

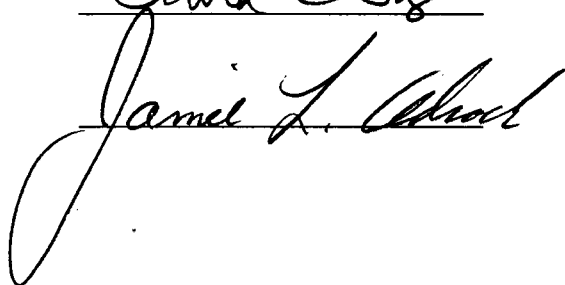
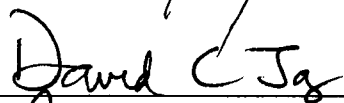
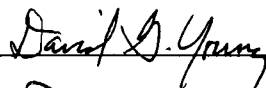
To the Graduate Council:

I am submitting herewith a dissertation written by Xiaozhan Liu entitled "Synthesis of a Silyl Complex and Studies of Mechanistic Pathways in Chemical Vapor Deposition of Metal-Silicon-Nitrogen Ternary and Zirconium Carbide Thin Films." I have examined the final 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.



Ziling Xue, Major Professor

We have read this dissertation  
and recommend its acceptance:



Accepted for the Council:



Associate Vice Chancellor and  
Dean of The Graduate School

**Synthesis of a Silyl Complex and Studies of Mechanistic  
Pathways in Chemical Vapor Deposition of Metal-Silicon-  
Nitrogen Ternary and Zirconium Carbide Thin Films**

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Xiaozhan Liu

December 1999

## **DEDICATION**

**This dissertation is dedicated to  
my mother Wanwan Lian  
and my grandmother Manwen Zhao**

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## ABSTRACT

This dissertation describes research on the synthesis of a tantalum silyl complex, chemical vapor deposition (CVD) of Ti-Si-N ternary thin films, and mechanistic pathways in the CVD processes to form the Ti-Si-N ternary thin films and zirconium carbide (ZrC). An overview of the Ph.D. research appears in Chapter 1.

Chapter 2 describes the preparation of a thermally unstable bis(alkylidene) complex  $(RCH_2)_4Ta_2(=CHR)_2(Cl)_2$  ( $R = SiMe_3$ , **1**) and kinetic studies of its conversion to an unstable alkylidene-alkylidyne complex  $(RCH_2)_3Ta_2(=CHR)(\equiv CR)(Cl)_2$  (**3**). The synthesis and characterization of the first silyl bis(alkylidyne) complex  $(RCH_2)(R_3Si)Ta(\mu-CR)_2Ta(CH_2R)_2$  (**4**) are also reported.

Chapter 3 presents CVD of Ti-Si-N ternary thin films from the reaction of  $Ti(NMe_2)_4$  with  $SiH_4$ . Analyses of the thin films by XPS (X-ray photoelectron spectroscopy), RBS (Rutherford backscattering spectrometry), and SEM (scanning electron microscopy) showed that the films likely contained TiN and  $Si_3N_4$ . The reaction between  $Ti(NMe_2)_4$  and  $SiH_4$  at room temperature yielded  $H_2$ ,  $HSi(NMe_2)_3$  and a black solid. The reaction mixture, after heating, gave powders which were found to be likely ternary materials containing TiN and  $Si_3N_4$ . The formation of these two solid compounds in both the CVD processes and room temperature reaction (followed by heating), rather than a single phase Ti-Si-N solid,  $TiSi_n-Si_3N_4$  or  $TiSi_n-TiN$ , is discussed with the use of a Ti-Si-N ternary phase diagram.

The reaction between  $Ti(NMe_2)_4$  and  $SiH_4$ , and the mechanistic pathways to TiN and  $Si_3N_4$  were further investigated. These studies are described in Chapter 4. The

reactions of  $M(NMe_2)_4$  ( $M = Ti, Zr, Hf$ ) with  $H_2SiR'_2$  ( $R'_2 = HPh, Ph_2, MePh$ ) were found to give aminosilanes and metal amide hydride species. Hydride amide complexes  $[(Me_2N)_3M(\mu-H)(\mu-NMe_2)_2]_2M$  [ $M = Zr$  (7);  $Hf$  (8)] were isolated from the reactions of  $M(NMe_2)_4$  ( $M = Zr, Hf$ ) with  $H_2SiPh_2$  and characterized by NMR and single-crystal X-ray crystallography. *Ab initio* quantum chemical calculations on the mechanism of the reactions of  $Ti(NR_2)_4$  ( $R = Me, H$ ) with  $SiH_4$  supported the experimental observations that these reactions preferentially gave aminosilanes and metal hydride amide species. An equilibrium,  $(Me_2N)_3ZrSi(SiMe_3)_3$  (5b) +  $H_2SiPh_2 \rightleftharpoons (Me_3Si)_3SiZr-(H)(NMe_2)_2$  (6) +  $HSi(NMe_2)Ph_2$ , was observed. This equilibrium suggested that the reactions between  $M-NR_2$  and  $H-Si$  bonds to give  $M-H$  and  $Si-NR_2$  bonds were reversible. The results here indicated that the role of  $SiH_4$  in its reaction with  $Ti(NMe_2)_4$  was to remove amide ligands as amidosilanes. The removal of amide ligands might be incomplete, and thus the reaction gave Ti amide hydride species as black solids. Subsequent heating of the black solids and aminosilanes perhaps yielded  $TiN$  and  $Si_3N_4$ , respectively, as the Ti-Si-N materials.

The mechanistic studies of CVD of ZrC from  $Zr(CH_2CMe_3)_4$  (11b) are described in Chapter 5. *Ab initio* MO calculations predicted that, unlike its titanium analogue, the first step in the thermolysis of  $Zr(CH_2CMe_3)_4$  (11b) was a  $\gamma$ -hydrogen abstraction reaction. Experimental studies were designed to confirm the theoretical prediction. Analyses of the volatile products in CVD of ZrC from  $Zr(CH_2CMe_3)_4$  (11b) and  $Zr(CD_2CMe_3)_4$  (11b- $d_8$ ) showed that the major products were neopentane and isobutene in a ratio of 2.3 : 1. In addition, the ratio of neopentane- $d_2$ /neopentane- $d_3$  produced in the CVD involving  $Zr(CD_2CMe_3)_4$  (11b- $d_8$ ) was ca. 4.9. These results are discussed in terms

of  $\gamma$ -hydrogen abstraction as the preferred first step in the thermolysis of  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$  (11b).

# TABLE OF CONTENTS

| CHAPTER                                                                                                  | PAGE |
|----------------------------------------------------------------------------------------------------------|------|
| 1. Introduction                                                                                          |      |
| 1.1 Metal Carbides, Silicides and Titanium-Silicon-Nitrogen Ternary Materials .....                      | 1    |
| 1.2 Chemical Vapor Deposition (CVD) of Thin Film Materials .....                                         | 2    |
| 1.3 Chemical Vapor Deposition of Metal Silicides and M-Si-N Ternary Materials .....                      | 4    |
| 1.4 Current Dissertation .....                                                                           | 6    |
| 1.4.1 Chapter 2 .....                                                                                    | 7    |
| 1.4.2 Chapter 3 .....                                                                                    | 7    |
| 1.4.3 Chapter 4 .....                                                                                    | 8    |
| 1.4.4 Chapter 5 .....                                                                                    | 9    |
| References and Footnotes .....                                                                           | 11   |
| 2. Synthesis and Characterization of a Silyl Bis(alkylidyne) Complex                                     |      |
| 2.1 Introduction .....                                                                                   | 13   |
| 2.2 Results and Discussion .....                                                                         | 19   |
| 2.2.1 Synthesis of Bis(alkylidene) Complex 1 and Its Conversion to Alkylidene Alkylidyne Complex 3 ..... | 19   |

|       |                                                                                                                     |    |
|-------|---------------------------------------------------------------------------------------------------------------------|----|
| 2.2.2 | Chloride-Bridged vs. Alkyl-Bridged Structure for 1 and 3 .....                                                      | 26 |
| 2.2.3 | Synthesis and Structure of<br>$(RCH_2)(R_3Si)Ta(\mu-CR)_2Ta(CH_2R)_4$ (4) .....                                     | 27 |
| 2.3   | Experimental Section .....                                                                                          | 30 |
| 2.3.1 | General Procedure .....                                                                                             | 30 |
| 2.3.2 | Preparation of $(RCH_2)_3Ta_2(=CHR)(\equiv CR)(Cl)_2$ (3) .....                                                     | 46 |
| 2.3.3 | Kinetic Study of the Conversion of 1 to 3 .....                                                                     | 47 |
| 2.3.4 | Preparation of $(RCH_2)(R_3Si)Ta(\mu-CR)_2Ta(CH_2R)_2$ (4) .....                                                    | 47 |
| 2.3.5 | X-ray Crystal Structure Determination of 4 .....                                                                    | 49 |
|       | References and Footnotes .....                                                                                      | 51 |
| 3.    | Chemical Vapor Deposition of Ti-Si-N Thin Films from the Reaction of<br>Tetrakis(dimethylamido)titanium with Silane |    |
| 3.1   | Introduction .....                                                                                                  | 56 |
| 3.2   | Results and Discussion .....                                                                                        | 61 |
| 3.2.1 | Design of a CVD Reactor .....                                                                                       | 61 |
| 3.2.2 | Formation of Ti-Si-N Ternary Thin Films via Hot-Wall Low<br>Pressure Horizontal CVD .....                           | 64 |
| 3.2.3 | Preparation of Powders from the Reactions of $M(NMe_2)_4$ ( $M = Ti,$<br>$Zr$ ) with $SiH_4$ .....                  | 68 |
| 3.2.4 | Characterization of the Thin Films and Powders by XPS, RBS,                                                         |    |

|       |                                                                                                                                                    |     |
|-------|----------------------------------------------------------------------------------------------------------------------------------------------------|-----|
|       | Powder X-ray Diffraction (XRD) and SEM .....                                                                                                       | 68  |
| 3.3   | Experimental Section .....                                                                                                                         | 81  |
| 3.3.1 | General Procedure .....                                                                                                                            | 81  |
| 3.3.2 | Reaction of $M(NMe_2)_4$ with $SiH_4$ Conducted in a Static<br>Reaction Tube .....                                                                 | 83  |
| 3.3.3 | The Procedures of Thin Film Deposition Conducted in an Ultra-<br>High-Vacuum (UHV) CVD Chamber .....                                               | 88  |
|       | References and Footnotes .....                                                                                                                     | 89  |
| 4.    | Synthesis and Structures of Unusual Metal Amide Hydride Complexes.<br>Mechanistic Studies of the Reactions of Transition Metal Amides with Silanes |     |
| 4.1   | Introduction .....                                                                                                                                 | 93  |
| 4.2   | Results and Discussion .....                                                                                                                       | 95  |
| 4.2.1 | Reactions of $M(NMe_2)_4$ ( $M = Ti, Zr, Hf$ ) with Silanes .....                                                                                  | 95  |
| 4.2.2 | Syntheses and Characterization of Amide Hydride Complexes<br>$[(Me_2N)_3M(\mu-H)(\mu-NMe_2)_2]_2M$ ( $M = Zr, 7; Hf, 8$ ) .....                    | 99  |
| 4.2.3 | Crystal and Molecular Structures of 7 and 8 .....                                                                                                  | 101 |
| 4.2.4 | Variable Temperature NMR Study of 7 .....                                                                                                          | 134 |
| 4.2.5 | Reactions of $(Me_2N)_3ZrSi(SiMe_3)_3$ ( <b>5b</b> ) with Silanes .....                                                                            | 137 |
| 4.2.6 | <i>Ab Initio</i> MO Calculations of the Reactions between $Ti(NR_2)_4$<br>and $SiH_4$ .....                                                        | 138 |

|        |                                                                                                                                                                                                                                                                                           |     |
|--------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 4.2.7  | The First Step in the Reactions of $M(\text{NMe}_2)_4$ ( $M = \text{Ti, Zr, Hf}$ )<br>with Silanes – Mechanistic Considerations .....                                                                                                                                                     | 139 |
| 4.3    | Experimental Section .....                                                                                                                                                                                                                                                                | 144 |
| 4.3.1  | General Procedure .....                                                                                                                                                                                                                                                                   | 144 |
| 4.3.2  | Preparation of $[(\text{Me}_2\text{N})_3\text{Zr}(\mu\text{-H})(\mu\text{-NMe}_2)_2]_2\text{Zr}$ ( <b>7</b> ) .....                                                                                                                                                                       | 145 |
| 4.3.3  | Preparation of $[(\text{Me}_2\text{N})_3\text{Hf}(\mu\text{-H})(\mu\text{-NMe}_2)_2]_2\text{Hf}$ ( <b>8</b> ) .....                                                                                                                                                                       | 146 |
| 4.3.4  | Preparation of $[(\text{Me}_2\text{N})_3M(\mu\text{-D})(\mu\text{-NMe}_2)_2]_2M$ ( <b>7-d</b> , <b>8-d</b> ) .....                                                                                                                                                                        | 146 |
| 4.3.5  | Variable Temperature NMR Study of <b>7</b> .....                                                                                                                                                                                                                                          | 147 |
| 4.3.6  | Reaction of $M(\text{NMe}_2)_4$ ( $M = \text{Ti, Zr}$ ) with Excess $\text{SiH}_4$ .....                                                                                                                                                                                                  | 147 |
| 4.3.7  | Reaction of $\text{Zr}(\text{NMe}_2)_4$ with $\text{H}_2\text{SiPh}_2$ in the Presence<br>of $\text{HNMe}_2$ .....                                                                                                                                                                        | 148 |
| 4.3.8  | Reactions of $M(\text{NMe}_2)_4$ ( $M = \text{Ti, Zr, Hf}$ ) with Silanes ( $\text{H}_3\text{SiPh}$ ,<br>$\text{H}_2\text{SiPh}_2$ , $\text{H}_2\text{SiMePh}$ ) .....                                                                                                                    | 149 |
| 4.3.9  | Attempted Reactions of $M(\text{NMe}_2)_4$ ( $M = \text{Ti, Zr, Hf}$ ) with<br>$\text{H}_2\text{SiBu}^t$ , $\text{HSiEt}_3$ , $\text{HSiMeBu}^t$ , $\text{HSiPh}_3$ , $\text{HSiPr}^i_3$ and<br>$\text{HSi}(\text{NMe}_2)_3$ .....                                                        | 149 |
| 4.3.10 | Reaction of $(\text{Me}_2\text{N})_3\text{ZrSi}(\text{SiMe}_3)_3$ ( <b>5b</b> ) with $\text{H}_2\text{SiPh}_2$ .....                                                                                                                                                                      | 149 |
| 4.3.11 | Confirmation of the Equilibrium: $(\text{Me}_2\text{N})_3\text{ZrSi}(\text{SiMe}_3)_3$ ( <b>5b</b> ) +<br>$\text{H}_2\text{SiMePh} \rightleftharpoons (\text{Me}_2\text{N})_2\text{Zr}(\text{H})\text{Si}(\text{SiMe}_3)_3$ ( <b>6</b> ) +<br>$\text{HSi}(\text{NMe}_2)\text{MePh}$ ..... | 150 |
| 4.3.12 | Identification of the Aminosilane Products and $\text{H}_2$ .....                                                                                                                                                                                                                         | 150 |

|        |                                                                                                                                                     |     |
|--------|-----------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 4.3.13 | X-ray Crystal Structure Determination of <b>7</b>                                                                                                   | 151 |
| 4.3.14 | X-ray Crystal Structure Determination of <b>8</b>                                                                                                   | 152 |
|        | References and Footnotes                                                                                                                            | 153 |
| 5.     | Mechanistic Studies of Thermal Decomposition of Tetraneopentylzirconium to Zirconium Carbide                                                        |     |
| 5.1    | Introduction                                                                                                                                        | 158 |
| 5.2    | Results and Discussion                                                                                                                              | 164 |
| 5.2.1  | Summary of <i>Ab Initio</i> Quantum Chemical Calculations of the Structure and Thermolysis of $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$ ( <b>11b</b> ) | 164 |
| 5.2.2  | Experimental Studies of the Thermolysis of $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$ ( <b>11b</b> ) in the CVD of Zirconium Carbide                    | 169 |
| 5.3    | Experimental Section                                                                                                                                | 179 |
| 5.3.1  | General Procedure                                                                                                                                   | 179 |
| 5.3.2  | Synthesis of $\text{Zr}(\text{CD}_2\text{CMe}_3)_4$ ( <b>11b-<i>d</i><sub>3</sub></b> )                                                             | 179 |
| 5.3.3  | Dynamic Vacuum CVD                                                                                                                                  | 180 |
| 5.3.4  | The Analyses of the Volatile Products                                                                                                               | 181 |
|        | References and Footnotes                                                                                                                            | 184 |
|        | Vita                                                                                                                                                | 188 |

## LIST OF TABLES

| TABLE                                                                                                                                   | PAGE |
|-----------------------------------------------------------------------------------------------------------------------------------------|------|
| 2.1 Rate Constants $k_i$ for the Conversion 1 $\rightarrow$ 3 .....                                                                     | 25   |
| 2.2 Crystal Data for 4 .....                                                                                                            | 32   |
| 2.3 Interatomic Distances ( $\text{\AA}$ ) in 4 .....                                                                                   | 33   |
| 2.4 Intramolecular Bond Angles ( $^\circ$ ) in 4 .....                                                                                  | 34   |
| 2.5 Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement<br>Parameters ( $\text{\AA}^2 \times 10^3$ ) for 4 ..... | 36   |
| 2.6 Anisotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for 4 .....                                                      | 39   |
| 2.7 Hydrogen Coordinates ( $\times 10^4$ ) and Isotropic Displacement Parameters<br>( $\text{\AA}^2 \times 10^3$ ) for 4 .....          | 42   |
| 3.1 CVD Conditions .....                                                                                                                | 67   |
| 3.2 Features of Various Analytical Methods Discussed in This Thesis .....                                                               | 70   |
| 3.3 XPS Chemical Shifts of Compounds Related to Ti-Si-N Ternary Alloys and<br>the Samples in This Study .....                           | 71   |
| 3.4 Composition by RBS of Films Prepared at Different Delivery<br>Temperatures .....                                                    | 76   |
| 3.5 Summary of Experimental Procedures and Analysis Methods .....                                                                       | 85   |
| 4.1 Reactions of Metal Amide Complexes $M(\text{NMe}_2)_4$ ( $M = \text{Ti, Zr, Hf}$ )<br>with Silanes .....                            | 98   |

|      |                                                                                                                                                                                                                                                                                                                     |     |
|------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 4.2  | Crystal Data for <b>7</b> .....                                                                                                                                                                                                                                                                                     | 104 |
| 4.3  | Interatomic Distances ( $\text{\AA}$ ) in <b>7</b> .....                                                                                                                                                                                                                                                            | 106 |
| 4.4  | Intramolecular Bond Angles ( $^{\circ}$ ) in <b>7</b> .....                                                                                                                                                                                                                                                         | 107 |
| 4.5  | Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement<br>Parameters ( $\text{\AA}^2 \times 10^3$ ) for <b>7</b> .....                                                                                                                                                                          | 110 |
| 4.6  | Anisotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for <b>7</b> .....                                                                                                                                                                                                                               | 112 |
| 4.7  | Hydrogen Coordinates ( $\times 10^4$ ) and Isotropic Displacement Parameters<br>( $\text{\AA}^2 \times 10^3$ ) for <b>7</b> .....                                                                                                                                                                                   | 114 |
| 4.8  | Crystal Data for <b>8</b> .....                                                                                                                                                                                                                                                                                     | 118 |
| 4.9  | Interatomic Distances ( $\text{\AA}$ ) in <b>8</b> .....                                                                                                                                                                                                                                                            | 120 |
| 4.10 | Intramolecular Bond Angles ( $^{\circ}$ ) in <b>8</b> .....                                                                                                                                                                                                                                                         | 121 |
| 4.11 | Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement<br>Parameters ( $\text{\AA}^2 \times 10^3$ ) for <b>8</b> .....                                                                                                                                                                          | 124 |
| 4.12 | Anisotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for <b>8</b> .....                                                                                                                                                                                                                               | 126 |
| 4.13 | Hydrogen Coordinates ( $\times 10^4$ ) and Isotropic Displacement Parameters<br>( $\text{\AA}^2 \times 10^3$ ) for <b>8</b> .....                                                                                                                                                                                   | 128 |
| 5.1  | Properties of Zirconium Carbide .....                                                                                                                                                                                                                                                                               | 159 |
| 5.2  | Calculated Changes of Energies ( $\Delta E$ , kcal/mol), Thermal Energies ( $\Delta\Delta H_{298}^{\circ}$ ,<br>kcal/mol) and Entropies ( $\Delta S_{298}$ , eu) for the Formation of Transition Structures<br>and Products for Alkane Elimination from $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$ ( <b>11b</b> ) ..... | 168 |

|     |                                                                                                                                                                                              |     |
|-----|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 5.3 | Mass Spectra ( $m/e = 72 - 75$ ) Generated upon 6 kV Ionization of the Volatile<br>Products in the CVD with $\text{Zr}(\text{CD}_2\text{CMe}_3)_4$ ( <b>11b-<i>d</i><sub>8</sub></b> ) ..... | 175 |
|-----|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|

## LIST OF FIGURES

| FIGURE                                                                                                                                                                        | PAGE |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| 1.1 Illustration showing the fundamental steps in the CVD involving a metal-organic molecule .....                                                                            | 3    |
| 1.2 The structure of complexes 7 and 8 .....                                                                                                                                  | 9    |
| 2.1 Proposed reactions of $\text{SiH}_4$ with $\text{M}(\text{CH}_2\text{R})_4$ , $(\text{RCH}_2)_3\text{M}=\text{CHR}$ , and $(\text{RCH}_2)_3\text{M}\equiv\text{CR}$ ..... | 14   |
| 2.2 (a) Proposed intermediates, (b) Model complexes .....                                                                                                                     | 15   |
| 2.3 Cp-free silyl compounds prepared by our group: (a) Group 4 alkyl silyl complexes; (b) Group 5 alkylidene silyl complexes; (c) Group 6 alkylidyne silyl complexes .....    | 17   |
| 2.4 The formation of 4 from 2 .....                                                                                                                                           | 20   |
| 2.5 Proposed mechanism of the alkylidene to alkylidyne conversion in the formation of 3 from 1 .....                                                                          | 21   |
| 2.6 Kinetic plots of the decomposition of $(\text{RCH}_2)_4\text{Ta}_2\text{Cl}_2(=\text{CHR})_2$ (1) .....                                                                   | 23   |
| 2.7 Eyring plot of decomposition of 1 .....                                                                                                                                   | 24   |
| 2.8 Five possible isomers of 3 .....                                                                                                                                          | 28   |
| 2.9 NOSEY spectrum of 3 at $-45^\circ\text{C}$ in toluene- $d_8$ .....                                                                                                        | 29   |
| 2.10 ORTEP view of 4, showing 50% thermal ellipsoids .....                                                                                                                    | 31   |
| 2.11 Labeling scheme for 3-C .....                                                                                                                                            | 48   |

|     |                                                                                                                                                                             |     |
|-----|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 3.1 | Schematic representations of various diffusion barriers: (a) sacrificial barrier;<br>(b) stuffed barrier; (c) passive barrier; (d) amorphous barrier .....                  | 58  |
| 3.2 | Diagram of a hot-wall CVD reactor .....                                                                                                                                     | 62  |
| 3.3 | Diagram of a cold-wall CVD reactor .....                                                                                                                                    | 63  |
| 3.4 | Hot wall horizontal CVD apparatus for deposition of Ti-Si-N thin films .....                                                                                                | 65  |
| 3.5 | Rutherford backscattering spectra (RBS) of films deposited on Si wafers:<br>(a) film 1 - precursor delivered at 350 °C; (b) film 3 - precursor delivered<br>at 280 °C ..... | 75  |
| 3.6 | XPS of film 3 after sputtering: (a) Ti 2p <sub>3/2</sub> ; (b) N 1s; (c) Si 2p .....                                                                                        | 78  |
| 3.7 | SEM of Ti-Si-N film 3 (thickness = 2169.9 Å) .....                                                                                                                          | 79  |
| 3.8 | Schematic representation of phase equilibria in the Ti-Si-N system at<br>1000 °C .....                                                                                      | 80  |
| 3.9 | Schematic diagram of a static reaction tube for the reactions of M(NMe <sub>2</sub> ) <sub>4</sub><br>with SiH <sub>4</sub> .....                                           | 84  |
| 4.1 | Reactions of metal amide complexes .....                                                                                                                                    | 94  |
| 4.2 | Possible pathways of the first step in the reactions of metal amide complexes<br>with silanes .....                                                                         | 96  |
| 4.3 | ORTEP diagram of 7, showing 50% ellipsoids .....                                                                                                                            | 102 |
| 4.4 | ORTEP diagram of 8, showing 50% ellipsoids .....                                                                                                                            | 103 |
| 4.5 | Packing diagram of 7 .....                                                                                                                                                  | 132 |
| 4.6 | Packing diagram of 8 .....                                                                                                                                                  | 133 |

|      |                                                                                                                                                                                                                                                                                                                                                                                                                                                        |     |
|------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 4.7  | NOSEY spectrum of <b>7</b> at 213 K .....                                                                                                                                                                                                                                                                                                                                                                                                              | 135 |
| 4.8  | Variable temperature $^1\text{H}$ NMR spectra of <b>7</b> .....                                                                                                                                                                                                                                                                                                                                                                                        | 136 |
| 4.9  | Exchanges between <b>5b</b> and <b>6</b> .....                                                                                                                                                                                                                                                                                                                                                                                                         | 138 |
| 4.10 | Transition structures (HF/HW3) for the reactions of $\text{Ti}(\text{NH}_2)_4$ and $\text{Ti}(\text{NMe}_2)_4$<br>with $\text{SiH}_4$ , and MP2/HW3 activation enthalpies .....                                                                                                                                                                                                                                                                        | 140 |
| 4.11 | Schematic diagram of the reaction between a M-N (M = Ta, Zr) bond and<br>a Si-H bond .....                                                                                                                                                                                                                                                                                                                                                             | 143 |
| 4.12 | Reaction of a tantalum alkylidene complex with silanes .....                                                                                                                                                                                                                                                                                                                                                                                           | 144 |
| 5.1  | Hydrogen abstraction reactions in the thermolysis of $\text{M}(\text{CH}_2\text{R})_4$ .....                                                                                                                                                                                                                                                                                                                                                           | 162 |
| 5.2  | Possible first steps in the thermolysis of $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$ ( <b>11b</b> ) .....                                                                                                                                                                                                                                                                                                                                                 | 163 |
| 5.3  | The calculated structures of $\text{M}(\text{CH}_2\text{CMe}_3)_4$ (M = Ti, <b>11a</b> ; Zr, <b>11b</b> in<br>parentheses) .....                                                                                                                                                                                                                                                                                                                       | 165 |
| 5.4  | The calculated structures of transition states ( <b>C1</b> , <b>C3</b> ) and products ( <b>C2</b> , <b>C4</b> )<br>for the $\alpha$ -hydrogen and $\gamma$ -hydrogen abstraction reactions of $\text{M}(\text{CH}_2\text{CMe}_3)_4$<br>( <b>11a-b</b> ) with the MP2/HW3 activation and reaction enthalpies (kcal/mol).<br>Selected geometrical parameters calculated with HF/3-21G method are<br>given for M = Ti ( <b>a</b> ), Zr ( <b>b</b> ) ..... | 166 |
| 5.5  | (a) $^1\text{H}$ NMR spectrum of isobutene and neopentane from decomposition of<br>$\text{Zr}(\text{CH}_2\text{CMe}_3)_4$ ( <b>11b</b> ). (b) $^1\text{H}$ NMR spectrum of isobutene and neopentane<br>from decomposition of $\text{Zr}(\text{CD}_2\text{CMe}_3)_4$ ( <b>11b-d<sub>8</sub></b> ). (c) $^2\text{H}$ NMR spectrum of<br>isobutene and neopentane from decomposition of <b>11b-d<sub>8</sub></b> .....                                    | 170 |

|     |                                                                                                                                                                      |     |
|-----|----------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 5.6 | FI-MS mass spectrum of volatile products from the thermolysis of<br>Zr(CD <sub>2</sub> CMe <sub>3</sub> ) <sub>4</sub> ( <b>11b-d<sub>8</sub></b> ) .....            | 174 |
| 5.7 | GC/MS spectrum of the volatile organic products from CVD using<br>Zr(CD <sub>2</sub> CMe <sub>3</sub> ) <sub>4</sub> ( <b>11b-d<sub>8</sub></b> ) as precursor ..... | 177 |
| 5.8 | CVD apparatus for the deposition of zirconium carbide .....                                                                                                          | 180 |

## NUMBERING SCHEME FOR COMPOUNDS IN THE TEXT

1.  $(\text{Me}_3\text{SiCH}_2)_4\text{Ta}_2(=\text{CHSiMe}_3)_2(\text{Cl})_2$
2.  $(\text{Me}_3\text{SiCH}_2)_4\text{Ta}_2(\mu\text{-CSiMe}_3)_2$
3.  $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}_2(=\text{CHSiMe}_3)(\equiv\text{CSiMe}_3)(\text{Cl})_2$
4.  $(\text{Me}_3\text{SiCH}_2)[(\text{Me}_3\text{Si})_3\text{Si}]\text{Ta}(\mu\text{-CR})_2\text{Ta}(\text{CH}_2\text{SiMe}_3)_2$
- 5a.  $"(\text{Me}_2\text{N})_3\text{ZrSi}(\text{H})\text{Ph}_2"$
- 5b.  $(\text{Me}_2\text{N})_3\text{ZrSi}(\text{SiMe}_3)_3$
- 5c.  $"(\text{Me}_2\text{N})_3\text{M}(\text{SiH}_3)"$  (M = Ti, Zr, Hf)
6.  $(\text{Me}_2\text{N})_2\text{Zr}(\text{H})\text{Si}(\text{SiMe}_3)_3$
7.  $[(\text{Me}_2\text{N})_3\text{Zr}(\mu\text{-H})(\mu\text{-NMe}_2)_2]_2\text{Zr}$
- 7- $d_2$ .  $[(\text{Me}_2\text{N})_3\text{Zr}(\mu\text{-D})(\mu\text{-NMe}_2)_2]_2\text{Zr}$
8.  $[(\text{Me}_2\text{N})_3\text{Hf}(\mu\text{-H})(\mu\text{-NMe}_2)_2]_2\text{Hf}$
- 8- $d_2$ .  $[(\text{Me}_2\text{N})_3\text{Hf}(\mu\text{-D})(\mu\text{-NMe}_2)_2]_2\text{Hf}$
9.  $"\text{HM}(\text{NMe}_2)_3"$  (M = Ti, Zr, Hf)
10.  $"\text{H}_2\text{M}(\text{NMe}_2)_2"$  (M = Ti, Zr, Hf)
- 11a.  $\text{Ti}(\text{CH}_2\text{CMe}_3)_4$
- 11b.  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$
- 11b- $d_3$ .  $\text{Zr}(\text{CD}_2\text{CMe}_3)_4$

# Chapter 1

## Introduction

### 1.1 Metal Carbides, Silicides and Titanium-Silicon-Nitrogen Ternary Materials

Transition metal carbides and silicide materials have been widely used in coating, electronic and nuclear industries largely because of their unique chemical and physical properties.<sup>1-9</sup> Their hardness has given them applications in cutting tools, golf clubs, and snow tires.<sup>9</sup> Their thermal stability allows them to be used on rocket nozzles, drill bits, and support for catalysis under extreme conditions.<sup>1</sup> The optical, electronic and magnetic properties of these materials are employed on optical coating,<sup>1</sup> electrical contacts,<sup>2</sup> diffusion barriers,<sup>3</sup> and other usages.<sup>4</sup> In particular, metal silicides are important components of very-large-scale-integration (VLSI) devices, and high-temperature and IR detector materials,<sup>5</sup> as they are known to have metal-like resistivities and stability to high temperatures and oxidation. Silicides are thus used to replace metals as low-resistivity contacts and new interconnection metallization in VLSI circuits.

Molecular approaches to titanium silicides (e.g.,  $\text{TiSi}_2$ ), zirconium carbide ( $\text{ZrC}$ ) and titanium-silicon-nitrogen (Ti-Si-N) ternary materials are the focus of this dissertation.  $\text{TiSi}_2$  is among the most popular metal silicides in submicron contact applications, and has been routinely used for local interconnects.<sup>5b</sup>  $\text{ZrC}$  is an efficient coating for atomic fuel particles to prolong the life of the graphite components in nuclear reactors.<sup>10</sup> Ti-Si-N ternary materials have been explored as new diffusion barriers for microelectronics metallization.

## **1.2 Chemical Vapor Deposition (CVD) of Thin Film Materials**

Chemical vapor deposition (CVD) is a general method to produce thin films of metal carbides, silicides and Ti-Si-N ternary materials. A thermal CVD process is essentially the deposition of a solid on the heated substrate surface from a chemical reaction in the vapor phase or on the surface (Figure 1.1).<sup>8</sup>

Physical vapor deposition (PVD) is another prevalent commercial method to give thin films of metal carbides and metal silicides.<sup>8</sup> PVD includes evaporation, sputtering, molecular beam epitaxy, ion plating, ion implantation, and pack cementation. Chemical vapor deposition (CVD) is known to have the following important advantages over physical vapor deposition (PVD).<sup>8</sup>

1. PVD is a line-of-sight technique. It has a long mean-free path and a high sticking coefficient. In contrast, a CVD process requires smaller mean-free path and sticking coefficients, and thus leads to a more conformal surface coverage.
2. PVD usually requires a much higher temperature than CVD. In a deposition process, the ratio of  $T/T_m$  ( $T$ : growth temperature;  $T_m$ : melting temperature of deposited material) is among the most important factors for film microstructure. Reduced temperatures usually give good film microstructures. In addition, high temperature may also lead to high residual stresses and grain growth in the films.
3. Ultra-high vacuum is usually obligatory for a PVD process. Most CVD processes, on the other hand, are operated in the range of 0.1 - 760 torr, and are more economical and flexible.
4. CVD usually gives a high deposition rate and thick coating.

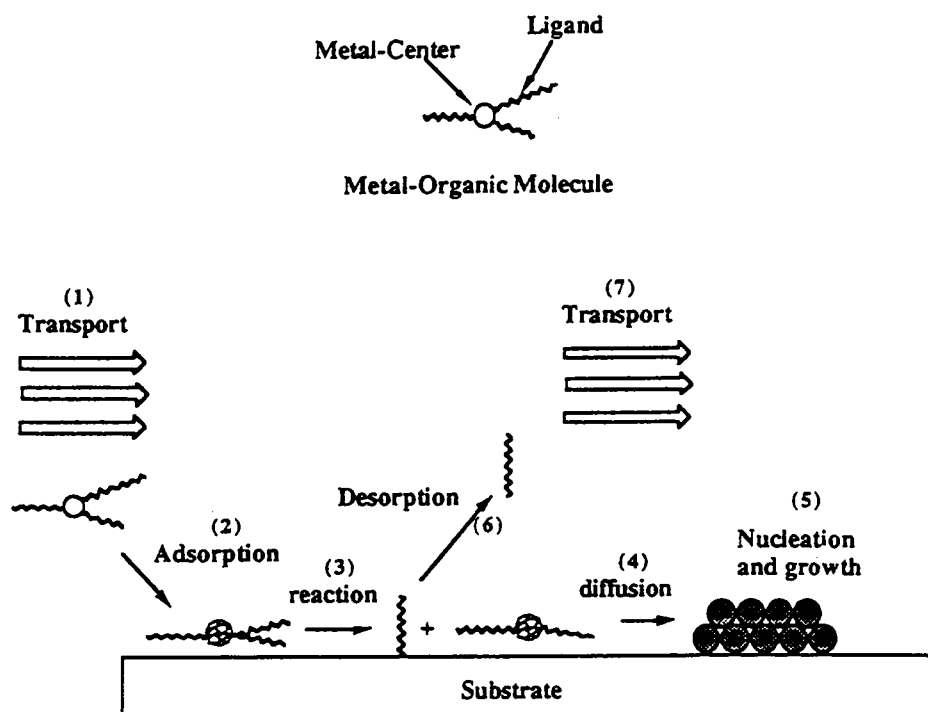


**Figure 1.1** Illustration showing the fundamental steps in the CVD involving a metal-organic molecule.<sup>8</sup>

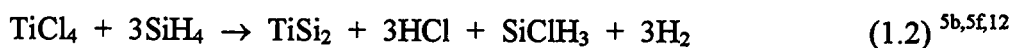
Based on the methods to provide energy for CVD reactions, CVD is often classified into the following categories: thermal CVD, plasma CVD, laser CVD, and photo CVD.<sup>9</sup> Thermal CVD, the first CVD process developed, is also known as “conventional” CVD. Conventional thermal CVD processes are often conducted at high temperatures (800 - 2000 °C).

In 1968, Manasevit reported CVD of gallium arsenide (GaAs) employing volatile metal-organic complexes.<sup>11</sup> Gaseous trimethylgallium (GaMe<sub>3</sub>) reacted with AsH<sub>3</sub> to give gallium arsenide GaAs thin films (Equation 1.1). This has led to the development of a new technique - metallo-organic chemical vapor deposition (MOCVD). One feature of MOCVD is that it often requires lower deposition temperatures than conventional thermal CVD processes.



### 1.3 Chemical Vapor Deposition of Metal Silicides and M-Si-N Ternary Materials

Current chemical processes to silicide thin films mainly involve chemical vapor deposition from metal halides and silane as precursors (e.g., Equation 1.2). The use of



metal halides as precursors for CVD is usually undesired for the following reasons: (i) metal halides do not normally decompose below 500 °C; (ii) they may yield halide-contaminated films; (iii) the volatility of metal halides is often low, and they may thus

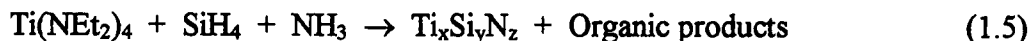
give low deposition rates. The single-precursor CVD approach has been explored to deposit late transition-metal silicide films CoSi, FeSi<sub>2</sub> and Mn<sub>2</sub>Si from H<sub>3</sub>SiCo(CO)<sub>4</sub>, (H<sub>3</sub>Si)<sub>2</sub>Fe(CO)<sub>4</sub> and Mn<sub>2</sub>(CO)<sub>10</sub>(μ-SiH<sub>2</sub>), respectively.<sup>13</sup> However, this approach has been impeded by a small pool of polysilyl complexes as precursors. Developing new MOCVD routes for metal silicides is of intense current interest. Volatile ML<sub>n</sub> (L = alkyl, carbene, carbyne, amide) complexes are potential candidates for CVD processes. Recently a patent was issued for the formation of TiSi<sub>n</sub> films from the reaction of Ti(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>4</sub> with SiH<sub>4</sub> (Equation 1.3).<sup>14</sup>



Related to metal silicides MSi<sub>n</sub> are M-Si-N ternary materials that have been explored as diffusion barriers in microelectronic devices. Excellent barrier property of sputtered Ti-N-Si thin films has been demonstrated.<sup>7</sup> Three patents were recently issued for CVD of TiSi<sub>n</sub>/TiN films from the reactions of Ti(NR<sub>2</sub>)<sub>4</sub> with silanes (Equation 1.4).<sup>15</sup> Smith and Custer also reported CVD of Ti-Si-N thin films through the reaction of Ti(NEt<sub>2</sub>)<sub>4</sub> with silane and ammonia gases (Equation 1.5).<sup>16</sup> However, the patents for CVD of TiSi<sub>n</sub>/TiN films from the reactions in Equation 1.4 only described the processes,<sup>15</sup> and no studies of the chemistry involved in the reactions have been reported.



R = Me, Et



We are particularly interested in the mechanistic pathways in these reactions. The reactions of Cp-free early transition-metal complexes  $\text{ML}_n$  ( $\text{L}$  = alkyl, carbene, carbyne, amide) with  $\text{SiH}_4$ , a largely unexplored area, are linked to the chemistry of Cp-free silyl complexes. Early transition-metal silyl chemistry has been mostly focused on metallocene-based complexes such as  $\text{Cp}_2\text{Zr}(\text{SiR}_3)\text{R}'$ , or those containing supporting ligands such as CO, -OR or  $\text{PR}_3$ .<sup>17</sup> Much progress has been made in understanding the chemistry of these early transition-metal Cp-silyl complexes, and applications of these complexes in, e.g., catalytic dehydropolymerization of organosilanes.<sup>17</sup> The relatively unreactive cyclopentadienyl ligands in these complexes are believed to contribute to the enhanced stability of, e.g., 16-e  $\text{Cp}_2\text{M}(\text{SiR}_3)\text{R}'$ . However, our pursuit of the mechanistic pathways in the reactions between  $\text{ML}_n$  ( $\text{L}$  = alkyl, carbene, carbyne, amide) and  $\text{SiH}_4$  calls for the studies of Cp-free early transition-metal silyl chemistry. Unlike, e.g., Group 4 metallocene-based complexes " $\text{Cp}_2\text{M}$ ", multiple-reactive sites are present in  $\text{ML}_n$ . The studies of these Cp-free complexes may help discover reactions involving pairs or triads of reactive ligands, and establish selectivity among these ligands.

#### 1.4 Current Dissertation

The preparation of a novel metal silyl complex and the mechanistic pathways in the formation of Ti-Si-N ternary materials and metal carbides are the focuses of this Ph.D. study.

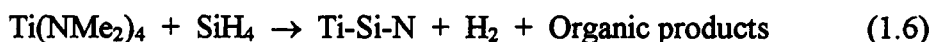
### 1.4.1 Chapter 2

In chapter 2, our study of Cp-free tantalum silyl chemistry is reported. An unstable bis(alkylidene) complex  $(RCH_2)_4Ta_2(=CHR)_2(Cl)_2$  ( $R = SiMe_3$ , **1**), prepared by the addition of 2 equiv of HCl to a symmetrically bridging bis(alkylidyne) complex  $(RCH_2)_4Ta_2(\mu-CR)_2$  (**2**), decomposes through elimination of  $SiMe_4$  to form an unstable alkylidene-alkylidyne complex  $(RCH_2)_3Ta_2(=CHR)(\equiv CR)(Cl)_2$  (**3**). This conversion of an alkylidene to alkylidyne ligand was found to follow first-order kinetics with  $\Delta H_1^\ddagger = 14.1(0.8)$  kcal/mol and  $\Delta S_1^\ddagger = -12(3)$  eu. This is, to our knowledge, the second reported kinetic study of alkylidene  $\rightarrow$  alkylidyne conversion, and the kinetics of this conversion is in contrast to that of  $(RCH_2)_3Ta=CHR \rightarrow (RCH_2)_4Ta_2(\mu-CR)_2$  (**2**) reported earlier.<sup>18</sup> Substitution of the chlorides by  $SiR_3^-$  ( $R = SiMe_3$ ) leads to a preferential elimination of  $HSiR_3$  and formation of the first silyl bis(alkylidyne) complex  $(RCH_2)(R_3Si)Ta(\mu-CR)_2Ta(CH_2R)_2$  (**4**). Complex **4** was found to be thermally stable and was characterized by X-ray crystallography.

### 1.4.2 Chapter 3

Recent patents on CVD of  $TiSi_x/TiN$  thin films<sup>15</sup> prompted us to study the reaction of  $Ti(NMe_2)_4$  with  $SiH_4$ . The results of the study are presented in Chapter 3. An ultra-high vacuum (UHV) chemical vapor deposition chamber with a residual gas analyzer (RGA) was assembled. Thin Ti-Si-N films were deposited on a silicon (100) wafer at various temperatures and pressures (Equation 1.6). The films were found to be amorphous even after being heated up to 750 °C, and their thickness was measured by ellipsometry. The films were characterized by X-ray photoelectron spectroscopy (XPS)

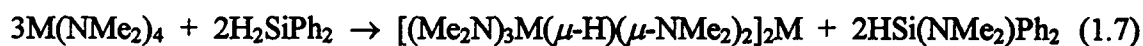
and Rutherford backscattering spectrometry (RBS). The XPS results revealed that the films consisted of  $\text{TiN}_x$  and  $\text{Si}_3\text{N}_4$ . The composition of the films was found to be Ti : Si : N = 16 : 13 : 30 by RBS. A view of scanning electron microscopy (SEM) of the film indicates that the film deposited by this technique is smooth.



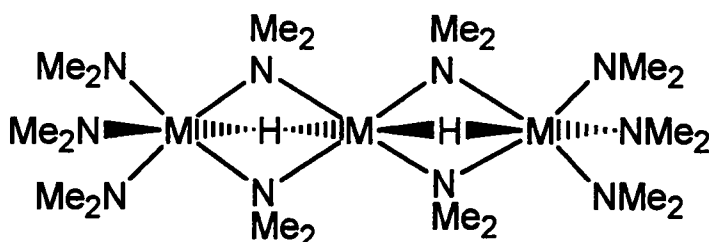
### 1.4.3 Chapter 4

Chapter 4 reports our mechanistic studies of the reaction between metal amido complexes and silanes. The reactions of  $\text{M}(\text{NMe}_2)_4$  ( $\text{M} = \text{Ti}, \text{Zr}$ ) with  $\text{SiH}_4$  were found to give  $\text{H}_2$ ,  $\text{HSi}(\text{NMe}_2)_3$ , and other unknown species.  $\text{H}_2\text{Si}(\text{NMe}_2)_2$  was seen as an intermediate, and no  $\text{HNMe}_2$  was observed in these reactions. The reactions between  $\text{Zr}(\text{NMe}_2)_4$  and  $\text{H}_2\text{SiR}'_2$  ( $\text{R}'_2 = \text{Ph}_2, \text{MePh}, \text{HPh}$ ) were found to yield  $\text{H}_2$ ,  $\text{HSi}(\text{NMe}_2)\text{R}'_2$ , and an unusual trinuclear complex  $[(\text{Me}_2\text{N})_3\text{Zr}(\mu\text{-H})(\mu\text{-NMe}_2)_2]_2\text{Zr}$  (7) (Equation 1.7 and Figure 1.2). The structure of 7 was determined by X-ray crystallography. Its hafnium analogue  $[(\text{Me}_2\text{N})_3\text{Hf}(\mu\text{-H})(\mu\text{-NMe}_2)_2]_2\text{Hf}$  (8) was also synthesized and characterized by X-ray crystallography. The structure of the hafnium complex was found to be similar to that of the zirconium complex 7. *Ab initio* quantum chemical calculations were conducted by the research group of Professor Yun-Dong Wu at the Hong Kong University of Science and Technology to investigate the mechanism of the reactions between  $\text{Ti}(\text{NR}_2)_4$  ( $\text{R} = \text{Me}, \text{H}$ ) and  $\text{SiH}_4$ . These theoretical studies showed that the formation of aminosilanes and  $\text{HTi}(\text{NR}_2)_3$  was favored. The reactions of  $(\text{Me}_2\text{N})_3\text{ZrSi}(\text{SiMe}_3)_3$  (5) with  $\text{H}_n\text{SiR}'_2$  were found to give aminosilanes and

(Me<sub>2</sub>N)<sub>2</sub>Zr(H)Si(SiMe<sub>3</sub>)<sub>3</sub> (6), and these reactions were reversible through unusual equilibria such as (Me<sub>2</sub>N)<sub>3</sub>ZrSi(SiMe<sub>3</sub>)<sub>3</sub> (5) + H<sub>2</sub>SiPh<sub>2</sub> → (Me<sub>2</sub>N)<sub>2</sub>Zr(H)Si(SiMe<sub>3</sub>)<sub>3</sub> (6) + HSi(NMe<sub>2</sub>)Ph<sub>2</sub> [*K*<sub>eq</sub> = 0.11(0.01) and Δ*G*<sup>0</sup> = 1.20(0.05) kcal/mol at 0 °C].



M = Zr, Hf



M = Zr, Hf

**Figure 1.2** The structure of complexes 7 and 8.

### 1.3.4 Chapter 5

Chapter 5 reports our study of the mechanistic pathways in the thermal decomposition of tetraneopentylzirconium Zr(CH<sub>2</sub>CMe<sub>3</sub>)<sub>4</sub> to give zirconium carbide thin films. Both experimental and theoretical studies of the thermolysis of its titanium analog Ti(CH<sub>2</sub>CMe<sub>3</sub>)<sub>4</sub> to TiC showed that the first step is an α-hydrogen abstraction reaction.<sup>19</sup> *Ab initio* quantum chemical calculations of the decomposition of Zr(CH<sub>2</sub>CMe<sub>3</sub>)<sub>4</sub> by

Professor Yun-Dong Wu and his research group revealed that the activation energy of  $\gamma$ -hydrogen abstraction was much lower than that of  $\alpha$ -hydrogen abstraction. In other words,  $\gamma$ -hydrogen abstraction was expected to be the primary pathway in the thermal decomposition of  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$  to  $\text{ZrC}$ . Experimental studies were then conducted in our group to investigate the thermal decomposition of  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$  and  $\text{Zr}(\text{CD}_2\text{CMe}_3)_4$ . The results of our studies support the theoretical predictions. In the thermal decomposition of both  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$  and  $\text{Zr}(\text{CD}_2\text{CMe}_3)_4$ , the major volatile products are neopentane and isobutene, with a ratio of approximately 2.3. In the case of  $\text{Zr}(\text{CD}_2\text{CMe}_3)_4$ , the molar ratios of neopentane- $d_2$ /neopentane- $d_3$  and isobutene- $d_2$ /isobutene- $d_0$  are about 4.9 and 1.52, respectively. These results are discussed in terms of a thermolysis involving  $\gamma$ -hydrogen abstraction as the first step.

