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I am submitting herewith a dissertation written by Jaime Renee Blanton entitled "Chemistry of Silicon-containing Compounds and Molecular Approaches to Materials for Silicon-based Microelectronics. Preparation of Metal Silyl Complexes, Studies of Reactions Between Alkylidenes and Silanes, and Deposition of Titanium Oxide Thin Films." I have examined the final paper copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

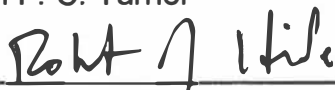


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**CHEMISTRY OF SILICON-CONTAINING COMPOUNDS AND
MOLECULAR APPROACHES TO MATERIALS FOR SILICON-
BASED MICROELECTRONICS. PREPARATION OF METAL
SILYL COMPLEXES, STUDIES OF REACTIONS BETWEEN
ALKYLIDENES AND SILANES, AND DEPOSITION OF
TITANIUM OXIDE THIN FILMS**

A Dissertation

Presented for the

Doctor of Philosophy Degree

The University of Tennessee, Knoxville

Jaime Renee Blanton

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DEDICATION

This dissertation is dedicated in loving memory of my
father, William Michael (Bill) Blanton

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ABSTRACT

This dissertation describes studies of the chemistry of silicon-containing compounds and molecular approaches to silicon-based microelectronic materials. The preparation of new silyl dianions and transition metal silyl complexes, our studies of the mechanism of reactions between alkylidenes and silanes, and the fabrication of TiO₂ thin films on Si as microelectronic gate materials are presented.

Chapter 1 provides a brief overview of the field of early transition metal silyl chemistry and experimental techniques used in the research, and a summary of the research conducted in each subsequent chapter. In Chapter 2 are described the synthesis and characterization of new complexes [K(18-crown-6)]₂[(Me₃Si)₂Si-(CH₂)_n-Si(SiMe₃)₂] (n = 1, 4; 2, 5; 3, 6) containing silyl dianions. These compounds represent some of the few known disilyl dianion complexes. In addition, the crystal structures of the starting materials to **5** and **6**, (Me₃Si)₃Si-(CH₂)_n-Si(SiMe₃)₃, (n = 2, 2; 3, 3) were determined by single-crystal X-ray diffraction studies. The preparation and characterization of novel Zr and Zn silyl complexes from the reactions of **5** with (Me₂N)₃ZrCl and ZnCl₂, respectively, are presented in Chapter 3. Both complexes are anionic with K(18-crown-6)⁺ as the counterion. {(Me₂N)₃Zr[η²-(Me₃Si)₂Si-(CH₂)₂-Si(SiMe₃)₂]}⁻ (**7**) consists of a five-coordinate Zr center with a distorted trigonal bipyramidal geometry. [K(18-

crown-6)]₂{[η²-(Me₃Si)₂Si-(CH₂)₂-Si(SiMe₃)₂]Zn₂[μ-(Me₃Si)₂Si-(CH₂)₂-Si(SiMe₃)₂]} (8) is, to our knowledge, the first trisilyl Zn complex. 8 is a dimer with each Zn metal center coordinated by a chelating disilyl ligand and a disilyl ligand bridging each Zn center. Chapter 4 presents some new mechanistic insights into the reactions of a Ta alkylidene complex (Me₃SiCH₂)₃Ta(PMe₃)(=CHSiMe₃) (9) with silane H₂SiMePh. Such reactions yielded new silyl-substituted alkylidene complexes. Experiments conducted in the presence of 20-fold PMe₃ were found to be 19 times slower than those conducted with no added phosphine. Mass spectral analysis of the gaseous products from the reaction conducted in the presence of H₂ suggested hydrogen scrambling. Finally, in Chapter 5 are discussed the preparation and characterization of TiO₂ thin films on a Si wafer from the reaction of Ti(NMe₂)₄ with O₂ by chemical vapor deposition (CVD) processes. These films were characterized by X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD), infrared spectroscopy (IR), ellipsometry and scanning electron microscopy (SEM), and found to be amorphous before annealing but crystalline anatase after annealing at 600 °C for 1 h in air. Importantly, analyses by XPS, XRD and IR suggested that the films were C-free and contained no TiN or TiO_xN_y species.

TABLE OF CONTENTS

Chapter	Page
1	Introduction and Background.....1
1.1	Introduction.....1
1.2	Characterization Techniques.....5
1.2.1	Nuclear Magnetic Resonance (NMR).....5
1.2.2	Ellipsometry.....6
1.2.3	Scanning Electron Microscopy (SEM).....6
1.2.4	X-ray Photoelectron Spectroscopy (XPS).....7
1.2.5	Infrared Spectroscopy (IR).....8
1.2.6	X-ray Diffraction.....8
1.3	Summary of Research.....10
1.3.1	Chapter 2.....10
1.3.2	Chapter 3.....11
1.3.3	Chapter 4.....11
1.3.4	Chapter 5.....12
2	Synthesis and Characterization of Bis[tris(trimethylsilyl)silyl] propane and Dianionic Bis(silyl)alkane Salts.....13
2.1	Introduction.....13
2.2	Results and Discussion.....15

2.2.1	Synthesis of Bis[tris(trimethylsilyl)silyl]propane (Me ₃ Si) ₃ Si-(CH ₂) ₃ -Si(SiMe ₃) ₃ (3).....	15
2.2.2	X-ray Crystal Structures of 2 and 3	16
2.2.3	Metalation of 1 , 2 and 3 . Synthesis of [K(18-crown-6)] ₂ [(Me ₃ Si) ₂ Si-(CH ₂) _n -Si(SiMe ₃) ₂] (n = 1, 4 ; 2, 5 ; 3, 6).....	21
2.2.4	X-ray Crystal Structure of 5	29
2.3	Experimental Section.....	36
2.3.1	General Procedures.....	36
2.3.2	Preparation of (Me ₃ Si) ₃ Si-(CH ₂) ₃ -Si(SiMe ₃) ₃ (3).....	37
2.3.3	Preparation of [K(18-crown-6)] ₂ [(Me ₃ Si) ₂ Si-CH ₂ - Si(SiMe ₃) ₂] (4).....	37
2.3.4	Preparation of [K(18-crown-6)] ₂ [(Me ₃ Si) ₂ Si-(CH ₂) ₂ - Si(SiMe ₃) ₂] (5).....	38
2.3.5	Preparation of [K(18-crown-6)] ₂ [(Me ₃ Si) ₂ Si-(CH ₂) ₃ - Si(SiMe ₃) ₂] (6).....	39
2.3.6	X-ray Crystal Structure Determinations of 2 , 3 and 5	40
3	Preparation of Transition Metal Complexes Containing [(Me ₃ Si) ₂ Si-(CH ₂) _n -Si(SiMe ₃) ₂] ²⁻ Ligands.....	41
3.1	Introduction.....	41
3.2	Results and Discussion.....	46

3.2.1	Attempted Synthesis of Persilyl Complexes from MCl ₄	46
3.2.2	Preparation and Characterization of Zr Silyl Amide Complex K(18-crown-6) _{3/2} {(Me ₂ N) ₃ Zr[η ² -(Me ₃ Si) ₂ Si- (CH ₂) ₂ -Si(SiMe ₃) ₂]} (7).....	52
3.2.3	X-ray Crystal Structure of 7.....	56
3.2.4	Preparation and Characterization of Trisilyl Zn Complex [K(18-crown-6)] ₂ {[η ² -(Me ₃ Si) ₂ Si-(CH ₂) ₂ - Si(SiMe ₃) ₂]Zn ₂ [μ-(Me ₃ Si) ₂ Si-(CH ₂) ₂ -Si(SiMe ₃) ₂]} (8).....	66
3.2.5	X-ray Crystal Structure of 8.....	71
3.3	Experimental Section.....	78
3.3.1	General Procedures.....	78
3.3.2	Attempted Preparation of Persilyl Group IV Complexes.....	79
3.3.3	Preparation of the Zr Silyl Amide Complex K(18- crown-6) _{3/2} {(Me ₂ N) ₃ Zr[η ² -(Me ₃ Si) ₂ Si-(CH ₂) ₂ - Si(SiMe ₃) ₂]} (7).....	79
3.3.4	Preparation of the Zn Complex [K(18-crown-6)] ₂ {[η ² - (Me ₃ Si) ₂ Si-(CH ₂) ₂ -Si(SiMe ₃) ₂]Zn ₂ [μ-(Me ₃ Si) ₂ Si- (CH ₂) ₂ -Si(SiMe ₃) ₂]} (8).....	80
3.3.5	X-ray Crystal Structure Determinations of 7 and 8.....	81

4	New Mechanistic Insights into the Reactions of Tantalum	
	Alkylidene Complexes with Silanes.....	83
4.1	Introduction.....	83
4.2	Results and Discussion.....	84
4.2.1	Mechanistic Considerations and Kinetics Plots.....	84
4.2.2	Mass Spectral Analysis of Volatiles.....	89
4.2.3	NMR Analysis of the Remaining Silane.....	92
4.2.4	Mechanisms of the Reactions between 9 and Silanes.....	98
4.3	Experimental Section.....	104
4.3.1	General Procedures.....	104
4.3.2	Preparation of NMR Samples for Kinetics.....	104
4.3.3	Preparation of Samples for Mass Spectral Analysis.....	105
4.3.4	Preparation of Samples for NMR Analysis of Remaining Silane.....	106
5	Chemical Vapor Deposition of TiO ₂ Thin Films from the Reaction of Tetrakis(dimethylamido)titanium with Oxygen.....	107
5.1	Introduction.....	107
5.2	Results and Discussion.....	110
5.2.1	Design of CVD Reactors.....	110

5.2.2	Formation of TiO ₂ Thin Films via Hot-Wall Low Pressure Horizontal CVD.....	113
5.2.3	Characterization of TiO ₂ Thin Films by Ellipsometry, IR, Powder XRD, XPS, and SEM.....	115
5.3	Experimental Section.....	123
5.3.1	General Procedures.....	123
5.3.2	Procedure for Thin Film Deposition in an Ultra- High-Vacuum (UHV) CVD Chamber.....	128
	References.....	130
	Appendix.....	145
	Vita.....	278

LIST OF SCHEMES

Scheme	Page
2.1 Preparation of 4-6.....	28
3.1 CVD routes to metal silicides from metal alkyls or halides.....	42
3.2 Formation of metal carbenes and carbynes. Some formed unexpectedly in attempts to prepare peralkyl complexes.....	43
3.3 Reported synthesis of Zn disilyl complexes.....	45
3.4 New transition metal (multi)silyl complexes prepared from the reactions of MCl_x with $[K(18\text{-crown-}6)]_2[(Me_3Si)_2Si-(CH_2)_2-Si(SiMe_3)_2]$	47
3.5 Attempted preparation of persilyl Zr and Hf complexes.....	48
3.6 Preparation of Zr amide disilyl complex 7.....	52
3.7 Preparation of Zn persilyl complex 8.....	68
4.1 Reaction of 9 with silanes.....	83
4.2 Originally proposed mechanism.....	85
4.3 Mechanistic considerations.....	86
4.4 Modified mechanisms.....	100
4.5 Actions of Schrock-type alkylidenes and metal amido complexes with hydrosilanes.....	102
5.1 Tris(pyrazolyl)borate (Tp^-) ion.....	109

LIST OF FIGURES

Figure	Page
1.1 Schematic of integrated microelectronic transistor.....	2
1.2 Formation of silicides between the metal and Si, e.g., in the source and drain in ULSI transistors.....	4
1.3 The use of metal silicides as metallization layers for, e.g., source and drain in ULSI transistors.....	4
1.4 Diffraction described by Equation 1.2.....	9
2.1 ORTEP diagram of 2 showing 10% ellipsoids.....	20
2.2 Packing diagram of 2 . View down the <i>a</i> axis.....	22
2.3 ORTEP diagram of 3 showing 10% ellipsoids.....	26
2.4 Packing diagram of 3 . View down the <i>a</i> axis.....	27
2.5 ORTEP diagram of 5 showing 30% ellipsoids.....	34
2.6 Packing diagram of 5 . View down the <i>a</i> axis.....	35
3.1 ¹ H NMR (at 400 MHz) of the –NMe ₂ region of 7 at 293 K (top), 283 K and 258 K (bottom).....	54
3.2 ¹ H NMR (at 400 MHz) of the –SiMe ₃ region of 7 at 293 K (top), 283 K and 258 K (bottom).....	55
3.3 ¹³ C{ ¹ H} NMR spectrum of the –NMe ₂ region of 7 at 296 K (top) and 258 K (bottom).....	57
3.4 ORTEP diagram of 7 showing 30% probability thermal ellipsoids....	62

3.5	ORTEP diagram of Zr(1) portion of 7 showing 30% ellipsoids.....	63
3.6	ORTEP diagram of cationic K(18-crown-6) ⁺ portions of 7	64
3.7	Packing diagram of 7 . View down the <i>a</i> axis.....	65
3.8	ORTEP diagram of 8 showing 30% ellipsoids.....	75
3.9	ORTEP diagram of the Zn dianion in 8 showing 30% ellipsoids.....	76
3.10	Packing diagram in 8 . Viewing down the <i>a</i> axis.....	77
4.1	Kinetics plot of the reaction of 9 with 5.3 equiv of H ₂ SiMePh without added PMe ₃ – Control experiment.....	90
4.2	Kinetics plot of the reaction of 9 with 5.4 equiv of H ₂ SiMePh and 20 equiv of PMe ₃	91
4.3	Mass spectrum of Sample A	93
4.4	Mass spectrum of Sample B	94
4.5	Mass spectrum of Sample C	95
4.6	NMR of remaining silane in the reaction of D ₂ SiMePh with 9 in a 15:1 ratio.....	97
4.7	NMR of remaining silane in the reaction of D ₂ SiMePh with 9 in a 5:1 ratio in the presence of 1 atm H ₂ (Sample C)	99
5.1	Schematic of integrated microelectronic transistor.....	108
5.2	Cold-wall CVD reactor.....	111
5.3	Hot-wall CVD reactor.....	111
5.4	The hot wall, horizontal CVD apparatus used in the deposition of TiO ₂ thin films in this dissertation.....	114
5.5	Film pattern on Si wafer including thickness and refractive	

	index obtained from ellipsometry (Kf1 is the correction factor)	118
5.6	IR spectra of Film 3 before and after annealing.....	119
5.7	XRD spectrum of Film 3 (annealed).....	120
5.8	XPS spectrum of Film 2	124
5.9	XPS spectrum of a cleaned Si wafer.....	125
5.10	SEM of Film 2	126

LIST OF TABLES

Table	Page
2.1 Crystal Data for 2	17
2.2 Selected Bond Distances (Å) in 2	19
2.3 Selected Bond Angles (deg) in 2	19
2.4 Crystal Data for 3	23
2.5 Selected Bond Distances (Å) in 3	25
2.6 Selected Bond Angles (deg) in 3	25
2.7 Crystal Data for 5	30
2.8 Selected Bond Distances (Å) in 5	32
2.9 Selected Bond Angles (deg) in 5	32
3.1 Summary of Unsuccessful Attempts to Prepare Zr and Hf Persilyl Complexes.....	49
3.2 Key NMR Data of 7 and Relevant Complexes at 23 °C.....	58
3.3 Crystal Data for 7	59
3.4 Selected Bond Distances (Å) in 7	61
3.5 Selected Bond Angles (deg) in 7	61
3.6 Key NMR Data of 8 and Relevant Complexes at 23 °C.....	69
3.7 Crystal Data for 8	72
3.8 Selected Bond Distances (Å) for 8	74
3.9 Selected Bond Angles (deg) for 8	74

4.1	Mass Spectral Distribution of Gaseous Products.....	96
5.1	CVD Conditions.....	116
5.2	XPS Chemical Shifts of Films 2-4 and Other Relevant Materials...	122
A1	Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in 2.....	146
A2	Bond Distances ($\text{\AA}$) in 2.....	148
A3	Bond Angles (deg) in 2.....	149
A4	Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in 2.....	151
A5	Hydrogen Coordinates ($\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in 2.....	152
A6	Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in 3.....	155
A7	Bond Distances ($\text{\AA}$) in 3.....	157
A8	Bond Angles (deg) in 3.....	158
A9	Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in 3.....	160
A10	Hydrogen Coordinates ($\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in 3.....	162
A11	Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in 5.....	166
A12	Bond Distances ($\text{\AA}$) in 5.....	170
A13	Bond Angles (deg) in 5.....	172
A14	Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in 5.....	176

A15	Hydrogen Coordinates ($\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in 5.....	180
A16	Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in 7.....	185
A17	Bond Distances ($\text{\AA}$) in 7.....	199
A18	Bond Angles (deg) in 7.....	207
A19	Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in 7.....	222
A20	Hydrogen Coordinates ($\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in 7.....	236
A21	Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in 8.....	257
A22	Bond Distances ($\text{\AA}$) in 8.....	261
A23	Bond Angles (deg) in 8.....	263
A24	Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in 8.....	268
A25	Hydrogen Coordinates ($\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in 8.....	272

NUMBERING SCHEME FOR COMPOUNDS IN TEXT

1. $(\text{Me}_3\text{Si})_3\text{Si}-\text{CH}_2-\text{Si}(\text{SiMe}_3)_3$
2. $(\text{Me}_3\text{Si})_3\text{Si}-(\text{CH}_2)_2-\text{Si}(\text{SiMe}_3)_3$
3. $(\text{Me}_3\text{Si})_3\text{Si}-(\text{CH}_2)_3-\text{Si}(\text{SiMe}_3)_3$
4. $[\text{K}(18\text{-crown-}6)]_2[(\text{Me}_3\text{Si})_2\text{Si}-\text{CH}_2-\text{Si}(\text{SiMe}_3)_2]$
5. $[\text{K}(18\text{-crown-}6)]_2[(\text{Me}_3\text{Si})_2\text{Si}-(\text{CH}_2)_2-\text{Si}(\text{SiMe}_3)_2]$
6. $[\text{K}(18\text{-crown-}6)]_2[(\text{Me}_3\text{Si})_2\text{Si}-(\text{CH}_2)_3-\text{Si}(\text{SiMe}_3)_2]$
7. $\text{K}(18\text{-crown-}6)_{3/2}\{(\text{Me}_2\text{N})_3\text{Zr}[\eta^2-(\text{Me}_3\text{Si})_2\text{Si}-(\text{CH}_2)_2-\text{Si}(\text{SiMe}_3)_2]\}$
8. $[\text{K}(18\text{-crown-}6)]_2\{[\eta^2-(\text{Me}_3\text{Si})_2\text{Si}-(\text{CH}_2)_2-\text{Si}(\text{SiMe}_3)_2]\text{Zn}_2[\mu-(\text{Me}_3\text{Si})_2\text{Si}-(\text{CH}_2)_2-\text{Si}(\text{SiMe}_3)_2]\}$
9. $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}(\text{PMe}_3)(=\text{CHSiMe}_3)$
- 9a. “ $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}(=\text{CHSiMe}_3)$ ”
- 9b. “ $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}(\text{PMe}_3)(\text{H})[\text{CH}(\text{SiMe}_3)(\text{SiHMePh})]$ ”
10. $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}[=\text{C}(\text{SiMe}_3)(\text{SiHMePh})]$
- 10-d₁. $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}[=\text{C}(\text{SiMe}_3)(\text{SiDMePh})]$
- 10a. $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}[=\text{C}(\text{SiMe}_3)(\text{SiHPh}_2)]$
11. “ $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}(\text{H})[\text{CH}(\text{SiMe}_3)(\text{SiHMePh})]$ ”
- 11-d₁. “ $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}(\text{H})[\text{CH}(\text{SiMe}_3)(\text{SiDMePh})]$ ”
- 11-d₂. “ $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}(\text{D})[\text{CH}(\text{SiMe}_3)(\text{SiDMePh})]$ ”
12. “ $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}(\text{SiHMePh})[\text{CH}(\text{SiMe}_3)(\text{SiHMePh})]$ ”
- 12-d₁. “ $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}(\text{SiDMePh})[\text{CH}(\text{SiMe}_3)(\text{SiHMePh})]$ ”

NOMENCLATURE AND ABBREVIATIONS

Å	angstrom
ACS	American Chemical Society
ALD	atomic layer deposition
atm	atmosphere
BE	binding energy
°C	degrees Celsius
cm ⁻¹	wavenumbers or reciprocal centimeters
Cp	η^5 -cyclopentadienyl (C ₅ H ₅ ⁻)
CVD	chemical vapor deposition
diglyme	2-methoxyethyl ether
DME	1,2-dimethoxyethane
DRAM	dynamic random access memory
Eq	equation
equiv	equivalent(s)
ESCA	electron spectroscopy for chemical analysis
Et ₂ O	diethyl ether
eV	electron volt
g	gram
h	Planck's constant (6.626 x 10 ⁻³⁴ J/sec)
h	hour
I	nuclear spin quantum number

IR	infrared
κ	dielectric constant
K	Kelvin
KE	kinetic energy
k_{obs}	observed rate constant
kV	kilovolts
m	meter
mA	milliamps
MHz	mega Hertz
min	minutes
mL	milliliter
mmol	millimole
MOCVD	metal organic chemical vapor deposition
MS	mass spectrometry
nm	nanometer
NMR	nuclear magnetic resonance
ORTEP	Oak Ridge Thermal Ellipsoid Program
pm	picometer
ppm	parts per million
RGA	residual gas analyzer
SEM	scanning electron microscopy
T_2	spin-spin relaxation
TCE	tetrachloroethylene

THF	tetrahydrofuran
Tp	tris(pyrazolyl)borate
θ	theta, glancing angle
ULSI	ultra-large-scale-integration
ν	frequency
v/v	volume per volume
vs	versus
λ	wavelength
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
>>	much greater than

CHAPTER 1

Introduction and Background

1.1 Introduction

The area of transition-metal silyl chemistry is a diverse and exciting field with applications in areas ranging from catalysis to microelectronics. Beginning with the first transition-metal silyl complex, $\text{Cp}(\text{CO})_2\text{FeSiMe}_3$, prepared in 1956,¹ this area has been rapidly growing. Although numerous transition-metal silyl complexes have now been prepared, many, particularly those of the early transition metals, contain stabilizing ligands such as Cp (η^5 -cyclopentadienyl), alkoxides^{2,3} or amides.⁴ The area of early transition-metal silyl chemistry, especially chemistry of complexes free of stabilizing ligands, is a relatively new field of research that our group has been actively involved in developing.

Our interest in preparing Cp-free, early transition-metal silyl complexes is two-fold. First, because few such complexes have been reported, we are interested in their fundamental chemistry including their synthesis, structures and reactivities. Secondly, such complexes could be used as single-source precursors to silicon-based microelectronic materials. In a microelectronic device (Figure 1.1), the metal and Si layers often undergo solid-state reactions to form a metal silicide layer. The formation of such a layer decreases the

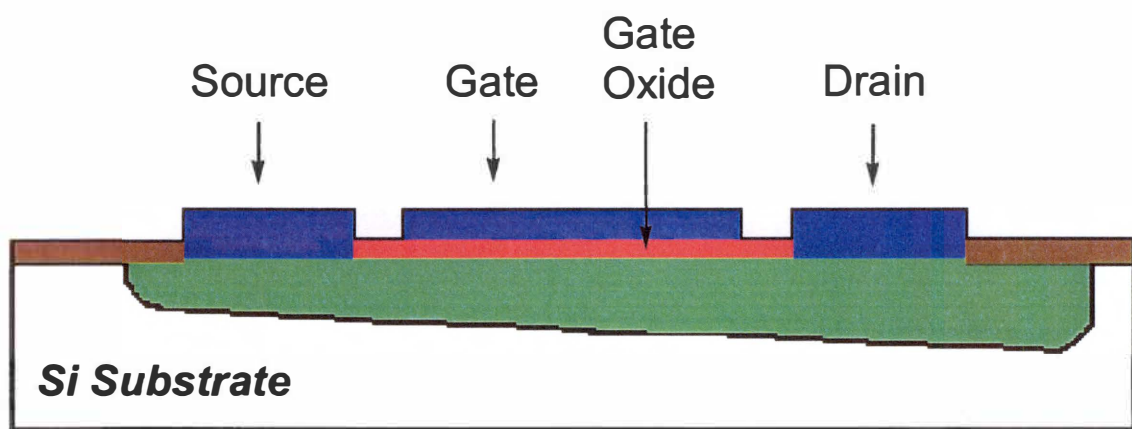


Figure 1.1 Schematic of integrated microelectronic transistor

efficiency of the device and shortens its lifetime (Figure 1.2). One solution is to use conductive metal silicide thin films to replace metals as the metallization layer on Si. Metal silicides (MSi_n) are thermodynamically more stable with respect to reactions with Si than metals themselves, and are thus unlikely to react with the Si substrate (Figure 1.3).

In addition to the preparation of M-Si bonded species, we are also interested in reactions of metal complexes with silanes, and the mechanistic pathways in these reactions. These reactivities and pathways may help elucidate mechanistic pathways by which metal silicide materials are formed via, e.g., chemical vapor deposition processes involving silane, SiH_4 .

Our most recent work has led us to study a new class of compounds potentially useful as gate oxide materials in ultra-large-scale integrated (ULSI) microelectronic transistors (Figure 1.1). SiO_2 ($\kappa = 3.9$) is currently the material used as an insulating gate oxide. However, as the thickness of this layer decreases, the leakage current increases. Once the thickness of the SiO_2 layer is less than 20 Å, the leakage current will become too great for practical use. Hence, new materials with a high dielectric constant (κ) are required as new gate materials. TiO_2 is studied as a gate oxide replacement for SiO_2 thin films because of its high dielectric constant ($\kappa = 80\text{-}180$ for the rutile form).

Our group has been actively studying the reactions of early-transition-metal amides with silanes⁴⁻⁹ and serendipitously, their reactions with O_2 .¹⁰ Although numerous methods have been utilized to prepare thin films of TiO_2 , our

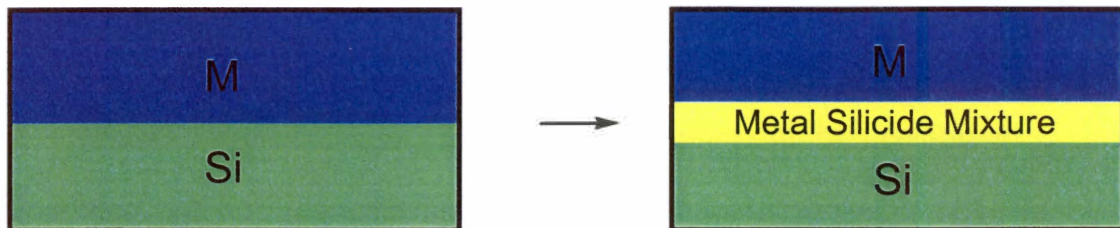


Figure 1.2 Formation of silicides between the metal and Si, e.g., in the source and drain in ULSI transistors

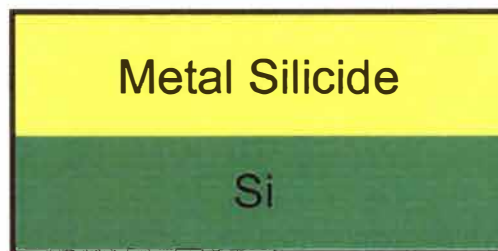


Figure 1.3 The use of metal silicides as metallization layers for, e.g., source and drain in ULSI transistors

hope was to prepare the films from the reaction of an amide precursor $\text{Ti}(\text{NMe}_2)_4$ with O_2 .

1.2 Characterization Techniques

Numerous methods were utilized for the characterization of compounds and materials prepared in this dissertation. One of the primary methods of characterization of the new compounds prepared in Chapters 2 and 3 was nuclear magnetic resonance (NMR) spectroscopy. This technique was also of great importance to the kinetic studies conducted in Chapter 4. Ellipsometry, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (IR), and X-ray diffraction (XRD) were used in the characterization of the thin films prepared and discussed in Chapter 5. Single-crystal X-ray diffraction was also important for the structural characterization of complexes discussed in Chapters 2 and 3. Below is a brief summary of each of these techniques.

1.2.1 *Nuclear Magnetic Resonance (NMR)*

NMR is probably the most important characterization technique used in organic and organometallic chemistries. NMR involves a flip of the nuclear spin of an atom. Every isotope of every element has a nuclear spin (I). Isotopes with $I = 0$ are not NMR active. The most commonly and easily studied isotopes have $I = 1/2$ but other spin values are also useful. The nuclei with $I > 1/2$, however,

have a nuclear quadrupole moment in addition to their magnetic moments. These quadrupole moments shorten T_2 (spin-spin relaxation time which controls the redistribution of energy between spins of different nuclei), leading to broadened resonances. The chemical shift, multiplicity and integration of NMR resonances are useful for determining the functional groups present and the connectivity of these groups in the complex of interest.

1.2.2 *Ellipsometry*

Because ellipsometry is a non-destructive method of characterization, it is a technique widely used in the microelectronics industry for measuring the thickness and refractive indices of dielectric films deposited on a semiconductor substrate (Si). Ellipsometry involves the reflection of light from a surface and is based on the fact that the polarization of a monochromatic electromagnetic wave changes its state when it hits an interface between two dielectric media at an angle other than 90° . The index of refraction describes the interaction of light with the film.¹¹

1.2.3 *Scanning Electron Microscopy (SEM)*

Scanning electron microscopy (SEM) is used to study the surface of solids. It has been extensively utilized to monitor the fabrication of microelectronic devices. To acquire an SEM micrograph, electrons are focused at the surface of the sample of interest and they are scanned across it in a

pattern of parallel lines. A signal can be collected for every position of the incident electron beam. The brightness of the image on the cathode-ray tube is varied by changing the signal amplification. Usually, the magnification range of the microscope can be 10–200,000 times.¹²

1.2.4 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a characterization technique used to determine the elemental composition of a solid sample. In XPS, X-ray photons bombard the sample, leading to the ejection of core level electrons. The kinetic energy (KE) of the electrons is measured. Because the energy of the incident photon is known, one can derive the binding energy (BE) from Eq. 1.1.

$$h\nu = BE + KE \quad (\text{Eq. 1.1})$$

Most elements have at least one characteristic line within the 50-12,000 eV range of binding energies. Bonding to form molecules has little effect on the chemical shift of the element of interest in XPS because it is the valence rather than core electrons that are involved in the bonding process. However, chemical shifts are not completely unaffected by bonding, and slight chemical shift differences, usually on the order of a few eVs, do arise from the formation of molecules when compared to pure elements.

1.2.5 *Infrared Spectroscopy (IR)*

Infrared spectroscopy is useful as a supplement to other characterization techniques. IR is used to detect the vibrations of molecules. The energy of absorption is usually on the order of $400\text{--}4000\text{ cm}^{-1}$. Vibrational motions such as bond stretching, bending, rocking, wagging, and twisting can be observed. In order for a compound to be IR active, i.e., to be observed by infrared spectroscopy, there must be a change in dipole during the vibration. Thus, the stretching mode of homonuclear diatomics, such as H_2 , is not detected by IR but that of heteronuclear diatomics, such as HCl , is. The atomic masses of the elements present, force constant of the bonds and geometry of the molecule play a role in the energy at which an IR absorption occurs. Thus, isotopically labeled compounds can be distinguished.

1.2.6 *X-ray Diffraction*

X-ray diffraction is used to determine the structure of a compound. X-rays have wavelengths that are on the order of ca. $1\text{ \AA}$. These wavelengths are on the order of the separation of atoms in a crystal ($\text{\AA}$), and thus they can be diffracted. A bright reflection from constructive interference is observed when Bragg's law is obeyed and the spacing is a multiple of the wavelength of the X-ray. Bragg's law is expressed in Equation 1.2 where λ is the wavelength of the X-ray, d is the distance between the lattice planes, and θ is the glancing angle.

$$n \lambda = 2 d \sin \theta$$

(Eq. 1.2)

Figure 1.4 demonstrates how diffraction occurs. Both single crystal and polycrystalline (powder) samples diffract in this manner and can be analyzed by X-ray diffraction.

Because X-rays are diffracted off of electrons, the intensity of scattering is dependent on the atomic numbers of the atoms in the crystal. Thus, it is difficult to locate light atoms, such as H, in the presence of heavier atoms by single crystal X-ray diffraction. From the electron density map, atoms are located by the areas with the highest electron density. An ellipsoid is generated for each atom, and it describes the amplitudes and directions of motion of the atoms. After the structure has been fully refined, an ORTEP (Oak Ridge Thermal Ellipsoid Program) diagram can be produced to show the identity, connectivity and geometry of atoms in the crystal. The ORTEP gives a “picture” of how the compound looks.

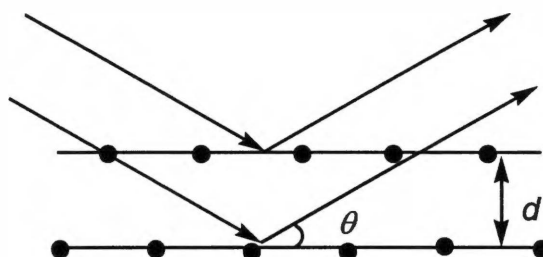


Figure 1.4 Diffraction described by Equation 1.2

When used in addition to other characterization methods such as NMR, IR and elemental analysis, single-crystal X-ray diffraction is a very useful technique for unambiguously characterizing a compound. However, this method does have some drawbacks. First and most importantly, only the crystalline form of a compound is analyzed, and thus crystals of the compound are required for single-crystal X-ray diffraction. Because only one crystal in a batch of sample is studied, the crystal picked for the diffraction studies may be that of an impurity and not actually represent the bulk sample. When solving the structure, assumptions are made about the identity of atoms present. Finally, some compounds exhibit disorders making structural determination difficult.

In powder X-ray diffraction, on the other hand, many small crystals are randomly oriented, and each crystal in each different orientation diffracts. Like single-crystal XRD, the crystallites diffract in the normal way and each reflection has a particular Bragg angle. Powder XRD is particularly useful in investigating structural changes associated with phase changes.

1.3 Summary of Research

1.3.1 *Chapter 2*

The syntheses of new disilyl dianions are discussed in Chapter 2. The new disilyl dianions, $[(\text{Me}_3\text{Si})_2\text{Si}-(\text{CH}_2)_n-\text{Si}(\text{SiMe}_3)_2]^{2-}$ ($n = 1, 4; 2, 5; 3, 6$), were isolated as $[\text{K}(18\text{-crown-6})]^+$ salts. Each new complex was fully characterized by

NMR (^1H , ^{13}C and ^{29}Si) and elemental analysis, and the structure of **5** was also determined by single-crystal X-ray crystallography. The structures of the precursors to dianions **5** and **6**, $(\text{Me}_3\text{Si})_3\text{Si}-(\text{CH}_2)_n-\text{Si}(\text{SiMe}_3)_3$ ($n = 2, 2; 3, 3$) were also determined by single-crystal X-ray diffraction studies.

1.3.2 Chapter 3

In Chapter 3 the preparation of new Zr and Zn silyl complexes containing the silyl ligands in Chapter 2 are discussed. Attempts to prepare a persilyl Zr complex from ZrCl_4 were unsuccessful. However, a new bis(silyl) Zr anion $\{(\text{Me}_2\text{N})_3\text{Zr}(\eta^2-[(\text{Me}_3\text{Si})_2\text{Si}-(\text{CH}_2)_2-\text{Si}(\text{SiMe}_3)_2])\}^-$ (**7**) containing amide ligands was prepared and characterized. The Zr anion exists in an ionic pair with a $\text{K}^+(18\text{-crown-6})_{1.5}$ cation. The reaction of ZnCl_2 with 1.5 equiv $[\text{K}(18\text{-crown-6})]_2[(\text{Me}_3\text{Si})_2\text{Si}-(\text{CH}_2)_2-\text{Si}(\text{SiMe}_3)_2]$ (**5**) led to the isolation of a new three-coordinate, trisilyl Zn complex $[\text{K}(18\text{-crown-6})]_2[[\eta^2-(\text{Me}_3\text{Si})_2\text{Si}-(\text{CH}_2)_2-\text{Si}(\text{SiMe}_3)_2]\text{Zn}[\mu-(\text{Me}_3\text{Si})_2\text{Si}-(\text{CH}_2)_2-\text{Si}(\text{SiMe}_3)_2]\text{Zn}[\eta^2-(\text{Me}_3\text{Si})_2\text{Si}-(\text{CH}_2)_2-\text{Si}(\text{SiMe}_3)_2]]$ (**8**). Both **7** and **8** were characterized by ^1H , ^{13}C and ^{29}Si NMR and single-crystal X-ray crystallography.

1.3.3 Chapter 4

Some new mechanistic insights into the reactions of a Ta alkylidene complex $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}(\text{PMe}_3)(=\text{CHSiMe}_3)$ (**9**) with H_2SiMePh and D_2SiMePh are presented in Chapter 4. Reactions with H_2SiMePh conducted without added

PMe₃ gave $k_{\text{obs}} = 1.5 \times 10^{-2} \text{ min}^{-1}$ while those carried out under a 20-fold excess of PMe₃ yielded $k_{\text{obs}} = 8.1 \times 10^{-4} \text{ min}^{-1}$. In other words, the reactions under a large excess of PMe₃ were found to be 19 times slower than those performed with no additional PMe₃. In the reaction of **9** with D₂SiMePh, mass spectrometric analyses of H₂, HD and D₂, and NMR studies of the remaining silanes indicated hydrogen scrambling among the gaseous reaction products and silane. New mechanistic pathways for the reaction between (Me₃SiCH₂)₃Ta(PMe₃)(=CHSiMe₃) (**9**) with H₂SiMePh are discussed.

1.3.4 Chapter 5

Preparation and characterization of TiO₂ thin films from the reaction of tetrakis(dimethylamido)titanium Ti(NMe₂)₄ with O₂ by metal-organic chemical vapor deposition (MOCVD) processes are discussed in Chapter 5. We found that thin films of TiO₂, free of C contamination, could be fabricated from these processes. The thin films prepared were characterized by ellipsometry, SEM, IR, powder XRD and XPS. Before annealing, the films were found to be amorphous and the surface was smooth and featureless. After annealing at 600 °C in air for 1 h the films were found to be crystalline anatase TiO₂.

CHAPTER 2

Synthesis and Characterization of Bis[tris(trimethylsilyl)silyl]propane and Dianionic Bis(silyl)alkane Salts

2.1 Introduction

Organosilicon compounds are important for the preparation of the new chelating silyl complexes, and they are also widely used reagents in both synthetic inorganic¹³⁻¹⁷ and organic chemistry.^{18,19} In particular, silyl anions play an important role in the preparation of new silicon-containing compounds.²⁰ Of intense interest to us are those involved in the preparation of transition-metal silyl complexes.^{3,4,7,13-17,21-43}

Preparation of new silyl anions and dianions has been actively studied by many research groups.²⁵⁻³¹ However, in comparison to carbanions and dicarbanions, there are a smaller number and variety of silyl anions²⁵⁻³¹ and dianions.^{25-31,44-66} Dilithio- and dipotassio-oligosilanes are one major source of silyl dianions, and are usually prepared from the cleavage of Si-Si bonds by alkali metals,^{44,45,47,49,51} MeLi,⁵² or (Me₃Si)₃SiLi.⁴⁶ Silole dianions (R₄C₄Si)²⁻, analogs of the cyclopentadienyl ligand, are another source and are usually yielded from the reactions of R₄C₄SiX₂ (X₂ = Cl₂,^{57-59,64-66} Br₂,^{61,62} MeH⁶³) with

alkali metals.

Our group has been interested in the chemistry of cyclopentadienyl-free, d^0 early transition metal silyl complexes, and has reported such novel metal-Si bonded complexes over the past several years.^{3,10,17,37,38,40,41} The Cp-free silyl compounds we have prepared usually contain only one silyl ligand. A few rare Zr and Ta bis(silyl) complexes have also been reported.^{4,7} In these studies, either tris(trimethylsilyl)silyl, $-\text{Si}(\text{SiMe}_3)_3$, or t-butyldiphenylsilyl, $-\text{Si}^t\text{BuPh}_2$, ligands were utilized in the preparation of both mono- and bis(silyl) complexes. Our success in this area prompted us to investigate the synthesis and reactivities of silyl complexes containing different silyl ligands. We are interested in chelating bis(silyl) ligands, as the chelating effect may enhance the stability of the metal silyl complexes. Hence, bis(silyl)alkane compounds were chosen as ligand precursors.

In addition to the methods previously mentioned, reactions of alkoxides (MOR') with disilanes $\text{R}_3\text{Si}-\text{SiR}_3$ and polysilanes have also been used to make silyl anions (Equation 2.1)⁶⁷⁻⁷⁰ and dianions.⁵⁵



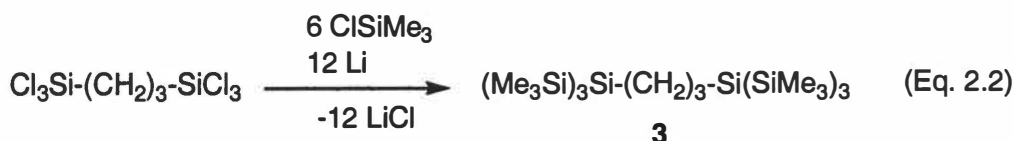
In research presented in this dissertation we found that reactions of $(\text{Me}_3\text{Si})_3\text{Si}-(\text{CH}_2)_n-\text{Si}(\text{SiMe}_3)_3$ ($n = 1, 1; 2, 2; 3, 3$) with t-BuOK in the presence of 18-crown-6 gave silyl dianions $[(\text{Me}_3\text{Si})_2\text{Si}-(\text{CH}_2)_n-\text{Si}(\text{SiMe}_3)_2]^{2-}$.⁷¹ The reactions

were fast and complete within ca. 5 min. These anions were readily isolated as salts of the formula $[K(18\text{-crown-6})]_2[(\text{Me}_3\text{Si})_2\text{Si}(\text{CH}_2)_n\text{Si}(\text{SiMe}_3)_2]$ ($n = 1, 4; 2, 5; 3, 6$). Reported in this chapter is the preparation of **4-6** and X-ray crystal structure of **5**. The silyl dianions described here add to the list of known silyl dianions as potential precursors to silicon-containing compounds. Improved synthesis of **3**,⁷² a precursor to **6**, and X-ray structures of silyl dianion precursors **2** and **3** are also reported.

2.2 Results and Discussion

2.2.1 Synthesis of Bis[tris(trimethylsilyl)silyl]propane $(\text{Me}_3\text{Si})_3\text{Si}(\text{CH}_2)_3\text{Si}(\text{SiMe}_3)_3$ (**3**)

$(\text{Me}_3\text{Si})_3\text{Si}(\text{CH}_2)_3\text{Si}(\text{SiMe}_3)_3$ (**3**) was prepared from the reaction of 1 equiv of $\text{Cl}_3\text{Si}(\text{CH}_2)_3\text{SiCl}_3$ with 6 equiv of ClSiMe_3 and 12 equiv of Li in 85.5% yield by an improved reported procedure (Equation 2.2).⁶⁴ The yield of **3** was higher than those of its analogs $(\text{Me}_3\text{Si})_3\text{Si}(\text{CH}_2)_n\text{Si}(\text{SiMe}_3)_3$ ($n = 1, 1; 2, 2$) with shorter hydrocarbon bridges. It is likely that this approach to make bis(silyl)alkane compounds may be extended to other lengths of hydrocarbon chains.



Compound **3** was characterized by ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectroscopy. Its ^1H and ^{13}C NMR spectra are consistent with those given in the literature.^{72,73} **3** has not been previously characterized by ^{29}Si NMR. The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **3** shows two signals, one for $-\text{SiMe}_3$ at -12.70 ppm and the other for the quaternary Si atom at -82.97 ppm. The ^{29}Si chemical shift of this quaternary Si is comparable to those in **1** and **2**⁷³ as well as other compounds of the type $\text{RSi}(\text{SiMe}_3)_3$ such as $\text{MeSi}(\text{SiMe}_3)_3$ (-89.9 ppm),⁷⁴ $\text{EtSi}(\text{SiMe}_3)_3$ (-78.6 ppm),⁷⁰ and a bis(silyl)ethylene compound $(\text{Me}_3\text{Si})_3\text{Si}-\text{CH}=\text{CH}-\text{Si}(\text{SiMe}_3)_3$ (-80.9 ppm).⁷⁵

2.2.2 X-ray Crystal Structures of **2** and **3**

The crystal data for **2**, selected bond distances, and selected bond angles are given in Tables 2.1, 2.2, and 2.3, respectively. The crystal structure of $(\text{Me}_3\text{Si})_3\text{Si}-(\text{CH}_2)_2-\text{Si}(\text{SiMe}_3)_3$ (**2**, Figure 2.1) shows the $-\text{Si}(\text{SiMe}_3)_3$ groups to be in an *anti* configuration. The C atoms of the Me_3Si groups were found to be disordered. Attempts to obtain crystallographic data sets at a lower temperature failed. The crystal cracked during cooling to a lower temperature. The inability to obtain crystal data at low temperature (73 K) is likely due to a phase change, as observed for $\text{Si}(\text{SiMe}_3)_4$ at 225 K and $\text{C}(\text{SiMe}_3)_4$ at 268 K.⁷⁶ The C(1)-Si(1) bond length in **2** [$1.907(7)$ Å] is comparable to that in **1** [$1.896(4)$ Å].⁷³ The C(1A)-C(1)-Si(1) bond angle of $119.4(8)^\circ$ is larger from that expected for tetrahedral geometry signifying steric bulkiness in **2**. This angle is, however,

Table 2.1 Crystal Data for **2**

Empirical formula	$\text{C}_{20} \text{H}_{58} \text{Si}_8$	
Formula weight	523.38	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 9.2943(19)$ Å	$\alpha = 109.39(3)^\circ$
	$b = 9.6650(19)$ Å	$\beta = 93.05(3)^\circ$
	$c = 13.014(3)$ Å	$\gamma = 117.63(3)^\circ$
Volume	946.5(3) Å ³	
<i>Z</i>	1	
Density (calculated)	0.918 Mg/m ³	
Absorption coefficient	0.290 mm ⁻¹	
<i>F</i> (000)	290	
Crystal size	0.50 x 0.30 x 0.30 mm ³	
θ range for data collection	2.47 to 22.50°	
Index ranges	$-10 \leq h \leq 0, -10 \leq k \leq 10, -13 \leq l \leq 13$	
Reflections collected	2654	
Independent reflections	2468 [$R(\text{int}) = 0.0278$]	

Table 2.1 (continued)

Completeness to $\theta = 22.50^\circ$	100.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9180 and 0.8685
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2468 / 0 / 155
Goodness-of-fit on F^2	1.035
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0751$, $wR2 = 0.1706$
R indices (all data)	$R1 = 0.1431$, $wR2 = 0.2149$
Largest diff. peak and hole	0.282 and -0.244 e. $\text{\AA}^{-3}$

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$$

Table 2.2 Selected Bond Distances (Å) in **2**

Si(1)-C(1)	1.906(7)	Si(1)-Si(3)	2.329(3)
Si(1)-Si(4)	2.338(3)	Si(1)-Si(2)	2.340(3)
Si(2)-C(2A)	1.79(3)	Si(3)-C(5)	1.839(9)
Si(4)-C(10)	1.854(10)	C(1)-C(1A)	1.436(14)

Table 2.3 Selected Bond Angles (deg) in **2**

C(1)-Si(1)-Si(3)	111.4(3)	C(1A)-C(1)-Si(1)	119.3(8)
C(1)-Si(1)-Si(2)	110.2(3)	C(1)-Si(1)-Si(4)	102.9(3)
C(4)-Si(2)-Si(1)	108.1(9)	C(5)-Si(3)-Si(1)	111.8(3)
C(6)-Si(3)-C(7)	107.4(6)	C(8)-Si(4)-C(9)	107.3(6)
Si(3)-Si(1)-Si(2)	111.58(12)	Si(3)-Si(1)-Si(4)	110.03(11)

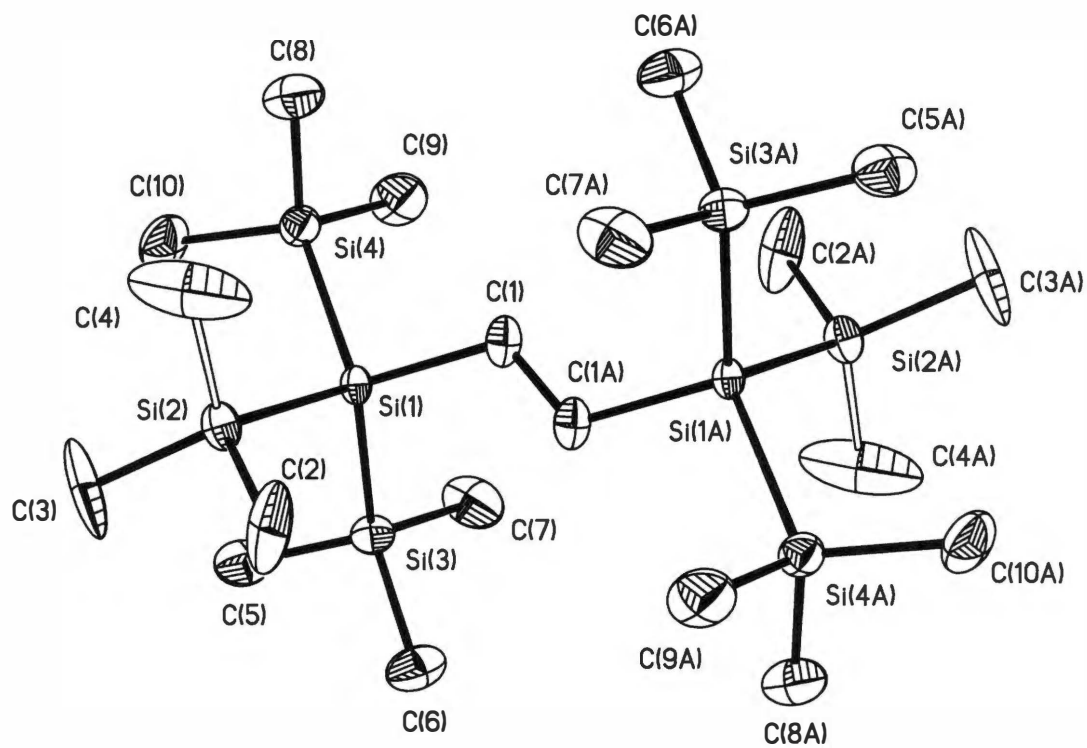


Figure 2.1 ORTEP diagram of 2 showing 10% ellipsoids

much smaller than 136.2° observed for the highly strained Si-C-Si angle in (Me₃Si)₃Si-CH₂-Si(SiMe₃)₃ (**1**).⁷³ A packing diagram of **2** is shown in Figure 2.2.

Similar to **2**, data sets of **3** at a low temperature were not acquired due to cracking of the crystal. The crystal structure of **3** was solved at room temperature. The crystal data for (Me₃Si)₃Si-(CH₂)₃-Si(SiMe₃)₃ (**3**), selected bond distances, and selected bond angles are given in Tables 2.4, 2.5, and 2.6, respectively. The crystal structure of **3** (Figure 2.3) shows that, unlike the ethylene-bridged **2**, the -Si(SiMe₃)₃ groups in **3** are *syn* to each other. As in **2**, the geometry around the bridge carbon atoms in **3** is distorted. The central bridge atom, C(2), has the smallest bond angle [C(3)-C(2)-C(1) = 114.4(2)°] whereas the angle between the outer bridge carbon atoms and bulky -Si(SiMe₃)₃ groups are larger [Si(2)-C(3)-C(2) = 118.1(2)° and C(2)-C(1)-Si(1) = 117.51(19)°]. A packing diagram of **3** is shown in Figure 2.4.

