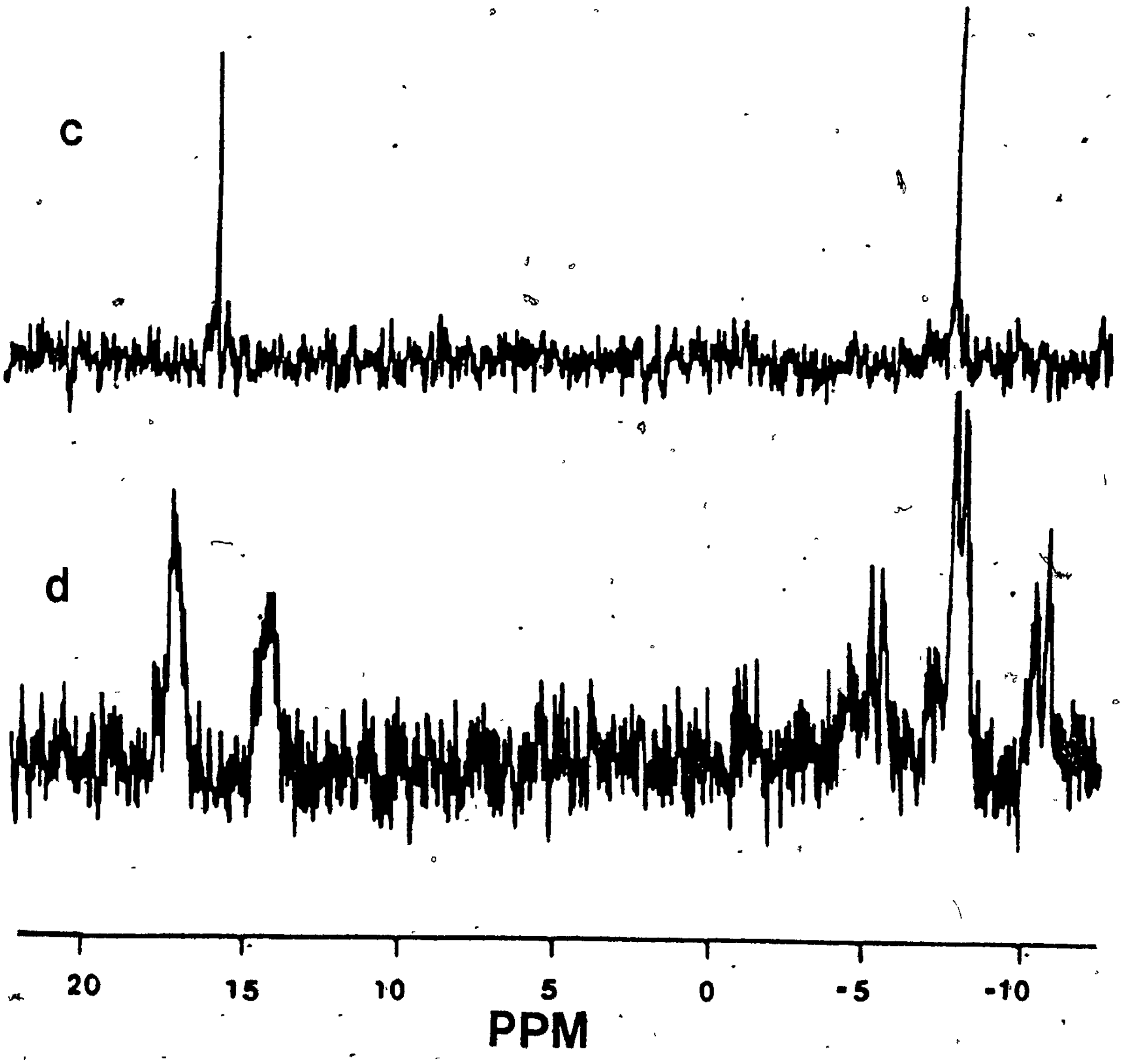
[c] peaks due to diethyl ether

complex provided the first structural evidence for the existence of the $Zr(\mu-H)_2Zr$ linkage in binuclear zirconium hydride complexes. As already discussed, Cp_2M fragments have been shown to possess three frontier orbitals (142). In XVIII, it seems likely therefore that these may be used to form two bridging Zr-H-Zr bonds, and one terminal Zr-Si bond at each zirconium centre. Attempts to obtain an X-ray structural analysis of XVIII were not successful, due to problems with disorder in the crystal. Preliminary results obtained from Professor A. Beauchamp, Laboratoire de Diffraction des Rayons-X, Université de Montréal, show that the crystals studied were monoclinic, $P2_1/c$, where a = 8.86, b = 16.34, c = 10.25 Å, β = 90.82°. The structure was solved in this space group and consisted of pairs of centrosymmetrically related $(\eta^5-C_5H_5)_2Zr$ units whose relative orientation and Zr-Zr separation was similar to that for $\{(\eta^5-C_5H_4Me)_2ZrH(\mu-H)\}_2$ (117). Thus it seems likely that the two units of the dimer are held by a similar pair of bridging hydrides. One of the C_5H_5 groups was severely disordered and the electron density for the $Si-CH_3$ group was more consistent with half occupancy at the two sites of the dimer. However there was not disorder of the Si atoms corresponding to reflection through the plane perpendicular to the Si-Zr-Zr-Si plane, indicating that the crystal contains a single diastereomer. The present level of refinement (R = 12) does not allow an interpretation of the disorder in terms of superimposed ordered chemical units.

A natural abundance ^{29}Si NMR spectrum (THF-d_8) of XVIII, obtained using a DEPT pulse sequence, is shown in FIGURE III.17. The decoupled spectrum clearly shows the presence of two types of silicon atom (at 16 and -8 ppm). The coupled spectrum shows a doublet for the peak at 16 ppm (J = 168 Hz), assigned to $\underline{Si}$-H(CH_3), and a triplet of doublets at -8 ppm ($^1J_{Si-H}$ = 158 Hz, $^2J_{Si-H}$ = 4.4 Hz) assigned to $\underline{Si}$-H_2. Both chemical shift positions for the silicon atoms of XVIII are to high field of those obtained for most transition metal silyl complexes. This is probably a result of the absence of any d electrons in the complex, where both Zr atoms are in the +4 oxidation state. The fact that the $\underline{Si}$-H_2 group is present in the coupled spectrum (FIGURE III.17) as a triplet of doublets suggests that the Si atom is coupled to one of the bridging hydrides.

Decomposition of XVIII occurred slowly in toluene-d_8 over a period of several days at ambient temperature, to produce $MePhSiH_2$ and $PhSiH_3$, identified by ^1H NMR. A complex pattern of bands in the cyclopentadienyl region appeared at 6.50 - 5.91 ppm. Thermolysis and photolysis studies (119) have shown that $[(\eta^5\text{-}C_5H_4Me)_2ZrH(\mu\text{-}H)]_2$ reductively eliminates H_2, and initially forms a paramagnetic zirconium hydride, as detected by ESR. Evidence for paramagnetic hydrides and a mixed valent hydride analogous to $\{[(\eta^5\text{-}C_5H_5)_2TiH]_2(\mu\text{-}H)\}$ upon photolysis of solutions of XVIII has been obtained from ESR spectroscopy (166).

FIGURE III.17: ^{29}Si DEPT NMR SPECTRUM OF $\{(\eta^5\text{-}C_5H_5)_2(SiHMePh)\text{-}Zr(\mu\text{-}H)_2Zr(SiH_2Ph)(\eta^5\text{-}C_5H_5)_2\}^{a,b}$



[a] at ambient temperature

[b] in THF-d_8

[c] decoupled

[d] coupled

The preparation of $\{(\eta^5\text{-}C_5H_5)_2Zr(\mu\text{-}H)(SiH_2Ph)\}_2$, XIX, was attempted by treating $[Cp_2ZrH_2]_n$ with an excess of $PhSiH_3$ (1:4.5 mole ratio) in THF. A slow gas evolution was noted, with the colour of the solution gradually darkening from colourless to dark orange/brown over a period of approximately 16 hours. At the end of this time, the $[Cp_2ZrH_2]_n$ had been consumed to give a clear, viscous solution. Despite various attempts, precipitation of solid material could not be induced and the volatiles were removed to give an oily gum. ^1H NMR (C_6D_6) showed this contained mainly oligophenylsilane together with some XIX. A singlet in the Cp region appeared at 5.40 ppm, and a singlet at -4.94 ppm was assigned to the bridging Zr-$\underline{H}_2$-Zr group. Peaks in a broad range (6.37-4.41 ppm) were assigned to the Si-$\underline{H}$ resonances of the oligosilane. It is possible that the fine structure observed at the low field end of this broad band contains other cyclopentadienyl protons. This band extends further downfield than that observed for the polymer only, the ^1H NMR spectrum of which will be discussed later. Peaks attributed to the cyclopentadienyl protons of decomposed XVIII, as already mentioned, appear from 6.50-5.91 ppm. Thus similar decomposition products may be present here. Complex XIX could not be isolated as a pure compound. This might be due to a number of reasons. In particular, the low solubility of $[Cp_2ZrH_2]_n$ necessitated an excess of $PhSiH_3$.

When a 1:1 ratio was used, the reaction did not appear to go to completion. It is possible that in this case, formation of an active species analogous to that postulated to be formed during the reaction of Cp_2ZrMe_2 with $PhSiH_3$ (SCHEME III.6), $\{Cp_2(SiH_2Ph)Zr(\mu\text{-}H)[\mu\text{-}Si(H)(Ph)]ZrCp_2\}$, might occur. Such a species, even if present in low concentration, might subsequently proceed to react with silane at a faster rate than with H_2 (leading to the production of polysilylmetal species rather than XIX) and at a faster rate than reaction of $(Cp_2ZrH_2]_n$ with $PhSiH_3$, eventually resulting in $(HPhSi)_n$ and unreacted hydride. XIX could not be isolated from the reaction even when an excess of silane was used. In this case, reaction of $\{Cp_2(SiH_2Ph)Zr(\mu\text{-}H)[\mu\text{-}Si(H)(Ph)]ZrCp_2\}$ with $PhSiH_3$ could be favoured over its reaction with H_2, leading to the production of polysilylmetal species. The suggested structure of XIX has been shown in FIGURE III.15. It is somewhat surprising that even in the presence of a large excess of $PhSiH_3$, no XIX was detected during the reaction of $PhSiH_3$ with Cp_2ZrMe_2, with XVIII being formed preferentially.

In conclusion, the reaction of $PhSiH_3$ with Cp_2ZrMe_2 was observed to give one main organometallic complex, XVIII. The difference in the reactivity of Cp_2ZrMe_2 vs. Cp_2TiMe_2 appears to be due to the ready accessibility and relative stability of lower oxidation states of the latter.

III.7 THE REACTION BETWEEN $BzSiH_3$ AND Cp_2ZrMe_2 (3:1 MOLAR RATIO)

Solid material was isolated from the reaction of $BzSiH_3$ with Cp_2ZrMe_2 (3:1 molar ratio) in Et_2O. Due to the low solubility of the ~~solid~~ in C_6D_6, the ^1H NMR spectrum was obtained in THF-d_8. The solid was found to consist of two complexes, analogous to XVIII and XIX. These were $\{(\eta^5\text{-}C_5H_5)_2(SiHMeBz)Zr(\mu\text{-}H)_2Zr(SiH_2Bz)\}$, XX and $\{(\eta^5\text{-}C_5H_5)_2Zr(\mu\text{-}H)(SiH_2Bz)\}_2$, XXI, present in a ratio of 2:1. Evidence of decomposition was observed in the ^1H NMR spectrum of the mixture, in the form of a low field cyclopentadienyl region (6.35-5.85 ppm), similar to that observed for the decomposition products of XVIII. ^1H NMR studies on the reaction of $BzSiH_3$ with Cp_2ZrMe_2 have shown that methane is evolved as the reaction proceeds, but no $MeBzSiH_2$ was observed. Decomposition of XX, however, eventually led to its formation. The supernatant was found to contain oligobenzylsilane, produced from the polymerisation of excess $BzSiH_3$. In conclusion it is likely that the structures of XX and XXI are completely analogous to XVIII and XIX. A diagram of the proposed structure has been shown in FIGURE III.15.

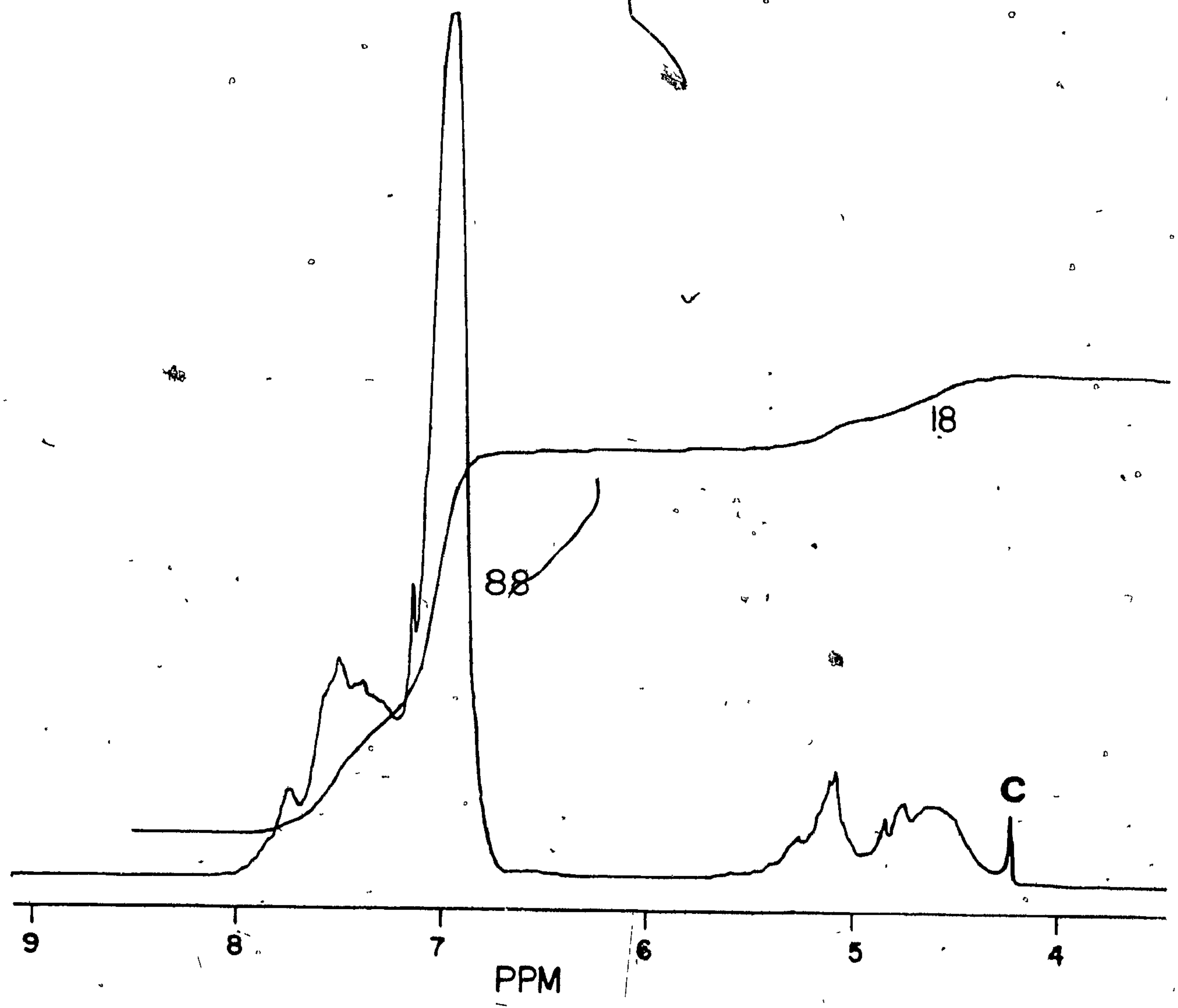
III.8 THE CHARACTERISATION OF OLIGOPHENYLSILANE AND OLIGOHEXYLSILANE

III.8.1 Oligophenylsilane

Oligophenylsilane, $(HPhSi)_n$, was prepared via the reaction of $PhSiH_3$ with Cp_2TiMe_2 and Cp_2ZrMe_2, and was obtained in all cases as a brittle white glass. ^1H NMR spectroscopy (C_6D_6) provided little information since in all cases, a broadened phenyl region (8.00-6.72 ppm), together with a broad massif to low field of the Si-H resonances of $PhSiH_3$ (5.43-4.29 ppm), were evident. The integrals obtained for these were consistent with those expected for an $(HPhSi)_n$ oligomer. The spectrum of oligophenylsilane (C_6D_6) prepared from $PhSiH_3/Cp_2TiMe_2$ (2 mol %) is shown in FIGURE III.18. In the ^{29}Si NMR spectrum (DEPT pulse sequence), two types of silicon atoms were differentiated according to the number of attached protons, i.e. SiH and SiH_2. The Si-H resonances were at high field (-59 to -66 ppm) relative to the Si-H_2 resonances (-55 to -59 ppm). Qualitatively this confirmed the presence of Si-H_2 end groups in the oligomer, thus providing evidence for a linear as opposed to a cyclic structure.