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## Chapter 2

### Synthesis and Characterization of a Silyl Bis(alkylidyne) Complex

#### 2.1 Introduction

Novel molecular approaches to metal silicide thin films are of intense interest. The conventional route for the formation of a metal silicide is through the reaction of a metal chloride with silane (Equation 1.1). We are interested in the reactions of  $d^0$  alkyls  $(RCH_2)_4M$  ( $M = Ti, Zr, Hf$ ),<sup>1</sup> alkylidenes  $(RCH_2)_3M=CHR$  ( $M = Ta, Nb$ ),<sup>2</sup> and alkylidynes  $(RCH_2)_3M\equiv CR$  ( $M = Mo, W$ )<sup>3</sup> with  $SiH_4$ , and the potentials of these reactions to lead to the formation of metal silicides (Figure 2.1). A Japanese patent was issued recently for the formation of  $TiSi_2$  from the reaction of  $Ti(CH_2SiMe_3)_4$  with  $SiH_4$ .<sup>4</sup> In our proposed new routes (Figure 2.1), alkyl, alkylidene, and alkylidyne ligands may be cleanly eliminated as alkanes. Possible intermediates in the first steps of these reactions are shown in Figure 2.2. We have not been able to directly observe these reactive intermediates. A series of stable silyl complexes have been prepared to model these intermediates. The studies of these stable model complexes may give a better understanding of the reaction pathways in these reactions.

We are also interested in the fundamental chemistry of the model metal silyl complexes (syntheses, structures, and reactivity) in Figure 2.2(b).<sup>5</sup> Since the report of the first silyl complex,  $Cp(CO)_2FeSiMe_3$ , transition metal silyl chemistry has been the subject of intense study. Many silyl complexes are those of late transition-metal

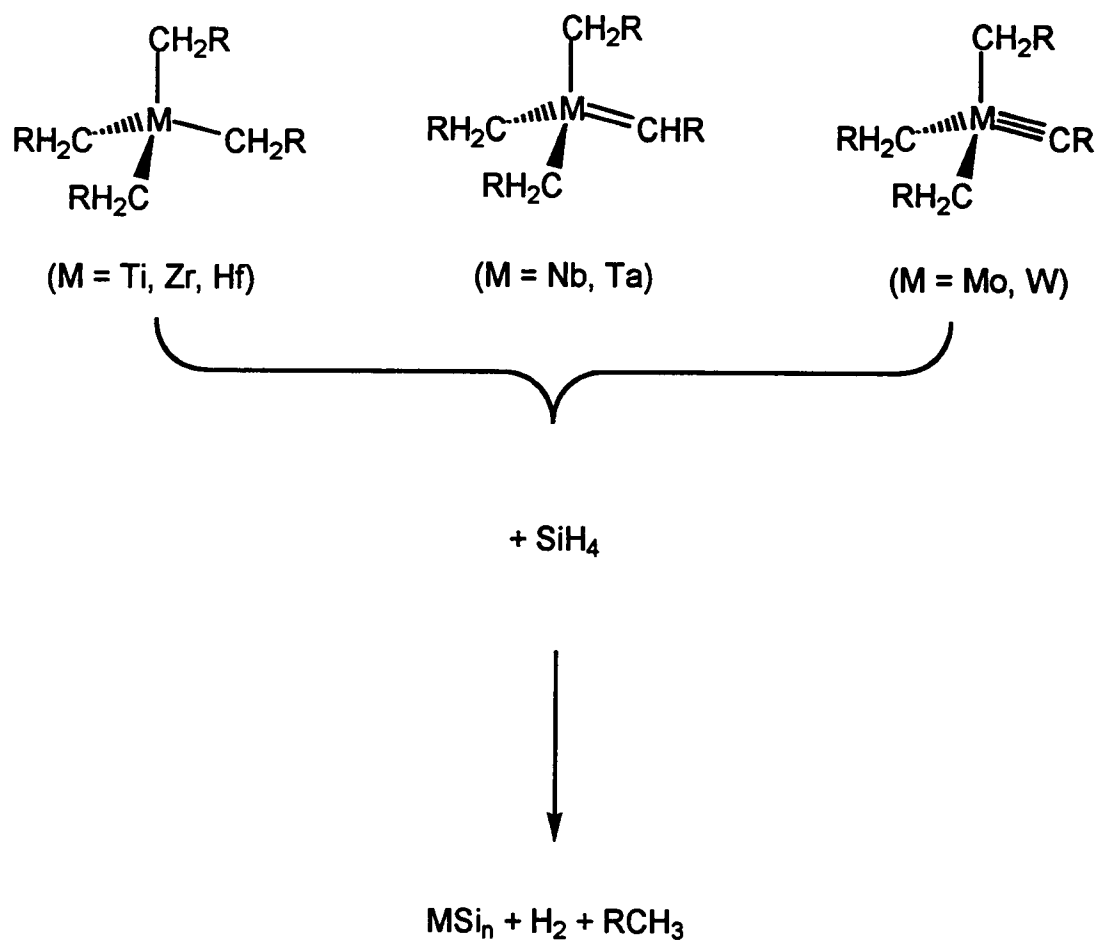


**Figure 2.1** Proposed reactions of  $\text{SiH}_4$  with  $\text{M}(\text{CH}_2\text{R})_4$ ,  $(\text{RCH}_2)_3\text{M}=\text{CHR}$ , and  $(\text{RCH}_2)_3\text{M}\equiv\text{CR}$ .

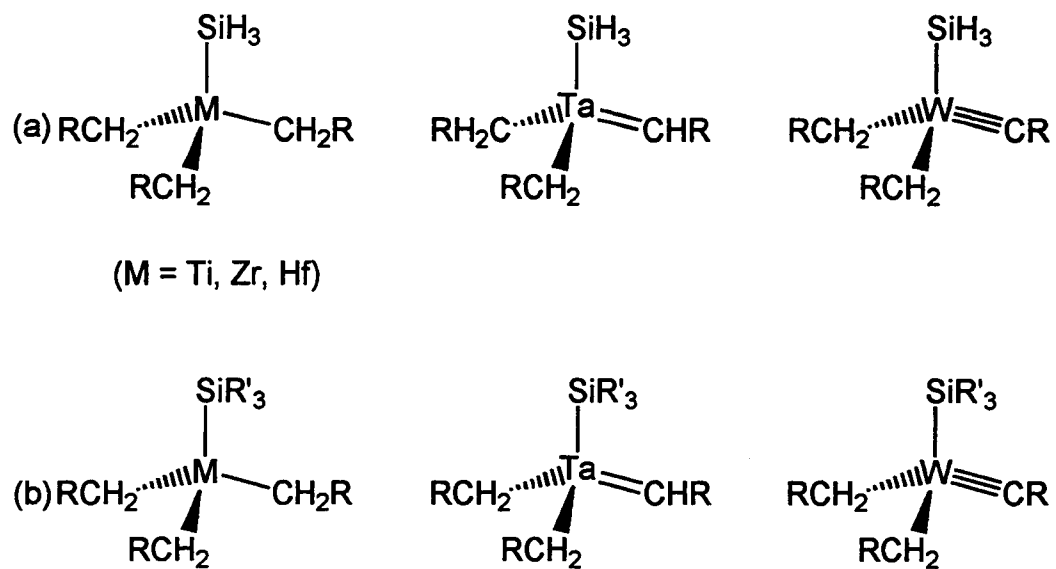
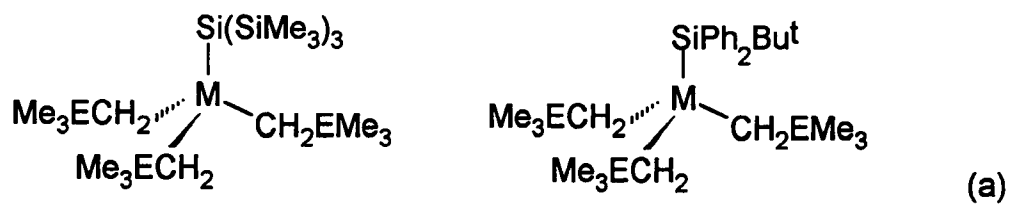


**Figure 2.2** (a) Proposed intermediates; (b) Model complexes.

elements. These coordinatively saturated electron-rich transition-metal silyl complexes are usually stable. The chemistry of electron-deficient early transition-metal silyl compounds, on the other hand, is a relatively young area.<sup>6</sup> The studies in this area have been focused on silyl compounds supported by cyclopentadienyl (Cp) or analogous anionic  $\pi$ -ligands.<sup>6-7</sup> The work of many researchers has laid a solid foundation in this area.<sup>6</sup> The presence of such ligands in, e.g.,  $\text{Cp}_2\text{Zr}(\text{SiR}_3)\text{R}'$ ,<sup>7f</sup>  $\text{Cp}_2\text{Ta}(=\text{CH}_2)\text{SiH}\text{Bu}^t_2$ ,<sup>7k</sup> and  $\text{Cp}_2\text{W}(\eta^2\text{-Me}_2\text{Si}=\text{SiMe}_2)$ ,<sup>7l</sup> is believed to contribute to the enhanced stability of these silyl compounds. The few known Cp-free early transition-metal silyl complexes, such as  $(\text{Me}_3\text{CO})_3\text{MSi}(\text{SiMe}_3)_3$  ( $\text{M} = \text{Zr}, \text{Hf}$ ),<sup>8a</sup>  $\text{V}(\text{CO})_6\text{SiH}_3$ ,<sup>8b</sup> and  $(\text{Me}_3\text{P})_3\text{W}(\text{H})_2\text{I}(\text{SiMe}_3)$ ,<sup>8c</sup> usually contain carbonyls, alkoxides or phosphines as ancillary ligands. The model Cp-free early transition-metal silyl complexes in Figure 2.2(b) were unknown before we started our studies.

Our research group thus has studied these complexes with dual interests: (1) these complexes as models for possible intermediates in the formation of metal silicides; (2) the fundamental chemistry of these new Cp-free silyl complexes.<sup>5</sup> Our group has successfully synthesized a series of mono-nuclear Cp-free silyl complexes  $(\text{RCH}_2)_3\text{M-Si}(\text{SiMe}_3)_3$  ( $\text{R} = \text{Me}_3\text{C}, \text{Me}_3\text{Si}; \text{M} = \text{Ti}, \text{Zr}$ ),  $(\text{RCH}_2)_2\text{Ta}(=\text{CHR})\text{SiR}'_3$  [ $\text{R}'_3 = (\text{SiMe}_3)_3, \text{Bu}^t\text{Ph}_2$ ], and  $(\text{Bu}^t\text{CH}_2)_2\text{W}(=\text{CBu}^t)\text{SiR}'_3$  (Figure 2.3). However, we have not obtained a precise structure of these Cp-free alkylidene or alkylidyne complexes. Disordering of the alkyl and alkylidene ligands was observed in the crystal structures of  $(\text{RCH}_2)_2\text{Ta}(=\text{CHR})\text{Si}(\text{SiMe}_3)_3$ .<sup>5b-c</sup> More severe disorderings in  $(\text{Bu}^t\text{CH}_2)_2\text{W}(=\text{CBu}^t)\text{SiR}'_3$  prevented us from obtaining the crystal structures of the silyl alkylidyne complexes.<sup>5b</sup>



E = C, Si

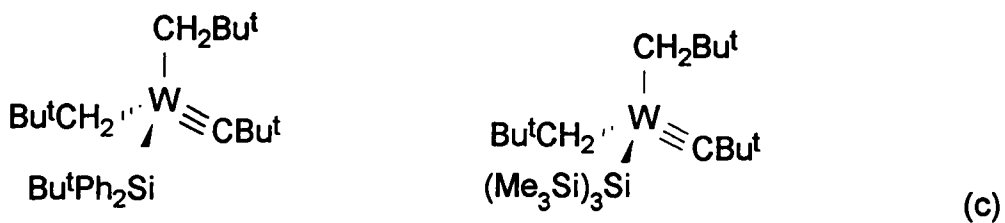
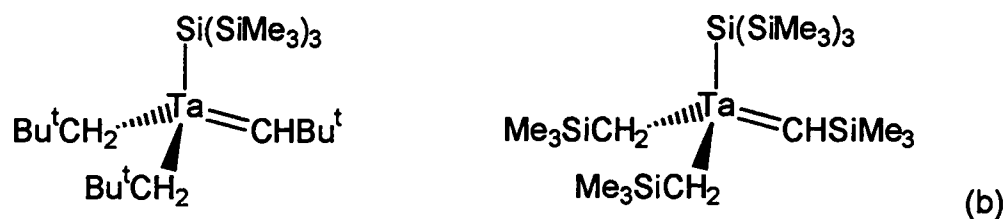


**Figure 2.3** Cp-free silyl compounds prepared by our group: (a) Group 4 alkyl silyl complexes; (b) Group 5 alkylidene silyl complexes; (c) Group 6 alkylidyne silyl complexes.

$(\text{RCH}_2)_2\text{Ta}(=\text{CHR})\text{SiBu}^t\text{Ph}_2$  were found to be thermally unstable, and observed only in solution.<sup>5d</sup>

We thus turned to new Cp-free bridging silyl complexes in the hope that the bridging ligands could eliminate or limit the disordering in the crystals of silyl alkylidene and alkylidyne complexes. An attempt was thus made to synthesize a new Cp-free dinuclear silyl complex  $(\text{R}_3\text{Si})(\text{RCH}_2)\text{Ta}(\mu\text{-CR})_2\text{Ta}(\text{CH}_2\text{R})_2$  ( $\text{R} = \text{SiMe}_3$ , **4**). In the multi-step synthesis of **4**, a new bis(alkylidene) intermediate  $(\text{RCH}_2)_4\text{Ta}_2(=\text{CHR})_2(\text{Cl})_2$  (**1**) was prepared. **1** was found to be extremely thermally unstable and decompose to yield a new alkylidene alkylidyne complex  $(\text{RCH}_2)_3\text{Ta}_2(=\text{CHR})(\equiv\text{CR})(\text{Cl})_2$  (**3**) through  $\alpha$ -hydrogen abstraction. **3** was not stable above  $-25^\circ\text{C}$ . The structures of **2** and **3** were predicted through the combination of 2D NMR and molecular-modeling. The reaction of **3** with 2 equiv of  $\text{Li}(\text{THF})_3\text{SiR}_3$  ( $\text{R} = \text{SiMe}_3$ ) gave the new dinuclear silyl complex  $(\text{R}_3\text{Si})(\text{RCH}_2)\text{Ta}(\mu\text{-CR})_2\text{Ta}(\text{CH}_2\text{R})_2$  (**4**). The reaction of alkylidene complex **1** with 2 equiv of  $\text{Li}(\text{THF})_3\text{SiR}_3$  gave  $(\text{RCH}_2)_4\text{Ta}_2(\mu\text{-CR})_2$  (**2**).<sup>9</sup> **4** is the silyl analog of **2**, one of the first reported high-oxidation-state alkylidyne complexes.<sup>3,9</sup>

The mechanistic pathway in the conversion of unstable alkylidene complex **1** to alkylidene alkylidyne complex **3** was investigated. The mechanistic pathways in the formation of the archetypal alkylidyne complexes  $(\text{RCH}_2)_3\text{M}\equiv\text{CR}$  ( $\text{R} = \text{Me}_3\text{C}$ ,  $\text{Me}_3\text{Si}$ ;  $\text{M} = \text{Mo}$ ,  $\text{W}$ ) are, to our knowledge, unknown.<sup>3</sup> However,  $\alpha$ -hydrogen abstraction is believed to be involved in the conversion of an alkyl ligand (through an alkylidene) to the alkylidyne ligand in  $(\text{RCH}_2)_3\text{M}\equiv\text{CR}$ .<sup>3</sup> To our knowledge, the only previous attempt to study the mechanistic pathway in the conversion of an alkylidene ligand  $\text{M}=\text{CHR}$  to an

alkylidyne ligand  $M\equiv CR$  was the investigation of the formation of **2** from  $(Me_3SiCH_2)_3Ta=CHSiMe_3$ .<sup>10</sup> The conversion from **1** to **3** offered another unique chance to study in detail the conversion of an alkylidene to an alkylidyne ligand.

## 2.2 Results and Discussion

### 2.2.1 Synthesis of Bis(alkylidene) Complex **1** and Its Conversion to Alkylidene

#### Alkylidyne Complex **3**

The addition of 2 equiv of HCl to  $(RCH_2)_2Ta(\mu-CR)_2Ta(CH_2R)_2$  ( $R = SiMe_3$ ) (**2**) leads to almost quantitative formation of the thermally unstable bis(alkylidene) complex  $(RCH_2)_4(Cl)_2Ta_2(=CHR)_2$  (**1**). The two molecules of HCl were found to add to the  $Ta=C$  bonds instead of reacting with the  $Ta-CH_2R$  bonds to eliminate  $SiMe_4$  (Figure 2.4). **1** formed a yellow solution in ethyl ether and was found to decompose above  $-50\text{ }^\circ\text{C}$  to give **3**. The first step in the thermal decomposition of the chloro-alkylidene dimer  $(RCH_2)_4(Cl)_2Ta_2(=CHR)_2$  (**1**) was found to be an  $\alpha$ -hydrogen abstraction between an alkyl ligand and the  $\alpha$ -hydrogen atom of an alkylidene ligand, leading to the formation of an unusual dinuclear alkylidene/alkylidyne complex  $(RCH_2)_3(Cl)_2Ta_2(=CHR)(\equiv CR)$  (**3**) containing an alkylidyne ligand (Figure 2.5). High-oxidation-state  $d^0$  alkylidyne complexes comprise a large and varied class of compounds.<sup>3</sup> However, there is no firm conclusion regarding the mechanistic pathways leading to the formation of archetypal alkylidyne complexes  $(RCH_2)_3M\equiv CR_3$  ( $R = Me_3C, Me_3Si$ ;  $M = Mo, W$ ).  $\alpha$ -Hydrogen abstraction is believed to be involved in the  $M-CH_2R \rightarrow M=CHR \rightarrow M\equiv CR$

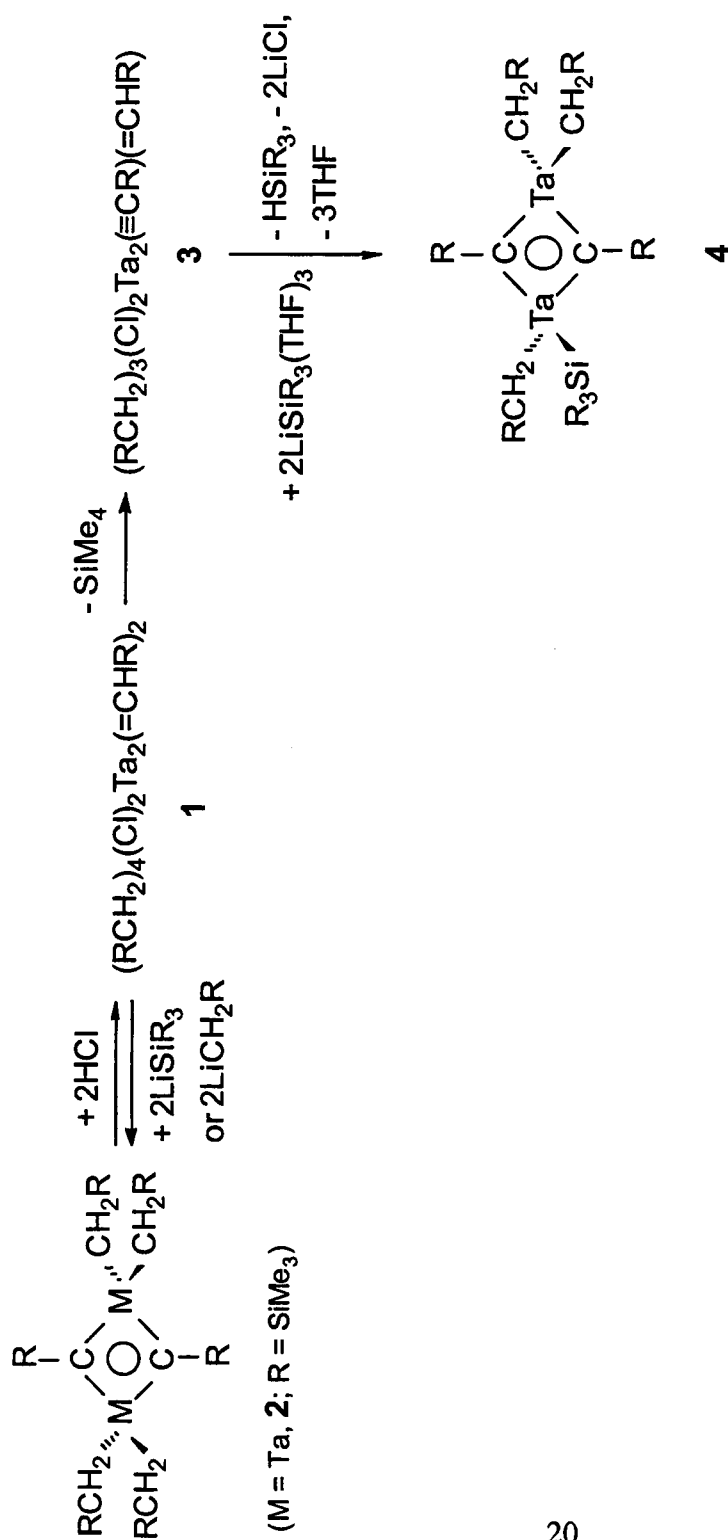


**Figure 2.4** The formation of 4 from 2.

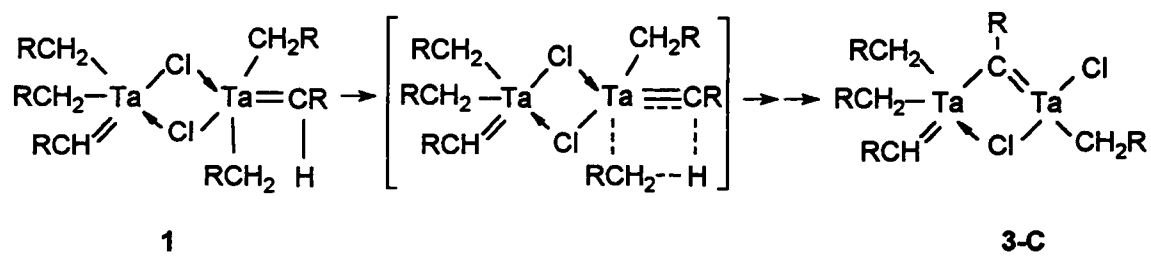


**Figure 2.5** Proposed mechanism of the alkylidene to alkylidyne conversion in the formation of **3** from **1**.

conversions in the formation of  $(\text{RCH}_2)_3\text{M}\equiv\text{CR}$ .<sup>3</sup> Earlier we reported a study of the conversion of an alkylidene complex  $(\text{RCH}_2)_3\text{Ta}=\text{CHR}$  ( $\text{R} = \text{SiMe}_3$ ) to the dimeric alkylidyne complex  $(\text{RCH}_2)_4\text{Ta}_2(\mu\text{-CR})_2$  (**2**).<sup>10</sup> This conversion was found to follow second-order kinetics with a small activation enthalpy [ $\Delta H^\ddagger = 6.2(0.3)$  kcal/mol] and a very negative activation entropy [ $\Delta S^\ddagger = -61.6(0.8)$  eu].<sup>10</sup> To our knowledge, this was the only reported kinetic study of the alkylidene to alkylidyne conversion.<sup>3</sup> We thus decided to investigate, in the current study, the alkylidene  $\rightarrow$  alkylidyne conversion in the formation of **3** from **1**. The elimination of  $\text{SiMe}_4$  in this conversion was found to follow first-order kinetics. The kinetic plots and the Eyring plot are shown in Figures 2.6 and 2.7, respectively. The rate constants of the conversion **1**  $\rightarrow$  **3** determined between 217 - 244 K are listed in Table 2.1. The activation enthalpy and entropy of this alkylidene to alkylidyne conversion thus determined are  $\Delta H_1^\ddagger = 14.1(0.8)$  kcal/mol and  $\Delta S_1^\ddagger = -12(3)$  eu. The negative value for  $\Delta S_1^\ddagger$  indicates a transition state where the rotation of bonds involved is restricted and the symmetry of the molecule descends. Such negative  $\Delta S^\ddagger$  have been observed in C-H bond activation processes and are attributed to concerted four-center transition states, especially those involving cyclometalation.<sup>11,12</sup> The proposed reaction mechanism for the conversion of **1**  $\rightarrow$  **3** is shown in Figure 2.5. The kinetics and mechanism of this conversion are in contrast to those of alkylidene to alkylidyne conversion in the formation of dimeric **2** from  $(\text{RCH}_2)_3\text{Ta}=\text{CHR}$ . The second-order kinetics observed in the  $(\text{RCH}_2)_3\text{Ta}=\text{CHR} \rightarrow \textbf{2}$  conversion, the small activation enthalpy  $\Delta H^\ddagger$ , and the very negative activation entropy  $\Delta S^\ddagger$ , were attributed to dimerization of  $(\text{RCH}_2)_3\text{Ta}=\text{CHR}$  as an integral part of the mechanism.<sup>10</sup>

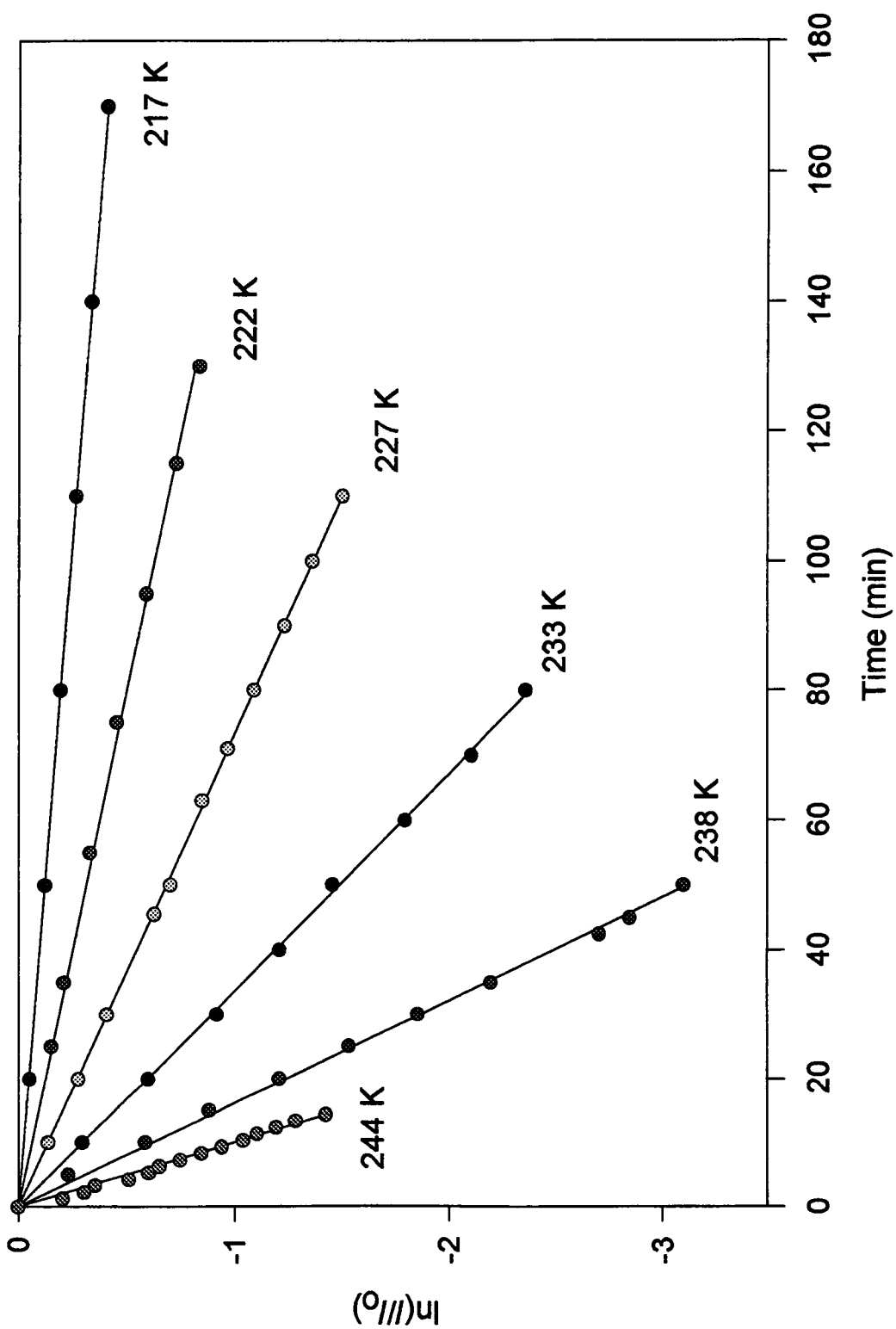


Figure 2.6 Kinetic plots of the decomposition of  $(RCH_2)_4Ta_2Cl_2(=CHR)_2$  (1).

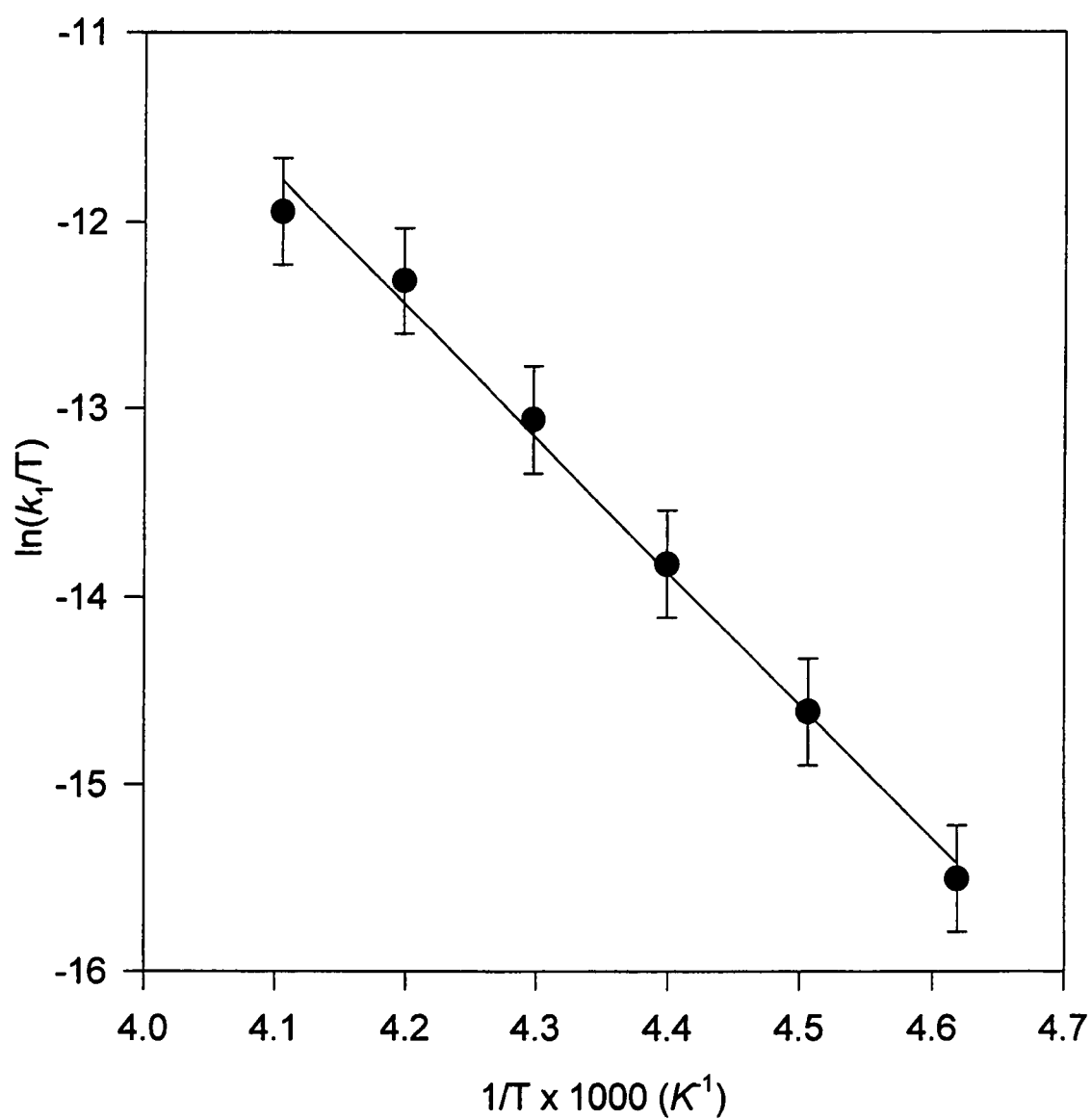


**Figure 2.7** Eyring plot of the decomposition of 1.

**Table 2.1** Rate Constants  $k_1$  for the Conversion  $1 \rightarrow 3^a$ 

| $T$ (K)     | $(k_1 \pm \delta k_{1(\text{ran})}) \times 10^4 \text{ (s}^{-1}\text{)}$ |
|-------------|--------------------------------------------------------------------------|
| $217 \pm 1$ | $0.400 \pm 0.013$                                                        |
| $222 \pm 1$ | $0.996 \pm 0.033$                                                        |
| $227 \pm 1$ | $2.25 \pm 0.07$                                                          |
| $233 \pm 1$ | $4.95 \pm 0.16$                                                          |
| $238 \pm 1$ | $10.7 \pm 0.3$                                                           |
| $244 \pm 1$ | $15.8 \pm 0.5$                                                           |

<sup>a</sup> The total uncertainty  $\delta k_1/k_1$  of 6.0% was calculated from  $\delta k_{1(\text{ran})}/k_1 = 3.3\%$  and  $\delta k_{1(\text{sys})}/k_1 = 5\%$ .<sup>10</sup>

### 2.2.2 Chloride-Bridged vs. Alkyl-Bridged Structure for 1 and 3

There are two possible structures for **1** that are consistent with its NMR spectra and reactivities. Complex **1** may contain either alkylidene (**1-A**) or  $\text{Cl}^-$  (**1-B**) as the bridging ligand.<sup>13</sup> For structure **1-A**, the NMR spectra at  $-50\text{ }^\circ\text{C}$  are consistent with a *trans* configuration of the two bridging alkylidene ligands in the dimetallacyclobutadiene moiety.<sup>13</sup> The presence of a center of inversion in the molecule makes the two  $\alpha$ -hydrogen atoms of the two bridging alkylidene ligands magnetically equivalent, as seen in the  $^1\text{H}$  NMR spectra. However, there is no mirror plane passing through the molecule, thus making the  $\alpha$ -hydrogen atoms in each of the two  $-\text{CH}_2\text{R}$  ligands in **1-A** diastereotopic, as observed in the  $^1\text{H}$  NMR data. In a *trans* configuration with  $\text{Cl}^-$  as the bridging ligands (**1-B**) and the alkylidene ligands in axial positions, the  $\alpha$ -hydrogen atoms of the  $-\text{CH}_2\text{R}$  are diastereotopic, as there is no mirror plane passing through the molecule.

**1** is an electron-deficient compound. The dative bonds formed by the lone-pair electrons on the bridging  $\text{Cl}^-$  ligands in **1-B** increase the electron count on tantalum to 12. In comparison, the metal atoms in **1-A** are 10-electron centers. Thus, it seems likely that **1-B** is the preferred structure for this thermally unstable chloro-alkylidene dimer. Such preferential halide-bridging structures in the presence of alkylidene ligands have been observed in  $[\text{Ta}(=\text{CHBu}^t)(\text{PMe}_3)\text{Cl}_3]_2$ ,<sup>14a</sup>  $\{\text{W}[=\text{C}(\text{CH}_2)_4](\text{OCH}_2\text{Bu}^t)_2\text{Br}_2\}_2$ ,<sup>14b</sup> and  $[\text{Re}(=\text{CBu}^t)(=\text{CHBu}^t)(\text{NH}_2\text{R})\text{Cl}_2]_2$  ( $\text{R} = \text{Bu}^t$ , 2,6- $\text{C}_6\text{H}_3\text{Me}_2$ ).<sup>3h</sup> On the other hand, the formation of alkylidyne-bridged  $(\text{Me}_3\text{P})_2(\text{Cl})\text{Ta}(\mu\text{-CR})_2\text{Ta}(\text{Cl})(\text{CH}_2\text{R})_2$  ( $\text{R} = \text{SiMe}_3$ ) from **1** suggests that **1-A** is favored, as the conversion  $\mathbf{1} \rightarrow (\text{Me}_3\text{P})_2(\text{Cl})\text{Ta}(\mu\text{-CR})_2\text{Ta}(\text{Cl})(\text{CH}_2\text{R})_2$  would not require ligand transfers between metal centers.<sup>15</sup>

There are five possible isomers for **3** (Figure 2.8). The NOESY (nuclear Overhauser enhancement spectroscopy) spectrum of **3** (Figure 2.9) showed that (1) the SiMe<sub>3</sub> group on the alkylidyne ( $\equiv\text{CSiMe}_3$ ) ligand has NOE to five of the six -CH<sub>2</sub>- protons, and (2) the SiMe<sub>3</sub> group on the alkylidene ( $=\text{CHSiMe}_3$ ) ligand has NOE to two protons on two different -CH<sub>2</sub> groups. On the basis of the NOESY spectrum, isomers **3-A**, **3-D**, and **3-E** may be ruled out. Furthermore, on the basis of electron count, **3-C** with a chloride bridge may be favored, as the dative bond by a lone electron pair on the chloride ligand alleviates the electron deficiency in **3**. Such structures with preferential halide bridges have been reported earlier.<sup>3h,14a-b</sup> As in the structure of **1**, the formation of alkylidyne-bridged **4** suggests that **3-B** with alkylidene alkylidyne bridges is preferred, as the conversion **3**  $\rightarrow$  **4** would not require ligand transfers between metal centers.

### 2.2.3 Synthesis and Structure of $(\text{RCH}_2)(\text{R}_3\text{Si})\text{Ta}(\mu\text{-CR})_2\text{Ta}(\text{CH}_2\text{R})_2$ (**4**)

The first silyl bis(alkylidyne) complex **4** was prepared through the substitution of a chloride ligand in **3** by LiSiR<sub>3</sub>(THF)<sub>3</sub> (R = SiMe<sub>3</sub>). This Cp-free silyl complex is of particular interest. It is a silyl analog of the archetypical alkyl bis(alkylidyne) compound  $(\text{RCH}_2)_2\text{Ta}(\mu\text{-CR})_2\text{Ta}(\text{CH}_2\text{R})_2$  (**2**),<sup>9,16</sup> and, to our knowledge, the first structurally characterized d<sup>0</sup> silyl alkylidyne complex.

**4** may be regarded as an adduct between " $(\text{RCH}_2)(\text{R}_3\text{Si})\text{Ta}=\text{CR}$ " and " $(\text{RCH}_2)_2\text{Ta}=\text{CR}$ " through bridging alkylidyne ligands. The fact that this complex is dinuclear is consistent with what is observed for other structurally characterized alkylidyne complexes of tantalum,<sup>9,16</sup> and indicates that the bulky Si(SiMe<sub>3</sub>)<sub>3</sub> ligand is not sufficiently sterically demanding to result in the dissociation of **4** to a monomeric

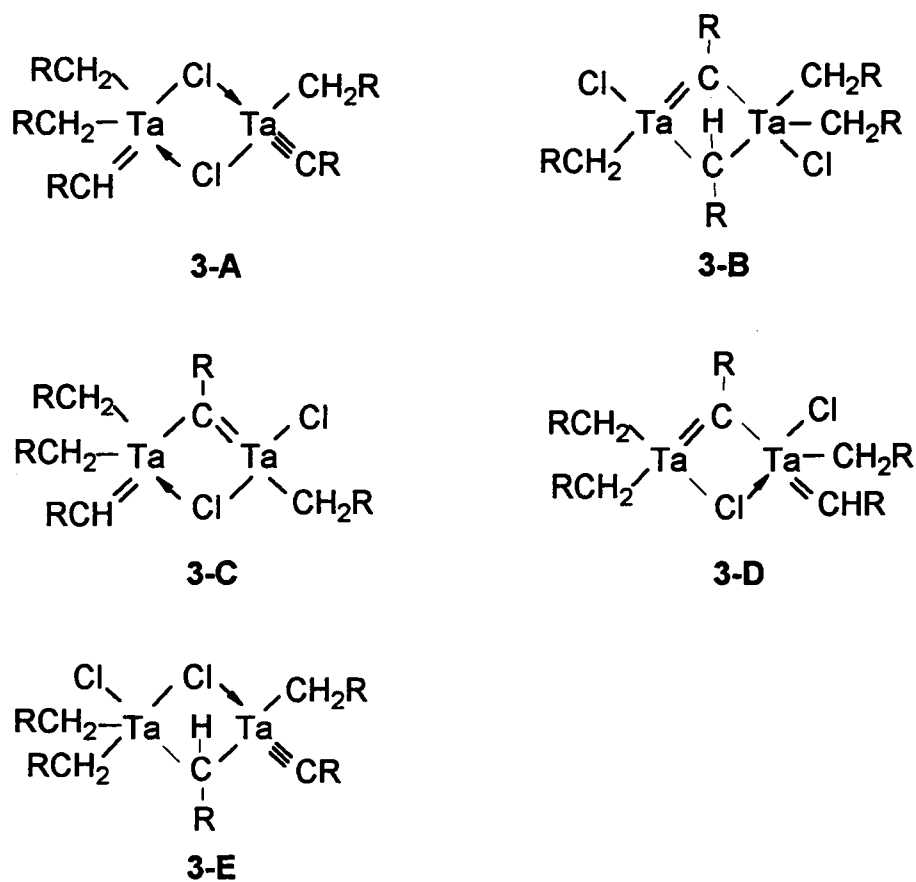


**Figure 2.8** Five possible isomers of 3.

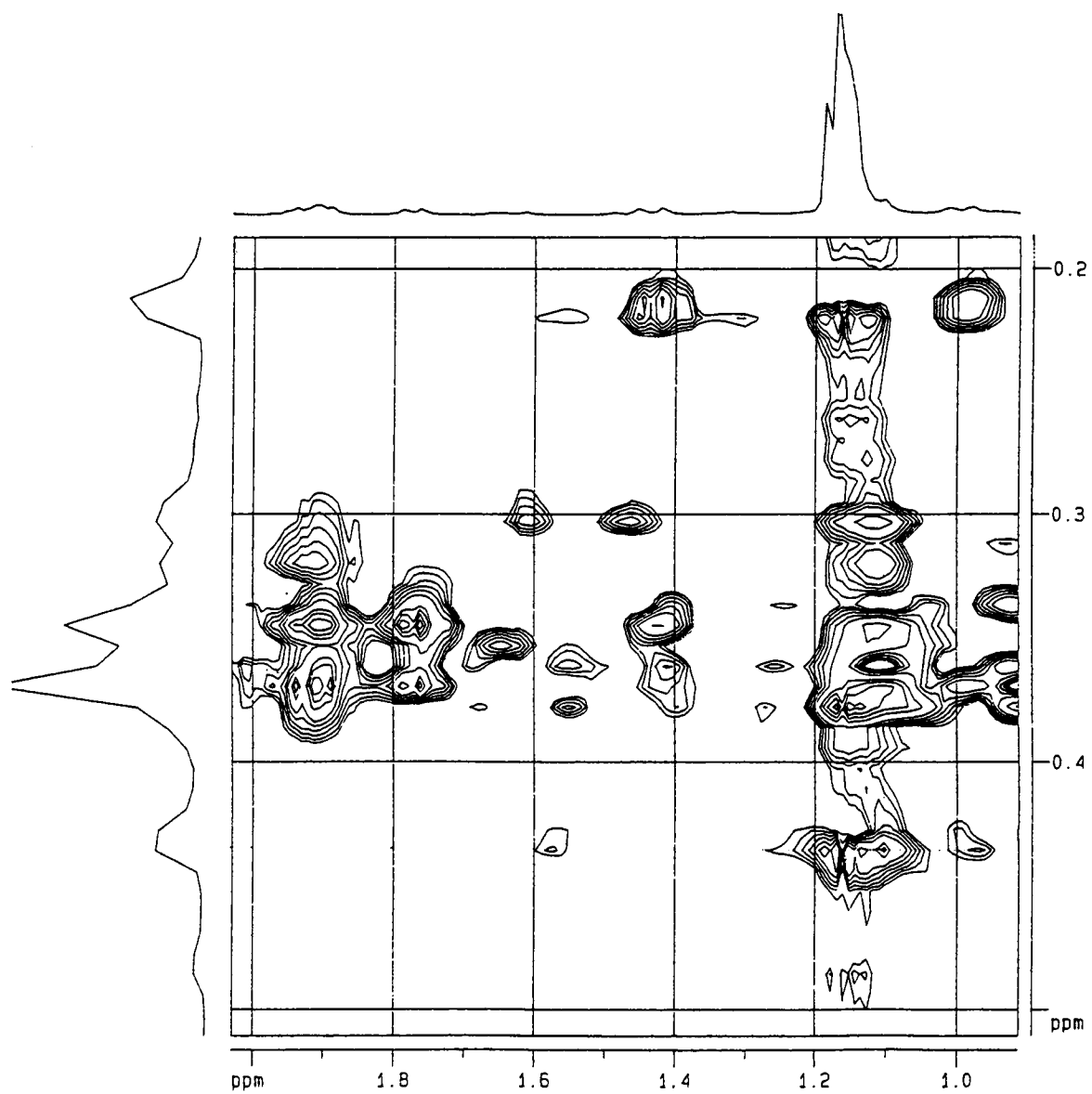


**Figure 2.9** NOSEY spectrum of **3** at -45 °C in toluene-*d*<sub>8</sub>.

complex "(RCH<sub>2</sub>)(R<sub>3</sub>Si)Ta=CR". In contrast, Group 6 alkylidyne compounds such as (Bu<sup>t</sup>CH<sub>2</sub>)<sub>3</sub>W≡CSiMe<sub>3</sub> are monomeric.<sup>12i</sup> An ORTEP view of **4** is shown in Figure 2.10, and crystal data in **4** are given in Tables 2.3 - 2.8. The structure of this silyl bis(alkylidyne) **4** shares many features with that of its alkyl analog **2** and (RCH<sub>2</sub>)<sub>2</sub>Nb( $\mu$ -CR<sub>2</sub>)Nb(CH<sub>2</sub>R)<sub>2</sub>, which were first reported by Wilkinson and coworkers.<sup>9,16</sup> The two Ta-C(bridging) bond lengths are identical within estimated standard deviation; the average [1.9867(11) Å] is identical to that in **2**. The Ta-Si bond length of 2.666(3) Å is comparable to other reported Ta-Si bond lengths. The two bridging carbon atoms and the Ta atoms are co-planar with a deviation of 0.001 Å, and the ring formed by these four atoms is conjugated. The Ta-Ta distance of 2.9 Å represents a non-bonding distance between the two metal atoms, and the Ta-C(bridging) bonds have a multiple (e.g., 1.5) bond order. These bonding features are consistent with the diamagnetism of the complex.

## 2.3 Experimental Section

### 2.3.1 General Procedure

All manipulations, unless noted, were performed under a dry nitrogen atmosphere with the use of either a drybox or standard Schlenk techniques. All solvents were purified by distillation from potassium/benzophenone ketyl. Benzene-*d*<sub>6</sub> and toluene-*d*<sub>8</sub> were dried over activated molecular sieves and stored under N<sub>2</sub>. NMR spectra, unless noted, were recorded at 23 °C on a Bruker AC-250 or AMX-400 Fourier transform spectrometer and referenced to solvents (residual protons in the <sup>1</sup>H spectra).