2.2.3 Metalation of **1**, **2** and **3**. Synthesis of [K(18-crown-6)]₂

[(Me₃Si)₂Si-(CH₂)_n-Si(SiMe₃)₂] (n = 1, 4; 2, 5; 3, 6)

Reactions of (Me₃Si)₃Si-(CH₂)_n-Si(SiMe₃)₃ (n = 2, 2; 3, **3**) with t-BuOK in THF were found by Marschner and co-workers to slowly give silyl dianion salts K₂[(Me₃Si)₂Si-(CH₂)_n-Si(SiMe₃)₂]. Their preparation, however, required heating at 60 °C in a sealed tube for several days. Isolation of the dianion required trapping with EtBr.⁵⁵

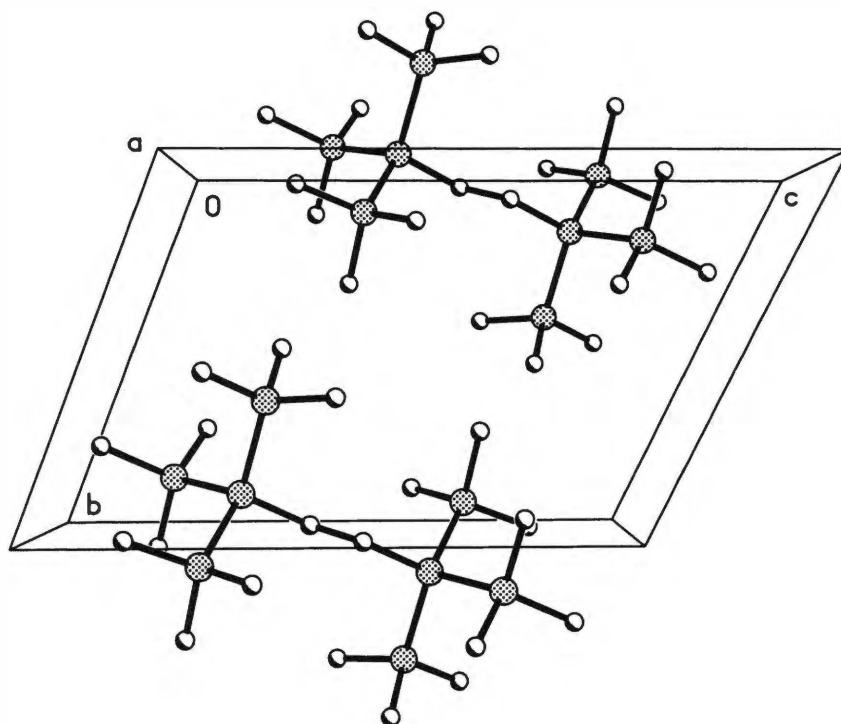


Figure 2.2 Packing diagram of **2**. View down the *a* axis

Table 2.4 Crystal Data for **3**

Empirical formula	$\text{C}_{21} \text{H}_{60} \text{Si}_8$	
Formula weight	537.41	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	$a = 12.9940(12)$ Å	$\alpha = 90^\circ$
	$b = 17.8317(17)$ Å	$\beta = 97.712(2)^\circ$
	$c = 16.7937(16)$ Å	$\gamma = 90^\circ$
Volume	3856.0(6) Å ³	
<i>Z</i>	4	
Density (calculated)	0.926 Mg/m ³	
Absorption coefficient	0.286 mm ⁻¹	
<i>F</i> (000)	1192	
Crystal size	0.15 x 0.11 x 0.07 mm ³	
θ range for data collection	1.67 to 23.32°	
Index ranges	$-14 \leq h \leq 14, -19 \leq k \leq 19, -18 \leq l \leq 18$	
Reflections collected	23488	
Independent reflections	5574 [$R(\text{int}) = 0.1074$]	

Table 2.4 (continued)

Completeness to $\theta = 23.32^\circ$	99.7%
Max. and min. transmission	0.9802 and 0.9583
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5574 / 0 / 280
Goodness-of-fit on F^2	1.049
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0496$, $wR2 = 0.1416$
R indices (all data)	$R1 = 0.0681$, $wR2 = 0.1552$
Largest diff. peak and hole	0.471 and -0.229 e.Å ⁻³

$$R1 = \Sigma ||F_c|| / \Sigma |F_o|; wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$$

Table 2.5 Selected Bond Distances (Å) in **3**

Si(1)-C(1)	1.902(3)	Si(1)-Si(7)	2.3401(13)
Si(1)-Si(8)	2.3400(13)	Si(1)-Si(6)	2.3445(13)
Si(2)-C(3)	1.905(3)	Si(6)-C(7)	1.815(5)
Si(7)-C(6)	1.835(6)	Si(7)-C(5)	1.866(4)
Si(7)-C(4)	1.878(5)	C(2)-C(3)	1.513(4)
Si(8)-C(9)	1.855(4)	C(2)-C(1)	1.518(4)

Table 2.6 Selected Bond Angles (deg) in **3**

C(1)-Si(1)-Si(7)	105.91(9)	C(3)-C(2)-C(1)	114.4(2)
C(2)-C(1)-Si(1)	117.51(19)	C(3)-Si(2)-Si(5)	110.15(11)
C(2)-C(3)-Si(2)	118.1(2)	C(16)-Si(5)-C(17)	107.9(2)
C(19)-Si(4)-C(20)	108.0(2)	Si(5)-Si(2)-Si(3)	110.37(5)

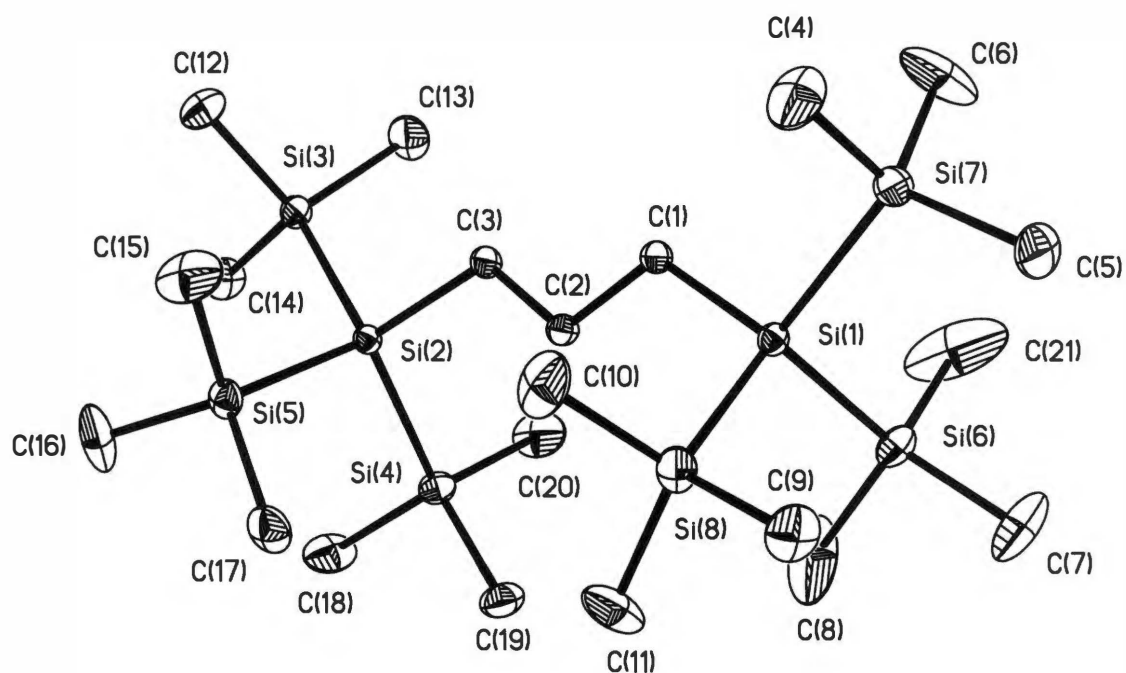


Figure 2.3 ORTEP diagram of **3** showing 10% ellipsoids

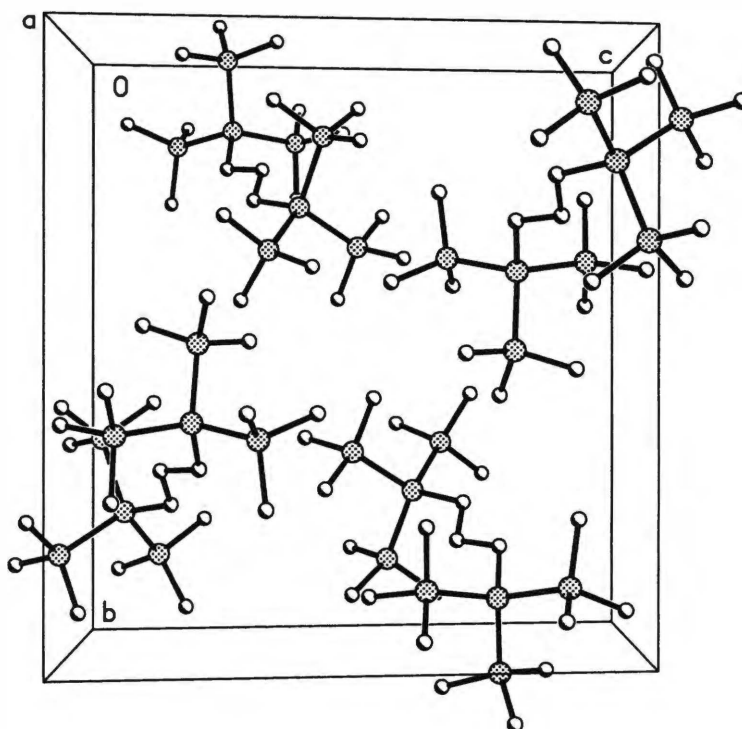
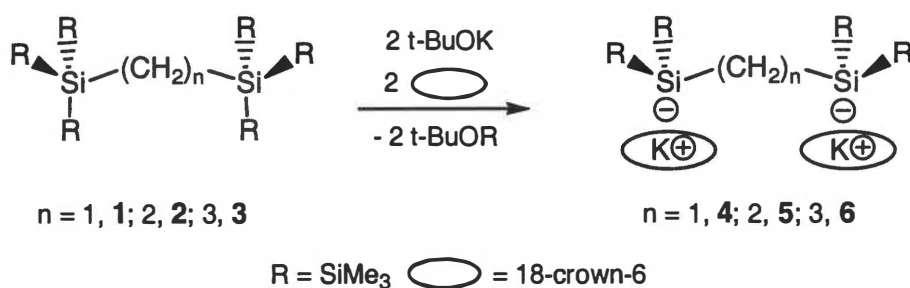


Figure 2.4 Packing diagram of **3**. View down the *a* axis

In the current study, when two equivalents of t-BuOK were reacted with **1**, **2** or **3** at room temperature in DME, no solid products could be isolated. 18-crown-6, which has been used in the formation of other silyl potassium salts,^{51,61,62,69,77,78,79} was added to the reaction mixture to give silyl dianions **4-6** as [K(18-crown-6)]⁺ salts (Scheme 2.1). Reactions among solids of 18-crown-6, t-BuOK, and **2** or **3** were observed, as the mixtures of colorless solids turned yellow before the solvent, DME, was added. In DME, reactions to give **5** and **6** were very fast. ¹H NMR indicated the reactions were clean and complete within 5 min. The removal of volatiles gave an analytically pure, yellow powdery solid of **5** or **6**.

The crystal structure of t-BuOK revealed that it exists as tetramer [t-BuOK]₄ in the solid state with a cubane-like structure.⁸⁰ In etheral solvents, this compound remains highly oligomerized⁸⁰ with reduced activity to attack Si atoms in **1-3**. Hence, it is not surprising that the reaction proceeds slowly in the



Scheme 2.1 Preparation of **4-6**

etheral solvent DME. Addition of 18-crown-6 to t-BuOK leads to complexation of K^+ ions by the crown molecules, and increases the activity of $t\text{-BuO}^-$ ions to attack the Si atoms in **1-3**.

A single resonance of the crown ether bonded to K^+ was observed around 3.3 ppm in the ^1H spectra of **4-6**. In the ^1H NMR spectra of **5** and **6**, the protons of both $-\text{SiMe}_3$ and the bridge $-(\text{CH}_2)_n-$ are downfield shifted from those of the neutral precursors **2** and **3**. In $[\text{K}(18\text{-crown-6})]_2[(\text{Me}_3\text{Si})_2\text{Si-CH}_2\text{-Si}(\text{SiMe}_3)_2]$ (**4**), only the $-\text{SiMe}_3$ protons are downfield shifted. The ^1H NMR resonance for the bridging $-\text{CH}_2\text{-Si}$ group in **4** was observed at 0.11 ppm, upfield shifted from that (0.22 ppm) in its neutral precursor $(\text{Me}_3\text{Si})_3\text{Si-CH}_2\text{-Si}(\text{SiMe}_3)_3$ (**1**),⁷³ and those of the $-\text{CH}_2\text{-Si}$ groups in ethylene-bridged **5** (1.33 ppm) and propylene-bridged **6** (1.54 ppm). The quaternary Si resonances in the ^{29}Si spectra of **4**, **5** and **6** were upfield shifted from those in **1**, **2** and **3** by 32.0, 35.2 and 34.6 ppm, respectively. These resonances, at -110.5 , -111.8 and -117.6 ppm for **4**, **5** and **6**, respectively, are comparable to those for $(\text{Me}_3\text{Si})_2\text{EtSiK}$ (-111.7 ppm).⁷⁰

2.2.4 X-ray Crystal Structure of 5

The molecular structure of **5** was difficult to obtain as **5** was found to be very air-sensitive and the crystals coated with paratone oil were difficult to quickly mount. The crystal structure of **5** was solved at 173 K. The crystal data for **5**, selected bond distances, and selected bond angles are given in Tables 2.7, 2.8, and 2.9, respectively. There are two independent molecules in a unit

Table 2.7 Crystal Data for 5

Empirical formula	$\text{C}_{38} \text{H}_{88} \text{K}_2 \text{O}_{12} \text{Si}_6$	
Formula weight	983.82	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	$a = 10.0755(10)$ Å	$\alpha = 72.346(2)^\circ$
	$b = 14.2497(15)$ Å	$\beta = 86.520(2)^\circ$
	$c = 22.082(2)$ Å	$\gamma = 75.028(2)^\circ$
Volume	2917.9(5) Å ³	
<i>Z</i>	2	
Density (calculated)	1.120 Mg/m ³	
Absorption coefficient	0.332 mm ⁻¹	
<i>F</i> (000)	1068	
Crystal size	0.41 x 0.32 x 0.11 mm ³	
θ range for data collection	1.55 to 26.46°	
Index ranges	$-12 \leq h \leq 12, -17 \leq k \leq 17, -27 \leq l \leq 27$	
Reflections collected	28466	
Independent reflections	11878 [<i>R</i> (int) = 0.0891]	

Table 2.7 (continued)

Completeness to $\theta = 26.46^\circ$	98.5%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9644 and 0.8759
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11878 / 0 / 535
Goodness-of-fit on F^2	0.808
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0551$, $wR2 = 0.1240$
R indices (all data)	$R1 = 0.1206$, $wR2 = 0.1535$
Largest diff. peak and hole	0.333 and -0.283 e.Å ⁻³

$$R1 = \Sigma ||F_c| | / \Sigma |F_o|; wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$$

Table 2.8 Selected Bond Distances (Å) in **5**

K(1)-O(6)	2.732(2)	K(1)-O(2)	2.761(2)
K(1)-O(4)	2.775(2)	K(1)-O(3)	2.889(2)
K(1)-O(1)	2.897(2)	K(1)-O(5)	2.892(2)
K(1)-Si(2)	3.4197(12)	Si(1)-C(28)	1.890(3)
Si(1)-Si(2)	2.3430(14)	Si(2)-C(25)	1.953(3)
Si(3)-Si(2)	2.3395(13)	O(5)-C(1)	1.423(4)
C(12)-C(1)	1.500(5)	C(25)-C(25A)	1.546(6)

Table 2.9 Selected Bond Angles (deg) in **5**

O(6)-K(1)-O(2)	118.35(7)	Si(3)-Si(2)-K(1)	118.44(5)
O(2)-K(1)-Si(2)	99.80(5)	C(2)-O(5)-K(1)	104.97(19)
O(1)-K(1)-C(2)	100.95(8)	C(26)-Si(1)-C(27)	104.56(17)
O(5)-C(2)-C(3)	109.5(3)	C(25)-Si(2)-Si(1)	100.18(12)
C(25)-Si(2)-Si(3)	102.67(10)	C(25)-Si(2)-K(1)	120.45(10)
Si(3)-Si(2)-Si(1)	99.95(5)		

cell of **5**, and its structure (Figure 2.5) shows the [K(18-crown-6)]⁺ groups to be *anti* to each other. There is no evidence of interaction between neighboring molecules of **5**, as revealed in a packing diagram of **5** (Figure 2.6). Two different ranges of K-O bond lengths were observed within each [K(18-crown-6)]⁺ cation [2.889(2)-2.897(2) Å for K(1)-O(1), K(1)-O(3) and K(1)-O(5), and 2.732-2.775 Å for K(1)-O(2), K(1)-O(4) and K(1)-O(6)]. The Si(2) anion and K(1) cation have an interatomic distance of 3.4197(12) Å suggesting some electrostatic interaction. The C(25)-C(25A) distance of 1.546(6) Å for the ethylene bridge is elongated compared to that in its neutral precursor **2** [C(1)-C(1A) = 1.433(14) Å]. Moreover, C(25)-Si(2)-Si(n) (n = 1, 3) and Si(1)-Si(2)-Si(3) bond angles around the anionic Si(2) are smaller than those in the neutral **1**,⁷³ **2** and **3**, indicating the steric effect of the bulky [K(18-crown-6)]⁺ cations in **5**.

In summary, new, isolated silyl dianions have been prepared and characterized by ¹H, ¹³C and ²⁹Si NMR spectroscopy, elemental analysis and, in the case of **5**, by single-crystal X-ray diffraction studies. These silyl anions are potential precursors to new silicon-containing compounds. In addition, the crystal structures of the silyl dianion precursors, **2** and **3**, were determined. The results presented in this chapter have been published in the literature.⁷¹

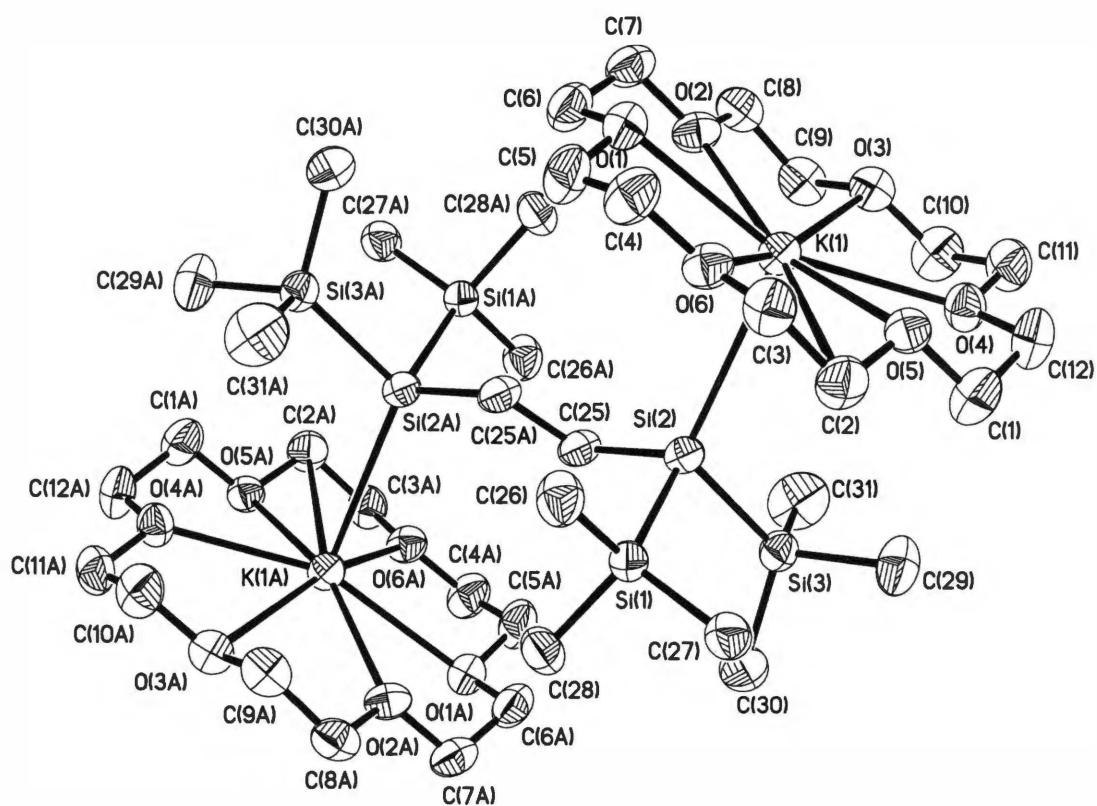


Figure 2.5 ORTEP diagram of **5** showing 30% ellipsoids

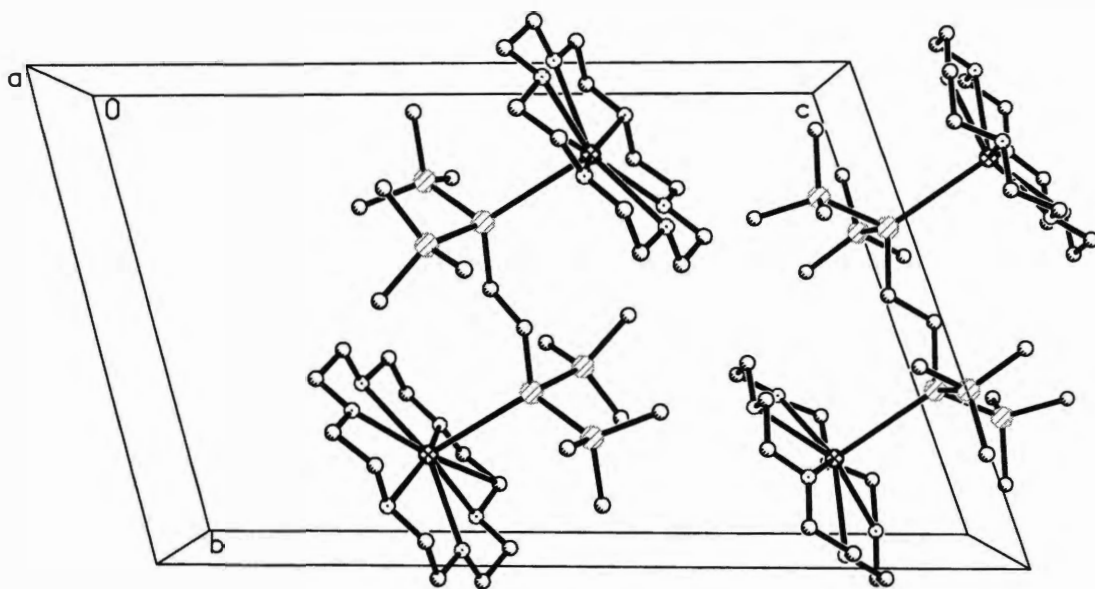


Figure 2.6 Packing diagram of **5**. View down the *a* axis

2.3 Experimental Section

2.3.1 General Procedures

All manipulations were performed under a dry nitrogen or argon atmosphere with the use of either a glovebox or standard Schlenk techniques. Hexanes (Fisher, Certified ACS) that were used to extract **1-3** from their reaction mixtures and to crystallize **2**, and acetone (Fisher, Certified ACS) were used as received. THF (Fisher, Certified), DME (Fisher, Certified), toluene (Fisher, Certified ACS), and hexanes (Fisher, Certified ACS) that were used to precipitate **4** were purified by distillation from potassium benzophenone ketyl. NMR solvents were dried and stored over 5 Å molecular sieves. ClSiMe_3 (Strem) was distilled before use. Li wire [high Na (1%) content, Aldrich], 18-crown-6 (Aldrich), $\text{Cl}_3\text{SiCH}_2\text{SiCl}_3$ (Gelest), $\text{Cl}_3\text{Si}(\text{CH}_2)_2\text{SiCl}_3$ (Gelest), and $\text{Cl}_3\text{Si}(\text{CH}_2)_3\text{SiCl}_3$ (Gelest) were used as received. *t*-BuOK was prepared by the literature procedure.⁸¹ $(\text{Me}_3\text{Si})_3\text{Si-CH}_2\text{-Si}(\text{SiMe}_3)_3$ (**1**) and $(\text{Me}_3\text{Si})_3\text{Si-CH}_2\text{CH}_2\text{-Si}(\text{SiMe}_3)_3$ (**2**) were prepared by the methods our group previously reported in the literature.⁷¹ A glass-coated stir bar was used in all reactions requiring Li metal or *t*-BuOK. NMR spectra were recorded on Bruker AC-250 and AMX-400 Fourier transform spectrometers. ^1H and ^{13}C NMR spectra were referenced to solvents (residual protons in the ^1H spectra). ^{29}Si chemical shifts were referenced to SiMe_4 . Elemental analyses were carried out by Complete Analysis Laboratories, Inc., Parsippany, New Jersey.

2.3.2 Preparation of $(\text{Me}_3\text{Si})_3\text{Si}-(\text{CH}_2)_3\text{Si}(\text{SiMe}_3)_3$ (3)

This compound was prepared earlier as a 2:1 mixture with $(\text{Me}_3\text{Si})_2\text{Si}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}(\text{SiMe}_3)_2$.⁷² In the current study, a flame-dried flask  was charged with a suspension of cut Li wire (0.4245 g, 61.16 mmol) and ClSiMe_3 (3.90 mL, 3.34 g, 30.7 mmol) in THF (40 mL). $\text{Cl}_3\text{Si}(\text{CH}_2)_3\text{SiCl}_3$ (1.515 g, 4.872 mmol) in THF (10 mL) at 0 °C was added dropwise with stirring to this suspension. After 2 h, the reaction mixture turned cloudy brown. The mixture was stirred for a total of 29 h, at which time the dark brown solution was filtered into 100 mL of 10% (v/v) HCl and the LiCl washed with hexanes. The organic phase was dried over MgSO_4 , and the solvent was removed resulting in a yellow residue. The residue was crystallized from acetone, producing 2.237 g of 3 [85.5% yield based on $\text{Cl}_3\text{Si}(\text{CH}_2)_3\text{SiCl}_3$]. ^1H NMR (250.1 MHz, benzene- d_6 , 23 °C) δ 1.71 (m, 2H, CH_2CH_2), 1.05 (m, 4H, CH_2Si), 0.27 (s, 54H, SiMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (62.9 MHz, benzene- d_6 , 23 °C) δ 29.85 (CH_2CH_2 , $^1J_{\text{C-H}} = 125.4$ Hz), 14.52 (CH_2Si , $^1J_{\text{C-H}} = 121.5$ Hz), 1.42 (SiMe_3 , $^1J_{\text{C-H}} = 119.6$ Hz). $^{29}\text{Si}\{^1\text{H}\}$ NMR (79.49 MHz, benzene- d_6 , 23 °C) δ -12.70 (Si-SiMe_3), -82.97 (Si-SiMe_3). Anal. Calcd. for $\text{C}_{21}\text{H}_{60}\text{Si}_8$: C, 46.94; H, 11.25. Found: C, 46.93; H, 11.31.

2.3.3 Preparation of $[\text{K}(18\text{-crown-6})]_2[(\text{Me}_3\text{Si})_2\text{Si}-\text{CH}_2-\text{Si}(\text{SiMe}_3)_2]$ (4)

$(\text{Me}_3\text{Si})_3\text{SiCH}_2\text{Si}(\text{SiMe}_3)_3$ (1) (0.900 g, 1.77 mmol) was degassed for 1.25 h under vacuum in a flame-dried flask. $t\text{-BuOK}$ (0.4180 g, 3.725 mmol) was added, and the two reagents were dissolved in DME (20 mL). After 2 h, all

volatiles were removed. The remaining orange oil was dissolved in toluene, and the resulting yellow-orange solution was treated dropwise with a solution of 18-crown-6 (1.520 g, 5.751 mmol) in DME. The reaction mixture turned orange-red, and was concentrated before cooling to $-20\text{ }^{\circ}\text{C}$. An orange oil, which was not soluble in hexanes, developed in 2.5 weeks. When toluene was added to the oil, a powder of **4** precipitated (0.283 g, 16.5% yield). ^1H NMR (250.1 MHz, benzene- d_6 , $23\text{ }^{\circ}\text{C}$) δ 3.34 (s, 48 H, $\text{CH}_2\text{-O}$), 0.76 (s, 36 H, SiMe_3), 0.11 (s, 2 H, $\text{CH}_2\text{-Si}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (62.9 MHz, benzene- d_6 , $23\text{ }^{\circ}\text{C}$) δ 70.18 ($\text{CH}_2\text{-O}$, $^1J_{\text{C-H}} = 141.2\text{ Hz}$), 6.23 (SiMe_3 , $^1J_{\text{C-H}} = 116.7\text{ Hz}$), -17.16 ($\text{CH}_2\text{-Si}$, $^1J_{\text{C-H}} = 115.2\text{ Hz}$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (79.49 MHz, benzene- d_6 , $23\text{ }^{\circ}\text{C}$) δ -6.7 (Si-SiMe_3), -110.5 (Si-SiMe_3). Anal. Calcd. for $\text{C}_{37}\text{H}_{86}\text{O}_{12}\text{Si}_6\text{K}_2$: C, 45.83; H, 8.94. Found: C, 45.75; H, 9.10.

2.3.4 Preparation of $[\text{K}(18\text{-crown-6})]_2[(\text{Me}_3\text{Si})_2\text{Si}(\text{CH}_2)_2\text{Si}(\text{SiMe}_3)_2]$ (**5**)

$(\text{Me}_3\text{Si})_3\text{Si}(\text{CH}_2)_2\text{Si}(\text{SiMe}_3)_3$ (**2**) (1.6839 g, 3.2174 mmol) in a flame-dried flask was degassed for 1.5 h under vacuum before $t\text{-BuOK}$ (0.7358 g, 6.557 mmol) was added. The reaction mixture turned yellow immediately after the reagents were dissolved in DME. After 2 h, 18-crown-6 (1.7188 g, 6.5027 mmol) in DME was added dropwise with stirring, and the mixture turned orange. After 25 min, volatiles were removed in vacuo yielding 2.710 g of a yellow powder (85.6% yield). Crystals suitable for X-ray diffraction studies were grown in toluene at $-20\text{ }^{\circ}\text{C}$ over a one-month period. ^1H NMR (250.1 MHz, benzene- d_6 ,

23 °C) δ 3.32 (s, 48 H, $\text{CH}_2\text{-O}$), 1.33 (s, 4 H, $\text{CH}_2\text{-Si}$), 0.64 (s, 36 H, SiMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (62.9 MHz, benzene- d_6 , 23 °C) δ 70.20 ($\text{CH}_2\text{-O}$, $^1J_{\text{C-H}} = 141.4$ Hz), 17.09 ($\text{CH}_2\text{-Si}$, $^1J_{\text{C-H}} = 122.4$ Hz), 5.74 (SiMe_3 , $^1J_{\text{C-H}} = 117.2$ Hz). $^{29}\text{Si}\{^1\text{H}\}$ NMR (79.49 MHz, benzene- d_6 , 23 °C) δ -6.8 (Si-SiMe_3), -111.8 (Si-SiMe_3). Anal. Calcd. for $\text{C}_{38}\text{H}_{88}\text{O}_{12}\text{Si}_6\text{K}_2$: C, 46.39; H, 9.02. Found: C, 45.98; H, 8.83.

2.3.5 Preparation of $[\text{K}(\text{18-crown-6})]_2[(\text{Me}_3\text{Si})_2\text{Si}(\text{CH}_2)_3\text{Si}(\text{SiMe}_3)_2]$ (**6**)

To a flame-dried flask containing degassed $(\text{Me}_3\text{Si})_3\text{Si}(\text{CH}_2)_3\text{Si}(\text{SiMe}_3)_3$ (**3**) (1.0329 g, 1.9221 mmol) was added t-BuOK (0.443 g, 3.95 mmol) and 18-crown-6 (1.0392 g, 3.9316 mmol). The solid reagents turned yellow before being dissolved in DME (30 mL). The reaction mixture in DME was bright yellow. After 20 min of stirring, hexanes (15 mL) were added. The two layers of solutions were mixed together followed by the removal of all volatiles to give a yellow-orange solid. This solid was washed with hexanes and dried to give **6** (1.515 g, 79.0% yield). ^1H NMR (250.1 MHz, benzene- d_6 , 23 °C) δ 3.29 (s, 48 H, $\text{CH}_2\text{-O}$), 2.078 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.54 (m, 4 H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 0.71 (s, 36 H, SiMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (62.9 MHz, benzene- d_6 , 25 °C) δ 70.21 ($\text{CH}_2\text{-O}$, $^1J_{\text{C-H}} = 141.9$ Hz), 40.29 ($\text{CH}_2\text{CH}_2\text{CH}_2$, $^1J_{\text{C-H}} = 124.2$ Hz), 19.68 ($\text{CH}_2\text{CH}_2\text{CH}_2$, $^1J_{\text{C-H}} = 117.8$ Hz), 5.85 (SiMe_3 , $^1J_{\text{C-H}} = 117.0$ Hz). $^{29}\text{Si}\{^1\text{H}\}$ NMR (79.49 MHz, benzene- d_6 , 23 °C) δ -6.5 (Si-SiMe_3), -117.6 (Si-SiMe_3). Anal. Calcd. for $\text{C}_{39}\text{H}_{90}\text{O}_{12}\text{Si}_6\text{K}_2$: C, 46.61; H, 9.00. Found: C, 46.94; H, 9.09.

2.3.6 X-ray Crystal Structure Determinations of 2, 3 and 5

The crystal structure of **2** was determined on a Siemens R3m/V diffractometer equipped with a graphite-monochromated Mo Source ($K\alpha$ radiation, 0.71073 Å). The unit cell parameters and orientation matrix were determined from a least-square fit of 30 reflections obtained from a rotation photograph and an automatic peak search routine. The crystal structures of **3** and **5** were determined on a Bruker AXS Smart 1000 X-ray diffractometer equipped with a CCD area detector and a graphite-monochromated Mo Source ($K\alpha$ radiation, 0.71073 Å) and fitted with an upgraded Nicolet LT-2 low temperature device. The crystals of **2** and **3** were directly mounted at room temperature on the diffractometer. A suitable crystal of **5** was coated with paratone oil (Exxon) and mounted on a glass fiber under a stream of nitrogen at 173(2) K. The structures of **2**, **3**, and **5** were solved by direct methods. Non-hydrogen atoms were anisotropically refined. All hydrogen atoms for **2** were placed in calculated positions and introduced into refinement as fixed contributors with an isotropic U value of 0.08 Å². All H atoms in **3** and **5** were treated as idealized contributions. Global refinements for the unit cells and data reductions of the data sets for **3** and **5** were conducted with the Saint program. The SHELXTL (Version 5.1) proprietary software package was used for all structure solution and refinement calculations.^{82,83}

CHAPTER 3

Preparation of Transition Metal Complexes Containing

$[(\text{Me}_3\text{Si})_2\text{Si}-(\text{CH}_2)_n-\text{Si}(\text{SiMe}_3)_2]^{2-}$ Ligands

3.1 Introduction

During the past decade, the field of early-transition-metal silyl chemistry has experienced a period of rapid growth and proliferation, as applications of metal silyl complexes in areas such as hydrosilylation and polysilane synthesis have either been developed or expanded.^{16,84-104} Moreover, silyl and persilyl complexes free of stabilizing ligands, such as η^5 -cyclopentadienyl (Cp), alkoxides, or amides, may find applications as single-source precursors for the preparation of metal silicides (MSi_x), a class of solid-state materials widely used in the electronic, aerospace and machine-tool industries.¹⁰⁵⁻¹¹⁰ Use of single-source precursors would be advantageous over current methods which involve the use of a pyrophoric reagent (SiH_4) and/or elimination of corrosive HCl (Scheme 3.1). Most known silyl complexes contain monodentate silyl ($-\text{SiR}_3$) ligands.

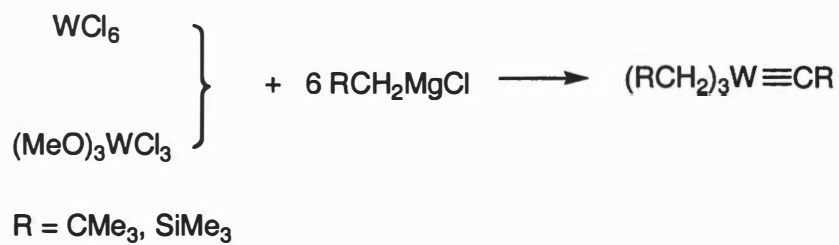
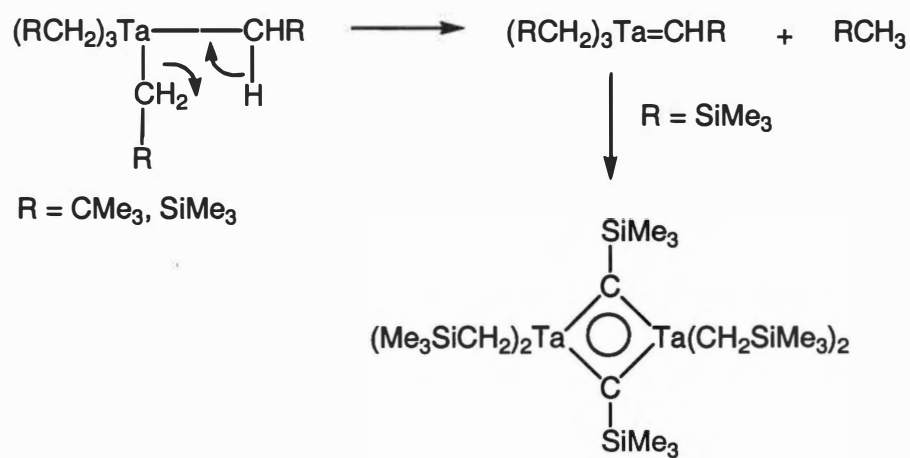
Early-transition-metal peralkyl complexes are known for $\text{M}(\text{CH}_2\text{R})_n$ ($n = 4$; $\text{M} = \text{Ti, Zr, Hf}$; $n = 5$, $\text{M} = \text{Ta}$; $n = 6$, $\text{M} = \text{W}$).¹¹¹⁻¹¹³ These peralkyl complexes have played a critical role in our understanding of M-C bonds and structures and reactivities of transition metal complexes. For example, a d^0 WMe_6 complex



Scheme 3.1 CVD routes to metal silicides from metal alkyls or halides

was recently reported to have a unique distorted trigonal prismatic structure with C_{3v} symmetry.^{114,115} The d^1 ReMe_6 complex showed a regular trigonal-prismatic symmetry.^{114,115} $\text{M}(\text{CH}_2\text{R})_4$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$; $\text{R} = \text{CMe}_3, \text{SiMe}_3$) are thermally stable at their sublimation temperatures (ca. 50 °C). Our earlier studies of $\text{Ta}(\text{CH}_2\text{R})_5$ ($\text{R} = \text{CMe}_3, \text{SiMe}_3$) showed that they were thermally unstable, and this thermal instability played a critical role in their conversion through α -H abstraction reactions to archetypical Schrock carbene complexes $(\text{RCH}_2)_3\text{Ta}=\text{CHR}$ and one of the first known carbyne complexes $(\text{Me}_3\text{SiCH}_2)_2\text{Ta}(\mu\text{-CSiMe}_3)_2\text{Ta}(\text{CH}_2\text{SiMe}_3)_2$ (Scheme 3.2).¹¹⁶ “ $\text{W}(\text{CH}_2\text{R})_6$ ” ($\text{R} = \text{CMe}_3, \text{SiMe}_3$) have not been observed, and the reactions of WCl_6 or $\text{WCl}_3(\text{OMe})_3$ with 6 equiv of RCH_2MgCl gave Schrock-type carbyne complexes $(\text{RCH}_2)_3\text{W}\equiv\text{CR}$.^{117,118}

Persilyl complexes $\text{M}(\text{SiR}_3)_n$, on the other hand, are much more difficult to prepare, and have been one of the major challenges in synthetic inorganic and organometallic chemistry. Previous attempts to prepare early-transition-metal



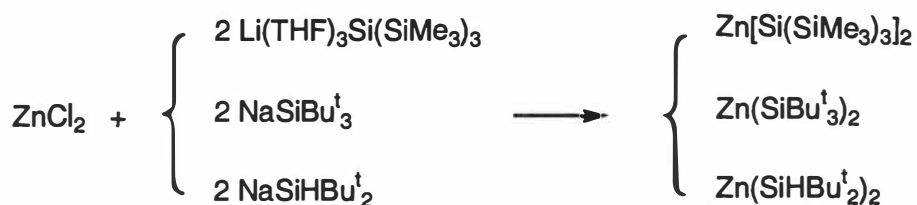
Scheme 3.2 Formation of metal carbenes and carbynes. Some formed unexpectedly in attempts to prepare peralkyl complexes.

polysilyl complexes by the reactions of MCl_n with n equivalents of silylating reagents have sometimes led to the formation of disilanes and reduced metal species (*vide infra*), presumably as the result of either reductive elimination from the metal center, or homolytic cleavage of the M-Si bonds to produce silyl radicals which combine to give disilanes. A report of $Ti(SiPh_3)_4$,¹¹⁹ prepared from $TiCl_4$ and $KSiPh_3$, was later refuted, and this compound was reformulated as $Ti(OSiPh_3)_4$.²⁵ It has also been reported to be difficult to prepare silyl complexes from the reactions of MCl_4 ($M = Zr, Hf$) and $TaCl_5$ with $Li(THF)_2SiHMe_2$.¹³

Late-transition-metal persilyl complexes such as $Zn(SiR_3)_2$ [$R_3 = Ph_3, (SiMe_3)_3; Bu^t_3; HBu^t_2$] (Scheme 3.3).¹²⁰⁻¹²³ and $M[Si(SiMe_3)_3]_2$ ($M = Cd, Hg$) have been reported. Base adducts such as $M[Si(SiMe_3)_3](bpy)$ ($M = Zn, Cd$) and $Zn(SiPh_3)_2(PMe_3)_2$,¹²⁴ have also been reported. However, it was found to be difficult to prepare silyl complexes from $FeCl_2$ and $Li(THF)_2SiHMe_2$.¹³

The zinc silyl complexes $Zn(SiR_3)_2$ have been prepared, in part, to study their reactivities as silylating reagents. Zinc alkyl complexes ZnR'_2 have often been used as alkylating reagents in organic and organometallic reactions, and the reactivities of these zinc complexes are usually milder than those of, e.g., lithium alkyls and Grignard reagents.¹²⁵

Whether zinc silyl derivatives are silylating reagents is of fundamental interest with potential applications in synthetic chemistry. Zn silyl complexes have been found to undergo transmetalation with alkali metals (M) to give



Scheme 3.3 Reported synthesis of Zn disilyl complexes

solvent-free MSiR_3 .¹²⁶

We recently reported the synthesis and characterization of the first Cp-free, d^0 , bis(silyl) complexes of zirconium and tantalum, $\text{Li(THF)}_4(\text{Me}_2\text{N})_3\text{Zr}(\text{SiPh}_2\text{Bu}^t)_2$ and $(\text{Me}_2\text{N})_3\text{Ta}[\text{Si}(\text{SiMe}_3)_3]_2$.⁴ These are among the few known complexes containing more than one silyl ligand. The silyl ligands in these two complexes are monodentate. Their syntheses were among the first steps to prepare early transition-metal persilyl complexes.

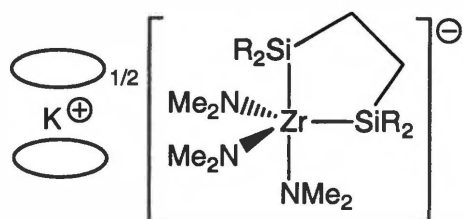
In the current work, bis(silyl)alkane compounds were chosen as potential ligand precursors that may chelate to a transition metal center. Such chelating ligands may serve to enhance the stability of the resulting metal complexes. Only a handful of such dianionic bis(silyl) ligand precursors have been previously reported, many of which contain an all silicon backbone. We chose to focus on ligands containing a hydrocarbon backbone to minimize the possibility of cleavage of the ligand backbone during reactions with transition metal halides.

The potassium salts prepared in Chapter 2, $[K(18\text{-crown-6})]_2[(\text{Me}_3\text{Si})_2\text{Si}(\text{CH}_2)_n\text{-Si}(\text{SiMe}_3)_2]$ ($n = 1, 4; 2, 5; 3, 6$), were thus chosen as possible disilyl ligands to prepare new metal silyl complexes. It was interesting to find that the reaction of $(\text{Me}_2\text{N})_3\text{Zr-Cl}$ with the silyl dianion salt **5** gave $K(18\text{-crown-6})_{3/2}[(\text{Me}_2\text{N})_3\text{Zr}[\eta^2\text{-(Me}_3\text{Si})_2\text{Si}(\text{CH}_2)_2\text{-Si}(\text{SiMe}_3)_2]]$ (**7**) containing a chelating bis(silyl) ligand. The reaction of 1.5 equiv of **5** with 1 equiv of anhydrous ZnCl_2 gave an unusual salt $[K(18\text{-crown-6})]_2[\eta^2\text{-(Me}_3\text{Si})_2\text{Si}(\text{CH}_2)_2\text{-Si}(\text{SiMe}_3)_2]_2\text{Zn}_2[\mu\text{-(Me}_3\text{Si})_2\text{Si}(\text{CH}_2)_2\text{-Si}(\text{SiMe}_3)_2]$ (**8**) containing Zn ions coordinated with three silicon atoms (Scheme 3.4). Our syntheses, characterization and structures of **7** and **8** are reported here. In addition, our unsuccessful attempts to prepare Zr and Hf persilyl complexes using these dianionic bis(silyl) ligand precursors are presented.

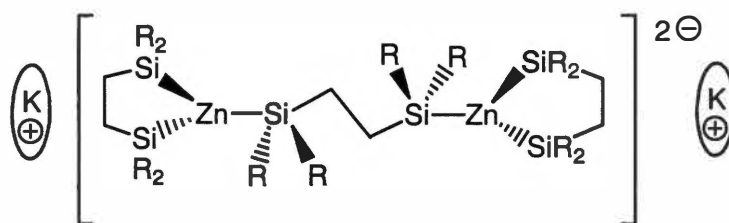
3.2 Results and Discussion

3.2.1 Attempted Synthesis of Persilyl Complexes from MCl_4

With the chelating silyl precursors $[K(18\text{-crown-6})]_2[(\text{Me}_3\text{Si})_2\text{Si}(\text{CH}_2)_n\text{-Si}(\text{SiMe}_3)_2]$ ($n = 1, 4; 2, 5; 3, 6$) discussed in Chapter 2, numerous efforts were made to prepare Zr or Hf persilyl metal complexes from reactions with MCl_4 ($\text{M} = \text{Zr, Hf}$). Unfortunately, our attempts failed to yield an identifiable M-Si bonded species (Scheme 3.5). These unsuccessful attempts are summarized in Table 3.1. All reagents denoted “X” were used in situ.



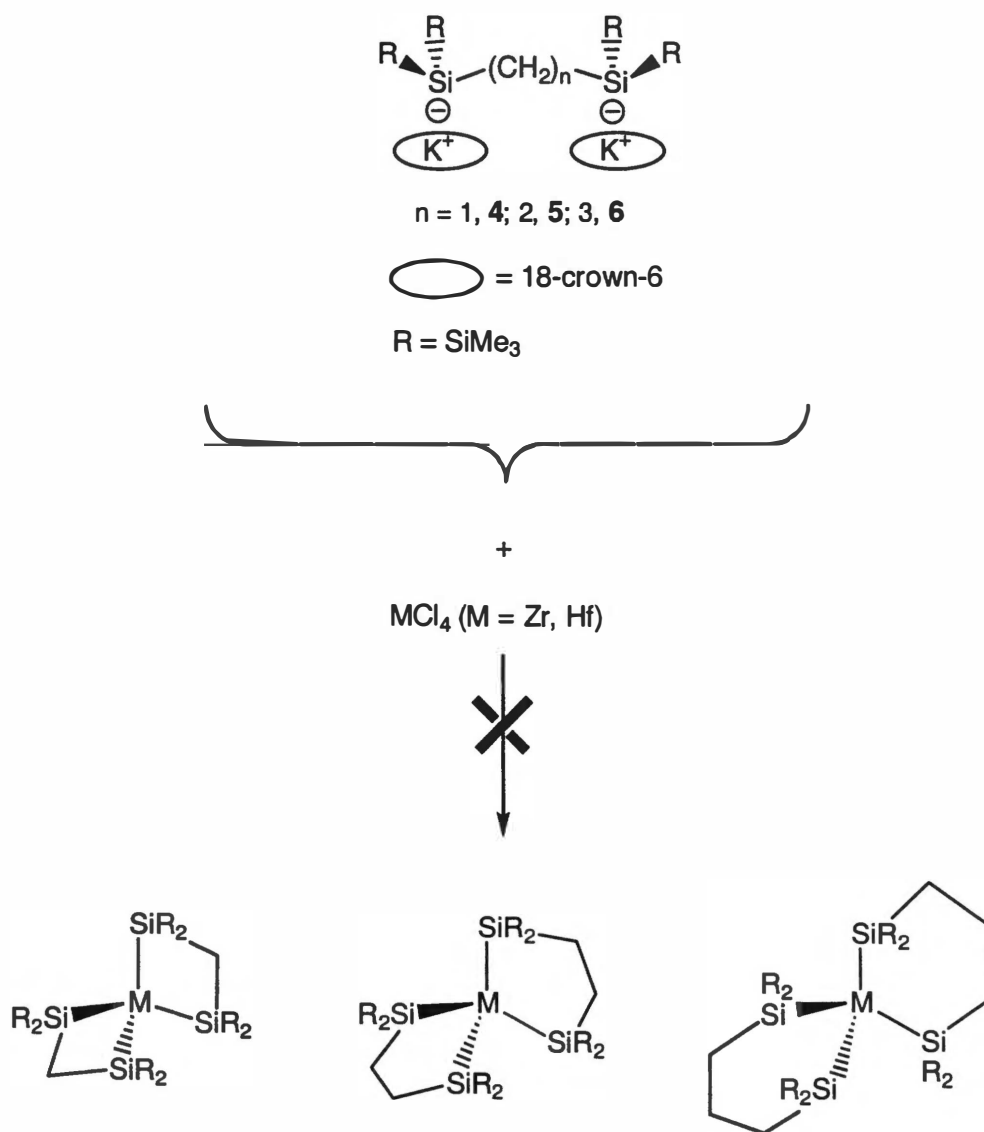
7



8

R = SiMe₃; ○ = 18-crown-6

Scheme 3.4 New transition metal (multi)silyl complexes prepared from
 $[K(18\text{-crown-}6)]_2[(\text{Me}_3\text{Si})_2\text{Si}-(\text{CH}_2)_2-\text{Si}(\text{SiMe}_3)_2]$



Scheme 3.5 Attempted preparation of persilyl Zr and Hf complexes

Table 3.1 Summary of Unsuccessful Attempts to Prepare Zr and Hf Persilyl Complexes

Reactants	Reaction Conditions	Outcome
HfCl ₄ + “[K(DME) ₃] ₂ [R ₂ Si-(CH ₂) ₂ -SiR ₂]” (R = SiMe ₃)	Solvent = DME; Silyl anion was added to HfCl ₄ at 0 °C. Reaction was stirred at 0 °C for 3 h. The solution was filtered, volatiles removed and residue redissolved in toluene.	Unidentified products
HfCl ₄ + 2	Both reagents added to same flask and toluene added. The reaction was heated to 70 °C and stirred overnight.	No reaction
HfCl ₄ + 5	Solvent = THF; HfCl ₄ added to solution of	No identifiable products

Table 3.1 (continued)

	the ligand at $-78\text{ }^{\circ}\text{C}$. Reaction was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h. It was then warmed to $23\text{ }^{\circ}\text{C}$ and stirred for 2 h. Volatiles were removed, and the residue was extracted with pentane.		
	$\text{ZrCl}_4 + \mathbf{2}$	Solvent = toluene; At $23\text{ }^{\circ}\text{C}$ 2 was added to ZrCl_4 and stirred for 22 h.	Little appreciable reaction observed by ^1H NMR
50	$\text{ZrCl}_4 +$ “ $[\text{K}(\text{diglyme})_2]_2[\text{R}_2\text{Si}-(\text{CH}_2)_3-\text{SiR}_2]$ ”	Solvent = diglyme; Silyl anion added to ZrCl_4 at $-20\text{ }^{\circ}\text{C}$. The mixture was gradually warmed to $23\text{ }^{\circ}\text{C}$ and stirred for 16 h. Volatiles were removed, and the residue was extracted with toluene.	Unidentified products

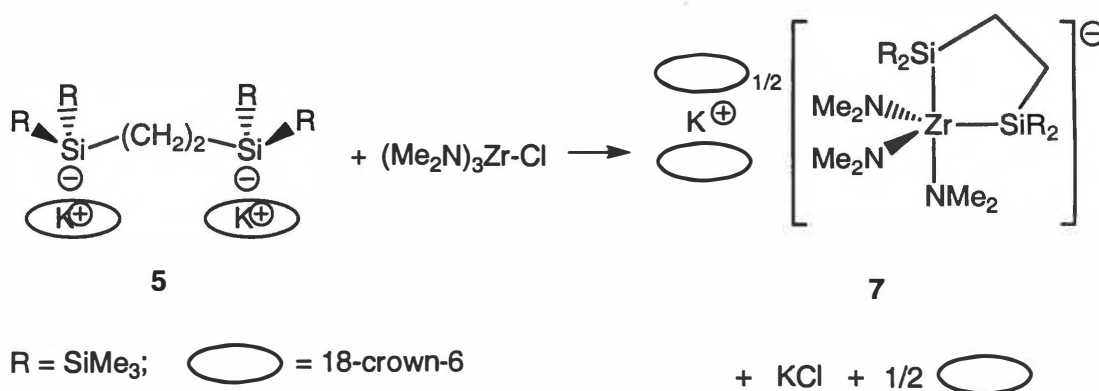
Table 3.1 (continued)

ZrCl ₄ + “[K(diglyme) ₂] ₂ [R ₂ Si-(CH ₂) ₃ -SiR ₂]”	Solvent = THF; ZrCl ₄ was added slowly, dropwise to the silyl anion at –35 °C. Reaction mixture was deep red by end of addition. The volatiles were immediately removed, and the oily residue was extracted with hexanes.	Unidentified products

Although we were not successful at synthesizing persilyl Zr and Hf complexes, we were able to prepare a Zr disilyl complex $K(18\text{-crown-6})_{3/2}\{(\text{Me}_2\text{N})_3\text{Zr}[\eta^2\text{-(Me}_3\text{Si)}_2\text{Si-(CH}_2)_2\text{-Si(SiMe}_3)_2]\}$ (**7**) and a Zn trisilyl complex $[K(18\text{-crown-6})]_2\{[\eta^2\text{-(Me}_3\text{Si)}_2\text{Si-(CH}_2)_2\text{-Si(SiMe}_3)_2]_2\text{Zn}_2[\mu\text{-(Me}_3\text{Si)}_2\text{Si-(CH}_2)_2\text{-Si(SiMe}_3)_2]\}$ (**8**) containing chelating disilyl ligands. These are the first disilyl and trisilyl complexes, respectively, of these chelating ligands, and provide valuable insights into the bonding of the ligands and structures of their complexes.