The IR spectrum of the oligomer as a film formed by evaporation of a pentane solution gave a strong ν(Si-H) band at 2086 cm^{-1}, significantly lower than that of $PhSiH_3$ (2150

FIGURE III.18: ^{1}H NMR SPECTRUM OF OLIGOPHENYLSILANE[a,b]



[a] in C_6D_6 at ambient temperature

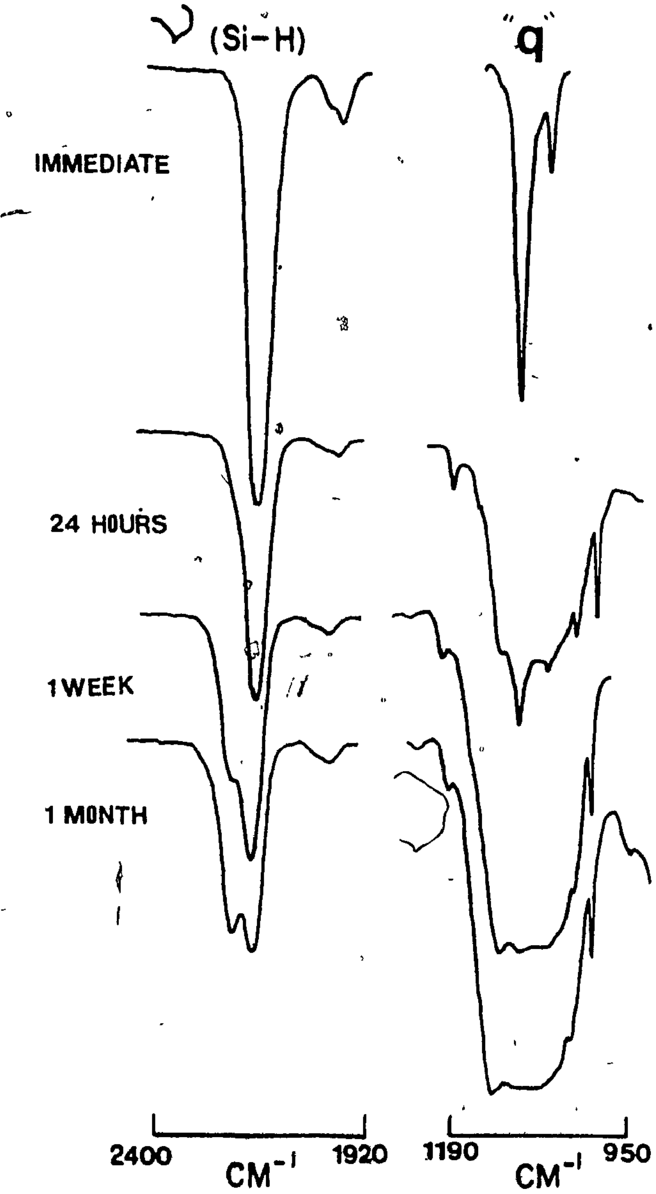
[b] prepared using $PhSiH_3/CpTiMe_2$ (2 mol %)

[c] $PhSiH_3$

cm^{-1}). It has been reported that ν(Si-H) shifts to a lower wavenumber as the degree of substitution at the silicon atom increased (171). The IR spectrum also supported the presence of SiH_2 end groups since a band was detected at 910 cm^{-1} (172). IR spectroscopy was useful in determining the degree of oxidation of $(HPhSi)_n$, leading to the formation of siloxanes. These were detected by the presence of a very strong band at approximately 1100 cm^{-1} which eventually masked a peak due to the ring vibration "q" (Whiffen's notation (141)) which for Ph-Si compounds also appears at approximately 1100 cm^{-1} (171). In addition, changes to the ν(Si-H) band were also apparent upon oxidation of the oligomer. The effect of exposing $(HPhSi)_n$ to air is shown in FIGURE III.19.

$(HPhSi)_n$ was prepared using a variety of reaction conditions (discussed in II.10) in a preliminary study of the effect of catalyst concentration and temperature on the molecular weight. Vapour pressure osmometry results are given in TABLE III.7. No significant difference in the molecular weight was observed, regardless of reaction conditions used. Furthermore, $(HPhSi)_n$ formed during the reaction of $PhSiH_3$ with $Cp_2Ti(Co)_2$ (~ 6 mol %) was shown by GPC to possess a molecular weight which corresponded to approximately 8 silicon atoms (173).

FIGURE III.19: THE EFFECT OF OXIDATION ON THE IR SPECTRUM OF $(HPhSi)_n$[a,b]



[a] as pentane film on KBR plates

[b] oligomer prepared from $PhSiH_3/Cp_2TiMe_2$ (2 mol %)

TABLE III.7: NUMBER AVERAGE MOLECULAR WEIGHTS OF $(HPhSi)_n$[a,b]

CONDITIONS UNDER WHICH MADE	MOLECULAR WEIGHT	NUMBER OF SILICON ATOMS
$PhSiH_3/Cp_2TiMe_2$ (2 mol %)[c]	843	8
$PhSiH_3/Cp_2TiMe_2$ (2 mol %)[d]	958	9
$PhSiH_3/Cp_2TiMe_2$ (10 mol %)[c]	1358	13
$PhSiH_3/Cp_2ZrMe_2$ (1 mol %)[c]	1732	16

[a] in toluene at 50°C

[b] in Daltons

[c] oligomer prepared at ambient temperature

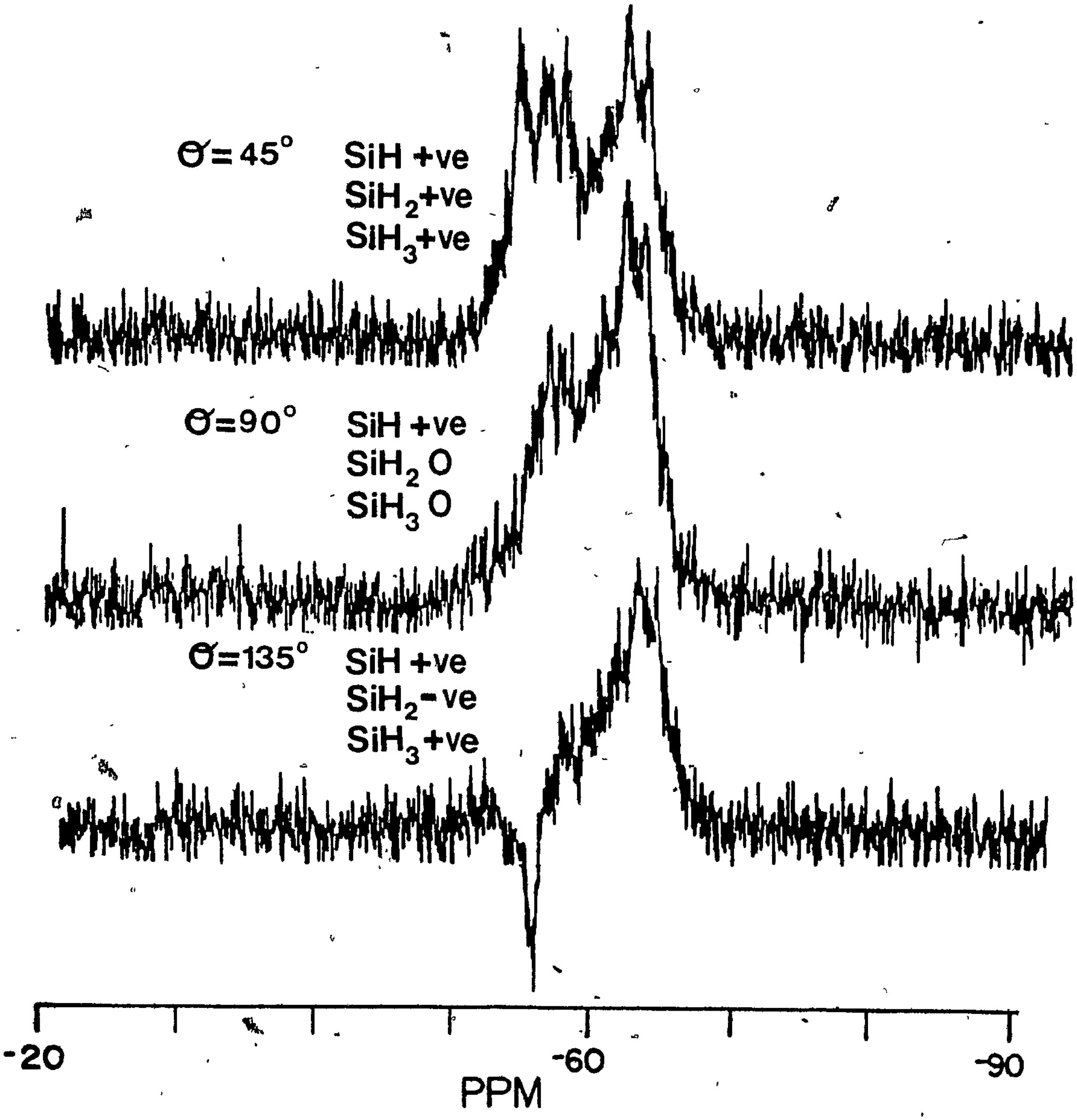
[d] oligomer prepared at 60°C/40 minutes followed by ambient temperature for 2 days

---

III.8.2 Oligohexylsilane

Oligohexylsilane, $(HHxSi)_n$, was obtained from the reaction of $HxSiH_3$ with Cp_2TiMe_2 (1 mol%) in toluene as a viscous oil whose ^1H NMR (C_6D_6) showed a broad band (4.13 - 3.81 ppm) due to the Si-H resonances, and a series of broadened bands (1.81-0.68 ppm) due to the hexyl protons, in the ratio of 1:13. As in the case of $(HPhSi)_n$, ^{29}Si NMR, using the DEPT pulse sequence, (FIGURE III.20) provided a means of differentiating the two types of silicon atoms detected according to their number of attached protons. The Si-H atoms

FIGURE III.20: ^{29}Si DEPT NMR SPECTRUM OF $(HHxSi)_n$[a]



[a] in C_6D_6 at ambient temperature

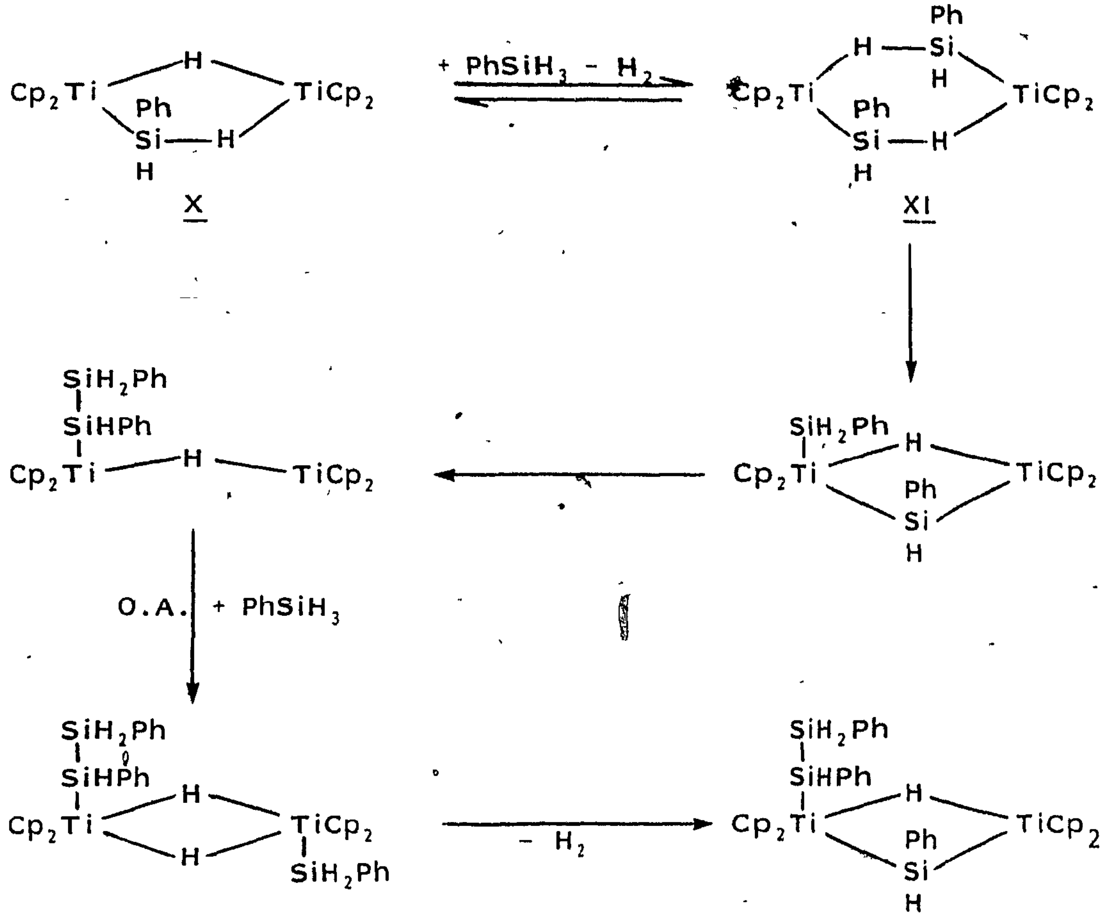
were found to be predominant, and at high field (-57 to -68 ppm) relative to the Si-H_2 atoms (-54 to -57 ppm). Once more the presence of the latter provided evidence for linear, as opposed to cyclic, oligomers.