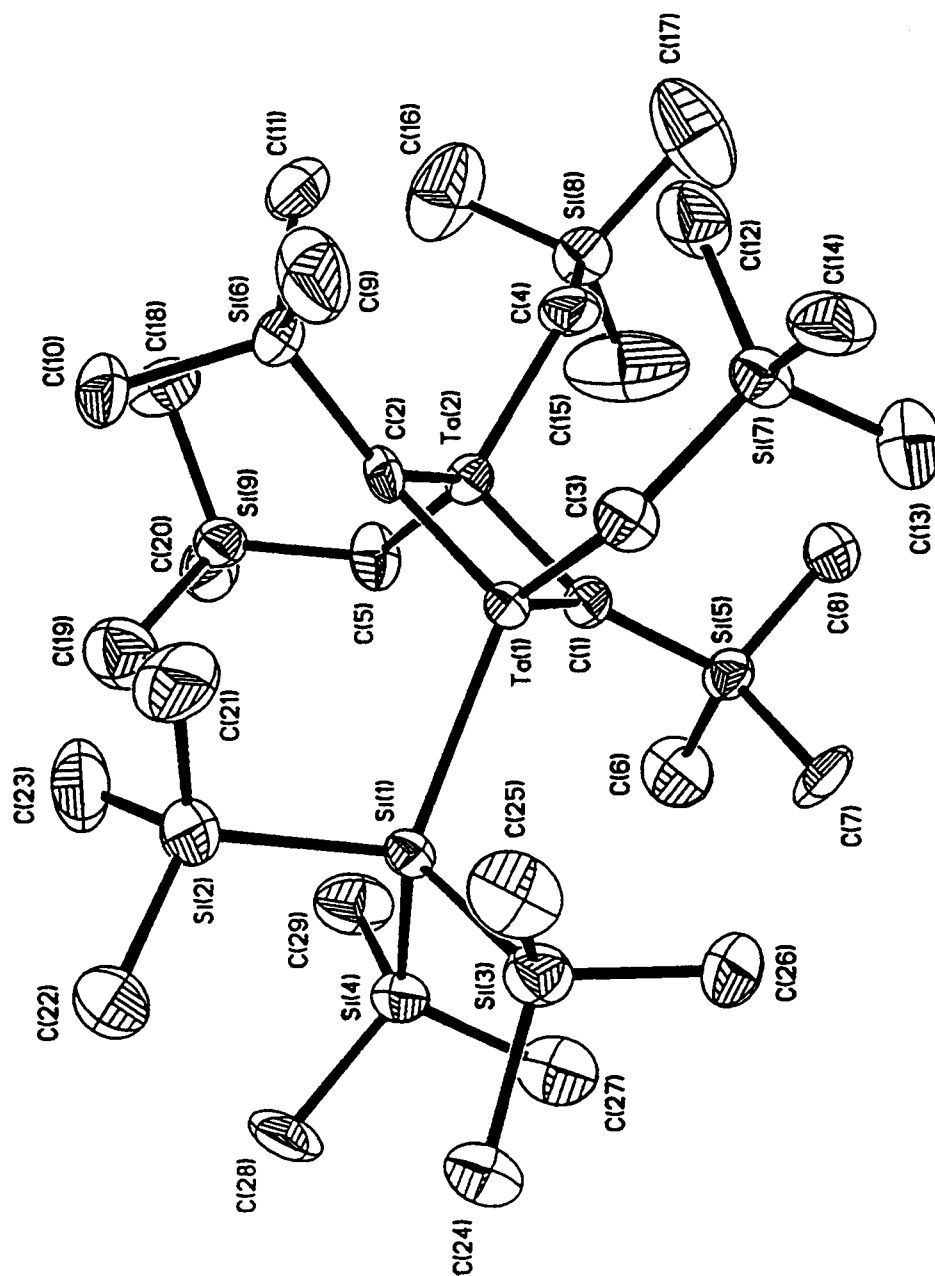


Figure 2.10 ORTEP view of 4, showing 50% thermal ellipsoids.

**Table 2.2** Crystal Data for 4

|                                                 |                                                                                                               |
|-------------------------------------------------|---------------------------------------------------------------------------------------------------------------|
| Formula (Formula weight)                        | C <sub>29</sub> H <sub>78</sub> Si <sub>9</sub> Ta <sub>2</sub> (1041.62)                                     |
| Crystal system                                  | monoclinic                                                                                                    |
| Space group                                     | <i>P</i> 2 <sub>1</sub> / <i>c</i>                                                                            |
| Lattice parameters                              | <i>a</i> (Å) = 10.907(5)<br><i>b</i> (Å) = 18.112(6)<br><i>c</i> (Å) = 25.095(8)<br><i>β</i> (deg) = 97.53(3) |
| <i>V</i> /Å <sup>3</sup>                        | 4915(3)                                                                                                       |
| <i>Z</i>                                        | 4                                                                                                             |
| <i>d</i> <sub>calcd</sub> (Mg m <sup>-3</sup> ) | 1.408                                                                                                         |
| <i>μ</i> (mm <sup>-1</sup> )                    | 4.686                                                                                                         |
| Temp (K)                                        | 173                                                                                                           |
| 2 <i>θ</i> (deg)                                | 3 - 45                                                                                                        |
| No. of data collected                           | 6907                                                                                                          |
| No. of independent data                         | 6465 ( <i>R</i> <sub>int</sub> = 0.0451)                                                                      |
| No. of variables                                | 361                                                                                                           |
| Refinement method                               | full-matrix least-squares on <i>F</i> <sup>2</sup>                                                            |
| <i>R</i> indices (obs. data)                    | 0.0441                                                                                                        |
| Weighted <i>R</i> <sup>a</sup>                  | 0.1115 ( <i>wR</i> <sup>2</sup> )                                                                             |
| Goodness-of-fit on <i>F</i> <sup>2 a</sup>      | 0.913                                                                                                         |

$$^a wR^2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}; R = \sum ||F_o| - |F_c|| / \sum |F_o|;$$

$$w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]; P = [2F_c^2 + \text{Max}(F_o^2, 0)] / 3$$

**Table 2.3** Interatomic Distances (Å) in **4**

|             |            |             |           |
|-------------|------------|-------------|-----------|
| Ta(1)-C(2)  | 1.979(11)  | Ta(1)-C(1)  | 1.994(11) |
| Ta(1)-C(3)  | 2.137(11)  | Ta(1)-Si(1) | 2.666(3)  |
| Ta(1)-Ta(2) | 2.8841(13) | Ta(2)-C(1)  | 1.960(11) |
| Ta(2)-C(2)  | 2.020(10)  | Ta(2)-C(5)  | 2.127(12) |
| Ta(2)-C(4)  | 2.157(12)  | Si(1)-Si(2) | 2.337(5)  |
| Si(1)-Si(4) | 2.340(5)   | Si(1)-Si(3) | 2.360(5)  |
| Si(2)-C(23) | 1.84(2)    | Si(2)-C(22) | 1.884(12) |
| Si(2)-C(21) | 1.885(14)  | Si(3)-C(26) | 1.875(13) |
| Si(3)-C(25) | 1.884(14)  | Si(3)-C(24) | 1.892(12) |
| Si(4)-C(28) | 1.854(12)  | Si(4)-C(27) | 1.86(2)   |
| Si(4)-C(29) | 1.893(13)  | Si(5)-C(1)  | 1.854(11) |
| Si(5)-C(8)  | 1.855(12)  | Si(5)-C(7)  | 1.869(12) |
| Si(5)-C(6)  | 1.875(14)  | Si(6)-C(2)  | 1.841(11) |
| Si(6)-C(10) | 1.854(12)  | Si(6)-C(9)  | 1.88(2)   |
| Si(6)-C(11) | 1.893(14)  | Si(7)-C(3)  | 1.840(12) |
| Si(7)-C(12) | 1.845(13)  | Si(7)-C(13) | 1.857(14) |
| Si(7)-C(14) | 1.864(13)  | Si(8)-C(15) | 1.81(2)   |
| Si(8)-C(16) | 1.84(2)    | Si(8)-C(17) | 1.85(2)   |
| Si(8)-C(4)  | 1.853(12)  | Si(9)-C(19) | 1.850(14) |
| Si(9)-C(18) | 1.853(13)  | Si(9)-C(20) | 1.866(14) |
| Si(9)-C(5)  | 1.866(12)  |             |           |

**Table 2.4** Intramolecular Bond Angles (°) in **4**

|                    |          |                    |           |
|--------------------|----------|--------------------|-----------|
| C(1)-Ta(1)-C(2)    | 87.1(4)  | C(2)-Ta(1)-C(3)    | 111.4(4)  |
| C(1)-Ta(1)-C(3)    | 116.7(5) | C(2)-Ta(1)-Si(1)   | 116.4(3)  |
| C(1)-Ta(1)-Si(1)   | 112.8(3) | C(3)-Ta(1)-Si(1)   | 110.7(3)  |
| C(2)-Ta(1)-Ta(2)   | 44.4(3)  | C(1)-Ta(1)-Ta(2)   | 42.7(3)   |
| C(3)-Ta(1)-Ta(2)   | 124.3(3) | Si(10)-Ta(1)-Ta(2) | 124.94(8) |
| C(1)-Ta(2)-C(2)    | 86.9(4)  | C(1)-Ta(2)-C(5)    | 111.7(5)  |
| C(2)-Ta(2)-C(5)    | 117.3(5) | C(1)-Ta(2)-C(4)    | 108.1(5)  |
| C(2)-Ta(2)-C(4)    | 114.1(5) | C(4)-Ta(2)-C(5)    | 114.9(5)  |
| C(1)-Ta(2)-Ta(1)   | 43.6(3)  | C(2)-Ta(2)-Ta(1)   | 43.3(3)   |
| C(5)-Ta(2)-Ta(1)   | 124.7(4) | C(4)-Ta(2)-Ta(1)   | 119.8(4)  |
| Si(2)-Si(1)-Si(4)  | 107.9(2) | Si(2)-Si(1)-Si(3)  | 105.2(2)  |
| Si(4)-Si(1)-Si(3)  | 106.2(2) | Si(2)-Si(1)-Ta(1)  | 109.2(2)  |
| Si(4)-Si(1)-Ta(1)  | 117.2(2) | Si(3)-Si(1)-Ta(1)  | 110.6(2)  |
| C(23)-Si(2)-C(22)  | 107.0(7) | C(23)-Si(2)-C(21)  | 108.9(8)  |
| C(22)-Si(2)-C(21)  | 106.3(7) | C(23)-Si(2)-Si(1)  | 110.0(5)  |
| C(22)-Si(20)-Si(1) | 114.3(5) | C(21)-Si(2)-Si(1)  | 110.1(5)  |
| C(26)-Si(3)-C(25)  | 107.4(7) | C(26)-Si(3)-C(24)  | 107.0(6)  |
| C(25)-Si(3)-C(24)  | 107.9(6) | C(26)-Si(30)-Si(1) | 112.6(5)  |
| C(25)-Si(3)-Si(1)  | 112.0(5) | C(24)-Si(3)-Si(1)  | 109.8(5)  |
| C(28)-Si(4)-C(27)  | 108.2(7) | C(28)-Si(4)-C(29)  | 108.6(7)  |
| C(27)-Si(4)-C(29)  | 108.2(7) | C(28)-Si(4)-Si(1)  | 110.8(5)  |

**Table 2.4** Continued

|                   |           |                   |           |
|-------------------|-----------|-------------------|-----------|
| C(27)-Si(4)-Si(1) | 110.6(5)  | C(29)-Si(4)-Si(1) | 110.4(5)  |
| C(1)-Si(5)-C(8)   | 110.6(6)  | C(1)-Si(5)-C(7)   | 110.6(6)  |
| C(8)-Si(5)-C(7)   | 108.2(6)  | C(1)-Si(5)-C(6)   | 109.5(6)  |
| C(8)-Si(5)-C(6)   | 107.8(6)  | C(7)-Si(5)-C(6)   | 110.0(7)  |
| C(2)-Si(6)-C(10)  | 110.9(6)  | C(2)-Si(6)-C(9)   | 112.2(7)  |
| C(10)-Si(6)-C(9)  | 106.9(7)  | C(2)-Si(6)-C(11)  | 111.7(6)  |
| C(10)-Si(6)-C(11) | 108.2(7)  | C(9)-Si(6)-C(11)  | 106.7(8)  |
| C(3)-Si(7)-C(12)  | 111.6(6)  | C(3)-Si(7)-C(13)  | 108.6(6)  |
| C(12)-Si(7)-C(13) | 109.9(7)  | C(3)-Si(7)-C(14)  | 111.5(6)  |
| C(12)-Si(7)-C(14) | 108.0(7)  | C(13)-Si(7)-C(14) | 107.2(7)  |
| C(15)-Si(8)-C(16) | 110.4(11) | C(15)-Si(8)-C(17) | 106.2(10) |
| C(16)-Si(8)-C(17) | 105.8(10) | C(15)-Si(8)-C(4)  | 114.4(7)  |
| C(16)-Si(8)-C(4)  | 109.6(7)  | C(17)-Si(8)-C(4)  | 110.1(7)  |
| C(19)-Si(9)-C(18) | 109.0(7)  | C(19)-Si(9)-C(20) | 107.9(7)  |
| C(18)-Si(9)-C(20) | 107.1(7)  | C(19)-Si(9)-C(5)  | 111.9(7)  |
| C(18)-Si(9)-C(5)  | 110.7(7)  | C(20)-Si(9)-C(5)  | 110.0(6)  |
| Si(5)-C(1)-Ta(2)  | 132.1(6)  | Si(5)-C(1)-Ta(1)  | 134.0(7)  |
| Ta(1)-C(1)-Ta(2)  | 93.7(5)   | Si(6)-C(2)-Ta(1)  | 137.3(6)  |
| Si(6)-C(2)-Ta(2)  | 125.6(6)  | Ta(1)-C(2)-Ta(2)  | 92.3(4)   |
| Si(7)-C(3)-Ta(1)  | 132.3(6)  | Si(8)-C(4)-Ta(2)  | 125.3(7)  |
| Si(9)-C(5)-Ta(2)  | 129.6(7)  |                   |           |

**Table 2.5** Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic DisplacementParameters ( $\text{\AA}^2 \times 10^3$ ) for **4<sup>a</sup>**

|       | x        | y       | z       | <i>U</i> (eq) |
|-------|----------|---------|---------|---------------|
| Ta(1) | 2334(1)  | 2091(1) | 980(1)  | 25(1)         |
| Ta(2) | 4497(1)  | 2585(1) | 1674(1) | 29(1)         |
| Si(1) | 1802(3)  | 2439(2) | -57(1)  | 30(1)         |
| Si(2) | 697(4)   | 3548(2) | -135(2) | 46(1)         |
| Si(3) | 456(3)   | 1554(2) | -509(1) | 40(1)         |
| Si(4) | 3462(4)  | 2551(2) | -555(1) | 38(1)         |
| Si(5) | 4970(3)  | 942(2)  | 1006(1) | 32(1)         |
| Si(6) | 1887(4)  | 3538(2) | 1894(1) | 39(1)         |
| Si(7) | 920(3)   | 775(2)  | 1810(1) | 35(1)         |
| Si(8) | 6410(3)  | 2210(2) | 2908(1) | 39(1)         |
| Si(9) | 6040(4)  | 4293(2) | 142(1)  | 38(1)         |
| C(1)  | 4081(10) | 1763(6) | 1174(5) | 31(3)         |
| C(2)  | 2730(10) | 2924(6) | 1483(4) | 26(3)         |
| C(3)  | 934(11)  | 1397(7) | 1231(5) | 36(3)         |
| C(4)  | 4904(12) | 2134(7) | 2473(5) | 41(3)         |
| C(5)  | 5908(11) | 3266(7) | 1427(6) | 42(3)         |
| C(6)  | 6316(13) | 1245(8) | 665(6)  | 58(4)         |
| C(7)  | 3963(13) | 299(7)  | 560(5)  | 45(4)         |

**Table 2.5 Continued**

|       | x         | y        | z        | <i>U</i> (eq) |
|-------|-----------|----------|----------|---------------|
| C(8)  | 590(12)   | 434(7)   | 1625(5)  | 43(3)         |
| C(9)  | 292(15)   | 3184(9)  | 1958(7)  | 76(5)         |
| C(10) | 1697(14)  | 4470(7)  | 1590(5)  | 52(4)         |
| C(11) | 2718(15)  | 3638(8)  | 2601(5)  | 60(4)         |
| C(12) | 1432(15)  | 1252(8)  | 2450(5)  | 62(4)         |
| C(13) | 1954(14)  | -20(8)   | 1728(6)  | 59(4)         |
| C(14) | -655(12)  | 395(8)   | 1845(5)  | 52(4)         |
| C(15) | 7728(16)  | 1939(14) | 2585(7)  | 118(9)        |
| C(16) | 6612(19)  | 3157(10) | 3172(8)  | 100(7)        |
| C(17) | 6423(17)  | 1605(11) | 3504(8)  | 104(7)        |
| C(18) | 5482(14)  | 4692(8)  | 2030(5)  | 60(4)         |
| C(19) | 5160(15)  | 4706(9)  | 818(6)   | 67(5)         |
| C(20) | 7693(13)  | 4569(7)  | 1444(6)  | 56(4)         |
| C(21) | -534(14)  | 3541(9)  | 327(6)   | 68(5)         |
| C(22) | -122(14)  | 3738(8)  | -829(5)  | 59(4)         |
| C(23) | 1746(15)  | 4327(7)  | 46(7)    | 69(5)         |
| C(24) | 318(12)   | 1715(8)  | -1260(5) | 46(3)         |
| C(25) | -1143(13) | 1607(9)  | -305(6)  | 61(4)         |
| C(26) | 1025(14)  | 585(7)   | -384(6)  | 51(4)         |
| C(27) | 3993(13)  | 1626(8)  | -750(60  | 55(4)         |

**Table 2.5 Continued**

|       | x        | y       | z        | $U(\text{eq})$ |
|-------|----------|---------|----------|----------------|
| C(28) | 3005(14) | 3092(8) | -1177(5) | 54(4)          |
| C(29) | 4807(14) | 3034(9) | -145(5)  | 58(4)          |

<sup>a</sup> $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

**Table 2.6** Anisotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for 4<sup>a</sup>

|       | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|-------|----------|----------|----------|----------|----------|----------|
| Ta(1) | 29(1)    | 24(1)    | 21(1)    | 2(1)     | 1(1)     | 3(1)     |
| Ta(2) | 30(1)    | 27(1)    | 29(1)    | -4(1)    | 3(1)     | -2(1)    |
| Si(1) | 35(2)    | 31(2)    | 21(2)    | 3(1)     | -1(1)    | 7(2)     |
| Si(2) | 55(3)    | 41(2)    | 40(2)    | 3(2)     | -2(2)    | 15(2)    |
| Si(3) | 42(2)    | 44(2)    | 33(2)    | -1(2)    | 2(2)     | -6(2)    |
| Si(4) | 47(2)    | 40(2)    | 27(2)    | -1(2)    | 5(2)     | -2(2)    |
| Si(5) | 32(2)    | 31(2)    | 32(2)    | -2(2)    | 14(2)    | 6(2)     |
| Si(6) | 48(2)    | 33(2)    | 39(2)    | 0(2)     | 1(2)     | 14(2)    |
| Si(7) | 35(2)    | 38(2)    | 30(2)    | 5(2)     | -7(2)    | -4(2)    |
| Si(8) | 28(2)    | 45(2)    | 39(2)    | -3(2)    | 4(2)     | 2(2)     |
| Si(9) | 49(2)    | 35(2)    | 31(2)    | -2(2)    | 13(5)    | -8(2)    |
| C(1)  | 33(7)    | 27(6)    | 33(7)    | 1(5)     | 6(5)     | 8(5)     |
| C(2)  | 23(6)    | 23(6)    | 33(7)    | 10(5)    | 0(6)     | 6(5)     |
| C(3)  | 33(7)    | 38(7)    | 34(7)    | 2(6)     | -2(6)    | -9(6)    |
| C(4)  | 50(8)    | 48(8)    | 24(6)    | -3(6)    | 11(6)    | 5(7)     |
| C(5)  | 34(7)    | 33(7)    | 61(9)    | 6(7)     | 15(8)    | -11(6)   |
| C(6)  | 49(9)    | 67(10)   | 62(10)   | 7(8)     | -3(7)    | 13(8)    |
| C(7)  | 58(9)    | 34(7)    | 41(8)    | -22(6)   | 2(7)     | 12(7)    |
| C(8)  | 50(9)    | 39(8)    | 40(8)    | 4(6)     | 11(6)    | 7(7)     |

**Table 2.6** Continued

|       | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|-------|----------|----------|----------|----------|----------|----------|
| C(9)  | 68(11)   | 70(11)   | 97(14)   | 29(10)   | 31(10)   | 33(9)    |
| C(10) | 64(10)   | 36(8)    | 53(9)    | 2(7)     | 0(8)     | 20(7)    |
| C(11) | 88(12)   | 50(9)    | 42(8)    | -10(7)   | 9(8)     | 25(9)    |
| C(12) | 85(12)   | 55(9)    | 38(8)    | 8(7)     | -17(8)   | -10(9)   |
| C(13) | 57(10)   | 43(9)    | 77(11)   | 8(8)     | 10(8)    | -1(7)    |
| C(14) | 55(10)   | 66(10)   | 40(8)    | 0(7)     | 20(7)    | -11(8)   |
| C(15) | 66(13)   | 226(28)  | 58(12)   | -18(15)  | -14(10)  | 17(16)   |
| C(16) | 104(16)  | 79(13)   | 103(15)  | -40(12)  | -40(12)  | 4(12)    |
| C(17) | 80(14)   | 105(16)  | 117(16)  | 52(13)   | -30(12)  | -24(12)  |
| C(18) | 67(11)   | 65(10)   | 48(9)    | -18(8)   | 10(8)    | 4(8)     |
| C(19) | 70(12)   | 71(11)   | 58(10)   | 2(8)     | -4(9)    | -1(9)    |
| C(20) | 61(10)   | 42(9)    | 68(10)   | -3(7)    | 19(8)    | -14(7)   |
| C(21) | 66(11)   | 80(12)   | 61(10)   | -5(9)    | 20(8)    | 37(9)    |
| C(22) | 66(10)   | 61(10)   | 42(8)    | 0(7)     | -22(7)   | 18(8)    |
| C(23) | 86(13)   | 37(9)    | 80(12)   | 7(8)     | -2(10)   | 13(8)    |
| C(24) | 43(8)    | 60(9)    | 35(8)    | 7(7)     | 1(6)     | -4(7)    |
| C(25) | 50(10)   | 74(11)   | 58(10)   | 5(8)     | 1(8)     | -17(8)   |
| C(26) | 69(10)   | 33(8)    | 50(9)    | -5(7)    | 2(8)     | -9(7)    |
| C(27) | 36(8)    | 78(11)   | 52(9)    | 4(8)     | 11(7)    | 13(8)    |
| C(28) | 76(10)   | 62(9)    | 23(7)    | 16(7)    | 9(7)     | -11(8)   |

**Table 2.6 Continued**

|       | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|-------|----------|----------|----------|----------|----------|----------|
| C(29) | 55(10)   | 76(11)   | 43(9)    | -4(8)    | 2(7)     | -21(8)   |

<sup>a</sup> The anisotropic displacement factor exponent takes the form:  $-2\pi^2[(ha^*)^2U_{11} + (kb^*)^2U_{22} + (lc^*)^2U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2lkc^*b^*U_{23}]$ .

**Table 2.7** Hydrogen Coordinates ( $\times 10^4$ ) and Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for **4**

|        | x        | y       | z       | $U(\text{eq})$ |
|--------|----------|---------|---------|----------------|
| H(3A)  | 229(11)  | 1735(7) | 1254(5) | 80             |
| H(3B)  | 678(11)  | 1079(7) | 915(5)  | 80             |
| H(4A)  | 4281(12) | 2347(7) | 2683(5) | 80             |
| H(4B)  | 4720(12) | 1600(7) | 2440(5) | 80             |
| H(5A)  | 6682(11) | 3092(7) | 1641(6) | 80             |
| H(5B)  | 5966(11) | 3116(7) | 1052(6) | 80             |
| H(6A)  | 6785(13) | 811(8)  | 576(6)  | 80             |
| H(6B)  | 6852(13) | 1569(8) | 906(6)  | 80             |
| H(6C)  | 6012(13) | 1513(8) | 335(6)  | 80             |
| H(7A)  | 4448(13) | -131(7) | 476(5)  | 80             |
| H(7B)  | 3642(13) | 555(7)  | 227(5)  | 80             |
| H(7C)  | 3272(13) | 136(7)  | 744(5)  | 80             |
| H(8A)  | 6057(12) | 3(7)    | 1529(5) | 80             |
| H(8B)  | 4903(12) | 272(7)  | 1813(5) | 80             |
| H(8C)  | 6137(12) | 760(7)  | 1861(5) | 80             |
| H(9A)  | -122(15) | 3526(9) | 2179(7) | 80             |
| H(9B)  | 353(15)  | 2696(9) | 2128(7) | 80             |
| H(9C)  | -186(15) | 3146(9) | 1600(7) | 80             |
| H(10A) | 1247(14) | 4787(7) | 1815(5) | 80             |

**Table 2.7 Continued**

|        | x         | y        | z       | $U(\text{eq})$ |
|--------|-----------|----------|---------|----------------|
| H(10B) | 1231(14)  | 4433(7)  | 1230(5) | 80             |
| H(10C) | 2513(14)  | 4684(7)  | 1565(5) | 80             |
| H(11A) | 2244(15)  | 3967(8)  | 2808(5) | 80             |
| H(11B) | 3542(15)  | 3847(8)  | 2588(5) | 80             |
| H(11C) | 2797(15)  | 3153(8)  | 2775(5) | 80             |
| H(12A) | 1414(15)  | 906(8)   | 2750(5) | 80             |
| H(12B) | 878(15)   | 1668(8)  | 2493(5) | 80             |
| H(12C) | 2277(15)  | 1436(8)  | 2449(5) | 80             |
| H(13A) | 1956(14)  | -356(8)  | 2034(6) | 80             |
| H(13B) | 2796(14)  | 160(8)   | 1712(6) | 80             |
| H(13C) | 1657(14)  | -283(8)  | 1395(6) | 80             |
| H(14A) | -632(12)  | 67(8)    | 2156(5) | 80             |
| H(14B) | -930(12)  | 116(8)   | 1516(5) | 80             |
| H(14C) | -1232(12) | 801(8)   | 1880(5) | 80             |
| H(15A) | 7608(16)  | 1435(14) | 2447(7) | 80             |
| H(15B) | 8478(16)  | 1959(14) | 2846(7) | 80             |
| H(15C) | 7813(16)  | 2277(14) | 2287(7) | 80             |
| H(16A) | 5892(19)  | 3296(10) | 3345(8) | 80             |
| H(16B) | 6694(19)  | 3499(10) | 2875(8) | 80             |
| H(16C) | 7360(19)  | 3181(10) | 3434(8) | 80             |

**Table 2.7 Continued**

|        | x         | y        | z        | <i>U</i> (eq) |
|--------|-----------|----------|----------|---------------|
| H(17A) | 5722(17)  | 1730(11) | 3694(8)  | 80            |
| H(17B) | 7197(17)  | 1677(11) | 3744(8)  | 80            |
| H(17C) | 6358(17)  | 1088(11) | 3888(8)  | 80            |
| H(18A) | 5944(14)  | 4475(8)  | 2354(5)  | 80            |
| H(18B) | 4600(14)  | 4584(8)  | 2022(5)  | 80            |
| H(18C) | 5608(14)  | 5227(8)  | 2033(5)  | 80            |
| H(19A) | 5450(15)  | 4497(9)  | 497(6)   | 80            |
| H(19B) | 5286(15)  | 5242(9)  | 823(6)   | 80            |
| H(19C) | 4278(15)  | 4598(9)  | 812(6)   | 80            |
| H(20A) | 8180(13)  | 4356(7)  | 1763(6)  | 80            |
| H(20B) | 7757(13)  | 5109(7)  | 1459(6)  | 80            |
| H(20C) | 8009(13)  | 4388(7)  | 1121(6)  | 80            |
| H(21A) | -1098(14) | 3127(9)  | 234(6)   | 80            |
| H(21B) | -998(14)  | 4005(9)  | 288(6)   | 80            |
| H(21C) | -145(14)  | 3488(9)  | 700(6)   | 80            |
| H(22A) | -693(14)  | 3332(8)  | -941(5)  | 80            |
| H(22B) | 487(14)   | 3780(8)  | -1082(5) | 80            |
| H(22C) | -587(14)  | 4201(8)  | -827(5)  | 80            |
| H(23A) | 2191(15)  | 4248(7)  | 407(7)   | 80            |
| H(23B) | 1266(15)  | 4785(7)  | 42(7)    | 80            |

**Table 2.7** Continued

|        | x         | y       | z        | $U(\text{eq})$ |
|--------|-----------|---------|----------|----------------|
| H(23C) | 2340(15)  | 4364(7) | -214(7)  | 80             |
| H(24A) | 22(12)    | 2218(8) | -1342(5) | 80             |
| H(24B) | -269(12)  | 1360(8) | -1445(5) | 80             |
| H(24C) | 1129(12)  | 1649(8) | -1381(5) | 80             |
| H(25A) | -1467(13) | 2109(9) | -366(6)  | 80             |
| H(25B) | -1106(13) | 1483(9) | 77(6)    | 80             |
| H(25C) | -1687(13) | 1258(9) | -520(6)  | 80             |
| H(26A) | 1858(14)  | 538(7)  | -487(6)  | 80             |
| H(26B) | 466(14)   | 242(7)  | -598(6)  | 80             |
| H(26C) | 1048(14)  | 467(7)  | -2(6)    | 80             |
| H(27A) | 4239(13)  | 1331(8) | -426(6)  | 80             |
| H(27B) | 4702(13)  | 1683(8) | -950(6)  | 80             |
| H(27C) | 3319(13)  | 1376(8) | -977(6)  | 80             |
| H(28A) | 2722(14)  | 3582(8) | -1083(5) | 80             |
| H(28B) | 2335(14)  | 2836(8) | -1402(5) | 80             |
| H(28C) | 3718(14)  | 3143(8) | -1375(5) | 80             |
| H(29A) | 5059(14)  | 2754(9) | 186(5)   | 80             |
| H(29B) | 4557(14)  | 3532(9) | -53(5)   | 80             |
| H(29C) | 5503(14)  | 3064(9) | -354(5)  | 80             |

$(\text{RCH}_2)_2\text{Ta}(\mu\text{-CR})_2\text{Ta}(\text{CH}_2\text{R})_2$  (**2**),<sup>9</sup>  $\text{Li}(\text{THF})_3\text{SiR}_3$ ,<sup>17</sup>  $\text{Li}(\text{THF})_2\text{SiPh}_2\text{Bu}^t$ ,<sup>18</sup> and  $\text{LiCH}_2\text{R}^{19}$  were prepared by the literature procedures. HCl in  $\text{Et}_2\text{O}$  (1.0 M, Aldrich),  $\text{ClSiPh}_2\text{Bu}^t$  (Aldrich), and Li wire (high Na content, Aldrich) were used as received. The elemental analysis of **4** was performed by E+R Microanalytical Laboratory, Corona, New York.

For the kinetic studies, the rate constants were obtained from at least two separate experiments at a given temperature, and their averages are listed. The *maximum* random uncertainty in the rate constants was combined with the estimated systematic uncertainty, ca. 5%.<sup>10</sup> The total uncertainties in the rate constants were used in the Eyring plot and error propagation calculations. The estimated uncertainty in the temperature measurements for a NMR probe was 1 K. The activation enthalpy ( $\Delta H_1^\ddagger$ ) and entropy ( $\Delta S_1^\ddagger$ ) were calculated from an unweighted nonlinear least-squares procedure contained in the SigmaPlot Scientific Graph System, which is available from Jandel Corporation. The uncertainties in  $\Delta H_1^\ddagger$  and  $\Delta S_1^\ddagger$  were computed from the error propagation formulas derived from the Eyring equation by Girolami and coworkers.<sup>20</sup>

### 2.3.2 Preparation of $(\text{RCH}_2)_3\text{Ta}_2(=\text{CHR})(\equiv\text{CR})(\text{Cl})_2$ (**3**)<sup>1b</sup>

**2** (0.111 g, 0.126 mmol) was weighed into a Schlenk flask and dissolved in  $\text{Et}_2\text{O}$ . HCl (0.252 mL, 1.0 M in  $\text{Et}_2\text{O}$ , 0.252 mmol) was then added to the solution of **2** at  $-50^\circ\text{C}$  with vigorous stirring. The resulting solution of **1** was warmed to  $-28^\circ\text{C}$  and held at this temperature for 1 h. The solvent was then removed, and the thermally unstable solid **3** was dissolved in toluene- $d_8$  and characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR,  $^1\text{H}$ - $^{13}\text{C}$  HETCOR, long-range HETCOR, and nuclear Overhauser enhancement spectroscopy (NOESY).  $^1\text{H}$

NMR (toluene- $d_8$ , -45 °C, 400.1 MHz; See Figure 2.11 for labeling scheme and Results and Discussion for the structure of **3**)  $\delta$  4.68 (s, 1H, H<sub>9</sub>), 1.93 [d, 1H, H<sub>3a</sub>,  $^2J(\text{H}_{3a}\text{-H}_{3b}) = 12.8$  Hz], 1.91 [d, 1H, H<sub>5a</sub>,  $^2J(\text{H}_{5a}\text{-H}_{5b}) = 10.4$  Hz], 1.79 (d, 1H, H<sub>5b</sub>), 1.44 [d, 1H, H<sub>7a</sub>,  $^2J(\text{H}_{7a}\text{-H}_{7b}) = 13.6$  Hz], 1.13 (d, 1H, H<sub>3b</sub>), 1.00 (d, 1H, H<sub>7b</sub>), 0.42 (s, 9H, H<sub>4</sub>), 0.36 (s, 18H, H<sub>2</sub> and H<sub>6</sub>), 0.34 (s, 9H, H<sub>1</sub>), 0.21 (s, 9H, H<sub>8</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (toluene- $d_8$ , -45 °C, 100.6 MHz)  $\delta$  376.39 (C<sub>10</sub>), 237.36 (C<sub>9</sub>,  $^1J_{\text{C-H}} = 104.3$  Hz), 91.51 (C<sub>5</sub>,  $^1J_{\text{C-H}} = 110.8$  Hz), 91.21 (C<sub>3</sub>,  $^1J_{\text{C-H}} = 108.3$  Hz), 78.29 (C<sub>7</sub>,  $^1J_{\text{C-H}} = 110.8$  Hz), 4.33 (C<sub>4</sub>,  $^1J_{\text{C-H}} = 120.4$  Hz), 3.52 (C<sub>1</sub>,  $^1J_{\text{C-H}} = 119.0$  Hz), 2.99 (C<sub>6</sub>,  $^1J_{\text{C-H}} = 118.9$  Hz), 2.11 (C<sub>2</sub> and C<sub>8</sub>,  $^1J_{\text{C-H}} = 119.4$  Hz).

### 2.3.3 Kinetic Study of the Conversion of **1** to **3**

**2** was weighed into a Schlenk flask, and then dissolved in Et<sub>2</sub>O. 2 equiv of HCl was added to the solution of **2** at -50 °C with vigorous stirring to make **1**. After removal of the solvent, **1** was dissolved in pre-cooled toluene- $d_8$ , and the solution was transferred to an NMR tube containing 4,4'-dimethylbiphenyl (0.2 mg) as an internal standard. The initial concentrations of **1** ranged from 0.145 M to 0.254 M, and the concentration of the internal standard was 0.219 M. The NMR spectra were taken at  $244 \pm 1$ ,  $238 \pm 1$ ,  $233 \pm 1$ ,  $227 \pm 1$ ,  $222 \pm 1$ , and  $217 \pm 1$  K, respectively. The concentrations of **1** were calculated from the integrations of its  $^1\text{H}$  NMR peaks with respect to that of the internal standard.

### 2.3.4 Preparation of (RCH<sub>2</sub>)(R<sub>3</sub>Si)Ta( $\mu$ -CR)<sub>2</sub>Ta(CH<sub>2</sub>R)<sub>2</sub> (**4**)

**1** was prepared by adding HCl/Et<sub>2</sub>O solution (1.0 M, 3.46 mL) to a stirred solution of **2** (1.18 g, 1.34 mmol) in Et<sub>2</sub>O at -50 °C. The resulting solution of **1** was

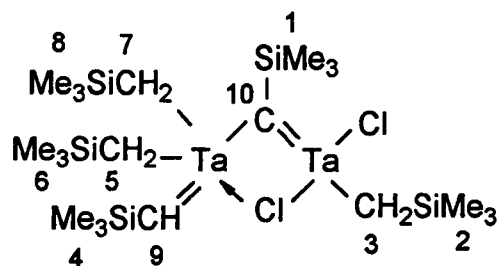


**Figure 2.11** Labeling scheme for 3-C.

warmed to -35 °C, and held at this temperature for 12 h to complete the decomposition of **1** to dark red-brown **3**. The solvent was removed *in vacuo*, and the solid was dissolved in toluene. To this solution at -50 °C was added  $\text{LiSiR}_3(\text{THF})_3$  (1.40 g, 2.97 mmol). The reaction mixture was warmed to room temperature and stirred for 30 min. After filtration, the solution was concentrated and cooled to -30 °C to give 0.59 g (0.566 mmol, 42.3% yield based on **2**) of **4** as maroon crystals.  $^1\text{H}$  NMR (toluene- $d_8$ , 400.1 MHz, 27 °C)  $\delta$  1.53 (s, 2H,  $\text{CH}_2\text{SiMe}_3$ ), 1.00 (s, 2H,  $\text{CH}_2\text{SiMe}_3$ ), 0.59 (s, 9H,  $\text{Me}_3\text{Si}$ ), 0.51 [s, 27H,  $(\text{Me}_3\text{Si})_3\text{Si}$ ], 0.38 (s, 2H,  $\text{CH}_2\text{SiMe}_3$ ), 0.30 (s, 9H,  $\text{Me}_3\text{Si}$ ), 0.26 (s, 9H,  $\text{Me}_3\text{Si}$ ), 0.15 (s, 18H, 2 $\text{Me}_3\text{Si}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (toluene- $d_8$ , 100.6 MHz, 27 °C)  $\delta$  424.07 ( $\equiv\text{CSiMe}_3$ ), 107.40 ( $\text{CH}_2\text{SiMe}_3$ ), 84.08 ( $\text{CH}_2\text{SiMe}_3$ ), 79.04 ( $\text{CH}_2\text{SiMe}_3$ ), 6.06 ( $\text{Me}_3\text{SiC}\equiv$ ), 5.81 [ $(\text{Me}_3\text{Si})_3\text{Si}$ ], 4.38 ( $\text{Me}_3\text{SiCH}_2$ ), 3.86 ( $\text{Me}_3\text{SiCH}_2$ ), 3.64 ( $\text{Me}_3\text{SiCH}_2$ ).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (benzene- $d_6$ , 79.5 MHz, 27 °C)  $\delta$  7.50 ( $\text{CH}_2\text{SiMe}_3$ ), 4.05 ( $\text{CH}_2\text{SiMe}_3$ ), 2.94 ( $\text{CH}_2\text{SiMe}_3$ ), 0.00 [ $\text{Si}(\text{SiMe}_3)_3$ ], -30.29 ( $\equiv\text{CSiMe}_3$ ), -35.85 [ $\text{Si}(\text{SiMe}_3)_3$ ]. Anal. Calcd for  $\text{C}_{29}\text{H}_{78}\text{Si}_9\text{Ta}_2$ : C, 33.44; H, 7.55. Found: C, 33.20; H, 7.53.

### 2.3.5 X-ray Crystal Structure Determination of **4**

The crystal structure of **4** was obtained at -100 °C on a Siemens R3m/V diffractometer fitted with a Nicolet LT-2 low temperature device. A suitable crystal of approximate dimensions 0.40 × 0.20 × 0.20 mm was cut from a larger crystal, coated in Paratone oil (Exxon), and mounted under a stream of nitrogen. The unit cell dimensions were calculated from the angular settings of 48 reflections located from a rotation photograph and an automatic peak search routine. **4** was found to crystallize in the

monoclinic system. 6907 reflections were collected using  $\omega$ -scans, of which 6465 were determined to be unique. Corrections for Lorentz and polarization effects were made during data reduction, and an absorption correction based on  $\psi$ -scans collected on 5 reflections with  $22^\circ < 2\theta < 42^\circ$  was applied to the data set. The  $|E^*E-1|$  statistics, as well as the observed systematic absences in the data, were uniquely consistent with the space group  $P2_1/c$ . The structure was solved by direct methods using the Siemens SHELXTL 93 (version 5.0) proprietary software package, completed by successive Fourier syntheses, and refined to convergence by successive Full-matrix least-squares refinements on  $F^2$ . All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were placed in calculated positions and introduced into the refinement as fixed contributors with isotropic  $U$  values of  $0.08 \text{ \AA}^2$ . Crystal, data collection, and refinement parameters are listed in Table 2.2.

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## **Chapter 3**

### **Chemical Vapor Deposition of Ti-Si-N Thin Films from the Reaction of Tetrakis(dimethylamido)titanium with Silane**

#### **3.1 Introduction**

Over the past decade, shrinking dimensions in microelectronic devices have demanded modification or replacement of existing metallization technologies. With each generation of metallization technology, new interconnect schemes have evolved to meet the rapidly increasing performance demands. Currently, aluminum is the prevalent interconnection metal. However, aluminum is a light metal and is susceptible to electromigration at high current densities.<sup>1,2</sup> In addition to diffusion into Si, aluminum has other undesirable properties. For instance, it has a much higher expansion coefficient when compared to SiO<sub>2</sub>. The combination of these two properties can produce hillocks (aluminum protrusion from the film surface), and result in interlevel short circuits or low voltage breakdown between interconnect levels. As the pitch becomes narrower, the lateral formation of hillocks may also lead to short circuits caused by bridging of adjacent metal lines.<sup>3</sup> Copper is now used as a replacement for aluminum in interconnect schemes because it exhibits better electromigration resistance, a better thermal expansion coefficient, and a lower tendency to form hillocks.<sup>4</sup> The use of copper in integrated circuits provides several challenges for barrier and contact layers. Copper is reactive towards most metals (Al, Au, Pd), metal silicides (CoSi<sub>2</sub>, CrSi<sub>2</sub>, TiSi<sub>2</sub>), and silicon based

oxides.<sup>5</sup> Significant progress has been made in developing diffusion barriers for copper interconnect. One of the most promising barrier materials for copper interconnect is Ti-Si-N, an amorphous ternary alloy first explored by Nicolet and coworkers.<sup>6</sup>

Diffusion barrier layers are often introduced between the metal layer and semiconductor to suppress their interaction.<sup>7</sup> As discussed by Nicolet, some of the characteristics necessary for diffusion barriers are:<sup>8</sup>

1. Good adhesion to adjacent materials.
2. Easily dry etched in combination with metallic conductors.
3. No excessive reaction with metals that would lead to large increases in resistance.
4. Manufacturable deposition process.
5. Low stress.
6. No degradation of electromigration characteristics of interconnects.

Barriers for diffusion in interconnection technology are classified according to the mechanisms by which they suppress the chemical interaction of the separated materials.<sup>9-10</sup> There are four types of barriers (Figure 3.1): sacrificial, stuffed, passive, and amorphous barriers. A sacrificial barrier is prepared through a reaction with either or both of the overlying and underlying materials during thermal processing cycles. The barrier is generally thick enough not to be totally consumed at the end of these thermal cycles, and helps to maintain the separation between the two layers. Sacrificial barriers are commonly yielded from pure metals and alloys and are depicted schematically in Figure 3.1a.<sup>3</sup>

A stuffed diffusion barrier (Figure 3.1b) refers to foreign material-filled or

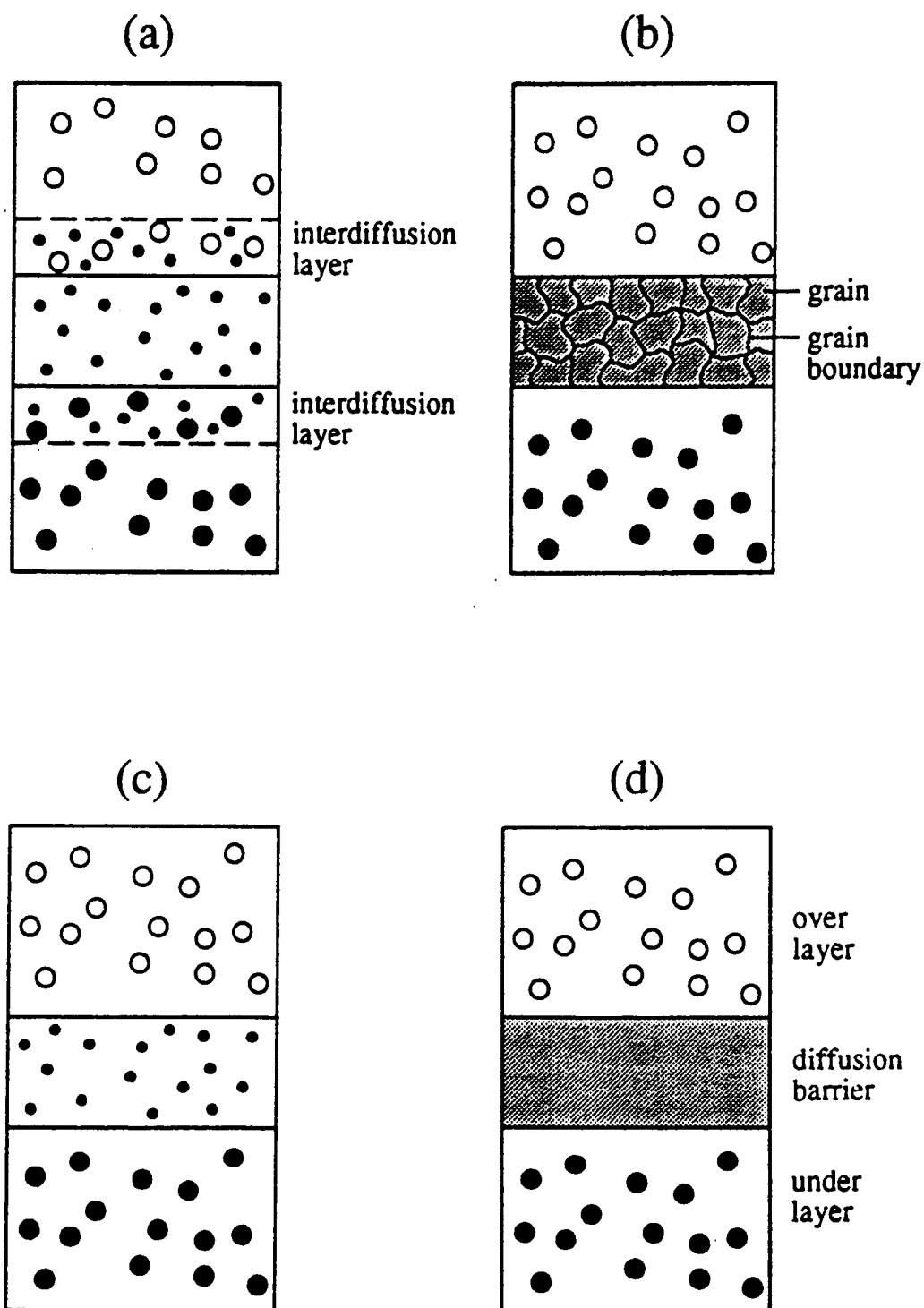


**Figure 3.1** Schematic representations of various diffusion barriers: (a) sacrificial barrier; (b) stuffed barrier; (c) passive barrier; (d) amorphous barrier.<sup>3</sup>

blocked grain boundaries during the deposition process.<sup>3</sup> In a polycrystalline barrier film, the grain boundaries of the film act as diffusion pathways for atoms of the overlying and underlying layers. If the grain boundaries are blocked, diffusion through these boundaries can be reduced. Stuffed diffusion barriers have been formed primarily from N-"stuffed" metals. For instance, nitrogen "stuffed" into the grain boundaries during the sputter deposition process serves to enhance the barrier properties of a Ti-W film.<sup>11</sup>

A passive diffusion barrier (Figure 3.1c) has a large negative free energy of formation and are therefore, chemically inert, strongly bonded compounds. They do not interact with the overlying or underlying materials and generally have a low solid solubility for silicon and metals such as aluminum.<sup>3</sup> These are properties preferred for barrier materials. Passive barriers are usually formed from metal nitrides. Titanium nitride (TiN) is so far the most thoroughly studied and most promising passive barrier, although it is not stable with respect to oxidation or decomposition to the elements at elevated temperatures.

An amorphous diffusion barrier (Figure 3.1d) usually has a very high crystallization temperature. Since diffusion barrier layers generally break down if polycrystalline grain boundaries are present,<sup>7</sup> elimination of the grain boundaries by using single crystal or amorphous materials is a potential solution. Deposition of single crystal films is a difficult process from a manufacturing standpoint, and, as a result, studies in microelectronics have focused on the development of amorphous barriers.

Sputtered titanium nitride (TiN) is an accepted diffusion barrier material for copper-based interconnect. The deposition of TiN into sub-0.5  $\mu\text{m}$  contact holes is

currently achieved by collimated reactive sputter deposition of titanium in a nitrogen ambient. However there is a need for CVD approaches to TiN thin films to improve step coverage. Integration of titanium nitride films through CVD into sub-0.5  $\mu\text{m}$  devices has recently been reported.<sup>12</sup> Film deposition was achieved through the reaction of titanium tetrachloride with ammonia and hydrogen at 700 - 800 °C. Films obtained by this process have excellent quality and are highly conformal in nature. However, the deposition process using this chemical route is generally performed at more than 700 °C and is therefore incompatible with processes used on layers past the first level of metallization.<sup>3</sup> The second CVD process uses metal-organic precursors such as  $\text{Ti}(\text{NMe}_2)_4$  (TDMAT) or  $\text{Ti}(\text{NEt}_2)_4$  (TDEAT) in combination with  $\text{NH}_3$ .<sup>13</sup> It is reportedly difficult, however, to produce TiN films from these metal-organic precursors with low resistivity, good conformality, and low impurity.<sup>14,15</sup> Furthermore, since these TiN films are often polycrystalline with grain-boundary diffusion, the barrier properties of TiN films may be inadequate, particularly at a thickness below 20 nm.