3.2.2 Preparation and Characterization of Zr Silyl Amide Complex $K(18\text{-crown-6})_{3/2}\{(\text{Me}_2\text{N})_3\text{Zr}[\eta^2\text{-(Me}_3\text{Si)}_2\text{Si-(CH}_2)_2\text{-Si(SiMe}_3)_2]\}$ (**7**)

The reaction of $(\text{Me}_2\text{N})_3\text{ZrCl}$ with $[K(18\text{-crown-6})]_2[(\text{Me}_3\text{Si)}_2\text{Si-(CH}_2)_2\text{-Si(SiMe}_3)_2]$ (**5**) in toluene was found to give **7** (Scheme 3.6).



Scheme 3.6 Preparation of Zr amide disilyl complex **7**

Large concentrations of both $(\text{Me}_2\text{N})_3\text{ZrCl}$ and **5** were found to be important to the success of the reaction. Solids of both reagents were mixed in one flask and dissolved in a small amount of toluene (5 mL) to start the reaction. The product, after washing with hexanes, was crystallized from toluene at -30°C to give crystals of **7**.

Four resonances were observed in the ^1H NMR spectrum of **7**. The $-\text{SiMe}_3$ resonance (0.67 ppm) of the disilyl ligand and $-\text{O}-\text{CH}_2$ resonances (3.32 ppm) of 18-crown-6, respectively, are only slightly shifted from those in the parent compound **5**. The $-\text{CH}_2-$ resonance in the $[(\text{Me}_3\text{Si})_2\text{Si}-(\text{CH}_2)_2-\text{Si}(\text{SiMe}_3)_2]^-$ ligand in **7** is 0.3 ppm downfield shifted from that of $[\text{K}(18\text{-crown-6})]_2[(\text{Me}_3\text{Si})_2\text{Si}-(\text{CH}_2)_2-\text{Si}(\text{SiMe}_3)_2]$ (**5**). Only one resonance attributed to the $-\text{NMe}_2$ ligands was observed at 296 K in the ^1H NMR spectrum of **7** at 250 MHz. However, in the ^1H NMR spectrum of **7** at 400 MHz, two nearly overlapping amide and $-\text{SiMe}_3$ peaks were found at 296 K. These peaks were slightly more separated at lower temperatures. The NMe_2 peak at 3.56 ppm in benzene- d_6 is downfield shifted from those in other silyl Zr amide complexes.^{4,7,41} Figure 3.1 shows the $-\text{NMe}_2$ region of the ^1H NMR spectrum of **7** at 400 MHz in toluene- d_8 at 293 K, 283 K and 258 K. Figure 3.2 shows the $-\text{SiMe}_3$ region of the ^1H spectrum at the same temperatures.

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **7** is also consistent with the structure assignment. As observed in the ^1H NMR spectrum, four resonances were observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **7**. In benzene- d_6 , the $-\text{SiMe}_3$

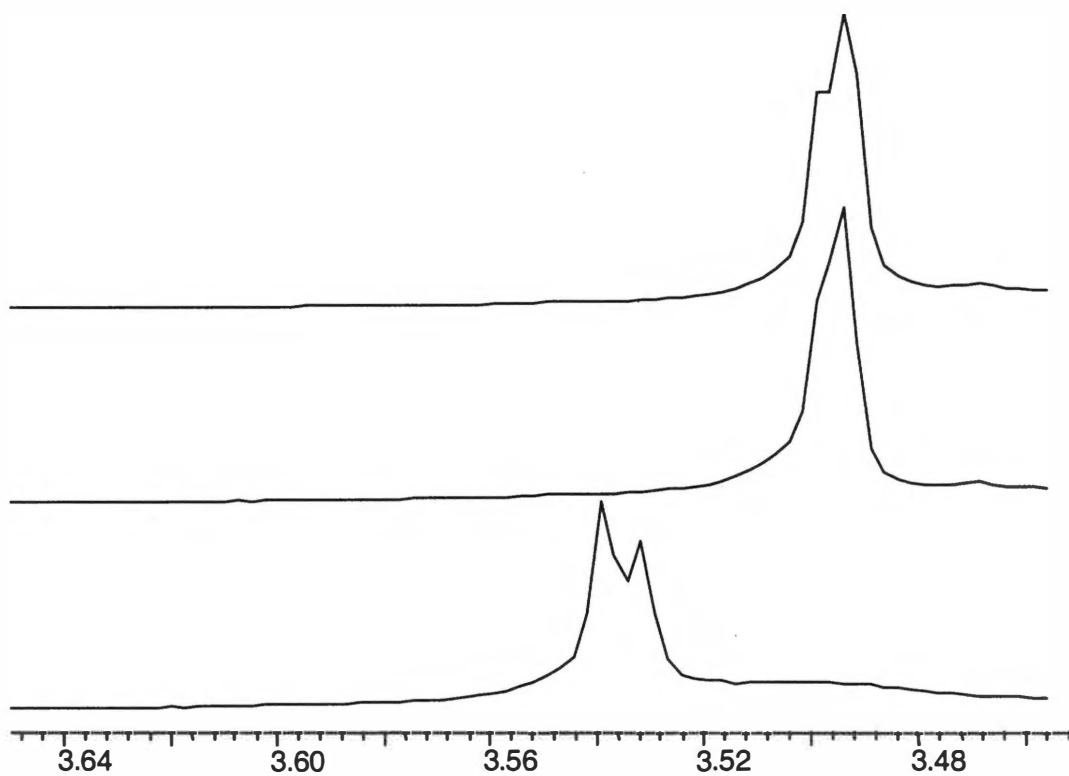


Figure 3.1 ^1H NMR (at 400 MHz) of the $-\text{NMe}_2$ region of **7** at
293 K(top), 283 K and 258 K (bottom)

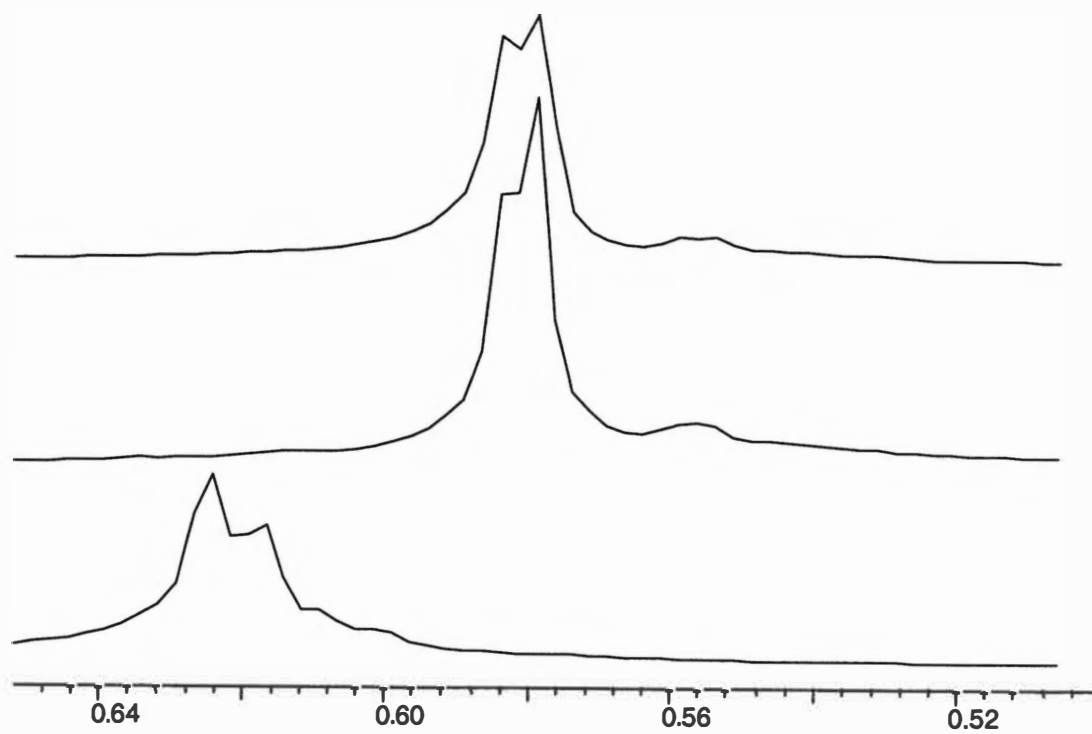


Figure 3.2 ^1H NMR (at 400 MHz) of the $-\text{SiMe}_3$ region of **7** at 293 K (top), 283 K and 258 K (bottom)

resonance at 4.48 ppm is significantly shifted from the parent dianion (5.74 ppm). One -NMe_2 peak was observed for **7** at 44.61 ppm at 296 K (Figure 3.3). At 258 K, two overlapping -NMe_2 peaks started to emerge (Figure 3.3). The $\text{-O-CH}_2\text{-}$ and $\text{-Si-CH}_2\text{-}$ resonances were found at 70.30 and 15.83 ppm, respectively, at 296 K.

In $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **7** at 296 K, two peaks were observed. One peak at -8.01 ppm was attributed to SiMe_3 atoms, and the other peak at -73.11 ppm was assigned to the Zr-Si-SiMe_3 atoms. The latter is consistent with those in other Zr-Si complexes such as $(\text{Me}_3\text{CCH}_2)_3\text{Zr-Si}(\text{SiMe}_3)_3$ (-85.5 ppm), $(\text{Me}_3\text{SiCH}_2)_3\text{Zr-Si}(\text{SiMe}_3)_3$ (-75.7 ppm)^{38,111} and $\text{Cp}_2\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$ (-85.5 ppm).¹²⁷ Table 3.2 lists key NMR data for **7** and some other related complexes.

3.2.3 X-ray Crystal structure of **7**

Single crystal X-ray diffraction studies of **7** revealed four independent Zr molecules in the unit cell. The crystal data for **7**, selected bond distances and bond angles in **7** are given in Tables 3.3-3.5. An ORTEP diagram of **7** is shown in Figure 3.4. Figure 3.5 gives the ORTEP of one $\{(\text{Me}_2\text{N})_3\text{Zr}[\eta^2\text{-(Me}_3\text{Si)}_2\text{Si-(CH}_2)_2\text{-Si(SiMe}_3)_2]\}^-$ anion. The ORTEPs of the $\text{K}^+(18\text{-crown-6})$ or $\text{K}^+(18\text{-crown-6})_2$ ions are shown in Figure 3.6. A packing diagram of **7** is given in Figure 3.7.

Each Zr center in **7** is five-coordinate (Figure 3.5) with one chelating bis(silyl)alkane ligand and three NMe_2 ligands. Unlike the trigonal bipyramidal

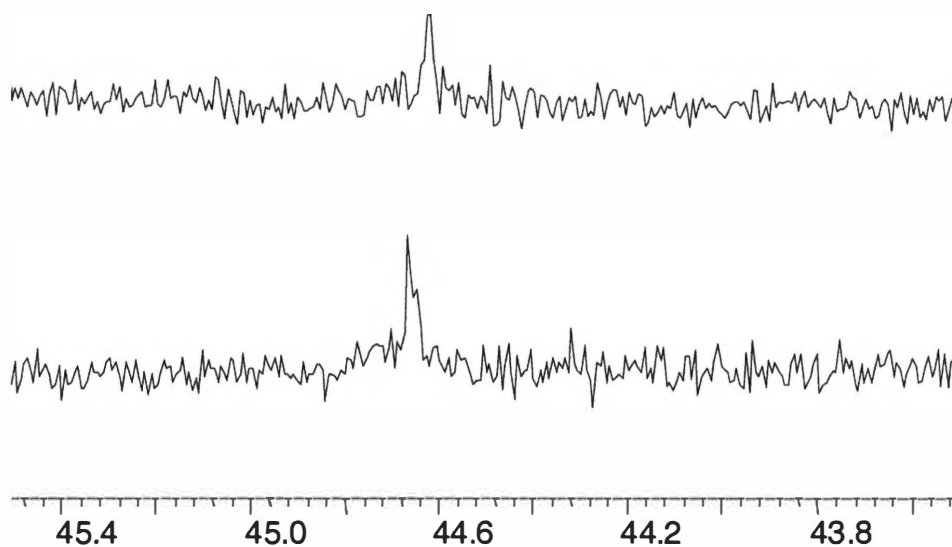


Figure 3.3 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the $-\text{NMe}_2$ region
of **7** at 296 K (top) and 258 K (bottom)

Table 3.2 Key NMR Data of **7** and Relevant Complexes at 23 °C

Complex	¹ H NMR	¹³ C{ ¹ H} NMR	²⁹ Si{ ¹ H} NMR
7	3.56 (NMe ₂)	44.64 (NMe ₂)	−8.0 (Si-SiMe ₃)
benzene- <i>d</i> ₆	1.63 (Si-CH ₂)	15.83 (Si-CH ₂)	−73.1 (Si-SiMe ₃)
	0.67 (SiMe ₃)	4.52 (SiMe ₃)	
(Me₂N)₃ZrSi(SiMe₃)₃	2.94 (NMe ₂)	40.2 (NMe ₂)	−4.4 (Si-SiMe ₃)
benzene- <i>d</i> ₆	0.39 (SiMe ₃)	5.1 (SiMe ₃)	−124.6 (Si-SiMe ₃)
[Li(THF)₄]⁺			
[(Me₂N)₃Zr(SiPh₂Bu^t)₂][−]	2.82 (NMe ₂)	40.6 (NMe ₂)	
benzene- <i>d</i> ₆	1.40 (SiCMe ₃)	31.3 (SiCMe ₃)	
		21.3 (SiCMe ₃)	

Table 3.3 Crystal Data for **7**

Empirical formula	$\text{C}_{360} \text{H}_{840} \text{K}_8 \text{N}_{24} \text{O}_{72} \text{Si}_{48} \text{Zr}_8$	
Formula weight	9049.44	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	$a = 13.077(3)$ Å	$\alpha = 101.06(3)^\circ$
	$b = 24.797(5)$ Å	$\beta = 92.00(3)^\circ$
	$c = 41.823(8)$ Å	$\gamma = 101.05(3)^\circ$
Volume	13028(5) Å ³	
<i>Z</i>	1	
Density (calculated)	1.153 g/cm ³	
Absorption coefficient	0.388 mm ⁻¹	
<i>F</i> (000)	4888	
Crystal size	0.45 × 0.40 × 0.20 mm ³	
θ range for data collection	1.07 to 27.05°	
Index ranges	$-16 \leq h \leq 16, -30 \leq k \leq 30, -52 \leq l \leq 52$	

Table 3.3 (continued)

Reflections collected	119093
Independent reflections	52829 [$R(\text{int}) = 0.1100$]
Completeness to $\theta = 27.05^\circ$	92.4%
Max. and min. transmission	0.9265 and 0.8448
Refinement method	Full-matrix-block least-squares on F^2
Data / restraints / parameters	52829 / 0 / 2419
Goodness-of-fit on F^2	0.991
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.1076$, $wR2 = 0.2790$
R indices (all data)	$R1 = 0.1912$, $wR2 = 0.3518$
Largest diff. peak and hole	2.538 and -1.098 e.Å ⁻³

$$R1 = \Sigma ||F_c| | / \Sigma |F_o|; wR2 = (\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [wF_o^2])^{1/2}$$

Table 3.4 Selected Bond Distances (Å) in **7**

Si(1)-Zr(1)	2.887(2)	Si(2)-Zr(1)	2.866(2)
N(1)-Zr(1)	2.078(8)	N(2)-Zr(1)	2.057(8)
N(3)-Zr(1)	2.076(8)		

Table 3.5 Selected Bond Angles (deg) in **7**

N(2)-Zr(1)-N(1)	98.8(3)	N(2)-Zr(1)-N(3)	110.6(3)
N(1)-Zr(1)-N(3)	97.6(3)	N(2)-Zr(1)-Si(2)	97.0(2)
N(3)-Zr(1)-Si(1)	122.6(2)	Si(2)-Zr(1)-Si(1)	69.42(7)
N(2)-Zr(1)-Si(1)	126.1(2)	N(1)-Zr(1)-Si(1)	83.4(2)
Si(5)-Si(2)-Zr(1)	116.73(11)	Si(6)-Si(2)-Zr(1)	114.32(11)
Si(4)-Si(1)-Zr(1)	118.09(11)	Si(3)-Si(1)-Zr(1)	117.11(10)

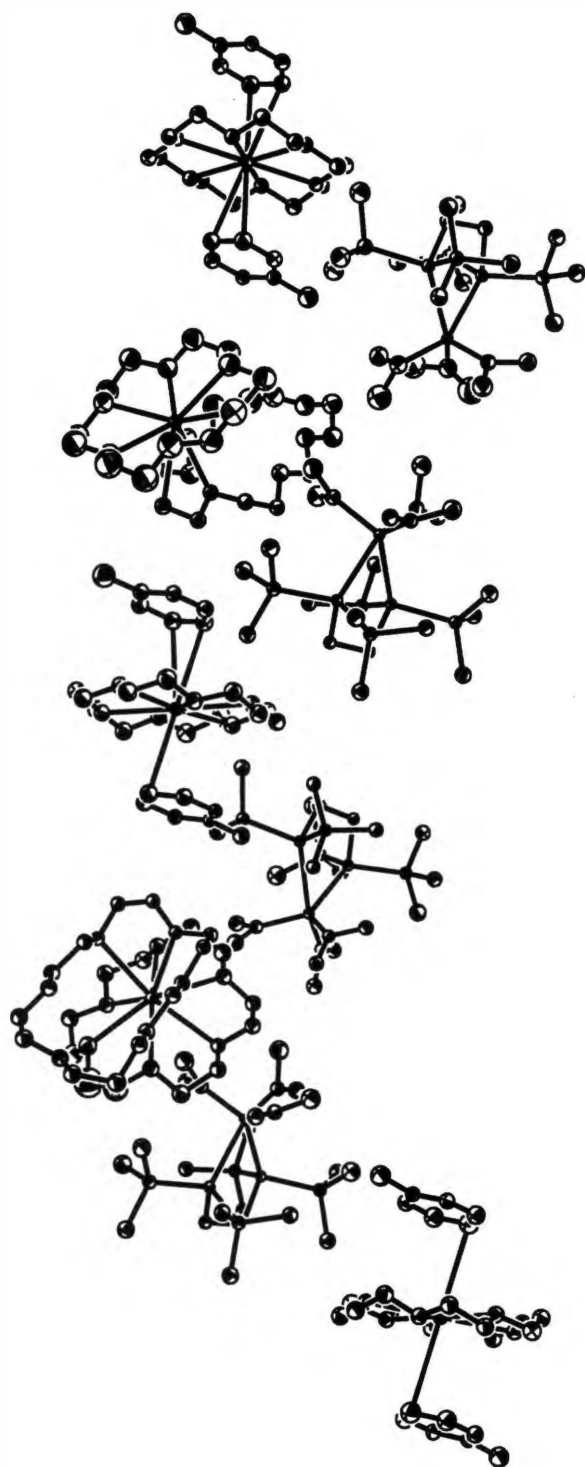


Figure 3.4 ORTEP diagram of **7** showing 30% probability thermal ellipsoids



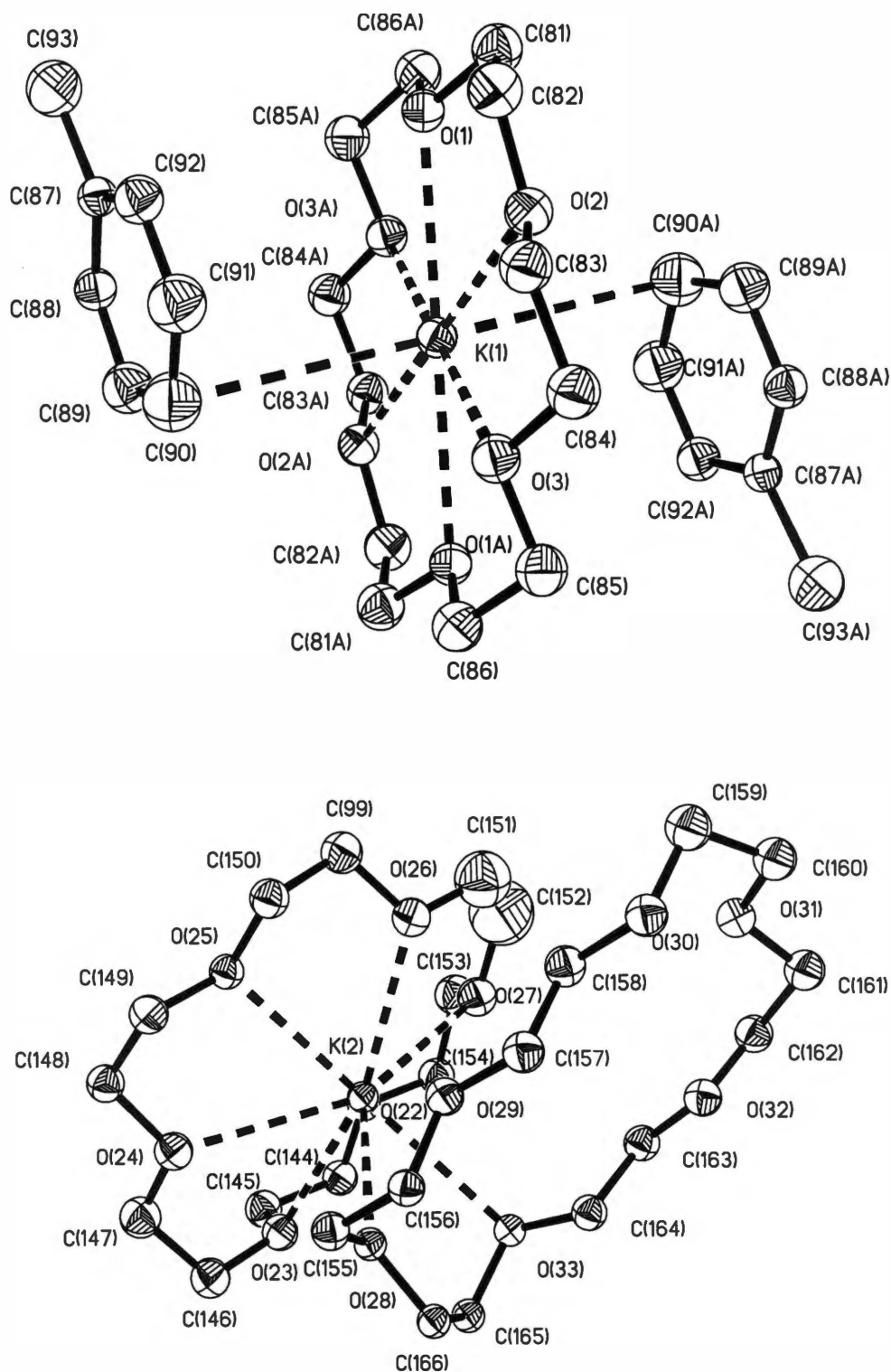


Figure 3.6 ORTEP diagram of cationic K(18-crown-6)^+ portions of 7

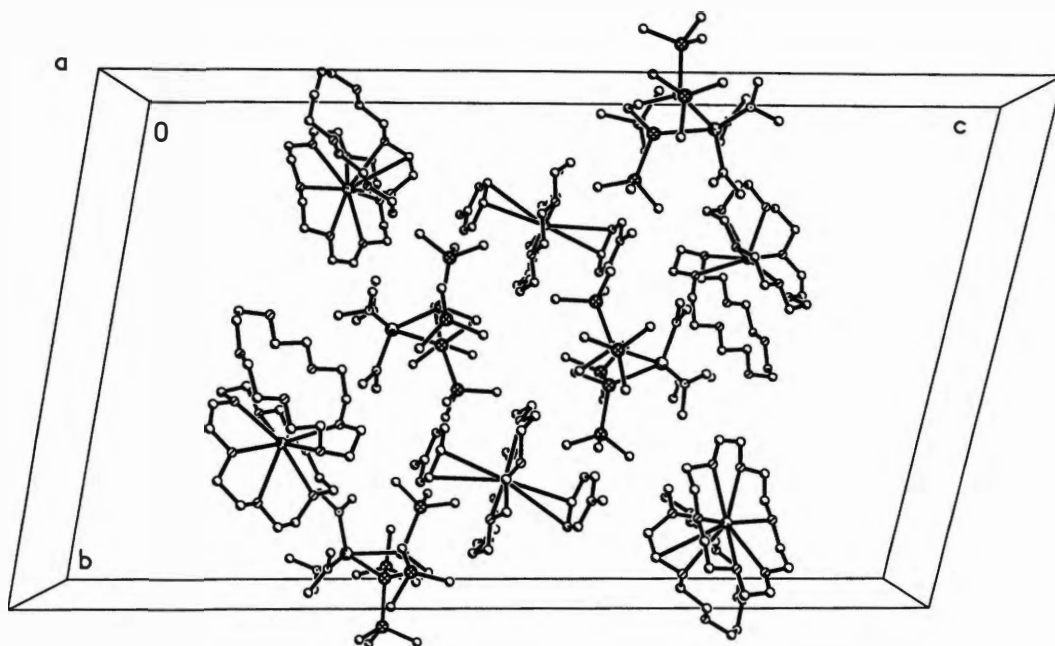
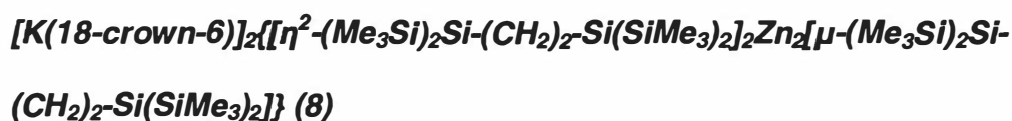


Figure 3.7 Packing diagram of **7**. View down the *a* axis

anion $[(\text{Me}_2\text{N})_3\text{Zr}(\text{SiPh}_2\text{Bu}^t)_2]^-$,⁴ the $\{(\text{Me}_2\text{N})_3\text{Zr}[\eta^2-(\text{Me}_3\text{Si})_2\text{Si}-(\text{CH}_2)_2-\text{Si}(\text{SiMe}_3)_2]\}^-$ anion in **7** is severely distorted from either trigonal bipyramidal or square pyramidal geometry. The Zr(1)-Si bond lengths [2.866(2)-2.887(2) Å] in **7** are in agreement with those in other Zr silyl complexes such as 2.9331(14) Å in $\text{Li}(\text{THF})_4(\text{Me}_2\text{N})_3\text{Zr}(\text{SiPh}_2\text{Bu}^t)_2$,⁴ 2.848(3) Å in $(\text{Me}_3\text{SiO})_3\text{Zr}(\text{SiPh}_2\text{Bu}^t)\text{Cl} \cdot 2\text{THF}$,³ 2.784(4) Å in $(\text{Me}_2\text{N})_3\text{ZrSi}(\text{SiMe}_3)_3$,⁴¹ and 2.803(2) Å in $(\text{Me}_2\text{N})_3\text{ZrSiPh}_2\text{Bu}^t$.⁴¹ The Zr(1)-N bond lengths [2.057(8)-2.078(8) Å] are also similar to 2.039(3)-2.063(5) Å in $\text{Li}(\text{THF})_4(\text{Me}_2\text{N})_3\text{Zr}(\text{SiPh}_2\text{Bu}^t)_2$,⁴ 2.018(7) Å in $(\text{Me}_2\text{N})_3\text{ZrSi}(\text{SiMe}_3)_3$,⁴¹ and 2.004(4)-2.034(4) Å in $(\text{Me}_2\text{N})_3\text{ZrSiPh}_2\text{Bu}^t$.⁴¹

There are two types of cations in **7**: $\text{K}^+(\text{18-crown-6})$ or $\text{K}^+(\text{18-crown-6})_2$. The K^+ ion in the former was coordinated to one 18-crown-6 molecule. There is also weak interaction between K^+ and two toluene molecules. In the latter, the two 18-crown-6 molecules use six and two O atoms, respectively, to bind to the K^+ ion.

3.2.4 Preparation and Characterization of the Trisilyl Zn Complex



The late-transition-metal Zn persilyl complex was prepared to offer insights into the synthesis, structure, and bonding of such a persilyl complexes containing a chelating ligand that we had prepared. In addition, Zn silyl complexes might be potential, milder silylating reagents. The first Zn silyl

complex was prepared in 1963¹²⁰ and several have been prepared since (Scheme 3.3). However, these complexes contained a linear Si-Zn-Si geometry and only one or two silyl ligands were attached to the Zn centers.¹²¹⁻¹²³

A slow addition of a freshly prepared solution of [K(18-crown-6)]₂ [(Me₃Si)₂Si-(CH₂)₂-Si(SiMe₃)₂] (5) (1.5 equiv) in mixed DME and toluene to a slurry of ZnCl₂ in Et₂O afforded an orange oil of 8 (Scheme 3.7). Washing of the oil with pentane gave a yellow solid of 8. In toluene, the solid turned into an oil, and cooling of the solution containing the oil at -30 °C gave crystals of the new Zn trisilyl complex [K(18-crown-6)]₂[[η²-(Me₃Si)₂Si-(CH₂)₂-Si(SiMe₃)₂]₂Zn₂[μ-(Me₃Si)₂Si-(CH₂)₂-Si(SiMe₃)₂]] (8) containing toluene solvent.

This compound was found to be insoluble in benzene-*d*₆ and only sparingly soluble in toluene-*d*₈. 8 was however found soluble in THF-*d*₈, in which the ¹H, ¹³C and ²⁹Si NMR spectra of 8 at 23 °C were taken. These NMR spectra agree with the structure shown in Scheme 3.7. As expected, two sets of ligand peaks were observed in the ¹H, ¹³C{¹H} and ²⁹Si{¹H} NMR spectra, one for the chelating ligand and the other for the bridging ligand (Table 3.6). Except for the ¹³C NMR resonance of the -SiMe₃ group in the bridging silyl ligand (4.52 ppm for Si-CH₃), the -SiMe₃ NMR resonances (¹H, ¹³C and ²⁹Si) of the terminal silyl ligands (0.03 ppm for Si-CH₃, 3.77 ppm for Si-CH₃ and -9.95 ppm for Si-SiMe₃) and bridging silyl ligands (0.18 ppm for Si-CH₃ and -11.15 ppm for Si-SiMe₃) in 8 are upfield-shifted from those in Zn[Si(SiMe₃)₃]₂ (0.35 ppm for Si-CH₃, 4.54 ppm for Si-CH₃ and -7.18 ppm for Si-SiMe₃) and Zn[Si(SiMe₃)₃]₂(bpy)

Table 3.6 Key NMR Data of **8** and Relevant Complexes at 23 °C

	¹ H	¹³ C	²⁹ Si
8	1.26 (CH ₂ -bridging)	14.63 (CH ₂ -bridging)	−9.95 (Si-SMe ₃ -terminal)
THF- <i>d</i> ₈	1.13 (CH ₂ -terminal)	12.17 (CH ₂ -terminal)	−11.15 (Si-SMe ₃ -bridging)
	0.18 (SiMe ₃ -bridging)	4.52 (SiMe ₃ -bridging)	−85.15 (Si-SiMe ₃ -bridging)
	0.03 (SiMe ₃ -terminal)	3.77 (SiMe ₃ -terminal)	−87.27 (Si-SiMe ₃ -terminal)
Zn[Si(SiMe₃)₃]₂ ¹²¹	0.35 (SiMe ₃)	4.54 (SiMe ₃)	−7.18 (Si-SMe ₃)
 benzene- <i>d</i> ₆			−123.9 (Si-SiMe ₃)
Zn[Si(SiMe₃)₃]₂(bpy) ¹²¹	0.27 (SiMe ₃)	5.11 (SiMe ₃)	−6.60 (Si-SMe ₃)
benzene- <i>d</i> ₆			−150.8 (Si-SiMe ₃)
5	0.64 (SiMe ₃)	5.74 (SiMe ₃)	−6.8 (Si-SMe ₃)
benzene- <i>d</i> ₆			−111.8 (Si-SiMe ₃)

(bpy = 2,2'-bipyridine; 0.27 ppm for Si-CH₃, 5.11 ppm for Si-CH₃ and -6.60 ppm for Si-SiMe₃) (Table 3.6).¹²¹ These upfield-shifted NMR resonances are consistent with the fact that $\{[\eta^2-(\text{Me}_3\text{Si})_2\text{Si}-(\text{CH}_2)_2-\text{Si}(\text{SiMe}_3)_2]_2\text{Zn}_2[\mu-(\text{Me}_3\text{Si})_2\text{Si}-(\text{CH}_2)_2-\text{Si}(\text{SiMe}_3)_2]\}^{2-}$ is a dianion. The two electrons in the anion are expected to provide more shielding than those in neutral complexes Zn[Si(SiMe₃)₃]₂ and Zn[Si(SiMe₃)₃]₂(bpy). It should be noted that the NMR spectra of **8** were taken in THF-*d*₈ solutions, while those of Zn[Si(SiMe₃)₃]₂, Zn[Si(SiMe₃)₃]₂(bpy) and **5** were obtained from their benzene-*d*₆ solutions.

Both **8** and [K(18-crown-6)]₂[(Me₃Si)₂Si-(CH₂)₂-Si(SiMe₃)₂] (**5**) are dianionic complexes. The X-ray structure of **5** (Figure 2.5) showed that the anionic Si(2)⁻ and Si(2A)⁻ atoms have direct interactions with the K⁺ cations surrounded by 18-crown-6 molecules. The X-ray structure of [K(18-crown-6)]₂{[η²-(Me₃Si)₂Si-(CH₂)₂-Si(SiMe₃)₂]₂Zn₂[μ-(Me₃Si)₂Si-(CH₂)₂-Si(SiMe₃)₂]} (**8**), to be discussed below, showed that, in comparison, the anionic centers Zn(Si-)₃⁻ in **8** are crowded with the terminal as well as the bridging disilyl ligands. Probably because of this steric crowding, the K(18-crown-6)⁺ cations in **8** stay on the two sides of the anions forming two charge-separated ions. The Zn trisilyl anion in **8** is thus expected to carry more negative charge than [(Me₃Si)₂Si-(CH₂)₂-Si(SiMe₃)₂]⁻ in **5**. The -SiMe₃ resonances of the terminal silyl ligands (0.03 ppm for Si-CH₃, 3.77 ppm for Si-CH₃ and -9.95 ppm for Si-SiMe₃) and bridging silyl ligands (0.18 ppm for Si-CH₃ and -11.15 ppm for Si-SiMe₃) in **8** are upfield-shifted from those in **5** (0.64 ppm for Si-CH₃, 5.74 ppm for Si-CH₃ and -6.8 ppm

for Si-SMe₃). These upfield shifts in NMR are consistent the structural differences between **8** and **5**. Only one 18-crown-6 resonance and one toluene resonance were observed in the ¹H and ¹³C NMR spectra of **8**.

3.2.5 X-ray Crystal Structure of **8**

The Zn trisilyl complex **8** was studied by X-ray crystallography. Crystallographic data for **8**, selected bond distances, and selected angles are given in Tables 3.7, 3.8 and 3.9, respectively. ORTEP diagrams of **8** and the anionic portion of **8**, and a packing diagram of **8** are given in Figures 3.8, 3.9 and 3.10, respectively. The X-ray structure showed two three-coordinate Zn centers bridged by a disilyl ligand. Each Zn atom has one terminal, chelating disilyl ligand and one bridging disilyl ligand linking it to another Zn metal center. Two 18-crown-6 molecules encapsulating K⁺ cations flank each side of the dimer to balance the charge of the complex. Two toluene molecules are also found in the crystal structure. The Zn(1)-Si bond lengths in **8** are in agreement with those in other zinc silyl complexes such as Zn[Si(SiMe₃)₃]₂ [2.342(4) Å],¹²¹ Zn(Si^tBu₃)₂ [2.384(1) Å], ^tBu₃SiZnBr [2.377(2) Å],¹²² and Zn[SiH(Si^tBu₃)₂]₂ [2.449(2) Å].¹²³ The lengths of the Zn-Si bonds for the chelating ligand [2.4368(8) Å and 2.4153(10) Å] are slightly longer than the Zn-Si bond length of the bridging ligand [2.4076(8) Å]. The geometry around each Zn center is Y-shaped with two widened angles [Si(3)-Zn-Si(2) = 138.45(3); Si(3)-Zn-Si(2) = 133.72(3)] and one narrow angle [Si(2)-Zn-Si(1) = 118.39(6)].

Table 3.7 Crystal Data for **8**

Empirical formula	$\text{C}_{80} \text{H}_{184} \text{K}_2 \text{O}_{12} \text{Si}_{18} \text{Zn}_2$	
Formula weight	2052.84	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 12.603(2)$ Å	$\alpha = 60.196(3)^\circ$
	$b = 16.901(3)$ Å	$\beta = 75.945(3)^\circ$
	$c = 16.917(3)$ Å	$\gamma = 78.761(3)^\circ$
Volume	3021.3(9) Å ³	
Z	1	
Density (calculated)	1.128 g/cm ³	
Absorption coefficient	0.689 mm ⁻¹	
$F(000)$	1110	
Crystal size	0.40 × 0.40 × 0.30 mm ³	
θ range for data collection	1.39 to 28.27°	
Index ranges	$-16 \leq h \leq 16, -22 \leq k \leq 22, -21 \leq l \leq 22$	
Reflections collected	32547	
Independent reflections	14040 [$R(\text{int}) = 0.0385$]	

Table 3.7 (continued)

Completeness to $\theta = 28.27^\circ$	93.6%
Max. and min. transmission	0.8199 and 0.7701
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14040 / 0 / 552
Goodness-of-fit on F^2	1.014
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0466$, $wR2 = 0.1059$
R indices (all data)	$R1 = 0.0779$, $wR2 = 0.1223$
Largest diff. peak and hole	0.917 and -0.952 e.Å ⁻³

$$R1 = \Sigma ||F_c|| / \Sigma |F_o|; wR2 = (\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [wF_o^2])^{1/2}$$

Table 3.8 Selected Bond Distances (Å) in **8**

Si(1)-Zn(1)	2.4368(8)	Si(2)-Zn(1)	2.4153(10)
Si(3)-Zn(1)	2.4076(8)	C(1)-C(2)	1.513(10)
C(1)-Si(1)	1.981(5)	C(2)-Si(2)	2.004(6)
C(3)-C(3A)	1.536(5)	C(3)-Si(3)	1.923(3)
C(1A)-Si(1)	2.008(5)	C(1A)-C(2A)	1.548(11)
Si(1)-Si(4)	2.3338(16)		

Table 3.9 Selected Bond Angles (deg) in **8**

Si(2)-Zn(1)-Si(1)	87.63(3)	Si(3)-Zn(1)-Si(1)	138.45(3)
Si(3)-Zn(1)-Si(2)	133.72(3)	Si(5)-Si(1)-Zn(1)	123.26(5)
Si(4)-Si(1)-Zn(1)	115.79(5)	C(1)-Si(1)-Zn(1)	102.97(15)
C(1A)-Si(1)-Zn(1)	100.62(16)	C(2A)-Si(2)-Zn(1)	104.86(19)
C(2)-Si(2)-Zn(1)	103.92(17)	Si(7)-Si(2)-Zn(1)	118.39(6)
Si(6)-Si(2)-Zn(1)	108.96(5)	C(3)-Si(3)-Zn(1)	114.83(8)
C(2)-C(1)-Si(1)	109.5(5)	C(1)-C(2)-Si(2)	108.7(5)
C(3A)-C(3)-Si(3)	117.7(2)	C(2A)-C(1A)-Si(1)	109.4(5)

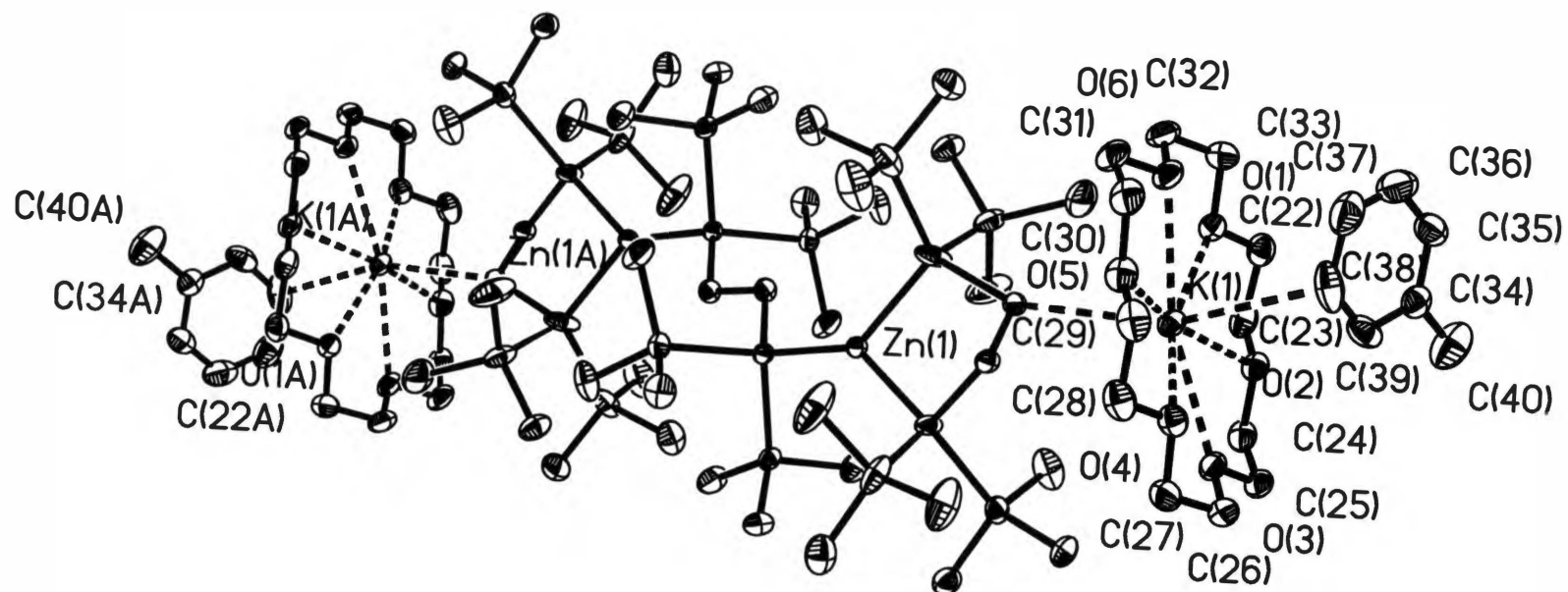


Figure 3.8 ORTEP diagram of 8 showing 30% ellipsoids

Figure 3.9 ORTEP diagram of the Zn dianion in **8** showing 30% ellipsoids

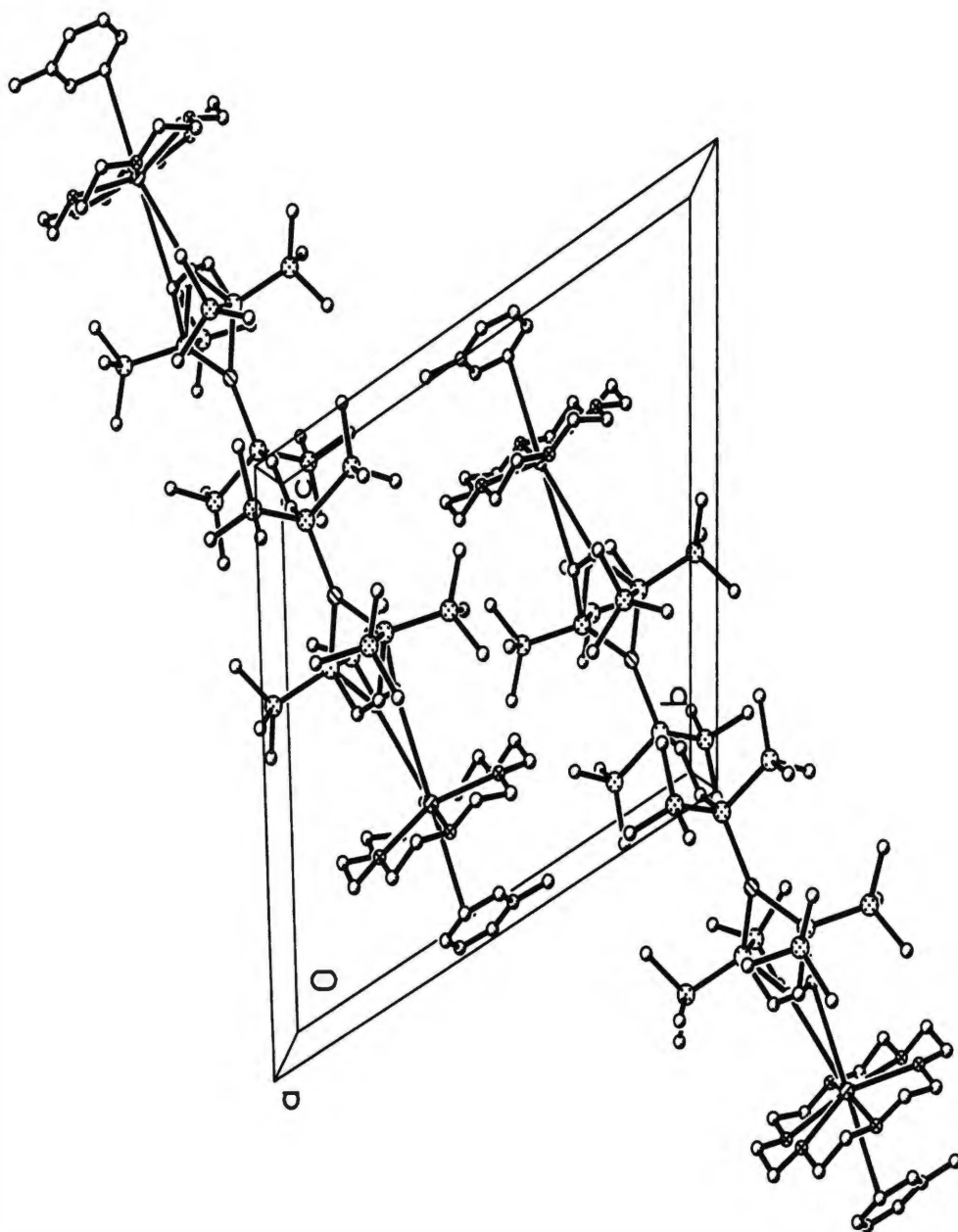


Figure 3.10 Packing diagram in **8**. View down the *a* axis

In summary, two new complexes containing chelating disilyl ligands have been prepared and characterized. $\text{K(18-crown-6)}_{3/2}\{(\text{Me}_2\text{N})_3\text{Zr}[\eta^2\text{-(Me}_3\text{Si)}_2\text{Si-(CH}_2)_2\text{-Si(SiMe}_3)_2]\}$ (**7**) is one of the few known Cp-free, d^0 early transition metal complexes containing two M-Si bonds. The Zn persilyl complex $[\text{K(18-crown-6)}]_2\{[\eta^2\text{-(Me}_3\text{Si)}_2\text{Si-(CH}_2)_2\text{-Si(SiMe}_3)_2]_2\text{Zn}_2[\mu\text{-(Me}_3\text{Si)}_2\text{Si-(CH}_2)_2\text{-Si(SiMe}_3)_2]\}$ (**8**) is, to our knowledge, the first trisilyl Zn complex.

3.3 Experimental Section

3.3.1 General Procedures

All manipulations were performed under a dry nitrogen or argon atmosphere with the use of either a glovebox or standard Schlenk techniques. NMR solvents were dried and stored over 5 Å molecular sieves. ZrCl_4 and HfCl_4 (Strem) were sublimed before use. $(\text{Me}_2\text{N})_3\text{ZrCl}$ was prepared by the literature procedure.¹²⁸ ZnCl_2 (Mallinckrodt, Analytical reagent) was purified by refluxing in SOCl_2 . SOCl_2 was then removed under vacuum at 10^{-3} torr. $[\text{K(18-crown-6)}]_2[(\text{Me}_3\text{Si)}_2\text{Si-(CH}_2)_n\text{-Si(SiMe}_3)_2]$ ($n = 1, 4; 2, 5; 3, 6$) were prepared by the method discussed in Chapter 2.⁷¹ Dimethoxyethane (Fisher, Certified), toluene (Fisher, Certified ACS), pentane (Fisher, Reagent grade) and Et_2O (Fisher, Certified ACS) were purified by distillation from potassium benzophenone ketyl. A glass-coated stir bar was used in all reactions involving **4-6**. NMR spectra were recorded on either a Bruker AC-250 or an AMX-400 Fourier transform spectrometer. ^1H and ^{13}C NMR spectra

were referenced to solvents (residual protons in the ^1H spectra). ^{29}Si chemical shifts were referenced to SiMe_4 . Elemental analyses were carried out by Complete Analysis Laboratory, Inc., Parsippany, New Jersey.

3.3.2 *Attempted Preparation of Persilyl Group IV Complexes*

In a general preparation attempt, MCl_4 ($\text{M} = \text{Zr}, \text{Hf}$) was dissolved in a polar solvent such as THF or diglyme and the resulting solution cooled to low temperatures. The ligand, usually either 5, 6 or analogs of 5 or 6 containing DME or diglyme rather than 18-crown-6, was dissolved in the same solvent as the metal chloride. Typically, the silyl anion solution was added slowly, dropwise to the MCl_4 solution. After stirring, all volatiles were removed and the resulting residue redissolved in a less polar solvent (toluene or hexanes), concentrated and placed in a freezer for crystallization.