The IR spectrum of the neat oil gave the strong ν(Si-H) band at 2080 cm^{-1} as compared to that of $HxSiH_3$ at 2140 cm^{-1}. The presence of a band at 940 cm^{-1}, as in the case of $(HPhSi)_n$, may indicate the presence of SiH_2 end groups. Oxidation of the oligomer proceeded slowly, and was indicated by the appearance of a band assigned to ν(Si-O) at approximately 1050 cm^{-1}.

A molecular weight of 984 D (corresponding to approximately 9 silicon atoms) was obtained for $(HHxSi)_n$ prepared from $HxSiH_3$ using Cp_2TiMe_2 (1 mol %) at ambient temperature. The chain length was thus found to be similar to that obtained for $(HPhSi)_n$.

III.8.3 Proposed mechanisms for the polymerisation of $RSiH_3$ using Cp_2TiMe_2 and Cp_2ZrMe_2

Several mechanisms may be postulated for the polymerisation of $RSiH_3$ using Cp_2TiMe_2. Using the case where R = Ph as an example, SCHEMES III.8, III.9 and III.10 may be suggested as plausible mechanisms, although it must be emphasised that they are of a speculative nature only. SCHEME III.8 involves repetitive insertion of a bridging silylene



SCHEME III.8

into a titanium-silicon bond, followed by oxidative addition of $PhSiH_3$ and subsequent loss of H_2. Chain termination could occur via reductive elimination of $H(HPhSi)_nH$, as shown in equation III.14:

$$\{Cp_2Ti[(SiHPh)_nSiH_2Ph](\mu\text{-}H)_2Ti(SiH_2Ph)Cp_2\} \longrightarrow$$

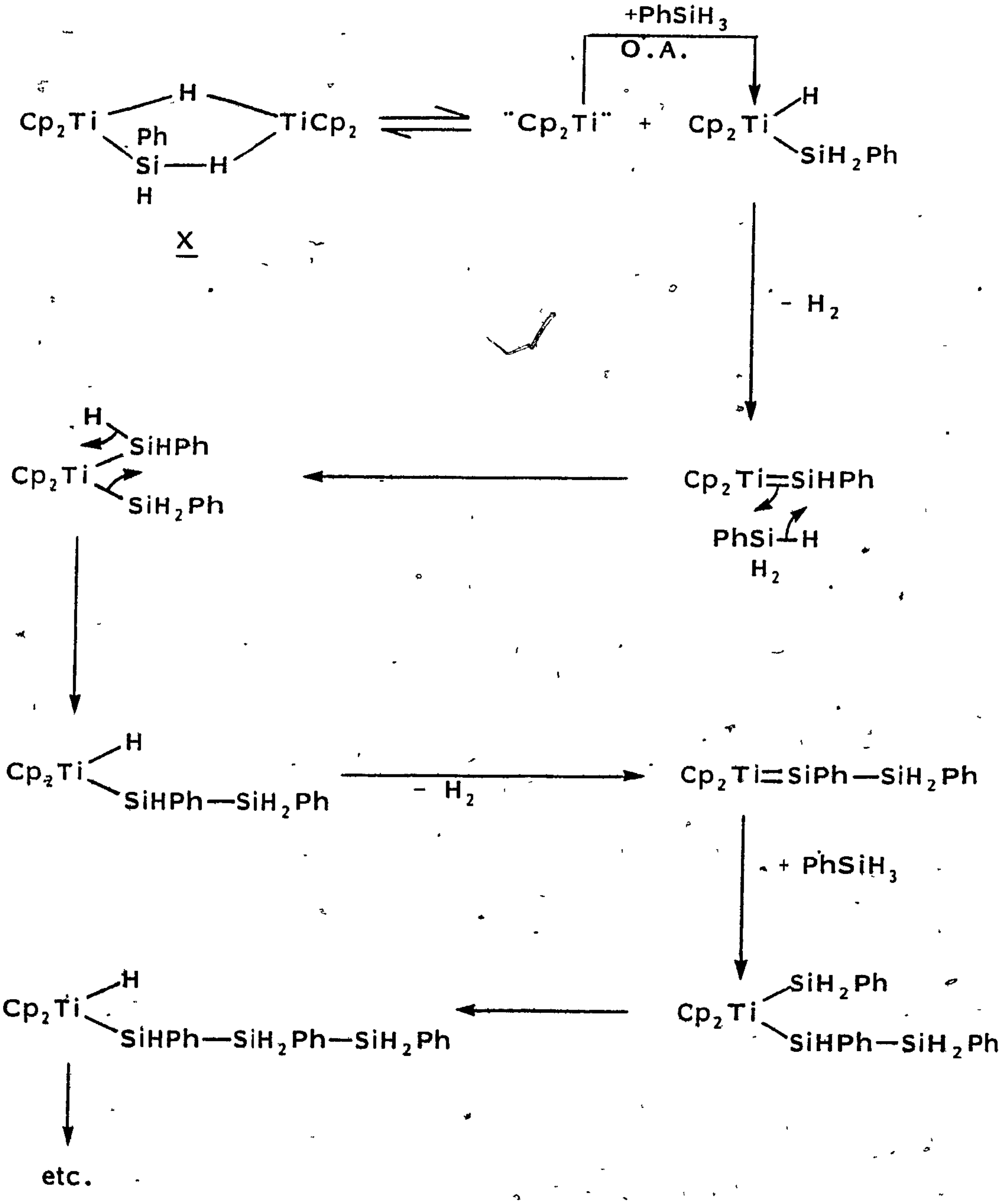
$$H(HPhSi)_nH + \underline{X} \qquad III.14$$

when secondary silanes such as Ph_2SiH_2 were reacted with Cp_2TiMe_2 (or Cp_2ZrMe_2), formation of the dimer was observed (174). In this case, for SCHEME III.8 to apply, one may postulate early termination by either reductive elimination (equation III.14, n = 1), or by preferential hydrogenolysis of $\{Cp_2(SiHR_2)Ti(\mu\text{-}H)(\mu\text{-}SiR_2)TiCp_2\}$ over further silylene insertion (equation III.15). Subsequent homolysis of the titanium-silyl bonds, followed by combination of the silyl radicals so formed could account for the disilane produced.

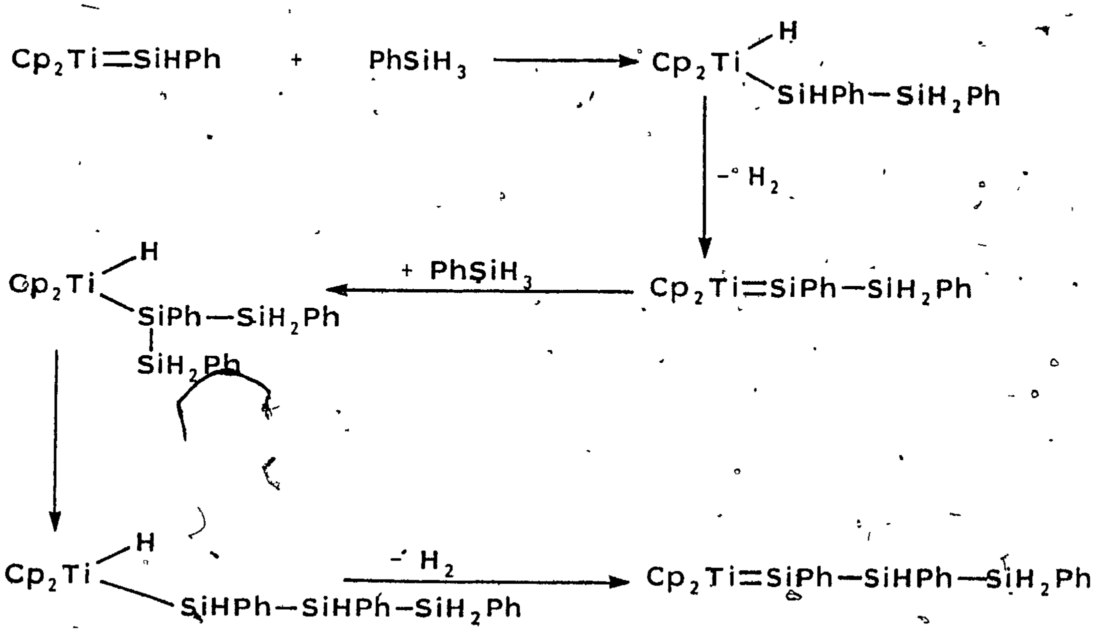
$$\{Cp_2(SiHR_2)Ti(\mu\text{-}H)(\mu\text{-}SiR_2)TiCp_2\} + H_2 \longrightarrow \{Cp_2Ti(\mu\text{-}H)(SiHR_2)\}_2 \qquad III.15$$

Two alternative mechanisms may be proposed whereby $PhSiH_3$ may be polymerised (SCHEMES III.9 and III.10). In both cases, formation of a terminal rather than a bridging silene is proposed. Both mechanisms involve the loss of H_2 from $Cp_2TiH(SiH_2Ph)$ to give $Cp_2Ti = SiHPh$. The way in which the silene is formed is the same for both mechanisms, and therefore is shown only once (SCHEME III.9). Subsequent reaction of this species with an Si-H bond of $PhSiH_3$ occurs differently, however, in the two mechanisms. As shown in SCHEME III.9, formation of an Si-H bond occurs prior to the formation of the Si-Si bond, whilst in the mechanism shown in SCHEME III.10, the Si-Si bond is formed first. The necessity for an α-hydride elimination in both mechanisms precludes the reaction of secondary silanes beyond the dimer, with reductive elimination of 1,1,2,2-tetraphenyldisilane (in the case of Ph_2SiH_2) from $Cp_2TiH(SiPh_2SiHPh_2)$ occurring. Furthermore, the mechanism shown in SCHEME III.9 preserves a linear polysilyl structure (as indicated by ^{29}Si NMR). In order to maintain a linear, as opposed to branched structure to the polysilyl moiety formed in SCHEME III.10, one may postulate a β-hydride elimination, followed by reinsertion into a Ti-H bond, assuming that as in the case of alkyl complexes, primary silyls are more stable to β-hydride elimination than are secondary silyls.

A possible mechanism for the reaction of $PhSiH_3$ with Cp_2ZrMe_2 to produce XVIII has been shown in SCHEME III.6. Polymerisation of the silane may be accounted for by the reaction of $\{Cp_2(SiHMePh)Zr(\mu\text{-}H)(\mu\text{-}SiHPh)ZrCp_2\}$ with $PhSiH_3$ rather than with H_2, as shown in SCHEME III.11. This mechanism does not, however, explain the observation of a significant amount of dimer (~ 30%) when secondary silanes such as Ph_2SiH_2 are used (174).

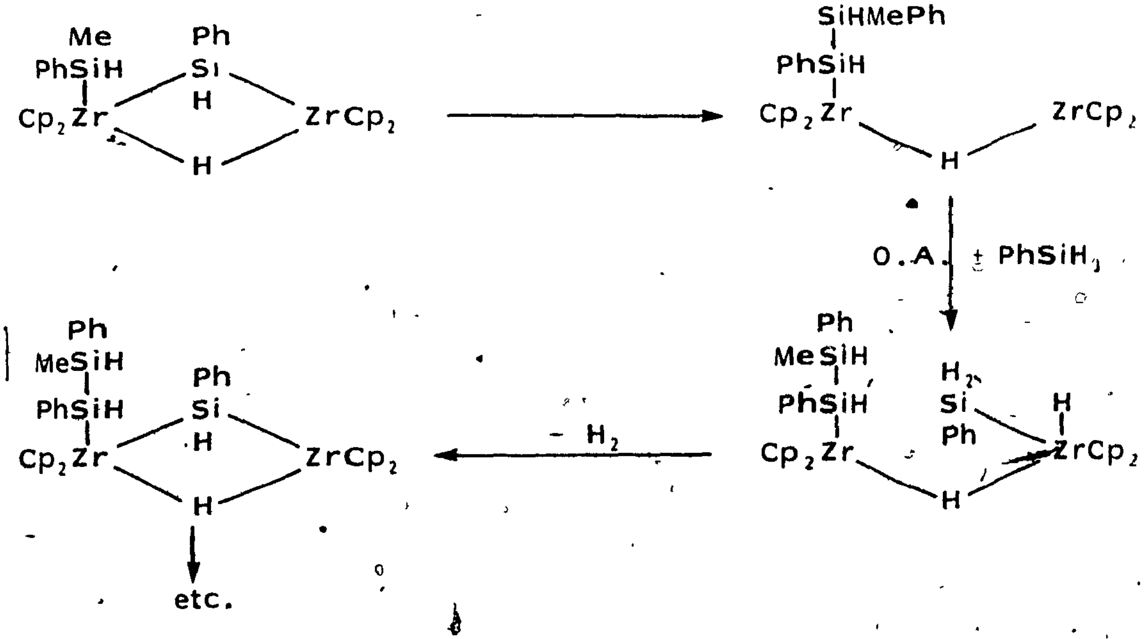

+PhSiH3
O.A.
Cp2Ti
H
Ph
Si
H
H
TiCp2
X
"Cp2Ti"
+
Cp2Ti
H
SiH2Ph
- H2
Cp2Ti=SiHPh
PhSi-H
H2
H
SiHPh
Cp2Ti
SiH2Ph
Cp2Ti
H
SiHPh—SiH2Ph
- H2
Cp2Ti=SiPh—SiH2Ph
+ PhSiH3
Cp2Ti
SiH2Ph
SiHPh—SiH2Ph
Cp2Ti
H
SiHPh—SiH2Ph—SiH2Ph
etc.

SCHEME III.9



SCHEME III.10

It is interesting to note that despite the reaction conditions used, the molecular weights of the oligosilanes obtained during the course of this work ($(HPhSi)_n$ and $(HHxSi)_n$) do not change significantly with reaction conditions. The reasons for this are as yet unclear.



SCHEME III.11

CONTRIBUTIONS TO ORIGINAL KNOWLEDGE

This work reports a series of hitherto unknown reactions whereby primary silanes are converted to linear polysilanes via catalytic dehydrogenation at ambient temperature and pressure. This has been accomplished by the reaction of $RSiH_3$ (R = alkyl/aryl) with a number of titanocenes and zirconocenes, primarily Cp_2TiMe_2 and Cp_2ZrMe_2. This new route is a major breakthrough in the synthesis of polysilanes. To date, the most commonly used preparative method for the production of catenated silicon compounds has been the Wurtz-type synthesis whereby halosilanes are reacted with highly electropositive metals such as lithium. Prior to the first report of the reaction between $PhSiH_3$ and Cp_2TiMe_2 (135) and the work presented in this thesis, there has been only one account of the formation of Si-Si bonds using a catalytic method (52). In this case $(Ph_3P)_3RhCl$ was reported to give small oligosilanes, consisting of at most, three silicon atoms.