Ternary amorphous metallic alloys such as Ta-Si-P, Ta-Si-N, W-Si-N, and Ti-Si-N are of intense current interest.<sup>3,16-19</sup> These phases have demonstrated superior diffusion barrier properties for copper and silicon at temperatures up to 700 and 900 °C, respectively, and the primary failure mechanism is the premature crystallization of the films at these temperatures. Although most of these amorphous barrier materials currently being evaluated have been deposited using physical vapor deposition (PVD) processes, there is an increased motivation to deposit these amorphous barriers by CVD processes to permit conformal coatings (uniform coating of non-planar surfaces) of

trenches and bias (vertical connections). Several research groups have investigated CVD of Ti-Si-N. Raajimaker first reported the CVD of Ti-Si-N thin films by using  $\text{Ti}(\text{NEt}_2)_4$ ,  $\text{NH}_3$ , and  $\text{SiH}_4$  in 1994.<sup>14</sup> Doan and Sandhu have patented a CVD process to films comprising mixtures of  $\text{TiSi}_n$  and TiN from precursors such as  $\text{Ti}(\text{NMe}_2)_4$  [or  $\text{Ti}(\text{NEt}_2)_4$ ] and silanes.<sup>20</sup> Li and coworkers developed a plasma-enhanced CVD process for the deposition of Ti-Si-N at 560 °C.<sup>21</sup> Smith and Nicolet have studied various CVD processes with  $\text{Ti}(\text{NEt}_2)_4$ ,  $\text{SiH}_4$ , and  $\text{NH}_3$  as precursors to give Ti-Si-N ternary films.<sup>16-17</sup>

We are interested in the CVD process to titanium silicide or Ti-Si-N ternary alloys through the reaction between  $\text{Ti}(\text{NR}_2)_4$  and  $\text{SiH}_4$  and the mechanistic pathways in the reactions between  $\text{M}(\text{NR}_2)_4$  and  $\text{SiH}_4$ . In this chapter, our studies of the CVD process involving  $\text{Ti}(\text{NMe}_2)_4$  and  $\text{SiH}_4$  are reported.

## 3.2 Results and Discussion

The studies of the reaction of  $\text{Ti}(\text{NMe}_2)_4$  and  $\text{SiH}_4$  to give solid materials were conducted both at room temperature in a Schlenk system and at high temperatures ( $\geq 300$  °C) in an ultra-high vacuum CVD reactor. The former gave powders which were used to better understand the reaction, and latter led to the deposition of thin films.

### 3.2.1 Design of a CVD Reactor

Chemical vapor deposition (CVD) reactors are often differentiated by the method employed for heating the wafer and the operating pressures. In a hot-wall reactor, the wafer as well as the reactor walls are externally heated (Figure 3.2). Hot-wall reactors

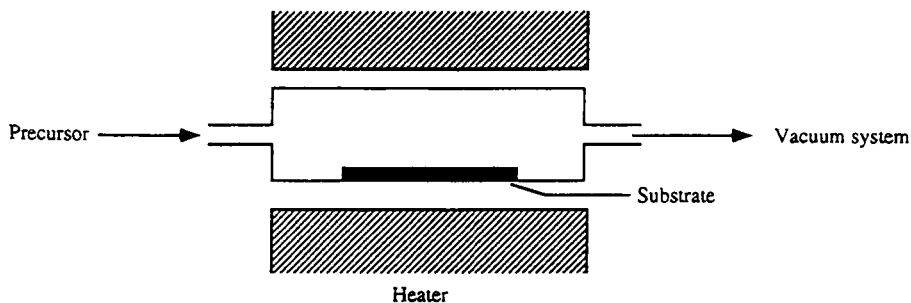


**Figure 3.2** Diagram of a hot-wall CVD reactor.

have been used in both industrial and laboratory CVD studies, although most CVD processes in industry are currently carried out in single-wafer, cold-wall systems. The advantages of hot-wall systems include (1) they are simple to operate; (2) they can accommodate several substrates; (3) they can be operated under a range of pressures and temperatures; and (4) they allow varied orientations of the substrate relative to the gas flow. The major disadvantage of the hot-wall system is that deposition can occur on the substrate as well as on the reactor walls. These deposits may eventually flake off the walls and contaminate the substrate. As a result, a hot-wall reactor is usually maintenance intensive. In addition, the correspondingly large consumption of the precursor can result in feed-rate-limited deposition at relatively low temperatures compared to cold-wall reactors. However, reactions usually occur on the walls and, in most cases, the fraction of the reactor surface covered with deposit can vary and lead to problems when reproducing deposition conditions. In addition, homogeneous gas-phase reactions in the heated gas can occur, which can lead to reduced deposition rates, particle

formation, and loss of selectivity. For these reasons, hot-wall reactors are used primarily at the laboratory scale to study a given precursor for CVD. They are also used to determine reaction-product distributions because the large heated surface area can consume the precursor completely and provide high yields of the reaction products. In a cold-wall reactor (also known as an adiabatic wall reactor), the substrate to be coated is heated directly. As a result, deposition takes place preferentially on the surfaces where the temperature is the highest, in this case the substrate, while the walls of the reactor, which are cooler, remain uncoated (Figure 3.3). Cold-wall reactors are advantageous, as they allow tailoring of the gas-flow directly over the wafer surface as well as suppressing precursor depletion because of the lack of deposition on the reactor walls. However, the throughput of cold-wall reactors is typically lower than for hot-wall reactors.

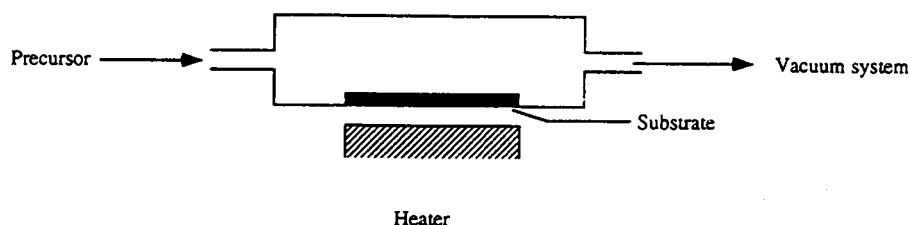


**Figure 3.3** Diagram of a cold-wall CVD reactor.

The CVD system that we built in the current studies is a hot-wall horizontal apparatus (Figure 3.4). The reactor consisted of a three-zone furnace, an introduction system, a glass bubbler, a residual gas analyzer (RGA), two turbo pumps, a mechanic pump, a silane tank containing 2% SiH<sub>4</sub> in Ar, and two mass flow controllers. The latter measured and controlled the gas (mass) flow. The three-zone furnace was adjusted to

## UHV/CVD Reactor

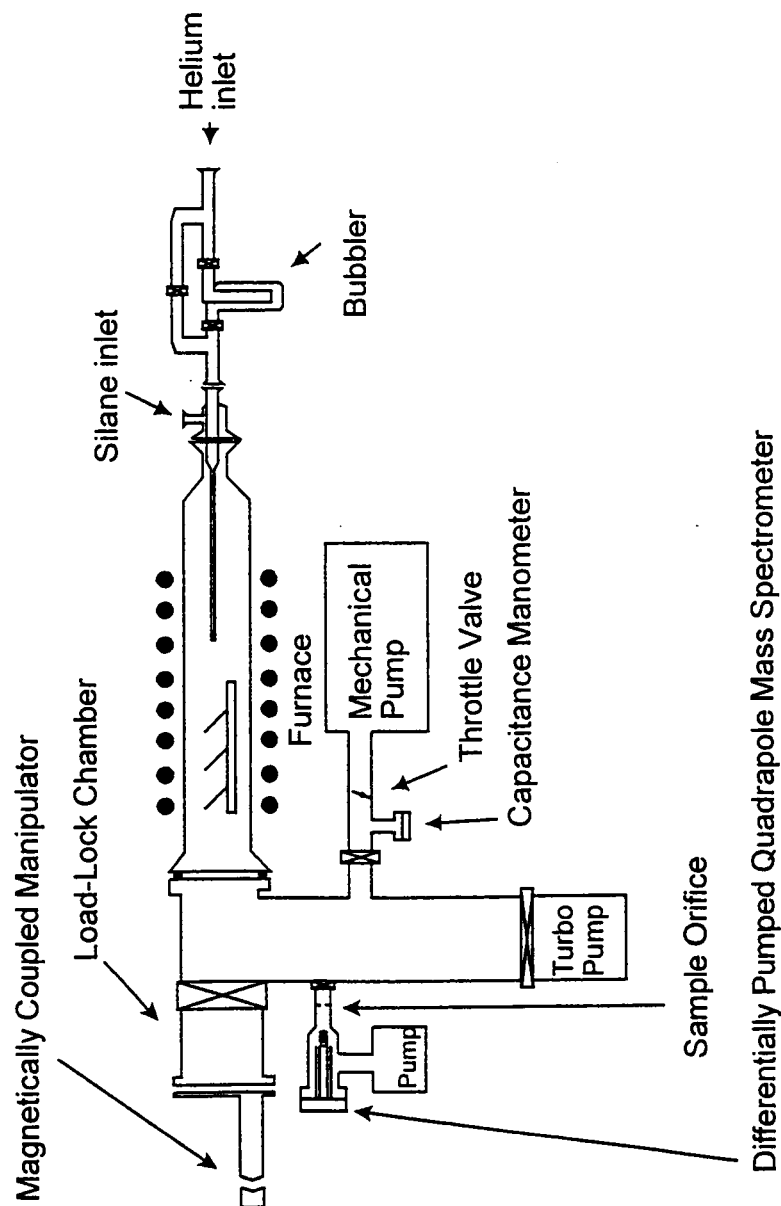


**Figure 3.4** Hot wall horizontal CVD apparatus for deposition of Ti-Si-N thin films.

give a constant temperature center zone of approximately 15 cm in length. The precursor was loaded into a glass bubbler in a drybox, and then connected to the system.

A residual gas analyzer was designed to analyze the rarified atmospheres in high vacuum systems. It consists of a quadrupole mass sensor, which functions only in the high vacuum environment, and electronic circuits which operate the sensor and display its output. The sensor analyzes the residual gases by ionizing some of the gas molecules, separating the resulting ions according to their respective masses, and measuring the quantity of ions at each mass.

### **3.3.2 Formation of Ti-Si-N Ternary Thin Films via Hot-Wall Low Pressure**

#### **Horizontal CVD**

The choice of a precursor is one of the key issues in CVD. A precursor ideally should meet the following criteria:

1. It is stable at room temperature so that it can be easily stored and transferred;
2. It reacts cleanly in the reaction zone;
3. It is sufficiently volatile at low temperatures and thus readily transported to the reaction zone without condensation in the transport zone;
4. It is easily prepared and purified;
5. It readily reacts to give deposition without side or parasitic reactions.

Ti(NMe<sub>2</sub>)<sub>4</sub>, currently commercially available, largely meets the above criteria. It is a volatile liquid at room temperature with a boiling point of 60 °C at 0.1 torr. Our current studies showed the reaction between Ti(NMe<sub>2</sub>)<sub>4</sub> and SiH<sub>4</sub> was rapid even at room

temperature.  $\text{HNMe}_2$  was not observed for this reaction at room temperature. However, it was detected by RGA during the CVD process employing  $\text{Ti}(\text{NMe}_2)_4$  and  $\text{SiH}_4$ . The temperature of the deposition zone (Figure 3.4) was 450 °C, and the observation of  $\text{HNMe}_2$  by RGA indicated the reaction between  $\text{Ti}(\text{NMe}_2)_4$  and  $\text{SiH}_4$  perhaps did not completely remove the amide ligands as amiosilanes.

The deposition conditions of our four experiments are shown in Table 3.1. To avoid premature reaction between the silane and  $\text{Ti}(\text{NMe}_2)_4$ , we designed our system to only allow the two precursors to mix exactly above the substrate in the heating zone. One feature of our process was that the deposition was direction-oriented. When the substrate was placed parallel to the gas flow in Exp. 4, no deposition occurred. We thus placed the substrate with one end slightly tilted in the direction of the gas flow in Exps. 1-3 to give the observed thin film deposition (Table 3.1).

$\text{Ti}(\text{NMe}_2)_4$  was reported to undergo thermal decomposition around 200 °C in a closed system.<sup>22</sup> In our flow system (with short residence time), no decomposition of this precursor was observed on the delivery inlet at 280 °C. At a higher delivery temperature of 350 °C (Exp. 1), the film growth rate was found to be slower than that at a lower delivery temperature of 264 °C. This suggested that the delivery temperature of 350 °C led to premature precursor decomposition in the delivery zone. In the current furnace, the minimum delivery zone temperature was 250 °C if the deposition temperature was set to 450 °C. A delivery temperature of 250 - 264 °C was thus used in the current study. Deposition temperature was also found to be a very important factor. The deposition at 300 °C was found to give a much thinner film (Exp. 2).

**Table 3.1 CVD Conditions**

|                       | Exp. 1             | Exp. 2             | Exp. 3             | Exp. 4                                      |
|-----------------------|--------------------|--------------------|--------------------|---------------------------------------------|
| Substrate             | Si(100) wafer      | Si(100) wafer      | Si(100) wafer      | Si(100) wafer                               |
| Delivery temperature  | 350 °C             | 250 °C             | 264 °C             | 251 °C                                      |
| Substrate temperature | 450 °C             | 300 °C             | 448 °C             | 447 °C                                      |
| Bubbler temperature   | 30 °C              | 30 °C              | 30 - 50 °C         | 40 - 50 °C                                  |
| Deposition pressure   | 2.0 torr           | 5.0 torr           | 5.0 torr           | 5.0 torr                                    |
| Carrier gas flow rate | Ar/400 sccm        | Ar/400 sccm        | Ar/450 sccm        | Ar/380 sccm                                 |
| Silane flow rate      | 145 sccm           | 150 sccm           | 140 sccm           | 130 sccm                                    |
| Resulting film        | thin film (film 1) | thin film (film 2) | thin film (film 3) | The deposition was too small to be detected |

Film 3 (0.2  $\mu\text{m}$  in thickness), deposited at above 450  $^{\circ}\text{C}$ , had a gold color and a dark blue black zone, reflecting some bluish gray light. Film 2, deposited at 300  $^{\circ}\text{C}$ , showed similar bluish black tint. Under the same conditions, films deposited on quartz substrates below 450  $^{\circ}\text{C}$  had very different appearances compared to those grown on a Si(100) wafer. They were very thin, transparent and quite yellow.

### **3.2.3 Preparation of Powders from the Reactions of $\text{M}(\text{NMe}_2)_4$ ( $\text{M} = \text{Ti, Zr}$ ) with $\text{SiH}_4$**

Liquid  $\text{Ti}(\text{NMe}_2)_4$  or solid  $\text{Zr}(\text{NMe}_2)_4$  at room temperature was exposed to  $\text{SiH}_4$  to give an immediate reaction with gas evolution. The gas was found to be  $\text{H}_2$  (Chapter 4). The reaction mixture involving  $\text{Ti}(\text{NMe}_2)_4$  turned darker with the formation of a black solid and  $\text{HSi}(\text{NMe}_2)_3$ . The black solid after heating gave amorphous powders with a metallic appearance under a microscope.

### **3.2.4 Characterization of the Thin Films and Powders by XPS, RBS, Powder X-ray Diffraction (XRD) and SEM**

Several techniques including X-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectrometry (RBS), and energy dispersive spectroscopy (EDS) were used to analyze the films and powders in the current studies.<sup>23-24</sup> In XPS,<sup>24</sup> the absorption of X-ray photons by the atoms in the target leads to the ejection of inner shell electrons, the photoelectrons, of these atoms in the target. The kinetic energies of the photoelectrons are measured to give the binding energies of the electrons in the atoms. The information

about bonding in, e.g., our thin films is obtained from chemical shifts of Ti 2p<sub>3/2</sub>, Si 2p, and N 1s peaks in XPS, in comparison to standards. In RBS,<sup>24-25</sup> light ions such as H<sup>+</sup> or He<sup>+</sup> at a high energy collide with the heavy atoms in the target surface and are scattered in a backward direction. The energies of the scattered ions are measured to give qualitative and quantitative analyses of the heavy atoms in the target. Since the collision and scattering are independent of chemical bonding, RBS is insensitive to chemical bonding within the target. For light elements such as H and D in the sample, the incident ions (e.g., He<sup>+</sup>) have a recoil collision with the atoms of these light elements. The energies of the recoiled H and D nuclei in the forward direction are measured by forward recoil spectrometry [also called forward recoil elastic spectrometry (FRES)] to determine H and D in the sample.<sup>24a</sup> EDS is one of the most common analytical attachments to SEM (scanning electron microscopy).<sup>24</sup> A high energy electron beam causes emission of a core electron in the target atom. An outer shell electron in the atom can fill the vacancy with emission of an X-ray photon which is characteristic of the element. The emitted X-ray can be detected in either the energy dispersive (EDS) or wavelength dispersive (WDS) mode to give an elemental analysis of the target. In conventional EDS, elements from sodium onwards can be analyzed accurately. The recent advent of windowless EDS (WEDS) extended the range to much lighter elements.<sup>24c</sup> A comparison of several surface analysis methods discussed in this thesis is given in Table 3.2.

The XPS chemical shifts of Ti 2p<sub>3/2</sub>, Si 2p, N 1s, and O 1s in the films 1 – 3, powder 8, and other known compounds related to Ti-Si-N ternary alloys are given in Table 3.3. Quantitative analyses of our samples by XPS were limited by several factors

**Table 3.2 Features of Several Analytical Methods Discussed in This Thesis<sup>a</sup>**

|      | Incident radiation | Emitted radiation | Elements detectable | Information level             | Quantification | Applicability to inorganics |
|------|--------------------|-------------------|---------------------|-------------------------------|----------------|-----------------------------|
|      |                    |                   |                     | E = elemental<br>C = Chemical |                |                             |
| AES  | $e^-$              | $e^-$             | Li onward           | E, C                          | good           | reasonable                  |
| XPS  | X-ray              | $e^-$             | He onward           | E, C                          | good           | good                        |
| EDS  | $e^-$              | X-ray             | Na onward           | E                             | good           | reasonable <sup>b</sup>     |
| WEDS | $e^-$              | X-ray             | B onward            | E                             | good           | reasonable <sup>b</sup>     |
| RBS  | ions               | ions              | Li onward           | E                             | poor           | good                        |
| FRES | ions               | ions              | mostly H and D      | E (isotopic)                  | good           |                             |

<sup>a</sup> adapted from references 24c (AES, XPS, EDS, WEDS, and RBS) and 24a-b (FRES).

<sup>b</sup> without conductive coating.

**Table 3.3** XPS Chemical Shifts of Compounds Related to Ti-Si-N Ternary Alloys and the Samples in This Study

| Compounds                                                                                                                | Binding energies (eV) |        |        |        |
|--------------------------------------------------------------------------------------------------------------------------|-----------------------|--------|--------|--------|
|                                                                                                                          | Ti 2p <sub>3/2</sub>  | Si 2p  | N 1s   | O 1s   |
| Ti <sub>0.49</sub> Si <sub>0.29</sub> (O, N) <sub>0.22 amorp</sub> + Ti <sub>5</sub> Si <sub>3</sub> (O,N) <sup>26</sup> | 454.4                 | 99.0   | 397.2  | 531.0  |
| Ti <sup>26</sup>                                                                                                         | 454.1                 |        |        |        |
| Ti <sub>5</sub> Si <sub>3</sub> (O) <sup>26</sup>                                                                        | 454.1                 | 98.8   |        | 530.9  |
| TiN(O) <sup>26</sup>                                                                                                     | 455.1                 |        | 397.3  | 531.5  |
| TiN <sub>0.75</sub> (O) <sup>26</sup>                                                                                    | 454.8                 |        | 397.3  | 531.5  |
| TiN <sup>13</sup>                                                                                                        | 454.8                 |        | 396.9  |        |
| TiSi <sup>28</sup>                                                                                                       | 453.3                 | 98.5   |        |        |
| TiO <sub>2</sub> <sup>28</sup>                                                                                           | 458.7                 |        |        |        |
| TiSi <sub>2</sub> <sup>28</sup>                                                                                          | 453.6                 | 99.0   |        |        |
| Si <sup>26</sup>                                                                                                         |                       | 99.5   |        |        |
| Si <sub>3</sub> N <sub>4</sub> (O) <sup>26</sup>                                                                         |                       | 101.7  | 397.5  | 531.3  |
| α-SiN <sub>x</sub> <sup>26</sup>                                                                                         |                       | 100.5  |        |        |
| Si <sub>3</sub> N <sub>4</sub> <sup>26</sup>                                                                             |                       | 104.5  | 400.50 |        |
| SiO <sub>2</sub> <sup>26</sup>                                                                                           |                       | 103.1  |        | 532.4  |
| TiC <sup>a</sup>                                                                                                         | 454.6                 |        |        |        |
| TiSi <sub>1.4</sub> N <sup>29</sup>                                                                                      | 455.5                 | 102.5  | 397.8  |        |
| Film 1 (after sputtering)                                                                                                | 457.90                | 102.60 | 398.10 | 532.50 |
| Film 3 (before sputtering)                                                                                               | 458.90                | 102.20 | 396.50 | 532.00 |

**Table 3.3** Continued

| Compounds                          | Binding energies (eV) |        |        |        |
|------------------------------------|-----------------------|--------|--------|--------|
|                                    | Ti 2p <sub>3/2</sub>  | Si 2p  | N 1s   | O 1s   |
| Film <b>3</b> (after sputtering)   | 455.50                | 102.00 | 397.00 | 531.00 |
| Powder <b>8</b> (after sputtering) | 454.90                | 101.20 | 396.60 | 531.40 |

<sup>a</sup> The binding energy of C in TiC is 281.4 eV.<sup>28</sup>

such as background signals, a complex intrinsic satellite structure in the Ti 2p<sub>3/2</sub> and 2p<sub>5/2</sub> spectral region, which depended on the sample composition, and severe peak overlapping in the XPS spectra. The Ti:Si:N ratios in the films were thus obtained from RBS.

The analyses of the powders were mainly achieved by EDS and windowless EDS (WEDS). In the current studies, only powder 1 was analyzed by conventional EDS. The errors in C, N, and O analysis by WEDS are in general higher than those in heavy element analysis. Other powders were analyzed by WEDS.

**Powder Analyses by XPS, EDS and XRD.** The powders from the reactions of Ti(NMe<sub>2</sub>)<sub>4</sub> were the focus of analyses. The XPS of powder 8 (Table 3.3) clearly revealed that it contained Ti, N, Si, O, and C. The binding energy of the Ti 2p<sub>3/2</sub> peak (454.90 eV) in powder 8 was nearly the same as that in TiN (454.8 eV).<sup>26</sup> In comparison, the binding energies of Ti 2p<sub>3/2</sub> peak in TiO<sub>2</sub> and TiSi<sub>2</sub> are 458.7 eV and 453.6 eV, respectively. The N 1s peak (396.60 eV) in powder 8 is close to that observed for TiN (396.9 eV) as well.<sup>13</sup> These results indicated that powder 8 contained TiN. The Si 2p peak (101.20 eV) in powder 8 is close to that in Si<sub>3</sub>N<sub>4</sub>(O) (101.7 eV), but significantly shifted from those of TiSi<sub>n</sub> and SiO<sub>2</sub> (Table 3.3).<sup>26</sup> In addition, the binding energies of Ti 2p<sub>3/2</sub>, N 1s, and Si 2p in powder 8 were close to those in the reported TiSi<sub>1.4</sub>N ternary alloy.<sup>29</sup> These XPS analyses indicated that TiN and Si<sub>3</sub>N<sub>4</sub>(O) were likely present in powder 8. The carbon binding energies in XPS showed the carbon in powder 8 was mainly hydrocarbons with some TiC. The oxygen peak on the powder surface was mainly from TiO<sub>2</sub>, signaling the oxidation of the sample in air.

A quantitative XPS analysis gave a Ti : Si : N ratio of 2.2 : 1 : 1 in powder 8. EDS analyses gave Ti : Si ratios between 1 : 1.5 in powder 1 to 1.5 : 1 in powder 8. These results showed that there was a large range of the Ti : Si ratios in these powders. Powder 6 after annealing at 1000 °C under vacuum, showed no powder XRD, indicating that the powder was amorphous. After powder 6 was heated at 1090 °C, XRD of TiN appeared. This appearance of TiN in the XRD of powder 6 was consistent with the observations of TiN binding energies in the XPS of powder 8.

**Film Analyses by RBS, XPS, XRD, SEM and Ellipsometry.** The Rutherford backscattering spectra (RBS) of films 1 and 3 are shown in Figure 3.5. Both films were not oriented since the random and aligned spectra for Ti, Si (in film), O, and N were identical. The Ti : Si : N ratios in films 1 and 3 by RBS (Table 3.4) were 16 : 17 : 19 and 16 : 13 : 30, respectively.

The XPS binding energies of films 1 and 3 are listed in Table 3.3 along with data reported in the literature. The binding energies of Ti 2p<sub>3/2</sub>, Si 2p, and N 1s peaks in film 3 after sputtering are close to those in the reported TiSi<sub>1.4</sub>N ternary alloy and in powder 8.<sup>26</sup> Another Si 2p peak was observed at 98.5 eV in film 3, which corresponded to Si wafer substrate. No Ti 2p<sub>3/2</sub> peak near that of TiO at 458.7 eV was observed. The Ti 2p<sub>3/2</sub>, Si 2p, and N 1s peaks in film 1, however, were shifted from those of TiSi<sub>1.4</sub>N and film 3.

The XPS analysis showed a large oxygen content in the films. The oxygen concentration varied from 20 to 35%. Since the precursors Ti(NMe<sub>2</sub>)<sub>4</sub> and SiH<sub>4</sub> contain

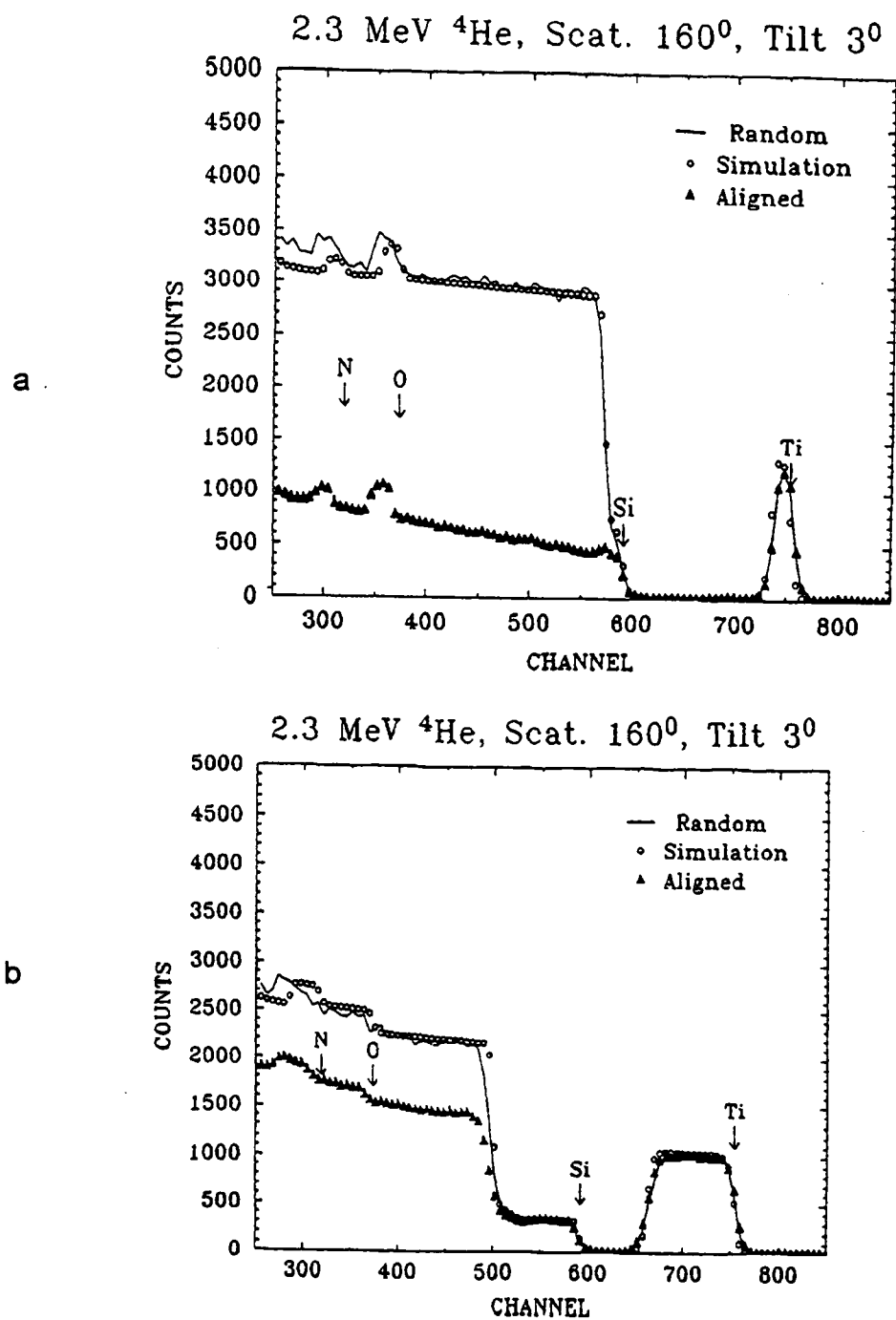


**Figure 3.5** Rutherford backscattering spectra (RBS) of films deposited on Si wafers: (a) film 1 - precursor delivered at  $350^\circ\text{C}$ ; (b) film 3 - precursor delivered at  $280^\circ\text{C}$ .

**Table 3.4** Composition by RBS of Films Prepared at Different Delivery Temperatures

| Film | Ratio of Ti : Si : N | Delivery temperature (°C) |
|------|----------------------|---------------------------|
| 1    | 16 : 17 : 19         | 350                       |
| 3    | 16 : 13 : 30         | 251                       |

no oxygen, it perhaps was incorporated during the deposition process. Similar oxygen incorporation has been reported in the deposition of TiN films from  $\text{Ti}(\text{NMe}_2)_4$  and  $\text{SiH}_4$ , especially when not enough  $\text{NH}_3$  was supplied.<sup>17,27</sup> Since both Ti(IV) and Si(IV) are oxophilic, this is perhaps not surprising. The oxygen contamination may come from: (1) the oxidized layer of the silicon wafer; (2) surface oxidization of the film; or (3) the reaction of with residual  $\text{O}_2$  in the XPS chamber during data collection. On the film surface, Ti was mainly bonded to oxygen, and the Ti  $2p_{3/2}$  binding energy was 458.9 eV, which matched 458.7 eV in  $\text{TiO}_2$ . However, after sputtering of the film surface, the binding energy of Ti  $2p_{3/2}$  peak shifted by  $-3.4$  eV to 455.5 eV, which matched 455.1 eV in  $\text{TiN}(\text{O})$ . This observation indicated that Ti in the bulk of the film did not bind to oxygen. In addition, the XPS depth profile showed the films had relatively constant composition. Two different types of carbon signals were present in the XPS of our films. One was at 282.0 eV, and the other was at 284.5 eV. The first was perhaps that of TiC, and the second was usually associated with hydrocarbons. In most of our film analyses, only the hydrocarbon peak was observed. Even when TiC was observed, hydrocarbon was the dominant peak in the C 1s region. Delivery temperature also could have played a

role in contributing to the carbon impurity. Film 3 had less TiC impurity than film 1. In other words, lowering delivery temperature helped reduce TiC impurity. XPS of Ti 2p<sub>3/2</sub>, N 1s, and Si 2p of film 3 after sputtering are shown in Figure 3.6.

Ellipsometry has found increasing use in monitoring the thickness and optical properties of thin films.<sup>30</sup> Two major attractions of ellipsometry are that it is nonperturbing and very sensitive to minute interfacial effects. The ellipsometry indicated that the thickness of film 3 was fairly uniform, giving an average of 2168.4 Å. The thickness obtained by ellipsometry was consistent with RBS measurement. Scanning electron microscopy (SEM, Figure 3.7) showed that film 3 was smooth. No pattern was observed in powder X-ray diffraction of film 3, indicating that the film was amorphous. Films 1 and 3 also passed the "Scotch tape test", showing good adhesion of the films to the Si substrate. A conductivity test indicated that film 3 was conductive.

The results in the current studies showed that the reaction between Ti(NMe<sub>2</sub>)<sub>4</sub> and SiH<sub>4</sub> likely gave Ti-Si-N ternary powders or films of similar compositions (mixtures of TiN-Si<sub>3</sub>N<sub>4</sub>) both at 23 °C (followed by heating) and at a high temperature in a CVD reactor. In other words, the compositions of the powders and films prepared at room and high temperatures suggested that similar chemistry and mechanistic pathways took place in a large temperature range. The ternary materials are likely TiN-Si<sub>3</sub>N<sub>4</sub>; i.e., they are neither one phase containing Ti, Si and N nor mixtures of TiSi<sub>n</sub>-Si<sub>3</sub>N<sub>4</sub> or TiSi<sub>n</sub>-TiN. The latter are two other possible combinations of binary phases in the Ti-Si-N ternary system.

The formation of these solid compounds in the current studies perhaps could be understood by an analysis of the Ti-Si-N phase diagram (Figure 3.8). The phase diagram

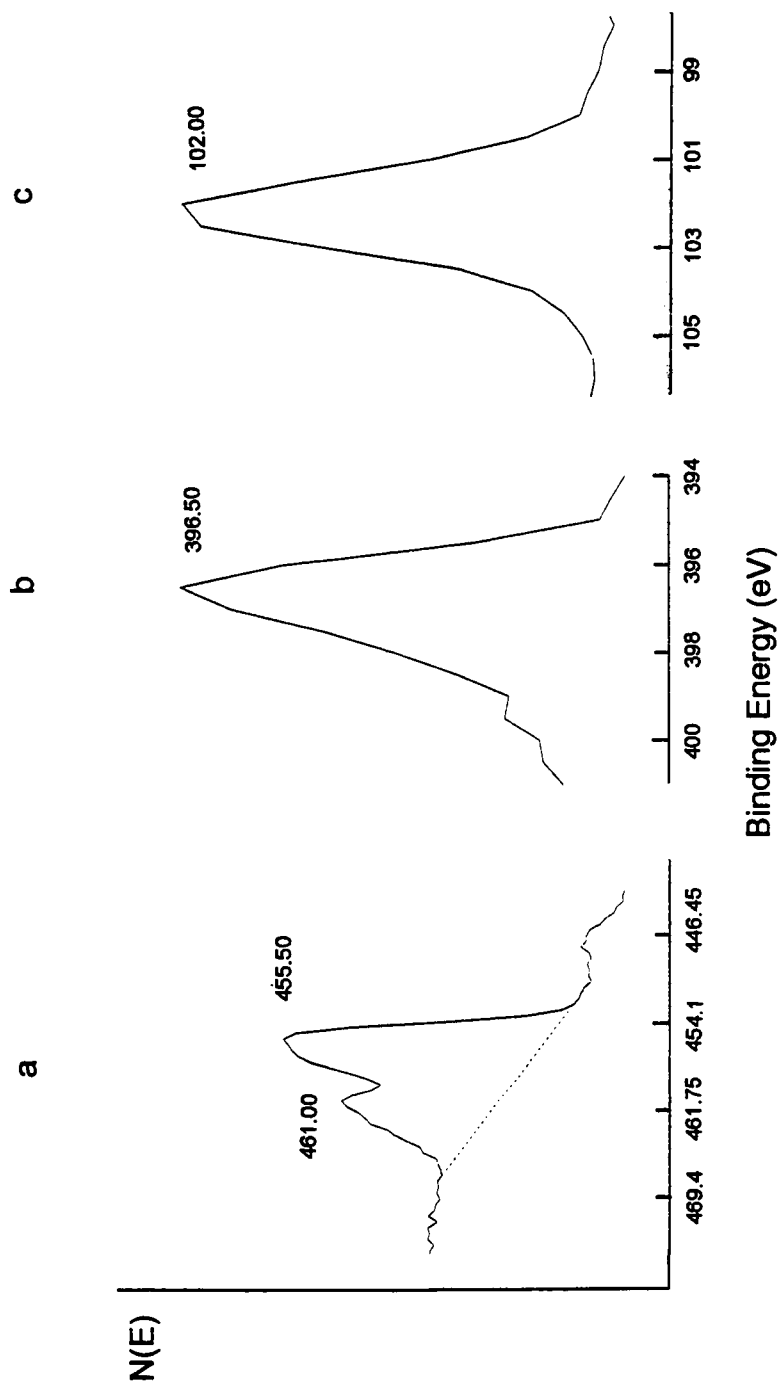


**Figure 3.6** XPS of film 3 after sputtering: (a) Ti 2p<sub>3/2</sub>; (b) N 1s; (c) Si 2p.

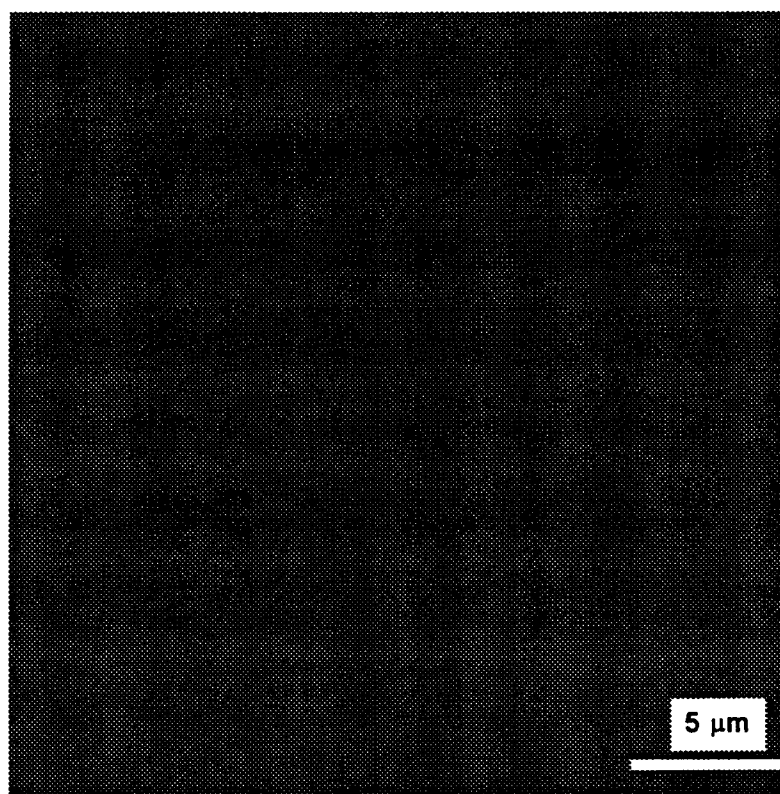


**Figure 3.7** SEM of Ti-Si-N film 3 (thickness = 2169.9 Å).

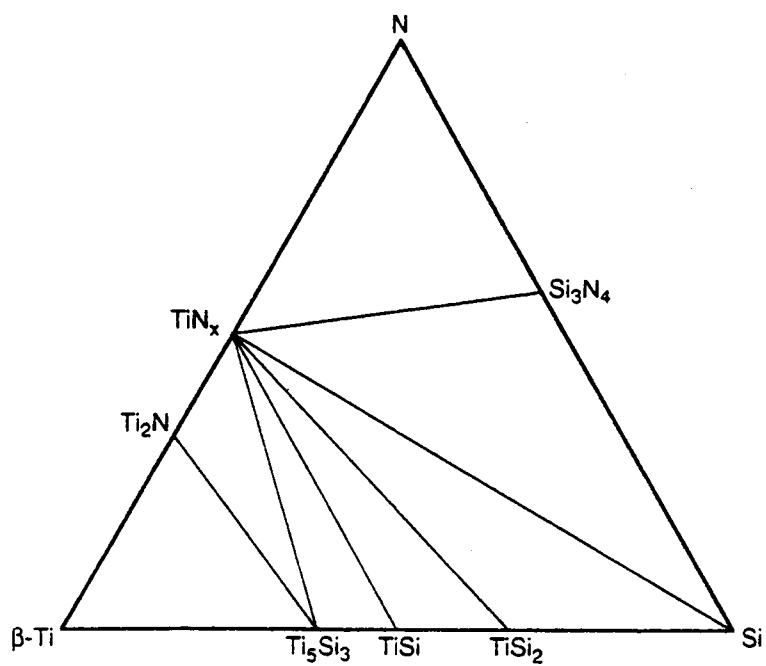


**Figure 3.8** Schematic representation of phase equilibria in the Ti-Si-N system at 1000 °C.<sup>31</sup>

indicates that these three elements do not form one phase. The formation of  $\text{TiSi}_n$  and  $\text{Si}_3\text{N}_4$  binary phases are thermodynamically forbidden, as there is no tie line between them in the phase diagram. The Ti, Si, and N composition in our films and powders place these solids near the  $\text{TiN-Si}_3\text{N}_4$  tie line. The use of this phase diagram is, however, tentative, as it was obtained at 1000 °C. It is, to our knowledge, the best simplified Ti-Si-N phase diagram in the literature.<sup>31</sup>

Similar ternary films ( $\text{TiN-Si}_3\text{N}_4$ ) have been reported by Smith and coworkers in the CVD from the reaction of  $\text{Ti}(\text{NET}_2)_4$  with  $\text{SiH}_4$  and  $\text{NH}_3$ , where  $\text{NH}_3$  was found necessary to give the desired materials.<sup>17</sup> The compositions of Ti, N, and Si in these films placed them near or above the  $\text{TiN}$  and  $\text{Si}_3\text{N}_4$  tie line as well in the Ti-Si-N phase diagram (Figure 3.8), even though these films were somewhat more N-rich. As the authors indicated that it was not clear what the reaction pathways were in these depositions, and how Si was incorporated into the films.

Our studies to explain why the reaction between  $\text{Ti}(\text{NMe}_2)_4$  and  $\text{SiH}_4$  yielded  $\text{TiN-Si}_3\text{N}_4$  binary phases (near their tie line in the phase diagram), but not other phases, are to be presented in Chapter 4.

### **3.3 Experimental Section**

#### **3.3.1 General Procedure**

All manipulations of precursors, unless noted, were performed under a dry nitrogen atmosphere with the use of either a drybox or standard Schlenk techniques. All solvents were purified by distillation from potassium/benzophenone ketyl.  $\text{SiH}_4$  [2% in

Ar (Air Products) and 5% in Ar (Air Products)] was used as received.  $\text{TiCl}_4$  (Aldrich) was used as purchased.  $\text{Ti}(\text{NMe}_2)_4$  was prepared by the literature procedures.<sup>32</sup>

EDS analyses were performed by Professor David C. Joy of the University of Tennessee. XRD spectra were obtained on a Phillips X-ray diffractometer. RBS analyses were performed by Drs. Catherine E. Vallet and Ray A. Zuhr using 2.3 MeV  $^4\text{He}^+$  with a standard silicon surface barrier detector placed at  $\sim 160^\circ$  scattering angle at Surface Modification and Characterization (SMAC) research center at Oak Ridge National Laboratory. XPS analyses of powder **8** were performed by Professor Zheng Xu of Nanjing University on a V. G. Scientific 5000 system. The pass energy was set to 100 eV with step sized set to 0.5 eV. The film thickness was measured with a Gartner ellipsometer.

XPS analyses of films **1** and **3** were carried out on a Perkin-Elmer ESCA/SAM system with a PE  $\Phi$  32-095 model X-ray source at 20 mA and 15 kV. The electron-energy analyzer was calibrated to the Au  $4f_{7/2}$  line at 84 eV. The Mg  $K_\alpha$  excitation (1253.6 eV) from an Al/Mg dual anode (PE  $\Phi$  04-500 model) was used to excite photoemission, and photoelectrons were detected at an angle of  $40^\circ$  with respect to the plane of the surface. Sputtering was done with a differentially pumped ion gun (PE  $\Phi$  04-300 model) providing an  $\text{Ar}^+$  current of 1  $\mu\text{A}$  at 3 keV, rastered over an area of  $3 \times 3 \text{ mm}^2$  with sputter rate of 30  $\text{\AA}/\text{min}$ . Base pressure in the XPS chamber was  $10^{-9}$  torr while the maximum pressure in chamber during sputtering was  $4.0 \times 10^{-7}$  torr. The electron-energy analyzer was set for a pass energy of 178 eV for general survey mode. The composition was determined according to the XPS multiplex spectrum. The pass

energy was set for 25 eV or lower. The multiplex data were collected for 10 cycles with 10 sweeps for each cycle. The depth profile of film 3 was obtained while the base pressure was  $10^{-7}$  torr with the  $\text{Ar}^+$  gun on. The pass energy was set at 17.90 eV.

### **3.3.2 Reactions of $\text{M}(\text{NMe}_2)_4$ with $\text{SiH}_4$ Conducted in a Static Reaction Tube**

The system to conduct these reactions consists of an oil diffusion pump, a Schlenk-type static reaction tube fitted into a tube furnace, and a 5% silane/Ar tank (Figure 3.9). The baseline pressure was  $10^{-5}$  torr. A silane (5%  $\text{SiH}_4$  in Ar) tank was connected to a static reaction flask through a stainless-steel tubing and a stainless-steel Cajon O-ring-type fitting.  $\text{SiH}_4$  was introduced as a flowing gas. Excess  $\text{SiH}_4$  was exhausted into a fume hood after passing through an aqueous KOH solution.

Detailed procedures for the reactions between  $\text{M}(\text{NMe}_2)_4$  and  $\text{SiH}_4$  to yield powders 1, 2 and 5 are given below. A summary of procedures to give these and other powders is given in Table 3.5.

**Preparation of Powder 1 [from the Reaction of  $\text{Ti}(\text{NMe}_2)_4$  and  $\text{SiH}_4$ ; Solid Handled in a Drybox].** A yellow liquid sample of  $\text{Ti}(\text{NMe}_2)_4$  (0.067 g, 0.30 mmol) was placed in a 125-mL Schlenk flask connected to a silane inlet. The flask was evacuated at  $-196^\circ\text{C}$ .  $\text{SiH}_4$  (5% in Ar) was then introduced. The color of the liquid changed instantaneously from yellow to orange, brown, and then black with gas evolution. A black solid precipitated from the dark liquid. When gas evolution had ceased, the system was cooled to  $-77^\circ\text{C}$ , and evacuated. The volatile products were collected in a liquid nitrogen trap.

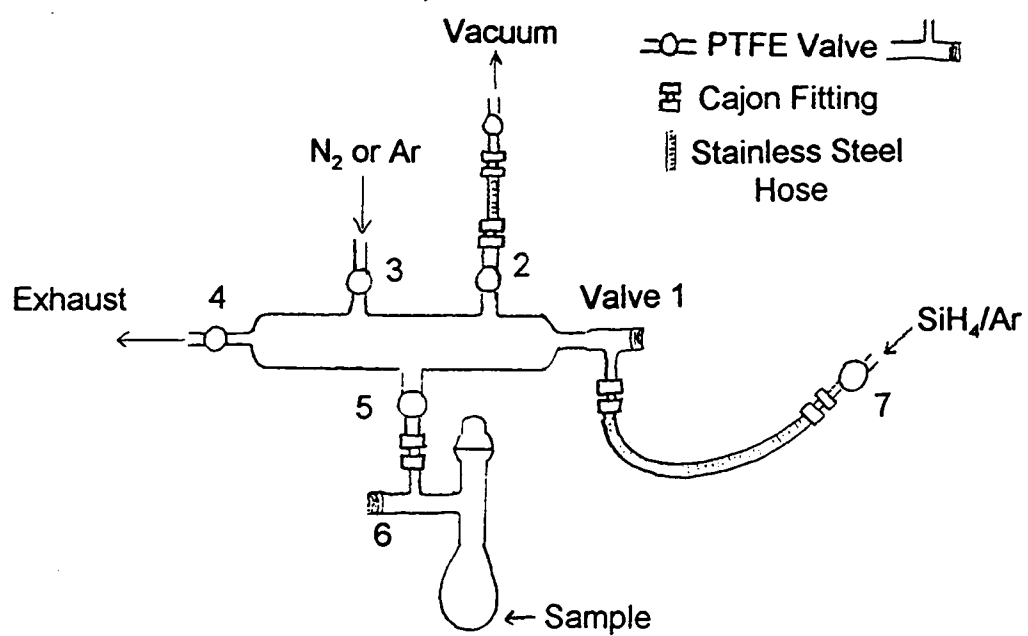


**Figure 3.9** Schematic diagram of a static reaction tube for the reactions of  $\text{M}(\text{NMe}_2)_4$  with  $\text{SiH}_4$ .