3.3.3 *Preparation of the Zr Silyl Amide Complex $\text{K}(18\text{-crown-6})_{3/2}$*



$(\text{Me}_2\text{N})_3\text{ZrCl}$ (0.2027 g, 0.6872 mmol) and 5 (0.6746 g, 0.6857 mmol) were added to one Schlenk flask and then dissolved in 5 mL of toluene. After 45 min of stirring, all volatiles were removed in vacuo. The resulting mixture of a yellow-orange solid and oil were washed with hexanes to give a bright yellow solid. This yellow powder was dissolved in toluene. An oil formed at the bottom of the flask. The flask containing the oil and the toluene solution was kept in a freezer at $-30\text{ }^\circ\text{C}$

for two weeks to give crystals of **7** (0.5919 g, 83.3% yield). ^1H NMR (250.1 MHz, benzene- d_6 , 23 °C) δ 3.56 (s, 18H, NMe_2), 3.32 (s, 36H, O-CH_2), 1.63 (s, 4H, Si-CH_2), 0.67 (s, 36H, SiMe_3); ^1H NMR (250.1 MHz, toluene- d_8 , 23 °C) δ 3.50 (s, 18H, NMe_2), 3.35 (s, 36H, O-CH_2), 1.56 (s, 4H, Si-CH_2), 0.59 (s, 36H, SiMe_3); ^1H NMR (400.1 MHz, THF- d_8 , 23 °C) δ 3.63 (s, 36H, O-CH_2), 2.99 (s, 18H, NMe_2), 1.07 (s, 4H, Si-CH_2), 0.51 (s, 36H, SiMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (62.9 MHz, benzene- d_6 , 23 °C) δ 70.30 (O-CH_2), 44.64 (NMe_2), 15.83 (Si-CH_2), 4.52 (SiMe_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (62.9 MHz, toluene- d_8 , 23 °C) δ 70.71 (O-CH_2), 44.60 (NMe_2), 15.82 (Si-CH_2), 4.43 (SiMe_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.62 MHz, THF- d_8 , 23 °C) δ 71.20 (O-CH_2), 44.50 (NMe_2), 15.61 (Si-CH_2), 4.12 (SiMe_3). $^{29}\text{Si}\{^1\text{H}\}$ NMR (79.48 MHz, THF- d_8 , 23 °C) δ -8.01 (SiMe_3), -73.11 (Si-SiMe_3). Anal. Calcd. for $\text{C}_{38}\text{H}_{94}\text{KN}_3\text{O}_9\text{Si}_6\text{Zr}$: C, 44.06; H, 9.15. Found: C, 43.89; H, 9.08.

3.3.4 Preparation of the Zn Complex $[\text{K}(18\text{-crown-6})]_2\{[\eta^2(\text{Me}_3\text{Si})_2\text{Si}(\text{CH}_2)_2\text{-Si}(\text{SiMe}_3)_2]_2\text{Zn}[\mu\text{-(Me}_3\text{Si)}_2\text{Si}(\text{CH}_2)_2\text{-Si}(\text{SiMe}_3)_2]\}$ (**8**)

Degassed $(\text{Me}_3\text{Si})_3\text{Si}(\text{CH}_2)_2\text{-Si}(\text{SiMe}_3)_3$ (**2**) (0.5168 g, 0.9874 mmol), *t*-BuOK (0.2218 g, 1.977 mmol) and 18-crown-6 (0.5221 g, 1.975 mmol) were added to a Schlenk flask. This mixture of solids was then dissolved in DME and toluene (a 50/50 volume mixture) and stirred for 15 min to give $\text{K}(18\text{-crown-6})]_2[(\text{Me}_3\text{Si})_2\text{Si}(\text{CH}_2)_2\text{-Si}(\text{SiMe}_3)_2]$ (**5**).

This ligand solution was added dropwise to ZnCl_2 (0.0910 g, 0.6677 mmol) suspended in Et_2O at room temperature. The mixture was stirred for 17 h, then

the solution was filtered. Removal of volatiles from the filtrate yielded an orange oil which, after washing with two 10 mL portions of pentane, turned to a yellow solid. The solid was dissolved in toluene and the resulting mixture of an oil and solution were placed in a freezer at $-20\text{ }^{\circ}\text{C}$ for crystallization. The supernatant was filtered and solid was washed with toluene to give 0.3585 g of crystalline **8**·(toluene)₂ (53.1% yield). ¹H NMR (250.1 MHz, THF-*d*₈, 23 °C) δ 3.61 (s, 48H, O-CH₂), 1.26 (s, 4H, CH₂-bridging), 1.13 (s, 8H, CH₂-chelating), 0.18 (s, 36H, SiMe₃-bridging), 0.03 (s, 72H, SiMe₃-chelating). ¹³C{¹H} NMR (62.9 MHz, THF-*d*₈, 23 °C) δ 71.27 (O-CH₂), 14.63 (CH₂-bridging), 12.17 (CH₂-chelating), 4.52 (SiMe₃-bridging), 3.77 (SiMe₃-chelating). ²⁹Si{¹H} NMR (79.49 MHz, THF-*d*₈, 23 °C) δ -9.95 (SiMe₃-chelating), -11.15 (SiMe₃-bridging), -85.15 (Si-SiMe₃-bridging), -87.27 (Si-SiMe₃-chelating). Anal. Calcd. for C₈₀H₁₈₄K₂O₁₂Si₁₈Zn₂ [**8**·(toluene)₂]: C 46.81; H 9.03. Found: C 46.97; H 9.10.

3.3.5 X-ray Crystal Structure Determinations of **7** and **8**

The crystal structures of **7** and **8** were determined on a Bruker AXS Smart 1000 X-ray diffractometer equipped with a CCD area detector and a graphite-monochromated Mo Source (K α radiation, 0.71073 Å) and fitted with an upgraded Nicolet LT-2 low temperature device. A suitable crystal of **7** or **8** was coated with paratone oil (Exxon) and mounted on a glass fiber under a stream of nitrogen at 173(2) K.

There were four large .raw files (about 0.80 Mb each) generated by the

SAINT (Bruker, 2000) program for **7**, and they were found to be too large to be processed by the earlier version of SADABS. The .hkl file (3.4 Mb) was thus converged by the latest version of SADABS (version 2.07, Bruker, 2003; <http://shelx.uni-ac.gwdg.de/axs/>). The structure of **7** was solved by direct methods. In SHELXTL, the normal L.S. 4 procedure was performed to refine non-hydrogen atoms isotropically. The L.S. 4 procedure could not be used in the anisotropic refinement because of the large size of the cell. The CGLS procedure is much faster and more suitable in most macromolecule refinements.^{82,83} Hence the CGLS and, subsequently, the L.S./BLOC procedures were used in the next, anisotropic refinement. The CGLS procedure does not provide estimated standard deviations (esd), therefore, in the final refinement, L.S. 1 and BLOC 1 procedures were used to obtain estimated standard deviations of bond lengths and bond angles in **7**.

The structure of **8** was solved by direct methods. Non-hydrogen atoms were anisotropically refined. All H atoms in **8** were treated as idealized contributions. Global refinements for the unit cells and data reductions of the data sets for **8** were conducted with the Saint program. The SHELXTL (Version 5.1) proprietary software package was used for all structure solution and refinement calculations.

CHAPTER 4

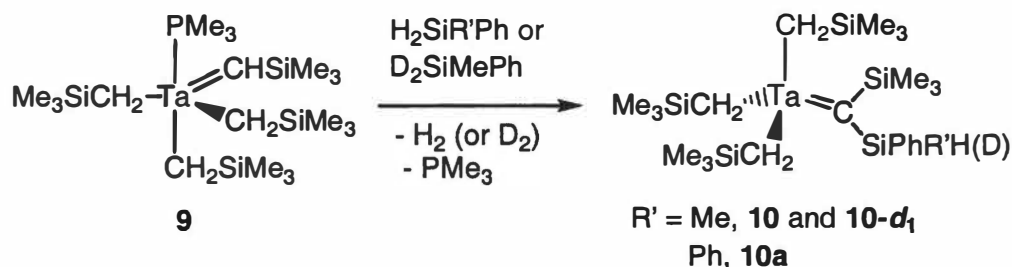
New Mechanistic Insights into the Reactions of Tantalum

Alkylidene Complexes with Silanes

4.1 Introduction

Early transition metal alkylidene chemistry has received much attention over the past 30 years. This class of compounds has been found to possess catalytic activities in alkene metathesis as well as olefin polymerization.

When the reactions of $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}(\text{PMe}_3)(=\text{CHSiMe}_3)$ (**9**) with H_2SiRPh ($\text{R} = \text{Me}, \text{Ph}$) were investigated by previous members of our group, we were surprised to observe that bis(silyl) substituted alkylidene complexes, $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}[\text{C}(\text{SiMe}_3)(\text{SiHRPh})]$ (**10**), were isolated (Scheme 4.1).^{8,129,130} The preparation of **10** by this route was unexpected, and prompted our study the mechanism of the reactions.



Scheme 4.1 Reaction of **9** with silanes

Based on earlier work done in our group, one mechanism in Scheme 4.2 was proposed to explain the formation of **10**.^{129,131} We conducted the additional studies discussed in this chapter to explore other possible mechanisms of the reactions.

4.2 Results and Discussion

4.2.1 Mechanistic Considerations and Kinetics Plots

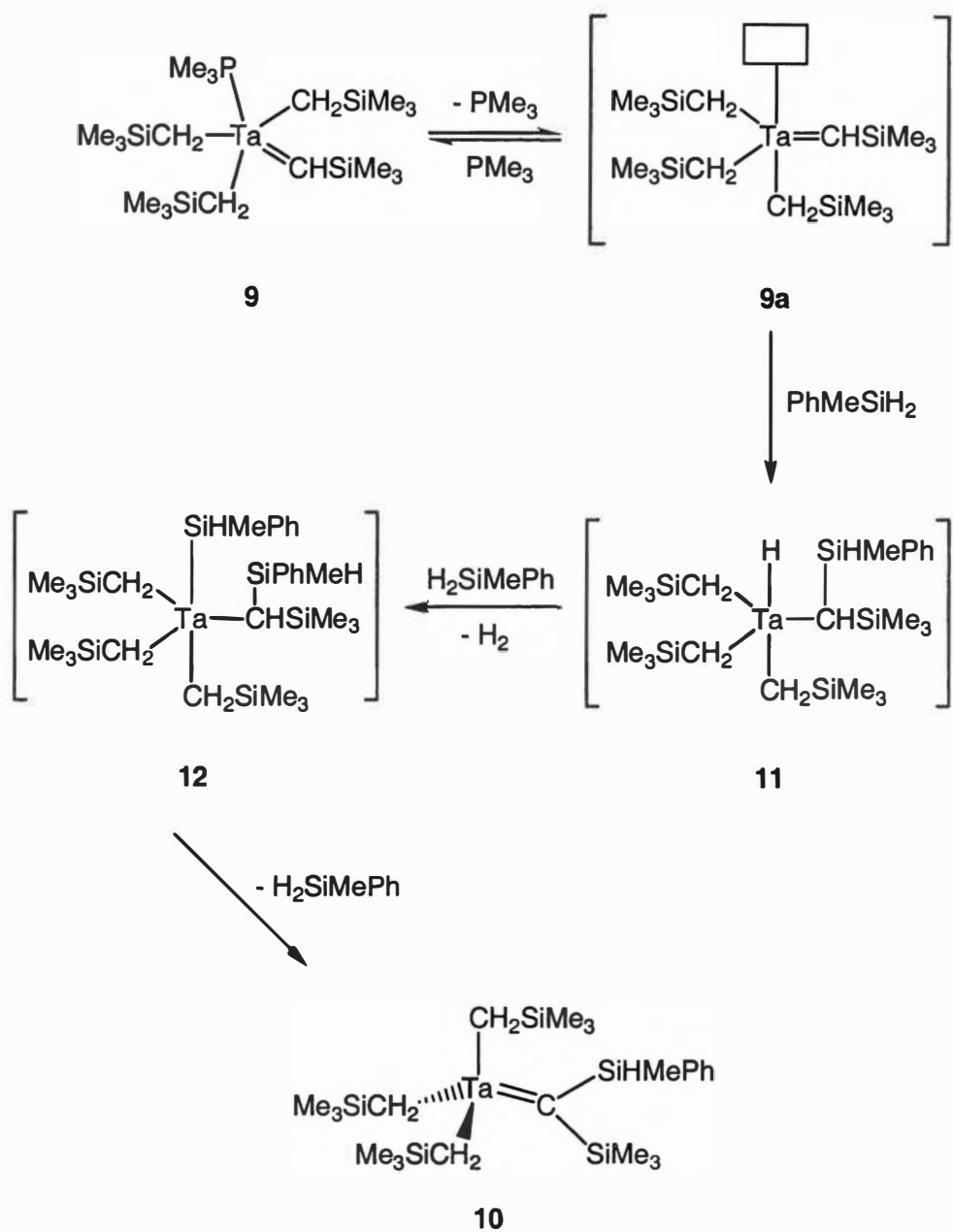
In the reaction of **9** with H₂SiMePh two possible pathways exist by which the product **10** could be formed, as shown in Scheme 4.3. **Path A** would involve loss of PMe₃ opening up a coordination site, followed by addition of the H-Si bond across the Ta=CHR bond. **Path B** would involve an addition of the silane to the Ta=C alkylidene bond, followed by loss of phosphine and conversion to products.

If the dissociative mechanism in **Path A** (Scheme 4.3) were operative in this reaction, the following relationships would exist:¹²⁹⁻¹³¹

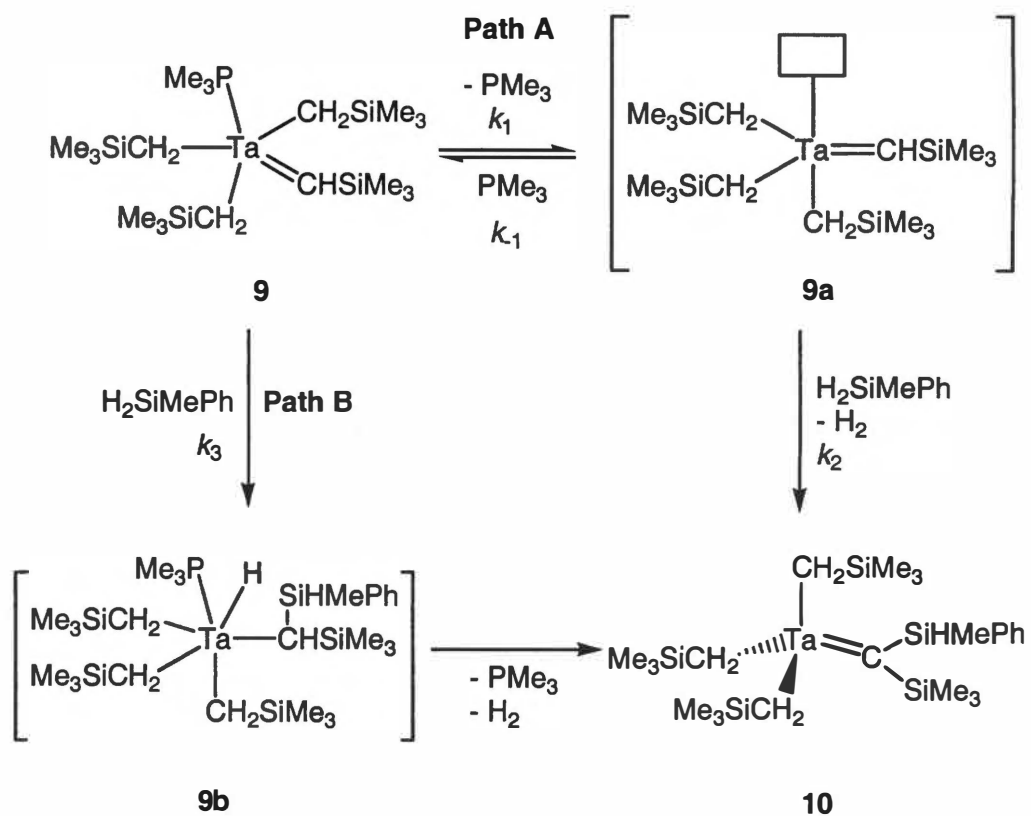
$$d[\mathbf{9}]/dt = k_{-1}[\mathbf{9a}][\text{PMe}_3] - k_1[\mathbf{9}] \quad (\text{Eq. 4.1})$$

$$d[\mathbf{9a}]/dt = k_1[\mathbf{9}] - k_{-1}[\mathbf{9a}][\text{PMe}_3] - k_2[\mathbf{9a}][\text{H}_2\text{SiMePh}] \quad (\text{Eq. 4.2})$$

Using a steady-state approximation ($d[\mathbf{9a}]/dt = 0$) and rearranging Eq. 4.2 gives



Scheme 4.2 Originally proposed mechanism



Scheme 4.3 Mechanistic considerations

$$[9a] = \frac{k_1[9]}{k_1[PMe_3] + k_2[H_2SiMePh]} \quad (\text{Eq. 4.3})$$

Substituting Eq. 4.3 into Eq. 4.1 gives

$$d[9]/dt = \frac{k_1 k_1 [PMe_3][9]}{k_1[PMe_3] + k_2[H_2SiMePh]} - k_1[9] \quad (\text{Eq. 4.4})$$

or

$$v = -d[9]/dt = \frac{k_1 k_2 [H_2SiMePh][9]}{k_1[PMe_3] + k_2[H_2SiMePh]} = k_{obs}[9] \quad (\text{Eq. 4.5})$$

where

$$k_{obs} = \frac{k_1 k_2 [H_2SiMePh]}{k_1[PMe_3] + k_2[H_2SiMePh]} \quad (\text{Eq. 4.6})$$

Integration using Eq. 4.5 gives

$$\ln \frac{[9]}{[9]_0} = -k_{obs} t \quad (\text{Eq. 4.7})$$

Eqs. 4.5-4.7 indicate that, with excess H_2SiMePh , pseudo-first order kinetics in $[\mathbf{9}]$ is expected. When $[\text{H}_2\text{SiMePh}] \gg [\text{PMe}_3]$, Eq. 4.6 is simplified to $k_{\text{obs}} \approx k_1$. In other words, one would observe saturation kinetics at large excesses of PhMeSiH_2 . Eq. 4.6 also indicates that increasing $[\text{PMe}_3]$, under constant $[\text{PhMeSiH}_2]$, would reduce the observed rate constant k_{obs} .

If the reaction proceeded by the associative mechanism in **Path B** (Scheme 4.3), and if the first step was rate-determining, a much simpler rate expression would be obtained:

$$d[\mathbf{9}]/dt = k_3[\mathbf{9}][\text{H}_2\text{SiMePh}] \quad (\text{Eq. 4.8})$$

For reactions conducted with an excess of H_2SiMePh , pseudo-first order kinetics was expected;

$$k_{\text{obs}} = k_3[\text{H}_2\text{SiMePh}] \quad (\text{Eq. 4.9})$$

Eqs. 4.8 and 4.9 suggest that, if the reaction proceeds by **Path B**, the observed rate constant would be independent of phosphine concentration $[\text{PMe}_3]$.

The kinetic studies of the reaction conducted earlier in our group were performed with the ratio of $[\text{H}_2\text{SiMePh}]/[\mathbf{9}]$ ranging from 5.34 to 34.8, and plots of $1/k_{\text{obs}}$ vs $[\text{PMe}_3]/[\text{H}_2\text{SiMePh}]$ were linear, lending support to **Path A**.^{130,131} In the current work, kinetics of the reaction with a large excess of PMe_3 was studied.

Path A involves PMe_3 dissociation before the reaction of silane with a Ta complex. If this is the operative pathway an excess of phosphine was expected to significantly slow the reaction, as Eq. 4.6 suggests.

In the current kinetic studies, two experiments were performed. In the control experiment, 5.3 equiv of H_2SiMePh was added to a J. Young NMR tube containing **9** and an internal standard, 4,4'-dimethylbiphenyl. Bubbles of H_2 were observed during the reaction. A plot of $\ln[\mathbf{9}]/[\mathbf{9}]_0$ vs time was linear (Figure 4.1) to give $k_{\text{obs}} = 1.5 \times 10^{-2} \text{ min}^{-1}$.

The second experiment was conducted by a process similar to the first except that 20 equiv PMe_3 was added to the J. Young NMR tube. By NMR the reaction with excess PMe_3 appeared to proceed much slower than the control without any added PMe_3 . After 12 h, only ca. 25% of the starting material had been consumed. However, after 25 h all starting material had been used. As in the control experiment, the plot of $\ln[\mathbf{9}]/[\mathbf{9}]_0$ vs time was linear (Figure 4.2) to give $k_{\text{obs}} = 8.1 \times 10^{-4} \text{ min}^{-1}$. Thus, the reaction with 20 equiv PMe_3 was 19 times slower than that without added PMe_3 . These results support **Path A** in Scheme 4.3. The first step in the reaction of **9** with H_2SiMePh to give the bis(silyl) substituted Ta alkylidene complex **10** is PMe_3 dissociation to open a coordination site.

4.2.2 Mass Spectral Analysis of Volatiles

The gaseous products from the reaction of **9** with ca. 1 equiv of D_2SiMePh were analyzed by mass spectrometry. The mass spectrum of **Sample A** (Figure

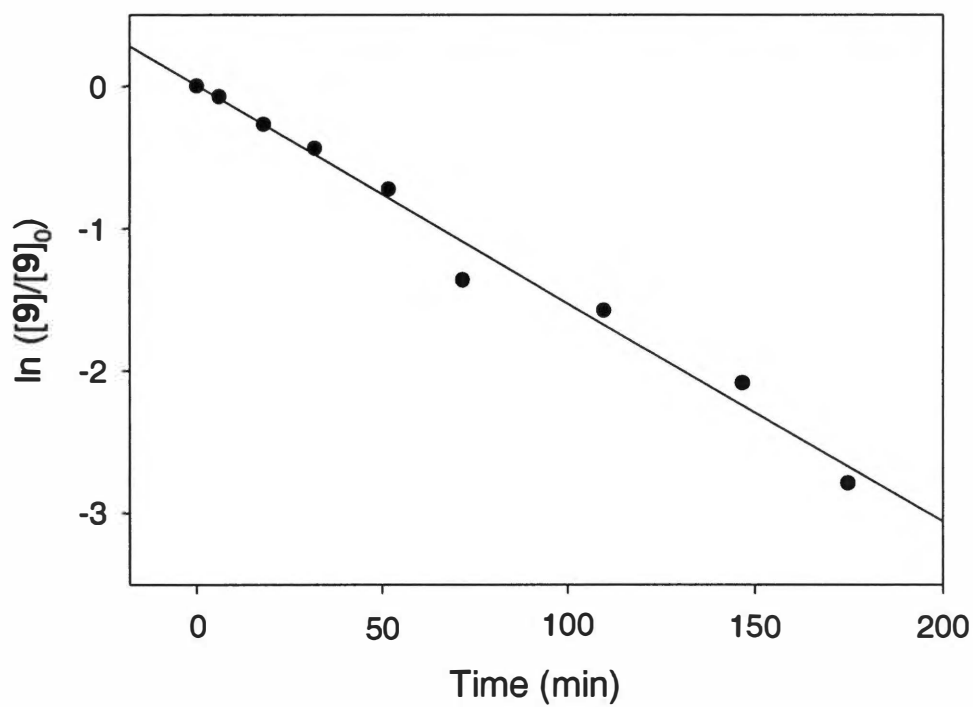


Figure 4.1 Kinetics plot of the reaction of **9** with 5.3 equiv of H₂SiMePh without added PMe₃ – Control experiment

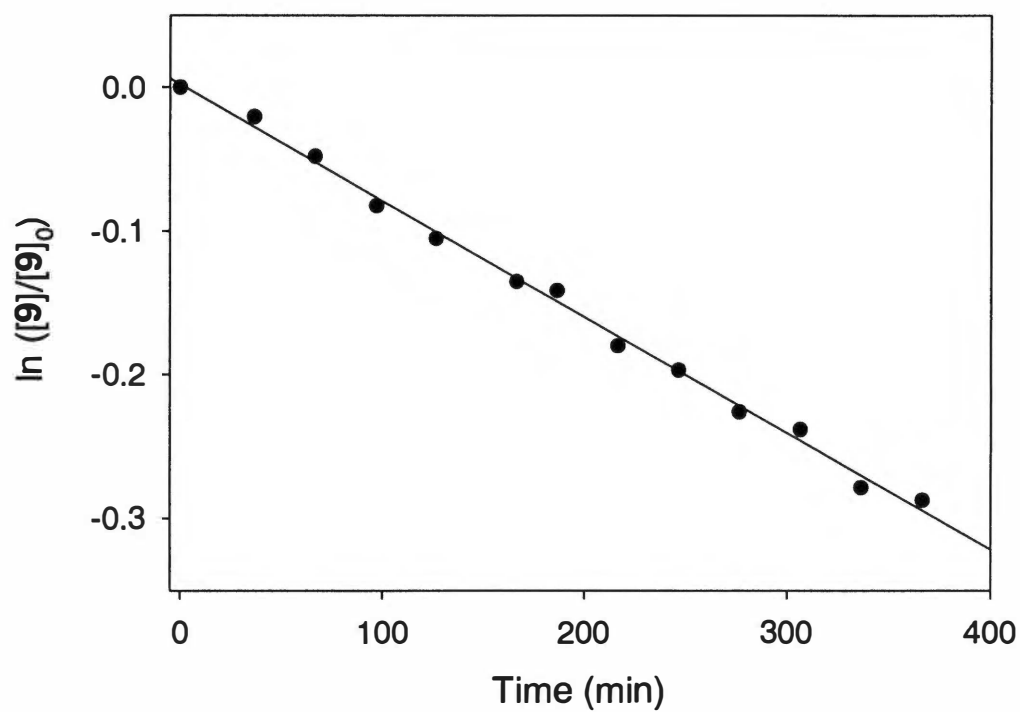


Figure 4.2 Kinetics plot of the reaction of **9** with 5.4 equiv of H_2SiMePh and 20 equiv of PMe_3

4.3) showed the products to be D₂, HD, and H₂ in an 86.6(0.3) : 12.5(0.3) : 0.86(0.03) ratio (by total ion current).¹³¹ In another experiment when **9** reacted with 4.5 equiv of D₂SiMePh (**Sample B**, Figure 4.4), the mass spectrum showed the gaseous products to be D₂, HD, and H₂ in an 89.6(1.2) : 9.1(1.1) : 1.26(0.01) ratio.¹³¹ In such a reaction between **9** and 4.5 equiv of D₂SiMePh, ¹H NMR spectra at 600 MHz showed the presence of 0.088 equiv of H₂SiMePh and 0.33 equiv of HDSiMePh. In the third experiment, the gaseous products from the reaction of **9** with 4.5 equiv of D₂SiMePh under excess H₂ (**Sample C**, Figure 4.5) were analyzed as well by mass spectrometry. The MS showed the products to be D₂, HD, and H₂ in a 24.5(0.1) : 13.4(0.1) : 62.1(0.1) ratio.¹³¹ A summary of these experimental results is listed in Table 4.1.

4.2.3 NMR Analyses of the Remaining Silane

NMR studies were undertaken to investigate whether there was hydrogen incorporation into the excess deuterated silane D₂SiMePh. In the reaction involving a 15 to 1 ratio of D₂SiMePh with **9**, a quartet of triplets was observed in the Si-*H* region of the ¹H NMR spectrum (Figure 4.6). The observation of a quartet of triplets signified the presence of HDSiMePh. The quartet appears to be a consequence of coupling between *H*-Si with the methyl protons while the triplet arises from coupling of *H*-Si with *D*-Si. The formation of HDSiMePh, when the reaction was conducted in the presence of a large excess of D₂SiMePh, supported the original mechanism in Scheme 4.2. The formation of HDSiMePh was

File:D849C Ident:1 Acq:15-NOV-2000 16:37:32 +5:04 Cal:D848»
 ZAB-SEQ4F EI+ Magnet BpI:1143961 TIC:18620904
 File Text:"1:1 Ta " (valve closed) s130 P1.8e-6 AFSe-6
 100% 4.0 2973mV

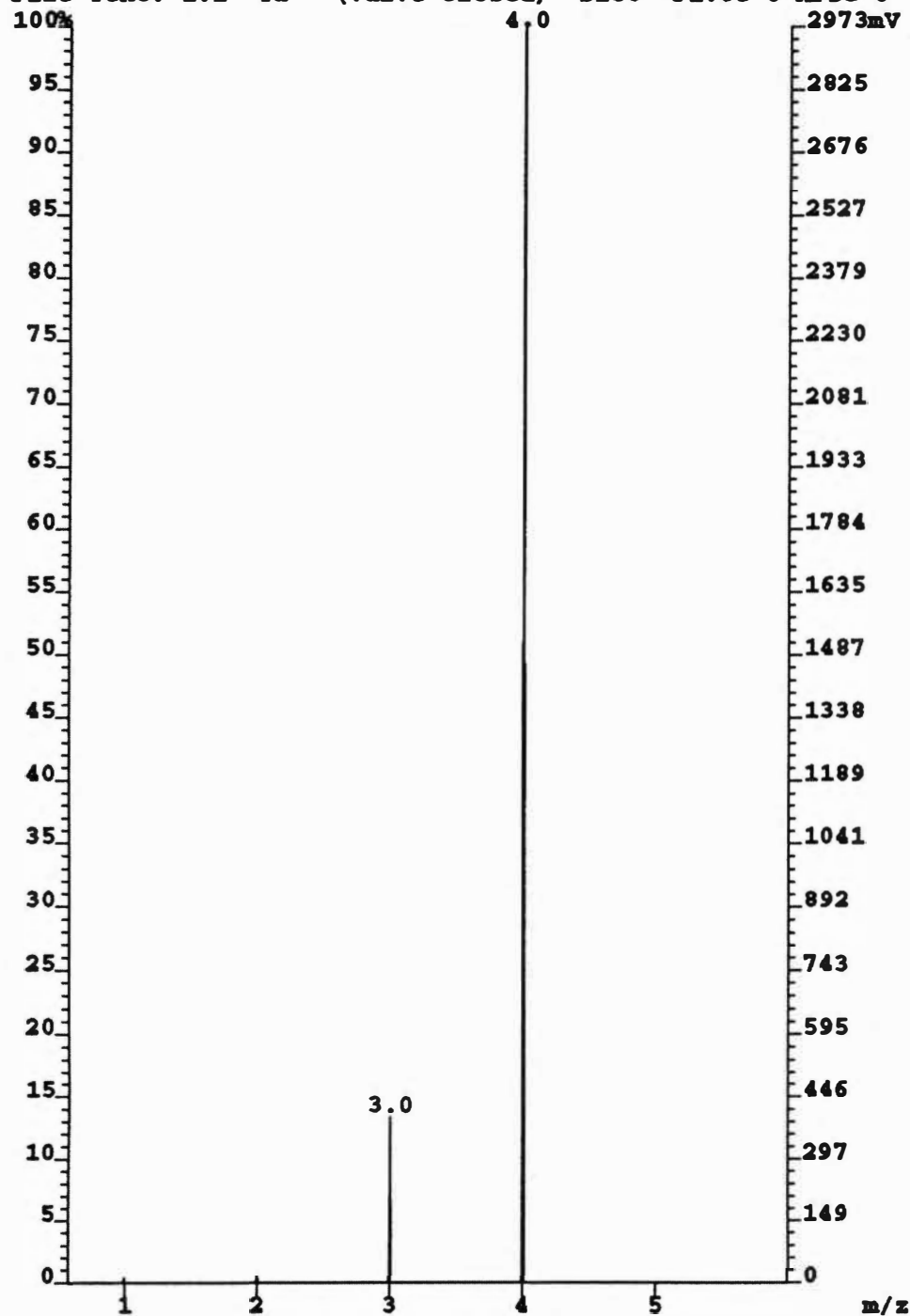


Figure 4.3 Mass spectrum of Sample A

File:D850C Ident:1 Acq:15-NOV-2000 17:08:32 +5:04 Cal:D848*
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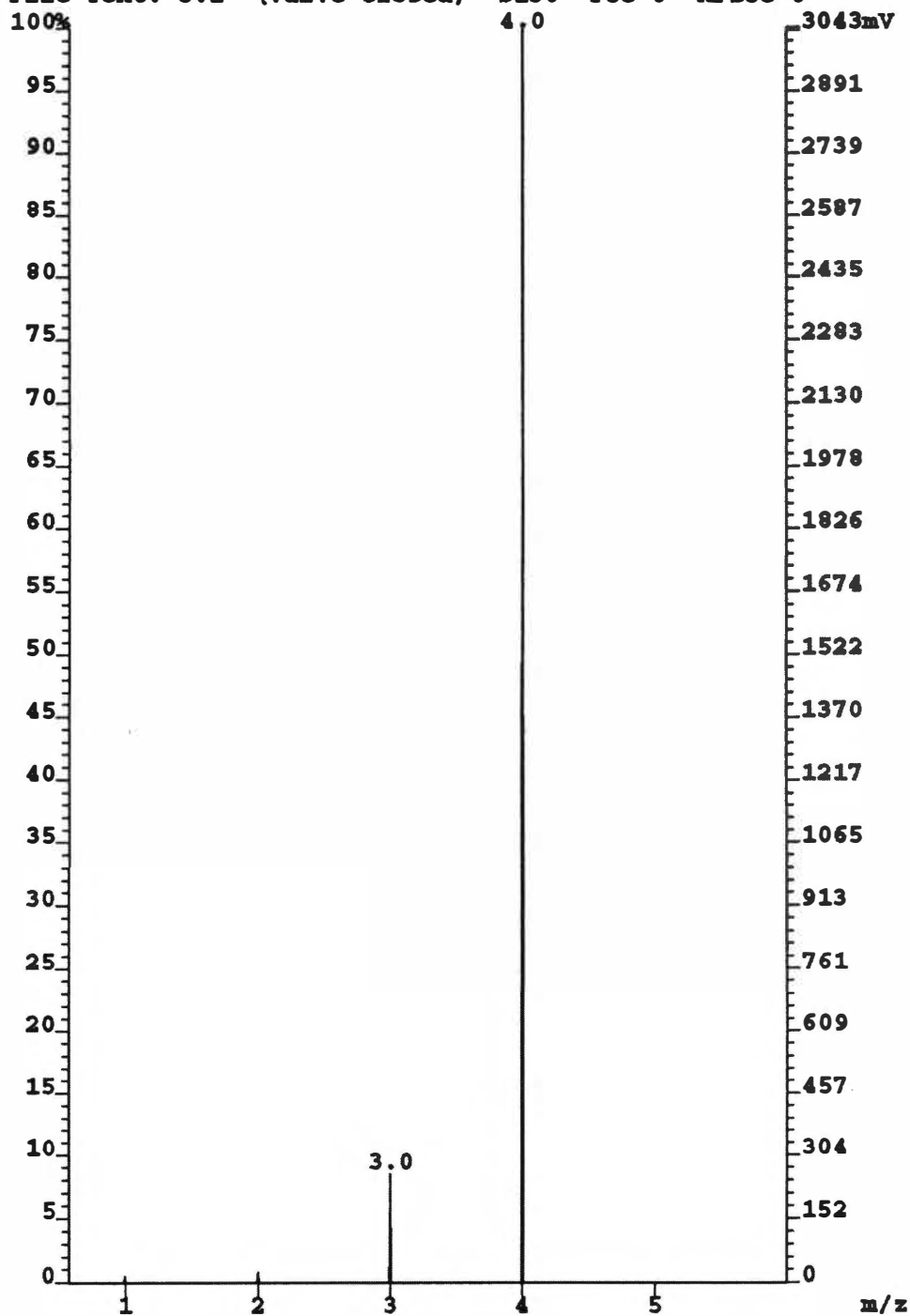


Figure 4.4 Mass spectrum of Sample B

File:D848C Ident:1 Acq:15-NOV-2000 17:23:53 +5:03 Cal:D848»
 ZAB-SEQ4F EI+ Magnet BpI:852550 TIC:16868932
 File Text:"5:1 +H2" (valve closed) s130 P1.4e-6 AFS2e-5»
 100% 2.0 1957mV

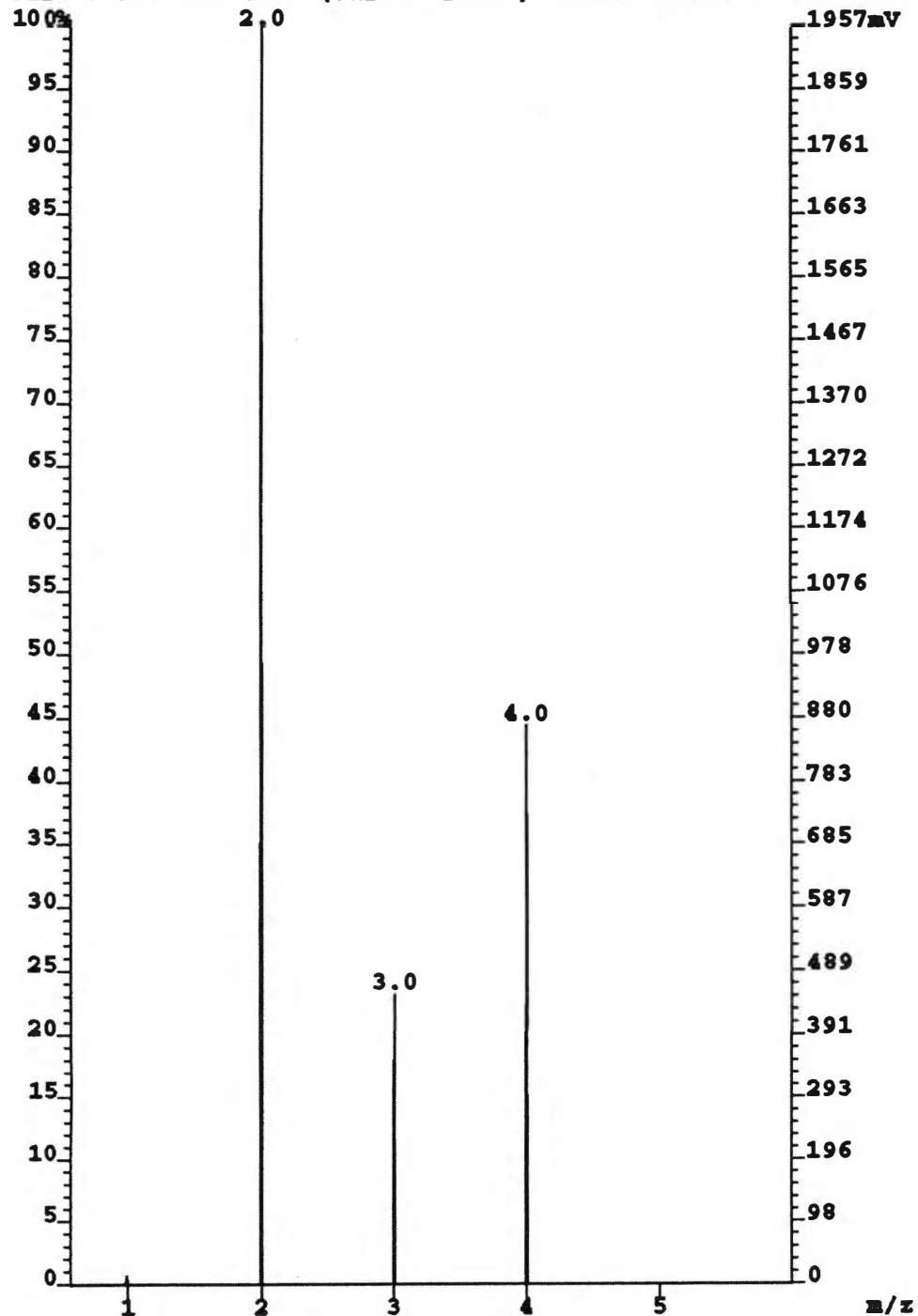


Figure 4.5 Mass spectrum of Sample C

Table 4.1 Mass Spectral Distribution of Gaseous Products

Samples	A	B	C
D ₂ SiMePh (equiv)	1	4.5	4.5 + H ₂ (1 atm)
MS ratio of D ₂ (%)	86.6	89.6	24.5
MS ratio of HD (%)	12.5	9.1	13.4
MS ratio of H ₂ (%)	0.86	1.26	62.1

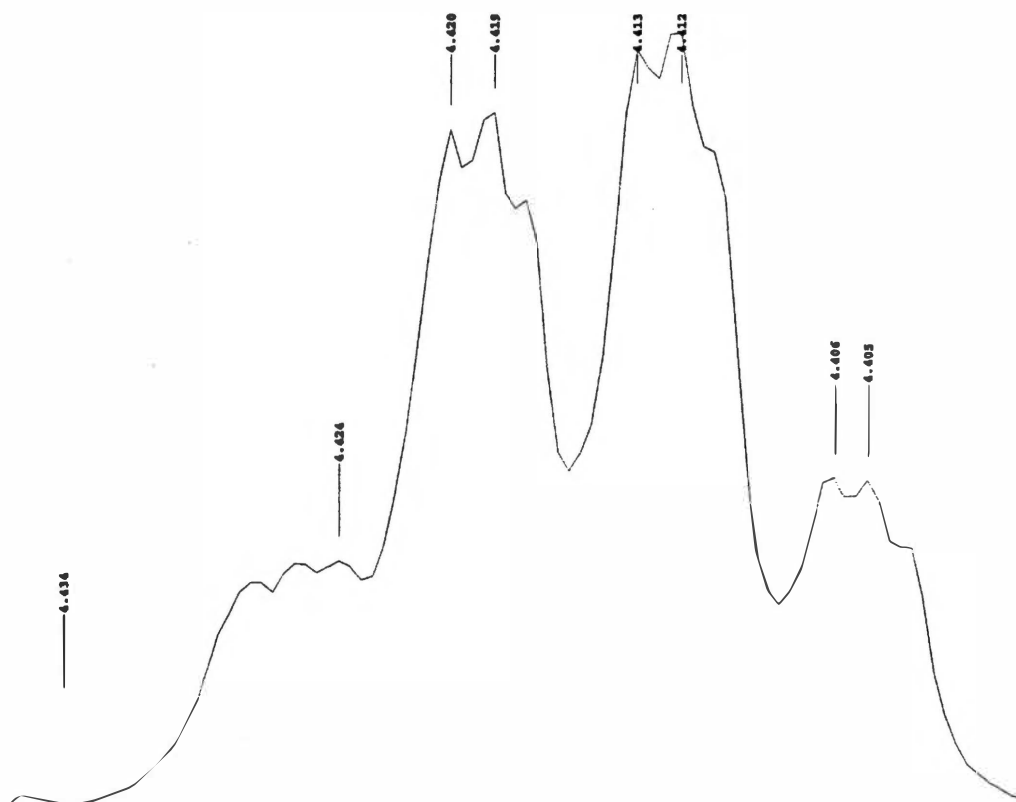


Figure 4.6 NMR of remaining silane in the reaction of $D_2SiMePh$ with **9** in a 15:1 ratio

observed earlier when this reaction conducted with 1 equiv of **9** and 2.85 equiv of D₂SiMePh.¹³⁰

The reaction of D₂SiMePh with **9** in a 5 to 1 ratio in the presence of H₂, however, revealed a different pattern in the Si-*H* region of the ¹H NMR spectrum (Figure 4.7). This reaction mixture showed both a quartet and a quartet of triplets in this region due to the presence of both H₂SiMePh and HDSiMePh, respectively. The hydrogen incorporation from H₂ into the deuterated silane indicated scrambling between gases in the reaction mixture and the silane.

4.2.4 Mechanisms of the Reactions between **9** and Silanes

The MS results from **Samples A** and **B** showed that D₂ is the major product in the reaction, and the ratios of D₂, HD, and H₂ changed slightly when the D₂SiMePh : **9** ratios varied from ca. 1 to 5. The MS and NMR results from **Sample C** with added H₂ in the reaction mixture indicated that products and H₂ added to the system undergo hydrogen scrambling.

In addition to our original mechanism in Scheme 4.2, two other mechanisms were proposed to account for the H incorporation into the remaining silane and the D₂ : HD : H₂ ratio when 1 atm of H₂ was used. These three mechanisms are given in Scheme 4.4.

Based on the kinetic studies, it appears that the first step in the reaction is dissociation of PMe₃ from **9** leaving an open coordination site. Silane then reacts with the alkylidene functionality to yield a deuteride intermediate **11-d₂**. This step

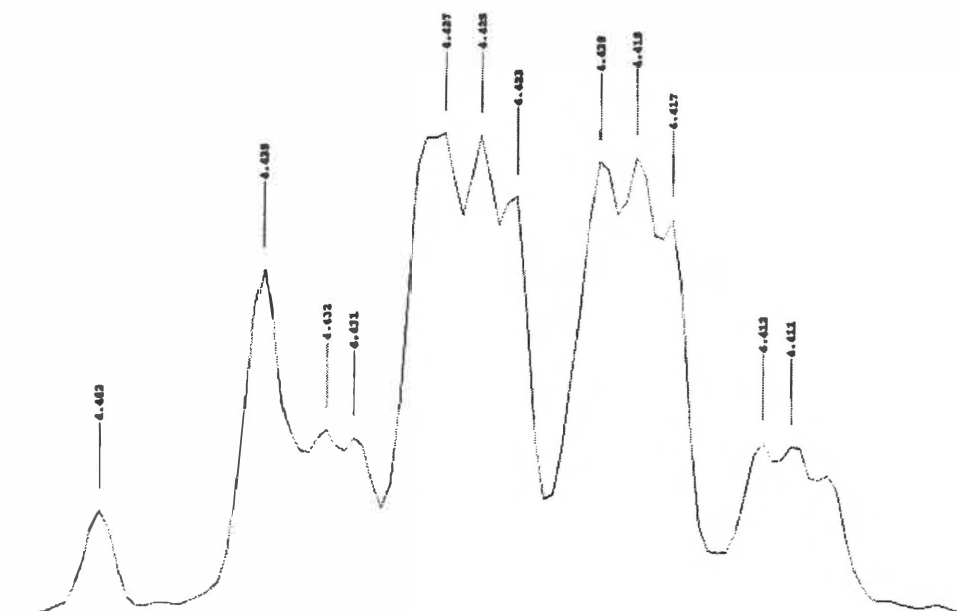
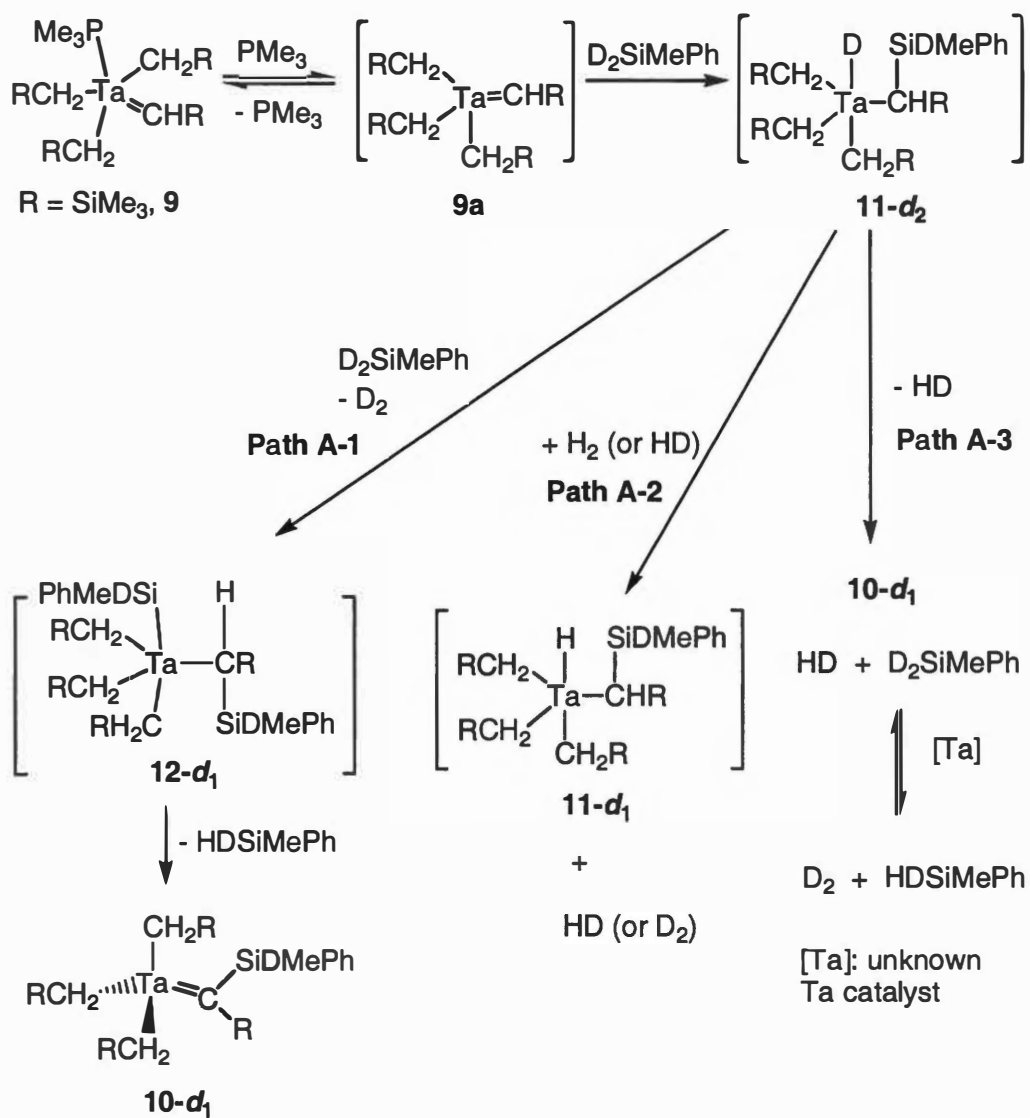


Figure 4.7 NMR of remaining silane in the reaction of D₂SiMePh with **9** in a 5:1 ratio in the presence of 1 atm H₂ (**Sample C**)

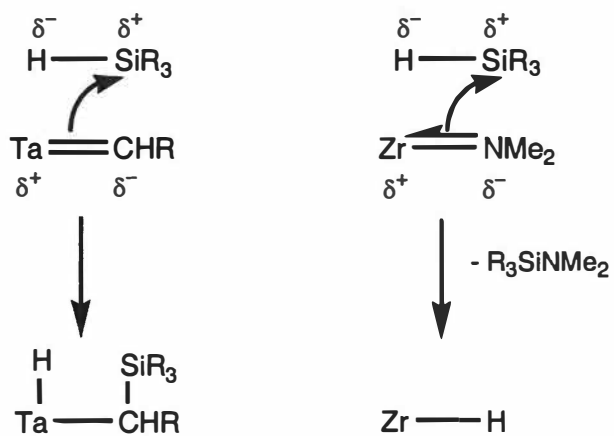


Scheme 4.4 Modified mechanisms

may proceed via nucleophilic attack on the silane by the π -electron density of the alkylidene bond. The $M=CHR$ moiety in Schrock-type alkylidenes have been shown to be nucleophilic in nature (Scheme 4.5). Similarly, reactions of amido complexes with silanes were found to give metal hydride complexes and amidosilanes.^{6,9,132}

The next step could occur via at least three processes. The first, **Path A-1**, would involve **11-d₂** reacting with another silane molecule through dehydrogenative coupling yielding D_2 and **12**. This process may help explain the observation that D_2 was the major gaseous product when the $D_2SiMePh$: **9** ratio was 1. The reactions of hydrides with silanes have been proposed to occur in the dehydrogenative polymerization of silanes.^{88,91,93,94,99-102,104} The silyl ligand in intermediate **12** could then undergo α -hydrogen abstraction to give $HDSiMePh$ and **10-d₁**. **Path A-1** is consistent with the observed dissociative mechanism obtained from the kinetic studies. This pathway also accounts for both the preferential formation of D_2 as the major gaseous product and the H incorporation into the $D_2SiMePh$ to give $HDSiMePh$. It should be noted that **Path A-1** initially requires $H-SiHMePh$ addition to the $Ta=C$ bond to give a $H-Ta-C'-Si$ moiety ($C' = CHR$), and in the last step requires elimination of $H-SiDMePh$ from **12** with $Si-Ta-C''-H$ moiety [$C'' = C(SiDMePh)R$] of opposite regiochemistry.