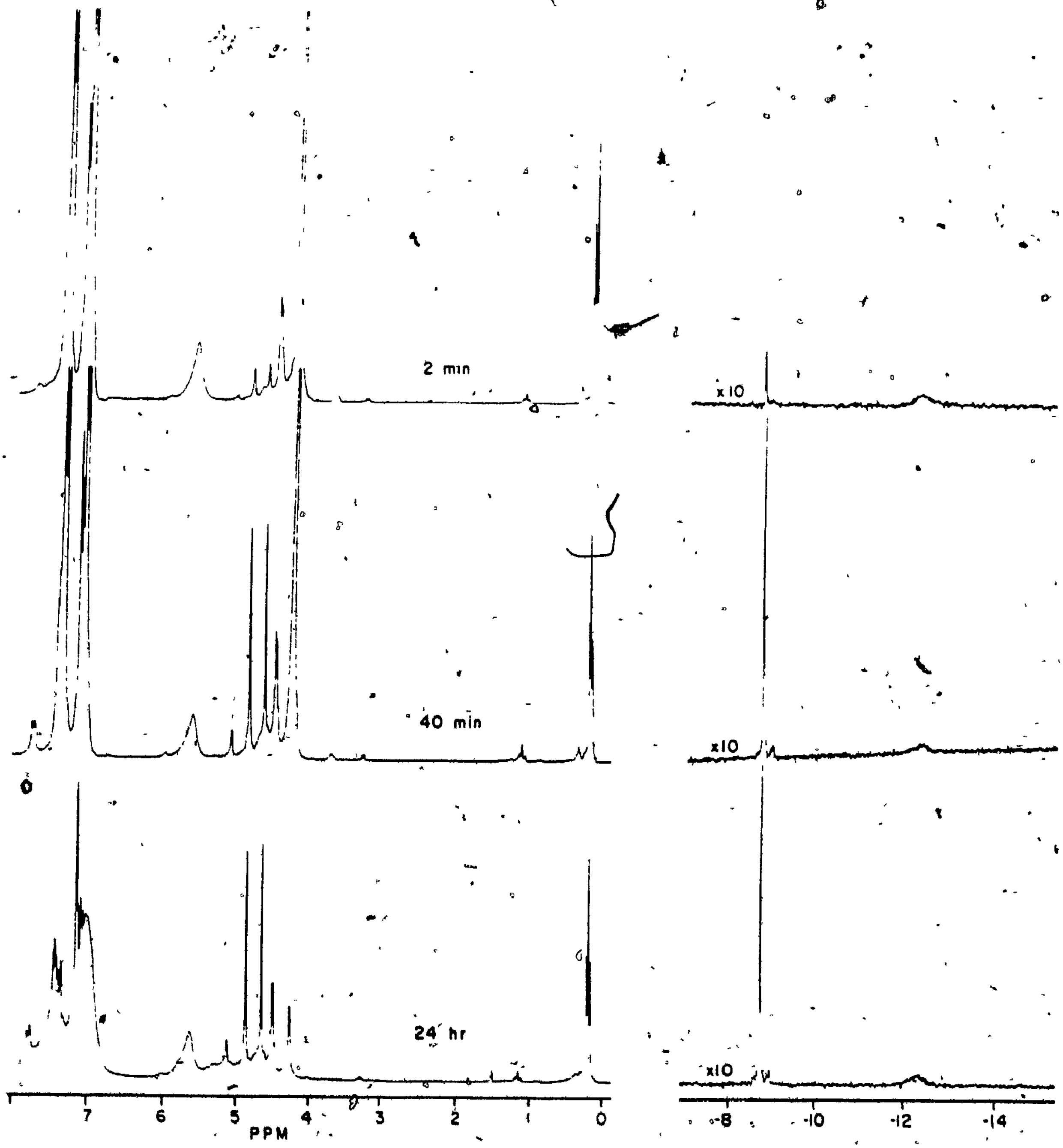
During the course of this work, novel organometallic complexes were isolated from the reactions and characterised as having Ti-H-Si-Ti bridges; the first such moieties to be observed. The structures of these complexes have been used as the basis for discussions of possible mechanisms for the polymerisation reactions.

APPENDIX I: ^{1}H NMR STUDIES OF THE Cp_2TiMe_2 CATALYSED POLYMERISATIONS OF $RSiH_3$, WHERE R = Ph, Hx AND Bz, AND OF $RSiD_3$, WHERE R = Ph AND BZ

AI-A: $PhSiH_3$

Reaction of $PhSiH_3$ with Cp_2TiMe_2 (20:1 molar ratio) in C_6D_6 was followed via ^{1}H NMR spectroscopy. Freshly recrystallised Cp_2TiMe_2 gave immediate reaction, with the colour changing from orange to blue/black accompanied by vigorous gas evolution. 1 minute after the addition of silane, the first ^{1}H NMR spectrum was obtained. At this time, it was broadened somewhat, probably due to the continuing gas evolution. Methane (a singlet at 0.17 ppm) and $MePhSiH_2$ (broadened multiplets at 4.48 ppm due to the Si-H resonances and 0.21 ppm due to the Si-CH_3 resonances) were observed. The peaks due to Cp_2TiMe_2 had been replaced by those of X predominantly, with traces of XI. After 2 minutes, the resolution of the spectrum had improved (FIGURE AI-A) and peaks due to XI had started to grow in intensity relative to X. After 10 minutes, peaks due to the cyclopentadienyl protons and Si-H-Ti of XI had increased further in intensity relative to the analogous peaks of X. At this point the methane peak was almost undetectable, possibly due to the purging action of H_2. H_2 was not observed, but since its peak appears at 4.64 ppm in C_6D_6 (175) it would be expected to be hidden under Si-H or Cp resonances. The triplet and quartet of $MePhSiH_2$ were now clearly evident. After 20 minutes, XI

FIGURE AI-A: ^{1}H NMR SPECTRUM OF $PhSiH_3/Cp_2TiMe_2$ (20:1 MOLAR RATIO) REACTION AT VARIOUS TIME INTERVALS[a]



[a] in C_6D_6 at ambient temperature

had further increased in intensity relative to X although no other change was apparent. After 40 minutes little change was apparent in the spectrum (FIGURE AI-A). After 165 minutes, slow gas evolution was still evident although the spectrum had not changed. The solution was left for 24 hours, during which time gas evolution continued, albeit more and more slowly. At this time the solution had significantly increased in viscosity. $PhSiH_3$, as shown by the weakness of its Si-H resonances (4.24 ppm), had almost entirely been converted to oligophenylsilane, as evidenced by the considerably broadened phenyl peaks. The Si-H resonances of the oligomer were however barely distinguishable from the baseline, and were buried beneath the cyclopentadienyl peaks of X and XI (FIGURE AI-A). After 43 hours the $PhSiH_3$ peaks had further decreased in intensity but there was no other change in the spectrum.

The reaction of $PhSiH_3$ with Cp_2TiMe_2 (9:1 molar ratio) was subsequently repeated in THF-d_8. The solution did not turn blue until 65 minutes after the addition of silane. At this time, vigorous gas evolution was also observed. The ^1H NMR spectrum showed peaks due to methane (0.19 ppm), $MePhSiH_2$ (0.40 ppm, t; 4.30 ppm, q), X and XI whilst those due to Cp_2TiMe_2 were no longer present. The reaction and spectral changes subsequently observed were qualitatively the same as those observed in C_6D_6.

In conclusion, the reaction of $PhSiH_3$ with Cp_2TiMe_2 gave ~~the~~ same products in both C_6D_6 and THF-d_8. There was no evidence for involvement of the solvent leading to the incorporation of deuterium into either methane or methylphenylsilane.

AI-B: $PhSiD_3$

The ^1H NMR study of the reaction of $PhSiD_3$ with Cp_2TiMe_2 (20:1 molar ratio) in C_6D_6 confirmed the assignments of the peaks in the $PhSiH_3$ reactions discussed above. In addition, CH_3D was detected (triplet at 0.17 ppm) which confirmed that the methane obtained its "proton" from the silane. The Cp resonances of the appropriately deuterated analogues of X and XI were detected, whilst the high field hydrides of these complexes were absent. The methyl group of $MePhSiD_2$ was detected as a singlet at 0.21 ppm. The reaction proceeded in the same way as had been observed for $PhSiH_3$, with slow gas evolution continuing for days. The eventual formation of oligophenylsilane was evidenced by the increasing viscosity of the solution, together with substantial broadening of the phenyl peaks in the ^1H NMR spectrum.

AI-C: $BzSiH_3$

The reaction of $BzSiH_3$ with Cp_2TiMe_2 (44:1 molar ratio) in C_6D_6 did not turn blue until 18 minutes after the addition of silane. At this point vigorous gas evolution occurred, and peaks due to Cp_2TiMe_2, methane and $MeBzSiH_2$

(-0.08 ppm, t, CH_3, $^3J_{H-H}$ = 5 Hz; 3.94 ppm, m, $Si-\underline{H}_2$) were detected in the ^1H NMR spectrum. Double irradiation of the $C\underline{H}_3$ triplet caused the multiplet at 3.94 ppm to collapse to a triplet, consistent with coupling to the $C\underline{H}_2$ protons of the benzyl group which were not identified. The cyclopentadienyl resonances of XVI and XVII were barely detectable. After 23 minutes, the peaks due to Cp_2TiMe_2 were absent whilst those due to methane, $MeBzSiH_2$, XVI and XVII had intensified. After 30 minutes, the peak due to methane had diminished. After 55 minutes, the peaks due to the cyclopentadienyl resonances and the high field hydrides $Si-\underline{H}-Ti$ of XVII had grown in intensity relative to those of XVI, and peaks for both isomers were observed. The peak due to methane had decreased in intensity. After 100 minutes all peaks due to XVII had grown larger. Furthermore, AB quartets were now visible for the CH_2 groups of both isomers of XVII. After 25 hours, the peaks due to the $C\underline{H}_2$ and $Si-\underline{H}$ resonances of benzylsilane had started to broaden. It is possible that this was due to the formation of oligobenzylsilane. The spectrum had otherwise not changed. After 6 days considerable fine structure was present on the low field side of the $C\underline{H}_2$ and $Si-\underline{H}$ peaks of benzylsilane. Both peaks were also considerably broadened. Peaks due to $MeBzSiH_2$, XVI and XVII were still present. After 13 days, further broadening of the $C\underline{H}_2$ and $Si-\underline{H}$ resonances of benzylsilane was evident and it is likely that this is due to the formation of oligobenzylsilane. Benzylsilane was still however present in the spectrum at this time. Slow gas evolution was still evident, and the viscosity of the solution had increased considerably.

AI-D: BzSiD$_3$

The ^{1}H NMR study of the reaction of BzSiD$_3$ with Cp$_2$TiMe$_2$ (45:1 molar ratio) in C_6D_6 confirmed the peak assignments made in the BzSiH$_3$ reaction discussed above. CH_3D was detected (0.17 ppm) confirming that the methane obtained its "proton" from the silane. MeBzSiD$_2$ was also produced (-0.08 ppm, s, CH_3). Furthermore, peaks at -9.73, -10.02 and -12.85 ppm, assigned to the hydrides Si-H-Ti of XVII and XVI were not observed.

AI-E: HxSiH$_3$

The reaction of HxSiH$_3$ with Cp$_2$TiMe$_2$ (15:1 molar ratio) in C_6D_6 did not turn blue until 12 minutes after the addition of silane. At this time vigorous gas evolution occurred and peaks due to methane, MeHxSiH$_2$ (3.91 ppm, bm, Si-H_2; 0.05 ppm, bm, CH_3), XIV and XV were detected in the somewhat broadened ^{1}H NMR spectrum. After 27 minutes, the peaks due to XIV and XV had increased in intensity. After 52 minutes the Si-H-Ti resonances at -10.08 and -10.20 ppm due to the 2 isomers of XV, as well as at -13.33 due to XIV, were observed. After 70 minutes the peak due to methane had almost entirely disappeared. The resolution of the spectrum until this time had not been good. After 220 minutes, the spectrum had sharpened considerably. The peak due to the $C\underline{H}_3$ group of $MeHxSiH_2$ was now clearly a triplet, and the $Si-H_2$ peak showed evidence of fine structure. Slow gas evolution continued for days and after 6.5 days, broadening of the hexyl peaks was observed. At this time $MeHxSiH_2$, XIV and XV were still present. After 20 days, further broadening of the hexyl peaks was observed, as well as the development of a broad band at approximately 4 ppm. It is likely that both observations are related to the formation of oligohexylsilane. Furthermore, $HxSiH_3$ (as shown by its $Si-\underline{H}$ peak at 3.62 ppm) had significantly decreased in intensity. After 27 days, the solution had increased considerably in viscosity. The ^1H NMR spectrum showed almost complete conversion of $HxSiH_3$ to $(HHxSi)_n$.

APPENDIX II: ^{1}H NMR STUDIES OF THE Cp_2ZrMe_2 CATALYSED POLYMERISATIONS OF $RSiH_3$, WHERE R = Ph AND Bz, AND OF $PhSiD_3$

AII-A: $PhSiH_3$

The reaction of $PhSiH_3$ with Cp_2ZrMe_2 (21:1 molar ratio) in C_6D_6 occurred immediately, and the solution rapidly darkened to orange. Gas evolution was so vigorous, however, that it was 15 minutes before the first spectrum could be obtained. At this time peaks due to Cp_2ZrMe_2, methane and XVIII were observed. In contrast with the analogous titanium reaction, $MePhSiH_2$ was not observed. After 45 minutes, the peaks due to Cp_2ZrMe_2 and methane had virtually disappeared. Those due to XVIII had increased in intensity. Furthermore the phenyl peaks had started to broaden. Slow gas evolution continued for 24 hours after which time oligophenylsilane was observed, as evidenced by the considerable broadening of the phenyl peaks as well as by the observation of a broad band at approximately 5 ppm, due to the Si-H of $(HPhSi)_n$. After 6 days, $MePhSiH_2$ was now present, presumably from the decomposition of XVIII. After 29 days, complete conversion of excess $PhSiH_3$ to $(HPhSi)_n$ had occurred. A large number of peaks were present at approximately 6 ppm, similar to those observed during the decomposition of XVIII. Furthermore, the peaks due to $MePhSiH_2$ had disappeared.

AII-B: PhSiD$_3$

The ^{1}H NMR study of the reaction of PhSiD$_3$ with Cp$_2$ZrMe$_2$ (20:1 molar ratio) in C$_6$D$_6$ confirmed the assignments of the peaks in the PhSiH$_3$ reaction discussed above. In this case, reaction did not start until 16 minutes after the addition of silane. At this time CH$_3$D was detected (triplet at 0.17 ppm) which confirmed that, as in the case of the analogous titanium reaction, the methane obtained its deuteron from the silane. Peaks due to the Cp and CH$_3$ resonances of the deuterated analogue of XVIII were detected whilst the AB quartet observed for XVIII (ca -5 ppm) was absent. The reaction subsequently proceeded in the same way as that for PhSiH$_3$, and slow gas evolution continued for days. Eventual disappearance of Cp$_2$ZrMe$_2$ and methane occurred, to leave only the peaks due to the deuterated analogue of XVIII and broadened phenyl peaks suggestive of (HPhSi)$_n$.