**Table 3.5** Summary of Experimental Procedures and Analysis Methods

| Powder No. | Starting Materials                 | Summary of Procedures                                                                                                                                                                                                                                                                                                        | Analysis Methods |
|------------|------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------|
| 1          | Ti(NMe <sub>2</sub> ) <sub>4</sub> | Reaction was first conducted at 23 °C for a day with four refills of SiH <sub>4</sub> , and then at 40 °C for 78 h with two refills of SiH <sub>4</sub> .<br><br>A portion of the powder was heated at 800 °C for 4 days, cooled down to 23 °C, heated again at 1300 °C for 2 days, and finally slowly cooled down to 23 °C. | XRD, EDS         |
| 2          | Ti(NMe <sub>2</sub> ) <sub>4</sub> | Reaction was conducted at 23 °C for 7 days with five refills of SiH <sub>4</sub> .                                                                                                                                                                                                                                           | IR               |
| 3          | Ti(NMe <sub>2</sub> ) <sub>4</sub> | Reaction was conducted at 23 °C for 7 days with seven refills of SiH <sub>4</sub> . The product powder was heated under vacuum at 500 °C for 2 days, and then heated at 1000 °C for 2 days.                                                                                                                                  | XRD, IR          |
| 4          | Ti(NMe <sub>2</sub> ) <sub>4</sub> | Reaction was conducted at 23 °C for 24 h with four refills of SiH <sub>4</sub> . The powder was then transferred and stored in a drybox.                                                                                                                                                                                     | IR               |

**Table 3.5 Continued**

| Powder No. | Starting Materials                     | Summary of Procedures                                                                                                                                                                                                                       | Analysis Methods |
|------------|----------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------|
| 5          | Zr(NMe <sub>2</sub> ) <sub>4</sub>     | Reaction was conducted at 23 °C for 2 days with five refills of SiH <sub>4</sub> . A portion of the product powder was flame dried, and then heated at 1100 °C for 57 h 40 min. The powder was gradually cooled down to 23 °C at 0.5 °C/min | WEDS, XRD        |
| 6          | Ti(NMe <sub>2</sub> ) <sub>4</sub>     | Reaction was conducted at 23 °C for 2 days with 5 refills of SiH <sub>4</sub> . Product powder was heated to 1090 °C for 60 h 48 min, then gradually cooled down at 0.05 °C/min to 350 °C.                                                  | XRD              |
| 7          | Ti(NMe <sub>2</sub> )<br>(Two samples) | Reaction was conducted at 23 °C for 2 days with 5 refills of SiH <sub>4</sub> . One sample was heated at 81 °C overnight. Another sample was heated at 297 °C for 48 h for Auger sample analysis.                                           | WEDS             |
| 8          | Ti(NMe <sub>2</sub> ) <sub>4</sub>     | Reaction was conducted at 23 °C for 2 days with 5 SiH <sub>4</sub> refills. The product powder was annealed at 700 °C right after its formation.                                                                                            | XPS, WEDS        |

SiH<sub>4</sub> (5% in Ar) was reintroduced. The procedure was repeated three times. At this point, no gas evolved when new SiH<sub>4</sub>/Ar gas was introduced into the system. The volatile products were found to contain HSi(NMe<sub>2</sub>)<sub>3</sub>. The black solid was washed with hexanes six times and dried under vacuum overnight before its IR and Raman spectra were obtained. The black solid (powder 1) was handled in a drybox.

A portion of the sample was transferred to a quartz tube, and the tube was flame-sealed under a mechanic-pump vacuum. The tube was heated to 500 °C in a furnace (Lindberg model 55035) for 2 days, and then cooled down gradually to room temperature. The powder was ground into fine powders in a marble mortar and analyzed by EDS and XRD.

**Preparation of Powder 2 [from the Reaction of Ti(NMe<sub>2</sub>)<sub>4</sub> and SiH<sub>4</sub>; Solid Directly Sealed under Vacuum].** Ti(NMe<sub>2</sub>)<sub>4</sub> was placed in a Schlenk-type quartz tube with a graded seal to a 9 mm Pyrex inlet. This inlet was connected to a 3/8 inch Cajon stainless-steel O-ring-fitting. The tube was evacuated at -196 °C, and SiH<sub>4</sub> (5% in Ar) was introduced into the tube. The reaction was conducted over a period of 7 days with a total of five refills of SiH<sub>4</sub>. The tube was then first heated under vacuum at 500 °C for 2 days, and then heated at 1000 °C for 2 more days. The resulting solid (powder 2) was analyzed by IR, Raman, and XRD.

**Powder 5 [from the Reaction of Zr(NMe<sub>2</sub>)<sub>4</sub> + SiH<sub>4</sub>; Solid Directly Sealed under Vacuum].** Zr(NMe<sub>2</sub>)<sub>4</sub> (0.0304 g) was placed in a quartz tube described in the preparation of powder 2. SiH<sub>4</sub> (5% in Ar) was then introduced to the tube. The reaction was conducted over a period of 2 days with a total of five refills of SiH<sub>4</sub>. The black solid

was flame-dried before being transferred to a quartz tube, and heated at 1100 °C under vacuum for 57 h 40 min. The tube containing the solid (powder 5) was then gradually cooled down to room temperature at a rate of 0.5 °C/min, and then ground to fine powders before EDS, XRD, and Raman analysis. The EDS result revealed the ratio of Zr to Si is 3:1.

### **3.3.3 The Procedures of Thin Film Deposition Conducted in an Ultra-High-Vacuum (UHV) CVD Chamber<sup>33</sup>**

In a typical experiment, the precursor  $\text{Ti}(\text{NMe}_2)_4$  was loaded into a bubbler in a drybox. The bubbler then was connected to the CVD apparatus. A Si(100) wafer as substrate was placed in the middle heating zone through a loading lock. Ultra-high-purity argon was used as carrier gas. The system was evacuated and purged for 30 min around 400 °C before each deposition. Under these conditions, analyses of the argon outflow by RGA showed that it contained no  $\text{O}_2$ . The precursor  $\text{Ti}(\text{NMe}_2)_4$  was evacuated at -193 °C before each deposition. After each deposition, the film was annealed to 750 °C under vacuum for 2 h, and then allowed to cool slowly in the reactor under vacuum. The reactor conditions (Exps. 1-3) for the deposition of films 1-3 are listed in Table 3.5. In another experiment (Exp. 4), no deposition was observed.

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more detailed Ti-Si-N phase diagram, see Sambasivan, S.; Petuskey, W. T. *J.*

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## Chapter 4

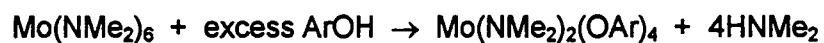
### Synthesis and Characterization of Unusual Metal Amide Hydride Complexes. Mechanistic Studies of the Reactions of Transition Metal Amides with Silanes

#### 4.1 Introduction

One important issue in chemical vapor deposition (CVD) of thin films is the mechanistic pathways in these reactions. Often such pathways are unknown, and the CVD processes are termed a "black box" art. However, an understanding of mechanistic pathways is often essential to the design of precursors, control of the CVD processes, and quality of the product materials thus produced. For the CVD of Ti-Si-N ternary films as TiN and Si<sub>3</sub>N<sub>4</sub> but not other solid compounds from the reaction of Ti(NMe<sub>2</sub>)<sub>4</sub> with SiH<sub>4</sub> (Chapter 3), its mechanistic pathways are of particular interest to us.

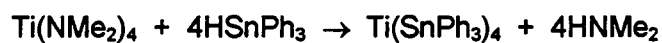
Reactions of transition metal amides with proton- or hydride-containing compounds,<sup>1</sup> such as H<sub>2</sub>O, HOR, HSnPh<sub>3</sub>,<sup>2</sup> and a silane HSi(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>,<sup>3</sup> are known to give amine HNR<sub>2</sub> (Figure 4.1). The patents of Doan and Sandhu indicated the formation of HNMe<sub>2</sub> in the CVD of TiN<sub>x</sub>/TiSi<sub>2</sub> thin films from reaction of Ti(NMe<sub>2</sub>)<sub>4</sub> with SiH<sub>4</sub>.<sup>4</sup> Andersen, Bergman, and coworkers recently reported that the reaction of Cp\*Ni(PET<sub>3</sub>)NHTol (Cp\* = pentamethylcyclopentadienyl) with HSiMe<sub>3</sub> yielded a late-transition metal hydride complex Cp\*Ni(PET<sub>3</sub>)H (Figure 4.1).<sup>5</sup> To our knowledge, this is the only report of the formation of a transition metal hydride from the reaction of an

- *With Protic Compounds*



(Ar = 2-Me-6-Bu<sup>i</sup>-phenyl)

- *With Hydride Compounds*



- *With Silanes*

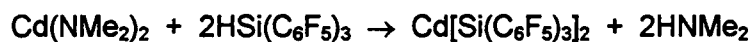


**Figure 4.1** Reactions of metal amide complexes.

amide complex with a silane. We thus decided to investigate the reactions of early transition metal amides  $M(\text{NMe}_2)_4$  ( $M = \text{Ti, Zr, Hf}$ ) with silanes. The results of such studies are reported here.

## 4.2 Results and Discussion

Two possible pathways in the first step of the reaction of  $M(\text{NMe}_2)_4$  with a silane (e.g.,  $\text{H}_2\text{SiPh}_2$ ) are shown in Figure 4.2. If the reaction occurs through Pathway 1, dimethylamine  $\text{HNMe}_2$  and a silyl complex " $(\text{Me}_2\text{N})_3\text{M-SiHPh}_2$ " (**5a**) are the major products. If Pathway 2 is the preferred process, aminosilane  $\text{HSi}(\text{NMe}_2)\text{Ph}_2$  and hydride " $\text{HM}(\text{NMe}_2)_3$ " (**9**) are expected. **9** may react with  $\text{H}_2\text{SiPh}_2$  in the next step to give **5a**.

### 4.2.1 Reactions of $M(\text{NMe}_2)_4$ ( $M = \text{Ti, Zr, Hf}$ ) with Silanes

When  $M(\text{NMe}_2)_4$  ( $M = \text{Ti, Zr, Hf}$ ) was exposed to excess  $\text{SiH}_4$  (5% in Ar) or  $\text{H}_2\text{SiR}'_2$  ( $\text{R}'_2 = \text{HPh, Ph}_2, \text{MePh}$ ) at 23 °C, instantaneous reactions were observed yielding aminosilanes [ $\text{HSi}(\text{NMe}_2)_3$ ,  $\text{HSi}(\text{NMe}_2)_2\text{Ph}$ ,  $\text{HSi}(\text{NMe}_2)\text{Ph}_2$ , and  $\text{HSi}(\text{NMe}_2)\text{MePh}$ , respectively],  $\text{H}_2$  and unknown black solids. No  $\text{HNMe}_2$  was detected. The formation of aminosilanes was found to be stepwise:  $\text{H}_2\text{Si}(\text{NMe}_2)_2$  and  $\text{H}_2\text{Si}(\text{NMe}_2)\text{Ph}$  were observed as intermediates when  $\text{SiH}_4$  and  $\text{H}_3\text{SiPh}$  were used, respectively. In the studies reported in Chapter 3, such black solids were then heated to give powders which were analyzed to reveal the solid compounds ( $\text{TiN}$  and  $\text{Si}_3\text{N}_4$ ) in the powders. In the investigations in the current chapter, the black solids (without heating) were studied directly by chemical and spectroscopic methods.

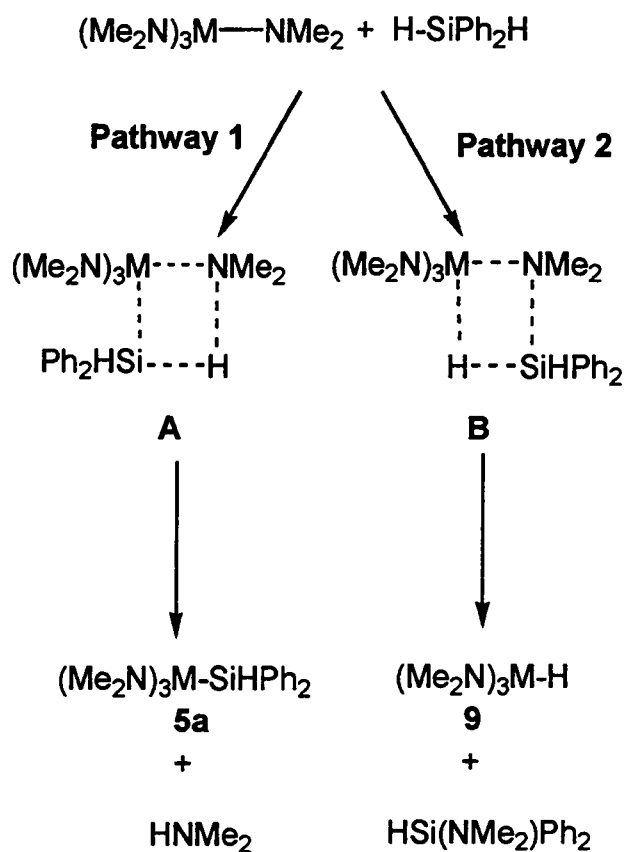


**Figure 4.2** Possible pathways of the first step in the reactions of metal amide complexes with silanes.

In the reactions of  $\text{Ti}(\text{NMe}_2)_4$  with silanes at room temperature, nearly 95% of the amido ligands were found to transfer from titanium metal to silanes to give aminosilanes. In the reactions of its zirconium and hafnium analogs  $\text{M}(\text{NMe}_2)_4$  ( $\text{M} = \text{Zr}, \text{Hf}$ ) with silanes at room temperature, the aminosilanes products accounted for only about 45% of the amido ligands in  $\text{M}(\text{NMe}_2)_4$ . This suggested that many amido ligands were left on the metal. The observation here was consistent with the carbon content by XPS of powder 8 in Chapter 3.

In contrast to the vigorous reactions between  $\text{Ti}(\text{NMe}_2)_4$  and  $\text{SiH}_4$  or phenylsilanes, no reactions were observed between this amido complex and alkylsilanes such as  $\text{H}_2\text{SiBu}^t_2$  and  $\text{HSiEt}_3$ , even at elevated temperatures (70 °C). At elevated temperatures, only the decomposition of the metal complexes was observed. The reactions and the aminosilane products are listed in Table 4.1.

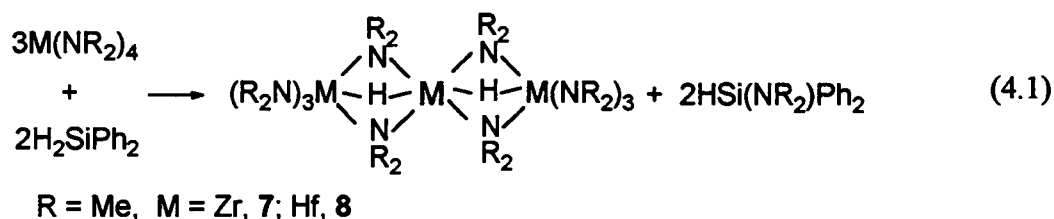
The black solids were not soluble in most common solvents. They were washed with hexanes six times and dried under vacuum (diffusion pump,  $10^{-5}$  torr) overnight before they were used in the following analyses and reactions. IR of the black solids showed no aminosilanes in the samples, as no Si-H stretch was observed. The black solids were extremely air-sensitive, pyrophoric, and readily hydrolyzed. They were found to react with acetone- $d_6$  to give  $\text{H}_2$ , HD, and  $\text{D}_2$  in a ratio of 100:8:7 by MS and an unknown white solid. The nature of this reaction is not clear. It, however, suggested that there were likely hydride ligands in the black solids. The reaction of the black solids with 1 M DCl in  $\text{D}_2\text{O}$  yielded  $\text{DNMe}_2$ , but no  $\text{HDSiR}'_2$  ( $\text{R}'_2 = \text{HPh}, \text{Ph}_2, \text{MePh}$ ) as analyzed by GC/MS. The Raman spectra of the solids showed M-N but no M-Si stretches. These results indicated that the black solids contained  $-\text{NMe}_2$  and  $-\text{H}$  ligands.

**Table 4.1** Reactions of Metal Amide Complexes  $M(NMe_2)_4$  ( $M = Ti, Zr, Hf$ ) with Silanes

| Silanes          | Observed aminosilane products       |
|------------------|-------------------------------------|
| $H_2SiBu^t_2$    | No reaction                         |
| $HSiEt_3$        | No reaction                         |
| $HSiMeBu^t_2$    | No reaction                         |
| $HSiPh_3$        | No reaction                         |
| $HSiPr^i_3$      | No reaction                         |
| $HSi(NMe_2)_3$   | No reaction                         |
| $SiH_4$          | $H_2Si(NMe_2)_2$ ; $HSi(NMe_2)_3$   |
| $H_3SiPh$        | $H_2Si(NMe_2)Ph$ ; $HSi(NMe_2)_2Ph$ |
| $H_2SiPh_2$      | $HSi(NMe_2)Ph_2$                    |
| $H_2SiMePh$      | $HSi(NMe_2)MePh$                    |
| $H_2Si(NMe_2)Ph$ | $HSi(NMe_2)_2Ph$                    |
| $HSi(NMe_2)_2Ph$ | $Si(NMe_2)_3Ph$                     |
| $HSi(NMe_2)Ph_2$ | $Si(NMe_2)_2Ph_2$                   |
| $HSi(NMe_2)MePh$ | $Si(NMe_2)_2MePh$                   |
| $H_2Si(NMe_2)_2$ | $HSi(NMe_2)_3$                      |
| $H_3Si(NMe_2)$   | $H_2Si(NMe_2)_2$ ; $HSi(NMe_2)_3$   |

#### 4.2.2 Syntheses and Characterization of Amide Hydride Complexes $[(\text{Me}_2\text{N})_3\text{M}(\mu\text{-H})(\mu\text{-NMe}_2)_2]_2\text{M}$ ( $\text{M} = \text{Zr}$ , **7**; $\text{Hf}$ , **8**)

The reactions of  $\text{Zr}(\text{NMe}_2)_4$  or  $\text{Hf}(\text{NMe}_2)_4$  with less than one equiv of  $\text{H}_3\text{SiPh}$ ,  $\text{H}_2\text{SiPh}_2$ ,  $\text{H}_2\text{SiMePh}$ , or  $\text{HSi}(\text{NMe}_2)\text{Ph}_2$  were found to yield amide hydride complexes  $[(\text{Me}_2\text{N})_3\text{M}(\mu\text{-H})(\mu\text{-NMe}_2)_2]_2\text{M}$  ( $\text{M} = \text{Zr}$ , **7**;  $\text{Hf}$ , **8**), respectively (Equation. 4.1). The reactions were instantaneous, although the reactions of  $\text{Hf}(\text{NMe}_2)_4$  were slightly slower. After dropwise addition of  $\text{H}_2\text{SiPh}_2$  in  $\text{Et}_2\text{O}$  to  $\text{M}(\text{NMe}_2)_4$  ( $\text{M} = \text{Zr}$ ,  $\text{Hf}$ ) in  $\text{Et}_2\text{O}$  at room temperature was complete [and additional 10 min stirring in the reaction of  $\text{Hf}(\text{NMe}_2)_4$ ], cooling of the reaction mixture to  $-35 - -40^\circ\text{C}$  yielded solids of **7** and **8**. The solid was washed with cold  $\text{Et}_2\text{O}$  at  $-35 - -40^\circ\text{C}$  to remove the unreacted  $\text{M}(\text{NMe}_2)_4$  and aminosilane  $\text{HSi}(\text{NMe}_2)\text{Ph}_2$ , and then recrystallized from  $\text{Et}_2\text{O}$  to give yellow crystals of **7** and colorless crystals of **8**. The reactions of  $\text{Zr}(\text{NMe}_2)_4$  or  $\text{Hf}(\text{NMe}_2)_4$  with less than one equiv of  $\text{D}_2\text{SiPh}_2$  were found to give  $[(\text{Me}_2\text{N})_3\text{M}(\mu\text{-D})(\mu\text{-NMe}_2)_2]_2\text{M}$  ( $\text{M} = \text{Zr}$ , **7-*d*<sub>2</sub>**;  $\text{Hf}$ , **8-*d*<sub>2</sub>**), indicating that the hydrides in **7** and **8** were from the silane. **7** and **8** are trinuclear complexes of yet unobserved " $\text{HM}(\text{NMe}_2)_3$ " (**9**) or " $\text{H}_2\text{M}(\text{NMe}_2)_2$ " (**10**) and unreacted  $\text{M}(\text{NMe}_2)_4$  ( $\text{M} = \text{Zr}$ ,  $\text{Hf}$ ).



The reactions between transition-metal complexes and silanes to give amide hydride complexes **7** and **8** are two of few known examples of such reactions. To our knowledge, the only other reported transition-metal amide reaction to give an isolated amide hydride complex involves a late transition-metal complex  $\text{Cp}^*\text{Ni}(\text{PEt}_3)\text{NHTol}$  (Figure 4.1),<sup>5</sup> although main group (tin) amides have been reported to yield hydrides and aminosilanes in their reactions with silanes.<sup>6</sup> Buchwald and coworkers reported the formation of " $\text{Cp}'_2\text{Ti-H}$ " [ $\text{Cp}' = (S,S)\text{-ethylenebis}(\eta^5\text{-tetrahydroindenyl})$ ] or its equivalent in the reaction of  $\text{Cp}'_2\text{TiF}_2$  with  $\text{H}_3\text{SiPh}$  and found it to be catalytically active for enantioselective imine hydrosilylation.<sup>7</sup> The proposed catalytic cycle involves reactions between " $\text{Cp}'_2\text{Ti-NR}(*\text{CHR}_1\text{R}_2)$ " and  $\text{H}_3\text{SiPh}$  to give " $\text{Cp}'_2\text{Ti-H}$ " and  $\text{PhH}_2\text{Si-NR}(*\text{CHR}_1\text{R}_2)$ . The reactions of  $\text{Cp}_2\text{MRR}'$  ( $\text{M} = \text{Ti, Zr}$ ;  $\text{R, R}' = \text{H, alkyl, silyl}$ )<sup>8a-d</sup> and  $\text{Cp}_2\text{Ti}(\text{OPh})_2$ <sup>8e</sup> with silanes were found to give  $\text{HR}$  ( $\text{HR}'$ ), disilanes, alkoxysilanes, and proposed  $\text{M-H}$  catalysts<sup>8f</sup> for polysilane synthesis. Such hydrides are believed to catalyze alkoxy- and siloxy-silane redistributions as well.<sup>9</sup> In the reactions of  $\text{M-L}$  multiple bonded complexes with silanes, Tilley and coworkers reported silane additions to  $\text{Ta}=\text{N}$  bonds, and  $\text{Si}$  intermediates containing  $\text{Si-N}$  bonds were proposed.<sup>10</sup> Lee and Bergman observed clean reactions of silanes with  $\text{Cp}_2\text{Zr}=\text{NBu}^t$ .<sup>11</sup> Silane additions to the  $\text{Ti}=\text{S}$  bond in  $\text{Cp}^*_2\text{Ti}(=\text{S})(\text{Py})$ ,<sup>12a</sup> the  $\text{Zr}=\text{O}$  bond in  $\text{Cp}^*_2\text{Zr}=\text{O}(\text{Py})$ ,<sup>12b</sup> and the  $\text{Ta}=\text{CHR}$  bond in  $(\text{RCH}_2)_3\text{Ta}(\text{PMe}_3)=\text{CHR}$  ( $\text{R} = \text{SiMe}_3$ )<sup>13</sup> have also been reported.

The solids of amide hydride complexes  $[(\text{Me}_2\text{N})_3\text{M}(\mu\text{-H})(\mu\text{-NMe}_2)_2]_2\text{M}$  ( $\text{M} = \text{Zr, Hf}$ , **8**) are stable at room temperature, but decompose slowly in solution. **8** is also slightly light sensitive. **7** and **8** were found to react with  $\text{H}_2\text{SiPh}_2$  and  $\text{HSi}(\text{NMe}_2)\text{Ph}_2$  instantaneously to give  $\text{H}_2$ ,  $\text{HSi}(\text{NMe}_2)\text{Ph}_2$ , and  $\text{Si}(\text{NMe}_2)_2\text{Ph}_2$ , respectively, and

unidentified species. Thus in the preparation of **7** and **8**, once the dropwise addition of  $\text{H}_2\text{SiPh}_2$  was complete, the mixture solution was cooled to  $-35 - -40\text{ }^\circ\text{C}$  to avoid further reactions of **7** and **8**.

#### 4.2.3 Crystal and Molecular Structures of **7** and **8**

The crystal structures of amide hydride complexes  $[(\text{Me}_2\text{N})_3\text{M}(\mu\text{-H})(\mu\text{-NMe}_2)_2]_2\text{M}$  ( $\text{M} = \text{Zr}$ , **7**;  $\text{Hf}$ , **8**) were determined by X-ray crystallography. ORTEPs of **7** and **8** are shown in Figures 4.3 and 4.4, respectively. The hydride ligands in **7** were located in an electron density map and independently refined. The crystal data, bond distances, bond angles, atomic coordinates, anisotropic displacement parameters, and hydrogen coordinates are given in Tables 4.2 – 4.7 for **7** and Tables 4.8 – 4.13 for **8**. The structure of **7** and **8** consists of two terminal  $\text{M}(\text{NMe}_2)_3$  moieties, one central  $\text{M}$  atom bridged to each terminal  $\text{M}(\text{NMe}_2)_3$  by one hydride and two amide ligands.

To our knowledge, **7** and **8** are among the few structurally characterized Cp-free Group 4 hydrides.<sup>14-16</sup> Others are  $[\text{P}_2\text{N}_2]\text{Zr}(\mu\text{-}\eta^2\text{-N}_2\text{H})(\mu\text{-H})\text{Zr}[\text{P}_2\text{N}_2]$  [ $\text{P}_2\text{N}_2 = \text{PhP}(\text{CH}_2\text{SiMe}_2\text{NSiMe}_2\text{CH}_2)_2\text{PPh}$ ],<sup>15a</sup>  $(2,6\text{-Pr}_2\text{C}_6\text{H}_3\text{O})_3\text{TiH}(\text{PMe}_3)$ ,<sup>15a</sup> an adduct of  $\text{NaH}$  to a Zr porphyrinogen  $[(\eta^5\text{-}\eta^1\text{-}\eta^1\text{-}\eta^1\text{-Et}_8\text{N}_4)\text{Zr}]_2(\mu\text{-NaH})_2$ ,<sup>15b</sup> and  $\text{BH}_4^-$  complexes.<sup>16</sup> Some other known Cp-free Group 4 hydrides include  $\text{MH}_2$  ( $\text{M} = \text{Ti}$ ,  $\text{Zr}$ ,  $\text{Hf}$ ),<sup>17</sup> silica-supported  $(\equiv\text{SiO})_3\text{Zr-H}$ ,<sup>18a</sup> and  $\text{HTi}[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]$ .<sup>18b</sup> The av. Zr---Zr distance of 3.232 Å in **7** reflects the constraints imposed by the bridging ligands.<sup>16a-b</sup> It is interesting to note that, in the structure of the only other known trinuclear Zr complex  $\text{Zr}_3\text{H}_6(\text{BH}_4)_6(\text{PMe}_3)_4$ ,<sup>16b</sup> the Zr atoms are arranged in a nonlinear fashion with the Zr---Zr

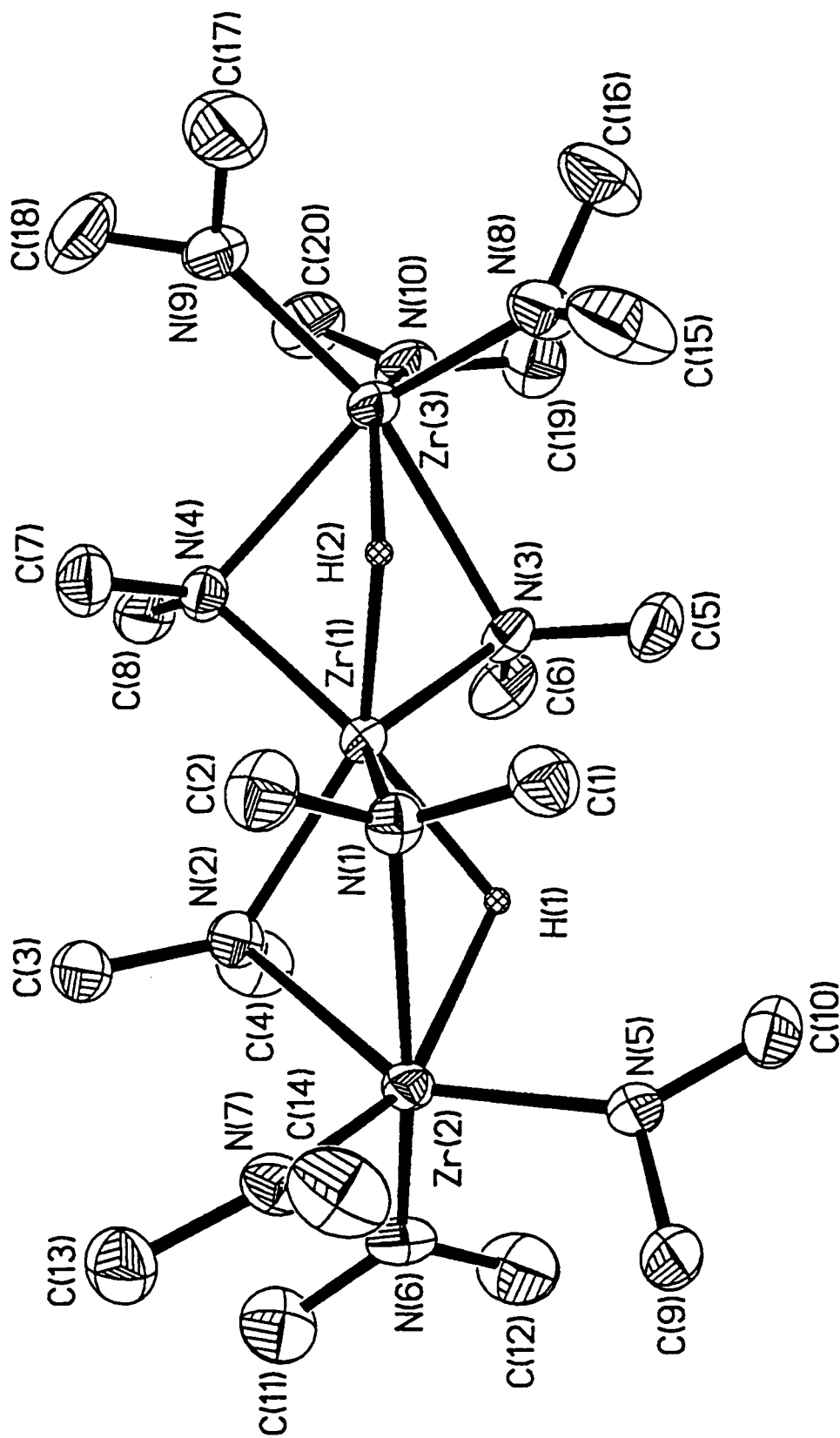


Figure 4.3 ORTEP diagram of 7, showing 50% ellipsoids.

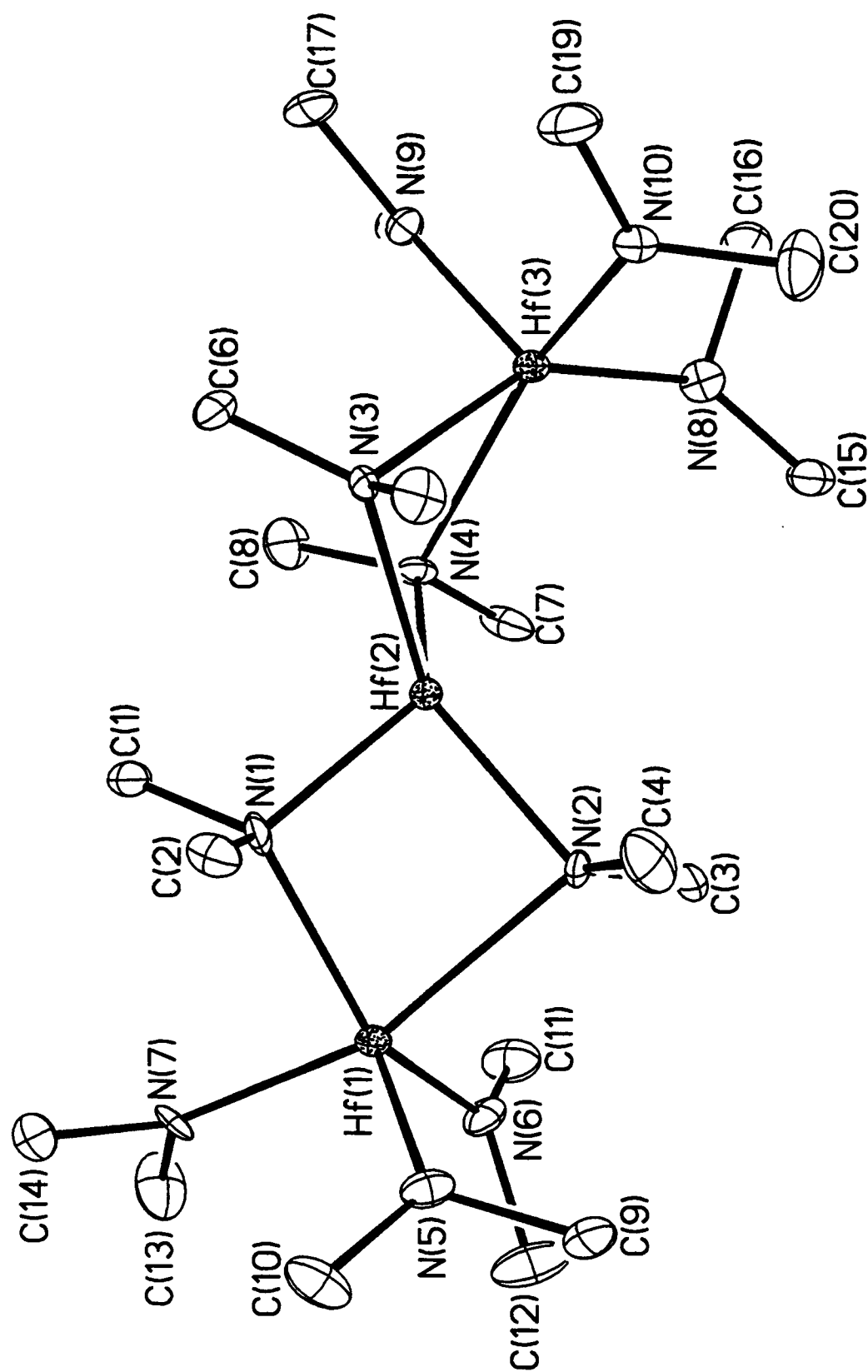


Figure 4.4 ORTEP diagram of **8**, showing 30% thermal ellipsoid.

**Table 4.2** Crystal Data for 7

|                                          |                                                                                                 |
|------------------------------------------|-------------------------------------------------------------------------------------------------|
| Formula (Formula weight)                 | C <sub>20</sub> H <sub>62</sub> N <sub>10</sub> Zr <sub>3</sub> (716.46)                        |
| Crystal system                           | monoclinic                                                                                      |
| Crystal color                            | yellow                                                                                          |
| Space group                              | <i>P</i> 2 <sub>1</sub> / <i>c</i>                                                              |
| Lattice parameters                       | $a$ (Å) = 15.475(3)<br>$b$ (Å) = 8.613(2)<br>$c$ (Å) = 26.154(4)<br>$\beta$ (deg) = 106.310(10) |
| $V$ (Å <sup>3</sup> )                    | 3345.7(11)                                                                                      |
| $Z$                                      | 4                                                                                               |
| $d_{\text{calcd}}$ (Mg m <sup>-3</sup> ) | 1.422                                                                                           |
| $\mu$ (mm <sup>-1</sup> )                | 0.941                                                                                           |
| $F(000)$                                 | 1488                                                                                            |
| Temp (K)                                 | 173                                                                                             |
| $2\theta$ (deg)                          | 3.24 – 45.1                                                                                     |
| No. of data collected                    | 4589                                                                                            |
| No. of independent data                  | 4397 ( $R_{\text{int}}$ = 0.0382)                                                               |
| Refinement method                        | full-matrix least-squares on $F^2$                                                              |
| $R$ indices (obs. data)                  | 0.0453                                                                                          |

**Table 4.2 Continued**

|                                   |                   |
|-----------------------------------|-------------------|
| Weighted $R^a$                    | 0.0952 ( $wR^2$ ) |
| Good-of-fit on $F^2$ <sup>a</sup> | 1.159             |

$$^a wR^2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}, R = \sum ||F_o| - |F_c|| / \sum |F_o|;$$

$$w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]; P = [2F_c^2 + \text{Max}(F_o^2, 0)] / 3$$

**Table 4.3** Interatomic Distances (Å) in 7

|             |           |             |           |
|-------------|-----------|-------------|-----------|
| Zr(1)–H(2)  | 1.89(4)   | Zr(1)–H(1)  | 1.93(4)   |
| Zr(1)–N(3)  | 2.122(4)  | Zr(1)–N(1)  | 2.127(4)  |
| Zr(1)–N(2)  | 2.215(4)  | Zr(1)–N(4)  | 2.230(4)  |
| Zr(1)–Zr(3) | 3.2296(8) | Zr(1)–Zr(2) | 3.2347(7) |
| Zr(2)–N(5)  | 2.049(4)  | Zr(2)–N(6)  | 2.066(4)  |
| Zr(2)–N(7)  | 2.075(4)  | Zr(2)–H(1)  | 2.017(4)  |
| Zr(2)–N(2)  | 2.393(4)  | Zr(2)–N(1)  | 2.560(4)  |
| Zr(3)–N(8)  | 2.041(4)  | Zr(3)–N(10) | 2.067(4)  |
| Zr(3)–N(9)  | 2.071(4)  | Zr(3)–H(2)  | 2.13(4)   |
| Zr(3)–N(4)  | 2.382(4)  | Zr(3)–N(3)  | 2.555(4)  |
| N(1)–C(2)   | 1.462(6)  | N(1)–C(1)   | 1.478(6)  |
| N(2)–C(3)   | 1.465(6)  | N(2)–C(4)   | 1.478(6)  |
| N(3)–C(5)   | 1.465(6)  | N(3)–C(6)   | 1.472(6)  |
| N(4)–C(7)   | 1.470(6)  | N(4)–C(8)   | 1.479(6)  |
| N(5)–C(10)  | 1.446(6)  | N(5)–C(9)   | 1.463(6)  |
| N(6)–C(12)  | 1.446(6)  | N(6)–C(11)  | 1.452(6)  |
| N(7)–C(13)  | 1.450(6)  | N(7)–C(14)  | 1.462(7)  |
| N(8)–C(15)  | 1.455(7)  | N(8)–C(16)  | 1.459(7)  |
| N(9)–C(17)  | 1.444(7)  | N(9)–C(18)  | 1.456(7)  |
| N(10)–C(19) | 1.451(6)  | N(10)–C(20) | 1.459(6)  |

**Table 4.4** Intramolecular Bond Angles (°) in **7**

|                  |            |                   |            |
|------------------|------------|-------------------|------------|
| H(2)–Zr(1)–H(1)  | 133(2)     | H(2)–Zr–N(3)      | 78.0(12)   |
| H(1)–Zr(1)–N(3)  | 82.7(11)   | H(2)–Zr(1)–N(1)   | 83.2(13)   |
| H(1)–Zr(1)–N(1)  | 77.0(12)   | N(3)–Zr(1)–N(1)   | 129.28(14) |
| H(2)–Zr(1)–N(2)  | 147.3(12)  | H(1)–Zr(1)–N(2)   | 72.9(12)   |
| N(3)–Zr(1)–N(2)  | 131.1(2)   | N(1)–Zr(1)–N(2)   | 85.88(14)  |
| H(2)–Zr(1)–N(4)  | 70.4(12)   | H(1)–Zr(1)–N(4)   | 149.2(12)  |
| N(3)–Zr(1)–N(4)  | 84.89(13)  | N(1)–Zr(1)–N(4)   | 131.43(14) |
| N(2)–Zr(1)–N(4)  | 94.93(13)  | H(2)–Zr(1)–Zr(3)  | 39.2(13)   |
| H(1)–Zr(1)–Zr(3) | 134.0(11)  | N(3)–Zr(1)–Zr(3)  | 52.19(10)  |
| N(1)–Zr(1)–Zr(3) | 122.29(10) | N(2)–Zr(1)–Zr(3)  | 141.79(9)  |
| N(4)–Zr(1)–Zr(3) | 47.52(9)   | H(2)–Zr(1)–Zr(2)  | 135.0(13)  |
| H(1)–Zr(1)–Zr(2) | 40.7(11)   | N(3)–Zr(1)–Zr(2)  | 123.38(10) |
| N(1)–Zr(1)–Zr(2) | 52.19(10)  | N(2)–Zr(1)–Zr(2)  | 47.71(9)   |
| N(4)–Zr(1)–Zr(2) | 141.86(10) | Zr(1)–Zr(2)–Zr(3) | 170.48(2)  |
| N(5)–Zr(2)–N(6)  | 96.2(2)    | N(5)–Zr(2)–N(7)   | 109.2(2)   |
| N(6)–Zr(2)–N(7)  | 103.9(2)   | N(5)–Zr(2)–H(1)   | 78.7(10)   |
| N(6)–Zr(2)–H(1)  | 102.3(11)  | N(7)–Zr(2)–H(1)   | 151.5(10)  |
| N(5)–Zr(2)–N(2)  | 144.05(14) | N(6)–Zr(2)–N(2)   | 91.42(14)  |
| N(7)–Zr(2)–N(2)  | 102.85(14) | H(1)–Zr(2)–N(2)   | 65.4(10)   |
| N(5)–Zr(2)–N(1)  | 91.77(14)  | N(6)–Zr(2)–N(1)   | 162.57(14) |
| N(7)–Zr(2)–N(1)  | 88.02(14)  | H(1)–Zr(2)–N(1)   | 6401(10)   |

**Table 4.4 Continued**

|                  |            |                   |            |
|------------------|------------|-------------------|------------|
| N(2)–Zr(2)–N(1)  | 73.28(12)  | N(5)–Zr(2)–Zr(10) | 105.14(10) |
| N(6)–Zr(2)–Zr(1) | 121.59(11) | N(7)–Zr(2)–Zr(1)  | 118.26(11) |
| H(1)–Zr(2)–Zr(1) | 35.4(10)   | N(2)–Zr(2)–Zr(1)  | 43.21(9)   |
| N(1)–Zr(2)–Zr(1) | 41.04(8)   | N(8)–Zr(3)–N(10)  | 107.5(2)   |
| N(8)–Zr(3)–N(9)  | 97.1(2)    | N(10)–Zr(3)–N(9)  | 102.9(2)   |
| N(8)–Zr(3)–H(2)  | 80.5(11)   | N(10)–Zr(3)–H(2)  | 151.6(12)  |
| N(9)–Zr(3)–H(2)  | 103.0(11)  | N(8)–Zr(3)–N(4)   | 144.1(2)   |
| N(10)–Zr(3)–N(4) | 104.4(2)   | N(9)–Zr(3)–N(4)   | 91.32(14)  |
| H(2)–Zr(3)–N(4)  | 63.6(11)   | N(8)–Zr(3)–N(3)   | 92.3(2)    |
| N(10)–Zr(3)–N(3) | 87.51(14)  | N(9)–Zr(3)–N(3)   | 163.02(14) |
| H(2)–Zr(3)–N(3)  | 64.6(11)   | N(4)–Zr(3)–N(3)   | 72.94(12)  |
| N(8)–Zr(3)–Zr(1) | 104.72(11) | N(10)–Zr(3)–Zr(1) | 119.25(11) |
| N(9)–Zr(3)–Zr(1) | 122.41(11) | H(2)–Zr(3)–Zr(1)  | 34.1(12)   |
| N(4)–Zr(3)–Zr(1) | 43.65(9)   | N(3)–Zr(3)–Zr(1)  | 41.00(8)   |
| C(2)–N(1)–C(1)   | 108.3(4)   | C(2)–N(1)–Zr(1)   | 114.6(3)   |
| C(1)–N(1)–Zr(2)  | 117.0(3)   | C(2)–N(1)–Zr(2)   | 117.6(3)   |
| C(3)–N(2)–C(4)   | 111.7(3)   | Zr(1)–N(1)–Zr(2)  | 86.77(13)  |
| C(3)–N(2)–C(4)   | 108.8(4)   | C(3)–N(2)–Zr(1)   | 127.7(3)   |
| C(4)–N(2)–Zr(1)  | 105.8(3)   | C(3)–N(2)–Zr(2)   | 112.5(3)   |
| C(4)–N(2)–Zr(2)  | 111.2(3)   | Zr(1)–N(2)–Zr(2)  | 89.07(13)  |
| C(5)–N(3)–C(6)   | 109.5(4)   | C(5)–N(3)–Zr(1)   | 114.5(3)   |

**Table 4.4 Continued**

|                   |          |                   |           |
|-------------------|----------|-------------------|-----------|
| C(6)–N(3)–Zr(1)   | 114.7(3) | C(5)–N(3)–Zr(3)   | 112.2(3)  |
| C(3)–N(3)–Zr(3)   | 117.8(3) | Zr(1)–N(3)–Zr(3)  | 86.81(12) |
| C(7)–N(4)–C(8)    | 108.5(4) | C(7)–N(4)–Zr(1)   | 104.2(3)  |
| C(8)–N(4)–Zr(1)   | 126.5(3) | C(7)–N(4)–Zr(3)   | 112.7(3)  |
| C(8)–N(4)–Zr(3)   | 114.8(3) | Zr(1)–N(4)–Zr(3)  | 88.83(12) |
| C(10)–N(5)–C(9)   | 109.9(4) | C(10)–N(5)–Zr(2)  | 138.4(3)  |
| C(9)–N(5)–Zr(2)   | 111.2(3) | C(12)–N(6)–C(11)  | 110.0(4)  |
| C(12)–N(6)–Zr(2)  | 124.4(3) | C(11)–N(6)–Zr(2)  | 125.6(3)  |
| C(13)–N(7)–C(14)  | 107.7(4) | C(13)–N(7)–Zr(2)  | 133.4(3)  |
| C(14)–N(7)–Zr(2)  | 118.8(3) | C(15)–N(8)–C(16)  | 108.2(4)  |
| C(15)–N(8)–Zr(3)  | 136.7(4) | C(16)–N(8)–Zr(3)  | 114.7(3)  |
| C(17)–N(9)–C(18)  | 107.6(5) | C(17)–N(9)–Zr(3)  | 124.8(4)  |
| C(18)–N(9)–Zr(3)  | 127.4(4) | C(19)–N(10)–C(20) | 108.6(4)  |
| C(19)–N(10)–Zr(3) | 123.6(3) | C(20)–N(10)–Zr(3) | 127.2(3)  |

**Table 4.5** Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic DisplacementParameters ( $\text{\AA}^2 \times 10^3$ ) for 7<sup>a</sup>

|       | x       | y       | z       | <i>U</i> (eq) |
|-------|---------|---------|---------|---------------|
| Zr(1) | 2383(1) | 6210(1) | 2899(1) | 19(1)         |
| Zr(2) | 2628(1) | 6170(1) | 1710(1) | 22(1)         |
| Zr(3) | 2413(1) | 5850(1) | 4133(1) | 25(1)         |
| N(1)  | 2332(2) | 4260(4) | 2392(2) | 25(1)         |
| N(2)  | 1698(2) | 7495(4) | 2163(2) | 28(1)         |
| N(3)  | 3415(2) | 6896(4) | 3583(2) | 27(1)         |
| N(4)  | 1446(2) | 7012(4) | 3354(2) | 26(1)         |
| N(5)  | 3888(2) | 5274(5) | 1798(1) | 32(1)         |
| N(6)  | 2825(3) | 8189(5) | 1332(2) | 32(1)         |
| N(7)  | 1701(3) | 4939(5) | 1123(2) | 32(1)         |
| N(8)  | 3256(3) | 4023(5) | 4407(2) | 37(1)         |
| N(9)  | 1321(3) | 5015(5) | 4360(2) | 39(1)         |
| N(10) | 2853(3) | 7687(5) | 4649(2) | 34(1)         |
| C(1)  | 3063(3) | 3105(6) | 2561(2) | 37(1)         |
| C(2)  | 1472(3) | 3431(6) | 2249(2) | 40(1)         |
| C(3)  | 743(3)  | 7449(6) | 1866(2) | 37(1)         |
| C(4)  | 1977(4) | 9133(6) | 2267(2) | 44(1)         |
| C(5)  | 4255(3) | 6015(7) | 3673(2) | 43(1)         |

**Table 4.5 Continued**

|       | x       | y       | z       | $U(\text{eq})$ |
|-------|---------|---------|---------|----------------|
| C(6)  | 3617(4) | 8570(6) | 3615(2) | 45(1)          |
| C(7)  | 621(3)  | 6108(6) | 3130(2) | 39(1)          |
| C(8)  | 1189(3) | 8636(6) | 3424(2) | 37(1)          |
| C(9)  | 4002(3) | 4785(8) | 1285(2) | 53(2)          |
| C(10) | 4737(3) | 5156(7) | 2207(2) | 47(2)          |
| C(11) | 2130(4) | 9052(6) | 948(2)  | 48(2)          |
| C(12) | 3679(4) | 8978(7) | 1426(2) | 56(2)          |
| C(13) | 862(3)  | 5358(7) | 736(2)  | 43(1)          |
| C(14) | 1889(4) | 3316(6) | 1031(2) | 54(2)          |
| C(15) | 3519(5) | 2608(7) | 4186(2) | 69(2)          |
| C(16) | 3644(4) | 3984(7) | 4984(2) | 55(2)          |
| C(17) | 1239(4) | 3452(8) | 4540(3) | 75(2)          |
| C(18) | 546(4)  | 5892(8) | 4413(2) | 59(2)          |
| C(19) | 3794(3) | 7976(7) | 4922(2) | 51(2)          |
| C(20) | 2301(4) | 8736(6) | 4863(2) | 48(2)          |

<sup>a</sup>  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

**Table 4.6** Anisotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for 7<sup>a</sup>

|       | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|-------|----------|----------|----------|----------|----------|----------|
| Zr(1) | 19(1)    | 20(1)    | 20(1)    | -1(1)    | 7(1)     | 0(1)     |
| Zr(2) | 24(1)    | 23(1)    | 19(1)    | 0(1)     | 7(1)     | 3(1)     |
| Zr(3) | 25(1)    | 31(1)    | 21(1)    | 0(1)     | 9(1)     | 0(1)     |
| N(1)  | 25(2)    | 23(2)    | 28(2)    | -4(2)    | 8(2)     | 2(2)     |
| N(2)  | 31(2)    | 25(2)    | 28(2)    | 0(2)     | 11(2)    | 10(2)    |
| N(3)  | 23(2)    | 32(2)    | 28(2)    | -7(2)    | 11(2)    | -6(2)    |
| N(4)  | 21(2)    | 29(2)    | 28(2)    | -1(2)    | 8(2)     | 2(2)     |
| N(5)  | 30(2)    | 44(3)    | 22(2)    | 1(2)     | 9(2)     | 9(2)     |
| N(6)  | 43(2)    | 31(2)    | 25(2)    | 2(2)     | 15(2)    | -2(2)    |
| N(7)  | 39(2)    | 31(2)    | 26(2)    | -4(2)    | 8(2)     | 0(2)     |
| N(8)  | 46(3)    | 36(3)    | 27(2)    | 3(2)     | 10(2)    | 10(2)    |
| N(9)  | 34(2)    | 53(3)    | 31(2)    | 7(2)     | 11(2)    | -7(2)    |
| N(10) | 37(2)    | 43(3)    | 26(2)    | -5(2)    | 15(2)    | -1(2)    |
| C(1)  | 41(3)    | 34(3)    | 37(3)    | 7(2)     | 10(2)    | 5(2)     |
| C(2)  | 39(3)    | 32(3)    | 51(3)    | 0(3)     | 14(3)    | -6(2)    |
| C(3)  | 37(3)    | 43(3)    | 33(3)    | 6(2)     | 13(2)    | 17(2)    |
| C(4)  | 64(4)    | 27(3)    | 44(3)    | -6(3)    | 18(3)    | 10(3)    |
| C(5)  | 29(3)    | 62(4)    | 40(3)    | -3(3)    | 14(2)    | 7(3)     |
| C(6)  | 43(3)    | 42(3)    | 56(4)    | -1(3)    | 24(3)    | -13(3)   |

**Table 4.6 Continued**

|       | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|-------|----------|----------|----------|----------|----------|----------|
| C(7)  | 26(3)    | 50(4)    | 39(3)    | -4(3)    | 5(2)     | -1(2)    |
| C(8)  | 40(3)    | 37(3)    | 39(3)    | 3(2)     | 18(2)    | 11(2)    |
| C(9)  | 41(3)    | 91(5)    | 29(3)    | -3(3)    | 12(3)    | 27(3)    |
| C(10) | 33(3)    | 71(4)    | 37(3)    | -3(3)    | 11(3)    | 12(3)    |
| C(11) | 56(4)    | 29(3)    | 58(4)    | 13(3)    | 16(3)    | 3(3)     |
| C(12) | 59(4)    | 59(4)    | 46(4)    | 4(3)     | 11(3)    | -25(3)   |
| C(13) | 35(3)    | 50(4)    | 40(3)    | -1(3)    | 4(2)     | -9(3)    |
| C(14) | 74(4)    | 39(3)    | 43(4)    | -13(3)   | 6(3)     | -1(3)    |
| C(15) | 115(6)   | 52(4)    | 39(4)    | 9(3)     | 20(4)    | 35(4)    |
| C(16) | 69(4)    | 61(4)    | 30(3)    | 7(3)     | 5(3)     | 22(3)    |
| C(17) | 50(4)    | 89(5)    | 75(5)    | 38(4)    | 1(3)     | -23(4)   |
| C(18) | 41(3)    | 89(5)    | 56(4)    | -7(4)    | 29(3)    | -11(3)   |
| C(19) | 43(3)    | 65(4)    | 42(3)    | -16(3)   | 6(3)     | -1(3)    |
| C(20) | 58(4)    | 48(4)    | 44(3)    | -13(3)   | 22(3)    | -3(3)    |

<sup>a</sup> The anisotropic displacement factor exponent takes the form:  $-2\pi^2[(ha^*)^2U_{11} + (kb^*)^2U_{22} + (lc^*)^2U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2lkc^*b^*U_{23}]$ .