Hydrogen scrambling in the products was also observed when H_2 was added to the system indicating **Paths A-2** and **A-3** may be occurring in the system. In **Path A-2** the deuteride in **11-d₂** undergoes σ -bond metathesis with H_2 (or HD) to



Scheme 4.5 Reactions of Schrock-type alkylidenes and metal amido complexes with hydrosilanes

give HD (or D₂) and **11-*d*₁**. This process may explain the increased HD percentage in **Sample C** in which the reaction was conducted under H₂. **Path A-3** in Scheme 4.4, in which HD is eliminated to give **11-*d*₁** followed by the exchange $\text{HD} + \text{D}_2\text{SiMePh} \rightleftharpoons \text{D}_2 + \text{HDSiMePh}$, may help explain the hydrogen scrambling process observed. Another process that may occur is a σ -bond metathesis reaction involving the α -C and H atoms in the Ta=CHR ligand in **9a** and the incoming D₂SiMePh, yielding HD and **11a-*d*₁** as products. Subsequent scrambling as shown in **Path A-3** may lead to the observed product hydrogen isotope distributions.

In conclusion, the reaction of (Me₃SiCH₂)₃Ta(PMe₃)(=CHSiMe₃) (**9**) with H₂SiMePh to give (Me₃SiCH₂)₃Ta[=CSiMe₃(SiHRPh)] (**10**) proceeds via a dissociative mechanism in which coordinated PMe₃ is initially lost opening up a site for silane addition. Although **Path A-1** in Scheme 4.4 is likely the major pathway, **Paths A-2** and **A-3** may exist and cannot be ruled out. **Path A-2** may explain the increased HD in **Sample C** and **Path A-3** may account for the D₂-HD-H₂ scrambling process. Mechanisms other than these in Scheme 4.4 may operate in these reactions as well.¹³³

4.3 Experimental Section

4.3.1 General Procedures

All manipulations were performed under a dry N₂ atmosphere using either standard Schlenk techniques or a glovebox. All solvents were purified by distillation from potassium/benzophenone ketyl. Toluene-*d*₈ was dried over activated molecular sieves and stored under nitrogen. NMR spectra were recorded on either a Bruker AC-250, AMX-400 or Varian INOVA 600 Fourier transform spectrometer and were referenced to solvents (residual protons in the ¹H spectra). Mass spectra were recorded on a VG ZAB-EQ hybrid high-performance mass spectrometer at an ionization voltage of 70 eV. (Me₃SiCH₂)₃Ta(PMe₃)(=CHSiMe₃) (**9**)¹³¹ and D₂SiMePh¹³⁴ were prepared by the literature procedures. H₂SiMePh (Gelest) was dried over activated molecular sieves and stored under nitrogen. 4,4'-dimethylbiphenyl (Aldrich) was used as received.

4.3.2 Preparation of NMR Samples for Kinetics

9 (28.1 mg, 0.04655 mmol), 4,4'-dimethylbiphenyl (1.3 mg) and toluene-*d*₈ (420 μL, 396 mg) were placed in an NMR tube. PMe₃ (97 μL, 71 mg, 0.94 mmol) and H₂SiMePh (34 μL, 30 mg, 0.25 mmol) were then added to this solution at 24 °C. The ratio of [H₂SiMePh]/[**9**]₀ was approximately 5.4. The reaction mixture was kept at 24 °C and monitored by both ¹H and ¹³C NMR.

In a control experiment, **9** (28.6 mg, 0.0473 mmol) and 4,4'-dimethylbiphenyl (5.1 mg) were dissolved in toluene-*d*₈ (536 μL, 504 mg). H₂SiMePh (34 μL, 30 mg, 0.25 mmol) was then added so that the ratio [H₂SiMePh]/[**9**]₀ was approximately 5.3. The reaction at 24 °C was monitored by ¹H NMR.

4.3.3 Preparation of Samples for Mass Spectral Analysis

Three separate samples were prepared for mass spectral analysis of the gaseous hydrogen products from the reaction of **9** with H₂SiMePh.

Sample A: To a J. Young valved NMR tube was added **9** (0.045 g, 0.074 mmol), toluene-*d*₈ (0.6 mL) and D₂SiMePh (9.5 μL, 0.068 mmol). The solution was immediately frozen in liquid nitrogen and the tube was evacuated to remove N₂. The Teflon valve on the tube was then sealed. The solution was allowed to thaw and was kept at 23 °C for 25 min at which time gas evolution from the reaction mixture had ceased. The solution was frozen again and the J. Young valved NMR tube connected to the mass spectrometer. The gaseous products were pumped into the mass spectrometer and analyzed.

Sample B: The same procedure was followed in the preparation of **Sample B** as **Sample A** except 47 μL (0.33 mmol, 4.5 equiv) of D₂SiMePh was added to the solution.

Sample C: To a precalibrated J. Young valved NMR tube was added 0.045 g (0.074 mmol) of **9**, 0.65 mL of toluene-*d*₈ and 47 μL (0.33 mmol) of D₂SiMePh

yielding 2.51 mL of headspace. The solution was immediately frozen in liquid nitrogen. A portion of the headspace was also cooled during this freezing process. Nitrogen in the tube was then removed in vacuo. One atmosphere of H₂ was added to the tube to fill the headspace. The solution was then allowed to thaw and was kept at 23 °C. When, after 25 min, gas evolution had ceased, the solution was frozen again and the tube was connected to the mass spectrometer. Gaseous products were then pumped into the mass spectrometer. After mass spectral analysis was complete, 4,4'-dimethylbiphenyl (4.1 mg, 0.022 mmol) was added to the solution as an internal standard for subsequent NMR studies.

4.3.4 Preparation of Samples for NMR Analysis of Remaining Silane

To **9** (0.45 g, 0.74 mmol) in toluene-*d*₈ (0.6 mL) in an NMR tube was added 47 µL (0.33 mmol) of D₂SiMePh. The internal standard 4,4'-dimethylbiphenyl (3.0 mg, 0.016 mmol) was then added. After the reaction was complete, ¹H NMR at 600 MHz revealed the presence of 0.0065 mmol (0.088 equiv) of H₂SiMePh and 0.024 mmol (0.33 equiv) of HDSiMePh in the product mixture. As a result of isotopic shift, the resonance attributed to HDSiMePh was 0.010 ppm upfield-shifted from that of H₂SiMePh. Also **Sample C**, prepared with 1 atm of H₂ gas for mass spectral analysis and containing, was checked by ¹H NMR at 600 MHz and showed the presence of ca. 0.0081 mmol (0.11 equiv) of H₂SiMePh and 0.074 mmol (1.0 equiv) of HDSiMePh.

CHAPTER 5

Chemical Vapor Deposition of TiO_2 Thin Films from the Reaction of Tetrakis(dimethylamido)titanium with Oxygen

5.1 Introduction

The dimensions of microelectronic devices are continuously shrinking. SiO_2 is the current gate insulating material used in ultra-large-scale-integration (ULSI) devices. However, SiO_2 (dielectric constant $\kappa = 3.9$) is an effective insulating material when the thickness of the SiO_2 layer is greater than 100 Å (Figure 5.1). When new generations of ULSI technology demand the insulating layer to be less than 20 Å thick, a material with a high dielectric constant (high- κ) is needed.¹³⁵ TiO_2 [$\kappa = 86$ -170 (rutile)] and Ta_2O_5 ($\kappa = 26$)¹³⁶ and mixed oxide materials MO_x - SiO_x , are presently studied for this application.^{135,137} In addition, Ta_2O_5 and TiO_2 are of current interest as replacement materials for SiO_2 in the new generation dynamic random access memories (DRAM).¹³⁸ TiO_2 has also been used as coatings for solar cells and photocatalysis as well.¹³⁹ Due to its high refractive index, TiO_2 is the most widely utilized white pigment,¹²⁵ and is used as building materials as well.

We were interested in preparing TiO_2 thin films from the reaction of tetrakis(dimethylamido)titanium $\text{Ti}(\text{NMe}_2)_4$ with O_2 by chemical vapor deposition

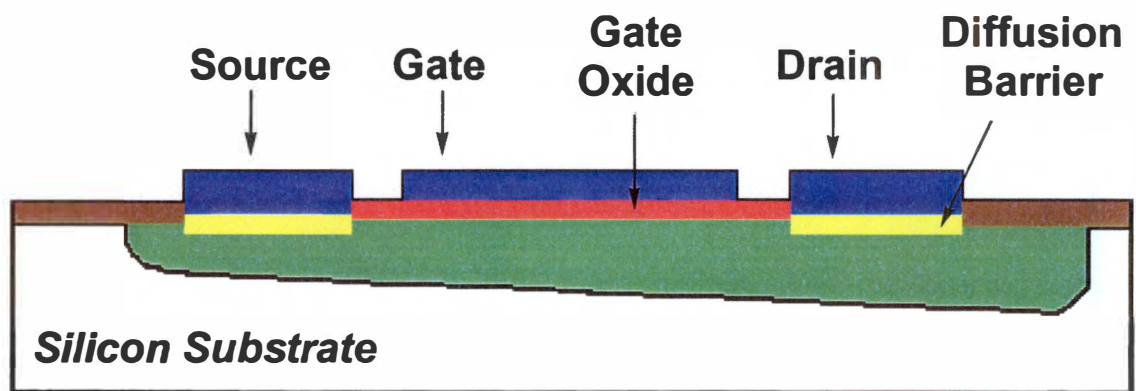
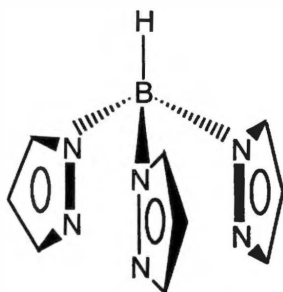


Figure 5.1 Schematic of integrated microelectronic transistor

(CVD). CVD is a process in which a volatile compound (usually either inorganic, metal-organic or organometallic) is carried by an inert gas into the reactor where it decomposes on a substrate. A solid film is deposited and volatile byproducts are removed.

Until now, most TiO_2 films were prepared by using a single source precursor, usually a titanium alkoxide, by a variety of methods such as sol-gel,^{140,141} metal-organic chemical vapor deposition (MOCVD),^{142,143,144} plasma CVD,^{145,146} reactive sputtering,¹⁴⁷⁻¹⁴⁹ atomic layer deposition (ALD),¹⁵⁰ ion beam assisted process,¹⁵¹ filtered arc deposition,¹⁵² cathodic electrodeposition,¹⁵³⁻¹⁵⁵ and electron beam evaporation.¹⁵⁶ Baum and coworkers filed a patent on the preparation of TiO_2 films from amide precursors.¹⁵⁷ Other group 4 oxides, ZrO_2 and HfO_2 , have been prepared by the reactions of $\text{M}(\text{NRR}')_4$ ($\text{M} = \text{Zr}, \text{Hf}$; $\text{NRR}' = \text{NMe}_2, \text{NMeEt}, \text{NEt}_2$) with H_2O via atomic layer deposition (ALD).¹⁵⁸ An alkoxy(pyrazolylborate)titanium(IV) complex $[\text{TpTi}(\text{OR})_3]$, Scheme 5.1] was used to prepare amorphous TiO_2 thin films via chemical vapor deposition.¹⁵⁹ Amide complexes of tantalum such as $\text{Ta}(\text{NR}_2)_5$ and $\text{Ta}(\text{NEt}_2)_3(=\text{N}^t\text{Bu})$ have been used to prepare Ta_2O_5 films.¹⁶⁰⁻¹⁶²



Scheme 5.1 Tris(pyrazolyl)borate (Tp^-) ion

Reactions of transition metal complexes with O₂ are also important in many biological and catalytic processes.¹⁶³ Most studies of reactions of transition metal complexes with O₂ have involved dⁿ metals.^{164,165} A few reports, however, have probed the reactions of d⁰ metal complexes with O₂.¹⁶⁶⁻¹⁷⁵ Oxygen was found to insert into the Zr-R bond of Cp₂ZrRCl forming Cp₂Zr(OR)Cl.^{169,176} Similarly, reactions of Cp₂ZrR₂ with O₂ were found to yield alkoxides Cp₂Zr(OR)₂ and reactions of (tritox)₂MMe₂ with O₂ gave (tritox)₂M(OMe)₂ [M = Ti, Zr, Hf; tritox = (Me₃C)₃CO].^{170,171} Tilley observed O insertion into a Zr-Si bond in the reaction of Cp₂Zr(SiMe₃)Cl with O₂.¹⁷² Our group recently reported the preparation of an O-insertion product (Me₂N)₃Ta(η²-ONMe₂)(OSiR₃) from the reaction of (Me₂N)₄TaSiR₃ with O₂,¹⁰ and such compounds may be intermediates in the formation of metal oxides such as Ta₂O₅.

We recently found that the reaction of Ti(NMe₂)₄ with O₂ gave TiO₂ thin films in chemical vapor deposition processes. The formation and characterization of the thin films and our studies of the CVD processes are reported in this chapter.

5.2 Results and Discussion

5.2.1 Design of CVD Reactors

There are two major designs of CVD reactors: hot-walled (Figure 5.2) and cold-walled (Figure 5.3).¹⁷⁷ Although most industrial processes utilize cold-wall systems, hot-wall reactors have been used extensively.

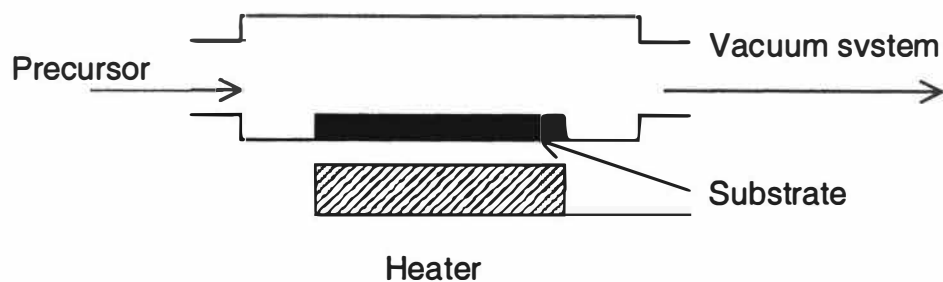


Figure 5.2 Cold-wall CVD reactor. Adapted from *Synthesis of Inorganic Materials*.¹⁷⁷

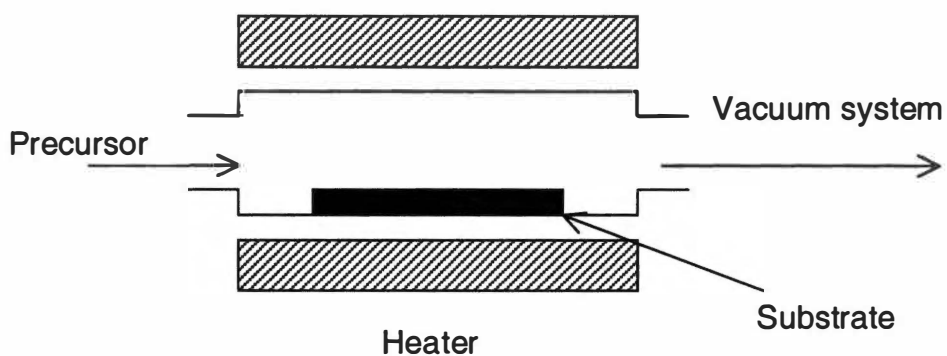


Figure 5.3 Hot-wall CVD reactor. Adapted from *Synthesis of Inorganic Materials*.¹⁷⁷

The design of a cold-wall reactor is such that only the substrate is heated. Thus deposition takes place on the substrate because its temperature is higher than on the reactor walls. The advantages of a cold-wall reactor include:

- (1) Efficient use of precursor due to limited gas-phase reactions
- (2) No deposition on reactor walls
- (3) High deposition rates

In the hot-wall reactor design, however, both the wafer and CVD reactor walls are externally heated. The advantages of a hot-wall system include:

- (1) Simple operation
- (2) Ability to accommodate multiple substrates
- (3) Large ranges of operating pressures and temperatures
- (4) A variety of wafer orientations with respect to gas flow

In a hot-wall reactor, however deposition may take place not only on the substrate but also on the reactor walls as well, requiring extensive maintenance and clean-up of the reactor. Deposition on the reactor walls may also peel off and contaminate the substrate. Moreover, a large amount of precursor is consumed. Due to these drawbacks hot-wall reactors are usually not used in industry, except for the production of semiconductors and oxides. They are used most often in

research laboratories to probe whether a compound could potentially be a CVD precursor.

The CVD reactor used in the current studies is a hot-wall, horizontal apparatus (Figure 5.4). The reactor consists of a three-zone furnace, an introduction system, a glass bubbler containing the precursor $\text{Ti}(\text{NMe}_2)_4$, two turbo pumps, a mechanical pump, a tank of 2% O_2 in Ar, a residual gas analyzer (RGA) and two mass flow controllers (model 2258 integrated flow meter and controller). The furnace (ATS) consisted of 3-in heating zones in the front and rear and one 6-in heating zone in the middle. A type-K thermocouple was used and the controllers were custom built. The three-zone furnace was designed so that the center heat zone was approximately 15 cm long. The $\text{Ti}(\text{NMe}_2)_4$ precursor was loaded into the glass bubbler in a glovebox, and then connected to the system. The length of the introduction system glass rod was varied but the inner diameter (2 mm) was kept the same and the residual gas analyzer was not used in the current studies.

5.2.2 Formation of TiO_2 Thin Films via Hot-Wall Low Pressure Horizontal CVD

An *ideal* precursor used in CVD needs to meet several criteria.¹⁷⁷ First, it must be volatile enough at low temperatures so that it is easily transported to the reaction zone while not condensing in the transport zone. An ideal precursor will also be stable at room temperature allowing for easy storage and transport. It should react cleanly to give deposition of the desired solid-state material without

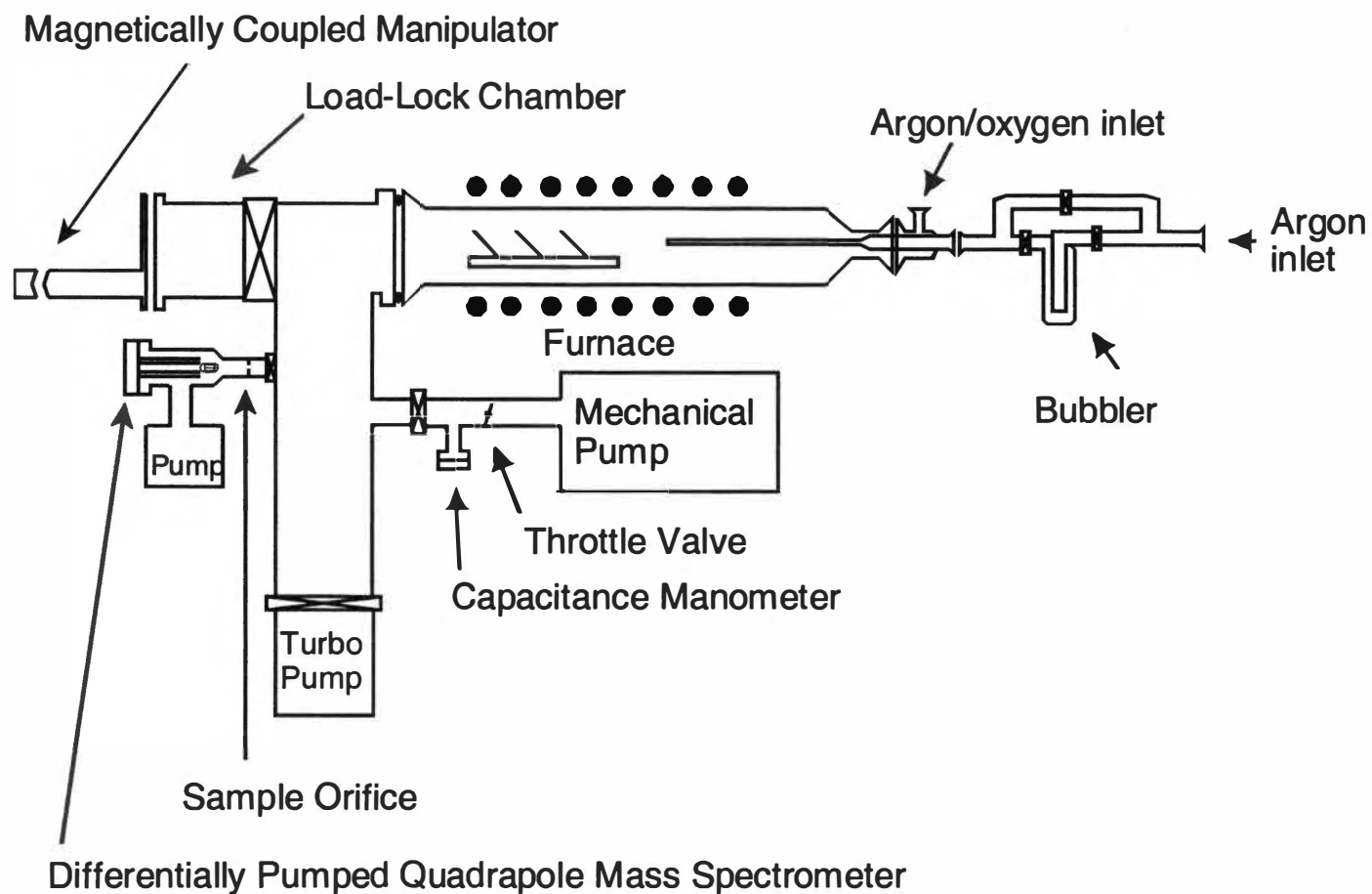


Figure 5.4 The hot-wall, horizontal CVD apparatus used in the deposition of TiO_2 thin films in this dissertation.

side reactions. These precursors should be easily prepared and purified. It should also be noted that liquid delivery techniques have been used recently in deposition of solid-state materials from non-volatile precursors.

Most CVD precursors however do not meet all the criteria. In the current study we chose $\text{Ti}(\text{NMe}_2)_4$ as the precursor. $\text{Ti}(\text{NMe}_2)_4$ is easily prepared from the reaction of $\text{TiCl}_4(\text{THF})_2$ with LiNMe_2 and purified.¹⁷⁸ At room temperature, $\text{Ti}(\text{NMe}_2)_4$ is a liquid with a boiling point of 60 °C at 0.1 torr. In the CVD reactor at elevated temperatures, the reaction between $\text{Ti}(\text{NMe}_2)_4$ and O_2 was found to be fast.

The conditions under which the TiO_2 films were grown are shown in Table 5.1. Unless noted otherwise, all films were deposited on cleaned Si(100) wafers. The carrier gas was Ar and the reactive gas was 2% O_2 in Ar. To eliminate untimely reaction between O_2 and $\text{Ti}(\text{NMe}_2)_4$ the reactor was designed so that the two precursors did not mix until they were in the heated reaction zone.

5.2.3 Characterization of TiO_2 Thin Films by Ellipsometry, IR, Powder XRD, XPS, and SEM

The TiO_2 films deposited by CVD were characterized by several methods. Films were initially studied by ellipsometry. Ellipsometry is a technique used to determine the thickness and refractive index of thin films.^{148,179,180} Our films showed a bullseye pattern on the Si wafer. The thickness of the film was the greatest near the top of the wafer and decreased closer to the bottom of the wafer

Table 5.1 CVD Conditions

Film	1	2	3	4^a	5^{a,b}
Substrate Temperature	350 °C	250 °C	300 °C	300 °C	300 °C
Bubbler Temperature	23 °C	23 °C	23-50 °C	0 °C	23 °C
Deposition Time	10 min	10 min	30 min	20 min	30 min
Resulting Film	No film	Thin film	Thin film	Thin Film	Thin Film
Annealing	N/A	No	Yes	No	Yes

^a Shorter delivery tube was used in deposition

^b Deposited on a Pt wafer [Si-SiO₂ (1000 Å)-Ti (200 Å)-Pt (1000 Å)]

(Figure 5.5). The film thickness was 306.0 Å near the center of the bullseye pattern, but increased to 965.3 Å in the ring furthest from the center of the film pattern. The refractive indices determined are consistent with those reported for TiO₂ (anatase 2.49–2.55; rutile 2.61–2.90).¹²⁵

Infrared spectroscopy (IR) was used to characterize these films to see if they contained TiO₂ and to observe whether organic materials remained on the film. By using IR, we could also detect if any other Ti species (such as TiC) were present. Figure 5.6 shows the IR spectra of **Film 3** before and after annealing. The IR spectrum of **Film 3** before annealing showed a broad peak at 443 cm⁻¹. Upon annealing of **Film 3** at 600 °C for 1 h in air, the peak sharpened indicating an ordering of the film. No organic materials were observed in the film as there were no C-H stretching or bending bands in the expected regions of 2800 or 1400 cm⁻¹, respectively.

Powder X-ray diffraction (XRD) was used to determine whether the film was crystalline and if so, which phase of TiO₂ was formed. Three common TiO₂ phases exist. They are anatase, rutile, and brookite. Anatase is tetragonal and is the low temperature form. Rutile is also tetragonal and is formed above 800 °C. Rutile is the most thermodynamically stable phase of TiO₂.

XRD of **Film 2**, which was not annealed, showed the film to be amorphous. No peaks indicating crystallinity were observed. **Film 3** after being annealed at 600 °C in air for 1 h, however, did show peaks in its XRD spectrum (Figure 5.7). Based on powder diffraction file 21-1272 from the library of reported XRD data,

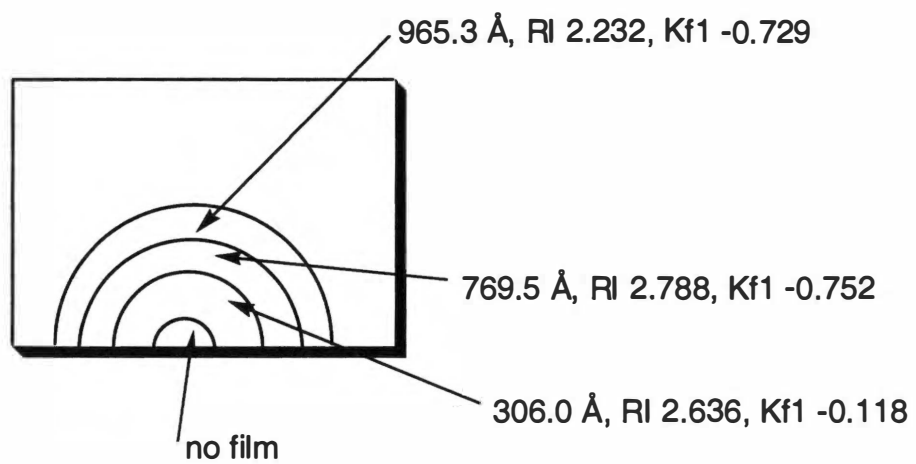


Figure 5.5 Film pattern on Si wafer including thickness and refractive index (RI) obtained from ellipsometry (Kf1 is the correction factor)

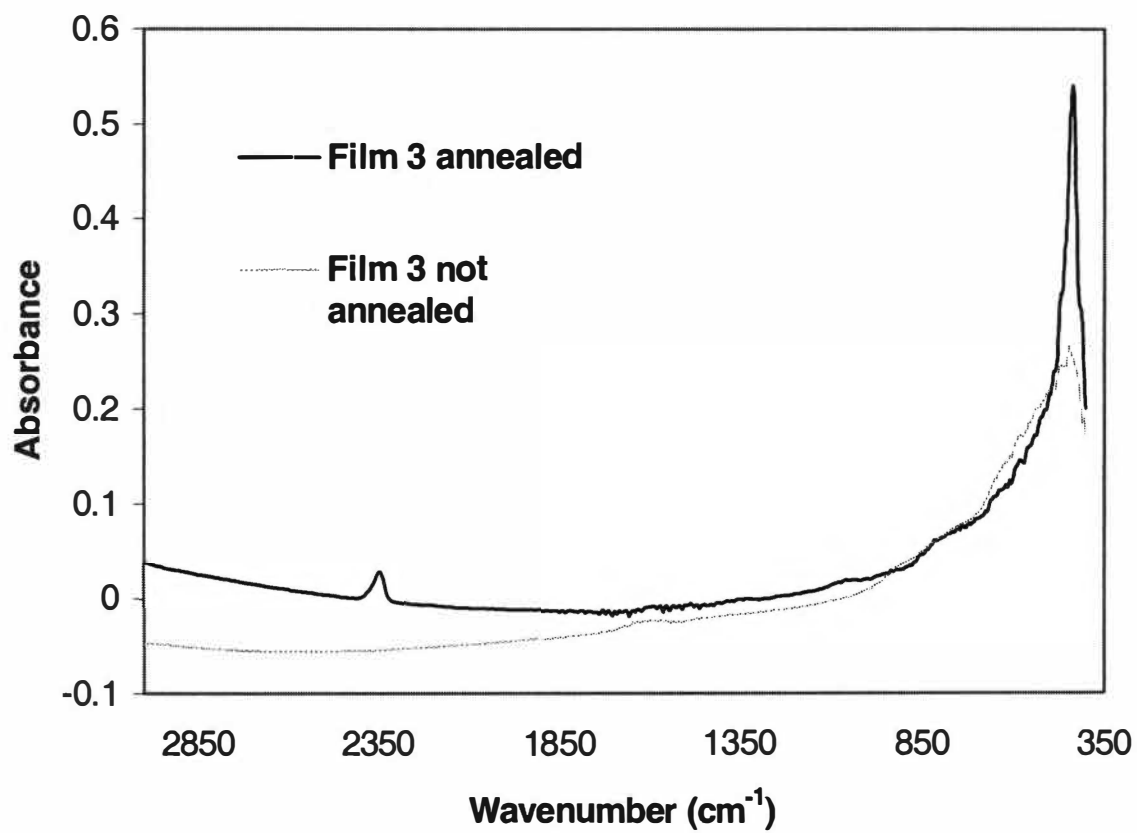


Figure 5.6 IR spectra of **Film 3** before and after annealing

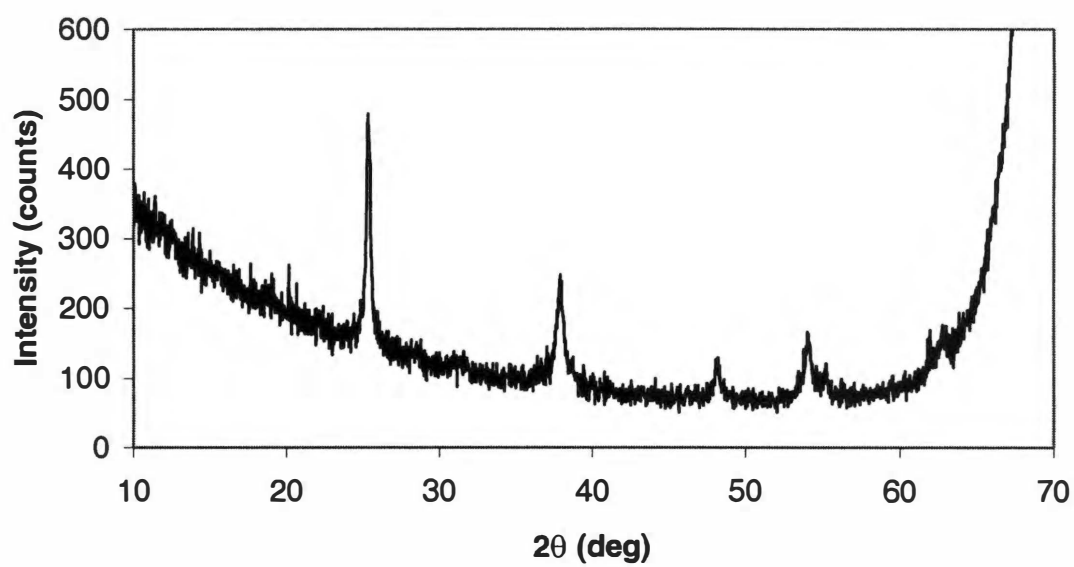


Figure 5.7 XRD spectrum of **Film 3** (annealed)

these peaks at $2\theta = 25.33^\circ$, 37.99° , 48.31° and 54.07° were found to be consistent with those of the anatase phase of TiO_2 . The very intense peak around $2\theta = 70^\circ$ arises from the single crystal Si (100) wafer.

X-ray photoelectron spectroscopy (XPS) was used to analyze the elements present in **Films 2-4**. The films prepared in the current studies contained peaks corresponding to four different elements, O 1s, Ti $2p_{3/2}$, Ti $2p_{1/2}$, and Ti 3p, C 1s and Si 2s and Si $2p^3$ [from the Si(100) wafer]. No N 1s peak at 397 eV was observed, suggesting that the formation of TiN in the CVD process using titanium amide $\text{Ti}(\text{NMe}_2)_4$ and O_2 as precursors could be ruled out. Similarly, no peaks of titanium oxynitride species $\text{TiN}(\text{O})$ [or $\text{TiN}_{0.75}(\text{O})$] were observed at 454.8-455.1 eV for Ti $2p_{3/2}$ or 397.3 eV for N 1s,¹⁸¹ indicating that their formation in the CVD process from O_2 and nitrogen in the amide ligands is unlikely.

The C(1s) peak could arise from two different sources: (1) contamination from organic graphitic substances; (2) formation of titanium carbide TiC. The chemical shifts of the Ti $2p_{3/2}$ and C 1s peaks in the XPS spectra were consistent with graphitic carbon (Table 5.2), and the C contamination of the XPS chamber was found to be source of the C 1s peak. The area of the graphitic C 1s peak of **Film 3** was found to equal ($\leq \pm 1\%$) the area of the C 1s peak of a cleaned Si(100) wafer, when both samples had about equal numbers of sweeps. Even after Ar^+ sputtering, significant C remained although the Ti peaks either decreased (**Film 3**) or disappeared completely (**Film 2**). These observations were consistent with the IR spectra of the films where no C-H stretches were observed around $2,800\text{ cm}^{-1}$.

Table 5.2 XPS Chemical Shifts of Films 2-4 and Other Relevant Materials

Film	Binding energies (eV)	
	O 1s	Ti 2p _{3/2}
Film 2	531.00	459.00
Film 2 sputtered	533.00	-----
Film 3	530.50	459.25
Film 3 annealed	530.75	459.50
Film 3 annealed; sputtered	533.00	459.00
Film 4	532.75	459.00
Cleaned Si(100) wafer	533.00	
TiO ₂ ¹⁸²	~531	458.5
TiN ¹⁸³ , ^a	-----	454.8
TiN(O) ¹⁸¹	531.5	455.1
TiN _{0.75} (O) ¹⁸¹	531.5	454.8
TiC ^b	454.6	

^a The binding energy of N in TiN is 396.9 eV.¹⁸³

^b The binding energy of C in TiC is 281.4 eV.¹⁸²

Figure 5.8 shows a typical XPS spectrum of the films prepared by the CVD process in the current studies. For comparison, the XPS spectrum of a cleaned Si wafer is shown in Figure 5.9. Table 5.2 lists O 1s and Ti 2p_{3/2} peaks observed in **Films 2-4** as well as other relevant compounds.

Scanning electron microscopy (SEM) was used to characterize the surface morphology of **Film 2**. **Film 2** was found to be smooth and featureless without any cracks, as expected for an amorphous film (Figure 5.10).

In summary, TiO₂ thin films have been deposited on Si(100) wafers via metal-organic chemical vapor deposition using Ti(NMe₂)₄ as the volatile precursor. The films were characterized by several techniques including ellipsometry, IR, XRD, SEM and XPS. Films that were not annealed were found to be amorphous. After annealing at 600 °C in air, the films were crystalline anatase. Annealing also sharpened the Ti-O stretching bands in the IR spectrum. XPS showed the presence of Ti and O at chemical shifts consistent with TiO₂, but, importantly, no nitride (TiN) or oxynitrided (TiO_xN_y) species were observed.

5.3 Experimental Section

5.3.1 General Procedures

All manipulations of the precursor Ti(NMe₂)₄ were performed under a dry N₂ atmosphere using either a glovebox or standard Schlenk techniques. Solvents were purified by distillation from potassium/benzophenone ketyl. O₂ (2% in Ar)

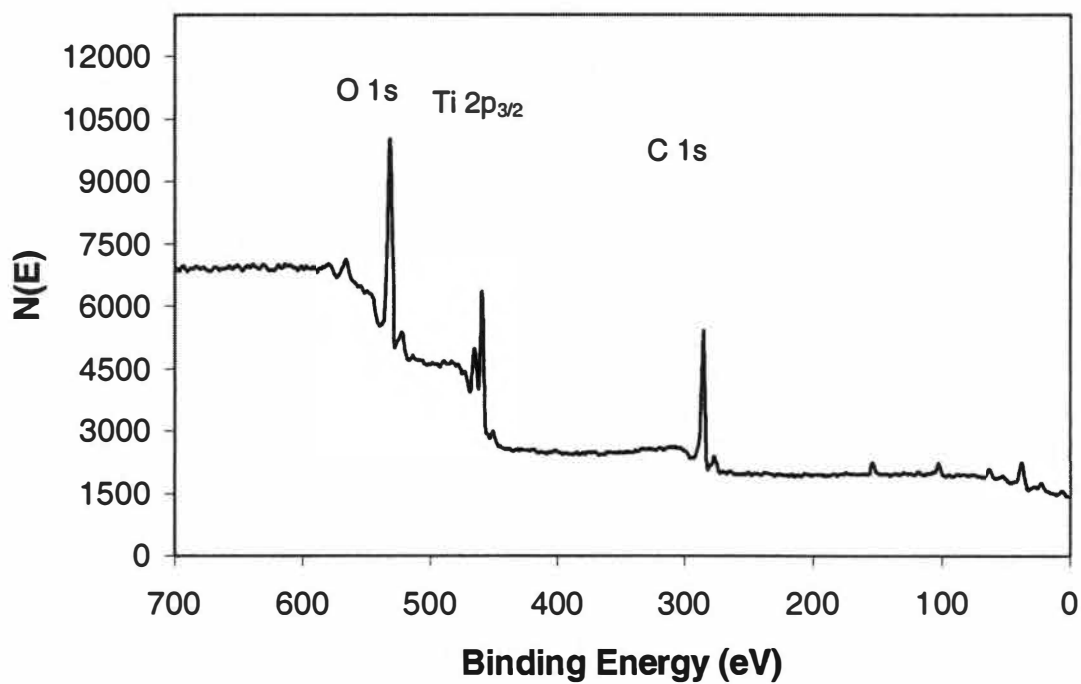


Figure 5.8 XPS spectrum of **Film 2**

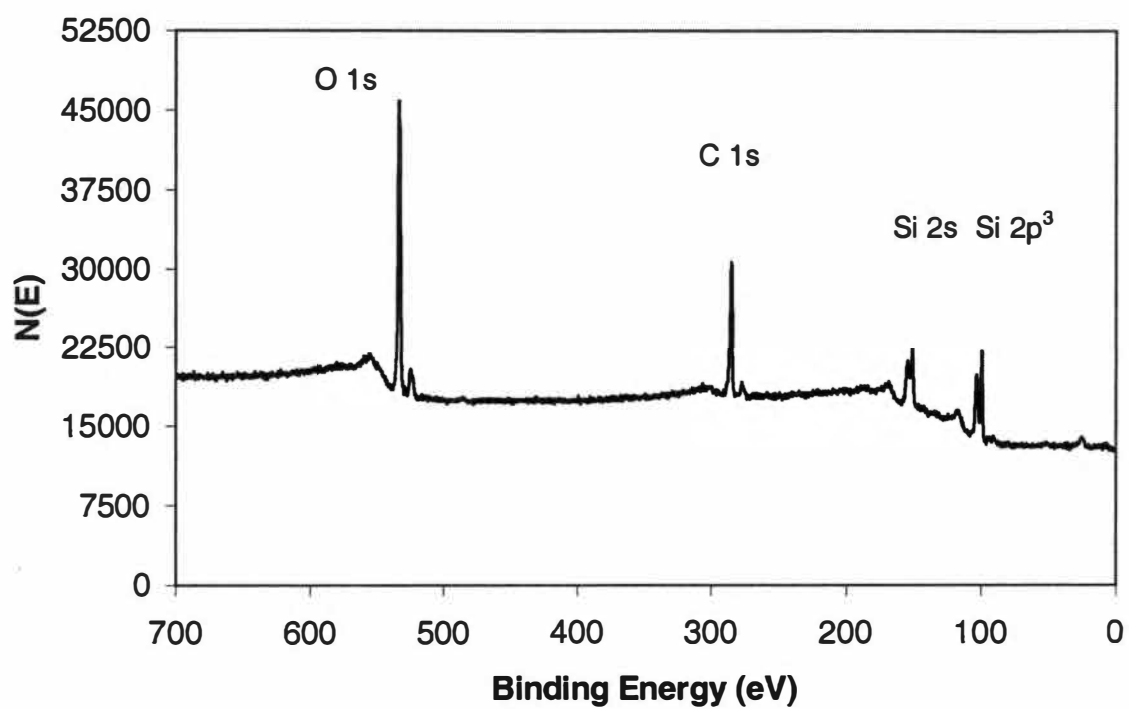


Figure 5.9 XPS spectrum of a cleaned Si wafer

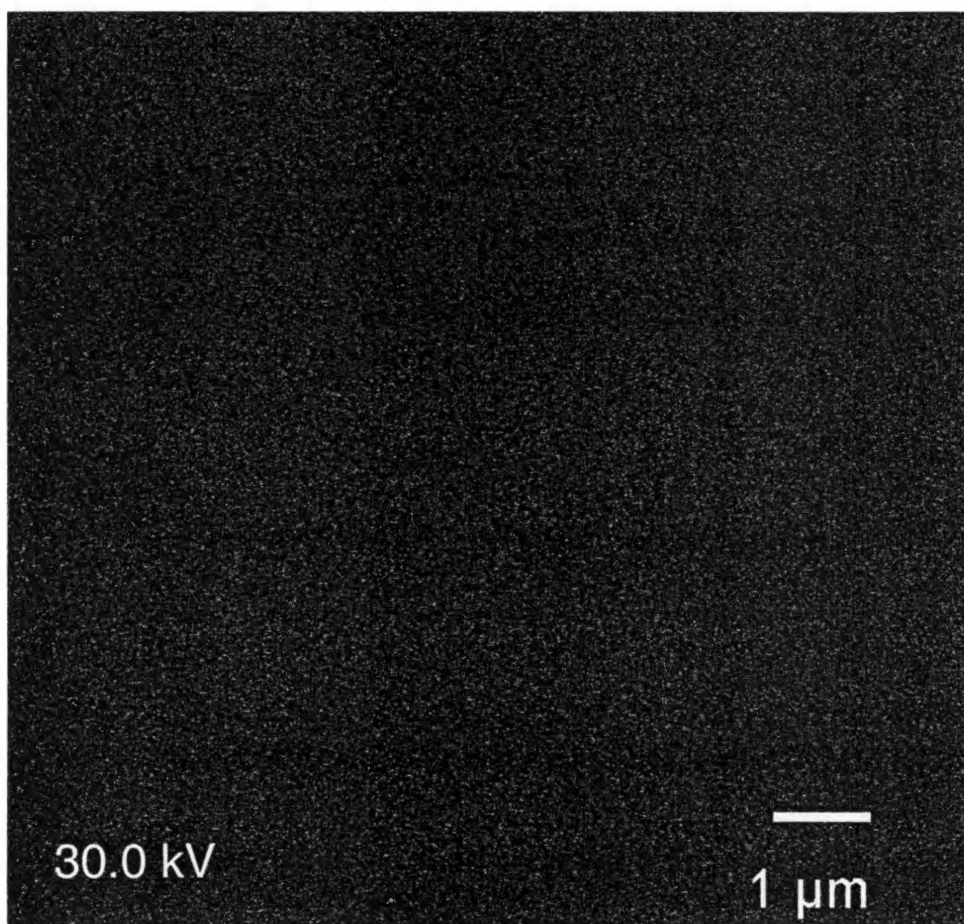


Figure 5.10 SEM of Film 2

and Ar were purchased from Air Liquide and used as received. TiCl_4 (Aldrich) was used as either a 1 M solution in toluene or as the solid $\text{TiCl}_4 \cdot 2\text{THF}$.¹⁸⁴ $\text{Ti}(\text{NMe}_2)_4$ was prepared by the literature procedure.¹⁷⁸

N-type Si(100) wafers were cleaned by the following process:

- (1) Degreased in hot (100 °C) tetrachloroethylene (TCE) for 15 min;
- (2) Rinsed with acetone and isopropanol followed by deionized water;
- (3) Soaked for 15 min in a 4:1 molar ratio solution of H_2SO_4 and H_2O_2 at 75 °C;
- (4) Dipped for 10 s in a 10% HF solution followed by a deionized water rinse;
- (5) Stored in deionized water until use, and then dried wafer by N_2 gas flow.

Ellipsometry measurements of film thickness and refractive index were made on a Gaertner Scientific L117 Ellipsometer. A monochromatic helium-neon light source with a fixed wavelength of 632.8 nm was used.

Infrared spectra to confirm the presence of TiO_2 and to determine the amount of surface organic contamination were recorded on a Bio-Rad FTS-60 with germanium optics. 1024 scans were acquired with a resolution of 8 cm^{-1} .

Powder X-ray diffraction data for annealed **Film 3** was collected on a model 1701 Phillips X-ray diffractometer. A Siemens D-5005 X-ray diffractometer with a KRISTALLOFLEX 760 X-ray generator was used to acquire data on **Film 2**.

X-ray photoelectron spectra (XPS) of **Films 2-4** were acquired on a Perkin-Elmer ESCA/SAM system with a PE Φ 32-095 model X-ray source 300 mA and 22

kV. The electron-energy analyzer was calibrated to the Au 4f_{7/2} line at 84 eV. The Mg K α excitation (1253.6 eV) from an Al/Mg dual anode (PE Φ 04-500 model) was used to excite photoemission. Photoelectrons were detected at an angle of 40° with respect to the plane of the surface. A differentially pumped ion gun (PE Φ 04-300 model) providing an Ar⁺ current of 15 mA at 3 keV was used for sputtering experiments. The base pressure in the XPS chamber was 10⁻⁹ torr, and the maximum pressure in the chamber during sputtering was 10⁻⁶ torr. The composition was determined according to the XPS multiplex spectrum. The pass energy was set for either 89.45 or 44.75 eV. The multiplex data were collected from 49 to 388 scans, depending on the film.

SEM images of the surface of the TiO₂ thin films were obtained using an Amray SEM 1830 microscope. This microscope contained a Kevex 48505 microscope interface module, an IXRF Systems Inc. 500 digital processor and EDS2000 microanalysis system software package.

5.3.2 Procedure for Thin Film Deposition in an Ultra-High-Vacuum (UHV)

CVD Chamber¹⁸⁵

In a typical experiment the Ti(NMe₂)₄ precursor was loaded into the glass bubbler in a glovebox. The bubbler was then connected to the CVD reactor. A Si(100) wafer in a ceramic holder was placed in the central heat zone area of the reactor through the loading lock. Ultra high purity Ar was used as the carrier gas. The flow rate of Ar was 100 sccm. O₂ (2% in Ar) was used as the reactive gas with

a flow rate of 500 sccm. $\text{Ti}(\text{NMe}_2)_4$ was evacuated at $-193\text{ }^\circ\text{C}$ before each deposition. After deposition of **Film 3**, the film was annealed at $600\text{ }^\circ\text{C}$ for 1 h in air.