AII-C: BzSiH$_3$

The ^{1}H NMR study of the reaction of BzSiH$_3$ with Cp$_2$ZrMe$_2$ (2:1 molar ratio) in C$_6$D$_6$ was performed using a low ratio of silane in order to optimise the observation of the organometallic species. The reaction was similar to that discussed above for PhSiH$_3$. Peaks due to methane and XX were observed during the reaction. MeBzSiH$_2$ was not evident until 26 hours after the addition of silane, presumably due to the decomposition of XX. At the same time oligobenzylsilane was present, as evidenced by broad bands which had appeared as low field shoulders on the $C\underline{H}_2$ and Si-$\underline{H}$ peaks of benzylsilane. Futhermore the benzyl aromatic groups had broadened also.

APPENDIX III: EXPERIMENTAL DETAILS FOR THE X-RAY CRYSTAL STRUCTURE DETERMINATION OF COMPLEXES X AND XI

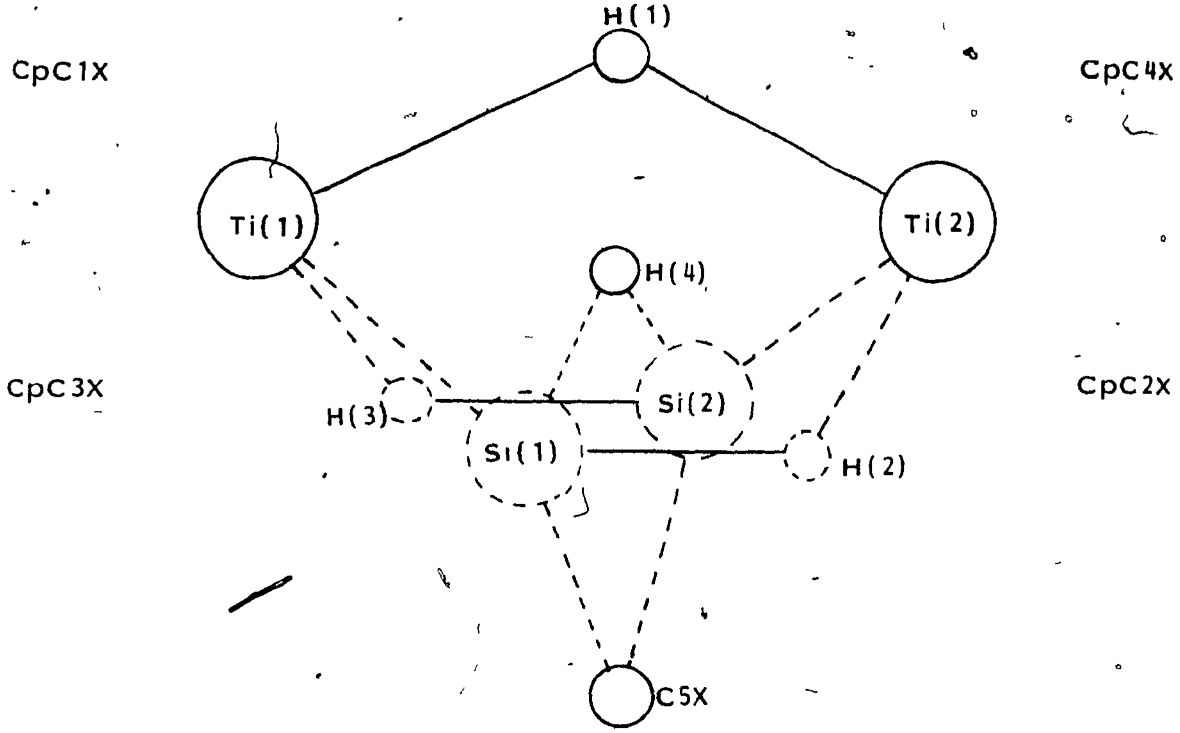
The X-ray structure determinations of complexes X and XI were performed by Dr. M. Simard, at the Laboratoire des structures aux Rayons-X, Université de Montréal. Samples were mounted under N_2 in a glass capillary. Measurements were made on an ENRAF-Nonius CAD-4 diffractometer. The unit cell was determined from a set of 25 reflections collected with the SEARCH procedure. The space group was determined by oscillation photographs, and subsequently confirmed by systematic absences in the complete data set ($h0\ell$, $\ell \neq 2n$ and $0k0$, $k \neq 2n$) to be $P2_1/c$. Intensity data were collected using the $\omega/2\theta$ technique with a fixed slit width of 4.0 mm and a scan range of $\omega_n = (1.00 + 0.35 \tan \theta)^0$, extended 25% on each side for background. Collection was at room temperature on a crystal of dimensions 0.30 x 0.35 x 0.45 mm for XI. Five standards were measured per hour and a variation of less than 2% was observed in their intensities. Data for X was collected on a crystal of dimensions 0.30 x 0.47 x 0.58 mm at -110°C, due to extensive decomposition in crystals irradiated at room temperature. The intensities of a set of seven standards decreased by less than 5% during the data collection at low temperature. Data was corrected for Lorenz and polarization effects but because of the low absorption coefficients, was not corrected for absorption.

In both structures, the Cp and phenyl groups were refined as ideal polygons (C-C: 1.420 Å for Cp and C-C: 1.395 Å for phenyl). For XI, isotropic refinement of all non-hydrogen atoms and anisotropic refinement of Si and Ti converged to R = 0.091. Anisotropic refinement of all non-hydrogen atoms converged to R = 0.062. The hydrogen atoms of Cp and phenyl groups were positioned using their ideal coordinates ($U = 0.01 Å^2$). Hydrogen atoms attached to silicon were located on a ΔF map and refined using constrained distances ($U = 0.05 Å^2$. In the final cycles, individual weights $\omega = 1/\sigma^2(F)$ based on counting statistics were applied. At convergence, the R factor was 0.048. The general background in the final ΔF map was lower than ± 0.4 $e/Å^3$. Using the same procedure the compound X refined to an R value of 0.061 for a six-membered ring (Ti_2SiH_3), but with a large anisotropy on the silicon atom. A disordered silicon was introduced into the model and the two occupancy factors refined. The final positions for the two Si atoms showed equal occupancy at a separation of 0.3 Å and this refinement converged to R = 0.046. The final ΔF map had a background of ± 0.5 $e/Å^3$.

The scattering curves were taken from Cromer and Waber (176) except for that of hydrogen which was from Stewart et al. (177).

APPENDIX IV: X-RAY CRYSTAL DATA FOR COMPLEX X

FIGURE AIV-A: DIAGRAMMATIC REPRESENTATION OF THE DISORDER OBSERVED FOR X



where: C1X, C2X, C3X and C4X are the cyclopentadienyl rings. C1X = C11-C15, C2X = C21-C25, C3X = C31-C35 and C4X = C41-C45.

Si(1), Si(2), correspond to ½ occupancy
H(2) and H(3) correspond to ½ occupancy

ϕ = phenyl group C5X = C51-C55

TABLE AIV-A: CRYSTAL DATA AND DATA COLLECTION PARAMETERS FOR X

formula	$C_{26}H_{28}SiTi_2$
fw, g/mol	464.4
space group	$P2_1/c$
a, Å	10.772 (3)
b, Å	11.129 (6)
c, Å	19.678 (8)
β, deg	112.94 (3)
v, $Å^3$	2172
z	4
cryst. size, mm	0.30 x 0.47 x 0.58
ρ_{calcd}, g/cm^3	1.420
λ, Å	0.71069 (Mo Kα)
μ, mm^{-1}	7.91
maximum 2θ, deg	45
scan rate, deg/min^{-1}/ max. scan time, sec	1.7/40
total no. of reflections	3507
reflections used	2303
background time, sec	3600
final no. of parameters	230
R^a	0.046
R_w^b	0.062

$^aR = \Sigma\ F_o - F_c\ / \Sigma\ F_o$

$^bR_w = [\Sigma w(\ F_o - F_c\ )^2/\Sigma w\ F_o\ ^2]^{\frac{1}{2}}$

$w = 1/\sigma^2(\ F_o\ )$

TABLE AIV-B: REFINED POSITIONAL PARAMETERS OF X (x 10^4; Ti AND Si, x 10^5; H x 10^3), (U_{eq}, x 10^3)^{a,b}

ATOM	X	Y	Z	UEQ
Ti(1)	29670 (8)	38803 (7)	24718 (4)	20
Ti(2)	13088 (8)	37093 (7)	36626 (4)	22
Si(1)	3334(22)	2312(14)	3517(11)	28
Si(2)	3234(22)	2300(14)	3628(11)	28
C(11)	1387 (3)	2401 (3)	1800 (2)	29
C(12)	2638 (3)	2068 (3)	1772 (2)	30
C(13)	3003 (3)	2968 (3)	1373 (2)	34
C(14)	1977 (3)	3858 (3)	1154 (2)	36
C(15)	978 (3)	3508 (3)	1418 (2)	32
C(21)	1052 (3)	5335 (3)	4379 (2)	35
C(22)	1554 (3)	4349 (3)	4868 (2)	35
C(23)	2864 (3)	4071 (3)	4902 (2)	29
C(24)	3171 (3)	4886 (3)	4434 (2)	28
C(25)	2051 (3)	5667 (3)	4110 (2)	32
C(31)	4987 (3)	4755 (3)	3366 (1)	31
C(32)	5263 (3)	4388 (3)	2748 (1)	29
C(33)	4455 (3)	5091 (3)	2132 (1)	30
C(34)	3680 (3)	5893 (3)	2370 (1)	28
C(35)	4008 (3)	5685 (3)	3133 (1)	30
C(41)	-1103 (3)	3774 (3)	3029 (2)	38
C(42)	-619 (3)	2971 (3)	2628 (2)	31
C(43)	-28 (3)	1970 (3)	3089 (2)	33
C(44)	-146 (3)	2156 (3)	3775 (2)	39
C(45)	-810 (3)	3271 (3)	3738 (2)	39
C(51)	4930 (3)	1980 (3)	4422 (1)	28
C(52)	6188 (3)	2026 (3)	4376 (1)	30
C(53)	7333 (3)	1632 (3)	4967 (1)	34
C(54)	7219 (3)	1193 (3)	5604 (1)	35
C(55)	5961 (3)	1148 (3)	5651 (1)	36
C(56)	4816 (3)	1541 (3)	5060 (1)	32
H(1)	151 (3)	437 (4)	279 (2)	30
H(2)	235 (6)	262 (5)	390 (4)	30
H(3)	372 (5)	290 (6)	307 (3)	30
H(4)	285 (4)	109 (2)	327 (2)	30

[a] estimated standard deviations are given in brackets

[b] numbered according to FIGURES III.I and AIV-A

TABLE AIV-C: CALCULATED POSITIONS FOR THE H ATOMS OF THE PHENYL GROUP AND Cp RINGS FOR X (x 10^4), (U_{eq}, x 10^3)[a,b]

ATOM	X	Y	Z	UEQ
H(11)	841(3)	1901(3)	2065(2)	50
H(12)	3212(3)	1270(3)	2013(2)	50
H(13)	3904(3)	2975(3)	1256(2)	50
H(14)	1960(3)	4660(3)	842(2)	50
H(15)	67(3)	3997(3)	1342(2)	50
H(21)	81(3)	5758(3)	4236(2)	50
H(22)	1032(3)	3891(3)	5162(2)	50
H(23)	3512(3)	3365(3)	5227(2)	50
H(24)	4094(3)	4907(3)	4340(2)	50
H(25)	1973(3)	6386(3)	3728(2)	50
H(31)	5441(3)	4391(3)	3918(1)	50
H(32)	5964(3)	3695(3)	2747(1)	50
H(33)	4434(3)	5028(3)	1580(1)	50
H(34)	2965(3)	6546(3)	2030(1)	50
H(35)	3588(3)	6153(3)	3475(1)	50
H(41)	-1605(3)	4620(3)	2830(2)	50
H(42)	-689(3)	3097(3)	2070(2)	50
H(43)	431(3)	1204(3)	2943(2)	50
H(44)	208(3)	1555(3)	4243(2)	50
H(45)	-1051(3)	3666(3)	4174(2)	50
H(52)	6276(3)	2366(3)	3882(1)	50
H(53)	8307(3)	1667(3)	4931(1)	50
H(54)	8105(3)	888(3)	6061(1)	50
H(55)	5873(3)	808(3)	6144(1)	50
H(56)	3841(3)	1506(3)	5096(1)	50

[a] estimated standard deviations are given in brackets

[b] numbered according to FIGURES III.1 and AIV-A

TABLE AIV-D: ANISOTROPIC THERMAL PARAMETERS FOR THE NON-HYDROGEN ATOMS OF X (x 10^3; Ti, x 10^4)[a,b]

ATOM	U11	U22	U33	U12	U13	U23
Ti(1)	188(5)	255(5)	172(5)	-6(4)	75(4)	2(4)
Ti(2)	188(5)	272(5)	208(5)	2(4)	96(4)	-15(4)
Si(1)	29(2)	27(1)	20(4)	4(1)	2(2)	-2(2)
Si(2)	29(2)	27(1)	20(4)	4(1)	2(2)	-2(2)
C(11)	27(3)	34(3)	21(3)	-4(2)	4(2)	-6(2)
C(12)	32(3)	34(3)	24(3)	-2(2)	10(2)	-14(2)
C(13)	38(3)	44(3)	24(3)	-6(3)	17(2)	-10(3)
C(14)	42(3)	44(3)	14(2)	-6(3)	2(2)	-1(2)
C(15)	23(3)	50(3)	15(2)	-3(2)	-1(2)	-7(2)
C(21)	41(3)	35(3)	30(3)	2(3)	17(3)	-11(2)
C(22)	42(3)	45(3)	25(3)	-5(3)	20(2)	-9(3)
C(23)	30(3)	34(3)	20(3)	-2(2)	6(2)	-2(2)
C(24)	30(3)	29(3)	21(3)	-5(2)	7(2)	-11(2)
C(25)	42(3)	27(3)	26(3)	-3(2)	12(2)	-8(2)
C(31)	23(3)	35(3)	30(3)	-11(2)	6(2)	-4(2)
C(32)	20(3)	36(3)	35(3)	-4(2)	15(2)	0(2)
C(33)	26(3)	36(3)	33(3)	-7(2)	17(2)	2(2)
C(34)	30(3)	26(3)	34(3)	-4(2)	17(2)	4(2)
C(35)	32(3)	25(3)	38(3)	-8(2)	19(2)	-4(2)
C(41)	16(2)	41(3)	53(4)	0(2)	11(2)	1(3)
C(42)	15(2)	46(3)	29(3)	-6(2)	6(2)	-4(3)
C(43)	25(3)	37(3)	37(3)	-10(2)	14(2)	-8(3)
C(44)	31(3)	50(4)	37(3)	-14(3)	15(3)	6(3)
C(45)	26(3)	51(4)	48(4)	-8(3)	24(3)	-7(3)
C(51)	30(3)	25(3)	23(3)	4(2)	5(2)	-6(2)
C(52)	32(3)	30(3)	26(3)	0(2)	9(2)	-7(2)
C(53)	26(3)	38(3)	33(3)	0(2)	7(2)	-7(3)
C(54)	29(3)	38(3)	28(3)	1(2)	2(2)	-4(2)
C(55)	37(3)	40(3)	26(3)	2(2)	8(3)	-3(2)
C(56)	29(3)	35(3)	32(3)	6(2)	12(2)	0(2)