**Table 4.7** Hydrogen Coordinates ( $\times 10^4$ ) and Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for 7

|       | x       | y       | z       | $U(\text{eq})$ |
|-------|---------|---------|---------|----------------|
| H(1A) | 3646(3) | 3639(6) | 2659(2) | 80             |
| H(1B) | 3037(3) | 2383(6) | 2268(2) | 80             |
| H(1C) | 2991(3) | 2528(6) | 2869(2) | 80             |
| H(2A) | 978(3)  | 4179(6) | 2135(2) | 80             |
| H(2B) | 1408(3) | 2853(6) | 2559(2) | 80             |
| H(2C) | 1455(3) | 2708(6) | 1957(2) | 80             |
| H(3A) | 551(3)  | 6367(6) | 1795(2) | 80             |
| H(3B) | 651(3)  | 8004(6) | 1528(2) | 80             |
| H(3C) | 387(3)  | 7945(6) | 2077(2) | 80             |
| H(4A) | 2616(4) | 9177(6) | 2465(2) | 80             |
| H(4B) | 1618(4) | 9625(6) | 2477(2) | 80             |
| H(4C) | 1882(4) | 9684(6) | 1928(2) | 80             |
| H(5A) | 4120(3) | 4901(7) | 3652(2) | 80             |
| H(5B) | 4653(3) | 6262(7) | 4026(2) | 80             |
| H(5C) | 4552(3) | 6292(7) | 3400(2) | 80             |
| H(6A) | 3055(4) | 9158(6) | 3555(2) | 80             |
| H(6B) | 3914(4) | 8847(6) | 3343(2) | 80             |
| H(6C) | 4016(4) | 8817(6) | 3968(2) | 80             |
| H(7A) | 779(3)  | 5027(6) | 3081(2) | 80             |

**Table 4.7 Continued**

|        | x       | y        | z       | U(eq) |
|--------|---------|----------|---------|-------|
| H(7B)  | 290(3)  | 6548(6)  | 2785(2) | 80    |
| H(7C)  | 242(3)  | 6147(6)  | 3373(2) | 80    |
| H(8A)  | 1733(3) | 9255(6)  | 3573(2) | 80    |
| H(8B)  | 808(3)  | 8664(6)  | 3666(2) | 80    |
| H(8C)  | 856(3)  | 9066(6)  | 3077(2) | 80    |
| H(9A)  | 3425(3) | 4867(8)  | 1010(2) | 80    |
| H(9B)  | 4211(3) | 3706(8)  | 1311(2) | 80    |
| H(9C)  | 4447(3) | 5455(8)  | 1192(2) | 80    |
| H(10A) | 4657(3) | 5485(7)  | 2550(2) | 80    |
| H(10B) | 5183(3) | 5827(7)  | 2115(2) | 80    |
| H(10C) | 4947(3) | 4078(7)  | 2234(2) | 80    |
| H(11A) | 1553(4) | 8511(6)  | 887(2)  | 80    |
| H(11B) | 2289(4) | 9134(6)  | 612(2)  | 80    |
| H(11C) | 2080(4) | 10095(6) | 1088(2) | 80    |
| H(12A) | 4144(4) | 8389(7)  | 1685(2) | 80    |
| H(12B) | 3632(4) | 10020(7) | 1566(2) | 80    |
| H(12C) | 3841(4) | 9060(7)  | 1091(2) | 80    |
| H(13A) | 718(3)  | 6444(7)  | 789(2)  | 80    |
| H(13B) | 378(3)  | 4688(7)  | 782(2)  | 80    |
| H(13C) | 923(3)  | 5226(7)  | 376(2)  | 80    |

**Table 4.7** Continued

|        | x       | y       | z       | <i>U</i> (eq) |
|--------|---------|---------|---------|---------------|
| H(14A) | 2455(4) | 3001(6) | 1288(2) | 80            |
| H(14B) | 1943(4) | 3199(6) | 668(2)  | 80            |
| H(14C) | 1397(4) | 2661(6) | 1075(2) | 80            |
| H(15A) | 3265(5) | 2612(7) | 3798(2) | 80            |
| H(15B) | 3292(5) | 1705(7) | 4336(2) | 80            |
| H(15C) | 4177(5) | 2555(7) | 4274(2) | 80            |
| H(16A) | 3474(4) | 4929(7) | 5141(2) | 80            |
| H(16B) | 4301(4) | 3923(7) | 5068(2) | 80            |
| H(16C) | 3416(4) | 3074(7) | 5130(2) | 80            |
| H(17A) | 1753(4) | 2832(8) | 4509(3) | 80            |
| H(17B) | 680(4)  | 2988(8) | 4320(3) | 80            |
| H(17C) | 1229(4) | 3476(8) | 4913(3) | 80            |
| H(18A) | 584(4)  | 6962(8) | 4293(2) | 80            |
| H(18B) | 542(4)  | 5896(8) | 4787(2) | 80            |
| H(18C) | -8(4)   | 5409(8) | 4194(2) | 80            |
| H(19A) | 4172(3) | 7278(7) | 4781(2) | 80            |
| H(19B) | 3901(3) | 7788(7) | 5304(2) | 80            |
| H(19C) | 3943(3) | 9055(7) | 4864(2) | 80            |
| H(20A) | 1663(4) | 8554(6) | 4682(2) | 80            |
| H(20B) | 2455(4) | 9814(6) | 4806(2) | 80            |

**Table 4.7** Continued

|        | x        | y        | z        | $U(\text{eq})$ |
|--------|----------|----------|----------|----------------|
| H(20C) | 2414(4)  | 8546(6)  | 5246(2)  | 80             |
| H(1)   | 3285(26) | 6696(46) | 2541(15) | 20(11)         |
| H(2)   | 2298(26) | 4678(52) | 3399(16) | 29(12)         |

**Table 4.8** Crystal Data for **8**

|                                                 |                                                                                                                      |
|-------------------------------------------------|----------------------------------------------------------------------------------------------------------------------|
| Formula (Formula weight)                        | C <sub>20</sub> H <sub>62</sub> N <sub>10</sub> Hf <sub>3</sub> (978.27)                                             |
| Crystal system                                  | monoclinic                                                                                                           |
| Crystal color (Habit)                           | colorless (plate)                                                                                                    |
| Space group                                     | <i>P</i> 2 <sub>1</sub> / <i>c</i>                                                                                   |
| Lattice parameters                              | <i>a</i> (Å) = 14.5901(4)<br><i>b</i> (Å) = 14.8647(5)<br><i>c</i> (Å) = 17.0738(3)<br><i>β</i> (deg) = 113.5665(13) |
| <i>V</i> (Å <sup>3</sup> )                      | 3394.05(19)                                                                                                          |
| <i>Z</i>                                        | 4                                                                                                                    |
| <i>d</i> <sub>calcd</sub> (Mg m <sup>-3</sup> ) | 1.914                                                                                                                |
| <i>μ</i> (mm <sup>-1</sup> )                    | 9.176                                                                                                                |
| <i>F</i> (000)                                  | 1872                                                                                                                 |
| Temp (K)                                        | 173                                                                                                                  |
| 2 <i>θ</i> (deg)                                | 3.04 – 56.42                                                                                                         |
| No. of data collected                           | 19538                                                                                                                |
| No. of independent data                         | 7792 ( <i>R</i> <sub>int</sub> = 0.0637)                                                                             |
| Refinement method                               | full-matrix least-squares on <i>F</i> <sup>2</sup>                                                                   |
| <i>R</i> indices (obs. data)                    | 0.0639                                                                                                               |

**Table 4.8** Continued

|                          |                   |
|--------------------------|-------------------|
| Weighted $R^a$           | 0.1524 ( $wR^2$ ) |
| Good-of-fit on $F^2{}^a$ | 1.281             |

$$^a wR^2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}; R = \sum ||F_o| - |F_c|| / \sum |F_o|;$$

$$w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]; P = [2F_c^2 + \text{Max}(F_o^2, 0)] / 3$$

**Table 4.9** Interatomic Distances (Å) in **8**

|             |           |             |           |
|-------------|-----------|-------------|-----------|
| Hf(1)-N(5)  | 2.073(10) | Hf(1)-N(6)  | 2.081(10) |
| Hf(1)-N(7)  | 2.094(9)  | Hf(1)-N(1)  | 2.383(10) |
| Hf(1)-N(2)  | 2.514(9)  | Hf(1)-Hf(2) | 3.2173(6) |
| Hf(2)-N(4)  | 2.151(9)  | Hf(2)-N(2)  | 2.160(9)  |
| Hf(2)-N(3)  | 2.215(9)  | Hf(2)-N(1)  | 2.215(10) |
| Hf(2)-Hf(3) | 3.2085(6) | Hf(3)-N(8)  | 2.062(11) |
| Hf(3)-N(9)  | 2.069(10) | Hf(3)-N(10) | 2.071(11) |
| Hf(3)-N(3)  | 2.400(9)  | Hf(3)-N(4)  | 2.571(10) |
| N(1)-C(2)   | 1.463(17) | N(1)-C(1)   | 1.504(15) |
| N(2)-C(3)   | 1.471(16) | N(2)-C(4)   | 1.493(18) |
| N(3)-C(6)   | 1.467(14) | N(3)-C(5)   | 1.470(15) |
| N(4)-C(8)   | 1.481(16) | N(4)-C(7)   | 1.489(18) |
| N(5)-C(10)  | 1.474(18) | N(5)-C(9)   | 1.473(17) |
| N(6)-C(11)  | 1.439(19) | N(6)-C(12)  | 1.472(17) |
| N(7)-C(14)  | 1.438(18) | N(7)-C(13)  | 1.465(19) |
| N(8)-C(15)  | 1.452(17) | N(8)-C(16)  | 1.499(17) |
| N(9)-C(18)  | 1.44(2)   | N(9)-C(17)  | 1.472(18) |
| N(10)-C(19) | 1.472(17) | N(10)-C(20) | 1.475(17) |

**Table 4.10** Intramolecular Bond Angles (°) in **8**

|                  |          |                   |             |
|------------------|----------|-------------------|-------------|
| N(5)-Hf(1)-N(6)  | 105.1(4) | N(5)-Hf(1)-N(7)   | 101.0(4)    |
| N(6)-Hf(1)-N(7)  | 97.1(4)  | N(5)-Hf(1)-N(1)   | 101.3(4)    |
| N(6)-Hf(1)-N(1)  | 149.9(4) | N(7)-Hf(1)-N(1)   | 91.5(4)     |
| N(5)-Hf(1)-N(2)  | 90.1(4)  | N(6)-Hf(1)-N(2)   | 92.2(4)     |
| N(7)-Hf(1)-N(2)  | 163.1(4) | N(1)-Hf(1)-N(2)   | 73.7(3)     |
| N(5)-Hf(1)-Hf(2) | 120.1(3) | N(6)-Hf(1)-Hf(2)  | 109.1(3)    |
| N(7)-Hf(1)-Hf(2) | 121.1(3) | N(1)-Hf(1)-Hf(2)  | 43.5(2)     |
| N(2)-Hf(1)-Hf(2) | 42.1(2)  | N(4)-Hf(2)-N(2)   | 130.5(4)    |
| N(4)-Hf(2)-N(3)  | 85.5(4)  | N(2)-Hf(2)-N(3)   | 129.9(4)    |
| N(4)-Hf(2)-N(1)  | 132.6(4) | N(2)-Hf(2)-N(1)   | 84.4(4)     |
| N(3)-Hf(2)-N(1)  | 94.1(3)  | N(4)-Hf(2)-Hf(3)  | 53.0(3)     |
| N(2)-Hf(2)-Hf(3) | 121.0(2) | N(3)-Hf(2)-Hf(3)  | 48.4(2)     |
| N(1)-Hf(2)-Hf(3) | 142.2(3) | N(4)-Hf(2)-Hf(1)  | 124.7(3)    |
| N(2)-Hf(2)-Hf(1) | 51.3(2)  | N(3)-Hf(2)-Hf(1)  | 140.9(2)    |
| N(1)-Hf(2)-Hf(1) | 47.8(3)  | Hf(3)-Hf(2)-Hf(1) | 169.717(19) |
| N(8)-Hf(3)-N(9)  | 104.4(4) | N(8)-Hf(3)-N(10)  | 95.9(4)     |
| N(9)-Hf(3)-N(10) | 106.1(4) | N(8)-Hf(3)-N(3)   | 149.4(4)    |
| N(9)-Hf(3)-N(3)  | 102.3(4) | N(10)-Hf(3)-N(3)  | 90.9(4)     |
| N(8)-Hf(3)-N(4)  | 91.9(4)  | N(9)-Hf(3)-N(4)   | 90.6(4)     |
| N(10)-Hf(3)-N(4) | 159.1(4) | N(3)-Hf(3)-N(4)   | 73.1(3)     |
| N(8)-Hf(3)-Hf(2) | 108.1(3) | N(9)-Hf(3)-Hf(2)  | 121.4(3)    |

**Table 4.10** Continued

|                   |           |                  |           |
|-------------------|-----------|------------------|-----------|
| N(10)-Hf(3)-Hf(2) | 117.3(3)  | N(3)-Hf(3)-Hf(2) | 43.6(2)   |
| N(4)-Hf(3)-Hf(2)  | 41.9(2)   | C(2)-N(1)-C(1)   | 111.0(10) |
| C(2)-N(1)-Hf(2)   | 129.9(8)  | C(1)-N(1)-Hf(2)  | 97.8(8)   |
| C(2)-N(1)-Hf(1)   | 114.3(8)  | C(1)-N(1)-Hf(1)  | 112.8(7)  |
| Hf(2)-N(1)-Hf(1)  | 88.7(3)   | C(3)-N(2)-C(4)   | 109.1(10) |
| C(3)-N(2)-Hf(2)   | 113.7(8)  | C(4)-N(2)-Hf(2)  | 113.7(9)  |
| C(3)-N(2)-Hf(1)   | 111.6(7)  | C(4)-N(2)-Hf(1)  | 120.6(8)  |
| Hf(2)-N(2)-Hf(1)  | 86.6(3)   | C(6)-N(3)-C(5)   | 108.4(10) |
| C(6)-N(3)-Hf(2)   | 127.3(8)  | C(5)-N(3)-Hf(2)  | 104.8(7)  |
| C(6)-N(3)-Hf(3)   | 113.7(7)  | C(5)-N(3)-Hf(3)  | 113.4(7)  |
| Hf(2)-N(3)-Hf(3)  | 88.0(3)   | C(8)-N(4)-C(7)   | 108.2(11) |
| C(8)-N(4)-Hf(2)   | 119.9(9)  | C(7)-N(4)-Hf(2)  | 112.5(8)  |
| C(8)-N(4)-Hf(3)   | 118.0(8)  | C(7)-N(4)-Hf(3)  | 111.7(8)  |
| Hf(2)-N(4)-Hf(3)  | 85.1(3)   | C(10)-N(5)-C(9)  | 110.2(11) |
| C(10)-N(5)-Hf(1)  | 127.4(9)  | C(9)-N(5)-Hf(1)  | 122.1(9)  |
| C(11)-N(6)-C(12)  | 108.9(12) | C(11)-N(6)-Hf(1) | 133.9(9)  |
| C(12)-N(6)-Hf(1)  | 116.8(11) | C(14)-N(7)-C(13) | 108.5(11) |
| C(14)-N(7)-Hf(1)  | 128.9(9)  | C(13)-N(7)-Hf(1) | 122.4(9)  |
| C(15)-N(8)-C(16)  | 106.5(11) | C(15)-N(8)-Hf(3) | 138.1(9)  |
| C(16)-N(8)-Hf(3)  | 113.1(8)  | C(18)-N(9)-C(17) | 107.7(11) |
| C(18)-N(9)-Hf(3)  | 122.4(9)  | C(17)-N(9)-Hf(3) | 129.8(10) |

**Table 4.10** Continued

|                   |           |                   |          |
|-------------------|-----------|-------------------|----------|
| C(19)-N(10)-C(20) | 108.4(12) | C(19)-N(10)-Hf(3) | 129.0(9) |
| C(20)-N(10)-Hf(3) | 122.4(9)  |                   |          |

**Table 4.11** Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic DisplacementParameters ( $\text{\AA}^2 \times 10^3$ ) for **8<sup>a</sup>**

|       | x         | y         | z         | <i>U</i> (eq) |
|-------|-----------|-----------|-----------|---------------|
| Hf(1) | 4123.1(3) | 7642.9(3) | 3398.6(3) | 19(1)         |
| Hf(2) | 6528.6(3) | 7673.2(3) | 4210.8(3) | 17(1)         |
| Hf(3) | 8894.4(3) | 7460.0(3) | 5270.0(3) | 19(1)         |
| N(1)  | 5398(7)   | 8521(7)   | 3230(6)   | 23(2)         |
| N(2)  | 5523(7)   | 7753(7)   | 4855(6)   | 23(2)         |
| N(3)  | 7798(7)   | 8554(6)   | 4319(5)   | 18(2)         |
| N(4)  | 7459(7)   | 6586(7)   | 4128(6)   | 22(2)         |
| N(5)  | 3335(7)   | 8621(7)   | 3736(7)   | 26(2)         |
| N(6)  | 3635(8)   | 6424(8)   | 3694(7)   | 27(2)         |
| N(7)  | 3307(7)   | 7584(8)   | 2074(6)   | 27(2)         |
| N(8)  | 9129(8)   | 6447(7)   | 6154(7)   | 27(2)         |
| N(9)  | 9836(8)   | 7146(9)   | 4670(6)   | 29(2)         |
| N(10) | 9614(7)   | 8455(8)   | 6151(7)   | 28(2)         |
| C(1)  | 5616(9)   | 8232(11)  | 2477(8)   | 32(3)         |
| C(2)  | 5235(9)   | 9493(9)   | 3217(9)   | 30(3)         |
| C(3)  | 5558(9)   | 6960(10)  | 5382(7)   | 30(3)         |
| C(4)  | 5656(12)  | 8582(11)  | 5384(9)   | 44(4)         |
| C(5)  | 7671(11)  | 9366(9)   | 4757(9)   | 32(3)         |

**Table 4.11** Continued

|       | x         | y        | z        | $U(\text{eq})$ |
|-------|-----------|----------|----------|----------------|
| C(6)  | 8097(9)   | 8830(10) | 3630(8)  | 30(3)          |
| C(7)  | 7246(10)  | 5727(10) | 4471(10) | 37(3)          |
| C(8)  | 538(12)   | 6391(12) | 3307(9)  | 43(4)          |
| C(9)  | 3222(10)  | 8595(12) | 4556(9)  | 40(3)          |
| C(10) | 2732(11)  | 9358(11) | 3198(10) | 42(3)          |
| C(11) | 3992(11)  | 5513(10) | 3767(12) | 44(4)          |
| C(12) | 2656(13)  | 6426(13) | 3754(15) | 60(5)          |
| C(13) | 2736(14)  | 6786(12) | 1647(10) | 52(4)          |
| C(14) | 3121(10)  | 8286(11) | 1450(8)  | 37(3)          |
| C(15) | 8608(10)  | 6041(14) | 6633(10) | 48(4)          |
| C(16) | 10212(10) | 6205(12) | 6616(10) | 42(4)          |
| C(17) | 10440(10) | 7741(13) | 4376(10) | 43(4)          |
| C(18) | 10039(11) | 6233(12) | 4509(11) | 44(4)          |
| C(19) | 10126(11) | 9268(11) | 6041(11) | 40(3)          |
| C(20) | 9597(14)  | 8482(12) | 7009(10) | 48(4)          |

<sup>a</sup>  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

**Table 4.12** Anisotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for **8<sup>a</sup>**

|       | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|-------|----------|----------|----------|----------|----------|----------|
| Hf(1) | 15(1)    | 24(1)    | 18(1)    | -1(1)    | 6(1)     | -2(1)    |
| Hf(2) | 14(1)    | 22(1)    | 16(1)    | 0(1)     | 6(1)     | -2(1)    |
| Hf(3) | 14(1)    | 23(1)    | 20(1)    | 1(1)     | 6(1)     | -1(1)    |
| N(1)  | 22(5)    | 31(5)    | 8(4)     | 4(4)     | 0(3)     | -5(4)    |
| N(2)  | 20(5)    | 40(6)    | 9(4)     | -1(4)    | 7(3)     | -7(4)    |
| N(3)  | 15(4)    | 24(5)    | 13(4)    | 5(3)     | 5(3)     | 4(3)     |
| N(4)  | 12(4)    | 28(5)    | 25(5)    | -7(4)    | 8(4)     | 2(4)     |
| N(5)  | 21(5)    | 22(5)    | 38(6)    | -10(4)   | 16(4)    | -3(4)    |
| N(6)  | 24(5)    | 31(6)    | 32(5)    | -6(4)    | 17(4)    | -12(4)   |
| N(7)  | 13(4)    | 41(6)    | 14(4)    | 3(4)     | -7(3)    | 3(4)     |
| N(8)  | 29(5)    | 20(5)    | 34(6)    | 1(4)     | 14(5)    | 2(4)     |
| N(9)  | 21(5)    | 50(7)    | 22(5)    | -3(5)    | 13(4)    | -1(5)    |
| N(10) | 19(5)    | 35(6)    | 27(5)    | 2(4)     | 7(4)     | -6(4)    |
| C(1)  | 17(5)    | 57(9)    | 22(5)    | -4(6)    | 8(5)     | -4(6)    |
| C(2)  | 21(6)    | 30(6)    | 34(6)    | 0(5)     | 5(5)     | -1(5)    |
| C(3)  | 19(5)    | 48(8)    | 18(5)    | 13(5)    | 4(4)     | -2(5)    |
| C(4)  | 47(9)    | 43(9)    | 31(7)    | -14(6)   | 6(6)     | -1(7)    |
| C(5)  | 37(7)    | 28(7)    | 34(7)    | -10(5)   | 15(6)    | 1(5)     |
| C(6)  | 22(6)    | 38(7)    | 32(6)    | 11(5)    | 14(5)    | -3(5)    |

**Table 4.12 Continued**

|       | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|-------|----------|----------|----------|----------|----------|----------|
| C(7)  | 17(6)    | 36(7)    | 46(8)    | 3(6)     | 0(6)     | -1(5)    |
| C(8)  | 44(8)    | 57(10)   | 26(7)    | -19(7)   | 12(6)    | -8(7)    |
| C(9)  | 26(7)    | 63(10)   | 36(7)    | -4(7)    | 17(6)    | 8(6)     |
| C(10) | 29(7)    | 39(8)    | 45(8)    | 3(7)     | 2(6)     | 15(6)    |
| C(11) | 35(8)    | 33(7)    | 65(10)   | 5(7)     | 21(7)    | -5(6)    |
| C(12) | 38(9)    | 52(10)   | 104(16)  | -15(10)  | 43(10)   | -19(8)   |
| C(13) | 64(11)   | 47(9)    | 34(7)    | -9(7)    | 7(7)     | -26(8)   |
| C(14) | 30(7)    | 53(9)    | 24(6)    | 2(6)     | 7(5)     | 0(6)     |
| C(15) | 21(6)    | 76(12)   | 40(8)    | 22(8)    | 6(6)     | -8(7)    |
| C(16) | 28(7)    | 52(9)    | 46(8)    | 15(7)    | 14(6)    | 12(6)    |
| C(17) | 21(6)    | 71(11)   | 45(8)    | -2(8)    | 21(6)    | -4(7)    |
| C(18) | 33(7)    | 52(9)    | 51(9)    | -10(7)   | 21(7)    | 2(7)     |
| C(19) | 27(7)    | 43(8)    | 52(9)    | 0(7)     | 17(7)    | -12(6)   |
| C(20) | 71(11)   | 47(9)    | 32(7)    | -9(7)    | 27(8)    | -12(8)   |

<sup>a</sup> The anisotropic displacement factor exponent takes the form:  $-2\pi^2[(ha^*)^2U_{11} + (kb^*)^2U_{22} + (lc^*)^2U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2lkc^*b^*U_{23}]$ .

**Table 4.13** Hydrogen Coordinates ( $\times 10^4$ ) and Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for **8**

|       | x    | y    | z    | $U(\text{eq})$ |
|-------|------|------|------|----------------|
| H(1A) | 4985 | 8153 | 1977 | 48             |
| H(1B) | 5983 | 7661 | 2609 | 48             |
| H(1C) | 6021 | 8692 | 2355 | 48             |
| H(2A) | 5234 | 9683 | 3766 | 45             |
| H(2B) | 4590 | 9642 | 2757 | 45             |
| H(2C) | 5772 | 9805 | 3119 | 45             |
| H(3A) | 6171 | 6976 | 5905 | 45             |
| H(3B) | 5550 | 6412 | 5060 | 45             |
| H(3C) | 4975 | 6963 | 5531 | 45             |
| H(4A) | 5107 | 8628 | 5574 | 65             |
| H(4B) | 5654 | 9111 | 5041 | 65             |
| H(4C) | 6294 | 8549 | 5883 | 65             |
| H(5A) | 8319 | 9664 | 5044 | 49             |
| H(5B) | 7405 | 9197 | 5180 | 49             |
| H(5C) | 7203 | 9777 | 4337 | 49             |
| H(6A) | 7627 | 9283 | 3273 | 44             |
| H(6B) | 8091 | 8306 | 3280 | 44             |
| H(6C) | 8772 | 9086 | 3877 | 44             |
| H(7A) | 6654 | 5442 | 4039 | 56             |

**Table 4.13** Continued

|        | x    | y    | z    | <i>U</i> (eq) |
|--------|------|------|------|---------------|
| H(7B)  | 7123 | 5850 | 4985 | 56            |
| H(7C)  | 7821 | 5322 | 4617 | 56            |
| H(8A)  | 8055 | 5935 | 3397 | 65            |
| H(8B)  | 7716 | 6943 | 3086 | 65            |
| H(8C)  | 6894 | 6167 | 2894 | 65            |
| H(9A)  | 3470 | 9160 | 4865 | 60            |
| H(9B)  | 3607 | 8090 | 4899 | 60            |
| H(9C)  | 2515 | 8520 | 4448 | 60            |
| H(10A) | 2046 | 9319 | 3163 | 63            |
| H(10B) | 2725 | 9309 | 2623 | 63            |
| H(10C) | 3024 | 9937 | 3449 | 63            |
| H(11A) | 4031 | 5254 | 4307 | 66            |
| H(11B) | 4658 | 5508 | 3754 | 66            |
| H(11C) | 3532 | 5156 | 3288 | 66            |
| H(12A) | 2233 | 5953 | 3385 | 90            |
| H(12B) | 2334 | 7012 | 3569 | 90            |
| H(12C) | 2749 | 6314 | 4347 | 90            |
| H(13A) | 2020 | 6928 | 1406 | 78            |
| H(13B) | 2869 | 6296 | 2062 | 78            |
| H(13C) | 2936 | 6601 | 1187 | 78            |

**Table 4.13 Continued**

|        | x     | y    | z    | $U(\text{eq})$ |
|--------|-------|------|------|----------------|
| H(14A) | 3354  | 8093 | 1011 | 55             |
| H(14B) | 3480  | 8831 | 1729 | 55             |
| H(14C) | 2402  | 8411 | 1182 | 55             |
| H(15A) | 8446  | 5415 | 6453 | 71             |
| H(15B) | 7989  | 6375 | 6524 | 71             |
| H(15C) | 9036  | 6061 | 7244 | 71             |
| H(16A) | 10605 | 6512 | 6347 | 63             |
| H(16B) | 10292 | 5553 | 6589 | 63             |
| H(16C) | 10444 | 6394 | 7215 | 63             |
| H(17A) | 11142 | 7554 | 4638 | 64             |

---Zr angle of  $124.14(1)^\circ$ . In contrast, the Zr atoms in **7** are almost linear with the Zr---Zr---Zr angle of  $170.48(2)^\circ$ . The middle and two terminal Zr atoms in **7** adopt a trigonal prismatic and trigonal antiprismatic geometries, respectively. The hydride ligands are closer to the central [av. Zr(1)-H =  $1.91(4)$  Å] than to the terminal Zr atoms [av. Zr-H =  $2.15(4)$  Å]. The Zr-H and Zr-N lengths are similar to those in other bridging Zr hydrides,<sup>8f,15a,16a-d,19</sup> and Zr amide complexes, respectively.<sup>20</sup> The Zr-N bonds between the bridging amides and central Zr(2) atom [Zr-N<sub>av</sub> =  $2.174(4)$  Å] are longer than the bonds between terminal amide ligands and terminal Zr(1) and Zr(3) atoms [Zr-N<sub>av</sub> =  $2.062(4)$  Å], but significantly shorter than the bonds between the bridging amides and the terminal Zr(1) and Zr(3) atoms [Zr-N<sub>av</sub> =  $2.473(4)$  Å]. The packing diagram of **7** shows that each unit cell contains four independent molecules of **7**.

The Hf amide hydride complex **8** is similar to its Zr analogue **7**. The data set for **8** was not good enough to reveal the two bridging hydride ligands. The three Hf atoms in **8** are nearly linear with an angle of  $169.717(19)^\circ$ . The Hf-N bonds between the bridging amides and central Hf(2) atom [Hf-N<sub>av</sub> =  $2.185(10)$  Å] are longer than the bonds between terminal amide ligands and terminal Hf(1) and Hf(3) atoms [Hf-N<sub>av</sub> =  $2.075(11)$  Å], but significantly shorter than the bonds between the bridging amides and the terminal Hf(1) and Hf(3) atoms [Hf-N<sub>av</sub> =  $2.467(10)$  Å]. The average terminal Hf-N length of  $2.075(11)$  Å in **8** is close to that [ $2.084(3)$  Å] in [(Aryl)NCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O]HfEt<sub>2</sub> (Aryl = 2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>) that Schrock and coworkers reported recently.<sup>21</sup>

Although the Zr and Hf amide hydride complexes are similar, the crystals of **7** and **8** are not isomorphous. In **8**, the length of *c* axis is  $17.0738(3)$  Å. In **7**, this length is  $26.154(4)$  Å. The packing diagrams of **7** and **8** are shown in Figures 4.5 and 4.6,

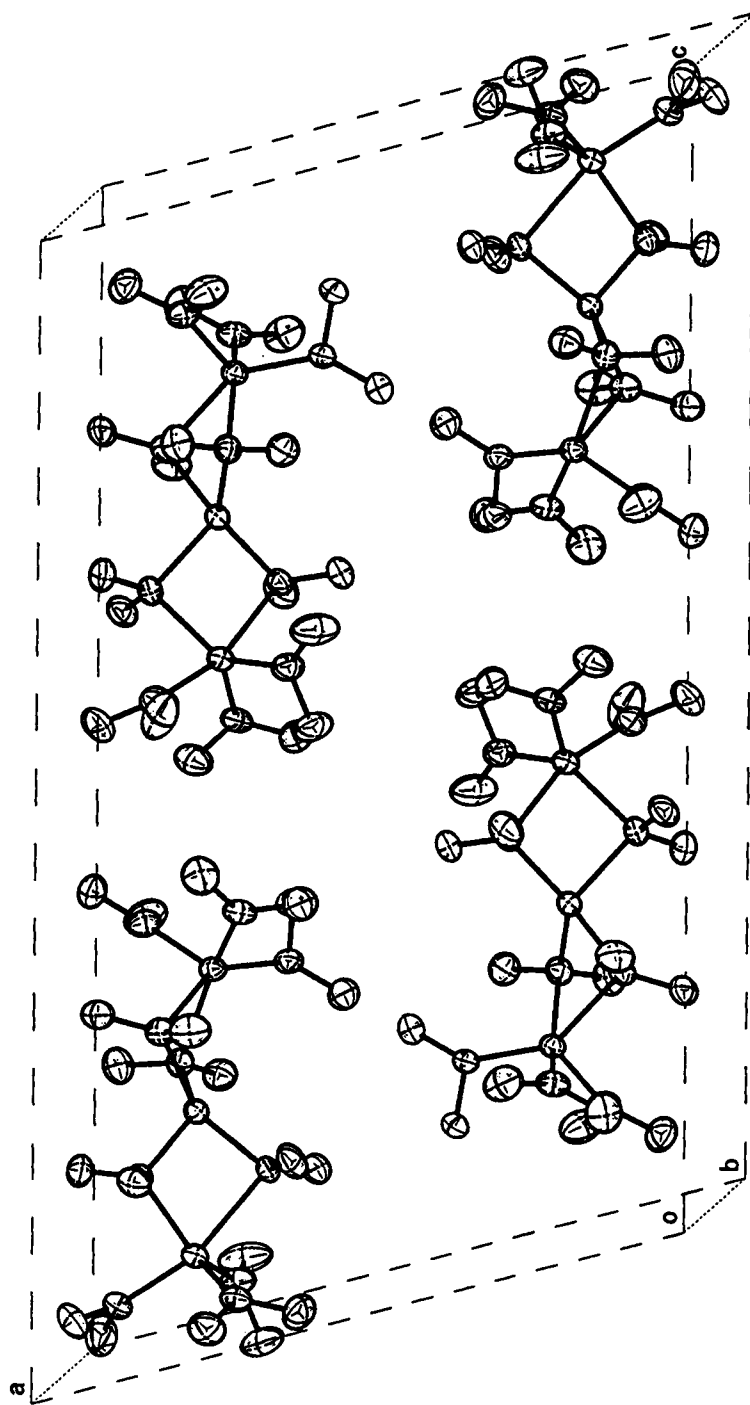


Figure 4.5 Packing diagram of 7.

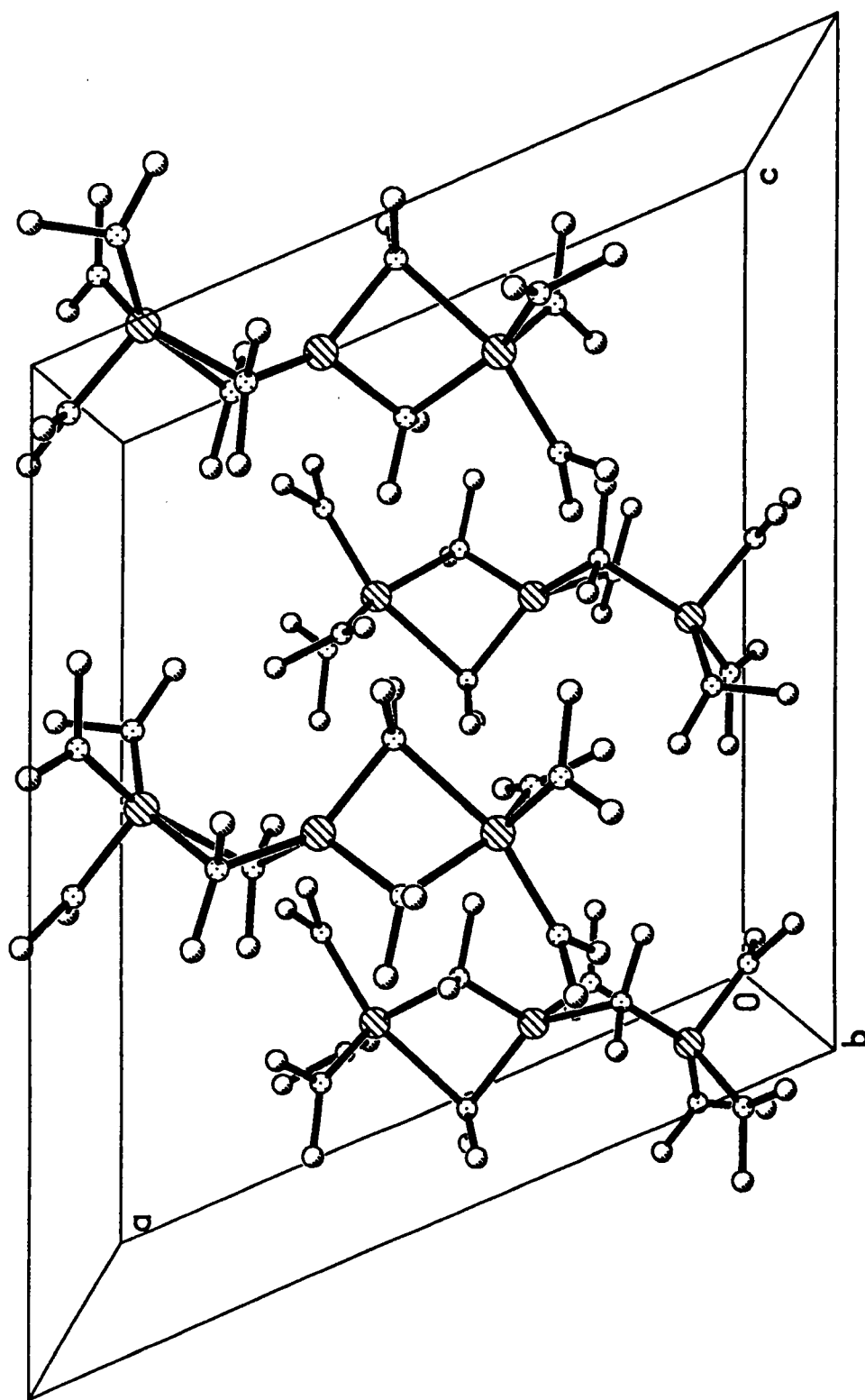


Figure 4.6 Packing diagram of 8.

respectively. There are four independent molecules in both unit cells. However, the four molecules of **8** are packed much tighter along the *c* direction. The  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and NOESY (Figures 4.7) spectrum of **7** is consistent with the X-ray structures.

#### 4.2.4 Variable Temperature NMR Study of **7**

The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of  $[(\text{Me}_2\text{N})_3\text{M}(\mu\text{-H})(\mu\text{-NMe}_2)_2]_2\text{M}$  ( $\text{M} = \text{Zr}$ , **7**;  $\text{Hf}$ , **8**) are consistent with the structure assignment. The bridging hydrides of **7** were observed at 5.21 ppm in  $^1\text{H}$  NMR at 23 °C. The resonance of bridging hydrides in **8** was down-field shifted to 9.87 ppm in  $^1\text{H}$  NMR at 23 °C. The amido resonances of **7** and **8** appear as one broad singlet at 2.98 (**7**) and 3.01 (**8**) ppm in  $^1\text{H}$  NMR and 44.54 (**7**) and 44.25 (**8**) ppm in  $^{13}\text{C}\{^1\text{H}\}$  NMR at 23 °C, indicating an exchange between the terminal and bridging amide ligands.

The variable-temperature  $^1\text{H}$  NMR spectra of **7** were studied, and are shown in Figure 4.8. Upon cooling a toluene- $d_8$  solution of **7**, the broad signal of the terminal and bridging amide ligands gradually disappeared to give separate bridging and terminal amide peaks. At -70 °C, there were one terminal and four distinct bridging amide resonances. At -50 °C, all bridging amide resonances first coalesced to give a single peak, along with the peak of the terminal amide ligands. The peaks of the bridging and terminal amide ligands coalesced at -20 °C. The first coalescence of the bridging amide resonances at -50 °C, followed by the coalescence of the bridging and terminal amide resonances, indicates that the rates of bridging/bridging ligand exchanges are faster than the bridging/terminal exchange. The estimated activation free energy of

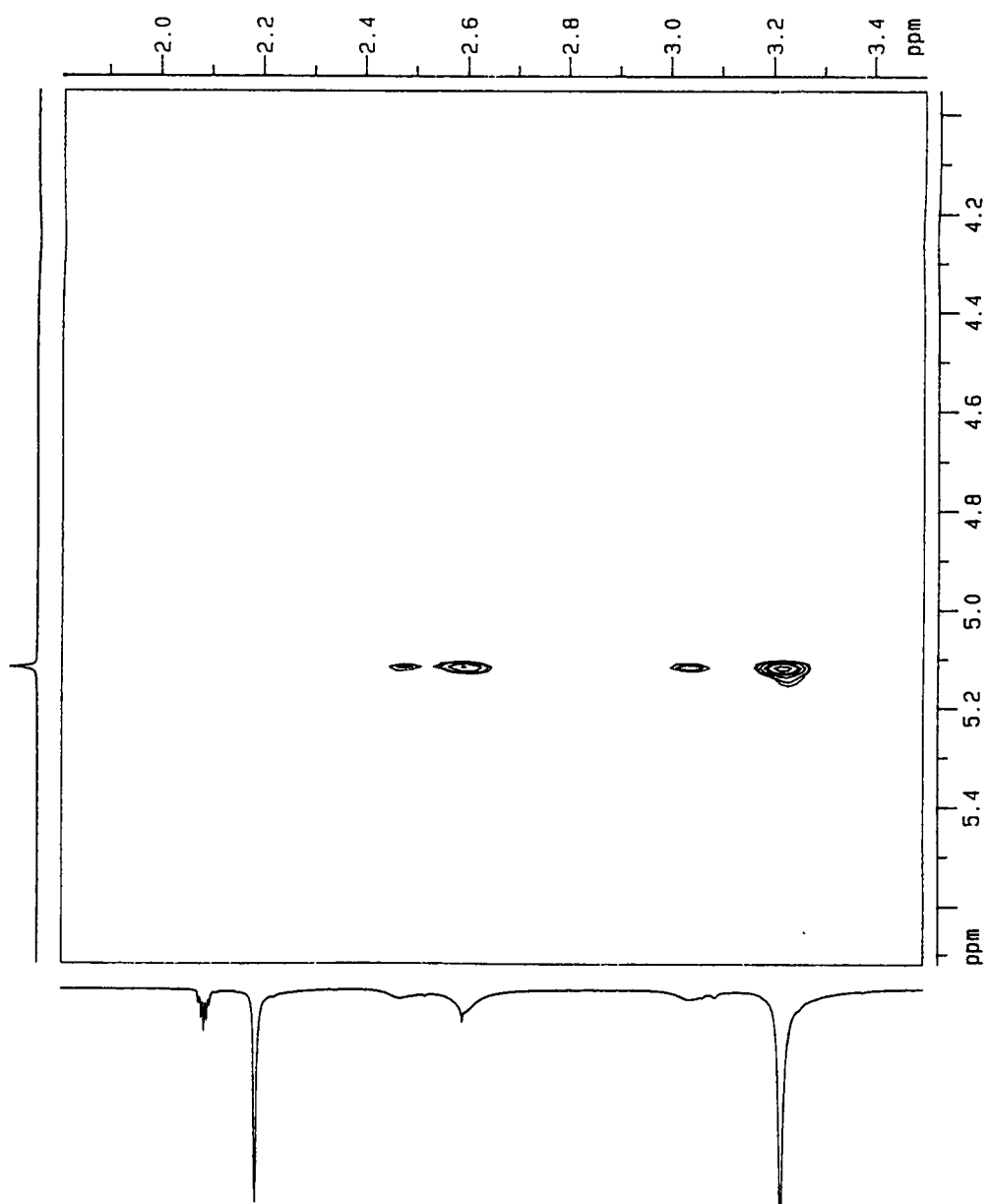


**Figure 4.7** NOSEY spectrum of **7** at 213 K.

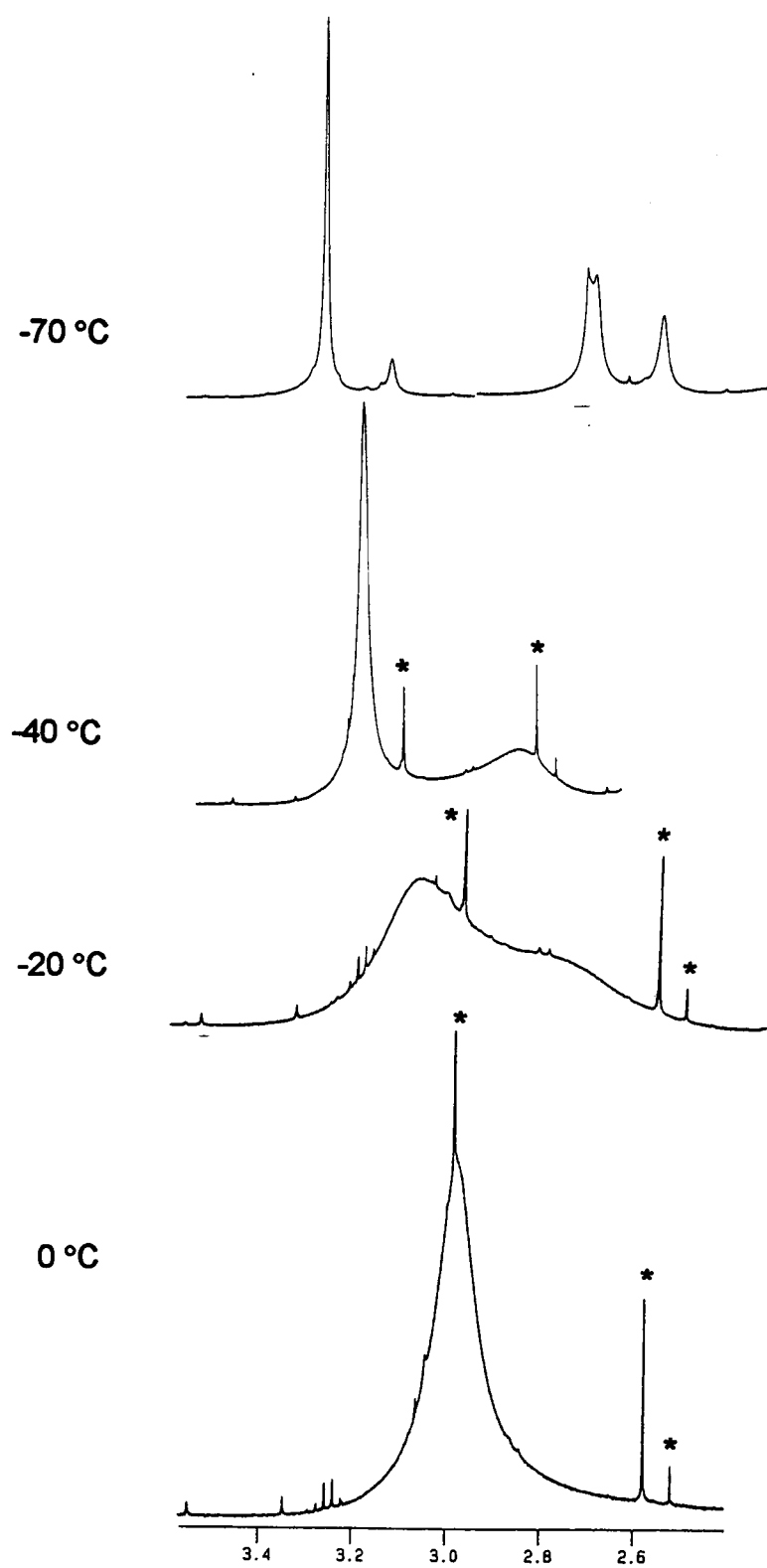


**Figure 4.8** Variable temperature  $^1\text{H}$  NMR spectra of 7. (\* Impurity)

bridging/bridging ligand exchange  $\Delta G^{\ddagger}_{222\text{ K}}$  is  $12.6 \pm 0.5$  kcal/mol. This bridging amide ligand exchange was perhaps the result of an internal rotation of the molecule with respect to Zr--Zr--Zr axis.