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APPENDIX

Table A1 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in **2**. $U(\text{eq})$ is Defined as One Third of the Trace of the Orthogonalized U^{ij} Tensor.

	x	y	z	$U(\text{eq})$
Si(1)	4945(2)	8845(2)	3095(2)	69(1)
Si(2)	4661(3)	6213(3)	2851(2)	94(1)
Si(3)	7588(3)	10729(3)	2987(2)	98(1)
Si(4)	2868(3)	8470(3)	1757(2)	102(1)
C(1)	4477(11)	9789(10)	4481(5)	106(3)
C(7)	7824(13)	12826(12)	3257(12)	203(6)
C(10)	2970(14)	7527(15)	288(7)	175(5)
C(6)	9279(11)	11072(15)	4005(9)	162(4)
C(9)	3058(15)	10527(14)	1965(11)	189(5)
C(8)	783(12)	7103(15)	1889(10)	180(5)
C(5)	7958(12)	9944(14)	1593(8)	155(4)
C(4A)	3070(40)	4980(30)	3470(20)	127(11)
C(3)	5380(70)	5410(60)	1650(40)	260(30)
C(2)	5680(60)	6110(30)	4010(30)	220(30)
C(4)	2530(40)	4760(40)	2690(40)	400(50)

Table A1 (continued)

C(3A)	4220(70)	4860(50)	1450(30)	300(30)
C(2A)	6550(40)	6550(30)	3600(30)	210(20)

Table A2 Bond Distances (Å) in **2**

Si(1)-C(1)	1.906(7)	Si(1)-Si(3)	2.329(3)
Si(1)-Si(4)	2.338(3)	Si(1)-Si(2)	2.340(3)
Si(2)-C(3A)	1.74(4)	Si(2)-C(4)	1.76(3)
Si(2)-C(2)	1.80(3)	Si(2)-C(2A)	1.79(3)
Si(2)-C(4A)	1.84(3)	Si(2)-C(3)	1.81(4)
Si(3)-C(6)	1.827(9)	Si(3)-C(5)	1.839(9)
Si(3)-C(7)	1.840(10)	Si(4)-C(8)	1.828(10)
Si(4)-C(9)	1.835(10)	Si(4)-C(10)	1.854(10)
C(1)-C(1)#1	1.436(14)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, -y+2, -z+1

Table A3 Bond Angles (deg) in **2**

C(1)-Si(1)-Si(3)	111.4(3)	C(1)-Si(1)-Si(4)	102.9(3)
Si(3)-Si(1)-Si(4)	110.03(11)	C(1)-Si(1)-Si(2)	110.2(3)
Si(3)-Si(1)-Si(2)	111.58(12)	Si(4)-Si(1)-Si(2)	110.38(12)
C(3A)-Si(2)-C(4)	82(2)	C(3A)-Si(2)-C(2)	123.8(15)
C(4)-Si(2)-C(2)	102(2)	C(3A)-Si(2)-C(2A)	108.5(18)
C(4)-Si(2)-C(2A)	131.6(16)	C(2)-Si(2)-C(2A)	32.3(16)
C(3A)-Si(2)-C(4A)	106.8(16)	C(4)-Si(2)-C(4A)	32.8(17)
C(2)-Si(2)-C(4A)	70.7(19)	C(2A)-Si(2)-C(4A)	102.3(14)
C(3A)-Si(2)-C(3)	30(3)	C(4)-Si(2)-C(3)	111(2)
C(2)-Si(2)-C(3)	106(2)	C(2A)-Si(2)-C(3)	82.0(19)
C(4A)-Si(2)-C(3)	128.0(17)	C(3A)-Si(2)-Si(1)	114.0(10)
C(4)-Si(2)-Si(1)	108.1(9)	C(2)-Si(2)-Si(1)	117.3(8)
C(2A)-Si(2)-Si(1)	109.6(8)	C(4A)-Si(2)-Si(1)	114.9(7)
C(3)-Si(2)-Si(1)	111.8(14)	C(6)-Si(3)-C(5)	106.4(5)
C(6)-Si(3)-C(7)	107.4(6)	C(5)-Si(3)-C(7)	107.6(5)
C(6)-Si(3)-Si(1)	112.5(3)	C(5)-Si(3)-Si(1)	111.8(3)
C(7)-Si(3)-Si(1)	110.9(3)	C(8)-Si(4)-C(9)	107.3(6)
C(8)-Si(4)-C(10)	108.1(6)	C(9)-Si(4)-C(10)	106.5(5)
C(8)-Si(4)-Si(1)	110.6(4)	C(9)-Si(4)-Si(1)	110.5(4)

Table A3 (continued)

C(10)-Si(4)-Si(1)	113.5(4)	C(1)#1-C(1)-Si(1)	119.3(8)

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1, -y+2, -z+1$

Table A4 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in **2**. The Anisotropic Displacement Factor Exponent Takes the Form: $-2\pi^2[h^2a^{*2}U^{11} + \dots + 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	87(1)	64(1)	58(1)	25(1)	24(1)	39(1)
Si(2)	129(2)	79(1)	96(2)	45(1)	43(2)	62(1)
Si(3)	87(2)	96(2)	114(2)	57(2)	28(1)	39(1)
Si(4)	103(2)	94(2)	106(2)	36(1)	10(1)	53(2)
C(1)	146(8)	83(5)	81(5)	24(5)	23(5)	60(6)
C(7)	146(10)	118(9)	346(19)	109(11)	101(11)	55(8)
C(10)	201(12)	190(11)	102(8)	34(7)	-21(7)	98(10)
C(6)	105(7)	197(11)	157(9)	90(9)	21(7)	45(7)
C(9)	194(12)	164(11)	230(13)	76(10)	-4(10)	115(10)
C(8)	116(8)	194(12)	207(12)	76(10)	13(8)	70(8)
C(5)	124(8)	205(11)	150(9)	104(9)	58(7)	70(8)
C(4A)	170(30)	85(15)	180(20)	88(17)	100(20)	81(17)
C(3)	500(70)	150(30)	250(50)	110(30)	300(60)	210(40)
C(2)	430(80)	72(18)	140(20)	31(18)	0(30)	120(30)
C(4)	190(40)	280(40)	980(140)	470(80)	220(60)	150(30)
C(3A)	710(110)	170(30)	130(20)	100(20)	150(50)	280(60)
C(2A)	180(30)	160(20)	370(60)	180(30)	50(30)	99(19)

Table A5 Hydrogen Coordinates ($\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in **2**

	x	y	z	U(eq)
H(1A)	4506	10820	4515	80
H(1B)	3336	8988	4452	80
H(7A)	8920	13582	3209	80
H(7B)	7685	13292	3995	80
H(7C)	6990	12699	2707	80
H(10A)	2089	7407	-218	80
H(10B)	2839	6426	132	80
H(10C)	4035	8259	189	80
H(6A)	10340	11854	3929	80
H(6B)	9217	10004	3868	80
H(6C)	9170	11539	4752	80
H(9A)	2199	10352	1409	80
H(9B)	4139	11276	1894	80
H(9C)	2935	11030	2702	80
H(8A)	-53	6962	1334	80
H(8B)	670	7621	2626	80

Table A5 (continued)

H(8C)	637	6009	1778	80
H(5A)	9056	10750	1580	80
H(5B)	7132	9806	1032	80
H(5C)	7880	8865	1439	80
H(4AA)	3032	3924	3336	80
H(4AB)	1990	4747	3142	80
H(4AC)	3352	5628	4271	80
H(3A)	5246	4329	1574	80
H(3B)	6543	6204	1752	80
H(3C)	4734	5260	979	80
H(2A)	5465	4974	3816	80
H(2B)	5260	6429	4656	80
H(2C)	6868	6888	4190	80
H(4A)	2384	3673	2586	80
H(4B)	1861	4651	2046	80
H(4C)	2187	5183	3350	80
H(3AA)	4126	3815	1417	80
H(3AB)	5103	5403	1124	80
H(3AC)	3179	4624	1049	80

Table A5 (continued)

H(2AA)	6429	5470	3499	80
H(2AB)	6753	7210	4387	80
H(2AC)	7470	7154	3320	80

Table A6 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in **3**. $U(\text{eq})$ is Defined as One Third of the Trace of the Orthogonalized U^{ij} Tensor.

	x	y	z	$U(\text{eq})$
C(1)	2853(2)	2499(2)	8134(2)	61(1)
C(2)	2016(2)	3062(2)	8265(2)	60(1)
C(3)	1134(2)	3112(2)	7581(2)	61(1)
C(4)	5787(5)	2139(4)	7701(3)	185(3)
C(5)	6248(4)	1299(3)	9254(3)	148(2)
C(6)	4529(6)	775(4)	7959(5)	227(4)
C(7)	4322(5)	1490(4)	10875(3)	189(3)
C(8)	2356(7)	2257(6)	10504(5)	337(8)
C(9)	5928(3)	3368(3)	10084(3)	126(2)
C(10)	4863(5)	4084(3)	8546(3)	168(3)
C(11)	3809(4)	4024(3)	10051(4)	161(2)
C(12)	-770(4)	4000(3)	5598(2)	111(1)
C(13)	-1362(4)	2587(2)	6409(3)	126(2)
C(14)	-2467(3)	4025(3)	6671(3)	112(1)
C(15)	1615(6)	5088(4)	6769(3)	183(3)

Table A6 (continued)

C(16)	-292(5)	5746(2)	7386(4)	169(3)
C(17)	1598(4)	5330(2)	8530(3)	116(2)
C(18)	-1743(3)	4351(3)	8895(3)	134(2)
C(19)	280(3)	3817(3)	9766(2)	107(1)
C(20)	-1185(5)	2696(3)	8853(3)	156(2)
C(21)	2712(10)	820(5)	9679(4)	371(10)
Si(1)	3946(1)	2346(1)	8991(1)	53(1)
Si(2)	81(1)	3843(1)	7651(1)	50(1)
Si(3)	-1182(1)	3620(1)	6539(1)	68(1)
Si(4)	-664(1)	3677(1)	8836(1)	74(1)
Si(5)	768(1)	5051(1)	7585(1)	78(1)
Si(6)	3321(1)	1697(1)	10043(1)	84(1)
Si(7)	5170(1)	1594(1)	8468(1)	88(1)
Si(8)	4676(1)	3499(1)	9426(1)	88(1)

Table A7 Bond Distances (Å) in **3**

Si(1)-C(1)	1.902(3)	Si(1)-Si(7)	2.3401(13)
Si(1)-Si(8)	2.3400(13)	Si(1)-Si(6)	2.3445(13)
Si(2)-C(3)	1.905(3)	Si(2)-Si(5)	2.3414(12)
Si(2)-Si(4)	2.3450(12)	Si(2)-Si(3)	2.3493(11)
Si(3)-C(14)	1.859(4)	Si(3)-C(12)	1.862(4)
Si(3)-C(13)	1.865(4)	Si(4)-C(18)	1.860(4)
Si(4)-C(19)	1.868(4)	Si(4)-C(20)	1.878(5)
Si(5)-C(16)	1.848(5)	Si(5)-C(17)	1.862(4)
Si(5)-C(15)	1.870(5)	Si(6)-C(7)	1.815(5)
Si(6)-C(21)	1.821(7)	Si(6)-C(8)	1.851(7)
Si(7)-C(6)	1.835(6)	Si(7)-C(5)	1.866(4)
Si(7)-C(4)	1.878(5)	C(2)-C(3)	1.513(4)
C(2)-C(1)	1.518(4)	Si(8)-C(10)	1.852(5)
Si(8)-C(9)	1.855(4)	Si(8)-C(11)	1.888(5)

Table A8 Bond Angles (deg) in **3**

C(1)-Si(1)-Si(7)	105.91(9)	C(1)-Si(1)-Si(8)	109.90(10)
Si(7)-Si(1)-Si(8)	110.69(5)	C(1)-Si(1)-Si(6)	110.00(11)
Si(7)-Si(1)-Si(6)	108.75(5)	Si(8)-Si(1)-Si(6)	111.43(5)
C(3)-Si(2)-Si(5)	110.15(11)	C(3)-Si(2)-Si(4)	110.39(10)
Si(5)-Si(2)-Si(4)	111.09(5)	C(3)-Si(2)-Si(3)	105.42(9)
Si(5)-Si(2)-Si(3)	110.37(5)	C(14)-Si(3)-C(12)	108.9(2)
C(14)-Si(3)-C(13)	107.3(2)	C(12)-Si(3)-C(13)	107.8(2)
C(14)-Si(3)-Si(2)	112.44(14)	C(12)-Si(3)-Si(2)	111.31(14)
C(13)-Si(3)-Si(2)	108.85(14)	C(18)-Si(4)-C(19)	106.5(2)
C(18)-Si(4)-C(20)	109.0(3)	C(18)-Si(4)-Si(2)	111.30(16)
C(19)-Si(4)-C(20)	108.0(2)	C(20)-Si(4)-Si(2)	108.72(16)
C(19)-Si(4)-Si(2)	113.14(14)	C(16)-Si(5)-C(15)	109.9(3)
C(16)-Si(5)-C(17)	107.9(2)	C(16)-Si(5)-Si(2)	110.20(18)
C(17)-Si(5)-C(15)	106.5(3)	C(15)-Si(5)-Si(2)	109.45(19)
C(17)-Si(5)-Si(2)	112.73(14)	C(7)-Si(6)-C(8)	104.1(4)
C(7)-Si(6)-C(21)	108.5(5)	C(7)-Si(6)-Si(1)	113.34(19)
C(21)-Si(6)-C(8)	108.2(6)	C(8)-Si(6)-Si(1)	111.8(2)
C(21)-Si(6)-Si(1)	110.6(2)	C(6)-Si(7)-C(4)	107.6(4)
C(6)-Si(7)-C(5)	110.9(3)	C(5)-Si(7)-C(4)	106.3(3)

Table A8 (continued)

C(6)-Si(7)-Si(1)	110.0(2)	C(5)-Si(7)-Si(1)	112.29(16)
C(4)-Si(7)-Si(1)	109.6(2)	C(3)-C(2)-C(1)	114.4(2)
C(2)-C(3)-Si(2)	118.1(2)	C(2)-C(1)-Si(1)	117.51(19)
C(10)-Si(8)-C(9)	110.3(3)	C(10)-Si(8)-C(11)	108.5(3)
C(9)-Si(8)-C(11)	105.8(2)	C(10)-Si(8)-Si(1)	109.73(18)
C(9)-Si(8)-Si(1)	111.16(16)	C(11)-Si(8)-Si(1)	111.21(18)

Table A9 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in **3**. The Anisotropic Displacement Factor Exponent Takes the Form: $-2\pi^2[h^2a^{*2}U^{11} + \dots + 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	55(2)	68(2)	57(2)	-3(1)	0(1)	13(2)
C(2)	52(2)	69(2)	56(2)	-6(1)	-1(1)	9(2)
C(3)	53(2)	67(2)	60(2)	-6(1)	-3(1)	13(2)
C(4)	142(5)	285(9)	146(5)	77(5)	85(4)	74(5)
C(5)	107(4)	207(6)	128(4)	15(4)	5(3)	93(4)
C(6)	182(7)	178(6)	323(10)	-160(7)	41(7)	8(5)
C(7)	149(5)	292(8)	119(4)	105(5)	-11(4)	-18(5)
C(8)	343(12)	428(14)	301(10)	254(11)	263(10)	249(11)
C(9)	82(3)	145(4)	139(4)	-4(3)	-30(3)	-27(3)
C(10)	213(7)	117(4)	163(5)	45(4)	-20(5)	-77(4)
C(11)	126(4)	139(4)	207(6)	-100(4)	-18(4)	19(4)
C(12)	107(3)	149(4)	73(2)	6(2)	-3(2)	-5(3)
C(13)	146(4)	88(3)	128(4)	-26(3)	-47(3)	-16(3)
C(14)	64(2)	154(4)	110(3)	-5(3)	-16(2)	29(3)
C(15)	225(7)	195(6)	143(5)	-4(4)	82(5)	-114(6)
C(16)	146(5)	68(3)	272(7)	24(4)	-49(5)	7(3)

Table A9 (continued)

C(17)	124(4)	76(3)	139(4)	-19(2)	-16(3)	-18(3)
C(18)	83(3)	211(6)	112(3)	-31(3)	30(3)	37(3)
C(19)	107(3)	148(4)	67(2)	-10(2)	15(2)	23(3)
C(20)	212(6)	137(4)	133(4)	4(3)	69(4)	-82(4)
C(21)	620(20)	345(13)	160(6)	-18(7)	84(10)	-381(15)
Si(1)	46(1)	59(1)	54(1)	3(1)	3(1)	3(1)
Si(2)	46(1)	51(1)	52(1)	-1(1)	3(1)	3(1)
Si(3)	61(1)	71(1)	66(1)	-3(1)	-12(1)	8(1)
Si(4)	70(1)	90(1)	65(1)	-2(1)	20(1)	-5(1)
Si(5)	86(1)	58(1)	88(1)	6(1)	4(1)	-14(1)
Si(6)	79(1)	106(1)	66(1)	22(1)	8(1)	-11(1)
Si(7)	72(1)	109(1)	81(1)	-1(1)	12(1)	33(1)
Si(8)	82(1)	72(1)	102(1)	-1(1)	-19(1)	-14(1)

Table A10 Hydrogen Coordinates ($\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in **3**

	x	y	z	U(eq)
H(1A)	3160	2656	7666	73
H(1B)	2519	2019	8006	73
H(2A)	1732	2928	8751	72
H(2B)	2332	3553	8348	72
H(3A)	802	2625	7522	73
H(3B)	1433	3208	7091	73
H(4A)	6153	2562	7956	278
H(4B)	5259	2312	7287	278
H(4C)	6266	1823	7470	278
H(5A)	6035	869	9534	222
H(5B)	6414	1703	9628	222
H(5C)	6849	1175	9005	222
H(6A)	5020	500	7694	341
H(6B)	3965	939	7568	341
H(6C)	4265	458	8347	341
H(7A)	4736	1930	11007	284

Table A10 (continued)

H(7B)	4755	1092	10725	284
H(7C)	4003	1338	11333	284
H(8A)	2104	1969	10921	506
H(8B)	1786	2383	10101	506
H(8C)	2676	2708	10728	506
H(9A)	6416	3128	9786	189
H(9B)	5821	3060	10535	189
H(9C)	6196	3847	10272	189
H(10A)	4855	4604	8692	253
H(10B)	4314	3987	8116	253
H(10C)	5519	3965	8373	253
H(11A)	4068	4524	10148	242
H(11B)	3802	3770	10555	242
H(11C)	3117	4044	9769	242
H(12A)	-191	3715	5462	167
H(12B)	-569	4515	5678	167
H(12C)	-1336	3964	5169	167
H(13A)	-1539	2373	6897	189
H(13B)	-729	2366	6285	189

Table A10 (continued)

H(13C)	-1910	2491	5978	189
H(14A)	-2939	3960	6185	168
H(14B)	-2389	4550	6790	168
H(14C)	-2735	3775	7105	168
H(15A)	1381	4724	6365	274
H(15B)	2319	4981	6991	274
H(15C)	1579	5580	6534	274
H(16A)	-672	5767	7838	253
H(16B)	-751	5600	6915	253
H(16C)	-3	6230	7302	253
H(17A)	1916	5806	8454	174
H(17B)	2128	4959	8666	174
H(17C)	1178	5369	8957	174
H(18A)	-2003	4292	9400	200
H(18B)	-2291	4255	8464	200
H(18C)	-1493	4854	8850	200
H(19A)	654	4276	9723	161
H(19B)	759	3405	9829	161
H(19C)	-89	3842	10224	161

Table A10 (continued)

H(20A)	-1566	2640	9301	235
H(20B)	-619	2346	8904	235
H(20C)	-1637	2600	8363	235
H(21A)	2178	690	9999	557
H(21B)	3224	429	9719	557
H(21C)	2411	877	9128	557

Table A11 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in **5**. $U(\text{eq})$ is Defined as One Third of the Trace of the Orthogonalized U^{ij} Tensor.

	x	y	z	U(eq)
K(1)	7518(1)	7984(1)	3472(1)	37(1)
K(2)	3918(1)	8185(1)	8459(1)	43(1)
Si(1)	7137(1)	6203(1)	5681(1)	35(1)
Si(3)	9754(1)	7550(1)	5523(1)	38(1)
Si(2)	8836(1)	6689(1)	4972(1)	37(1)
Si(4)	4681(1)	6717(1)	9963(1)	40(1)
Si(5)	3416(1)	7322(1)	10748(1)	46(1)
Si(6)	6919(1)	6664(1)	10219(1)	47(1)
O(4)	7630(2)	9872(2)	3547(1)	42(1)
O(5)	5097(2)	9363(2)	3772(1)	40(1)
O(2)	9485(2)	7039(2)	2774(1)	44(1)
O(1)	6958(2)	6555(2)	2889(1)	45(1)
O(3)	9710(2)	8889(2)	2880(1)	44(1)
O(6)	5063(2)	7466(2)	3653(1)	42(1)
O(8)	4578(3)	10139(2)	8171(1)	61(1)

Table A11 (continued)

O(7)	6504(3)	8448(2)	7975(1)	58(1)
O(9)	2102(3)	9802(2)	8741(1)	62(1)
O(11)	2771(3)	6890(2)	8061(1)	69(1)
O(12)	5379(3)	7061(2)	7643(1)	57(1)
O(10)	915(3)	8399(2)	8473(1)	66(1)
C(10)	9920(4)	9548(3)	3217(2)	56(1)
C(3)	3889(3)	8128(3)	3812(2)	49(1)
C(2)	4322(4)	8727(3)	4170(2)	51(1)
C(8)	10631(3)	7430(3)	2524(2)	47(1)
C(4)	4747(4)	6817(3)	3338(2)	55(1)
C(6)	8207(4)	5850(3)	2827(2)	53(1)
C(7)	9175(4)	6415(3)	2439(2)	49(1)
C(11)	8623(4)	10347(3)	3195(2)	53(1)
C(9)	10880(3)	8053(3)	2919(2)	49(1)
C(16)	1333(5)	6991(4)	8065(2)	84(2)
C(12)	6416(4)	10571(3)	3649(2)	54(1)
C(14)	504(4)	8793(4)	8989(2)	80(2)
C(5)	6028(4)	6042(3)	3287(2)	58(1)
C(1)	5534(4)	9969(3)	4087(2)	56(1)

Table A11 (continued)

C(21)	6721(4)	9439(4)	7775(2)	75(1)
C(24)	2363(5)	10781(4)	8540(2)	74(1)
C(15)	782(5)	7387(4)	8597(2)	85(2)
C(20)	7184(4)	7863(4)	7579(2)	76(2)
C(17)	3433(6)	6423(4)	7615(2)	84(2)
C(23)	3863(5)	10663(4)	8596(2)	74(1)
C(22)	6024(4)	10005(4)	8218(2)	74(1)
C(13)	682(4)	9842(4)	8808(2)	75(1)
C(19)	6794(5)	6875(4)	7771(2)	83(2)
C(18)	4943(6)	6151(3)	7753(2)	81(2)
C(25)	10207(3)	5387(3)	5133(2)	40(1)
C(32)	4712(4)	5280(3)	10245(2)	45(1)
C(28)	7795(4)	5139(3)	6431(2)	48(1)
C(27)	6012(3)	7276(3)	5957(2)	47(1)
C(26)	5896(4)	5723(3)	5318(2)	52(1)
C(35)	4095(4)	6906(3)	11597(2)	62(1)
C(29)	8710(4)	8909(3)	5397(2)	63(1)
C(30)	10040(4)	7033(3)	6413(2)	62(1)
C(33)	1720(4)	6956(4)	10839(2)	75(1)

Table A11 (continued)

C(34)	2971(4)	8761(3)	10523(2)	67(1)
C(31)	11498(4)	7683(4)	5210(2)	78(1)
C(38)	8195(4)	6167(4)	9664(2)	84(2)
C(36)	7160(5)	7946(4)	10151(3)	99(2)
C(37)	7623(5)	5807(5)	11027(2)	106(2)

Table A12 Bond Distances (Å) in **5**

K(1)-O(6)	2.732(2)	K(1)-O(2)	2.761(2)
K(1)-O(4)	2.775(2)	K(1)-O(3)	2.889(2)
K(1)-O(1)	2.897(2)	K(1)-O(5)	2.892(2)
K(1)-Si(2)	3.4197(12)	K(1)-C(2)	3.533(4)
K(2)-O(9)	2.756(3)	K(2)-O(11)	2.780(3)
K(2)-O(7)	2.828(3)	K(2)-O(12)	2.861(3)
K(2)-O(8)	2.903(3)	K(2)-O(10)	2.961(3)
K(2)-Si(4)	3.3550(13)	Si(1)-C(26)	1.890(3)
Si(1)-C(28)	1.890(3)	Si(1)-C(27)	1.893(4)
Si(1)-Si(2)	2.3430(14)	Si(3)-C(31)	1.884(4)
Si(3)-C(30)	1.890(4)	Si(3)-C(29)	1.894(4)
Si(3)-Si(2)	2.3395(13)	Si(2)-C(25)	1.953(3)
Si(4)-C(32)	1.944(4)	Si(4)-Si(6)	2.3339(14)
Si(4)-Si(5)	2.3332(14)	Si(5)-C(34)	1.893(4)
Si(5)-C(33)	1.894(4)	Si(5)-C(35)	1.899(4)
Si(6)-C(36)	1.864(5)	Si(6)-C(38)	1.876(4)
Si(6)-C(37)	1.887(4)	O(4)-C(11)	1.414(4)
O(4)-C(12)	1.419(4)	O(5)-C(2)	1.416(4)
O(5)-C(1)	1.423(4)	O(2)-C(7)	1.417(4)

Table A12 (continued)

O(2)-C(8)	1.420(4)	O(1)-C(5)	1.431(4)
O(1)-C(6)	1.422(4)	O(3)-C(10)	1.424(4)
O(3)-C(9)	1.428(4)	O(6)-C(4)	1.418(4)
O(6)-C(3)	1.409(4)	O(8)-C(23)	1.423(5)
O(8)-C(22)	1.426(5)	O(7)-C(20)	1.414(5)
O(7)-C(21)	1.417(5)	O(9)-C(13)	1.417(5)
O(9)-C(24)	1.420(5)	O(11)-C(17)	1.394(5)
O(11)-C(16)	1.419(5)	O(12)-C(19)	1.411(5)
O(12)-C(18)	1.423(5)	O(10)-C(14)	1.412(5)
O(10)-C(15)	1.424(5)	C(10)-C(11)	1.487(5)
C(3)-C(2)	1.479(5)	C(8)-C(9)	1.491(5)
C(4)-C(5)	1.490(5)	C(6)-C(7)	1.490(5)
C(16)-C(15)	1.472(7)	C(12)-C(1)	1.500(5)
C(14)-C(13)	1.482(6)	C(21)-C(22)	1.483(6)
C(24)-C(23)	1.485(6)	C(20)-C(19)	1.490(7)
C(17)-C(18)	1.496(6)	C(25)-C(25)#1	1.546(6)
C(32)-C(32)#2	1.532(6)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+2, -y+1, -z+1 #2 -x+1, -y+1, -z+2

Table A13 Bond Angles (deg) in **5**

O(6)-K(1)-O(2)	118.35(7)	Si(3)-Si(2)-K(1)	118.44(5)
O(6)-K(1)-O(4)	118.95(7)	Si(1)-Si(2)-K(1)	111.84(4)
O(2)-K(1)-O(4)	118.26(7)	C(32)-Si(4)-Si(6)	101.37(12)
O(6)-K(1)-O(3)	161.43(7)	C(32)-Si(4)-Si(5)	102.79(11)
O(2)-K(1)-O(3)	58.93(7)	Si(6)-Si(4)-Si(5)	101.99(5)
O(4)-K(1)-O(3)	59.38(7)	C(32)-Si(4)-K(2)	122.74(10)
O(6)-K(1)-O(1)	59.54(7)	Si(6)-Si(4)-K(2)	109.25(5)
O(2)-K(1)-O(1)	58.88(7)	Si(5)-Si(4)-K(2)	115.95(5)
O(4)-K(1)-O(1)	156.45(7)	C(34)-Si(5)-C(33)	106.2(2)
O(3)-K(1)-O(1)	113.68(7)	C(34)-Si(5)-C(35)	103.54(18)
O(6)-K(1)-O(5)	59.68(7)	C(33)-Si(5)-C(35)	103.39(19)
O(2)-K(1)-O(5)	160.45(7)	C(34)-Si(5)-Si(4)	111.80(14)
O(4)-K(1)-O(5)	59.29(6)	C(33)-Si(5)-Si(4)	109.15(14)
O(3)-K(1)-O(5)	115.89(7)	C(35)-Si(5)-Si(4)	121.55(14)
O(1)-K(1)-O(5)	114.59(7)	C(36)-Si(6)-C(38)	105.1(2)
O(6)-K(1)-Si(2)	96.77(5)	C(36)-Si(6)-C(37)	106.6(3)
O(2)-K(1)-Si(2)	99.80(5)	C(38)-Si(6)-C(37)	102.8(2)
O(4)-K(1)-Si(2)	94.55(5)	C(36)-Si(6)-Si(4)	112.80(16)
O(3)-K(1)-Si(2)	101.80(5)	C(38)-Si(6)-Si(4)	111.51(14)
O(1)-K(1)-Si(2)	108.99(5)	C(37)-Si(6)-Si(4)	116.94(16)

Table A13 (continued)

O(5)-K(1)-Si(2)	99.74(5)	C(11)-O(4)-C(12)	113.4(3)
O(6)-K(1)-C(2)	41.67(8)	C(11)-O(4)-K(1)	119.4(2)
O(2)-K(1)-C(2)	159.77(8)	C(12)-O(4)-K(1)	120.24(19)
O(4)-K(1)-C(2)	79.33(8)	C(2)-O(5)-C(1)	112.3(3)
O(3)-K(1)-C(2)	138.00(8)	C(2)-O(5)-K(1)	104.97(19)
O(1)-K(1)-C(2)	100.95(8)	C(1)-O(5)-K(1)	107.89(19)
O(5)-K(1)-C(2)	22.77(7)	C(7)-O(2)-C(8)	112.6(3)
Si(2)-K(1)-C(2)	87.88(7)	C(7)-O(2)-K(1)	121.25(19)
O(9)-K(2)-O(11)	116.41(9)	C(8)-O(2)-K(1)	121.8(2)
O(9)-K(2)-O(7)	117.99(9)	C(5)-O(1)-C(6)	110.8(3)
O(11)-K(2)-O(7)	117.92(9)	C(5)-O(1)-K(1)	107.8(2)
O(9)-K(2)-O(12)	155.50(8)	C(6)-O(1)-K(1)	109.60(19)
O(11)-K(2)-O(12)	58.98(9)	C(10)-O(3)-C(9)	112.4(3)
O(7)-K(2)-O(12)	59.04(8)	C(10)-O(3)-K(1)	108.62(19)
O(9)-K(2)-O(8)	59.53(9)	C(9)-O(3)-K(1)	105.4(2)
O(11)-K(2)-O(8)	148.39(8)	C(4)-O(6)-C(3)	113.2(3)
O(7)-K(2)-O(8)	58.63(9)	C(4)-O(6)-K(1)	120.8(2)
O(12)-K(2)-O(8)	110.37(9)	C(3)-O(6)-K(1)	120.45(19)
O(9)-K(2)-O(10)	58.39(9)	C(23)-O(8)-C(22)	111.1(3)

Table A13 (continued)

O(11)-K(2)-O(10)	58.35(10)	C(23)-O(8)-K(2)	108.8(2)
O(7)-K(2)-O(10)	158.39(8)	C(22)-O(8)-K(2)	110.6(2)
O(12)-K(2)-O(10)	114.26(9)	C(20)-O(7)-C(21)	111.5(4)
O(8)-K(2)-O(10)	111.99(9)	C(20)-O(7)-K(2)	118.4(2)
O(9)-K(2)-Si(4)	97.00(6)	C(21)-O(7)-K(2)	119.1(2)
O(11)-K(2)-Si(4)	97.81(6)	C(13)-O(9)-C(24)	112.8(3)
O(7)-K(2)-Si(4)	103.01(6)	C(13)-O(9)-K(2)	120.9(3)
O(12)-K(2)-Si(4)	107.41(6)	C(24)-O(9)-K(2)	120.2(3)
O(8)-K(2)-Si(4)	113.72(6)	C(17)-O(11)-C(16)	112.5(3)
O(10)-K(2)-Si(4)	98.60(6)	C(17)-O(11)-K(2)	120.5(3)
C(26)-Si(1)-C(28)	104.28(17)	C(16)-O(11)-K(2)	121.9(3)
C(26)-Si(1)-C(27)	104.56(17)	C(19)-O(12)-C(18)	112.8(4)
C(28)-Si(1)-C(27)	105.44(17)	C(19)-O(12)-K(2)	107.3(2)
C(26)-Si(1)-Si(2)	112.50(13)	C(18)-O(12)-K(2)	109.2(2)
C(28)-Si(1)-Si(2)	115.22(12)	C(14)-O(10)-C(15)	112.7(4)
C(27)-Si(1)-Si(2)	113.79(13)	C(14)-O(10)-K(2)	102.3(2)
C(31)-Si(3)-C(30)	103.8(2)	C(15)-O(10)-K(2)	104.5(2)
C(31)-Si(3)-C(29)	104.1(2)	O(3)-C(10)-C(11)	108.9(3)
C(30)-Si(3)-C(29)	103.67(19)	O(6)-C(3)-C(2)	109.0(3)

Table A13 (continued)

C(31)-Si(3)-Si(2)	110.22(15)	O(5)-C(2)-C(3)	109.5(3)
C(30)-Si(3)-Si(2)	120.78(13)	O(5)-C(2)-K(1)	52.26(15)
C(29)-Si(3)-Si(2)	112.73(12)	C(3)-C(2)-K(1)	82.7(2)
C(25)-Si(2)-Si(3)	102.67(10)	O(2)-C(8)-C(9)	108.0(3)
C(25)-Si(2)-Si(1)	100.18(12)	O(6)-C(4)-C(5)	108.9(3)
Si(3)-Si(2)-Si(1)	99.95(5)	O(1)-C(6)-C(7)	109.3(3)
C(25)-Si(2)-K(1)	120.45(10)	O(2)-C(7)-C(6)	108.1(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2, -y+1, -z+1 #2 -x+1, -y+1, -z+2

Table A14 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in **5**. The Anisotropic Displacement Factor Exponent Takes the Form: $-2\pi^2[h^2a^{*2}U^{11} + \dots + 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
K(1)	35(1)	40(1)	40(1)	-16(1)	4(1)	-11(1)
K(2)	48(1)	48(1)	36(1)	-10(1)	-1(1)	-17(1)
Si(1)	39(1)	32(1)	34(1)	-10(1)	-1(1)	-8(1)
Si(3)	38(1)	37(1)	41(1)	-14(1)	2(1)	-12(1)
Si(2)	43(1)	37(1)	32(1)	-14(1)	0(1)	-8(1)
Si(4)	49(1)	42(1)	31(1)	-12(1)	3(1)	-15(1)
Si(5)	51(1)	55(1)	37(1)	-21(1)	4(1)	-14(1)
Si(6)	51(1)	57(1)	35(1)	-10(1)	2(1)	-22(1)
O(4)	40(1)	37(2)	51(2)	-13(1)	8(1)	-12(1)
O(5)	40(1)	41(2)	39(1)	-13(1)	3(1)	-10(1)
O(2)	42(1)	54(2)	39(1)	-20(1)	7(1)	-9(1)
O(1)	46(1)	41(2)	48(2)	-17(1)	1(1)	-10(1)
O(3)	37(1)	48(2)	46(2)	-12(1)	0(1)	-10(1)
O(6)	39(1)	52(2)	42(1)	-18(1)	0(1)	-17(1)
O(8)	70(2)	60(2)	56(2)	-17(2)	1(1)	-26(2)
O(7)	55(2)	77(2)	44(2)	-17(2)	5(1)	-23(2)

Table A14 (continued)

O(9)	58(2)	60(2)	56(2)	-10(2)	-3(1)	-1(2)
O(11)	95(2)	82(2)	45(2)	-18(2)	-7(2)	-48(2)
O(12)	72(2)	55(2)	41(2)	-15(1)	1(1)	-11(2)
O(10)	60(2)	84(2)	46(2)	3(2)	3(1)	-33(2)
C(10)	42(2)	66(3)	72(3)	-26(2)	10(2)	-28(2)
C(3)	41(2)	51(3)	60(3)	-17(2)	10(2)	-19(2)
C(2)	51(2)	52(3)	55(3)	-22(2)	20(2)	-15(2)
C(8)	38(2)	49(2)	44(2)	-10(2)	7(2)	0(2)
C(4)	51(2)	64(3)	66(3)	-32(2)	3(2)	-27(2)
C(6)	60(2)	43(2)	56(3)	-25(2)	-5(2)	-2(2)
C(7)	51(2)	54(3)	45(2)	-26(2)	2(2)	-4(2)
C(11)	58(2)	47(3)	60(3)	-16(2)	12(2)	-28(2)
C(9)	34(2)	54(3)	53(2)	-10(2)	0(2)	-7(2)
C(16)	107(4)	95(4)	60(3)	0(3)	-23(3)	-67(3)
C(12)	52(2)	38(2)	78(3)	-24(2)	6(2)	-12(2)
C(14)	55(3)	110(5)	51(3)	0(3)	12(2)	-15(3)
C(5)	66(3)	49(3)	72(3)	-27(2)	4(2)	-25(2)
C(1)	53(2)	54(3)	71(3)	-33(2)	10(2)	-14(2)
C(21)	71(3)	107(4)	59(3)	-17(3)	11(2)	-55(3)

Table A14 (continued)

C(24)	89(3)	58(3)	70(3)	-23(3)	-10(3)	0(3)
C(15)	79(3)	107(4)	64(3)	15(3)	-9(3)	-63(3)
C(20)	47(2)	124(5)	63(3)	-42(3)	8(2)	-15(3)
C(17)	138(5)	80(4)	58(3)	-24(3)	-3(3)	-64(4)
C(23)	90(3)	58(3)	80(3)	-30(3)	-7(3)	-18(3)
C(22)	81(3)	84(4)	67(3)	-15(3)	1(3)	-49(3)
C(13)	59(3)	98(4)	50(3)	-16(3)	11(2)	3(3)
C(19)	81(3)	92(4)	63(3)	-34(3)	-10(3)	15(3)
C(18)	160(5)	40(3)	45(3)	-18(2)	22(3)	-27(3)
C(25)	43(2)	44(2)	35(2)	-18(2)	0(2)	-7(2)
C(32)	58(2)	49(2)	33(2)	-17(2)	12(2)	-18(2)
C(28)	54(2)	39(2)	44(2)	-2(2)	1(2)	-10(2)
C(27)	50(2)	42(2)	44(2)	-10(2)	2(2)	-6(2)
C(26)	53(2)	46(2)	59(3)	-14(2)	-8(2)	-17(2)
C(35)	73(3)	77(3)	45(2)	-27(2)	5(2)	-24(2)
C(29)	66(3)	45(3)	83(3)	-26(2)	-8(2)	-13(2)
C(30)	86(3)	61(3)	48(3)	-19(2)	-11(2)	-28(2)
C(33)	68(3)	118(4)	57(3)	-43(3)	13(2)	-39(3)
C(34)	77(3)	60(3)	66(3)	-36(2)	-8(2)	-1(2)

Table A14 (continued)

C(31)	56(3)	103(4)	93(4)	-42(3)	20(2)	-38(3)
C(38)	58(3)	120(5)	93(4)	-55(3)	18(3)	-33(3)
C(36)	89(4)	87(4)	149(5)	-59(4)	-2(3)	-40(3)
C(37)	65(3)	158(6)	62(3)	18(3)	-14(3)	-29(3)

Table A15 Hydrogen Coordinates ($\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in 5

	x	y	z	U(eq)
H(10A)	10667	9867	3021	67
H(10B)	10188	9155	3664	67
H(3A)	3274	7729	4074	59
H(3B)	3378	8590	3420	59
H(2A)	3503	9146	4319	62
H(2B)	4885	8262	4546	62
H(8A)	10440	7856	2077	56
H(8B)	11453	6864	2537	56
H(4A)	4360	7220	2909	66
H(4B)	4055	6476	3580	66
H(6A)	8022	5371	2617	63
H(6B)	8620	5452	3252	63
H(7A)	10027	5931	2368	59
H(7B)	8749	6839	2020	59
H(11A)	8779	10862	3381	64
H(11B)	8299	10694	2749	64

Table A15 (continued)

H(9A)	11056	7626	3367	59
H(9B)	11700	8311	2766	59
H(16A)	1139	6322	8123	100
H(16B)	904	7467	7658	100
H(12A)	5922	10965	3240	65
H(12B)	6648	11053	3842	65
H(14A)	1072	8363	9372	95
H(14B)	-470	8799	9086	95
H(5A)	6450	5669	3714	70
H(5B)	5814	5546	3102	70
H(1A)	6063	9527	4479	67
H(1B)	4725	10435	4209	67
H(21A)	6346	9801	7338	90
H(21B)	7718	9396	7772	90
H(24A)	1857	11196	8809	89
H(24B)	2047	11133	8094	89
H(15A)	-198	7381	8653	102
H(15B)	1289	6946	8994	102
H(20A)	8191	7741	7623	91

Table A15 (continued)

H(20B)	6914	8233	7129	91
H(17A)	3220	6894	7179	101
H(17B)	3124	5804	7648	101
H(23A)	4053	11341	8495	89
H(23B)	4185	10276	9038	89
H(22A)	6353	9620	8659	88
H(22B)	6238	10676	8107	88
H(13A)	186	10251	8402	90
H(13B)	299	10168	9139	90
H(19A)	7336	6425	7532	99
H(19B)	6993	6532	8231	99
H(18A)	5140	5728	8201	97
H(18B)	5447	5754	7475	97
H(25A)	11083	5510	4940	48
H(25B)	10369	5084	5597	48
H(32A)	5274	4947	10641	54
H(32B)	3764	5212	10346	54
H(28A)	8303	5379	6693	73
H(28B)	8405	4561	6320	73

Table A15 (continued)

H(28C)	7017	4925	6670	73
H(27A)	5623	7851	5587	70
H(27B)	6564	7492	6215	70
H(27C)	5266	7040	6213	70
H(26A)	5171	5574	5621	77
H(26B)	6388	5101	5216	77
H(26C)	5484	6244	4928	77
H(35A)	4974	7079	11600	94
H(35B)	4229	6168	11777	94
H(35C)	3432	7254	11851	94
H(29A)	9193	9259	5595	94
H(29B)	7809	8908	5591	94
H(29C)	8588	9263	4941	94
H(30A)	10418	7494	6562	93
H(30B)	10687	6359	6519	93
H(30C)	9163	6978	6620	93
H(33A)	1079	7370	11066	112
H(33B)	1869	6235	11080	112
H(33C)	1334	7073	10417	112

Table A15 (continued)

H(34A)	2455	8986	10866	100
H(34B)	2410	9049	10131	100
H(34C)	3818	8993	10455	100
H(31A)	11421	8043	4754	117
H(31B)	12127	7006	5282	117
H(31C)	11855	8070	5432	117
H(38A)	7956	6596	9226	126
H(38B)	8177	5467	9702	126
H(38C)	9117	6178	9774	126
H(36A)	8137	7894	10204	149
H(36B)	6636	8203	10481	149
H(36C)	6833	8413	9731	149
H(37A)	7480	5129	11092	159
H(37B)	7147	6093	11356	159
H(37C)	8609	5755	11052	159

Table A16 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in **7**. $U(\text{eq})$ is Defined as One Third of the Trace of the Orthogonalized U^{ij} Tensor.

	x	y	z	$U(\text{eq})$
C(1)	5981(9)	1345(5)	8216(3)	62
C(2)	5072(11)	1722(6)	7850(3)	82
C(3)	2633(11)	1155(5)	8199(3)	75
C(4)	2195(11)	1934(6)	7990(3)	78
C(5)	5759(11)	3130(6)	8229(3)	81
C(6)	4148(9)	3309(5)	8401(3)	58
C(7)	3244(8)	560(4)	9022(2)	47
C(8)	5064(8)	271(4)	8650(3)	51
C(9)	5268(8)	576(4)	9386(2)	50
C(10)	7723(9)	1341(5)	8955(3)	56
C(11)	7632(11)	2531(6)	8889(3)	77
C(12)	7437(9)	2206(5)	9541(3)	55
C(13)	4773(7)	2049(4)	9433(2)	35
C(14)	3619(7)	2099(4)	9417(2)	36
C(15)	947(10)	1685(5)	8946(3)	71

Table A16 (continued)

C(16)	1115(10)	2817(5)	8746(3)	67
C(17)	1083(9)	2738(5)	9467(3)	61
C(18)	5539(8)	3670(4)	9236(3)	51
C(19)	4139(9)	3550(5)	9791(3)	58
C(20)	3423(9)	3972(4)	9217(3)	54
C(21)	6893(9)	-41(5)	6906(3)	57
C(22)	6215(9)	651(5)	7247(3)	57
C(23)	3719(9)	87(5)	6895(3)	62
C(24)	3372(9)	910(5)	6718(3)	55
C(25)	7014(8)	1854(4)	6671(2)	48
C(26)	5637(8)	2021(4)	7026(2)	46
C(27)	4993(11)	-971(6)	6227(4)	85
C(28)	5809(11)	-1089(6)	5551(3)	76
C(29)	7120(10)	-1211(5)	6132(3)	71
C(30)	9077(9)	-24(5)	5733(3)	54
C(31)	9191(8)	1119(4)	6172(3)	51
C(32)	9300(10)	133(5)	6482(3)	67
C(33)	6610(6)	380(3)	5670(2)	30
C(34)	5474(7)	391(4)	5579(2)	38

Table A16 (continued)

C(35)	2560(9)	-125(4)	5907(3)	55
C(36)	2881(9)	355(5)	5302(3)	57
C(37)	2250(9)	1054(5)	5906(3)	59
C(38)	4643(7)	1861(4)	5434(2)	41
C(39)	6734(7)	1977(4)	5790(2)	42
C(40)	4908(7)	2280(4)	6163(2)	40
C(41)	6062(8)	3947(4)	3169(3)	51
C(42)	5182(10)	4394(5)	2814(3)	70
C(43)	2651(11)	3675(5)	3103(3)	78
C(44)	2141(10)	4476(5)	2955(3)	69
C(45)	5692(9)	5751(5)	3252(3)	67
C(46)	3994(8)	5858(4)	3381(2)	47
C(47)	3164(7)	3021(4)	3948(2)	43
C(48)	4965(8)	2800(4)	3547(2)	50
C(49)	5224(8)	3021(4)	4291(2)	48
C(50)	7667(8)	3897(4)	3951(3)	52
C(51)	7482(9)	5044(4)	3835(3)	54
C(52)	7293(8)	4782(4)	4508(2)	50
C(53)	795(9)	4181(5)	3820(3)	57

Table A16 (continued)

C(54)	1054(9)	5383(5)	3703(3)	57
C(55)	900(8)	5178(4)	4389(2)	48
C(56)	5419(7)	6110(4)	4238(2)	45
C(57)	4002(8)	5925(4)	4779(2)	50
C(58)	3324(8)	6452(4)	4240(3)	52
C(59)	3434(6)	4524(3)	4343(2)	28
C(60)	4592(6)	4483(3)	4378(2)	29
C(61)	5468(15)	1712(8)	1718(5)	131
C(62)	7096(18)	2199(10)	1916(5)	149
C(63)	4281(15)	2688(8)	2127(4)	118
C(64)	3817(10)	3344(5)	1869(3)	68
C(65)	6626(11)	4116(6)	2071(3)	80
C(66)	7959(9)	3728(5)	1781(3)	62
C(67)	4585(10)	1362(5)	822(3)	68
C(68)	5984(10)	1474(5)	286(3)	64
C(69)	6743(9)	1100(5)	879(3)	62
C(70)	8851(9)	2235(5)	529(3)	54
C(71)	9161(10)	2372(5)	1260(3)	66
C(72)	9087(9)	3392(5)	957(3)	59

Table A16 (continued)

C(73)	6358(7)	2954(4)	647(2)	43
C(74)	5227(8)	2978(4)	644(2)	45
C(75)	2630(11)	2843(6)	508(3)	82
C(76)	2439(11)	2319(6)	1103(4)	83
C(77)	2194(10)	3509(5)	1141(3)	74
C(78)	4608(9)	4474(5)	742(3)	61
C(79)	6633(9)	4513(5)	1115(3)	60
C(80)	4721(9)	4669(4)	1481(3)	53
C(81)	7318(10)	4326(5)	10063(3)	63
C(82)	7813(10)	3834(5)	9993(3)	68
C(83)	9401(9)	3538(5)	10046(3)	58
C(84)	10460(9)	3706(5)	10203(3)	59
C(85)	12070(9)	4365(5)	10230(3)	61
C(86)	12661(9)	4784(5)	10059(3)	61
C(87)	8672(7)	4639(4)	8955(2)	40
C(88)	9529(8)	5065(4)	8979(2)	48
C(89)	10481(10)	5032(5)	9093(3)	68
C(90)	10586(12)	4541(6)	9200(4)	84
C(91)	9701(11)	4112(6)	9176(3)	79

Table A16 (continued)

C(92)	8756(9)	4157(5)	9056(3)	56
C(93)	7614(11)	4696(6)	8807(3)	82
C(99)	1583(9)	4116(5)	8202(3)	62
C(118)	1154(10)	3867(5)	4797(3)	67
C(119)	2037(9)	3691(5)	4946(3)	59
C(120)	2846(9)	2929(5)	4963(3)	57
C(121)	2704(10)	2323(5)	4866(3)	64
C(122)	1648(11)	1461(5)	4913(3)	76
C(123)	759(10)	1221(6)	5071(3)	74
C(124)	-1062(9)	1127(5)	5101(3)	64
C(125)	-1990(10)	1238(5)	4943(3)	65
C(126)	-2795(10)	1978(5)	4837(3)	63
C(127)	-2697(9)	2582(5)	4912(3)	63
C(128)	-1659(10)	3452(5)	4859(3)	66
C(129)	-689(10)	3709(6)	4741(3)	75
C(130)	-1473(8)	2134(4)	3957(3)	50
C(131)	-643(8)	2569(4)	3967(2)	50
C(132)	328(9)	2527(5)	4065(3)	55
C(133)	498(10)	2040(5)	4146(3)	65

Table A16 (continued)

C(134)	-300(9)	1597(5)	4137(3)	63
C(135)	-1316(9)	1645(5)	4039(3)	59
C(136)	-2570(13)	2188(7)	3857(4)	105
C(137)	1426(7)	2823(3)	5848(2)	31
C(138)	1382(7)	3342(4)	5776(2)	36
C(139)	408(8)	3451(5)	5687(3)	53
C(140)	-488(10)	3054(5)	5675(3)	62
C(141)	-443(9)	2542(5)	5741(3)	52
C(142)	519(7)	2427(4)	5833(2)	43
C(143)	2453(9)	2696(5)	5954(3)	57
C(144)	-499(9)	1598(5)	7252(3)	58
C(145)	535(9)	1646(5)	7104(3)	61
C(146)	1614(9)	2223(5)	6784(3)	62
C(147)	2587(10)	2435(5)	6987(3)	65
C(148)	3499(8)	3183(4)	7408(3)	50
C(149)	3419(8)	3746(4)	7598(3)	51
C(150)	2480(8)	4221(4)	7979(3)	52
C(151)	-254(16)	3913(8)	8191(5)	123
C(152)	-920(20)	3469(11)	8152(6)	178

Table A16 (continued)

C(153)	-1255(11)	2502(5)	7957(3)	76
C(154)	-1405(9)	2052(5)	7662(3)	61
C(155)	1648(8)	3982(4)	6837(2)	45
C(156)	1345(7)	4548(4)	6940(2)	39
C(157)	583(8)	5068(4)	7355(2)	49
C(158)	54(8)	5040(4)	7670(3)	51
C(159)	-700(9)	5638(5)	8081(3)	63
C(160)	-1870(9)	5460(5)	8039(3)	58
C(161)	-3168(9)	4672(5)	7792(3)	58
C(162)	-3275(9)	4069(4)	7630(3)	54
C(163)	-2473(8)	3497(4)	7251(3)	50
C(164)	-1725(8)	3534(4)	6973(2)	46
C(165)	-825(7)	2948(4)	6626(2)	41
C(166)	35(7)	3421(4)	6579(2)	38
C(167)	-2477(8)	403(4)	-45(3)	49
C(168)	-1834(9)	801(5)	-201(3)	58
C(169)	-132(8)	1360(5)	-186(3)	55
C(170)	914(8)	1478(5)	-18(3)	55
C(171)	2392(9)	1074(5)	66(3)	55

Table A16 (continued)

C(172)	2783(9)	555(4)	-22(3)	54
C(173)	1294(8)	339(4)	992(2)	45
C(174)	495(8)	-119(4)	973(2)	44
C(175)	-494(9)	-116(5)	870(3)	54
C(176)	-720(10)	353(5)	770(3)	60
C(177)	78(10)	817(6)	788(3)	70
C(178)	1070(9)	807(5)	894(3)	53
C(179)	2394(12)	342(6)	1114(4)	90
C(228)	9104(13)	840(7)	1679(4)	102
C(229)	10105(16)	1163(8)	1774(5)	117
C(230)	11024(17)	2052(9)	2031(5)	127
C(231)	10895(14)	2578(7)	2104(4)	109
C(232)	9999(16)	3211(9)	2477(5)	129
C(233)	9485(14)	3258(7)	2724(4)	102
C(234)	7951(17)	2767(9)	3042(5)	138
C(235)	6940(20)	2409(10)	2940(6)	155
C(236)	6092(17)	1493(9)	2737(5)	127
C(237)	6248(13)	989(8)	2623(4)	102
C(238)	6953(14)	443(8)	2164(4)	106

Table A16 (continued)

C(239)	7472(14)	465(7)	1883(4)	102
C(240)	9973(9)	1461(4)	3244(3)	52
C(241)	9005(9)	1042(5)	3129(3)	57
C(247)	11032(8)	2276(4)	3111(3)	50
C(248)	12035(8)	2075(4)	3099(2)	47
C(249)	9765(11)	412(6)	2771(3)	81
C(250)	9615(11)	27(6)	2437(3)	80
C(251)	13011(10)	1548(5)	2730(3)	66
C(252)	12839(11)	1163(6)	2405(3)	75
C(253)	10415(15)	-556(7)	2071(5)	110
C(254)	11416(17)	-521(9)	1984(5)	137
C(255)	12978(12)	27(7)	2006(4)	89
C(259)	13634(12)	566(6)	2028(4)	86
K(1)	10000	5000	10000	43
K(2)	554(2)	3160(1)	7414(1)	37
K(3)	11(2)	2478(1)	4922(1)	35
K(4)	8790(2)	1708(1)	2465(1)	34
K(5)	0	0	0	37
N(1)	5255(6)	1689(3)	8196(2)	45

Table A16 (continued)

N(2)	2881(6)	1751(3)	8210(2)	45
N(3)	4837(6)	2907(3)	8368(2)	46
N(4)	6345(6)	401(3)	6904(2)	43
N(5)	4114(6)	550(3)	6735(2)	42
N(6)	6010(6)	1625(3)	6773(2)	35
N(7)	5300(6)	4295(3)	3154(2)	40
N(8)	2882(6)	4284(3)	3147(2)	42
N(9)	4713(6)	5488(3)	3358(2)	35
N(10)	6276(9)	2278(5)	1763(3)	72
N(11)	4533(8)	2984(4)	1871(2)	62
N(12)	6861(6)	3655(3)	1824(2)	45
O(1)	7815(5)	4744(3)	9906(2)	48
O(2)	8885(6)	3981(3)	10115(2)	52
O(3)	11063(6)	4160(3)	10069(2)	52
O(16)	185(6)	3599(3)	4888(2)	56
O(17)	1978(6)	3127(3)	4843(2)	52
O(18)	1840(6)	2058(3)	4994(2)	57
O(19)	-163(6)	1346(3)	4960(2)	55
O(20)	-1937(5)	1812(3)	4990(2)	51

Table A16 (continued)

O(21)	-1787(6)	2856(3)	4793(2)	56
O(22)	-425(5)	2059(3)	7520(2)	50
O(23)	732(6)	2158(3)	6971(2)	53
O(24)	2588(6)	2969(3)	7192(2)	54
O(25)	2545(5)	3696(3)	7787(2)	42
O(26)	651(6)	3953(3)	8006(2)	54
O(27)	-1013(6)	3031(3)	7869(2)	66
O(28)	811(5)	3512(2)	6834(1)	36
O(29)	933(5)	4569(3)	7254(2)	44
O(30)	-243(5)	5575(3)	7769(2)	50
O(31)	-2148(5)	4864(3)	7933(2)	51
O(32)	-2603(5)	4041(3)	7372(2)	51
O(33)	-1259(5)	3061(3)	6936(2)	39
O(34)	-791(5)	938(3)	-54(2)	47
O(35)	1379(5)	983(3)	-82(2)	48
O(36)	2146(5)	119(3)	111(2)	41
O(101)	8529(8)	777(4)	1938(2)	83
O(102)	10059(9)	1715(5)	1937(3)	98
O(103)	10264(9)	2718(5)	2406(3)	97