---

[a] estimated standard deviations are given in brackets

[b] numbered according to FIGURES III.1 and AIV-A

TABLE AIV-E: CALCULATED (F_c) AND OBSERVED (F_o) STRUCTURE FACTOR AMPLITUDES FOR X[a]

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR (TI)2 (SI)1 (H)3 (PHENYL)1 (CP)4 PAGE 1

H	K	L	FOBS	FCAL	SIG	H	K	L	FOBS	FCAL	SIG	H	K	L	FOBS	FCAL	SIG	H	K	L	FOBS	FCAL	SIG	H	K	L	FOBS	FCAL	SIG
1	0	0	170	-186	4	4	5	0	275	-294	6	-3	1	1	416	-387	8	10	3	1	143	134	7	6	6	1	401	-414	9
2	0	0	353	-334	11	5	5	0	57	65	12*	-2	1	1	86	90	4	-10	4	1	73	68	12*	7	6	1	616	-622	13
3	0	0	279	300	6	6	5	0	217	-218	6	-1	1	1	630	-636	13	-9	4	1	57	-61	13*	8	6	1	70	-72	13*
4	0	0	367	-390	8	7	5	0	113	-102	7	0	1	1	698	638	14	-8	4	1	28	30	28*	9	6	1	106	-131	9
5	0	0	1444	-1459	29	8	5	0	28	23	28*	1	1	1	1830	1929	37	-7	4	1	407	429	9	-8	7	1	181	186	7
6	0	0	439	445	9	9	5	0	125	123	8	2	1	1	455	-450	9	-6	4	1	219	226	6	-7	7	1	91	-96	9
7	0	0	700	707	14	1	6	0	161	176	5	3	1	1	422	-408	9	-5	4	1	219	-240	5	-6	7	1	636	684	13
8	0	0	212	211	6	2	6	0	534	574	11	4	1	1	392	-382	8	-4	4	1	744	760	15	-5	7	1	84	-114	10
9	0	0	49	-41	16*	3	6	0	347	-384	7	5	1	1	623	-622	13	-3	4	1	137	153	5	-4	7	1	383	-427	8
10	0	0	456	437	10	4	6	0	138	157	6	6	1	1	282	-292	6	-2	4	1	107	-142	5	-3	7	1	77	86	8
1	1	0	1215	-1340	25	5	6	0	120	-109	7	7	1	1	171	161	6	-1	4	1	246	-264	5	-2	7	1	112	-109	7
2	1	0	169	-152	4	6	6	0	222	-228	6	8	1	1	347	346	8	0	4	1	260	335	6	-1	7	1	297	-293	7
3	1	0	680	643	14	7	6	0	139	-136	7	9	1	1	28	-16	28*	1	4	1	217	-255	5	0	7	1	179	202	5
4	1	0	465	-494	9	8	6	0	167	161	7	10	1	1	80	96	12	2	4	1	22	18	22*	1	7	1	399	432	8
5	1	0	688	706	14	9	6	0	48	52	18*	-10	2	1	353	343	8	3	4	1	22	47	23*	2	7	1	272	279	6
6	1	0	1087	1062	22	1	7	0	758	794	15	-9	2	1	205	213	6	4	4	1	300	294	7	3	7	1	212	229	6
7	1	0	358	-356	8	2	7	0	128	132	6	-8	2	1	358	360	8	5	4	1	104	-106	7	4	7	1	129	-148	7
8	1	0	36	-62	14*	3	7	0	86	-98	9	-7	2	1	248	247	6	6	4	1	596	583	12	5	7	1	224	-234	6
9	1	0	28	-6	28*	4	7	0	352	397	8	-6	2	1	430	-422	9	7	4	1	28	6	28*	6	7	1	181	-182	6
10	1	0	322	-320	7	5	7	0	152	-144	6	-5	2	1	1444	-1427	29	8	4	1	117	115	8	7	7	1	169	-191	7
0	2	0	490	-507	10	6	7	0	465	-478	10	-4	2	1	249	-261	5	9	4	1	87	108	10	8	7	1	30	21	30*
1	2	0	677	-722	14	7	7	0	135	147	7	-3	2	1	606	-560	12	-9	5	1	199	-186	6	-8	8	1	219	222	7
2	2	0	48	15	8*	8	7	0	109	108	9	-2	2	1	506	-507	10	-8	5	1	28	-7	28*	-7	8	1	45	-32	20*
3	2	0	865	-861	17	0	8	0	621	613	13	-1	2	1	1058	1133	22	-7	5	1	40	-72	20*	-6	8	1	127	137	7
4	2	0	21	-11	22*	1	8	0	81	83	9	0	2	1	1630	1595	33	-6	5	1	500	-519	10	-5	8	1	47	-59	17*
5	2	0	132	132	5	2	8	0	415	-445	9	1	2	1	84	-113	4	-5	5	1	119	-124	6	-4	8	1	90	-100	9
6	2	0	159	-175	5	3	8	0	50	44	16*	2	2	1	363	-397	7	-4	5	1	565	631	11	-3	8	1	172	-198	6
7	2	0	40	71	18*	4	8	0	358	-384	8	3	2	1	310	-313	7	-3	5	1	174	-184	5	-2	8	1	67	60	11
8	2	0	99	-107	8	5	8	0	508	-548	11	4	2	1	307	-301	7	-2	5	1	36	-6	14*	-1	8	1	71	56	11
9	2	0	80	-75	10	6	8	0	125	137	7	5	2	1	801	-798	16	-1	5	1	815	820	16	0	8	1	182	188	6
10	2	0	104	98	9	7	8	0	415	429	9	6	2	1	298	304	7	0	5	1	462	-532	9	1	8	1	42	-54	17*
1	3	0	51	-47	8	1	9	0	311	-294	7	7	2	1	751	759	15	1	5	1	738	-887	15	2	8	1	255	269	6
2	3	0	736	-789	15	2	9	0	118	-122	8	8	2	1	520	-532	10	2	5	1	123	-127	5	3	8	1	94	116	9
3	3	0	264	274	6	3	9	0	303	-331	7	9	2	1	307	-307	7	3	5	1	246	273	6	4	8	1	209	-220	6
4	3	0	355	-376	7	4	9	0	38	2	22*	10	2	1	157	143	7	4	5	1	378	-414	8	5	8	1	202	204	6
5	3	0	24	10	24*	5	9	0	307	317	7	-10	3	1	313	302	7	5	5	1	286	316	7	6	8	1	149	171	7
6	3	0	398	413	8	6	9	0	30	-14	30*	-9	3	1	74	-56	11	6	5	1	39	33	19*	7	8	1	296	-295	7
7	3	0	64	-82	12*	7	9	0	31	10	30*	-8	3	1	199	188	6	7	5	1	221	-218	6	-7	9	1	31	-46	30*
8	3	0	438	-439	9	0	10	0	279	284	7	-7	3	1	172	-179	6	8	5	1	354	-354	8	-6	9	1	247	253	7
9	3	0	68	62	12*	1	10	0	154	-162	7	-6	3	1	147	-157	6	9	5	1	89	60	10	-5	9	1	212	-240	6
10	3	0	30	13	29*	2	10	0	132	-139	7	-5	3	1	418	-419	9	-9	6	1	213	-201	7	-4	9	1	102	-94	9
0	4	0	1130	-1172	23	3	10	0	380	403	8	-4	3	1	551	574	11	-8	6	1	142	-165	7	-3	9	1	47	-66	18*
1	4	0	447	-497	9	4	10	0	244	248	7	-3	3	1	21	25	22*	-7	6	1	496	-510	10	-2	9	1	28	53	28*
2	4	0	657	715	13	5	10	0	76	-57	12	-2	3	1	177	187	5	-6	6	1	221	227	6	-1	9	1	121	-127	7
3	4	0	250	261	6	1	11	0	340	-320	8	-1	3	1	455	-469	9	-5	6	1	471	540	10	0	9	1	142	-135	7
4	4	0	314	335	7	2	11	0	75	94	13*	0	3	1	1065	1144	22	-4	6	1	143	141	6	1	9	1	299	305	7
5	4	0	488	518	10	3	11	0	282	291	7	1	3	1	779	-918	16	-3	6	1	282	-300	6	2	9	1	51	-16	16*
6	4	0	287	289	7	4	11	0	127	-130	8	2	3	1	78	-71	6	-2	6	1	323	345	7	3	9	1	228	-232	6
7	4	0	588	-592	12	-10	1	1	153	-145	7	3	3	1	556	580	11	-1	6	1	630	-617	13	4	9	1	94	109	10
8	4	0	222	-219	6	-9	1	1	234	236	6	4	3	1	387	407	8	0	6	1	1151	-1229	23	5	9	1	92	-90	10
9	4	0	198	191	6	-8	1	1	159	-158	6	5	3	1	307	308	7	1	6	1	97	120	7	6	9	1	349	-336	8
10	4	0	282	-279	7	-7	1	1	131	121	6	6	3	1	500	500	10	2	6	1	518	605	11	-6	10	1	68	-78	14*
1	5	0	124	136	5	-6	1	1	530	545	11	7	3	1	123	-126	7	3	6	1	55	-93	12*	-5	10	1	173	-145	7
2	5	0	332	358	7	-5	1	1	61	-58	8	8	3	1	224	-229	6	4	6	1	336	341	7	-4	10	1	213	-213	7
3	5	0	401	448	8	-4	1	1	664	-669	13	9	3	1	200	-182	6	5	6	1	177	207	6	-3	10	1	29	41	29*

[a] Starred reflections represent unobserved reflections ($I/\sigma(I) < 3.0$)

TABLE AIV-F: INTERATOMIC DISTANCES (Å) AROUND Ti(1) AND Ti(2) FOR X[a,b]

Ti(1)-Ti(2)	3.461(1)		
Ti(1)-Si(1)	2.61(2)	Ti(2)-Si(2)	2.62(2)
Ti(1)-Si(2)	2.80(2)	Ti(2)-Si(1)	2.78(2)
Ti(1)-H(1)	1.97(4)	Ti(2)-H(1)	1.97(3)
Ti(1)-H(3)	1.58(6)	Ti(2)-H(2)	1.59(6)
Ti(1)-C(11)	2.366(3)	Ti(2)-C(21)	2.375(3)
Ti(1)-C(12)	2.389(3)	Ti(2)-C(22)	2.390(3)
Ti(1)-C(13)	2.402(3)	Ti(2)-C(23)	2.394(3)
Ti(1)-C(14)	2.388(3)	Ti(2)-C(24)	2.381(3)
Ti(1)-C(15)	2.366(3)	Ti(2)-C(25)	2.369(3)
Ti(1)-C(1G)[c]	2.054(3)	Ti(2)-C(2G)[c]	2.053(3)
Ti(1)-C(31)	2.407(3)	Ti(2)-C(41)	2.405(4)
Ti(1)-C(32)	2.384(4)	Ti(2)-C(42)	2.416(4)
Ti(1)-C(33)	2.380(3)	Ti(2)-C(43)	2.414(3)
Ti(1)-C(34)	2.401(3)	Ti(2)-C(44)	2.401(3)
Ti(1)-C(35)	2.418(3)	Ti(2)-C(45)	2.394(4)
Ti(1)-C(3G)[c]	2.072(3)	Ti(2)-C(4G)[c]	2.081(4)

[a] estimated standard deviations are given in brackets

[b] numbered according to FIGURES III.1 and AIV-A

[c] C(1G), C(2G), C(3G) and C(4G) are the ring centroids of the appropriate cyclopentadienyl ring.

TABLE AIV-G: INTERATOMIC DISTANCES (Å) AROUND Si(1) AND Si(2) FOR **X**[a,b]

Si(1)-Si(2)	0.28(3)		
Si(1)-Ti(1)	2.61(2)	Si(2)-Ti(2)	2.62(2)
Si(1)-Ti(2)	2.78(2)	Si(2)-Ti(1)	2.80(2)
Si(1)-C(51)	1.97(2)	Si(2)-C(51)	1.92(2)
Si(1)-H(2)	1.56(7)	Si(2)-H(3)	1.54(6)
Si(1)-H(4)	1.47(3)	Si(2)-H(4)	1.51(3)

[a] estimated standard deviations are given in brackets

[b] numbered according to FIGURES III.1 and AIV-A

TABLE AIV-H: ANGLES (°) AROUND Ti(1) AND Ti(2) FOR X[a,b,c]

Ti(2)-Ti(1)-Si(1)	52.3	(4)	Ti(1)-Ti(2)-Si(2)	52.6	(4)
Ti(2)-Ti(1)-Si(2)	48.1	(4)	Ti(1)-Ti(2)-Si(1)	47.9	(4)
Ti(2)-Ti(1)-C(1G)	112.99	(10)	Ti(1)-Ti(2)-C(2G)	111.32	(10)
Ti(2)-Ti(1)-C(3G)	114.78	(9)	Ti(1)-Ti(2)-C(4G)	115.59	(10)
Ti(2)-Ti(1)-H(3)	73	(2)	Ti(1)-Ti(2)-H(2)	75	(2)
H(1)-Ti(1)-H(3)	101	(2)	H(1)-Ti(2)-H(2)	103	(3)
Si(1)-Ti(1)-C(1G)	105.3	(5)	Si(2)-Ti(2)-C(2G)	107.8	(5)
Si(1)-Ti(1)-C(3G)	113.0	(5)	Si(2)-Ti(2)-C(4G)	110.8	(5)
Si(1)-Ti(1)-H(1)	80	(1)	Si(2)-Ti(2)-H(1)	81	(1)
Si(2)-Ti(1)-C(1G)	107.2	(4)	Si(1)-Ti(2)-C(2G)	109.5	(4)
Si(2)-Ti(1)-C(3G)	113.4	(4)	Si(1)-Ti(2)-C(4G)	111.5	(4)
Si(2)-Ti(1)-H(1)	76	(1)	Si(1)-Ti(2)-H(1)	76	(1)
C(1G)-Ti(1)-C(3G)	130.6	(1)	C(4G)-Ti(2)-C(2G)	131.1	(1)
C(1G)-Ti(1)-H(1)	104	(1)	C(4G)-Ti(2)-H(1)	104	(1)
C(1G)-Ti(1)-H(3)	106	(2)	C(4G)-Ti(2)-H(2)	102	(2)
C(3G)-Ti(1)-H(1)	111	(1)	C(2G)-Ti(2)-H(1)	110	(1)
C(3G)-Ti(1)-H(3)	99	(2)	C(2G)-Ti(2)-H(2)	102	(2)

[a] estimated standard deviations are given in brackets

[b] numbered according to FIGURES III.1 and AIV-A

[c] C(1G), C(2G), C(3G) and C(4G) are the ring centroids of the appropriate cyclopentadienyl ring.