Exchanges between bridging and terminal amide ligands are well known. Such an exchange was observed in  $(\text{Me}_2\text{N})_3\text{Zr}(\mu\text{-Cl})_2(\mu\text{-NMe}_2)\text{Zr}(\text{NMe}_2)_2(\text{THF})$ .<sup>20</sup> The activation free energy  $\Delta G^{\ddagger}$  of  $11.4 \pm 0.5$  kcal/mol for this exchange is comparable to that in 7.

#### 4.2.5 Reactions of $(\text{Me}_2\text{N})_3\text{ZrSi}(\text{SiMe}_3)_3$ (5b) with Silanes

In the reactions of  $\text{M}(\text{NMe}_2)_4$  with  $\text{SiH}_4$  to give M-Si-N ternary materials, the intermediates "HM(NMe<sub>2</sub>)<sub>3</sub>" (9, Figure 4.2) or  $[(\text{Me}_2\text{N})_3\text{M}(\mu\text{-H})(\mu\text{-NMe}_2)_2]_2\text{M}$  (M = Zr, 7; Hf, 8) may react with  $\text{SiH}_4$  further to give "H<sub>2</sub>M(NMe<sub>2</sub>)<sub>2</sub>" (10) or "(Me<sub>2</sub>N)<sub>3</sub>M-SiH<sub>3</sub>" (5c). We have not directly observed either 9 or 5c, and have thus studied the reactions of  $(\text{Me}_2\text{N})_3\text{ZrSi}(\text{SiMe}_3)_3$  (5b),<sup>22</sup> a model for 5a-c (Figure 4.2), with  $\text{H}_2\text{SiR}'_2$  (R' = HPh, Ph<sub>2</sub>, MePh). These reactions were found to give an unstable hydride complex  $(\text{Me}_2\text{N})_2\text{Zr}(\text{H})\text{Si}(\text{SiMe}_3)_3$  (6) and  $\text{HSi}(\text{NMe}_2)\text{R}'_2$ , and to reach equilibria (Figure 4.9). The equilibrium  $5\text{b} + \text{H}_2\text{SiPh}_2 \rightleftharpoons 6 + \text{HSi}(\text{NMe}_2)\text{Ph}_2$  was found to favor 5b and  $\text{H}_2\text{SiPh}_2$  at 0 °C, as shown in the equilibrium constant  $K_{\text{eq}}$  [0.11(0.01)] and  $\Delta G^\circ$  [1.20(0.05) kcal/mol] at this temperature. The addition of  $\text{HSi}(\text{NMe}_2)\text{Ph}_2$  to the equilibrium involving  $\text{H}_2\text{SiMePh}$  in Figure 4.9 yielded  $\text{H}_2\text{SiPh}_2$ . This observation confirmed that the reactions of these d<sup>0</sup> amide complexes with silanes to form hydrides and aminosilanes were reversible. To our knowledge, the current study represents the first direct

observation of hydrides in the reactions of transition metal amides with silanes through unusual equilibria.<sup>5,6,10,13</sup>

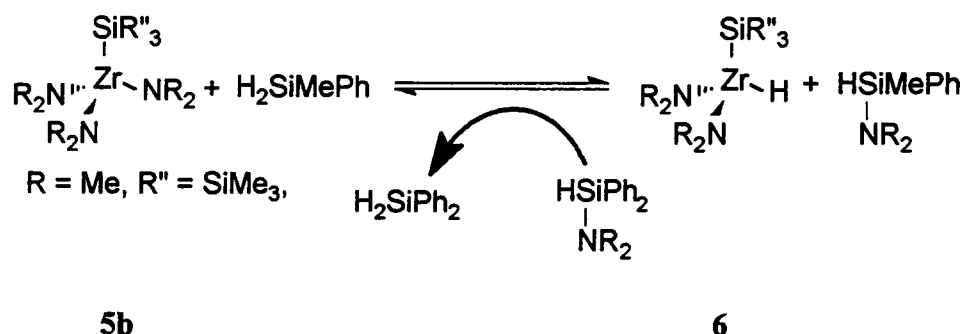


**Figure 4.9** Exchanges between 5b and 6.

#### 4.2.6 *Ab Initio* MO Calculations of the Reactions between $\text{Ti}(\text{NR}_2)_4$ and $\text{SiH}_4$

Theoretical calculations were carried out by Professor Yun-Dong Wu and his research group at the Hong Kong University of Science and Technology to study the reactions between model complexes  $\text{Ti}(\text{NR}_2)_4$  ( $\text{R} = \text{H}$  and  $\text{Me}$ ) and  $\text{SiH}_4$ . The results of these calculations support our experimental observations and are summarized here.

$\text{Ti}(\text{NH}_2)_4$  was chosen for  $\text{Ti}(\text{NMe}_2)_4$  in order to reduce the base matrix of the high level computing calculations required in this molecular orbital quantum mechanics analysis. This analysis through the calculations holds true only if the simplified model represents well the actual molecule. In this case, this assumption is valid, since the geometries of both simplified model and actual molecule are close.

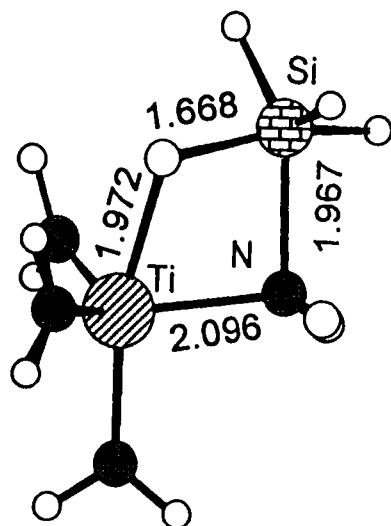
As indicated in Figure 4.2, there are two possible pathways for the  $\sigma$ -bond metathesis reactions between  $\text{Ti}(\text{NR}_2)_4$  and  $\text{SiH}_4$ . The two transition states **A** and **B** lead to the formation of aminosilane  $\text{H}_3\text{Si-NH}_2$  and ammonia  $\text{NH}_3$ , respectively. The two

calculated transition structures A and B (HF/HW3) and their energies (MP2/HW3) are listed in Figure 4.10. Transition state B would lead to the transfer of hydrogen from Si to a -NH<sub>2</sub> ligand. Transition state A giving aminosilane H<sub>3</sub>Si-NH<sub>2</sub> is lower than B by 18.8 kcal/mol. The transition state C for the reaction of Ti(NMe<sub>2</sub>)<sub>4</sub> with SiH<sub>4</sub> was also calculated, and is shown in Figure 4.10. The geometry of this transition state and activation energy of the reaction are essentially the same as A, suggesting that Ti(NH<sub>2</sub>)<sub>4</sub> was a correct model for Ti(NMe<sub>2</sub>)<sub>4</sub> in its reaction with SiH<sub>4</sub>.

#### 4.2.7 The First Step in the Reactions of M(NMe<sub>2</sub>)<sub>4</sub> (M = Ti, Zr, Hf) with Silanes – Mechanistic Considerations

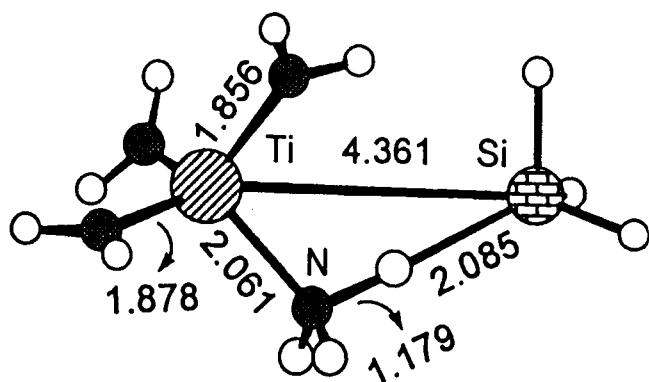
Both the experimental and theoretical studies suggested that M(NMe<sub>2</sub>)<sub>4</sub> (M = Ti, Zr, Hf) and silanes undergo  $\sigma$ -bond metathesis through transition state A (Figure 4.10). Nevertheless, if such reactions proceed through B, the amine HNR<sub>2</sub> (or NH<sub>3</sub>) thus produced could further react with silanes to form aminosilanes and H<sub>2</sub> in the presence of a catalyst.<sup>23</sup> In order to exclude this pathway, we investigated whether HNMe<sub>2</sub> could survive the conditions of the reaction between Zr(NMe<sub>2</sub>)<sub>4</sub> and H<sub>2</sub>SiPh<sub>2</sub>. Our studies suggest that the reaction of HNMe<sub>2</sub> with H<sub>2</sub>SiPh<sub>2</sub>, if occurred, would be much slower than that of Zr(NMe<sub>2</sub>)<sub>4</sub> with H<sub>2</sub>SiPh<sub>2</sub>. Although we cannot rule out transition state B, the isolation of 7 and 8, the observation of 10, and the *ab initio* MO calculations indicate that transition state A is more likely and favored. Such preference for A in these metathesis reactions between M <sup>$\delta^+$</sup> -N <sup>$\delta^-$</sup> Me<sub>2</sub> (M = Ti, Zr) *d-p*  $\pi$  and H <sup>$\delta^-$</sup> -Si <sup>$\delta^+$</sup>  bonds could perhaps also be explained by the electronegativity differences between M and N as well as between H

**Figure 4.10** Transition structures (HF/HW3) for the reactions of  $\text{Ti}(\text{NH}_2)_4$  and  $\text{Ti}(\text{NMe}_2)_4$  with  $\text{SiH}_4$ , and MP2/HW3 activation enthalpies.

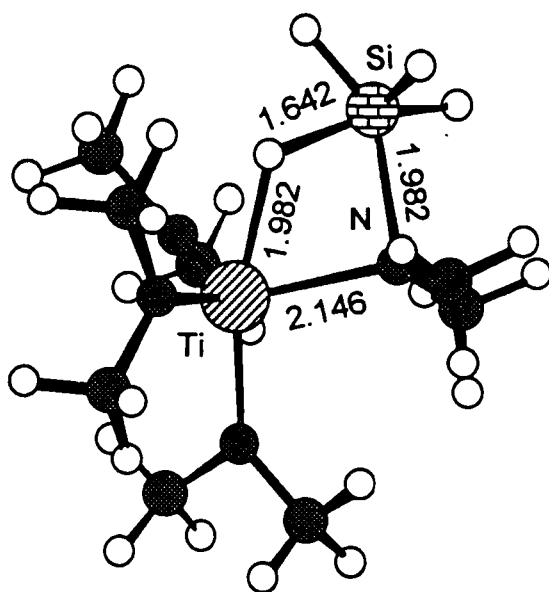


$\Delta H^\ddagger$  (kcal/mol)

A 18.2



B 37.0



C 19.5

and Si.<sup>24</sup> The zirconium-nitrogen bond reacts with polarized  $H^{\delta-}-Si^{\delta+}$  bonds to place the more electronegative group on zirconium and the less electronegative group on nitrogen (Figure 4.11). In other words, such a reaction is a nucleophilic attack on the incoming silane by the *d-p*  $\pi$  bond in  $M-NMe_2$ . The reactions of the  $Ta=CHR$   $\pi$  bond in a metal alkylidene complex  $(Me_3SiCH_2)_3Ta(PMe_3)[=CHSiMe_3]$  with phenyl-containing silanes  $H_2SiPhR$  ( $R = Me, Ph, H$ ), were found to follow similar pathways (Figure 4.12) with the formation of a disilylalkylidene product.<sup>13,25</sup>

The studies presented in this chapter indicated that the first step in the CVD of Ti-Si-N thin films involving  $Ti(NMe_2)_4$  and  $SiH_4$  yielded " $HTi(NMe_2)_3$ " and  $H_3Si(NMe_2)$ . The analyses of the black solids in the current chapter suggested that in the following steps similar reactions occurred to give black solids containing hydride and unreacted amide ligands. The role of silane here was to remove amide ligands [as aminosilanes  $H_nSi(NMe_2)_{4-n}$  ( $n = 1, 2$ )]. Subsequently the two types of products, the black solids containing  $-H$  and  $-NMe_2$ , and the aminosilanes  $H_nSi(NMe_2)_{4-n}$ , perhaps underwent *separate* thermal decompositions to give  $TiN$  and  $Si_3N_4$ , respectively. In other words, the reaction pathways led to the formation of the two types of intermediates (the black solids and aminosilanes) that likely yielded the two solid compounds observed in the Ti-Si-N ternary films in Chapter 3.  $H_nSi(NMe_2)_{4-n}$  have been used as precursors in chemical vapor deposition of  $Si_3N_4$ .<sup>26</sup> The reactivity of the  $Ti-NMe_2$  and  $H-Si$  bonds seemed to forbid the formation of intermediates with  $Ti-Si$  bonds. This perhaps explained why silicides  $TiSi_n$  were either not present or not the major products in the Ti-Si-N ternary films.

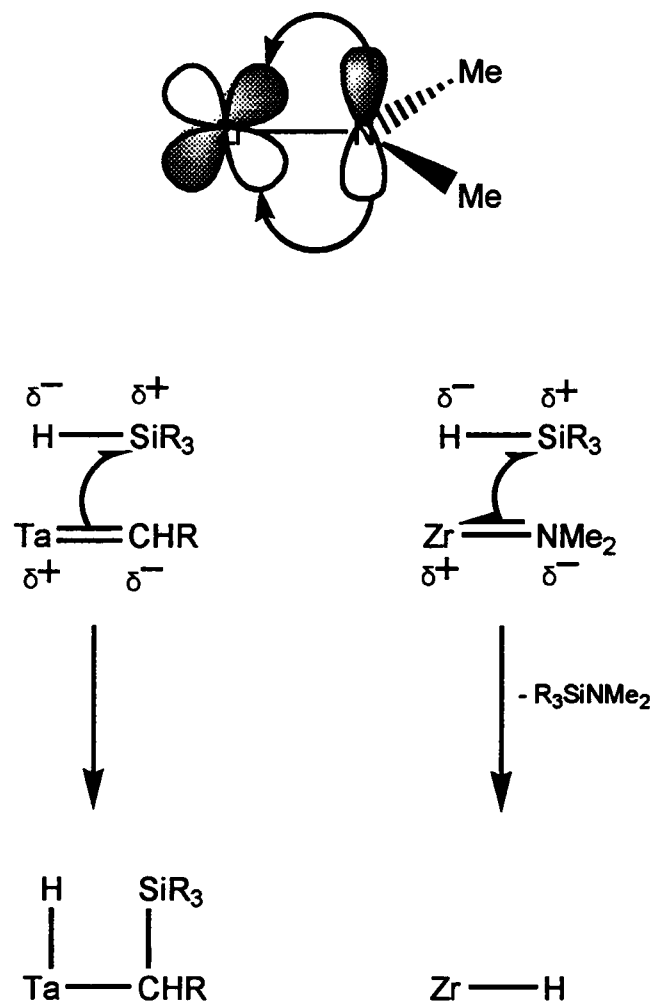


**Figure 4.11** Schematic diagram of the reaction between a M-N ( $M = \text{Ta}, \text{Zr}$ ) bond and a Si-H bond.

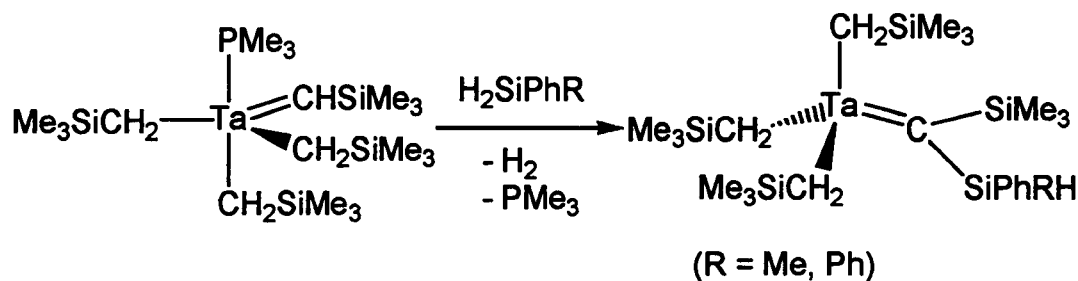


**Figure 4.12** Reactions of a tantalum alkylidene complex with silanes.

### 4.3 Experimental Section

#### 4.3.1 General Procedure

All manipulations, unless noted, were performed under a dry nitrogen atmosphere with the use of either a drybox or standard Schlenk techniques. All solvents were purified by distillation from potassium/benzophenone ketyl. Silanes were dried by molecular sieves, and degassed by  $\text{N}_2$ . Benzene- $d_6$  and toluene- $d_8$  were dried over activated molecular sieves and stored under  $\text{N}_2$ .  $\text{H}_3\text{SiPh}$  (Aldrich),  $\text{H}_2\text{SiPh}_2$  (Aldrich), and  $\text{H}_2\text{SiMePh}$  (Gelest) were stored under  $\text{N}_2$  and used as received. 5%  $\text{SiH}_4$  in Ar was used as received from Air Products; a glass manifold with PTFE vales and stainless steel hoses was used for gas transfers at near-ambient pressures.  $\text{Ph}_2\text{SiCl}_2$  (Gelest) was purified by distillation at 100 °C/0.05 Torr.  $\text{ZrCl}_4$  (Strem) and  $\text{HfCl}_4$  (Strem) were freshly sublimed.  $\text{Zr}(\text{NMe}_2)_4$ ,<sup>27</sup>  $\text{Hf}(\text{NMe}_2)_4$ ,<sup>27a</sup> and  $(\text{Me}_2\text{N})_3\text{ZrSi}(\text{SiMe}_3)_3$  (**5b**)<sup>22</sup> were prepared by the literature procedures.  $\text{D}_2\text{SiPh}_2$  was prepared by  $\text{LiAlD}_4$  reduction of  $\text{Ph}_2\text{SiCl}_2$ .<sup>28</sup> Dimethylamine gas was generated by bubbling  $\text{N}_2$  through a 40 wt.% aqueous solution of  $\text{HNMe}_2$  (Aldrich), dried over a KOH-filled column, and then condensed as a liquid at -78 °C.  $\text{DCl}$  (37 wt.% solution in  $\text{D}_2\text{O}$ , 100 g) was purchased

from Aldrich, and then diluted with 103 g of D<sub>2</sub>O to form a 1 M solution.

One-dimensional <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra, unless noted, were recorded at 23 °C on a Bruker AC-250 or AMX-400 spectrometer and referenced to solvents (residual protons in the <sup>1</sup>H spectra). The <sup>29</sup>Si{<sup>1</sup>H} (DEPT) NMR spectra were referenced to SiMe<sub>4</sub>. <sup>2</sup>H chemical shifts were referenced to external toluene-*d*<sub>8</sub>. FT/IR spectra of KBr pellets were obtained from a Bio-Rad FTS-60A spectrometer. Mass spectra (MS) were recorded on a VG ZAB-EQ hybrid high performance mass spectrometer at an ionization voltage of 70 eV. A Hewlett-Packard 6890 gas chromatograph (GC) with a 5793 mass selective (MS) detector (MSD) was used to obtain GC/MS data. The column used was a Hewlett-Packard DB5MS capillary column (30 m × 250 μm; coating: 0.25 μm 5% phenyl methyl siloxane film). Elemental analyses were performed by E+R Microanalytical Laboratory, Corona, New York.

#### 4.3.2 Preparation of [(Me<sub>2</sub>N)<sub>3</sub>Zr(μ-H)(μ-NMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>Zr (7)

To a solution of Zr(NMe<sub>2</sub>)<sub>4</sub> (0.32 g, 1.2 mmol) in Et<sub>2</sub>O (10 mL) was added H<sub>2</sub>SiPh<sub>2</sub> (0.22 mL, 1.2 mmol) in Et<sub>2</sub>O (5 mL). After the addition, the reaction solution was cooled to -40 °C immediately, and the solvent was removed in vacuo. The yellow residue was washed with cold Et<sub>2</sub>O several times to remove organic products. Recrystallization from cold Et<sub>2</sub>O afforded 0.11 g (0.15 mmol) of 7 as yellow blocks [38% yield based on Zr(NMe<sub>2</sub>)<sub>4</sub>]. <sup>1</sup>H and <sup>13</sup>C NMR, HMQC, and NOSEY were used in structure assignments. Data for 7: <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 250.1 MHz, 23 °C) δ 5.21 (s, 2H, Zr-*H*), 2.98 (s, 60H, NMe<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} (benzene-*d*<sub>6</sub>, 62.9 MHz, 23 °C) δ 44.54 (NMe<sub>2</sub>). <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 400.1 MHz, -70 °C) δ 5.11 (s, 2H, Zr-*H*), 3.24 (s, 36H,

terminal  $\text{NMe}_2$ ), 3.05 (s, 6H, bridging  $\text{NMe}_2$ ); 2.60 (s, 6H, bridging  $\text{NMe}_2$ ), 2.58 (s, 6H, bridging  $\text{NMe}_2$ ), 2.46 (s, 6H, bridging  $\text{NMe}_2$ );  $^{13}\text{C}\{^1\text{H}\}$  (toluene- $d_8$ , 100.6 MHz,  $-70^\circ\text{C}$ )  $\delta$  45.32 (terminal  $\text{NMe}_2$ ); 43.25 (bridging  $\text{NMe}_2$ ); 43.06 (bridging  $\text{NMe}_2$ ); 42.14 (bridging  $\text{NMe}_2$ ). Anal. Calcd for  $\text{C}_{20}\text{H}_{62}\text{N}_{10}\text{Zr}_3$ : C, 33.53; H, 8.72. Found: C, 33.20; H, 8.34.

#### 4.3.3 Preparation of $[(\text{Me}_2\text{N})_3\text{Hf}(\mu\text{-H})(\mu\text{-NMe}_2)_2]_2\text{Hf}$ (**8**)

To a solution of  $\text{Hf}(\text{NMe}_2)_4$  (1.015 g, 2.861 mmol) in 10 mL of  $\text{Et}_2\text{O}$  was added dropwise 0.53 mL of  $\text{H}_2\text{SiPh}_2$  (0.53 g, 3.0 mmol) in  $\text{Et}_2\text{O}$ . After the addition was complete, the mixture was stirred for 10 min, and then cooled to  $-35^\circ\text{C}$ . The volatile products were removed under vacuum, and the colorless solid was washed with cold  $\text{Et}_2\text{O}$  ( $-50^\circ\text{C}$ , 15 mL) three times to extract organic products. The solid was then dissolved in  $\text{Et}_2\text{O}$ , and solution was cooled to  $-30^\circ\text{C}$  yielding colorless crystals totaling 0.55 g [59% yield based on  $\text{Hf}(\text{NMe}_2)_4$ ].  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR and HMQC were used in structure assignments. Data for **8**:  $^1\text{H}$  NMR (benzene- $d_6$ , 250.1 MHz,  $23^\circ\text{C}$ )  $\delta$  9.87 (s, 2H, Hf- $\text{H}$ ), 3.01 (s, 60H,  $\text{NMe}_2$ );  $^{13}\text{C}\{^1\text{H}\}$  (benzene- $d_6$ , 62.9 MHz,  $23^\circ\text{C}$ )  $\delta$  44.25 ( $\text{NMe}_2$ ). Anal. Calcd for  $\text{C}_{20}\text{H}_{62}\text{N}_{10}\text{Hf}_3$ : C, 24.56; H, 6.39. Found: C, 24.22; H, 6.37.

#### 4.3.4 Preparation of $[(\text{Me}_2\text{N})_3\text{M}(\mu\text{-D})(\mu\text{-NMe}_2)_2]_2\text{M}$ (**7- $d_2$** , **8- $d_2$** )

To a solution of  $\text{Zr}(\text{NMe}_2)_4$  (0.0423 g, 0.158 mmol) in toluene was added  $\text{D}_2\text{SiPh}_2$  (0.029 mL, 0.16 mmol).<sup>30</sup> The color changed from pale yellow to intense lemon in the formation of **7- $d_2$** .  $^2\text{H}$  (toluene, 61.4 MHz) of **7- $d_2$**   $\delta$  5.24 (s, 2D, Zr- $\text{D}$ ). The hafnium analogue was prepared similarly.  $^2\text{H}$  (toluene, 61.4 MHz) of **8- $d_2$**   $\delta$  9.98 (s, 2D, Hf- $\text{D}$ ).

#### 4.3.5 Variable Temperature NMR Study of 7

7 (0.053 g, 0.074 mmol), 4,4'-dimethylbiphenyl (0.2 mg, an internal standard), and toluene- $d_8$  were placed in a valved J. Young NMR tube. NMR spectra were recorded on a Bruker AMX-400 spectrometer between  $-80$  and  $0$  °C at a  $5$  °C interval.

#### 4.3.6 Reaction of $M(NMe_2)_4$ ( $M = Ti, Zr$ ) with Excess $SiH_4$

A yellow liquid sample of  $Ti(NMe_2)_4$  (0.067 g, 0.30 mmol) was placed in a 125-mL Schlenk flask, and the flask was evacuated at  $-196$  °C. Then 5%  $SiH_4/Ar$  was introduced. The color of the liquid changed instantaneously from yellow to orange, brown, and then black with gas evolution. A black solid precipitated from the dark liquid. When gas evolution had ceased, the system was cooled again to  $-77$  °C, and evacuated. The volatile products were collected in a liquid nitrogen trap. Then 5%  $SiH_4/Ar$  was reintroduced. The procedure was repeated for a total of four times. At this point, no gas evolved when new  $SiH_4/Ar$  gas was introduced into the system. The volatile products were found to contain  $HSi(NMe_2)_3$ . In a separate experiment,  $Ti(NMe_2)_4$  (0.0116 g, 0.0517 mmol) was dissolved in toluene- $d_8$  in a valved J. Young NMR tube. After evacuating the system at  $-196$  °C, excess 5%  $SiH_4/Ar$  was introduced. The system was slowly warmed to  $23$  °C, and the reaction mixture was monitored by  $^1H$  NMR at  $-35$ ,  $-24$ ,  $-15$  and  $23$  °C.  $H_2$ ,  $H_2Si(NMe_2)_2$  and  $HSi(NMe_2)_3$  were identified as the reaction products. The reaction with  $Zr(NMe_2)_4$  solid was similarly conducted at  $23$  °C, except no initial cooling to  $-196$  °C was used during evacuation.

#### 4.3.7 Reaction of $\text{Zr}(\text{NMe}_2)_4$ with $\text{H}_2\text{SiPh}_2$ in the Presence of $\text{HNMe}_2$

$\text{H}_2\text{SiPh}_2$  (0.115 mL, 0.621 mmol) was added to  $\text{Zr}(\text{NMe}_2)_4$  (27.7 mg, 0.104 mmol) and 4,4-dimethylbiphenyl (an internal standard) in benzene- $d_6$  in a valved J. Young NMR tube (Tube A). The mixture was then immediately cooled to  $-70^\circ\text{C}$ .  $\text{HNMe}_2$  (0.0774 mmol) was vacuum transferred to the NMR tube. The mixture was then warmed to room temperature, and the reaction was monitored by NMR. As in the reaction without external  $\text{HNMe}_2$ , the formation of  $\text{HSi}(\text{NMe}_2)\text{Ph}_2$  and  $\text{H}_2$  was observed, and the peak of  $\text{Zr}(\text{NMe}_2)_4$  disappeared in ca. 5 min.

Three new peaks in  $^1\text{H}$  NMR [2.21 (s,  $\text{CH}_3$ ), 2.19 (s,  $\text{CH}_3$ ) and 0.18 (br,  $\text{H-N}$ ) ppm] and one new peak in  $^{13}\text{C}\{^1\text{H}\}$  (38.8 ppm) were observed, respectively, in the reaction mixture. [In comparison  $\text{HNMe}_2$  in a benzene- $d_6$  solution of  $\text{H}_2\text{SiPh}_2$  was found to be at 2.20 ppm (s, 6H,  $\text{CH}_3$ ) and 0.33 ppm (br, 1H,  $\text{H-N}$ ) in  $^1\text{H}$  and 38.9 ppm in  $^{13}\text{C}\{^1\text{H}\}$  NMR.] The integrals of these two peaks in  $^1\text{H}$  NMR decreased by 10% in 6 hrs after the addition of  $\text{HNMe}_2$ .

The nature of the chemical species giving these new NMR peaks was investigated. A portion of the volatile products in the reaction mixture was vacuum transferred to another valved J. Young NMR tube (Tube B) containing benzene- $d_6$  and the internal standard. The integrals of these two  $^1\text{H}$  NMR peaks in the remaining mixture (Tube A) were found to have decreased, and  $\text{HNMe}_2$  was observed in Tube B. The volatile products in Tube B were then transferred back to Tube A, and the integrals of these two  $^1\text{H}$  NMR peaks were found to have increased. Although we do not know the nature of the chemical species that give(s) these new NMR peaks, they are perhaps  $\text{HNMe}_2$  coordinated to colloidal Zr species. The observation that these two new peaks

decreased by 10% in 6 h indicated that the reaction of  $\text{HNMe}_2$  with  $\text{H}_2\text{SiPh}_2$ , if occurring in the reaction mixture, was much slower than that of  $\text{Zr}(\text{NMe}_2)_4$  with  $\text{H}_2\text{SiPh}_2$ . Thus it is unlikely that  $\text{HNMe}_2$  is formed by transition state B in Figure 4.10, and then reacted with  $\text{H}_2\text{SiPh}_2$  to give the aminosilane.

#### 4.3.8 Reactions of $\text{M}(\text{NMe}_2)_4$ ( $\text{M} = \text{Ti, Zr, Hf}$ ) with Silanes ( $\text{H}_3\text{SiPh}$ , $\text{H}_2\text{SiPh}_2$ , $\text{H}_2\text{SiMePh}$ )

One equiv of a silane was added to the solution of  $\text{M}(\text{NMe}_2)_4$  in benzene- $d_6$ . The solution turned dark yellow immediately. When more than one equiv of the silane was used, the solution turned black instantaneously with gas evolution. The organic products were identified by NMR as  $\text{HSi}(\text{NMe}_2)\text{Ph}_2$ ,  $\text{HSi}(\text{NMe}_2)\text{MePh}$ , and  $\text{HSi}(\text{NMe}_2)_2\text{Ph}$ , respectively.

#### 4.3.9 Attempted Reactions of $\text{M}(\text{NMe}_2)_4$ ( $\text{M} = \text{Ti, Zr, Hf}$ ) with $\text{H}_2\text{SiBu}^t_2$ , $\text{HSiEt}_3$ , $\text{HSiMeBu}^t_2$ , $\text{HSiPh}_3$ , $\text{HSiPr}^i_3$ and $\text{HSi}(\text{NMe}_2)_3$

Silane was added to a solution of  $\text{M}(\text{NMe}_2)_4$  in benzene- $d_6$ . No reaction was observed over a one week period.

#### 4.3.10 Reaction of $(\text{Me}_2\text{N})_3\text{ZrSi}(\text{SiMe}_3)_3$ (**5b**) with $\text{H}_2\text{SiPh}_2$

**5b** (30 mg, 0.064 mmol) was dissolved in benzene- $d_6$  at room temperature in an NMR tube. To this solution was added 4 equiv of  $\text{H}_2\text{SiPh}_2$  (47.2 mg, 0.256 mmol). The color of the solution gradually changed from pale yellow to red. The reaction was monitored by  $^1\text{H}$  NMR.  $(\text{Me}_2\text{N})_2\text{Zr}(\text{H})\text{Si}(\text{SiMe}_3)_3$  (**6**) and  $\text{HSi}(\text{NMe}_2)\text{Ph}_2$  were observed,

and the reaction was found to reach equilibrium. Two separate samples were used to measure the equilibrium constant for this reaction at 0 °C. **6** was found to slowly decompose to  $\text{HSi}(\text{SiMe}_3)_3$  and unidentified precipitates. Similarly, reactions of **5b** with  $\text{H}_3\text{SiPh}$  and  $\text{H}_2\text{SiMePh}$  were found to give **6** and  $\text{HSi}(\text{NMe}_2)\text{MePh}$  and  $\text{H}_2\text{Si}(\text{NMe}_2)\text{Ph}$ , respectively. Data for **6**:  $^1\text{H}$  NMR (benzene- $d_6$ , 250.1 MHz, 23 °C)  $\delta$  5.68 (s, 1H,  $\text{ZrH}$ ), 2.83 (s, 12H,  $\text{NMe}_2$ ), 0.40 (s, 27H,  $\text{SiMe}_3$ );  $^{13}\text{C}$  (benzene- $d_6$ , 62.9 MHz, 23 °C)  $\delta$  40.98 ( $\text{NMe}_2$ ), 5.67 ( $\text{SiMe}_3$ );  $^{29}\text{Si}\{^1\text{H}\}$  NMR (benzene- $d_6$ , 79.5 MHz, 23 °C)  $\delta$  -5.2 ( $\text{SiMe}_3$ ), -126.1 ( $\text{SiSiMe}_3$ ).

#### 4.3.11 Confirmation of the Equilibrium: $(\text{Me}_2\text{N})_3\text{ZrSi}(\text{SiMe}_3)_3$ (**5b**) + $\text{H}_2\text{SiMePh} \rightleftharpoons (\text{Me}_2\text{N})_2\text{Zr}(\text{H})\text{Si}(\text{SiMe}_3)_3$ (**6**) + $\text{HSi}(\text{NMe}_2)\text{MePh}$

**5b** (30 mg, 0.064 mmol) was dissolved in benzene- $d_6$  at room temperature in an NMR tube. To this solution was added 1 equiv of  $\text{H}_2\text{SiMePh}$  (7.8 mg, 0.064 mmol). Once the reaction reached equilibrium (as monitored by NMR), 1 equiv of  $\text{HSi}(\text{NMe}_2)\text{Ph}_2$  (14.5 mg, 0.064 mmol) was added to the reaction mixture. The NMR spectra of the reaction mixture showed the formation of  $\text{H}_2\text{SiPh}_2$ .

#### 4.3.12 Identification of the Aminosilane Products and $\text{H}_2$

The assignments of aminosilanes were based on reported NMR [ $^1\text{H}$  NMR of  $\text{Si}(\text{NMe}_2)_2\text{MePh}$ ,  $^{29\text{a-b}}\text{Si}\{^1\text{H}\}$  NMR of  $\text{HSi}(\text{NMe}_2)\text{Ph}_2$  and  $\text{HSi}(\text{NMe}_2)\text{MePh}$ ,  $^{29\text{c}}\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR of  $\text{H}_2\text{Si}(\text{NMe}_2)\text{Ph}$ ,  $\text{HSi}(\text{NMe}_2)_2\text{Ph}$  and  $\text{HSi}(\text{NMe}_2)\text{Ph}_2$ ,  $^{29\text{d}}$  and  $^1\text{H}$  NMR of  $\text{HSi}(\text{NMe}_2)_3$  and  $\text{H}_2\text{Si}(\text{NMe}_2)_2$ ,  $^{29\text{e}}$ ] and standard MS [ $\text{Si}(\text{NMe}_2)_2\text{Ph}_2$  in the NBS43k.1 MS library in the Hewlett-Packard 6890 GC/5793 MSD]. In some cases, aminosilanes were

independently prepared for spectroscopic comparison with the products.  $\text{H}_2$  was identified by its  $^1\text{H}$  NMR at  $\delta$  4.46 in benzene- $d_6$ . The NMR data of the following aminosilanes are listed, as they are either not available or reported in different solvents.

(a) Data for  $\text{HSi}(\text{NMe}_2)\text{MePh}$ :  $^1\text{H}$  NMR (benzene- $d_6$ , 250.1 MHz)  $\delta$  7.55 - 7.15 (m, 5H,  $\text{C}_6\text{H}_5$ ), 5.04 (q, 1H, SiH), 2.43 (s, 6H,  $\text{NMe}_2$ ), 0.30 (d, 3H, SiMe,  $^3J_{\text{H-H}} = 3.4$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  (benzene- $d_6$ , 62.9 MHz)  $\delta$  137.01, 134.36, 128.19, 127.81 ( $\text{C}_6\text{H}_5$ ), 38.71 ( $\text{NMe}_2$ ), -3.79 (SiMe);  $^{29}\text{Si}\{^1\text{H}\}$  (benzene- $d_6$ , 79.5 MHz)  $\delta$  -7.54. (b) Data for  $\text{Si}(\text{NMe}_2)_2\text{MePh}$ :  $^1\text{H}$  NMR (benzene- $d_6$ , 250.1 MHz)  $\delta$  7.57 - 7.20 (m, 5H,  $\text{C}_6\text{H}_5$ ), 2.49 (s, 12H,  $\text{NMe}_2$ ), 0.31 (s, 3H, SiMe).  $^{13}\text{C}\{^1\text{H}\}$  (benzene- $d_6$ , 62.9 MHz)  $\delta$  138.36, 134.77, 129.30, 128.00 ( $\text{C}_6\text{H}_5$ ), 38.02 ( $\text{NMe}_2$ ), -4.18 (SiMe). (c) Data for  $\text{HSi}(\text{NMe}_2)\text{Ph}_2$ :  $^{22\text{c-d}}\text{Si}\{^1\text{H}\}$  (benzene- $d_6$ , 79.5 MHz)  $\delta$  -11.47. (d) Data for  $\text{Si}(\text{NMe}_2)_2\text{Ph}_2$ :  $^1\text{H}$  NMR (benzene- $d_6$ , 250.1 MHz)  $\delta$  7.58 - 7.20 (m, 10H,  $\text{C}_6\text{H}_5$ ), 2.57 (s, 12H,  $\text{NMe}_2$ );  $^{13}\text{C}\{^1\text{H}\}$  (benzene- $d_6$ , 62.9 MHz)  $\delta$  136.38, 135.42, 129.51, 127.99 ( $\text{C}_6\text{H}_5$ ), 38.68 ( $\text{NMe}_2$ ). (e) Data for  $\text{H}_2\text{Si}(\text{NMe}_2)_2$ :  $^1\text{H}$  NMR (toluene- $d_8$ , 400.1 MHz)  $\delta$  4.65 (s, Si-H, 2H), 2.53 (s,  $\text{NMe}_2$ , 12H);  $^{13}\text{C}\{^1\text{H}\}$  (toluene- $d_8$ , 100.6 MHz)  $\delta$  37.97 ( $\text{NMe}_2$ ). (f) Data for  $\text{HSi}(\text{NMe}_2)_3$ :  $^1\text{H}$  NMR (benzene- $d_6$ , 250.1 MHz)  $\delta$  4.36 (s, 1H, SiH), 2.44 (s, 18H,  $\text{NMe}_2$ );  $^{13}\text{C}\{^1\text{H}\}$  (benzene- $d_6$ , 62.9 MHz)  $\delta$  36.86 ( $\text{NMe}_2$ ).

#### 4.3.13 X-ray Crystal Structure Determination of 7

A yellow crystal of 7 was selected in Paratone oil and mounted on a Siemens R3m/V diffractometer ( $\text{MoK}\alpha$  radiation, 0.71073 Å) equipped with a Nicolet LT-2 low-temperature device under a stream of nitrogen at -100 °C. The unit cell parameters and

orientation matrix were determined from a least-squares fit of 30 reflections obtained from a rotation photograph and an automatic peak search routine. All non-hydrogen atoms were refined anisotropically. The two hydride atoms were located and refined isotopically, and the remaining H atoms were placed in calculated positions and introduced into the refinements as fixed contributors with an isotropic  $U$  value of  $0.08 \text{ \AA}^2$ . All calculations were performed using the Siemens SHLEXTL 93 (version 5.0) proprietary software package.

#### 4.3.14 X-ray Crystal Structure Determination of 8

The single crystal X-ray diffraction experiment for **8** was performed on a Siemens P4/CCD diffractometer. Systematic absences and diffraction symmetry were uniquely consistent for the assigned space group. The structure was solved by direct methods, completed by subsequent difference Fourier syntheses and refined by a full-matrix, least-squares procedure. All non-hydrogen atoms were refined with anisotropic coefficients and all hydrogen atoms, except as noted below, were treated as idealized contributions. An empirical absorption correction was applied to the data of both compounds using the program DIFABS. The bridging hydrides could not be located from the difference map and were ignored in the refinement, but not in the global parameters.

All software and sources of the scattering factors are contained in the SHELXTL (5.10) program library (G. Sheldrick, Siemens XRD, Madison, WI). The program DIFABS is described by N. Walker and D. Stuart.<sup>31</sup>

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## Chapter 5

### Mechanistic Studies of Thermal Decomposition of Tetraneopentylzirconium to Zirconium Carbide

#### 5.1 Introduction

Zirconium carbide (ZrC) is a refractory solid with a high micro-hardness (2700 kg/mm<sup>2</sup>) and a high melting point (3670 °C).<sup>1a</sup> It also has a large Modulus of elasticity of 348 in comparison to other transition metal carbides.<sup>1a</sup> The physical properties of ZrC are listed in Table 5.1. The high chemical and thermal stabilities and metal-like properties of ZrC have made it an efficient catalyst for redox-type processes. It has been used in, e.g., the adsorption and activation of oxygen, hydrogen, ammonia, methane, and carbon monoxide.<sup>1b</sup> The most significant application of ZrC so far is in the coating materials for atomic fuel particles, owing largely to its exceptional hardness and thermal stability.<sup>1b,1c</sup> The NERVA/ROVER (Nuclear Engine for Rocket Vehicle Applications) project<sup>2</sup> demonstrated that a ZrC coating could extend the life of graphite components in high-temperature (1828 – 2928 °C) vacuum furnaces and mitigate H<sub>2</sub> corrosion of graphite-based fuel elements and components at high temperature (727 - 2227 °C) and high pressure ( $\approx$  600 psia).<sup>3</sup>

CVD (chemical vapor deposition) is a common technique for the manufacture of metal carbide coatings.<sup>1c</sup> In a conventional thermal CVD of ZrC, zirconium tetrachloride and methane are usually used as the precursors (Equation 5.1).<sup>1c,4</sup> Compared to

**Table 5.1** Properties of Zirconium Carbide

|                                |                                 |
|--------------------------------|---------------------------------|
| Crystal structure              | face centered cubic (f.c.c. B1) |
| Density                        | 6.57 g/cm <sup>3</sup>          |
| Melting point                  | 3670 °C                         |
| Vickers hardness               | 2000 kg/mm <sup>2</sup>         |
| Thermal conductivity (20 °C)   | 0.20 W/cm.°C                    |
| Thermal expansion (20 °C)      | 6.0 ppm                         |
| Electrical resistivity (25 °C) | 57-75 $\mu$ ohm-cm              |
| Modulus of elasticity          | 348 GPa                         |



conventional CVD, MOCVD (metallo-organic chemical vapor deposition), a process in which metallo-organic compounds are used as precursors, can lead to deposition at lower temperatures and better control of the stoichiometry of the films. The use of lower temperatures and better control of stoichiometry help reduce residual stresses and grain growth commonly occurred at high temperatures.<sup>5a</sup> Recent studies have focused on MOCVD of metal carbides and the thermal decomposition of organometallic precursors to these carbides.<sup>5</sup> Several transition metal carbides, including zirconium carbide, have been successfully prepared by the use of metal alkyl complexes as single-source precursors.<sup>6-10</sup> Girolami and coworkers first conducted the MOCVD of titanium carbide from tetraneopentyltitanium  $\text{Ti}(\text{CH}_2\text{CMe}_3)_4$  (11a) at as low as 150 °C, and further studied the mechanistic pathways of pyrolysis of  $\text{Ti}(\text{CH}_2\text{CMe}_3)_4$  (11a) in solution and under CVD conditions.<sup>6</sup> The amorphous products were found to contain Ti and C in a ratio of 1 : 0.93 with little hydrogen. Smith and coworkers reported the MOCVD of ZrC from tetraneopentylzirconium  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$  (11b) as a precursor at 500 °C under CVD condition (Equation 5.2).<sup>7</sup> The ratios of metal to carbon of the thin crystalline films were found to be about 1 : 2 by Auger electron spectroscopy (AES) depth profiling. Moreover, their forward recoil spectrometry (FRES) analysis showed a large amount of hydrogen (up to 16%) in the zirconium carbide films. These CVD results imply that different mechanisms might be involved in the thermolysis of  $\text{Ti}(\text{CH}_2\text{CMe}_3)_4$  (11a) and  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$  (11b).