Table A16 (continued)

O(104)	8491(10)	2830(5)	2765(3)	124
O(105)	7045(9)	1872(5)	2831(3)	102
O(106)	6798(7)	942(4)	2315(2)	82
O(107)	8971(5)	727(3)	2804(2)	48
O(108)	10112(5)	1839(3)	3029(2)	46
O(112)	12065(6)	1764(3)	2783(2)	60
O(113)	10425(8)	-241(4)	2397(3)	95
O(114)	11984(8)	39(4)	1978(3)	91
O(117)	13709(7)	943(4)	2343(2)	81
Si(1)	5198(2)	1737(1)	9003(1)	25
Si(2)	3415(2)	2509(1)	9077(1)	26
Si(3)	4708(2)	770(1)	9011(1)	32
Si(4)	7028(2)	1946(1)	9094(1)	35
Si(5)	1612(2)	2454(1)	9058(1)	40
Si(6)	4152(2)	3443(1)	9333(1)	36
Si(7)	6776(2)	202(1)	6097(1)	27
Si(8)	4887(2)	840(1)	5928(1)	27
Si(9)	6165(2)	-781(1)	6001(1)	43
Si(10)	8608(2)	336(1)	6127(1)	35

Table A16 (continued)

Si(11)	3112(2)	537(1)	5763(1)	36
Si(12)	5282(2)	1756(1)	5825(1)	29
Si(13)	5080(2)	4228(1)	3955(1)	23
Si(14)	4624(2)	3250(1)	3933(1)	30
Si(15)	6917(2)	4479(1)	4062(1)	30
Si(16)	3263(2)	4978(1)	4025(1)	24
Si(17)	1468(2)	4936(1)	3988(1)	35
Si(18)	4009(2)	5883(1)	4321(1)	31
Si(19)	6680(2)	2550(1)	986(1)	31
Si(20)	5992(2)	1609(1)	745(1)	42
Si(21)	8469(2)	2617(1)	933(1)	40
Si(22)	4790(2)	3252(1)	1067(1)	34
Si(23)	2974(2)	2997(1)	960(1)	47
Si(24)	5179(2)	4238(1)	1102(1)	38
Zr(1)	4276(1)	2125(1)	8475(1)	28
Zr(2)	5596(1)	778(1)	6580(1)	26
Zr(3)	4229(1)	4669(1)	3431(1)	27
Zr(4)	5846(1)	2941(1)	1600(1)	29

Table A17 Bond Distances (Å) in **7**

C(1)-N(1)	1.404(13)	C(2)-N(1)	1.477(16)
C(3)-N(2)	1.441(15)	C(4)-N(2)	1.454(15)
C(5)-N(3)	1.419(15)	C(6)-N(3)	1.456(13)
C(7)-Si(3)	1.890(10)	C(8)-Si(3)	1.892(10)
C(9)-Si(3)	1.890(11)	C(10)-Si(4)	1.907(11)
C(11)-Si(4)	1.885(13)	C(12)-Si(4)	1.880(11)
C(13)-C(14)	1.538(12)	C(13)-Si(1)	1.959(8)
C(14)-Si(2)	1.937(9)	C(15)-Si(5)	1.900(12)
C(16)-Si(5)	1.885(13)	C(17)-Si(5)	1.923(11)
C(18)-Si(6)	1.876(10)	C(19)-Si(6)	1.884(11)
C(20)-Si(6)	1.885(11)	C(21)-N(4)	1.421(13)
C(22)-N(4)	1.476(13)	C(23)-N(5)	1.458(13)
C(24)-N(5)	1.448(13)	C(25)-N(6)	1.440(12)
C(26)-N(6)	1.463(11)	C(27)-Si(9)	1.860(14)
C(28)-Si(9)	1.893(13)	C(29)-Si(9)	1.919(13)
C(30)-Si(10)	1.900(10)	C(31)-Si(10)	1.915(10)
C(32)-Si(10)	1.908(12)	C(33)-C(34)	1.529(12)
C(33)-Si(7)	1.933(8)	C(34)-Si(8)	1.933(9)
C(35)-Si(11)	1.881(11)	C(36)-Si(11)	1.892(11)
C(37)-Si(11)	1.890(11)	C(38)-Si(12)	1.897(10)

Table A17 (continued)

C(39)-Si(12)	1.893(9)	C(40)-Si(12)	1.877(9)
C(41)-N(7)	1.445(12)	C(42)-N(7)	1.499(14)
C(43)-N(8)	1.455(15)	C(44)-N(8)	1.443(14)
C(45)-N(9)	1.447(13)	C(46)-N(9)	1.428(12)
C(47)-Si(14)	1.892(9)	C(48)-Si(14)	1.898(10)
C(49)-Si(14)	1.899(10)	C(50)-Si(15)	1.890(10)
C(51)-Si(15)	1.889(11)	C(52)-Si(15)	1.883(10)
C(53)-Si(17)	1.896(11)	C(54)-Si(17)	1.902(11)
C(55)-Si(17)	1.896(10)	C(56)-Si(18)	1.887(10)
C(57)-Si(18)	1.900(10)	C(58)-Si(18)	1.886(11)
C(59)-C(60)	1.540(11)	C(59)-Si(16)	1.931(8)
C(60)-Si(13)	1.935(8)	C(61)-N(10)	1.56(2)
C(62)-N(10)	1.29(2)	C(63)-N(11)	1.424(19)
C(64)-N(11)	1.412(15)	C(65)-N(12)	1.475(15)
C(66)-N(12)	1.434(13)	C(67)-Si(20)	1.885(12)
C(68)-Si(20)	1.883(12)	C(69)-Si(20)	1.891(12)
C(70)-Si(21)	1.905(10)	C(71)-Si(21)	1.870(12)
C(72)-Si(21)	1.919(11)	C(73)-C(74)	1.491(13)
C(73)-Si(19)	1.962(10)	C(74)-Si(22)	1.918(10)

Table A17 (continued)

C(75)-Si(23)	1.878(14)	C(76)-Si(23)	1.906(14)
C(77)-Si(23)	1.845(13)	C(78)-Si(24)	1.896(12)
C(79)-Si(24)	1.889(11)	C(80)-Si(24)	1.918(10)
C(81)-O(1)	1.400(13)	C(81)-C(82)	1.475(16)
C(82)-O(2)	1.428(14)	C(83)-O(2)	1.386(13)
C(83)-C(84)	1.461(15)	C(84)-O(3)	1.461(13)
C(85)-O(3)	1.413(13)	C(85)-C(86)	1.486(16)
C(86)-O(1)#1	1.412(13)	C(87)-C(92)	1.363(14)
C(87)-C(88)	1.371(14)	C(87)-C(93)	1.538(16)
C(88)-C(89)	1.340(16)	C(89)-C(90)	1.405(18)
C(90)-C(91)	1.400(19)	C(91)-C(92)	1.351(17)
C(99)-O(26)	1.390(13)	C(99)-C(150)	1.537(15)
C(118)-O(16)	1.414(14)	C(118)-C(119)	1.469(16)
C(119)-O(17)	1.369(13)	C(120)-O(17)	1.433(13)
C(120)-C(121)	1.453(15)	C(121)-O(18)	1.373(13)
C(122)-O(18)	1.424(14)	C(122)-C(123)	1.443(17)
C(123)-O(19)	1.387(15)	C(124)-O(19)	1.397(13)
C(124)-C(125)	1.457(16)	C(125)-O(20)	1.388(13)
C(126)-O(20)	1.436(13)	C(126)-C(127)	1.448(16)

Table A17 (continued)

C(127)-O(21)	1.410(13)	C(128)-O(21)	1.428(13)
C(128)-C(129)	1.454(17)	C(129)-O(16)	1.377(15)
C(130)-C(131)	1.369(14)	C(130)-C(135)	1.374(15)
C(130)-C(136)	1.517(19)	C(131)-C(132)	1.350(15)
C(132)-C(133)	1.369(16)	C(133)-C(134)	1.356(16)
C(134)-C(135)	1.410(16)	C(137)-C(142)	1.379(13)
C(137)-C(138)	1.388(12)	C(137)-C(143)	1.508(14)
C(138)-C(139)	1.403(14)	C(139)-C(140)	1.371(15)
C(140)-C(141)	1.362(15)	C(141)-C(142)	1.400(14)
C(144)-O(22)	1.425(12)	C(144)-C(145)	1.499(15)
C(145)-O(23)	1.466(13)	C(146)-O(23)	1.415(13)
C(146)-C(147)	1.453(16)	C(147)-O(24)	1.432(13)
C(148)-O(24)	1.422(12)	C(148)-C(149)	1.490(14)
C(149)-O(25)	1.410(12)	C(150)-O(25)	1.415(12)
C(151)-C(152)	1.25(3)	C(151)-O(26)	1.43(2)
C(152)-O(27)	1.43(3)	C(153)-O(27)	1.412(15)
C(153)-C(154)	1.475(16)	C(154)-O(22)	1.431(13)
C(155)-O(28)	1.436(11)	C(155)-C(156)	1.520(13)
C(156)-O(29)	1.431(11)	C(157)-O(29)	1.396(12)

Table A17 (continued)

C(157)-C(158)	1.517(14)	C(158)-O(30)	1.444(12)
C(159)-O(30)	1.448(13)	C(159)-C(160)	1.503(16)
C(160)-O(31)	1.429(13)	C(161)-O(31)	1.396(13)
C(161)-C(162)	1.497(15)	C(162)-O(32)	1.413(12)
C(163)-O(32)	1.391(12)	C(163)-C(164)	1.550(13)
C(164)-O(33)	1.407(11)	C(165)-O(33)	1.434(10)
C(165)-C(166)	1.508(12)	C(166)-O(28)	1.402(11)
C(167)-O(36)#2	1.425(11)	C(167)-C(168)	1.441(15)
C(168)-O(34)	1.428(13)	C(169)-O(34)	1.432(12)
C(169)-C(170)	1.466(15)	C(170)-O(35)	1.457(12)
C(171)-O(35)	1.401(12)	C(171)-C(172)	1.461(15)
C(172)-O(36)	1.445(12)	C(173)-C(174)	1.375(13)
C(173)-C(178)	1.381(14)	C(173)-C(179)	1.507(17)
C(174)-C(175)	1.350(14)	C(175)-C(176)	1.388(16)
C(176)-C(177)	1.385(16)	C(177)-C(178)	1.362(16)
C(228)-O(101)	1.359(18)	C(228)-C(229)	1.40(2)
C(229)-O(102)	1.42(2)	C(230)-C(231)	1.33(2)
C(230)-O(102)	1.37(2)	C(231)-O(103)	1.551(19)
C(232)-C(233)	1.25(2)	C(232)-O(103)	1.32(2)

Table A17 (continued)

C(233)-O(104)	1.55(2)	C(234)-O(104)	1.40(2)
C(234)-C(235)	1.44(3)	C(235)-O(105)	1.35(2)
C(236)-C(237)	1.31(2)	C(236)-O(105)	1.40(2)
C(237)-O(106)	1.490(18)	C(238)-O(106)	1.334(18)
C(238)-C(239)	1.38(2)	C(239)-O(101)	1.436(18)
C(240)-O(108)	1.412(12)	C(240)-C(241)	1.475(15)
C(241)-O(107)	1.426(12)	C(241)-K(4)	3.523(12)
C(247)-O(108)	1.439(12)	C(247)-C(248)	1.491(14)
C(248)-O(112)	1.402(12)	C(249)-O(107)	1.410(15)
C(249)-C(250)	1.516(18)	C(250)-O(113)	1.353(16)
C(251)-O(112)	1.446(14)	C(251)-C(252)	1.487(17)
C(252)-O(117)	1.364(15)	C(253)-C(254)	1.36(2)
C(253)-O(113)	1.435(19)	C(254)-O(114)	1.45(2)
C(255)-O(114)	1.307(17)	C(255)-C(259)	1.428(19)
C(259)-O(117)	1.450(16)	K(1)-O(3)	2.769(7)
K(1)-O(3)#1	2.769(7)	K(1)-O(2)	2.800(7)
K(1)-O(2)#1	2.800(7)	K(1)-O(1)#1	2.803(7)
K(1)-O(1)	2.803(7)	K(1)-C(90)#1	3.481(14)
K(2)-O(28)	2.741(6)	K(2)-O(26)	2.833(7)

Table A17 (continued)

K(2)-O(23)	2.855(7)	K(2)-O(27)	2.859(8)
K(2)-O(22)	2.908(7)	K(2)-O(25)	2.928(7)
K(2)-O(24)	2.941(8)	K(2)-O(33)	2.988(7)
K(3)-O(21)	2.765(8)	K(3)-O(16)	2.776(8)
K(3)-O(19)	2.809(8)	K(3)-O(18)	2.815(8)
K(3)-O(20)	2.812(7)	K(3)-O(17)	2.827(7)
K(4)-O(108)	2.803(7)	K(4)-O(102)	2.811(11)
K(4)-O(105)	2.840(11)	K(4)-O(101)	2.828(10)
K(4)-O(106)	2.885(10)	K(4)-O(103)	2.910(11)
K(4)-O(104)	2.927(13)	K(4)-O(107)	3.083(7)
K(5)-O(34)#2	2.763(7)	K(5)-O(34)	2.763(7)
K(5)-O(36)#2	2.777(6)	K(5)-O(36)	2.777(6)
K(5)-O(35)#2	2.826(7)	K(5)-O(35)	2.826(7)
K(5)-C(176)#2	3.385(11)	K(5)-C(177)#2	3.509(12)
N(1)-Zr(1)	2.078(8)	N(2)-Zr(1)	2.057(8)
N(3)-Zr(1)	2.076(8)	N(4)-Zr(2)	2.103(8)
N(5)-Zr(2)	2.075(8)	N(6)-Zr(2)	2.059(7)
N(7)-Zr(3)	2.089(8)	N(8)-Zr(3)	2.049(8)
N(9)-Zr(3)	2.090(7)	N(10)-Zr(4)	2.062(11)

Table A17 (continued)

N(11)-Zr(4)	2.098(10)	N(12)-Zr(4)	2.036(8)
O(1)-C(86)#1	1.412(13)	O(36)-C(167)#2	1.425(11)
Si(1)-Si(4)	2.352(3)	Si(1)-Si(3)	2.366(3)
Si(1)-Zr(1)	2.887(2)	Si(2)-Si(5)	2.334(4)
Si(2)-Si(6)	2.357(3)	Si(2)-Zr(1)	2.866(2)
Si(7)-Si(10)	2.350(3)	Si(7)-Si(9)	2.366(4)
Si(7)-Zr(2)	2.908(2)	Si(8)-Si(11)	2.334(3)
Si(8)-Si(12)	2.354(3)	Si(8)-Zr(2)	2.891(2)
Si(13)-Si(14)	2.365(3)	Si(13)-Si(15)	2.368(3)
Si(13)-Zr(3)	2.907(2)	Si(16)-Si(17)	2.329(3)
Si(16)-Si(18)	2.352(3)	Si(16)-Zr(3)	2.866(2)
Si(19)-Si(21)	2.335(4)	Si(19)-Si(20)	2.347(4)
Si(19)-Zr(4)	2.893(3)	Si(22)-Si(23)	2.342(4)
Si(22)-Si(24)	2.374(4)	Si(22)-Zr(4)	2.884(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2, -y+1, -z+2 #2 -x, -y, -z

Table A18 Bond angles (deg) in **7**

C(14)-C(13)-Si(1)	111.7(6)	C(13)-C(14)-Si(2)	107.5(6)
C(34)-C(33)-Si(7)	111.6(6)	C(33)-C(34)-Si(8)	111.4(6)
C(60)-C(59)-Si(16)	108.9(5)	C(59)-C(60)-Si(13)	110.5(5)
C(74)-C(73)-Si(19)	108.6(7)	C(73)-C(74)-Si(22)	113.3(7)
O(1)-C(81)-C(82)	109.9(10)	O(2)-C(82)-C(81)	110.5(10)
O(2)-C(83)-C(84)	109.8(9)	O(3)-C(84)-C(83)	110.4(10)
O(3)-C(85)-C(86)	108.7(10)	O(1)#1-C(86)-C(85)	109.2(9)
C(92)-C(87)-C(88)	120.2(10)	C(92)-C(87)-C(93)	119.6(10)
C(88)-C(87)-C(93)	120.2(10)	C(89)-C(88)-C(87)	123.2(11)
C(88)-C(89)-C(90)	117.6(13)	C(91)-C(90)-C(89)	118.5(14)
C(92)-C(91)-C(90)	122.2(14)	C(91)-C(92)-C(87)	118.3(12)
O(26)-C(99)-C(150)	108.0(9)	O(16)-C(118)-C(119)	111.9(10)
O(17)-C(119)-C(118)	110.6(10)	O(17)-C(120)-C(121)	111.3(10)
O(18)-C(121)-C(120)	111.2(10)	O(18)-C(122)-C(123)	111.0(11)
O(19)-C(123)-C(122)	112.2(12)	O(19)-C(124)-C(125)	110.8(10)
O(20)-C(125)-C(124)	109.9(10)	O(20)-C(126)-C(127)	111.4(10)
O(21)-C(127)-C(126)	111.5(10)	O(21)-C(128)-C(129)	110.8(10)
O(16)-C(129)-C(128)	113.2(12)	C(131)-C(130)-C(135)	119.9(11)
C(131)-C(130)-C(136)	120.7(11)	C(135)-C(130)-C(136)	119.4(11)

Table A18 (continued)

C(130)-C(131)-C(132)	120.6(11)	C(131)-C(132)-C(133)	120.2(11)
C(134)-C(133)-C(132)	121.2(12)	C(133)-C(134)-C(135)	118.6(12)
C(130)-C(135)-C(134)	119.5(11)	C(142)-C(137)-C(138)	119.8(8)
C(142)-C(137)-C(143)	119.6(9)	C(138)-C(137)-C(143)	120.6(8)
C(137)-C(138)-C(139)	119.0(9)	C(140)-C(139)-C(138)	120.6(11)
C(141)-C(140)-C(139)	120.4(12)	C(140)-C(141)-C(142)	119.9(11)
C(137)-C(142)-C(141)	120.3(10)	O(22)-C(144)-C(145)	108.0(9)
O(23)-C(145)-C(144)	108.7(9)	O(23)-C(146)-C(147)	112.6(10)
O(24)-C(147)-C(146)	111.4(10)	O(24)-C(148)-C(149)	108.5(9)
O(25)-C(149)-C(148)	109.9(9)	O(25)-C(150)-C(99)	107.1(9)
C(152)-C(151)-O(26)	121(2)	C(151)-C(152)-O(27)	123(2)
O(27)-C(153)-C(154)	109.8(11)	O(22)-C(154)-C(153)	108.5(10)
O(28)-C(155)-C(156)	114.0(8)	O(29)-C(156)-C(155)	108.0(8)
O(29)-C(157)-C(158)	108.3(8)	O(30)-C(158)-C(157)	105.7(8)
O(30)-C(159)-C(160)	111.4(10)	O(31)-C(160)-C(159)	109.3(9)
O(31)-C(161)-C(162)	107.8(9)	O(32)-C(162)-C(161)	108.3(9)
O(32)-C(163)-C(164)	106.6(8)	O(33)-C(164)-C(163)	107.3(8)
O(33)-C(165)-C(166)	112.7(7)	O(28)-C(166)-C(165)	108.0(7)
O(36)#2-C(167)-C(168)	109.8(9)	O(34)-C(168)-C(167)	110.1(9)

Table A18 (continued)

O(34)-C(169)-C(170)	108.6(9)	O(35)-C(170)-C(169)	110.5(9)
O(35)-C(171)-C(172)	108.2(9)	O(36)-C(172)-C(171)	109.4(9)
C(174)-C(173)-C(178)	118.2(10)	C(174)-C(173)-C(179)	122.2(10)
C(178)-C(173)-C(179)	119.6(10)	C(175)-C(174)-C(173)	121.9(10)
C(174)-C(175)-C(176)	119.9(11)	C(175)-C(176)-C(177)	118.5(12)
C(178)-C(177)-C(176)	120.7(13)	C(177)-C(178)-C(173)	120.6(11)
O(101)-C(228)-C(229)	112.0(16)	C(228)-C(229)-O(102)	111.1(17)
C(231)-C(230)-O(102)	107.6(19)	C(230)-C(231)-O(103)	115.3(16)
C(233)-C(232)-O(103)	112(2)	C(232)-C(233)-O(104)	123.7(18)
O(104)-C(234)-C(235)	108.5(19)	O(105)-C(235)-C(234)	110(2)
C(237)-C(236)-O(105)	110.7(19)	C(236)-C(237)-O(106)	113.8(17)
O(106)-C(238)-C(239)	113.1(16)	C(238)-C(239)-O(101)	114.3(16)
O(108)-C(240)-C(241)	107.8(9)	O(107)-C(241)-C(240)	115.9(9)
O(107)-C(241)-K(4)	60.6(5)	C(240)-C(241)-K(4)	87.7(7)
O(108)-C(247)-C(248)	114.5(8)	O(112)-C(248)-C(247)	107.5(8)
O(107)-C(249)-C(250)	109.6(11)	O(113)-C(250)-C(249)	109.0(12)
O(112)-C(251)-C(252)	106.6(10)	O(117)-C(252)-C(251)	109.2(11)
C(254)-C(253)-O(113)	109.0(17)	C(253)-C(254)-O(114)	115.5(18)
O(114)-C(255)-C(259)	112.7(15)	C(255)-C(259)-O(117)	115.1(13)

Table A18 (continued)

O(3)-K(1)-O(3)#1	180.0(3)	O(3)-K(1)-O(2)	60.8(2)
O(3)#1-K(1)-O(2)	119.2(2)	O(3)-K(1)-O(2)#1	119.2(2)
O(3)#1-K(1)-O(2)#1	60.8(2)	O(2)-K(1)-O(2)#1	180.000(2)
O(3)-K(1)-O(1)#1	60.6(2)	O(3)#1-K(1)-O(1)#1	119.4(2)
O(2)-K(1)-O(1)#1	119.9(2)	O(2)#1-K(1)-O(1)#1	60.1(2)
O(3)-K(1)-O(1)	119.4(2)	O(3)#1-K(1)-O(1)	60.6(2)
O(2)-K(1)-O(1)	60.1(2)	O(2)#1-K(1)-O(1)	119.9(2)
O(1)#1-K(1)-O(1)	180.000(2)	O(3)-K(1)-C(90)#1	101.8(3)
O(3)#1-K(1)-C(90)#1	78.2(3)	O(2)-K(1)-C(90)#1	81.2(3)
O(2)#1-K(1)-C(90)#1	98.8(3)	O(1)#1-K(1)-C(90)#1	98.8(3)
O(1)-K(1)-C(90)#1	81.2(3)	O(28)-K(2)-O(26)	120.3(2)
O(28)-K(2)-O(23)	77.2(2)	O(26)-K(2)-O(23)	160.0(2)
O(28)-K(2)-O(27)	138.7(2)	O(26)-K(2)-O(27)	58.8(2)
O(23)-K(2)-O(27)	115.6(2)	O(28)-K(2)-O(22)	128.4(2)
O(26)-K(2)-O(22)	108.7(2)	O(23)-K(2)-O(22)	58.5(2)
O(27)-K(2)-O(22)	58.6(2)	O(28)-K(2)-O(25)	102.29(19)
O(26)-K(2)-O(25)	58.5(2)	O(23)-K(2)-O(25)	111.2(2)
O(27)-K(2)-O(25)	107.8(2)	O(22)-K(2)-O(25)	116.8(2)
O(28)-K(2)-O(24)	72.0(2)	O(26)-K(2)-O(24)	115.1(2)

Table A18 (continued)

O(23)-K(2)-O(24)	58.6(2)	O(27)-K(2)-O(24)	149.1(2)
O(22)-K(2)-O(24)	101.9(2)	O(25)-K(2)-O(24)	56.69(19)
O(28)-K(2)-O(33)	58.43(18)	O(26)-K(2)-O(33)	116.3(2)
O(23)-K(2)-O(33)	80.1(2)	O(27)-K(2)-O(33)	84.2(2)
O(22)-K(2)-O(33)	87.11(19)	O(25)-K(2)-O(33)	156.05(19)
O(24)-K(2)-O(33)	121.10(19)	O(21)-K(3)-O(16)	61.5(2)
O(21)-K(3)-O(19)	118.6(2)	O(16)-K(3)-O(19)	179.8(2)
O(21)-K(3)-O(18)	174.9(2)	O(16)-K(3)-O(18)	119.1(2)
O(19)-K(3)-O(18)	60.8(2)	O(21)-K(3)-O(20)	61.1(2)
O(16)-K(3)-O(20)	120.8(2)	O(19)-K(3)-O(20)	59.3(2)
O(18)-K(3)-O(20)	119.4(2)	O(21)-K(3)-O(17)	119.5(2)
O(16)-K(3)-O(17)	60.2(2)	O(19)-K(3)-O(17)	119.8(2)
O(18)-K(3)-O(17)	59.8(2)	O(20)-K(3)-O(17)	178.7(2)
O(108)-K(4)-O(102)	107.1(3)	O(108)-K(4)-O(105)	92.8(3)
O(102)-K(4)-O(105)	157.5(3)	O(108)-K(4)-O(101)	123.8(2)
O(102)-K(4)-O(101)	58.7(3)	O(105)-K(4)-O(101)	118.4(3)
O(108)-K(4)-O(106)	125.1(2)	O(102)-K(4)-O(106)	114.2(3)
O(105)-K(4)-O(106)	58.5(3)	O(101)-K(4)-O(106)	59.9(3)
O(108)-K(4)-O(103)	80.5(3)	O(102)-K(4)-O(103)	59.0(3)

Table A18 (continued)

O(105)-K(4)-O(103)	116.2(3)	O(101)-K(4)-O(103)	117.3(3)
O(106)-K(4)-O(103)	152.4(3)	O(108)-K(4)-O(104)	83.7(3)
O(102)-K(4)-O(104)	112.7(4)	O(105)-K(4)-O(104)	58.1(4)
O(101)-K(4)-O(104)	152.2(3)	O(106)-K(4)-O(104)	110.2(3)
O(103)-K(4)-O(104)	58.1(3)	O(108)-K(4)-O(107)	57.36(19)
O(102)-K(4)-O(107)	111.0(3)	O(105)-K(4)-O(107)	88.3(3)
O(101)-K(4)-O(107)	76.8(2)	O(106)-K(4)-O(107)	74.7(2)
O(103)-K(4)-O(107)	132.8(3)	O(104)-K(4)-O(107)	128.0(3)
O(108)-K(4)-C(241)	41.4(2)	O(102)-K(4)-C(241)	127.5(3)
O(105)-K(4)-C(241)	74.6(3)	O(101)-K(4)-C(241)	100.4(3)
O(106)-K(4)-C(241)	84.2(3)	O(103)-K(4)-C(241)	121.9(3)
O(104)-K(4)-C(241)	104.4(3)	O(107)-K(4)-C(241)	23.8(2)
O(34)#2-K(5)-O(34)	180.0(4)	O(34)#2-K(5)-O(36)#2	118.52(19)
O(34)-K(5)-O(36)#2	61.48(19)	O(34)#2-K(5)-O(36)	61.48(19)
O(34)-K(5)-O(36)	118.52(19)	O(36)#2-K(5)-O(36)	180.0(3)
O(34)#2-K(5)-O(35)#2	60.7(2)	O(34)-K(5)-O(35)#2	119.3(2)
O(36)#2-K(5)-O(35)#2	59.23(19)	O(36)-K(5)-O(35)#2	120.77(19)
O(34)#2-K(5)-O(35)	119.3(2)	O(34)-K(5)-O(35)	60.7(2)
O(36)#2-K(5)-O(35)	120.77(19)	O(36)-K(5)-O(35)	59.23(19)

Table A18 (continued)

O(35)#2-K(5)-O(35)	180.0(3)	O(34)#2-K(5)-C(176)#2	80.2(2)
O(34)-K(5)-C(176)#2	99.8(2)	O(36)#2-K(5)-C(176)#2	101.5(2)
O(36)-K(5)-C(176)#2	78.5(2)	O(35)#2-K(5)-C(176)#2	103.2(2)
O(35)-K(5)-C(176)#2	76.8(2)	O(34)#2-K(5)-C(177)#2	72.3(3)
O(34)-K(5)-C(177)#2	107.7(3)	O(36)#2-K(5)-C(177)#2	86.3(2)
O(36)-K(5)-C(177)#2	93.7(2)	O(35)#2-K(5)-C(177)#2	80.5(3)
O(35)-K(5)-C(177)#2	99.5(3)	C(176)#2-K(5)-C(177)#2	23.1(3)
C(1)-N(1)-C(2)	108.7(9)	C(1)-N(1)-Zr(1)	142.2(7)
C(2)-N(1)-Zr(1)	108.9(7)	C(3)-N(2)-C(4)	113.3(10)
C(3)-N(2)-Zr(1)	111.8(7)	C(4)-N(2)-Zr(1)	133.8(8)
C(5)-N(3)-C(6)	109.1(9)	C(5)-N(3)-Zr(1)	132.4(8)
C(6)-N(3)-Zr(1)	118.0(7)	C(21)-N(4)-C(22)	108.0(8)
C(21)-N(4)-Zr(2)	141.0(7)	C(22)-N(4)-Zr(2)	110.9(6)
C(23)-N(5)-C(24)	112.5(8)	C(23)-N(5)-Zr(2)	128.3(7)
C(24)-N(5)-Zr(2)	118.9(6)	C(25)-N(6)-C(26)	112.9(7)
C(25)-N(6)-Zr(2)	110.3(6)	C(26)-N(6)-Zr(2)	135.8(6)
C(41)-N(7)-C(42)	109.3(8)	C(41)-N(7)-Zr(3)	142.4(7)
C(42)-N(7)-Zr(3)	108.1(7)	C(44)-N(8)-C(43)	111.3(9)
C(44)-N(8)-Zr(3)	134.2(7)	C(43)-N(8)-Zr(3)	114.3(7)

Table A18 (continued)

C(46)-N(9)-C(45)	110.0(8)	C(46)-N(9)-Zr(3)	120.1(6)
C(45)-N(9)-Zr(3)	129.6(7)	C(62)-N(10)-C(61)	105.5(15)
C(62)-N(10)-Zr(4)	135.6(14)	C(61)-N(10)-Zr(4)	118.9(10)
C(64)-N(11)-C(63)	106.7(11)	C(64)-N(11)-Zr(4)	128.6(8)
C(63)-N(11)-Zr(4)	124.2(10)	C(66)-N(12)-C(65)	111.4(9)
C(66)-N(12)-Zr(4)	121.2(7)	C(65)-N(12)-Zr(4)	127.0(7)
C(86)#1-O(1)-C(81)	113.5(8)	C(86)#1-O(1)-K(1)	114.7(6)
C(81)-O(1)-K(1)	115.1(6)	C(83)-O(2)-C(82)	113.0(8)
C(83)-O(2)-K(1)	114.5(6)	C(82)-O(2)-K(1)	115.5(7)
C(85)-O(3)-C(84)	112.4(8)	C(85)-O(3)-K(1)	113.3(6)
C(84)-O(3)-K(1)	114.2(6)	C(129)-O(16)-C(118)	115.6(10)
C(129)-O(16)-K(3)	113.4(7)	C(118)-O(16)-K(3)	115.9(7)
C(119)-O(17)-C(120)	113.8(8)	C(119)-O(17)-K(3)	113.0(6)
C(120)-O(17)-K(3)	113.9(6)	C(121)-O(18)-C(122)	115.0(9)
C(121)-O(18)-K(3)	115.6(7)	C(122)-O(18)-K(3)	112.2(7)
C(124)-O(19)-C(123)	115.7(9)	C(124)-O(19)-K(3)	113.6(6)
C(123)-O(19)-K(3)	113.6(7)	C(125)-O(20)-C(126)	115.4(9)
C(125)-O(20)-K(3)	116.7(7)	C(126)-O(20)-K(3)	113.0(6)
C(127)-O(21)-C(128)	113.6(9)	C(127)-O(21)-K(3)	115.2(7)

Table A18 (continued)

C(128)-O(21)-K(3)	114.0(7)	C(144)-O(22)-C(154)	110.8(8)
C(144)-O(22)-K(2)	117.0(6)	C(154)-O(22)-K(2)	113.1(6)
C(146)-O(23)-C(145)	115.2(8)	C(146)-O(23)-K(2)	113.7(6)
C(145)-O(23)-K(2)	115.3(6)	C(148)-O(24)-C(147)	113.9(8)
C(148)-O(24)-K(2)	119.3(6)	C(147)-O(24)-K(2)	116.3(6)
C(150)-O(25)-C(149)	110.9(7)	C(150)-O(25)-K(2)	110.8(6)
C(149)-O(25)-K(2)	114.8(6)	C(99)-O(26)-C(151)	113.1(11)
C(99)-O(26)-K(2)	118.8(6)	C(151)-O(26)-K(2)	117.4(9)
C(153)-O(27)-C(152)	110.2(13)	C(153)-O(27)-K(2)	116.3(7)
C(152)-O(27)-K(2)	116.9(12)	C(166)-O(28)-C(155)	114.5(7)
C(166)-O(28)-K(2)	125.5(5)	C(155)-O(28)-K(2)	116.0(5)
C(157)-O(29)-C(156)	110.8(7)	C(158)-O(30)-C(159)	113.3(8)
C(161)-O(31)-C(160)	113.8(8)	C(163)-O(32)-C(162)	112.6(8)
C(164)-O(33)-C(165)	112.2(7)	C(164)-O(33)-K(2)	115.1(5)
C(165)-O(33)-K(2)	103.2(5)	C(168)-O(34)-C(169)	112.4(8)
C(168)-O(34)-K(5)	112.8(6)	C(169)-O(34)-K(5)	116.6(6)
C(171)-O(35)-C(170)	113.3(8)	C(171)-O(35)-K(5)	116.0(6)
C(170)-O(35)-K(5)	112.9(6)	C(167)#2-O(36)-C(172)	113.9(7)
C(167)#2-O(36)-K(5)	112.7(5)	C(172)-O(36)-K(5)	115.8(6)

Table A18 (continued)

C(228)-O(101)-C(239)	119.3(13)	C(228)-O(101)-K(4)	117.1(9)
C(239)-O(101)-K(4)	112.7(9)	C(230)-O(102)-C(229)	113.3(15)
C(230)-O(102)-K(4)	111.2(10)	C(229)-O(102)-K(4)	111.7(10)
C(232)-O(103)-C(231)	119.7(15)	C(232)-O(103)-K(4)	120.2(12)
C(231)-O(103)-K(4)	108.7(9)	C(234)-O(104)-C(233)	130.2(15)
C(234)-O(104)-K(4)	106.0(12)	C(233)-O(104)-K(4)	107.9(9)
C(235)-O(105)-C(236)	113.9(17)	C(235)-O(105)-K(4)	117.1(13)
C(236)-O(105)-K(4)	118.3(11)	C(238)-O(106)-C(237)	119.7(13)
C(238)-O(106)-K(4)	108.9(9)	C(237)-O(106)-K(4)	106.6(8)
C(249)-O(107)-C(241)	111.2(9)	C(249)-O(107)-K(4)	126.1(7)
C(241)-O(107)-K(4)	95.7(6)	C(240)-O(108)-C(247)	114.2(8)
C(240)-O(108)-K(4)	123.0(6)	C(247)-O(108)-K(4)	122.7(6)
C(248)-O(112)-C(251)	114.1(8)	C(250)-O(113)-C(253)	112.3(13)
C(255)-O(114)-C(254)	106.8(13)	C(252)-O(117)-C(259)	113.9(11)
C(13)-Si(1)-Si(4)	101.5(3)	C(13)-Si(1)-Si(3)	99.2(3)
Si(4)-Si(1)-Si(3)	104.84(12)	C(13)-Si(1)-Zr(1)	113.4(3)
Si(4)-Si(1)-Zr(1)	118.09(11)	Si(3)-Si(1)-Zr(1)	117.11(10)
C(14)-Si(2)-Si(5)	101.7(3)	C(14)-Si(2)-Si(6)	102.5(3)
Si(5)-Si(2)-Si(6)	105.25(13)	C(14)-Si(2)-Zr(1)	114.5(3)

Table A18 (continued)

Si(5)-Si(2)-Zr(1)	116.73(11)	Si(6)-Si(2)-Zr(1)	114.32(11)
C(7)-Si(3)-C(8)	105.7(5)	C(7)-Si(3)-C(9)	104.9(5)
C(8)-Si(3)-C(9)	105.8(5)	C(7)-Si(3)-Si(1)	110.4(3)
C(8)-Si(3)-Si(1)	115.9(4)	C(9)-Si(3)-Si(1)	113.3(3)
C(12)-Si(4)-C(11)	105.5(6)	C(12)-Si(4)-C(10)	105.7(5)
C(11)-Si(4)-C(10)	106.6(6)	C(12)-Si(4)-Si(1)	111.0(4)
C(11)-Si(4)-Si(1)	111.3(5)	C(10)-Si(4)-Si(1)	116.1(4)
C(16)-Si(5)-C(15)	107.5(6)	C(16)-Si(5)-C(17)	106.9(5)
C(15)-Si(5)-C(17)	105.0(5)	C(16)-Si(5)-Si(2)	113.8(4)
C(15)-Si(5)-Si(2)	108.1(4)	C(17)-Si(5)-Si(2)	114.9(4)
C(18)-Si(6)-Si(2)	112.9(3)	C(20)-Si(6)-Si(2)	113.7(4)
C(33)-Si(7)-Si(10)	96.8(3)	C(33)-Si(7)-Si(9)	103.6(3)
Si(10)-Si(7)-Si(9)	105.47(13)	C(33)-Si(7)-Zr(2)	113.2(3)
Si(10)-Si(7)-Zr(2)	124.26(11)	Si(9)-Si(7)-Zr(2)	111.09(11)
C(34)-Si(8)-Si(11)	100.0(3)	C(34)-Si(8)-Si(12)	104.6(3)
Si(11)-Si(8)-Si(12)	103.77(12)	C(34)-Si(8)-Zr(2)	115.0(3)
Si(11)-Si(8)-Zr(2)	118.67(11)	Si(12)-Si(8)-Zr(2)	113.04(10)
C(27)-Si(9)-C(28)	108.0(6)	C(27)-Si(9)-C(29)	104.0(6)
C(28)-Si(9)-C(29)	104.7(6)	C(27)-Si(9)-Si(7)	111.6(5)

Table A18 (continued)

C(28)-Si(9)-Si(7)	111.7(4)	C(29)-Si(9)-Si(7)	116.3(4)
C(30)-Si(10)-C(32)	107.8(5)	C(30)-Si(10)-C(31)	105.7(5)
C(32)-Si(10)-C(31)	103.5(5)	C(30)-Si(10)-Si(7)	110.9(4)
C(32)-Si(10)-Si(7)	118.7(4)	C(31)-Si(10)-Si(7)	109.2(3)
C(35)-Si(11)-C(37)	106.8(5)	C(35)-Si(11)-C(36)	105.7(5)
C(37)-Si(11)-C(36)	105.5(5)	C(35)-Si(11)-Si(8)	110.8(4)
C(37)-Si(11)-Si(8)	115.9(4)	C(36)-Si(11)-Si(8)	111.6(4)
C(40)-Si(12)-C(39)	107.2(4)	C(40)-Si(12)-C(38)	106.0(4)
C(39)-Si(12)-C(38)	104.9(4)	C(40)-Si(12)-Si(8)	111.7(3)
C(39)-Si(12)-Si(8)	110.4(3)	C(38)-Si(12)-Si(8)	116.0(3)
C(60)-Si(13)-Si(14)	98.5(3)	C(60)-Si(13)-Si(15)	102.2(3)
Si(14)-Si(13)-Si(15)	106.17(12)	C(60)-Si(13)-Zr(3)	114.0(3)
Si(14)-Si(13)-Zr(3)	118.00(10)	Si(15)-Si(13)-Zr(3)	115.60(10)
C(49)-Si(14)-C(47)	105.0(4)	C(49)-Si(14)-C(48)	107.1(5)
C(47)-Si(14)-C(48)	105.3(4)	C(49)-Si(14)-Si(13)	113.5(3)
C(47)-Si(14)-Si(13)	110.6(3)	C(48)-Si(14)-Si(13)	114.6(3)
C(52)-Si(15)-C(51)	106.1(5)	C(52)-Si(15)-C(50)	105.3(5)
C(51)-Si(15)-C(50)	106.5(5)	C(52)-Si(15)-Si(13)	111.4(3)
C(51)-Si(15)-Si(13)	110.3(4)	C(50)-Si(15)-Si(13)	116.5(4)

Table A18 (continued)

C(59)-Si(16)-Si(17)	103.1(3)	C(59)-Si(16)-Si(18)	101.6(3)
Si(17)-Si(16)-Si(18)	105.73(12)	C(59)-Si(16)-Zr(3)	113.8(2)
Si(17)-Si(16)-Zr(3)	117.50(10)	Si(18)-Si(16)-Zr(3)	113.38(10)
C(55)-Si(17)-C(53)	107.7(5)	C(55)-Si(17)-C(54)	105.0(5)
C(53)-Si(17)-C(54)	107.7(5)	C(55)-Si(17)-Si(16)	114.9(3)
C(53)-Si(17)-Si(16)	108.1(4)	C(54)-Si(17)-Si(16)	113.1(4)
C(58)-Si(18)-C(56)	106.3(5)	C(58)-Si(18)-C(57)	105.0(5)
C(56)-Si(18)-C(57)	105.9(5)	C(58)-Si(18)-Si(16)	114.8(3)
C(56)-Si(18)-Si(16)	112.3(3)	C(57)-Si(18)-Si(16)	111.9(3)
C(73)-Si(19)-Si(21)	99.3(3)	C(73)-Si(19)-Si(20)	103.2(3)
Si(21)-Si(19)-Si(20)	102.47(13)	C(73)-Si(19)-Zr(4)	112.4(3)
Si(21)-Si(19)-Zr(4)	122.36(12)	Si(20)-Si(19)-Zr(4)	114.50(11)
C(68)-Si(20)-C(67)	103.7(6)	C(68)-Si(20)-C(69)	105.7(5)
C(67)-Si(20)-C(69)	106.6(6)	C(68)-Si(20)-Si(19)	112.3(4)
C(67)-Si(20)-Si(19)	114.0(4)	C(69)-Si(20)-Si(19)	113.6(4)
C(71)-Si(21)-C(70)	105.9(5)	C(71)-Si(21)-C(72)	107.4(5)
C(70)-Si(21)-C(72)	104.9(5)	C(71)-Si(21)-Si(19)	114.1(4)
C(70)-Si(21)-Si(19)	116.0(4)	C(72)-Si(21)-Si(19)	107.9(4)
C(74)-Si(22)-Si(23)	100.1(3)	C(74)-Si(22)-Si(24)	102.1(3)

Table A18 (continued)

Si(23)-Si(22)-Si(24)	104.53(14)	C(74)-Si(22)-Zr(4)	114.5(3)
Si(23)-Si(22)-Zr(4)	121.86(12)	Si(24)-Si(22)-Zr(4)	111.41(11)
C(77)-Si(23)-C(75)	106.2(6)	C(77)-Si(23)-C(76)	106.3(6)
C(75)-Si(23)-C(76)	105.7(6)	C(77)-Si(23)-Si(22)	117.3(4)
C(75)-Si(23)-Si(22)	110.0(5)	C(76)-Si(23)-Si(22)	110.6(5)
C(79)-Si(24)-C(78)	105.0(5)	C(79)-Si(24)-C(80)	105.3(5)
C(78)-Si(24)-C(80)	105.1(5)	C(79)-Si(24)-Si(22)	111.3(4)
C(78)-Si(24)-Si(22)	114.3(4)	C(80)-Si(24)-Si(22)	115.0(4)
N(2)-Zr(1)-N(1)	98.8(3)	N(2)-Zr(1)-N(3)	110.6(3)
N(1)-Zr(1)-N(3)	97.6(3)	N(2)-Zr(1)-Si(2)	97.0(2)
N(1)-Zr(1)-Si(2)	152.9(2)	N(3)-Zr(1)-Si(2)	97.3(2)
N(2)-Zr(1)-Si(1)	126.1(2)	N(1)-Zr(1)-Si(1)	83.4(2)
N(3)-Zr(1)-Si(1)	122.6(2)	Si(2)-Zr(1)-Si(1)	69.42(7)
N(6)-Zr(2)-N(5)	103.6(3)	N(6)-Zr(2)-N(4)	104.6(3)
N(5)-Zr(2)-N(4)	95.2(3)	N(6)-Zr(2)-Si(8)	98.4(2)
N(5)-Zr(2)-Si(8)	95.6(2)	N(4)-Zr(2)-Si(8)	151.5(2)
N(6)-Zr(2)-Si(7)	122.7(2)	N(5)-Zr(2)-Si(7)	132.4(2)
N(4)-Zr(2)-Si(7)	83.9(2)	Si(8)-Zr(2)-Si(7)	69.46(7)
N(8)-Zr(3)-N(7)	99.4(3)	N(8)-Zr(3)-N(9)	110.2(3)

Table A18 (continued)

N(7)-Zr(3)-N(9)	98.5(3)	N(8)-Zr(3)-Si(16)	96.9(2)
N(7)-Zr(3)-Si(16)	153.2(2)	N(9)-Zr(3)-Si(16)	95.7(2)
N(8)-Zr(3)-Si(13)	124.2(2)	N(7)-Zr(3)-Si(13)	84.1(2)
N(9)-Zr(3)-Si(13)	124.4(2)	Si(16)-Zr(3)-Si(13)	69.09(6)
N(12)-Zr(4)-N(10)	107.8(4)	N(12)-Zr(4)-N(11)	101.8(3)
N(10)-Zr(4)-N(11)	97.4(4)	N(12)-Zr(4)-Si(22)	105.0(2)
N(10)-Zr(4)-Si(22)	144.0(3)	N(11)-Zr(4)-Si(22)	89.9(3)
N(12)-Zr(4)-Si(19)	106.5(2)	N(10)-Zr(4)-Si(19)	87.7(3)
N(11)-Zr(4)-Si(19)	148.2(3)	Si(22)-Zr(4)-Si(19)	69.09(7)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2, -y+1, -z+2 #2 -x, -y, -z

Table A19 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in 7. The Anisotropic Displacement Factor Exponent Takes the Form: $-2\pi^2[h^2a^{*2}U^{11} + \dots + 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	62	62	62	12	5	12
C(2)	82	82	82	17	6	17
C(3)	75	75	75	15	6	15
C(4)	78	78	78	16	6	16
C(5)	81	81	81	16	6	16
C(6)	58	58	58	12	4	12
C(7)	47	47	47	10	4	10
C(8)	51	51	51	10	4	10
C(9)	50	50	50	10	4	10
C(10)	56	56	56	11	4	11
C(11)	77	77	77	15	6	15
C(12)	55	55	55	11	4	11
C(13)	35	35	35	7	3	7
C(14)	36	36	36	7	3	7
C(15)	71	71	71	14	5	14
C(16)	67	67	67	14	5	14

Table A19 (continued)

C(17)	61	61	61	12	5	12
C(18)	51	51	51	10	4	10
C(19)	58	58	58	12	4	12
C(20)	54	54	54	11	4	11
C(21)	57	57	57	12	4	12
C(22)	57	57	57	12	4	12
C(23)	62	62	62	13	5	13
C(24)	55	55	55	11	4	11
C(25)	48	48	48	10	4	10
C(26)	46	46	46	9	3	9
C(27)	85	85	85	17	6	17
C(28)	76	76	76	15	6	15
C(29)	71	71	71	14	5	14
C(30)	54	54	54	11	4	11
C(31)	51	51	51	10	4	10
C(32)	67	67	67	14	5	14
C(33)	30	30	30	6	2	6
C(34)	38	38	38	8	3	8
C(35)	55	55	55	11	4	11

Table A19 (continued)

C(36)	57	57	57	11	4	11
C(37)	59	59	59	12	4	12
C(38)	41	41	41	8	3	8
C(39)	42	42	42	9	3	9
C(40)	40	40	40	8	3	8
C(41)	51	51	51	10	4	10
C(42)	70	70	70	14	5	14
C(43)	78	78	78	16	6	16
C(44)	69	69	69	14	5	14
C(45)	67	67	67	13	5	13
C(46)	47	47	47	9	3	9
C(47)	43	43	43	9	3	9
C(48)	50	50	50	10	4	10
C(49)	48	48	48	10	4	10
C(50)	52	52	52	10	4	10
C(51)	54	54	54	11	4	11
C(52)	50	50	50	10	4	10
C(53)	57	57	57	12	4	12
C(54)	57	57	57	12	4	12

Table A19 (continued)

C(55)	48	48	48	10	4	10
C(56)	45	45	45	9	3	9
C(57)	50	50	50	10	4	10
C(58)	52	52	52	10	4	10
C(59)	28	28	28	6	2	6
C(60)	29	29	29	6	2	6
C(61)	131	131	131	27	10	26
C(62)	149	149	149	30	11	30
C(63)	118	118	118	24	9	24
C(64)	68	68	68	14	5	14
C(65)	80	80	80	16	6	16
C(66)	62	62	62	13	5	13
C(67)	68	68	68	14	5	14
C(68)	64	64	64	13	5	13
C(69)	62	62	62	13	5	13
C(70)	54	54	54	11	4	11
C(71)	66	66	66	13	5	13
C(72)	59	59	59	12	4	12
C(73)	43	43	43	9	3	9

Table A19 (continued)

C(74)	45	45	45	9	3	9
C(75)	82	82	82	17	6	17
C(76)	83	83	83	17	6	17
C(77)	74	74	74	15	6	15
C(78)	61	61	61	12	5	12
C(79)	60	60	60	12	4	12
C(80)	53	53	53	11	4	11
C(81)	63	63	63	13	5	13
C(82)	68	68	68	14	5	14
C(83)	58	58	58	12	4	12
C(84)	59	59	59	12	4	12
C(85)	61	61	61	12	5	12
C(86)	61	61	61	12	5	12
C(87)	40	40	40	8	3	8
C(88)	48	48	48	10	4	10
C(89)	68	68	68	14	5	14
C(90)	84	84	84	17	6	17
C(91)	79	79	79	16	6	16
C(92)	56	56	56	11	4	11

Table A19 (continued)

C(93)	82	82	82	17	6	17
C(99)	62	62	62	13	5	13
C(118)	67	67	67	13	5	13
C(119)	59	59	59	12	4	12
C(120)	57	57	57	12	4	12
C(121)	64	64	64	13	5	13
C(122)	76	76	76	15	6	15
C(123)	74	74	74	15	6	15
C(124)	64	64	64	13	5	13
C(125)	65	65	65	13	5	13
C(126)	63	63	63	13	5	13
C(127)	63	63	63	13	5	13
C(128)	66	66	66	13	5	13
C(129)	75	75	75	15	6	15
C(130)	50	50	50	10	4	10
C(131)	50	50	50	10	4	10
C(132)	55	55	55	11	4	11
C(133)	65	65	65	13	5	13
C(134)	63	63	63	13	5	13

Table A19 (continued)

C(135)	59	59	59	12	4	12
C(136)	105	105	105	21	8	21
C(137)	31	31	31	6	2	6
C(138)	36	36	36	7	3	7
C(139)	53	53	53	11	4	11
C(140)	62	62	62	12	5	12
C(141)	52	52	52	11	4	11
C(142)	43	43	43	9	3	9
C(143)	57	57	57	11	4	11
C(144)	58	58	58	12	4	12
C(145)	61	61	61	12	5	12
C(146)	62	62	62	12	5	12
C(147)	65	65	65	13	5	13
C(148)	50	50	50	10	4	10
C(149)	51	51	51	10	4	10
C(150)	52	52	52	10	4	10
C(151)	123	123	123	25	9	25
C(152)	178	178	178	36	13	36
C(153)	76	76	76	15	6	15

Table A19 (continued)