TABLE AIV-I: INTERATOMIC ANGLES (°) AROUND Si(1), Si(2), H(1), H(2), AND H(3) FOR X[a,b]

Ti(1)-Si(1)-Ti(2)	79.8(6)	Ti(2)-Si(2)-Ti(1)	79.3(6)
Ti(1)-Si(1)-C(51)	130.5(9)	Ti(2)-Si(2)-C(51)	127.0(9)
Ti(1)-Si(1)-H(2)	108 (3)	Ti(2)-Si(2)-H(3)	104 (2)
Ti(1)-Si(1)-H(4)	116 (2)	Ti(2)-Si(2)-H(4)	118 (2)
Ti(2)-Si(1)-C(51)	117.1(9)	Ti(1)-Si(2)-C(51)	122.8(9)
Ti(2)-Si(1)-H(4)	111 (2)	Ti(1)-Si(2)-H(4)	105 (2)
Ti(2)-Si(1)-H(3)	105 (3)	Ti(1)-Si(2)-H(2)	107 (3)
C(51)-Si(1)-H(2)	97 (3)	C(51)-Si(2)-H(3)	100 (2)
C(51)-Si(1)-H(4)	101 (2)	C(51)-Si(2)-H(4)	102 (2)
C(51)-Si(1)-H(3)	108 (3)	C(51)-Si(2)-H(2)	109 (3)
H(2)-Si(1)-H(3)	132 (4)	H(3)-Si(2)-H(2)	132 (4)
H(2)-Si(1)-H(4)	98 (3)	H(3)-Si(2)-H(4)	100 (3)
H(3)-Si(1)-H(4)	114 (3)	H(2)-Si(2)-H(4)	109 (4)
Ti(1)-H(1)-Ti(2)	123 (2)		
Ti(2)-H(2)-Si(1)	124 (4)	Ti(1)-H(3)-Si(2)	128 (4)

[a] estimated standard deviations are given in brackets

[b] numbered according to FIGURES III.1 and AIV-A

TABLE AIV-J: SELECTED LEAST SQUARES PLANES FOR X

Plane 1

Equation: $0.474\,x + 0.599\,y + 0.646\,z = 6.094$

Distances from plane (A)

Ti(1)*	0.0000(8)	Ti(2)*	0.0000(8)	Si(1)*	0.02(2)
Si(2)*	-0.02(2)	H(1)	0.16(4)	H(2)	0.06(6)
H(3)	-0.22(6)				

*Atoms used in the plane calculation

Plane 2

Equation: $0.166\,x + 0.498\,y + 0.851\,z = 4.125$

Cyclopentadienyl bound to Ti(1) on the side of H(4)

Plane 3

Equation: $0.108\,x + 0.634\,y + 0.765\,z = 9.600$

Cyclopentadienyl bound to Ti(2) on the side of the phenyl group

Plane 4

Equation: $0.695\,x + 0.681\,y + 0.230\,z = 6.948$

Cyclopentadienyl bound to Ti(1) on the side of the phenyl group

Plane 5

Equation: $0.812\,x + 0.468\,y + 0.349\,z = 1.032$

Cyclopentadienyl bound to Ti(2) on the side of H(4)

Plane 6

Equation: $0.010\,x - 0.923\,y - 0.385\,z = -5.098$

Plane of the phenyl group attached to Si(1) and Si(2)

Angles between planes (degrees)

plane 1 and plane 2	22.1	plane 1 and plane 3	22.3
plane 1 and plane 4	27.6	plane 1 and plane 5	27.1
plane 1 and plane 6	37.2		

APPENDIX V: X-RAY CRYSTAL DATA FOR COMPLEX XI

TABLE AV-A: CRYSTAL DATA AND DATA COLLECTION PARAMETERS FOR XI

formula	$C_{32}H_{34}Si_2Ti_2$
fw, g/mol	570.6
space group	$P2_1/c$
a, Å	15.276 (6)
b, Å	11.466 (3)
c, Å	20.151 (8)
β, deg	129.19 (3)
V, $Å^3$	2736
Z	4
cryst. size, mm	0.30 x 0.35 x 0.45
ρ_{calcd}, g/cm^3	1.385
λ, Å	0.71069 (Mo Kα)
μ, mm^{-1}	6.83
maximum 2θ, deg	48
scan rate, deg/min^{-1}/ max. scan time, sec	1.7/40
total no. of reflections	5056
reflections used	4259
background time, sec	3600
final no. of parameters	278
R^a	0.048
R_w^b	0.057

$^a R = \Sigma\ F_o - F_c\ /\Sigma\ F_o$

$^b R_w = [\Sigma w(\ F_o - F_c\ )^2/\Sigma w\ F_o^{\ 2}]^{\frac{1}{2}}$

$w = 1/\sigma^2(\ F_o\ )$

TABLE AV-B: REFINED POSITIONAL PARAMETERS OF XI (x 10^4; Ti AND Si, x 10^5; H, x 10^3) (U_{eq}, x 10^3)[a,b]

ATOM	X	Y	Z	UEQ
Ti(1)	18283 (7)	10194 (8)	79907(5)	39
Ti(2)	33617 (7)	9583 (8)	70181(5)	37
Si(1)	33246(12)	23789(12)	81613(9)	43
Si(2)	16169(11)	-1490(12)	66240(8)	40
C(11)	1994 (3)	-724 (4)	8711(3)	67
C(12)	1879 (3)	218 (4)	9109(3)	80
C(13)	2837 (3)	953 (4)	9494(3)	81
C(14)	3543 (3)	465 (4)	9335(3)	70
C(15)	3022 (3)	-571 (4)	8851(3)	60
C(21)	5330 (3)	543 (3)	7960(3)	61
C(22)	4888 (3)	85 (3)	8349(3)	55
C(23)	4124 (3)	-826 (3)	7820(3)	55
C(24)	4095 (3)	-930 (3)	7103(3)	58
C(25)	4840 (3)	-84 (3)	7190(3)	61
C(31)	652 (4)	2284 (4)	8072(2)	69
C(32)	1051 (4)	2919 (4)	7705(2)	77
C(33)	597 (4)	2396 (4)	6908(2)	93
C(34)	-83 (4)	1437 (4)	6781(2)	97
C(35)	-49 (4)	1368 (4)	7500(2)	76
C(41)	1913 (3)	1246 (3)	5520(2)	61
C(42)	2949 (3)	1129 (3)	5668(2)	61
C(43)	3646 (3)	2091 (3)	6173(2)	59
C(44)	3041 (3)	2802 (3)	6337(2)	56
C(45)	1970 (3)	2280 (3)	5934(2)	60
C(51)	4707 (3)	2859 (3)	9266(2)	48
C(52)	5742 (3)	2831 (3)	9432(2)	54
C(53)	6707 (3)	3276 (3)	10200(2)	62
C(54)	6637 (3)	3749 (3)	10803(2)	72
C(55)	5602 (3)	3778 (3)	10637(2)	87
C(56)	4637 (3)	3333 (3)	9869(2)	72
C(61)	1507 (3)	-1798 (3)	6378(2)	45
C(62)	1310 (3)	-2081 (3)	5620(2)	64
C(63)	1318 (3)	-3245 (3)	5423(2)	73
C(64)	1523 (3)	-4126 (3)	5983(2)	75
C(65)	1720 (3)	-3843 (3)	6740(2)	82
C(66)	1712 (3)	-2679 (3)	6938(2)	67
H(1)	286 (3)	350 (2)	771(2)	50
H(2)	54 (2)	31 (4)	586(2)	50
H(3)	394 (3)	208 (3)	778(2)	50
H(4)	128 (3)	-10 (3)	722(2)	50

[a] estimated standard deviations are given in brackets

[b] numbered according to FIGURE III.7

TABLE AV-C: CALCULATED POSITIONS FOR THE H ATOMS OF THE PHENYL GROUP AND Cp RINGS FOR XI (x 10^4) (U_{eq}, x 10^3)[a,b]

ATOM	X	Y	Z	UEQ
H(11)	1403(3)	-1433(4)	8363(3)	100
H(12)	1186(3)	352(4)	9116(3)	100
H(13)	2999(3)	1744(4)	9847(3)	100
H(14)	4337(3)	820(4)	9546(3)	100
H(15)	3350(3)	-1143(4)	8628(3)	100
H(21)	5933(3)	1246(3)	8207(3)	100
H(22)	5096(3)	377(3)	8943(3)	100
H(23)	3650(3)	-1348(3)	7940(3)	100
H(24)	3594(3)	-1545(3)	6584(3)	100
H(25)	5005(3)	58(3)	6749(3)	100
H(31)	847(4)	2466(4)	8679(2)	100
H(32)	1604(4)	3668(4)	7984(2)	100
H(33)	743(4)	2677(4)	6473(2)	100
H(34)	-544(4)	862(4)	6233(2)	100
H(35)	-480(4)	731(4)	7596(2)	100
H(41)	1206(3)	652(3)	5157(2)	100
H(42)	3168(3)	432(3)	5436(2)	100
H(43)	4489(3)	2253(3)	6393(2)	100
H(44)	3343(3)	3600(3)	6705(2)	100
H(45)	1313(3)	2611(3)	5940(2)	100
H(52)	5796(3)	2464(3)	8965(2)	100
H(53)	7508(3)	3254(3)	10328(2)	100
H(54)	7384(3)	4094(3)	11398(2)	100
H(55)	5547(3)	4144(3)	11104(2)	100
H(56)	3835(3)	3355(3)	9741(2)	100
H(62)	1152(3)	-1399(3)	5187(2)	100
H(63)	1166(3)	-3464(3)	4836(2)	100
H(64)	1529(3)	-5027(3)	5830(2)	100
H(65)	1878(3)	-4525(3)	7174(2)	100
H(66)	1864(3)	-2460(3)	7524(2)	100

[a] estimated standard deviations are given in brackets

[b] numbered according to FIGURE III.7

TABLE AV-D: ANISOTROPIC THERMAL PARAMETERS FOR THE NON-HYDROGEN ATOMS OF XI (x 10^3; Ti and Si, x 10^4)[a,b]

ATOM	U11	U22	U33	U12	U13	U23
Ti(1)	348(5)	450(6)	340(5)	50(4)	209(4)	32(4)
Ti(2)	370(5)	364(5)	355(5)	0(4)	217(4)	45(4)
Si(1)	461(8)	410(8)	416(8)	35(7)	270(7)	32(7)
Si(2)	396(8)	403(8)	355(7)	0(6)	210(6)	5(6)
C(11)	67(4)	68(4)	58(4)	-11(3)	37(3)	20(3)
C(12)	101(6)	101(6)	71(4)	24(5)	69(5)	29(4)
C(13)	127(6)	59(4)	36(3)	19(5)	42(4)	7(3)
C(14)	52(4)	77(5)	38(3)	-10(3)	9(3)	27(3)
C(15)	77(4)	56(4)	52(3)	19(3)	43(3)	23(3)
C(21)	32(3)	55(4)	74(4)	6(3)	22(3)	5(3)
C(22)	46(3)	61(4)	42(3)	24(3)	21(3)	14(3)
C(23)	51(3)	49(4)	65(4)	19(3)	37(3)	24(3)
C(24)	54(3)	50(3)	66(4)	16(3)	36(3)	3(3)
C(25)	55(4)	64(4)	72(4)	14(3)	44(3)	8(3)
C(31)	64(4)	78(5)	72(4)	18(4)	47(4)	2(4)
C(32)	67(4)	54(4)	118(6)	25(3)	61(4)	22(4)
C(33)	69(5)	145(8)	79(5)	77(5)	53(4)	64(5)
C(34)	48(4)	155(8)	62(4)	41(5)	22(3)	-17(5)
C(35)	42(3)	86(5)	97(5)	10(3)	43(4)	-9(4)
C(41)	63(4)	64(4)	35(3)	-18(3)	21(3)	8(3)
C(42)	86(4)	58(4)	46(3)	-1(3)	45(3)	8(3)
C(43)	67(4)	58(4)	53(3)	-11(3)	38(3)	8(3)
C(44)	78(4)	37(3)	44(3)	-6(3)	33(3)	9(2)
C(45)	59(4)	66(4)	48(3)	11(3)	29(3)	21(3)
C(51)	52(3)	46(3)	50(3)	-7(3)	34(3)	-1(3)
C(52)	58(4)	55(4)	51(3)	-8(3)	36(3)	2(3)
C(53)	63(4)	65(4)	54(4)	-5(3)	35(3)	3(3)
C(54)	76(4)	67(5)	53(4)	-23(3)	31(3)	-4(3)
C(55)	102(5)	94(6)	78(5)	-32(4)	64(5)	-33(4)
C(56)	73(4)	86(5)	63(4)	-22(4)	45(4)	-34(4)
C(61)	41(3)	42(3)	49(3)	-1(2)	27(3)	-2(3)
C(62)	81(4)	52(4)	41(3)	3(3)	30(3)	0(3)
C(63)	85(5)	58(4)	50(4)	9(4)	30(3)	-10(3)
C(64)	82(5)	45(4)	86(5)	-7(3)	48(4)	-17(4)
C(65)	129(6)	48(4)	102(5)	-10(4)	88(5)	-2(4)
C(66)	108(5)	42(3)	82(4)	-11(3)	75(4)	-4(3)

[a] estimated standard deviations are given in brackets

[b] numbered according to FIGURE III.7

TABLE AV-E: CALCULATED (F_c) AND OBSERVED (F_o) STRUCTURE FACTOR AMPLITUDES FOR XI[a]

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR (TI)2 (SI)2 (H)4 (PHENYL)2 (CP)4 PAGE 1