C(154)	61	61	61	12	5	12
C(155)	45	45	45	9	3	9
C(156)	39	39	39	8	3	8
C(157)	49	49	49	10	4	10
C(158)	51	51	51	10	4	10
C(159)	63	63	63	13	5	13
C(160)	58	58	58	12	4	12
C(161)	58	58	58	12	4	12
C(162)	54	54	54	11	4	11
C(163)	50	50	50	10	4	10
C(164)	46	46	46	9	3	9
C(165)	41	41	41	8	3	8
C(166)	38	38	38	8	3	8
C(167)	49	49	49	10	4	10
C(168)	58	58	58	12	4	12
C(169)	55	55	55	11	4	11
C(170)	55	55	55	11	4	11
C(171)	55	55	55	11	4	11
C(172)	54	54	54	11	4	11

Table A19 (continued)

C(173)	45	45	45	9	3	9
C(174)	44	44	44	9	3	9
C(175)	54	54	54	11	4	11
C(176)	60	60	60	12	4	12
C(177)	70	70	70	14	5	14
C(178)	53	53	53	11	4	11
C(179)	90	90	90	18	7	18
C(228)	102	102	102	21	8	21
C(229)	117	117	117	24	9	24
C(230)	127	127	127	26	9	26
C(231)	109	109	109	22	8	22
C(232)	129	129	129	26	10	26
C(233)	102	102	102	21	8	21
C(234)	138	138	138	28	10	28
C(235)	155	155	155	31	12	31
C(236)	127	127	127	26	9	26
C(237)	102	102	102	21	8	21
C(238)	106	106	106	22	8	22
C(239)	102	102	102	21	8	21

Table A19 (continued)

C(240)	52	52	52	11	4	11
C(241)	57	57	57	11	4	11
C(247)	50	50	50	10	4	10
C(248)	47	47	47	10	4	10
C(249)	81	81	81	16	6	16
C(250)	80	80	80	16	6	16
C(251)	66	66	66	13	5	13
C(252)	75	75	75	15	6	15
C(253)	110	110	110	22	8	22
C(254)	137	137	137	28	10	28
C(255)	89	89	89	18	7	18
C(259)	86	86	86	17	6	17
K(1)	43	43	43	9	3	9
K(2)	37	37	37	7	3	7
K(3)	35	35	35	7	3	7
K(4)	34	34	34	7	3	7
K(5)	37	37	37	7	3	7
N(1)	45	45	45	9	3	9
N(2)	45	45	45	9	3	9

Table A19 (continued)

N(3)	46	46	46	9	3	9
N(4)	43	43	43	9	3	9
N(5)	42	42	42	8	3	8
N(6)	35	35	35	7	3	7
N(7)	40	40	40	8	3	8
N(8)	42	42	42	8	3	8
N(9)	35	35	35	7	3	7
N(10)	72	72	72	15	5	15
N(11)	62	62	62	12	5	12
N(12)	45	45	45	9	3	9
O(1)	48	48	48	10	4	10
O(2)	52	52	52	11	4	11
O(3)	52	52	52	11	4	11
O(16)	56	56	56	11	4	11
O(17)	52	52	52	11	4	11
O(18)	57	57	57	12	4	12
O(19)	55	55	55	11	4	11
O(20)	51	51	51	10	4	10
O(21)	56	56	56	11	4	11

Table A19 (continued)

O(22)	50	50	50	10	4	10
O(23)	53	53	53	11	4	11
O(24)	54	54	54	11	4	11
O(25)	42	42	42	9	3	9
O(26)	54	54	54	11	4	11
O(27)	66	66	66	13	5	13
O(28)	36	36	36	7	3	7
O(29)	44	44	44	9	3	9
O(30)	50	50	50	10	4	10
O(31)	51	51	51	10	4	10
O(32)	51	51	51	10	4	10
O(33)	38	38	38	8	3	8
O(34)	47	47	47	9	3	9
O(35)	48	48	48	10	4	10
O(36)	41	41	41	8	3	8
O(101)	83	83	83	17	6	17
O(102)	98	98	98	20	7	20
O(103)	97	97	97	20	7	20
O(104)	124	124	124	25	9	25

Table A19 (continued)

O(105)	102	102	102	21	8	21
O(106)	82	82	82	17	6	17
O(107)	49	49	49	10	4	10
O(108)	46	46	46	9	3	9
O(112)	60	60	60	12	4	12
O(113)	95	95	95	19	7	19
O(114)	91	91	91	18	7	18
O(117)	81	81	81	16	6	16
Si(1)	25	25	25	5	2	5
Si(2)	26	26	26	5	2	5
Si(3)	32	32	32	7	2	7
Si(4)	35	35	35	7	3	7
Si(5)	40	40	40	8	3	8
Si(6)	36	36	36	7	3	7
Si(7)	27	27	27	6	2	6
Si(8)	27	27	27	5	2	5
Si(9)	43	43	43	9	3	9
Si(10)	35	35	35	7	3	7
Si(11)	36	36	36	7	3	7

Table A19 (continued)

Si(12)	29	29	29	6	2	6
Si(13)	23	23	23	5	2	5
Si(14)	30	30	30	6	2	6
Si(15)	30	30	30	6	2	6
Si(16)	24	24	24	5	2	5
Si(17)	35	35	35	7	3	7
Si(18)	31	31	31	6	2	6
Si(19)	31	31	31	6	2	6
Si(20)	42	42	42	8	3	8
Si(21)	40	40	40	8	3	8
Si(22)	34	34	34	7	3	7
Si(23)	47	47	47	9	3	9
Si(24)	38	38	38	8	3	8
Zr(1)	31	36	18	8	2	9
Zr(2)	29	26	22	5	5	5
Zr(3)	23	36	20	5	0	4
Zr(4)	27	37	22	4	1	4

Table A20. Hydrogen Coordinates ($\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in **7**

	x	y	z	U(eq)
H(1A)	5709	977	8088	93
H(1B)	6106	1320	8440	93
H(1C)	6625	1502	8135	93
H(2A)	5730	1823	7760	123
H(2B)	4664	2001	7837	123
H(2C)	4703	1365	7730	123
H(3A)	1894	1038	8211	113
H(3B)	3002	1071	8379	113
H(3C)	2837	961	7997	113
H(4A)	2315	1788	7768	117
H(4B)	2337	2337	8029	117
H(4C)	1480	1799	8028	117
H(5A)	5575	3284	8046	122
H(5B)	6134	2838	8158	122
H(5C)	6190	3421	8390	122
H(6A)	4459	3636	8562	87

Table A20 (continued)

H(6B)	3487	3141	8468	87
H(6C)	4045	3414	8195	87
H(7A)	2906	630	8831	71
H(7B)	3025	775	9214	71
H(7C)	3058	168	9027	71
H(8A)	4765	-108	8664	77
H(8B)	5810	318	8652	77
H(8C)	4796	350	8451	77
H(9A)	5028	780	9578	75
H(9B)	6017	670	9395	75
H(9C)	5044	181	9375	75
H(10A)	8448	1455	9031	84
H(10B)	7661	1241	8721	84
H(10C)	7410	1024	9043	84
H(11A)	7308	2847	8954	115
H(11B)	7528	2405	8656	115
H(11C)	8367	2638	8952	115
H(12A)	8181	2250	9575	82
H(12B)	7098	1940	9663	82

Table A20 (continued)

H(12C)	7241	2561	9614	82
H(13A)	4880	1809	9584	42
H(13B)	5207	2417	9515	42
H(14A)	3450	2298	9625	43
H(14B)	3170	1730	9367	43
H(15A)	219	1647	8982	107
H(15B)	1264	1477	9079	107
H(15C)	1024	1541	8720	107
H(16A)	1269	2645	8532	100
H(16B)	1451	3207	8793	100
H(16C)	374	2785	8753	100
H(17A)	1180	3139	9500	91
H(17B)	1454	2638	9642	91
H(17C)	353	2578	9462	91
H(18A)	5803	4050	9348	76
H(18B)	5567	3646	9005	76
H(18C)	5958	3429	9306	76
H(19A)	4534	3307	9869	88
H(19B)	3431	3464	9849	88

Table A20 (continued)

H(19C)	4445	3933	9887	88
H(20A)	2716	3891	9277	81
H(20B)	3425	3953	8986	81
H(20C)	3758	4342	9330	81
H(21A)	7495	89	7059	85
H(21B)	7110	-159	6691	85
H(21C)	6443	-351	6968	85
H(22A)	5652	416	7327	86
H(22B)	6060	1017	7258	86
H(22C)	6849	682	7378	86
H(23A)	3358	220	7080	94
H(23B)	4293	-63	6965	94
H(23C)	3247	-201	6744	94
H(24A)	2725	691	6609	83
H(24B)	3646	1193	6598	83
H(24C)	3253	1086	6935	83
H(25A)	6955	2161	6567	72
H(25B)	7249	1569	6519	72
H(25C)	7508	1986	6858	72

Table A20 (continued)

H(26A)	6126	2124	7214	69
H(26B)	4969	1847	7085	69
H(26C)	5572	2350	6944	69
H(27A)	4397	-887	6121	128
H(27B)	5108	-760	6447	128
H(27C)	4871	-1365	6228	128
H(28A)	5565	-1487	5522	114
H(28B)	6414	-1014	5431	114
H(28C)	5269	-923	5474	114
H(29A)	7332	-1079	6360	107
H(29B)	7722	-1169	6007	107
H(29C)	6782	-1600	6094	107
H(30A)	9820	95	5734	80
H(30B)	8742	74	5550	80
H(30C)	8905	-423	5716	80
H(31A)	9939	1177	6188	76
H(31B)	8962	1325	6365	76
H(31C)	8962	1248	5984	76
H(32A)	9034	-255	6484	101

Table A20 (continued)

H(32B)	9176	361	6684	101
H(32C)	10037	190	6456	101
H(33A)	7045	744	5669	36
H(33B)	6844	103	5508	36
H(34A)	5065	11	5532	46
H(34B)	5437	544	5383	46
H(35A)	2587	-48	6142	83
H(35B)	2963	-404	5833	83
H(35C)	1847	-260	5821	83
H(36A)	3271	77	5215	85
H(36B)	3104	686	5215	85
H(36C)	2150	211	5243	85
H(37A)	1538	889	5828	88
H(37B)	2472	1388	5822	88
H(37C)	2302	1146	6140	88
H(38A)	3904	1824	5452	62
H(38B)	4769	1584	5253	62
H(38C)	4932	2229	5398	62
H(39A)	6900	2370	5785	63

Table A20 (continued)

H(39B)	6927	1765	5592	63
H(39C)	7112	1910	5974	63
H(40A)	5321	2298	6361	60
H(40B)	4181	2168	6197	60
H(40C)	5029	2643	6106	60
H(41A)	5836	3596	3018	76
H(41B)	6133	3879	3387	76
H(41C)	6723	4134	3113	76
H(42A)	5844	4576	2755	105
H(42B)	4681	4628	2804	105
H(42C)	4947	4041	2665	105
H(43A)	1965	3554	3171	117
H(43B)	3157	3559	3233	117
H(43C)	2678	3511	2877	117
H(44A)	2161	4314	2728	103
H(44B)	2318	4878	2986	103
H(44C)	1451	4365	3022	103
H(45A)	5574	5830	3039	100
H(45B)	6176	5504	3243	100

Table A20 (continued)

H(45C)	5974	6095	3404	100
H(46A)	4314	6213	3516	70
H(46B)	3378	5699	3476	70
H(46C)	3806	5910	3167	70
H(47A)	2970	2620	3884	64
H(47B)	2807	3190	3801	64
H(47C)	2974	3138	4166	64
H(48A)	5702	2896	3525	75
H(48B)	4591	2865	3361	75
H(48C)	4773	2411	3559	75
H(49A)	5088	3250	4492	72
H(49B)	5965	3063	4276	72
H(49C)	4922	2635	4288	72
H(50A)	8380	4029	4038	77
H(50B)	7645	3786	3718	77
H(50C)	7356	3582	4042	77
H(51A)	7100	5342	3875	81
H(51B)	7430	4889	3605	81
H(51C)	8203	5189	3910	81

Table A20 (continued)

H(52A)	8041	4867	4545	75
H(52B)	7004	4514	4635	75
H(52C)	7027	5119	4571	75
H(53A)	990	3946	3960	86
H(53B)	1003	4063	3604	86
H(53C)	52	4152	3812	86
H(54A)	315	5365	3706	85
H(54B)	1221	5243	3485	85
H(54C)	1419	5764	3775	85
H(55A)	159	5038	4368	71
H(55B)	1042	5580	4443	71
H(55C)	1213	5037	4558	71
H(56A)	5479	6061	4006	68
H(56B)	5835	5887	4327	68
H(56C)	5662	6499	4338	68
H(57A)	4313	6300	4891	75
H(57B)	4395	5667	4841	75
H(57C)	3296	5831	4837	75
H(58A)	3660	6804	4375	78

Table A20 (continued)

H(58B)	2607	6364	4288	78
H(58C)	3357	6479	4014	78
H(59A)	3218	4692	4552	33
H(59B)	3002	4152	4272	33
H(60A)	4674	4223	4519	35
H(60B)	5008	4848	4478	35
H(61A)	5779	1411	1612	197
H(61B)	4864	1731	1586	197
H(61C)	5264	1647	1928	197
H(62A)	7098	1855	1973	179
H(62B)	7682	2488	1969	179
H(63A)	4738	2866	2318	177
H(63B)	4363	2308	2059	177
H(63C)	3570	2692	2176	177
H(64A)	3119	3125	1828	102
H(64B)	3966	3556	1701	102
H(64C)	3881	3596	2077	102
H(65A)	6901	4094	2283	120
H(65B)	5883	4086	2071	120

Table A20 (continued)

H(65C)	6941	4469	2020	120
H(66A)	8179	4054	1690	93
H(66B)	8095	3403	1637	93
H(66C)	8336	3775	1989	93
H(67A)	4164	1593	743	102
H(67B)	4524	1388	1052	102
H(67C)	4350	979	710	102
H(68A)	5735	1081	199	96
H(68B)	6680	1587	224	96
H(68C)	5533	1685	202	96
H(69A)	6451	726	762	93
H(69B)	6698	1116	1109	93
H(69C)	7462	1199	834	93
H(70A)	9585	2357	511	82
H(70B)	8463	2316	352	82
H(70C)	8699	1838	522	82
H(71A)	8947	1973	1234	99
H(71B)	8989	2551	1470	99
H(71C)	9902	2468	1244	99

Table A20 (continued)

H(72A)	9002	3605	1168	88
H(72B)	8749	3530	791	88
H(72C)	9817	3428	924	88
H(73A)	6779	3331	693	51
H(73B)	6515	2763	436	51
H(74A)	4818	2605	558	54
H(74B)	5083	3219	498	54
H(75A)	1911	2862	467	123
H(75B)	2733	2474	414	123
H(75C)	3069	3114	410	123
H(76A)	2603	2372	1333	125
H(76B)	2751	2024	990	125
H(76C)	1695	2221	1057	125
H(77A)	2440	3861	1078	111
H(77B)	2265	3561	1375	111
H(77C)	1473	3371	1065	111
H(78A)	4792	4876	774	92
H(78B)	3861	4357	725	92
H(78C)	4881	4310	545	92

Table A20 (continued)

H(79A)	6900	4342	918	90
H(79B)	6971	4423	1300	90
H(79C)	6768	4912	1134	90
H(80A)	5077	4617	1674	80
H(80B)	3981	4548	1489	80
H(80C)	4875	5059	1470	80
H(81A)	6584	4217	9987	76
H(81B)	7367	4470	10296	76
H(82A)	7446	3539	10094	82
H(82B)	7766	3692	9759	82
H(83A)	9429	3427	9812	69
H(83B)	9024	3219	10125	69
H(84A)	10431	3831	10437	71
H(84B)	10801	3387	10169	71
H(85A)	12433	4058	10229	74
H(85B)	12013	4538	10456	74
H(86A)	13379	4898	10151	74
H(86B)	12664	4620	9829	74
H(88)	9446	5392	8913	58

Table A20 (continued)

H(89)	11052	5324	9101	81
H(90)	11228	4501	9285	101
H(91)	9765	3785	9246	95
H(92)	8178	3867	9042	67
H(93A)	7565	4560	8575	123
H(93B)	7560	5084	8852	123
H(93C)	7058	4481	8902	123
H(99A)	1676	3823	8318	75
H(99B)	1574	4455	8361	75
H(11D)	1229	4270	4865	80
H(11E)	1165	3779	4561	80
H(11F)	2688	3895	4886	71
H(11G)	2032	3780	5182	71
H(12D)	2924	3036	5200	69
H(12E)	3481	3104	4880	69
H(12F)	2626	2217	4630	77
H(12G)	3319	2205	4941	77
H(12H)	2260	1333	4982	92
H(12I)	1520	1336	4679	92

Table A20 (continued)

H(12J)	692	817	5032	89
H(12K)	875	1363	5305	89
H(12L)	-1007	1296	5332	76
H(12M)	-1124	726	5080	76
H(12N)	-2038	1078	4711	78
H(12O)	-2609	1064	5035	78
H(12P)	-3445	1802	4913	75
H(12Q)	-2819	1850	4603	75
H(12R)	-3305	2679	4815	76
H(12S)	-2675	2710	5147	76
H(12T)	-1654	3590	5092	79
H(12U)	-2243	3557	4753	79
H(12V)	-705	3573	4507	91
H(12W)	-639	4112	4779	91
H(131)	-749	2897	3907	60
H(132)	883	2829	4078	66
H(133)	1174	2012	4207	78
H(134)	-179	1270	4195	76
H(135)	-1876	1346	4030	70

Table A20 (continued)

H(13C)	-2812	2443	4026	157
H(13D)	-3029	1826	3823	157
H(13E)	-2564	2328	3658	157
H(138)	1988	3613	5786	44
H(139)	370	3797	5637	64
H(140)	-1130	3135	5621	74
H(141)	-1049	2269	5724	62
H(142)	547	2082	5885	52
H(14C)	2326	2352	6033	85
H(14D)	2809	2996	6125	85
H(14E)	2877	2658	5771	85
H(14F)	-1045	1606	7090	69
H(14G)	-671	1247	7327	69
H(14H)	1085	1662	7270	73
H(14I)	526	1322	6932	73
H(14J)	1536	2479	6641	74
H(14K)	1644	1863	6649	74
H(14L)	2687	2169	7122	78
H(14M)	3165	2471	6848	78

Table A20 (continued)

H(14N)	4116	3215	7286	60
H(14O)	3558	2931	7556	60
H(14P)	4049	3906	7740	61
H(14Q)	3349	3994	7449	61
H(15D)	2341	4475	7841	62
H(15E)	3132	4388	8110	62
H(15F)	-7	4009	8420	147
H(15G)	-614	4204	8150	147
H(15H)	-1599	3577	8165	213
H(15I)	-824	3303	8339	213
H(15J)	-1887	2474	8073	91
H(15K)	-692	2460	8102	91
H(15L)	-1654	1691	7719	74
H(15M)	-1919	2113	7507	74
H(15N)	1898	3955	6620	54
H(15O)	2221	3960	6985	54
H(15P)	1952	4847	6952	47
H(15Q)	824	4594	6782	47
H(15R)	94	5117	7188	59

Table A20 (continued)

H(15S)	1169	5385	7390	59
H(15T)	-557	4738	7634	61
H(15U)	530	4977	7836	61
H(15V)	-512	6028	8194	76
H(15W)	-420	5414	8215	76
H(16D)	-2166	5571	8245	69
H(16E)	-2147	5641	7880	69
H(16F)	-3308	4892	7633	69
H(16G)	-3662	4708	7959	69
H(16H)	-3087	3855	7786	65
H(16I)	-3992	3913	7545	65
H(16J)	-3140	3255	7167	60
H(16K)	-2174	3347	7422	60
H(16L)	-2111	3536	6771	55
H(16M)	-1195	3875	7028	55
H(16N)	-1376	2885	6453	49
H(16O)	-551	2608	6607	49
H(16P)	323	3322	6370	45
H(16Q)	-239	3758	6582	45

Table A20 (continued)

H(16R)	-2426	546	189	59
H(16S)	-3202	350	-126	59
H(16T)	-1832	642	-432	70
H(16U)	-2118	1138	-181	70
H(16V)	-417	1698	-155	66
H(16W)	-95	1229	-419	66
H(17D)	1354	1784	-93	65
H(17E)	867	1594	215	65
H(17F)	2384	1179	301	66
H(17G)	2843	1375	-10	66
H(17H)	2760	442	-258	64
H(17I)	3503	615	64	64
H(174)	639	-441	1033	53
H(175)	-1022	-428	865	65
H(176)	-1394	356	692	72
H(177)	-64	1138	728	83
H(178)	1601	1118	900	64
H(17J)	2476	468	1347	135
H(17K)	2877	590	1014	135

Table A20 (continued)

H(17L)	2529	-30	1058	135
H(228)	8860	686	1462	122
H(229)	10721	1033	1737	141
H(230)	11654	1932	2041	152
H(23D)	10545	2660	1917	131
H(23E)	11579	2824	2144	131
H(232)	10173	3491	2357	154
H(233)	9713	3568	2892	123
H(23F)	7865	3131	3160	165
H(23G)	8341	2603	3186	165
H(235)	6311	2528	2948	186
H(236)	5438	1587	2753	152
H(237)	6036	687	2724	123
H(238)	6735	113	2240	128
H(239)	7163	292	1676	122
H(24D)	9918	1661	3465	63
H(24E)	10564	1278	3246	63
H(24F)	8903	781	3277	68
H(24G)	8422	1233	3144	68

Table A20 (continued)

H(24H)	10992	2487	3330	60
H(24I)	11036	2532	2962	60
H(24J)	12622	2390	3147	56
H(24K)	12074	1841	3259	56
H(24L)	9739	191	2939	97
H(24M)	10443	662	2795	97
H(25D)	8964	-245	2418	96
H(25E)	9584	244	2268	96
H(25F)	13147	1348	2900	80
H(25G)	13602	1853	2733	80
H(25H)	12240	863	2403	89
H(25I)	12700	1366	2237	89
H(25J)	9821	-751	1939	132
H(25K)	11404	-754	1769	164
H(25L)	11796	-676	2136	164
H(25M)	13231	-297	2011	107
H(25N)	13373	744	1863	103
H(25O)	14330	514	1976	103

Table A21 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in **8**. U(eq) is Defined as One Third of the Trace of the Orthogonalized U^{ij} Tensor.

	x	y	z	U(eq)
C(1)	6662(6)	7609(5)	4968(3)	37(2)
C(2)	7796(6)	7741(5)	5010(4)	37(2)
C(3)	9806(2)	9770(2)	526(2)	38(1)
C(4)	4330(3)	7515(3)	3139(3)	73(1)
C(5)	4033(4)	7082(3)	5140(3)	97(2)
C(6)	4417(5)	8992(3)	3633(3)	119(2)
C(7)	6946(3)	5617(2)	3359(2)	57(1)
C(8)	6359(3)	5102(2)	5384(2)	55(1)
C(9)	8636(3)	5561(3)	4399(3)	79(1)
C(10)	10696(5)	7592(3)	3319(4)	112(2)
C(11)	10570(4)	7744(3)	5043(3)	90(1)
C(12)	11063(3)	9385(2)	3156(2)	62(1)
C(13)	6386(3)	10480(4)	4055(3)	106(2)
C(14)	8455(3)	10369(3)	4680(3)	72(1)
C(15)	8461(3)	11180(3)	2650(2)	76(1)

Table A21 (continued)

C(16)	6841(3)	7865(2)	984(2)	53(1)
C(17)	9181(3)	7162(2)	1352(2)	56(1)
C(18)	8756(3)	8407(2)	-596(2)	62(1)
C(19)	7094(3)	10842(3)	-985(2)	73(1)
C(20)	5663(3)	10276(3)	879(2)	62(1)
C(21)	7365(3)	11608(2)	227(3)	72(1)
C(22)	120(3)	4197(2)	2425(2)	58(1)
C(23)	336(3)	4746(2)	2819(2)	56(1)
C(24)	1628(3)	5641(2)	2715(2)	55(1)
C(25)	2718(3)	5991(2)	2204(2)	58(1)
C(26)	4601(3)	5510(2)	1945(2)	61(1)
C(27)	5408(3)	4687(3)	2257(2)	62(1)
C(28)	5957(3)	3280(3)	2242(3)	67(1)
C(29)	5706(3)	2684(3)	1903(3)	66(1)
C(30)	4404(3)	1725(2)	2135(3)	68(1)
C(31)	3298(3)	1418(2)	2655(3)	69(1)
C(32)	1423(3)	1954(2)	2751(3)	63(1)
C(33)	670(3)	2799(2)	2379(3)	61(1)
C(34)	8026(3)	4454(2)	108(2)	56(1)

Table A21 (continued)

C(35)	8412(3)	4973(3)	373(3)	67(1)
C(36)	7887(5)	5788(3)	283(3)	90(1)
C(37)	6968(5)	6117(3)	-64(3)	94(2)
C(38)	6533(4)	5638(4)	-342(3)	85(1)
C(39)	7057(3)	4798(3)	-258(2)	69(1)
C(40)	8605(4)	3580(3)	194(4)	108(2)
C(1A)	7303(6)	7225(5)	4986(4)	31(2)
C(2A)	7325(7)	8156(6)	4948(4)	35(2)
K(1)	2995(1)	3591(1)	2634(1)	43(1)
O(1)	867(2)	3400(1)	2676(1)	48(1)
O(2)	1389(2)	5076(1)	2393(1)	48(1)
O(3)	3531(2)	5236(1)	2386(1)	49(1)
O(4)	5180(2)	4062(2)	2003(1)	53(1)
O(5)	4657(2)	2365(2)	2362(2)	57(1)
O(6)	2517(2)	2190(1)	2365(2)	56(1)
Si(1)	6732(1)	7438(1)	3880(1)	54(1)
Si(2)	8353(1)	8826(1)	3832(1)	74(1)
Si(3)	8367(1)	9337(1)	992(1)	31(1)
Si(4)	4834(1)	7750(1)	3948(1)	65(1)

Table A21 (continued)

Si(5)	7152(1)	5901(1)	4249(1)	45(1)
Si(6)	10220(1)	8384(1)	3850(1)	64(1)
Si(7)	7924(1)	10236(1)	3816(1)	59(1)
Si(8)	8289(1)	8187(1)	633(1)	37(1)
Si(9)	7097(1)	10542(1)	240(1)	40(1)
Zn(1)	7834(1)	8651(1)	2647(1)	30(1)

Table A22 Bond Distances (Å) in **8**

C(1)-C(2)	1.513(10)	C(1)-Si(1)	1.981(5)
C(2)-Si(2)	2.004(6)	C(2)-K(1)#1	3.460(6)
C(3)-C(3)#2	1.536(5)	C(3)-Si(3)	1.923(3)
C(4)-Si(4)	1.869(4)	C(5)-Si(4)	1.885(4)
C(6)-Si(4)	1.887(4)	C(7)-Si(5)	1.877(3)
C(8)-Si(5)	1.878(3)	C(9)-Si(5)	1.887(3)
C(10)-Si(6)	1.891(4)	C(11)-Si(6)	1.875(4)
C(12)-Si(6)	1.868(3)	C(13)-Si(7)	1.889(4)
C(14)-Si(7)	1.871(4)	C(15)-Si(7)	1.881(4)
C(16)-Si(8)	1.877(3)	C(17)-Si(8)	1.885(3)
C(18)-Si(8)	1.877(3)	C(19)-Si(9)	1.873(3)
C(20)-Si(9)	1.876(3)	C(21)-Si(9)	1.885(4)
C(22)-O(1)	1.418(4)	C(22)-C(23)	1.477(5)
C(23)-O(2)	1.420(4)	C(24)-O(2)	1.418(4)
C(24)-C(25)	1.488(5)	C(25)-O(3)	1.423(4)
C(26)-O(3)	1.414(4)	C(26)-C(27)	1.494(5)
C(27)-O(4)	1.419(4)	C(28)-O(4)	1.423(4)
C(28)-C(29)	1.491(5)	C(29)-O(5)	1.416(4)
C(30)-O(5)	1.424(4)	C(30)-C(31)	1.489(5)

Table A22 (continued)

C(31)-O(6)	1.418(4)	C(32)-O(6)	1.416(4)
C(32)-C(33)	1.486(5)	C(33)-O(1)	1.418(4)
C(34)-C(35)	1.367(5)	C(34)-C(39)	1.395(5)
C(34)-C(40)	1.468(5)	C(35)-C(36)	1.357(6)
C(36)-C(37)	1.323(7)	C(37)-C(38)	1.362(7)
C(38)-C(39)	1.397(6)	C(38)-K(1)#3	3.354(4)
C(1A)-C(2A)	1.548(11)	C(1A)-Si(1)	2.008(5)
C(1A)-K(1)#1	3.494(5)	C(2A)-Si(2)	1.945(6)
K(1)-O(1)	2.742(2)	K(1)-O(5)	2.772(2)
K(1)-O(3)	2.793(2)	Si(3)-Zn(1)	2.4076(8)
K(1)-O(6)	2.818(2)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, -y+1, -z+1 #2 -x+2, -y+2, -z #3 -x+1, -y+1, -z

Table A23 Bond Angles (deg) in **8**

C(2)-C(1)-Si(1)	109.5(5)	C(1)-C(2)-Si(2)	108.7(5)
C(1)-C(2)-K(1)#1	83.6(3)	Si(2)-C(2)-K(1)#1	157.6(3)
C(3)#2-C(3)-Si(3)	117.7(2)	O(1)-C(22)-C(23)	109.0(3)
O(2)-C(23)-C(22)	109.1(3)	O(2)-C(24)-C(25)	108.4(2)
O(3)-C(25)-C(24)	109.0(3)	O(3)-C(26)-C(27)	108.9(3)
O(4)-C(27)-C(26)	109.2(3)	O(4)-C(28)-C(29)	108.8(3)
O(5)-C(29)-C(28)	109.3(3)	O(5)-C(30)-C(31)	108.8(3)
O(6)-C(31)-C(30)	108.3(3)	O(6)-C(32)-C(33)	108.4(3)
O(1)-C(33)-C(32)	108.4(3)	C(35)-C(34)-C(39)	116.9(4)
C(35)-C(34)-C(40)	122.0(4)	C(39)-C(34)-C(40)	121.2(4)
C(36)-C(35)-C(34)	122.1(4)	C(37)-C(36)-C(35)	121.3(5)
C(36)-C(37)-C(38)	119.9(5)	C(37)-C(38)-C(39)	120.0(4)
C(37)-C(38)-K(1)#3	114.8(3)	C(39)-C(38)-K(1)#3	87.3(2)
C(34)-C(39)-C(38)	119.8(4)	C(2A)-C(1A)-Si(1)	109.4(5)
C(2A)-C(1A)-K(1)#1	82.9(3)	Si(1)-C(1A)-K(1)#1	150.8(3)
C(1A)-C(2A)-Si(2)	105.3(5)	O(1)-K(1)-O(5)	119.09(7)
O(1)-K(1)-O(3)	119.63(6)	O(5)-K(1)-O(3)	119.23(7)
O(1)-K(1)-O(6)	59.72(6)	O(5)-K(1)-O(6)	59.39(7)
O(3)-K(1)-O(6)	164.64(7)	O(1)-K(1)-O(4)	162.37(7)

Table A23 (continued)

O(5)-K(1)-O(4)	60.09(7)	O(3)-K(1)-O(4)	59.26(7)
O(6)-K(1)-O(4)	116.09(7)	O(1)-K(1)-O(2)	60.69(6)
O(5)-K(1)-O(2)	164.73(7)	O(3)-K(1)-O(2)	58.94(6)
O(6)-K(1)-O(2)	117.76(7)	O(4)-K(1)-O(2)	114.92(7)
O(1)-K(1)-C(38)#3	88.80(9)	O(5)-K(1)-C(38)#3	75.82(9)
O(3)-K(1)-C(38)#3	91.10(11)	O(6)-K(1)-C(38)#3	73.63(11)
O(4)-K(1)-C(38)#3	73.81(10)	O(2)-K(1)-C(38)#3	88.96(9)
O(1)-K(1)-C(2)#1	80.35(12)	O(5)-K(1)-C(2)#1	97.33(16)
O(3)-K(1)-C(2)#1	106.29(12)	O(6)-K(1)-C(2)#1	88.90(12)
O(4)-K(1)-C(2)#1	117.22(13)	O(2)-K(1)-C(2)#1	97.60(16)
C(38)#3-K(1)-C(2)#1	162.40(15)	O(1)-K(1)-C(1A)#1	95.05(12)
O(5)-K(1)-C(1A)#1	101.51(15)	O(3)-K(1)-C(1A)#1	87.71(11)
O(6)-K(1)-C(1A)#1	107.64(11)	O(4)-K(1)-C(1A)#1	102.39(12)
O(2)-K(1)-C(1A)#1	93.63(15)	C(38)#3-K(1)-C(1A)#1	176.07(15)
C(2)#1-K(1)-C(1A)#1	19.66(13)	C(22)-O(1)-C(33)	112.8(2)
C(22)-O(1)-K(1)	117.41(18)	C(33)-O(1)-K(1)	118.79(18)
C(24)-O(2)-C(23)	111.9(2)	C(24)-O(2)-K(1)	112.40(17)
C(23)-O(2)-K(1)	109.74(16)	C(26)-O(3)-C(25)	112.7(2)
C(26)-O(3)-K(1)	119.06(19)	C(25)-O(3)-K(1)	119.49(18)

Table A23 (continued)

C(27)-O(4)-C(28)	111.9(3)	C(27)-O(4)-K(1)	113.69(18)
C(28)-O(4)-K(1)	112.5(2)	C(29)-O(5)-C(30)	112.4(3)
C(29)-O(5)-K(1)	117.78(19)	C(30)-O(5)-K(1)	119.12(19)
C(31)-O(6)-C(32)	112.6(3)	C(31)-O(6)-K(1)	112.2(2)
C(32)-O(6)-K(1)	112.66(18)	C(1)-Si(1)-C(1A)	26.9(2)
C(1)-Si(1)-Si(5)	110.8(2)	C(1A)-Si(1)-Si(5)	91.1(2)
C(1)-Si(1)-Si(4)	91.7(2)	C(1A)-Si(1)-Si(4)	115.9(2)
Si(5)-Si(1)-Si(4)	107.49(4)	C(1)-Si(1)-Zn(1)	102.97(15)
C(1A)-Si(1)-Zn(1)	100.62(16)	Si(5)-Si(1)-Zn(1)	123.26(5)
Si(4)-Si(1)-Zn(1)	115.79(5)	C(2A)-Si(2)-C(2)	23.5(2)
C(2A)-Si(2)-Si(7)	96.6(3)	C(2)-Si(2)-Si(7)	116.1(2)
C(2A)-Si(2)-Si(6)	118.0(3)	C(2)-Si(2)-Si(6)	97.3(3)
Si(7)-Si(2)-Si(6)	110.01(4)	C(2A)-Si(2)-Zn(1)	104.86(19)
C(2)-Si(2)-Zn(1)	103.92(17)	Si(7)-Si(2)-Zn(1)	118.39(6)
Si(6)-Si(2)-Zn(1)	108.96(5)	C(3)-Si(3)-Si(8)	109.97(10)
C(3)-Si(3)-Si(9)	108.60(9)	Si(8)-Si(3)-Si(9)	106.84(4)
C(3)-Si(3)-Zn(1)	114.83(8)	Si(8)-Si(3)-Zn(1)	104.75(3)
Si(9)-Si(3)-Zn(1)	111.53(3)	C(4)-Si(4)-C(5)	107.5(2)
C(4)-Si(4)-C(6)	107.4(2)	C(5)-Si(4)-C(6)	105.2(2)

Table A23 (continued)

C(4)-Si(4)-Si(1)	112.42(12)	C(5)-Si(4)-Si(1)	113.30(16)
C(6)-Si(4)-Si(1)	110.6(2)	C(7)-Si(5)-C(8)	106.92(15)
C(7)-Si(5)-C(9)	107.57(18)	C(8)-Si(5)-C(9)	104.64(17)
C(7)-Si(5)-Si(1)	114.46(11)	C(8)-Si(5)-Si(1)	113.46(12)
C(9)-Si(5)-Si(1)	109.19(15)	C(12)-Si(6)-C(11)	108.07(19)
C(12)-Si(6)-C(10)	106.95(19)	C(11)-Si(6)-C(10)	106.5(2)
C(12)-Si(6)-Si(2)	111.85(13)	C(11)-Si(6)-Si(2)	113.43(16)
C(10)-Si(6)-Si(2)	109.7(2)	C(14)-Si(7)-C(15)	106.08(19)
C(14)-Si(7)-C(13)	105.1(2)	C(15)-Si(7)-C(13)	107.83(19)
C(14)-Si(7)-Si(2)	116.71(13)	C(15)-Si(7)-Si(2)	110.55(15)
C(13)-Si(7)-Si(2)	110.09(19)	C(18)-Si(8)-C(16)	106.96(16)
C(18)-Si(8)-C(17)	106.54(16)	C(16)-Si(8)-C(17)	108.23(15)
C(18)-Si(8)-Si(3)	118.84(11)	C(16)-Si(8)-Si(3)	108.95(10)
C(17)-Si(8)-Si(3)	106.92(12)	C(19)-Si(9)-C(20)	106.49(17)
C(19)-Si(9)-C(21)	107.10(19)	C(20)-Si(9)-C(21)	107.02(18)
C(19)-Si(9)-Si(3)	115.76(13)	C(20)-Si(9)-Si(3)	110.59(12)
C(21)-Si(9)-Si(3)	109.47(13)	Si(3)-Zn(1)-Si(2)	133.72(3)

Table A23 (continued)

Si(3)-Zn(1)-Si(1)	138.45(3)	Si(2)-Zn(1)-Si(1)	87.63(3)

Symmetry transformations used to generate equivalent atoms:

#1	-x+1, -y+1, -z+1	#2	-x+2, -y+2, -z	#3	-x+1, -y+1, -z

Table A24 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in **8**. The Anisotropic Displacement Factor Exponent Takes the Form: $-2\pi^2[h^2a^{*2}U^{11} + \dots + 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	44(4)	39(3)	26(3)	-11(2)	2(2)	-19(3)
C(2)	45(4)	39(4)	26(3)	-14(3)	-2(2)	-13(3)
C(3)	36(1)	42(2)	30(1)	-11(1)	-1(1)	-13(1)
C(4)	59(2)	76(3)	61(2)	-18(2)	-6(2)	-2(2)
C(5)	103(3)	74(3)	54(2)	-7(2)	25(2)	7(2)
C(6)	186(6)	45(2)	80(3)	-23(2)	19(3)	17(3)
C(7)	71(2)	50(2)	46(2)	-18(2)	-3(2)	-19(2)
C(8)	62(2)	44(2)	42(2)	-8(1)	1(1)	-15(2)
C(9)	46(2)	121(4)	54(2)	-33(2)	-5(2)	-5(2)
C(10)	179(5)	73(3)	102(4)	-64(3)	22(3)	-46(3)
C(11)	119(4)	73(3)	54(2)	-10(2)	-2(2)	-32(3)
C(12)	80(2)	48(2)	53(2)	-23(2)	11(2)	-25(2)
C(13)	48(2)	165(5)	67(3)	-24(3)	-2(2)	-30(3)
C(14)	93(3)	71(3)	69(2)	-41(2)	-29(2)	-1(2)
C(15)	56(2)	96(3)	53(2)	-15(2)	-2(2)	-22(2)
C(16)	57(2)	48(2)	61(2)	-31(2)	-5(2)	-14(2)

Table A24. (continued)

C(17)	61(2)	41(2)	58(2)	-21(2)	-6(2)	3(2)
C(18)	99(3)	49(2)	39(2)	-23(2)	7(2)	-22(2)
C(19)	66(2)	98(3)	38(2)	-21(2)	-18(2)	7(2)
C(20)	49(2)	68(2)	62(2)	-30(2)	-3(2)	2(2)
C(21)	92(3)	35(2)	82(3)	-21(2)	-19(2)	-2(2)
C(22)	50(2)	53(2)	60(2)	-19(2)	-16(2)	3(2)
C(23)	53(2)	43(2)	55(2)	-18(2)	-5(2)	10(1)
C(24)	78(2)	41(2)	51(2)	-29(2)	-13(2)	12(2)
C(25)	90(3)	33(2)	54(2)	-23(2)	-20(2)	0(2)
C(26)	76(2)	53(2)	53(2)	-18(2)	-13(2)	-22(2)
C(27)	62(2)	70(2)	55(2)	-23(2)	-15(2)	-19(2)
C(28)	47(2)	85(3)	61(2)	-33(2)	-13(2)	7(2)
C(29)	58(2)	75(3)	60(2)	-35(2)	-9(2)	18(2)
C(30)	86(3)	50(2)	74(3)	-40(2)	-21(2)	24(2)
C(31)	95(3)	33(2)	78(3)	-28(2)	-21(2)	6(2)
C(32)	83(2)	43(2)	68(2)	-27(2)	-7(2)	-20(2)
C(33)	64(2)	61(2)	67(2)	-32(2)	-14(2)	-14(2)
C(34)	65(2)	53(2)	42(2)	-21(2)	4(2)	-10(2)
C(35)	65(2)	80(3)	61(2)	-33(2)	-13(2)	-16(2)

Table A24 (continued)

C(36)	114(4)	78(3)	86(3)	-40(3)	-3(3)	-37(3)
C(37)	141(5)	64(3)	58(3)	-23(2)	-2(3)	-4(3)
C(38)	73(3)	117(4)	39(2)	-26(2)	-10(2)	19(3)
C(39)	73(2)	101(3)	47(2)	-41(2)	1(2)	-32(2)
C(40)	130(4)	69(3)	95(4)	-38(3)	18(3)	5(3)
C(1A)	38(4)	30(3)	21(3)	-7(2)	-3(2)	-12(3)
C(2A)	41(4)	39(4)	28(3)	-20(3)	0(3)	-8(3)
K(1)	47(1)	34(1)	45(1)	-20(1)	-4(1)	-1(1)
O(1)	53(1)	41(1)	48(1)	-19(1)	-11(1)	-3(1)
O(2)	60(1)	37(1)	45(1)	-22(1)	-6(1)	3(1)
O(3)	64(1)	39(1)	41(1)	-16(1)	-5(1)	-9(1)
O(4)	50(1)	60(1)	47(1)	-23(1)	-8(1)	-5(1)
O(5)	60(1)	52(1)	59(1)	-32(1)	-7(1)	11(1)
O(6)	71(2)	33(1)	60(1)	-21(1)	-12(1)	0(1)
Si(1)	91(1)	50(1)	25(1)	-11(1)	-3(1)	-45(1)
Si(2)	105(1)	105(1)	30(1)	-31(1)	16(1)	-84(1)
Si(3)	34(1)	30(1)	24(1)	-10(1)	-1(1)	-9(1)
Si(4)	95(1)	33(1)	38(1)	-8(1)	15(1)	-1(1)
Si(5)	42(1)	50(1)	32(1)	-9(1)	-4(1)	-14(1)

Table A24 (continued)

Si(6)	111(1)	45(1)	39(1)	-22(1)	12(1)	-40(1)
Si(7)	45(1)	94(1)	37(1)	-24(1)	-3(1)	-26(1)
Si(8)	46(1)	31(1)	29(1)	-13(1)	1(1)	-8(1)
Si(9)	44(1)	37(1)	32(1)	-12(1)	-7(1)	-2(1)
Zn(1)	33(1)	31(1)	24(1)	-12(1)	-1(1)	-8(1)

Table A25 Hydrogen Coordinates ($\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) in **8**

	x	y	z	U(eq)
H(1A)	6152	8151	4921	45
H(1B)	6382	7066	5540	45
H(2A)	8298	7187	5090	44
H(2B)	7764	7844	5544	44
H(3A)	9834	10211	742	46
H(1A)	6152	8151	4921	45
H(1B)	6382	7066	5540	45
H(2A)	8298	7187	5090	44
H(2B)	7764	7844	5544	44
H(3A)	9834	10211	742	46
H(3B)	10343	9243	812	46
H(4A)	4521	6870	3293	110
H(4B)	4675	7903	2502	110
H(4C)	3531	7648	3197	110
H(5A)	3252	7296	5142	146
H(5B)	4297	7174	5586	146

Table A25 (continued)

H(5C)	4133	6430	5313	146
H(6A)	4680	9377	2974	178
H(6B)	4740	9156	3999	178
H(6C)	3615	9089	3764	178
H(7A)	7198	4973	3539	85
H(7B)	7368	6007	2757	85
H(7C)	6165	5722	3316	85
H(8A)	5581	5188	5337	83
H(8B)	6441	5232	5869	83
H(8C)	6642	4468	5540	83
H(9A)	8767	5693	4868	118
H(9B)	9110	5909	3810	118
H(9C)	8803	4905	4598	118
H(10A)	10568	7910	2679	168
H(10B)	10284	7048	3675	168
H(10C)	11481	7407	3329	168
H(11A)	11346	7510	5011	135
H(11B)	10112	7231	5429	135
H(11C)	10434	8157	5315	135

Table A25 (continued)

H(12A)	10918	9768	3461	93
H(12B)	10870	9745	2536	93
H(12C)	11844	9166	3105	93
H(13A)	6210	11113	3949	158
H(13B)	6100	10060	4699	158
H(13C)	6048	10395	3641	158
H(14A)	9259	10279	4576	108
H(14B)	8162	9914	5306	108
H(14C)	8223	10986	4611	108
H(15A)	8233	11772	2643	114
H(15B)	8164	11168	2172	114
H(15C)	9264	11093	2527	114
H(16A)	6379	8364	569	79
H(16B)	6561	7756	1621	79
H(16C)	6824	7308	946	79
H(17A)	9096	6637	1282	84
H(17B)	8960	7015	2003	84
H(17C)	9951	7300	1144	84
H(18A)	8711	7854	-633	93

Table A25 (continued)

H(18B)	9516	8569	-803	93
H(18C)	8282	8912	-992	93
H(19A)	6918	10312	-1003	109
H(19B)	7821	11017	-1355	109
H(19C)	6542	11356	-1239	109
H(20A)	5144	10795	564	93
H(20B)	5607	10168	1512	93
H(20C)	5489	9728	894	93
H(21A)	8096	11786	-128	108
H(21B)	7327	11487	862	108
H(21C)	6810	12104	-61	108
H(22A)	-643	4022	2664	69
H(22B)	212	4561	1743	69
H(23A)	-232	5267	2711	67
H(23B)	309	4364	3495	67
H(24A)	1642	5285	3387	66
H(24B)	1055	6159	2608	66
H(25A)	2703	6344	1532	69
H(25B)	2894	6402	2406	69

Table A25 (continued)

H(26A)	4764	5958	2106	73
H(26B)	4653	5806	1266	73
H(27A)	6163	4871	1967	75
H(27B)	5356	4391	2937	75
H(28A)	5917	2937	2921	80
H(28B)	6709	3473	1955	80
H(29A)	5718	3036	1228	80
H(29B)	6270	2158	2027	80
H(30A)	4962	1192	2303	82
H(30B)	4409	2014	1462	82
H(31A)	3121	949	2529	82
H(31B)	3286	1144	3327	82
H(32A)	1315	1672	3433	76
H(32B)	1268	1506	2588	76
H(33A)	802	3096	1695	73
H(33B)	-103	2646	2608	73
H(35)	9068	4757	628	80
H(36)	8186	6128	474	108
H(37)	6611	6688	-119	113

Table A25 (continued)

H(38)	5874	5874	-592	102
H(39)	6755	4461	-450	83
H(40A)	8986	3662	-417	161
H(40B)	8074	3123	448	161
H(40C)	9141	3371	607	161
H(1A1)	6824	6831	5560	37
H(1A2)	8052	6910	4989	37
H(2A1)	7576	8065	5501	42
H(2A2)	6586	8491	4918	42

VITA

Jaime Renee Blanton was born on July 13, 1976 in Prestonsburg, KY, to Vanessa Ann Penix Blanton and William Michael Blanton. She attended elementary school at Oil Springs School, and then high school at Johnson Central High School. She graduated as co-salutatorian in her class of 250 students in 1994. In the following August she began her undergraduate studies at Eastern Kentucky University in Richmond, KY. She conducted undergraduate research in the laboratory of Dr. Tom Otieno where she prepared coordination polymers of copper(II) thiocyanate. One compound she helped prepare was featured on the cover of an issue of the journal *Acta Crystallographica* [Otieno, T.; **Blanton, J. R.**; Hatfield, J.M.; Asher, S. L.; Parkin, S. "A copper(II)-pyrazole complex cation with $\bar{3}$ imposed symmetry" *Acta Cryst. Sec. C*. **2002**, C58, 182]. Jaime received her American Chemical Society (ACS)-certified B.S. degree in May 1998 and graduated with honors (Magna Cum Laude).

In August 1998 Jaime began her graduate studies in the chemistry department at the University of Tennessee, Knoxville. She soon joined Dr. Xue's group where she studied the preparation and characterization of new silyl ligands and early transition metal silyl complexes. Her research interests also led her to Oak Ridge National Laboratory (ORNL) where she worked on a collaborative project with Dr. David B. Beach studying the CVD of TiO₂ thin films as potential new microelectronic gate materials. She published five papers (listed below) by April 2003 for her graduate research. In addition, she presented her research at

at several meetings including national ACS meetings in San Francisco in Spring 2000 and Chicago in Fall 2001, a southeastern regional ACS meeting in Knoxville in 1999, the 2001 Organosilicon Symposium in White Plains, NY, and the 2002 Gordon Conference on Organometallic Chemistry in Newport, RI.

As a second year student, Jaime received a research merit award. In 2002, she was named the East Tennessee Section ACS graduate fellow. Jaime has also been an active member of the Association of Chemistry Graduate Students (ACGS) serving as treasurer in 1999 and 2001, and as the recruiting liaison between the graduate students and faculty in 2001.

Jaime's next position will be as an applications specialist with Degussa Corporation in their applied research & development laboratory in Calvert City, KY.

Publications (as of April 2003)

(1) Diminnie, J. B.; **Blanton, J. R.**; Cai, H.; Quisenberry, K. T.; Xue, Z., "Reactions of tantalum alkylidene complexes with silanes. Synthesis and characterization of novel metallasilacyclobutene complexes and kinetic and mechanistic studies of their formation" *Organometallics* **2001**, *20*, 1504.

(2) Diminnie, J. B.; Liu, X.; Cai, H.; Wu, Z.; **Blanton, J. R.**; Chen, T.; Tuinman, A. A.; Quisenberry, K. T.; Vallet, C. E.; Zuhre, R. A.; Beach, D. B.; Peng, Z.; Wu, Y.-D.; Concolino, T. E., Rheingold, A. L.; Xue, Z. "Reactions of d^0 alkylidene and amide complexes with silanes" *Pure Appl. Chem.* **2001**, *73*, 331.

- (3) **Blanton, J. R.**; Diminnie, J. B.; Chen, T.; Wiltz, A. M.; Xue, Z. " α,ω -Bis(potassiosilyl)alkanes. Synthesis and characterization of $[K(18\text{-crown-6})]_2[(\text{Me}_3\text{Si})_2\text{Si}(\text{CH}_2)_n\text{Si}(\text{SiMe}_3)_2]$ " *Organometallics* **2001**, *20*, 5542.
- (4) **Blanton, J. R.**; Chen, T.-N.; Diminnie, J.B.; Cai, H.; Wu, Z.; Li, L.; Sorasaene, K.R.; Quisenberry, K.T.; Pan, H.; Wang, C.-S.; Choi, S.-H.; Wu, Y.-D.; Lin, Z.; Guzei, I.A.; Rheingold, A. L.; Xue, Z. "Silyl-substituted alkylidenes: preparation of the novel complexes and mechanistic studies of their formation from the reactions of alkylidenes with silanes and silyl-to-alkylidyne migration" *J. Mol. Cat. A* **2002**, *190*, 101.
- (5) Wu, Z.; Cai, H., Yu, X.; **Blanton, J. R.**; Diminnie, J. B.; Xue, Z.; Bryan, J. C. "Synthesis of tantalum(V) amido silyl complexes and the unexpected formation of $(\text{Me}_2\text{N})_3\text{Ta}(\eta^2\text{-ONMe}_2)[\text{OSi}(\text{SiMe}_3)_3]$ from the reaction of $(\text{Me}_2\text{N})_4\text{Ta}[\text{Si}(\text{SiMe}_3)_3]$ with O_2 " *Organometallics* **2002**, *21*, 3973.