H	K	L	FOBS	FCAL	SIG	H	K	L	FOBS	FCAL	SIG	H	K	L	FOBS	FCAL	SIG	H	K	L	FOBS	FCAL	SIG	H	K	L	FOBS	FCAL	SIG
1	1	0	1116	-1064	22	5	5	0	327	328	8	6	10	0	282	275	8	-1	2	1	351	354	7	2	4	1	443	-438	9
2	1	0	658	633	13	6	5	0	183	-176	7	7	10	0	38	5	38*	0	2	1	1906	2009	38	3	4	1	379	-362	8
3	1	0	422	392	9	7	5	0	94	-54	13	8	10	0	103	-98	15	1	2	1	420	388	9	4	4	1	184	192	6
4	1	0	1096	-1043	22	8	5	0	302	307	8	1	11	0	90	-112	16*	2	2	1	196	-205	5	5	4	1	407	-384	9
5	1	0	133	162	7	9	5	0	37	-47	37*	2	11	0	37	17	37*	3	2	1	311	271	7	6	4	1	228	236	7
6	1	0	412	-379	9	10	5	0	216	-197	8	3	11	0	84	86	16*	4	2	1	27	-9	27*	7	4	1	145	-140	9
7	1	0	677	-685	14	11	5	0	147	143	11	4	11	0	37	17	38*	5	2	1	307	289	7	8	4	1	124	-93	11
8	1	0	628	631	13	12	5	0	38	-9	38*	5	11	0	56	-36	25*	6	2	1	983	978	20	9	4	1	37	-6	37*
9	1	0	190	212	8	1	6	0	286	299	7	6	11	0	64	-49	22*	7	2	1	311	-311	8	10	4	1	83	100	18*
10	1	0	119	142	12	2	6	0	664	673	14	7	11	0	38	-45	38*	8	2	1	432	-457	10	11	4	1	45	42	32*
11	1	0	52	68	26*	3	6	0	596	-611	12	1	12	0	69	-42	20*	9	2	1	266	249	8	12	4	1	38	-18	38*
12	1	0	151	-138	10	4	6	0	315	308	8	2	12	0	80	-85	18*	10	2	1	66	-50	20*	-12	5	1	229	229	9
13	1	0	131	-130	12	5	6	0	102	-104	11	3	12	0	38	24	38*	11	2	1	290	293	8	-11	5	1	98	-94	15
1	2	0	628	-548	13	6	6	0	174	-197	8	4	12	0	98	-103	16	12	2	1	162	142	10	-10	5	1	78	91	18*
2	2	0	269	-251	6	7	6	0	337	356	8	5	12	0	38	-12	38*	-13	3	1	79	-77	19*	-9	5	1	180	-196	9
3	2	0	943	-915	19	8	6	0	527	545	11	1	13	0	130	-125	12	-12	3	1	38	26	37*	-8	5	1	247	-236	8
4	2	0	402	371	8	9	6	0	242	-237	8	-13	1	1	294	-288	8	-11	3	1	37	5	37*	-7	5	1	43	-18	26*
5	2	0	298	322	7	10	6	0	38	-8	38*	-12	1	1	187	-183	9	-10	3	1	78	91	17*	-6	5	1	90	102	12
6	2	0	451	457	10	11	6	0	46	-21	31*	-11	1	1	325	325	8	-9	3	1	112	74	12	-5	5	1	523	-530	11
7	2	0	32	55	32*	12	6	0	123	-135	14	-10	1	1	272	288	8	-8	3	1	167	-157	8	-4	5	1	177	175	6
8	2	0	34	11	34*	1	7	0	983	1025	20	-9	1	1	145	132	9	-7	3	1	136	-130	8	-3	5	1	397	389	8
9	2	0	374	-369	9	2	7	0	46	61	23*	-8	1	1	42	-11	25*	-6	3	1	470	442	10	-2	5	1	437	-408	9
10	2	0	36	-3	36*	3	7	0	243	-237	7	-7	1	1	810	-807	17	-5	3	1	43	-19	18*	-1	5	1	420	434	9
11	2	0	99	107	14	4	7	0	213	215	7	-6	1	1	393	-372	8	-4	3	1	286	274	7	0	5	1	406	-407	9
12	2	0	111	103	13	5	7	0	594	-607	12	-5	1	1	1009	1051	20	-3	3	1	87	56	9	1	5	1	744	-755	15
13	2	0	38	-7	38*	6	7	0	36	-15	35*	-4	1	1	563	538	11	-2	3	1	192	-192	5	2	5	1	386	410	8
1	3	0	84	-76	8	7	7	0	677	669	14	-3	1	1	358	-333	7	-1	3	1	890	-877	18	3	5	1	797	815	16
2	3	0	252	-227	6	8	7	0	175	-202	9	-2	1	1	209	-195	5	0	3	1	1202	1128	24	4	5	1	40	-15	24*
3	3	0	956	881	19	9	7	0	143	-143	11	-1	1	1	1720	-1864	35	1	3	1	638	-610	13	5	5	1	58	18	18*
4	3	0	193	224	6	10	7	0	38	-33	38*	0	1	1	46	-103	6	2	3	1	517	529	11	6	5	1	238	-238	7
5	3	0	691	706	14	11	7	0	236	-218	9	1	1	1	2251	2367	46	3	3	1	211	194	6	7	5	1	317	-311	8
6	3	0	208	-211	7	1	8	0	91	77	13	2	1	1	587	-515	12	4	3	1	78	-65	10	8	5	1	263	250	8
7	3	0	239	-235	7	2	8	0	220	-208	7	3	1	1	413	-363	9	5	3	1	30	16	30*	9	5	1	527	527	11
8	3	0	35	19	35*	3	8	0	72	-54	17*	4	1	1	298	-282	7	6	3	1	177	-178	7	10	5	1	38	-20	38*
9	3	0	127	133	11	4	8	0	82	-29	15*	5	1	1	777	-773	16	7	3	1	139	-121	9	11	5	1	102	-69	15
10	3	0	94	62	14	5	8	0	110	107	12	6	1	1	228	216	7	8	3	1	88	114	14	12	5	1	192	-180	10
11	3	0	110	117	13	6	8	0	373	375	9	7	1	1	533	541	11	9	3	1	249	260	8	-12	6	1	145	-133	11
12	3	0	269	-269	8	7	8	0	125	-140	12	8	1	1	34	57	34*	10	3	1	37	-63	37*	-11	6	1	270	-255	8
13	3	0	39	-64	39*	8	8	0	199	-195	9	9	1	1	273	-299	8	11	3	1	38	20	38*	-10	6	1	37	10	37*
1	4	0	43	-8	17*	9	8	0	74	-66	19*	10	1	1	43	31	31*	12	3	1	92	-95	17*	-9	6	1	37	-34	37*
2	4	0	622	608	13	10	8	0	47	24	32*	11	1	1	193	-176	9	-13	4	1	59	-84	26*	-8	6	1	268	263	8
3	4	0	523	-522	11	1	9	0	183	173	8	12	1	1	38	-6	38*	-12	4	1	113	119	13	-7	6	1	203	-211	8
4	4	0	49	6	16*	2	9	0	42	30	30*	13	1	1	166	152	10	-11	4	1	204	193	9	-6	6	1	407	-424	9
5	4	0	598	-588	12	3	9	0	35	-61	35*	-13	2	1	152	-145	11	-10	4	1	316	-317	8	-5	6	1	304	-311	8
6	4	0	188	-169	7	4	9	0	53	-21	25*	-12	2	1	282	275	8	-9	4	1	204	225	8	-4	6	1	209	197	7
7	4	0	156	-147	8	5	9	0	181	-191	9	-11	2	1	148	174	10	-8	4	1	135	-125	9	-3	6	1	228	245	7
8	4	0	152	171	9	6	9	0	37	-11	37*	-10	2	1	61	-58	21*	-7	4	1	230	-230	7	-2	6	1	410	421	9
9	4	0	191	-210	8	7	9	0	221	210	8	-9	2	1	161	154	9	-6	4	1	578	570	12	-1	6	1	72	-92	12*
10	4	0	187	-168	8	8	9	0	38	-18	38*	-8	2	1	268	-276	7	-5	4	1	217	-200	6	0	6	1	731	-700	15
11	4	0	179	-181	9	9	9	0	89	75	17*	-7	2	1	397	-390	9	-4	4	1	570	-590	12	1	6	1	424	-461	9
12	4	0	39	-20	38*	1	10	0	40	-3	33*	-6	2	1	1308	1281	26	-3	4	1	192	-172	6	2	6	1	244	244	7
1	5	0	351	-371	8	2	10	0	209	-220	8	-5	2	1	381	370	8	-2	4	1	168	-134	6	3	6	1	239	252	7
2	5	0	321	305	7	3	10	0	268	-257	8	-4	2	1	267	228	6	-1	4	1	282	-260	6	4	6	1	45	29	23*
3	5	0	184	-179	6	4	10	0	191	-194	9	-3	2	1	428	410	9	0	4	1	566	612	12	5	6	1	94	91	12
4	5	0	824	-844	17	5	10	0	120	109	12	-2	2	1	890	-827	18	1	4	1	137	139	6	6	6	1	275	-278	8

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[a] Starred reflections represent unobserved reflections (I/σ(I) < 3.0)

TABLE AV-F: INTERATOMIC DISTANCES (Å) AROUND Ti(1) AND Ti(2) FOR XI[a]

Ti(1)-Ti(2)	3.890(2)		
Ti(1)-Si(1)	2.604(2)	Ti(2)-Si(2)	2.583(2)
Ti(1)-Si(2)	2.891(2)	Ti(2)-Si(1)	2.851(2)
Ti(1)-H(4)	1.76 (3)	Ti(2)-H(3)	1.76 (3)
Ti(1)-C(11)	2.388(4)	Ti(2)-C(21)	2.379(5)
Ti(1)-C(12)	2.389(5)	Ti(2)-C(22)	2.394(4)
Ti(1)-C(13)	2.379(4)	Ti(2)-C(23)	2.403(4)
Ti(1)-C(14)	2.374(4)	Ti(2)-C(24)	2.394(4)
Ti(1)-C(15)	2.379(4)	Ti(2)-C(25)	2.379(5)
Ti(1)-C(1G)[c]	2.053(4)	Ti(2)-C(2G)[c]	2.062(4)
Ti(1)-C(31)	2.394(6)	Ti(2)-C(41)	2.383(4)
Ti(1)-C(32)	2.371(5)	Ti(2)-C(42)	2.381(4)
Ti(1)-C(33)	2.367(4)	Ti(2)-C(43)	2.390(4)
Ti(1)-C(34)	2.388(5)	Ti(2)-C(44)	2.396(4)
Ti(1)-C(35)	2.404(6)	Ti(2)-C(45)	2.391(4)
Ti(1)-C(3G)[c]	2.056(5)	Ti(2)-C(4G)[c]	2.061(4)

[a] estimated standard deviations are given in brackets

[b] numbered according to FIGURE III.7

[c] C(1G), C(2G), C(3G) and C(4G) are the ring centroids of the appropriate cyclopentadienyl ring.

TABLE AV-G: INTERATOMIC DISTANCES (Å) AROUND Si(1) AND Si(2) FOR XI[a,b]

Si(1)-C(51)	1.943(4)	Si(2)-C(61)	1.935(4)
Si(1)-H(1)	1.47 (3)	Si(2)-H(2)	1.47 (3)
Si(1)-H(3)	1.58 (5)	Si(2)-H(4)	1.58 (4)

[a] estimated standard deviations are given in brackets

[b] numbered according to FIGURE III.7

TABLE AV-H: INTERATOMIC ANGLES (°) AROUND Ti(1) AND Ti(2) FOR XI[a,b,c]

Si(1)-Ti(1)-Si(2)	87.91(6)	Si(2)-Ti(2)-Si(1)	89.18(6)
Si(1)-Ti(1)-C(3G)	102.8 (2)	Si(2)-Ti(2)-C(4G)	102.7 (1)
Si(1)-Ti(1)-C(1G)	106.8 (1)	Si(2)-Ti(2)-C(2G)	104.5 (1)
Si(1)-Ti(1)-H(4)	116 (1)	Si(2)-Ti(2)-H(3)	119 (1)
Si(2)-Ti(1)-C(3G)	105.4 (2)	Si(1)-Ti(2)-C(4G)	108.4 (1)
Si(2)-Ti(1)-C(1G)	114.4 (1)	Si(1)-Ti(2)-C(2G)	110.8 (1)
C(3G)-Ti(1)-C(1G)	130.5 (2)	C(4G)-Ti(2)-C(2G)	132.0 (2)
C(3G)-Ti(1)-H(4)	100 (1)	C(4G)-Ti(2)-H(3)	100 (1)
C(1G)-Ti(1)-H(4)	101 (1)	C(2G)-Ti(2)-H(3)	100 (1)

[a] estimated standard deviations are given in brackets

[b] numbered according to FIGURE III.8

[c] C(1G), C(2G), C(3G) and C(4G) are the ring centroids of the appropriate cyclopentadienyl ring

TABLE AV-I: INTERATOMIC ANGLES (°) AROUND Si(1), Si(2), H(3) AND H(4) FOR XI[a,b]

Ti(1)-Si(1)-Ti(2)	90.88(6)	Ti(2)-Si(2)-Ti(1)	90.40(6)
Ti(1)-Si(1)-C(51)	123.3 (1)	Ti(2)-Si(2)-C(61)	117.7 (1)
Ti(1)-Si(1)-H(1)	114 (2)	Ti(2)-Si(2)-H(2)	114 (1)
Ti(1)-Si(1)-H(3)	123 (1)	Ti(2)-Si(2)-H(4)	121 (1)
Ti(2)-Si(1)-C(51)	121.7 (1)	Ti(1)-Si(2)-C(61)	129.5 (1)
Ti(2)-Si(1)-H(1)	104 (2)	Ti(1)-Si(2)-H(2)	102 (1)
C(51)-Si(1)-H(1)	102 (2)	C(61)-Si(2)-H(2)	103 (1)
C(51)-Si(1)-H(3)	94 (1)	C(61)-Si(2)-H(4)	102 (1)
H(1)-Si(1)-H(3)	95 (2)	H(2)-Si(2)-H(4)	96 (2)
Ti(1)-H(4)-Si(2)	120 (2)	Ti(2)-H(3)-Si(1)	117 (2)

[a] estimated standard deviations are given in brackets

[b] numbered according to FIGURE III.7

TABLE AV-J: SELECTED LEAST SQUARES PLANES FOR XI

Plane 1

Equation: $-0.285\,x + 0.654\,y - 0.701\,z = 5.817$

Distances from plane (Å)

Ti(1)*	0.0625(9)	Ti(2)*	0.0639(9)	Si(1)*	-0.181(2)
Si(2)*	-0.154(1)	H(3)	0.03(4)	H(4)	0.10(3)

*Atoms used in the plane calculation

Plane 2

Equation: $0.102\,x + 0.900\,y - 0.424\,z = -3.663$

Phenyl group attached to Si(1)

Plane 3

Equation: $0.878\,x - 0.064\,y - 0.475\,z = 0.509$

Phenyl group attached to Si(2)

Plane 4

Equation: $-0.652\,x + 0.603\,y - 0.459\,z = 1.847$

Cyclopentadienyl bound to Ti(1) on the side of H(1) and H(2)

Plane 5

Equation: $0.188\,x + 0.523\,y - 0.832\,z = -7.194$

Cyclopentadienyl bound to Ti(2) on the side of H(1) and H(2)

Plane 6

Equation: $0.066\,x + 0.528\,y - 0.846\,z = -12.487$

Cyclopentadienyl bound to Ti(1) on the side of the phenyl rings

TABLE AV-J: (cont'd)

Plane 7

Equation: $-0.557\ x + 0.661\ y - 0.503\ z = -4.726$

Cyclopentadienyl bound to Ti(2) on the side of the phenyl groups

Angles between planes (degrees)

plane 1 and plane 2	31.0	plane 1 and plane 4	25.6
plane 1 and plane 3	57.2	plane 1 and plane 5	29.4
plane 2 and plane 3	86.8	plane 1 and plane 6	23.1
		plane 1 and plane 7	19.4

Torsion angles (°) for the Ti_2-Si_2-H_4 moiety

H(1)-Si(1)-Ti(1)-H(4)	100(2)	H(2)-Si(2)-Ti(2)-H(3)	95(2)
H(3)-Si(1)-Ti(1)-H(4)	-14(2)	H(4)-Si(2)-Ti(2)-H(3)	-18(2)

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