The thermolysis of peralkyl complexes  $\text{M}(\text{CH}_2\text{R})_4$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ ;  $\text{R} = \text{H}, \text{CMe}_3, \text{SiMe}_3$ ) usually occurs via  $\alpha$ - or  $\gamma$ -hydrogen abstraction reactions (Figure 5.1). The intramolecular and intermolecular  $\alpha$ -hydrogen abstraction reactions, are shown in Figure 5.1a and 5.1b, respectively. When the R group is small, both experimental and theoretical studies have shown that the rate-determining step in, e.g.,  $\text{TaMe}_5$ , is the bimolecular intermolecular  $\alpha$ -hydrogen abstraction.<sup>11-13a</sup> If the alkyl group  $-\text{CH}_2\text{R}$  becomes bulkier (e.g.,  $\text{R} = \text{CMe}_3$ ), unimolecular  $\alpha$ -hydrogen abstraction becomes more favorable as it is expected to reduce steric interactions.<sup>12,14</sup> The kinetic studies of Girolami and coworkers showed that unimolecular  $\alpha$ -hydrogen abstraction is about 25 times faster than the  $\gamma$ -hydrogen abstraction reaction in the initial step of  $\text{Ti}(\text{CH}_2\text{CMe}_3)_4$  (11a) thermolysis,<sup>6</sup> as predicted by *ab initio* quantum chemical calculations.<sup>13b</sup> The conversions of  $\text{Ta}(\text{CH}_2\text{R})_5$  ( $\text{R} = \text{CMe}_3, \text{SiMe}_3$ ) to alkylidene complexes  $(\text{RCH}_2)_3\text{Ta}=\text{CHR}$  were also found to involve  $\alpha$ -hydrogen abstraction reactions.<sup>15</sup>

The mechanistic pathways in the thermal decomposition of  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$  (11b) is not known. In addition to  $\alpha$ - or  $\gamma$ -hydrogen abstraction reactions (Figure 5.2a-b), it could undergo a methyl abstraction (Figure 5.2c) or radical reaction (Figure 5.2d) in its thermolysis. An understanding of mechanistic pathways in the thermolysis of  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$  (11b) may help better control the process and the metal carbide materials thus formed. In collaboration with Professor Yun-Dong Wu and his research group at the Hong Kong University of Science and Technology, we have thus conducted theoretical

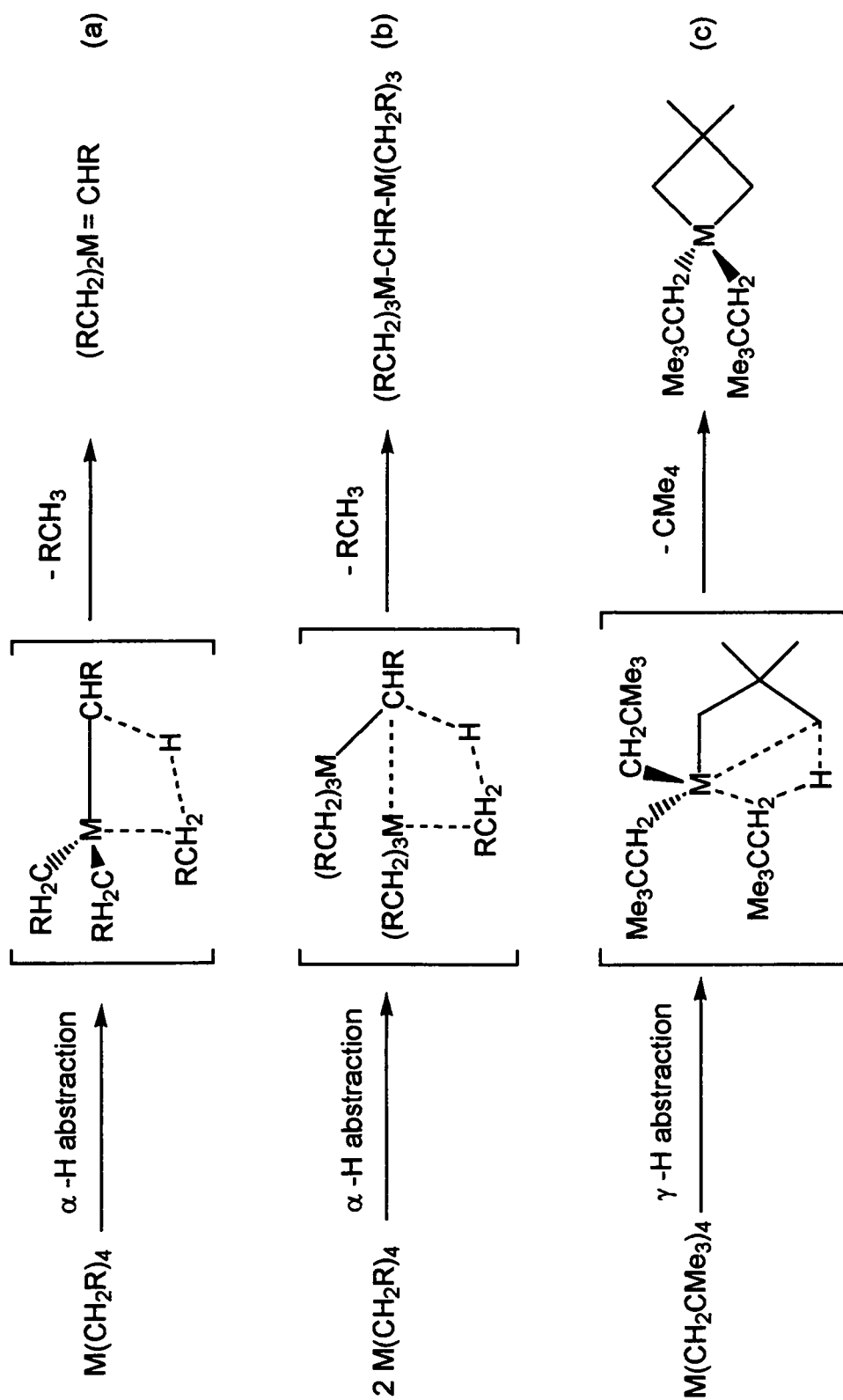
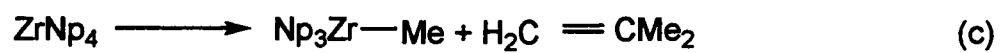
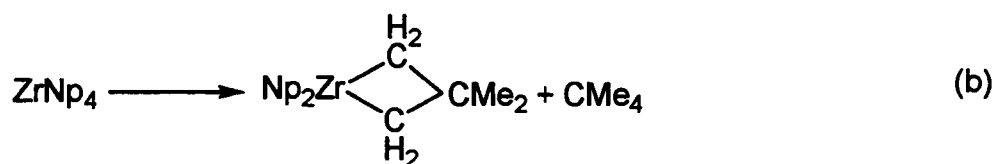


Figure 5.1 Hydrogen abstraction reactions in the thermolysis of  $\text{M}(\text{CH}_2\text{R})_4$ .



$\text{Np} = -\text{CH}_2\text{CMe}_3$

**Figure 5.2** Possible first steps in the thermolysis of  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$  (**11b**).

and experimental studies of the decomposition of  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$ . The results of our experimental studies are reported here, along with a summary of the theoretical studies by Professor Wu's research group.

## 5.2 Results and Discussion

### 5.2.1 Summary of *Ab Initio* Quantum Chemical Calculations of the Structure and Thermolysis of $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$ (11b)<sup>16</sup>

The calculated structure, shown in Figure 5.3, indicates that the geometry of  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$  (11b) is tetrahedral. Like its titanium analogue, it has  $S_4$  symmetry. The Zr-C bond length is 2.276 Å, which is longer than the Ti-C bond in  $\text{Ti}(\text{CH}_2\text{CMe}_3)_4$  (11a), and the Zr-C-C bond angle of 123.2° is relatively smaller than that in 11a by about 3°. Experimental studies have indicated that the first step in the thermolysis of  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$  is first order.<sup>17</sup> Thus, only unimolecular mechanisms were calculated in the present study. Figure 5.4 shows the calculated geometries of the transition structure (C1, C3) and products (C2, C4) of the  $\alpha$ -hydrogen and  $\gamma$ -hydrogen abstraction reactions for  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$  (11b). The activation and reaction enthalpies in Figure 5.4 were calculated based on those of MP2/HW3 energetics of  $\text{ZrMe}_4$  and  $\text{ZrPr}^n\text{Me}_3$  systems with correction of the steric interactions caused by the *tert*-butyl groups, which were calculated with the HF/3-21G method (see Table 5.2). For comparison, the data for  $\text{Ti}(\text{CH}_2\text{CMe}_3)_4$  (11a) are also listed in Figure 5.4.

In the thermolysis of  $\text{Ti}(\text{CH}_2\text{CMe}_3)_4$  (11a), as can be seen in Figure 5.4, the activation energy for the  $\alpha$ -hydrogen abstraction is lower than the  $\gamma$ -hydrogen abstraction by about 8.6 kcal/mol at the MP2/HW3 level. In contrast, the activation energy of the

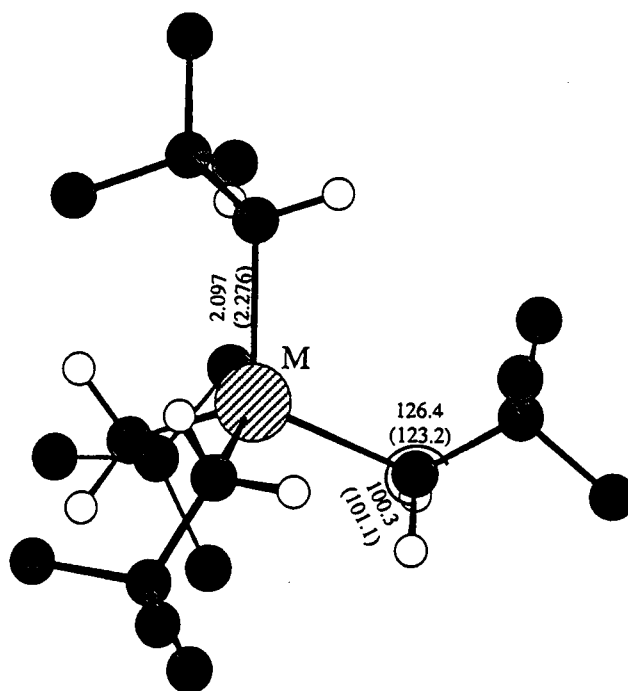
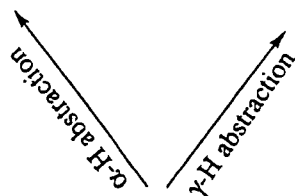
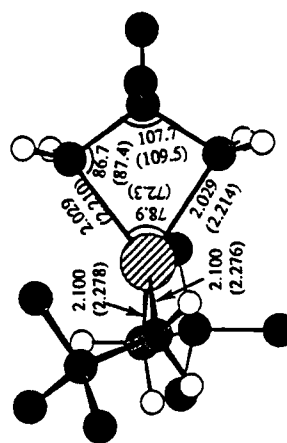
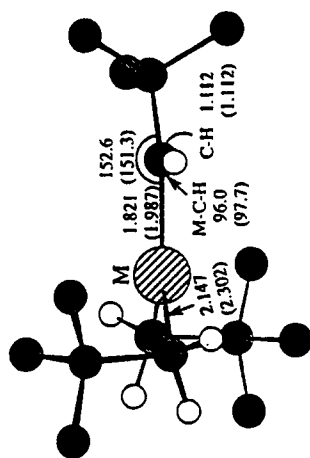
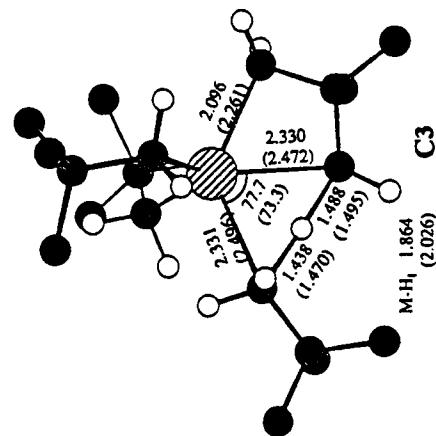
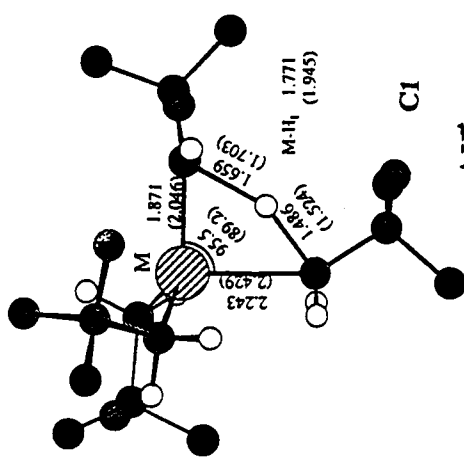


**Figure 5.3** The calculated structures of  $M(\text{CH}_2\text{CMe}_3)_4$  ( $M = \text{Ti}$ , 11a;  $\text{Zr}$ , 11b in parentheses).

**Figure 5.4** The calculated structures of transition states (C1, C3) and products (C2, C4) for the  $\alpha$ -hydrogen and  $\gamma$ -hydrogen abstraction reactions of  $M(\text{CH}_2\text{CMe}_3)_4$  (11a-b) with the MP2/HW3 activation and reaction enthalpies (kcal/mol). Selected geometrical parameters calculated with HF/3-21G method are given for  $M = \text{Ti}$  (a), Zr (b).



11

**Table 5.2.** Calculated Changes of Energies ( $\Delta E$ , kcal/mol), Thermal Energies ( $\Delta\Delta H^\circ_{298}$ , kcal/mol) and Entropies ( $\Delta S_{298}$ , eu) for the Formation of Transition Structures and Products for Alkane Elimination from  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$  (**11b**)<sup>18</sup>

| Entry | Reaction                                                     | HF/3-21G   |                              |                  | MP2/HW3    |
|-------|--------------------------------------------------------------|------------|------------------------------|------------------|------------|
|       |                                                              | $\Delta E$ | $\Delta\Delta H^\circ_{298}$ | $\Delta S_{298}$ | $\Delta E$ |
| 1     | <b>11b</b> $\rightarrow$ <b>C1b</b>                          | 61.5       | -3.0                         | 0.5              | 45.9       |
| 2     | <b>11b</b> $\rightarrow$ <b>C3b</b>                          | 54.3       | -3.1                         | -3.9             | 40.1       |
| 3     | <b>11b</b> $\rightarrow$ <b>C2b</b> + <b>CMe<sub>4</sub></b> | 36.8       | -1.8                         | 37.6             | 33.4       |
| 4     | <b>11b</b> $\rightarrow$ <b>C4b</b> + <b>CMe<sub>4</sub></b> | 10.3       | -2.4                         | 36.2             | 8.0        |

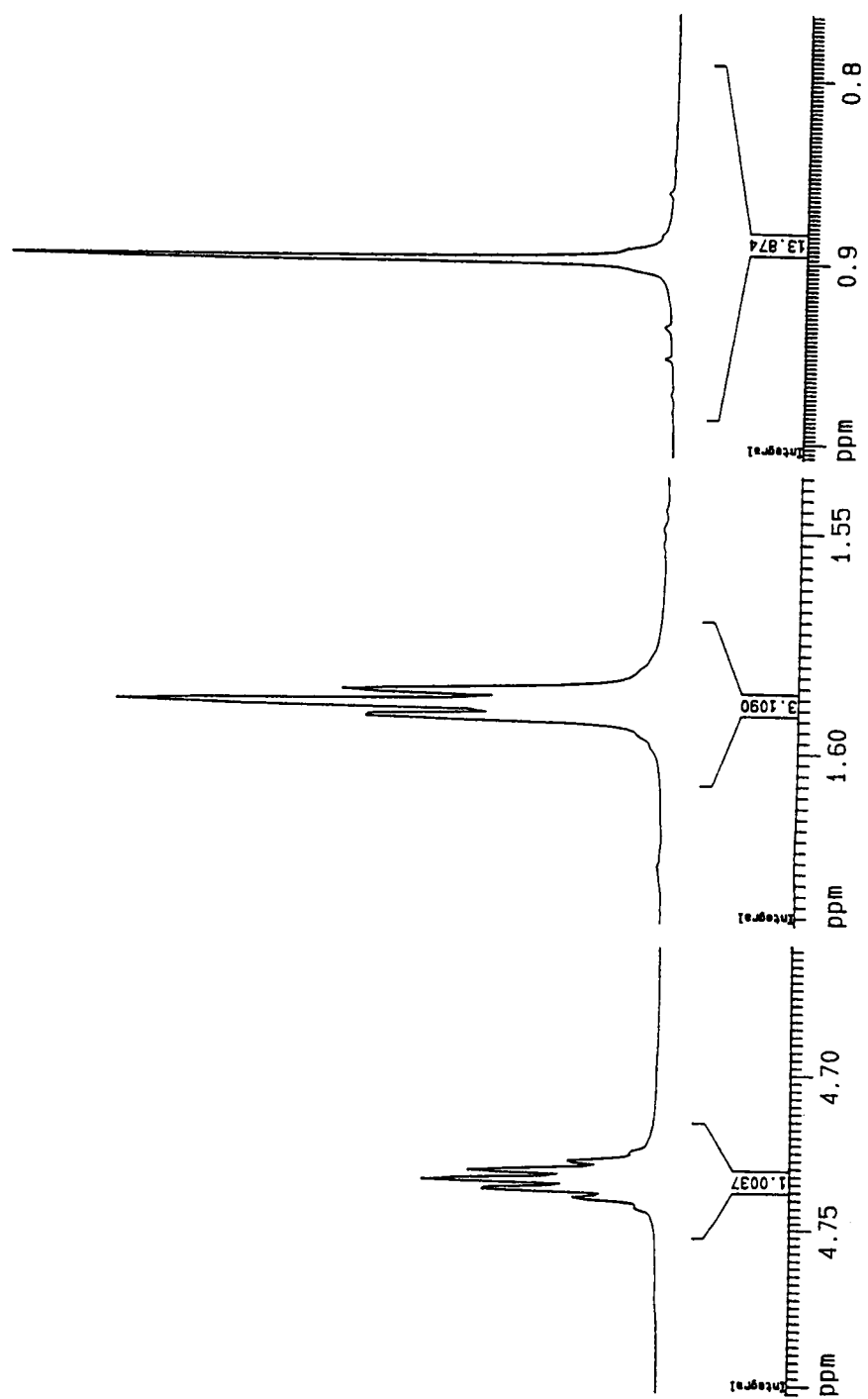
$\gamma$ -hydrogen abstraction of  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$  (**11b**) is smaller than the  $\alpha$ -hydrogen abstraction by 5.2 kcal/mol with the MP2/HW3 level. The *ab initio* quantum chemical calculations thus predict that, unlike its titanium analogue, the first step in the thermal decomposition of  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$  is a  $\gamma$ -hydrogen abstraction reaction.

### 5.2.2 Experimental Studies of the Thermolysis of $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$ (**11b**) in the CVD of Zirconium Carbide

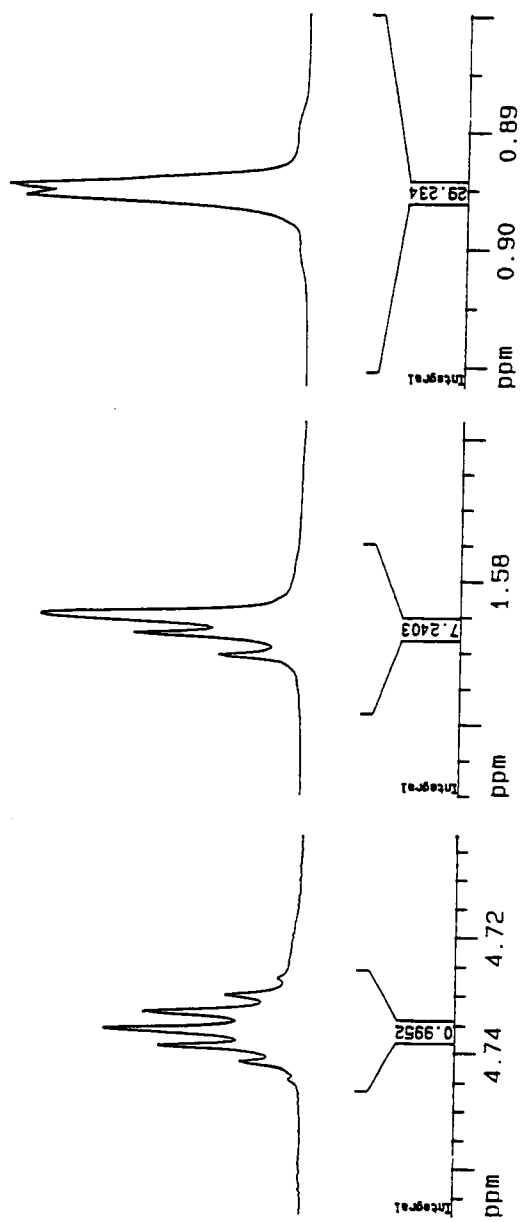
The results of these *ab initio* quantum chemical calculations of the decomposition of  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$  and the prediction that  $\gamma$ -hydrogen abstraction is preferred in this decomposition prompted us to study the decomposition experimentally.  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$  (**11b**) and deuterated  $\text{Zr}(\text{CD}_2\text{CMe}_3)_4$  (**11b-*d*<sub>8</sub>**) were prepared from  $\text{ZrX}_4$  ( $\text{X} = \text{Cl}, \text{Br}$ ) and  $\text{Me}_3\text{CCH}_2\text{Li}$  or  $\text{Me}_3\text{CCD}_2\text{MgBr}$ , respectively, and purified by sublimation. They were then used in chemical vapor decomposition (CVD) (400 - 500 °C, base pressure: ca.  $10^{-4}$  -  $10^{-5}$  torr similar to that reported by Smith and coworkers).<sup>7a</sup> The volatile products were collected in a liquid nitrogen trap and vacuum-transferred to a J. Young valved NMR tube.

The gases from the CVD with  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$  (**11b**) were analyzed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR and found to be mainly neopentane and isobutene. By NMR (Figure 5.5), 2.3(0.4) mol of neopentane and 1.0(0.1) mol of isobutene were produced per mole of  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$  (**11b**). Neopentane and isobutene account for 82(4)% of the mass released in the formation of  $\text{ZrC}$  from **11b**. The molar ratio of neopentane/isobutene in these volatile products was found to be 2.32(0.13) [or 69.9(1.2)% neopentane vs. 30.1(1.2)% isobutene].

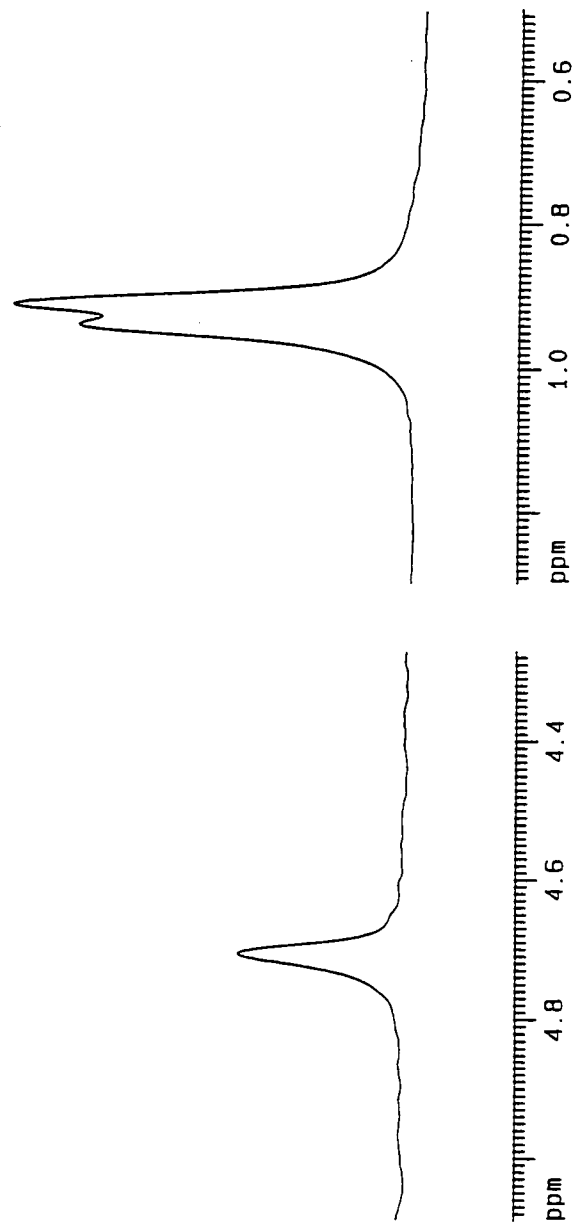
**Figure 5.5** (a)  $^1\text{H}$  NMR spectrum of isobutene and neopentane from the decomposition of  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$  (**11b**). (b)  $^1\text{H}$  NMR spectrum of isobutene and neopentane from the decomposition of  $\text{Zr}(\text{CD}_2\text{CMe}_3)_4$  (**11b-*d*<sub>8</sub>**). (c)  $^2\text{H}$  NMR spectrum of isobutene and neopentane from the decomposition of **11b-*d*<sub>8</sub>**.



B



**b**



**c**

The volatile products from the CVD with  $\text{Zr}(\text{CD}_2\text{CMe}_3)_4$  (**11b-d<sub>8</sub>**) were analyzed by field-ionization mass spectrometry (FI-MS) and NMR. Previous reports<sup>19</sup> have shown that field ionization in FI-MS provides the parent peak of neopentane, and reduces the fragmentation of neopentane to *tert*-butyl ions. In contrast, such fragmentation is essentially 100% in electron-impact mass spectrometry (EI-MS).<sup>6b</sup> An FI-MS spectrum of the volatile products and intensities of the peaks at mass 72 - 75 by FI-MS are shown in Figure 5.6 and Table 5.3, respectively. An analysis of these peaks showed the following distribution of neopentane isotopologues: 15%  $d_0$ , 14%  $d_1$ , 59%  $d_2$ , 12%  $d_3$ .<sup>20</sup> Neopentane- $d_2$  ( $\text{H}_3\text{C}$ )<sub>3</sub>C-CHD<sub>2</sub> was also observed in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum; -CHD<sub>2</sub> as a 1 : 2 : 3 : 2 : 1 quintet was identified at 31.21 ppm (isotopic shift  $^1\Delta$ :<sup>21</sup> +0.60 ppm). The ratio of neopentane- $d_2$ /neopentane- $d_3$  from FI-MS was 4.9. This ratio was much higher than that (0.57) observed in the decomposition of **11a-d<sub>8</sub>** under CVD conditions.<sup>6b</sup>

Two possible pathways are consistent with the formation of the large amount of neopentane- $d_2$ :  $\gamma$ -hydrogen abstraction and a radical mechanism [to form  $(\text{Me}_3\text{CCH}_2)_3\text{Zr}\cdot$  and  $\text{Me}_3\text{CCH}_2\cdot$  (Figure 5.2d)]; in contrast,  $\alpha$ -hydrogen abstraction predicts that the predominant neopentane isotopolog should be neopentane- $d_3$ . A GC/MS analysis showed there was no dineopentyl (2,2,5,5-tetramethylhexane), a possible product of  $\text{Me}_3\text{CCH}_2\cdot$  dimerization, in the volatile products from the CVD with  $\text{Zr}(\text{CD}_2\text{CMe}_3)_4$ . The lack of dineopentyl suggests that the radical mechanism is unlikely to be the major pathway. The large amount of neopentane- $d_2$  formed and the lack of dineopentyl indicate, as predicted by the *ab initio* quantum chemical calculations, that  $\gamma$ -hydrogen abstraction is likely to be the major thermal decomposition pathway. The formation of other neopentane isotopologues indicates that other processes occur in the CVD with

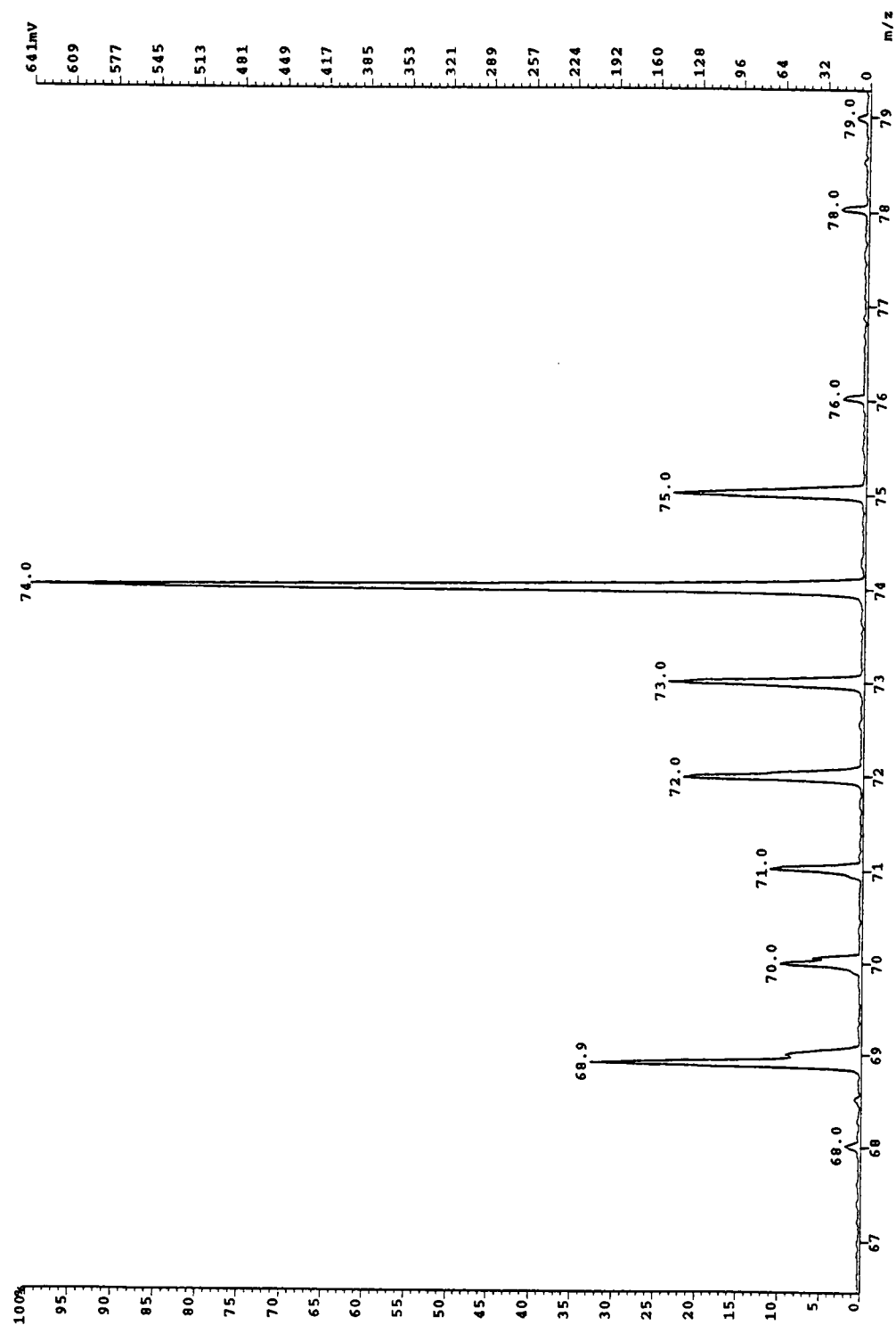


Figure 5.6 FI-MS mass spectrum of volatile products from the thermolysis of  $\text{Zr}(\text{CD}_2\text{CMe}_3)_4$  (11b- $d_8$ ).

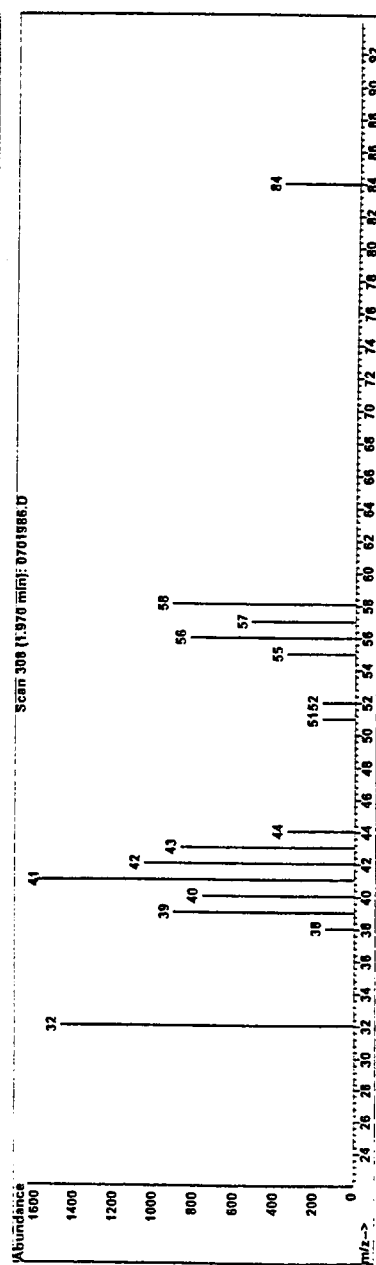
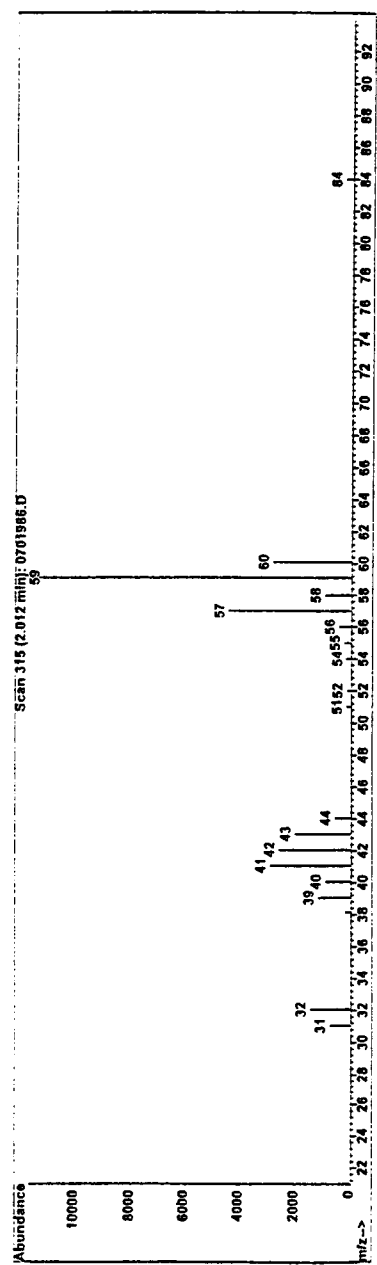
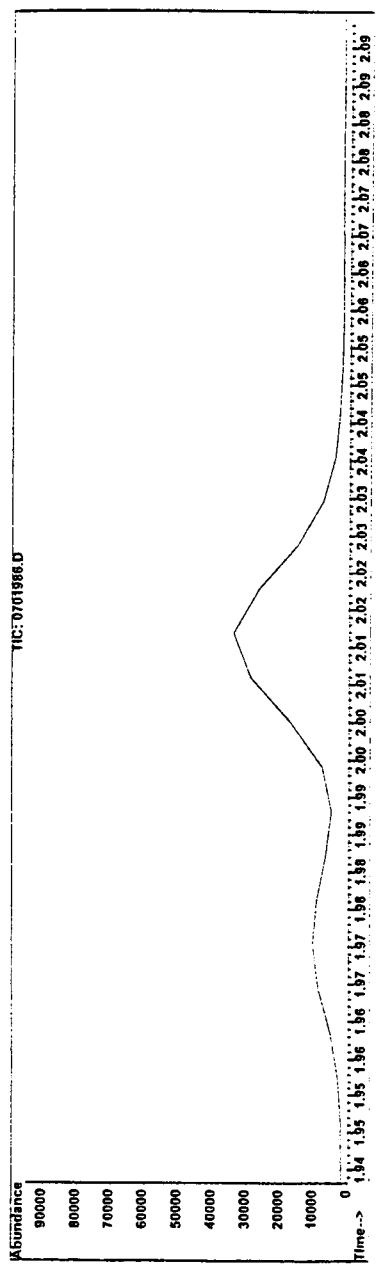
**Table 5.3** Mass Spectra ( $m/e = 72 - 75$ ) Generated upon 6 kV Ionization of the Volatile Products in the CVD with  $\text{Zr}(\text{CD}_2\text{CMe}_3)_4$  (**11b-*d*<sub>8</sub>**)

| $m/e$ | Relative Intensity <sup>a,20</sup> |
|-------|------------------------------------|
| 72    | 26.1                               |
| 73    | 24.9                               |
| 74    | 100                                |
| 75    | 25.3                               |

<sup>a</sup> All peaks are normalized to give the strongest peak an intensity of 100.

$\text{Zr}(\text{CD}_2\text{CMe}_3)_4$  (11b- $d_8$ ). These processes perhaps occur later in the decomposition sequence,<sup>22</sup> as close to 3 mole of neopentane are formed per mole of  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$  (11b). Neopentanes- $d_0$  and - $d_1$  were observed in the thermolysis of  $\text{Ti}(\text{CD}_2\text{CMe}_3)_4$  (11a- $d_8$ ) as well, and were attributed to unknown processes likely occurring later in the thermolysis sequence.<sup>6c</sup> A GC/MS analysis of the volatile products from the CVD with  $\text{Zr}(\text{CD}_2\text{CMe}_3)_4$  (Figure 5.7) showed the presence of both isobutene- $d_0$  and - $d_2$ .<sup>23</sup> The NMR of the volatile products from the CVD with  $\text{Zr}(\text{CD}_2\text{CMe}_3)_4$  (11b- $d_8$ ) is also consistent with the presence of both isobutene- $d_0$  and isobutene- $d_2$   $(\text{CH}_3)_2\text{C}=\text{CD}_2$ . The presence of isobutene- $d_1$   $(\text{CH}_3)_2\text{C}=\text{CHD}$  is unlikely, as it is not seen in either  $^1\text{H}$  (in the  $=\text{CHD}$  region),  $^2\text{H}\{^1\text{H}\}$ , or  $^{13}\text{C}\{^1\text{H}\}$  NMR. The molar ratio of isobutene- $d_2$ /isobutene- $d_0$  was obtained from  $^1\text{H}$  NMR and was found to be 1.52(0.10). The percentages of neopentane- $d_0$ , - $d_1$ , - $d_2$ , and - $d_3$  were then used in the analysis of the  $^1\text{H}$  NMR spectra to give the molar ratio 2.38(0.12) of neopentane/isobutene [or 70.4(1.1)% neopentane vs. 29.6(1.1)% isobutene] in the sample. It is interesting to note that this molar ratio in the volatile products from CVD with  $\text{Zr}(\text{CD}_2\text{CMe}_3)_4$  (11b- $d_8$ ) is about the same as that [2.32(0.13) or 69.9(1.2)% neopentane vs. 30.1(1.2)% isobutene] in the volatile products from the CVD with  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$  (11b). These observations suggest that both  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$  (11b) and  $\text{Zr}(\text{CD}_2\text{CMe}_3)_4$  (11b- $d_8$ ) follow similar pathways in their thermal decomposition, and are consistent with the prediction by the *ab initio* quantum chemical calculations that  $\gamma$ -hydrogen abstraction is preferred in their decomposition.

**Figure 5.7** GC/MS spectra of the volatile organic products from CVD using  $\text{Zr}(\text{CD}_2\text{CMe}_3)_4$  (**11b-*d*<sub>8</sub>**) as precursor.



## 5.3 Experimental Section

### 5.3.1 General Procedure

All manipulations were performed under a dry nitrogen or argon atmosphere with the use of either a glove box or standard Schlenk techniques. Solvents were purified by distillation from potassium/benzophenone ketyl and stored under dry nitrogen. Benzene- $d_6$  and toluene- $d_8$  were dried over activated molecular sieves and stored under  $N_2$ .  $ZrBr_4$  (Aldrich) and  $LiAlD_4$  (Aldrich, 98 atom% D, used for preparing  $Me_3CCD_2Br^{24}$ ) were used as received.  $Me_3CCD_2MgBr^{24}$  and  $Zr(CH_2CMe_3)_4$  (11b)<sup>11a,25</sup> were prepared by the literature methods. One-dimensional  $^1H$  and  $^{13}C$  NMR spectra, unless noted, were recorded at 23 °C on a Bruker AC-250 or AMX-400 Fourier transform spectrometer; shifts were referenced to solvents (residual proton peak).  $^2H\{^1H\}$  chemical shifts were referenced to external benzene- $d_6$ . CVD experiments with  $Zr(CD_2CMe_3)_4$  (11b- $d_8$ ) and  $Zr(CH_2CMe_3)_4$  (11b) were each performed twice, and the volatile products were analyzed by NMR, MS, and GC/MS.

All calculation were carried out by Professor Yun-Dong Wu's research group at the Hong Kong University of Science and Technology with the GAUSSIAN 94 program.<sup>26</sup> For the  $Zr(CH_2CMe_3)_4$  (11b) system, geometries were optimized with the HF/3-21G method, and thermal energies and reaction entropies were calculated based on vibration frequencies with the HF/STO-3G method.

### 5.3.2 Synthesis of $Zr(CD_2CMe_3)_4$ (11b- $d_8$ )

$ZrBr_4$  (0.840 g, 2.04 mmol) was stirred in 10 mL of  $Et_2O$  and cooled to -10 °C.  $Me_3CCD_2MgBr$  (0.195 M, 43 mL) was added dropwise at -10 °C with stirring. The

solution was then stirred at 0 °C for 4 h and slowly warmed to room temperature overnight. Ether was removed under vacuum, and the product was extracted with hexanes. After filtration and removal of hexanes by vacuum, the solid was sublimed at 60 °C (0.05 torr) to give 0.473 g (1.22 mmol, 60% yield) of **11b-d<sub>8</sub>**. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 250.1 MHz, 23 °C) δ 1.17 (CMe<sub>3</sub>).

### 5.3.3 Dynamic Vacuum CVD<sup>7a</sup>

CVD was conducted in a horizontal, hot-wall CVD reactor at 400 °C with a base pressure of ca. 10<sup>-4</sup> - 10<sup>-5</sup> torr (Figure 5.8). A process similar to this has been used by Smith and coworkers to prepare zirconium carbide thin films at 300 - 750 °C and 10<sup>-2</sup> - 10<sup>-4</sup> torr with either Zr(CH<sub>2</sub>CMe<sub>3</sub>)<sub>4</sub> (**11b**) or Zr(CD<sub>2</sub>CMe<sub>3</sub>)<sub>4</sub> (**11b-d<sub>8</sub>**) as the precursor.<sup>7a</sup> The precursor was heated at 45 °C. Volatile products were collected in a liquid nitrogen trap down stream from the CVD reactor. After the deposition, the volatile products were transferred under vacuum to a J. Young valved NMR tube cooled to -196 °C. An internal standard 4,4'-dimethylbiphenyl had been added to the NMR solvent, benzene-*d*<sub>6</sub>, to

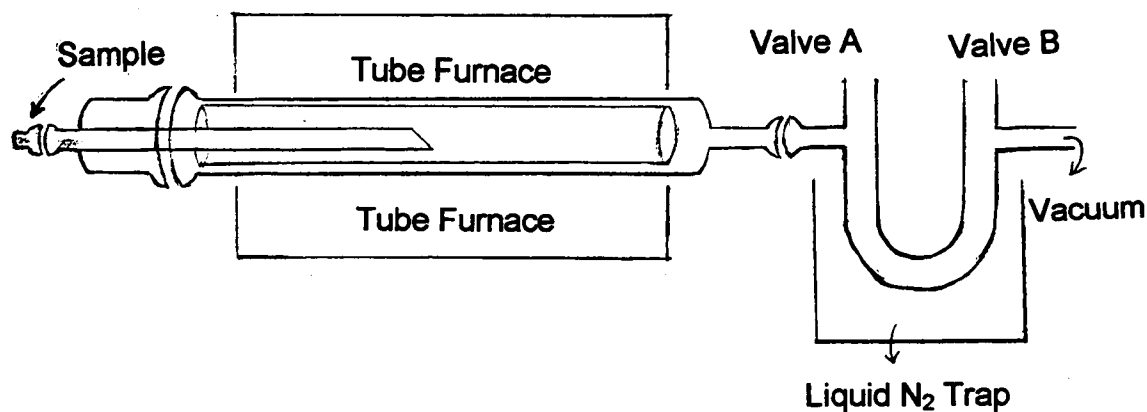


**Figure 5.8** CVD apparatus for the deposition of zirconium carbide.

measure the total hydrogen content in the volatile products. The procedures were repeated for the CVD using both **11b** and **11b-*d*<sub>8</sub>** as the precursor.

#### 5.3.4 The Analyses of the Volatile Products

**The Analysis of Volatile Products by NMR.** The sample was first analyzed by <sup>1</sup>H (400.1 MHz) and <sup>13</sup>C (100.6 MHz) NMR before the analysis by MS. A correction was made for the presence of volatile samples in the "head space" in the NMR tubes using a procedure detailed by Girolami and coworkers.<sup>6b</sup> The <sup>1</sup>H, <sup>2</sup>H{<sup>1</sup>H}, and <sup>13</sup>C{<sup>1</sup>H} NMR of the gases showed that the predominant organic products trapped were neopentane and isobutene isotopologues. Neopentane-*d*<sub>2</sub> (H<sub>3</sub>C)<sub>3</sub>C-CHD<sub>2</sub> was directly observed in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum: -CHD<sub>2</sub> was identified as a 1 : 2 : 3 : 2 : 1 quintet at 31.21 ppm with an isotopic shift <sup>1</sup>Δ of +0.60 ppm. Both isobutene-*d*<sub>0</sub> [<sup>1</sup>H δ 4.71 (2H, =CH<sub>2</sub>), 1.59 (6H, =CMe<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} δ 141.90 (=CMe<sub>2</sub>), 111.04 (=CH<sub>2</sub>), 24.02 (=CMe<sub>2</sub>)] and isobutene-*d*<sub>2</sub> Me<sub>2</sub>C=CD<sub>2</sub> were identified in the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, although the peak of the =CD<sub>2</sub> in (CH<sub>3</sub>)<sub>2</sub>C=CD<sub>2</sub> as a multiplet was not observed. The NMR isotopic shifts<sup>21</sup> for isobutene-*d*<sub>2</sub> were found: +0.0024 ppm (<sup>4</sup>Δ) for CH<sub>3</sub>, +0.10 ppm for CH<sub>3</sub> (<sup>3</sup>Δ), and +0.20 ppm for Me<sub>2</sub>C (<sup>2</sup>Δ). A partially resolved multiplet assigned to the CH<sub>3</sub> in (CH<sub>3</sub>)<sub>2</sub>C=CD<sub>2</sub> was seen at 24.26 ppm in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum. In addition, the ratio of integration of the CH<sub>3</sub> and =CH<sub>2</sub> groups was 7.3/1, rather than 3/1 as expected if only (CH<sub>3</sub>)<sub>2</sub>C=CH<sub>2</sub> is present. These observations are consistent with the presence of isobutene-*d*<sub>2</sub> as a volatile product in the CVD with Zr(CD<sub>2</sub>CMe<sub>3</sub>)<sub>4</sub> (**11b-*d*<sub>8</sub>**).

**The Analysis of Volatile Products by MS and GC/MS.** Field-ionization mass spectrometry (FI-MS) was conducted on a VG ZAB-EQ hybrid high performance spectrometer. The sample was introduced at *ca.*  $10^{-7}$  atm. The emitter voltage was maintained at 6 kV, while the counter electrode was kept at 0 kV. Such +6 kV ionization voltage was found to minimize the fragmentation of neopentane. In the FI-MS spectrum of a neopentane-*d*<sub>0</sub> control sample, the intensity of mass 71 (*M*-1) peak was found to be 0.8% of that of mass 72 (*M*) peak. In contrast, these two peaks were observed with *ca.* 50 : 50 ratio by Hindennach and Block.<sup>19a</sup> In obtaining the ratios of the neopentane isotopologues, corrections were made for (1) the *M*-1 peaks by using this ratio (0.8%), and (2) natural abundance <sup>13</sup>C isotopologues.

The gases produced from the CVD with Zr(CD<sub>2</sub>CMe<sub>3</sub>)<sub>4</sub> (**11b-d<sub>8</sub>**) were also analyzed by 70-eV electron-impact mass spectrometry (EI-MS). Girolami and coworkers have developed a method for the determination of the isotopic composition of samples of neopentane by EI-MS.<sup>6b</sup> Because neopentane does not give a parent peak in its 80-eV electron-impact mass spectrum, this method is based on the analysis of the intensities of the *tert*-butyl cations (H<sub>3</sub>C)<sub>3</sub>C<sup>+</sup>, (H<sub>3</sub>C)<sub>2</sub>(H<sub>2</sub>DC)C<sup>+</sup>, (H<sub>3</sub>C)<sub>2</sub>(HD<sub>2</sub>C)C<sup>+</sup>, and (H<sub>3</sub>C)<sub>2</sub>(D<sub>3</sub>C)C<sup>+</sup> at mass 57, 58, 59, and 60, respectively, as the products of neopentane ionization. However, in the current studies, the parent peaks of (CH<sub>3</sub>)<sub>2</sub>C=CD<sub>2</sub> and (H<sub>3</sub>C)<sub>2</sub>(H<sub>2</sub>DC)C<sup>+</sup> overlap at mass 58. Thus this method could not be readily used for the quantitative analysis of the gases produced from the CVD with Zr(CD<sub>2</sub>CMe<sub>3</sub>)<sub>4</sub> (**11b-d<sub>8</sub>**), and the EI-MS data were thus not used in the calculations.

The identifications of isobutene and neopentane isotopologues as well as the search for dineopentyl (2,2,5,5-tetramethylhexane) by GC/MS were conducted on a

Hewlett-Packard 6890 gas chromatograph (GC) with a 5793 mass selective detector (MSD). The column used was a Hewlett-Packard DB5MS capillary column (30 m  $\times$  250  $\mu$ m; coating: 0.25  $\mu$ m 5% phenyl methyl siloxane film). Dineopentyl (2,2,5,5-tetramethylhexane) was not observed in the GC/MS. A separation of isobutene and neopentane was achieved on the GC with a 0.5 mL/min Ar gas at 30 °C column temperature. The initial oven temperature was set to 26 °C, then increased to 27 °C at a rate of 0.5 °C/min. However, isobutene isotopologues were not separated by GC/MS. Isotubene- $d_2$  was directly observed in the GC/MS spectrum of isobutene isotopologues. Since the  $M-1$  (mass 57) and  $M-2$  (mass 56) peaks of isotubene- $d_2$   $(\text{CH}_3)_2\text{C}=\text{CD}_2$  overlap with those of parent isobutene- $d_1$   $(\text{CH}_3)_2\text{C}=\text{CDH}$  and - $d_0$   $(\text{CH}_3)_2\text{C}=\text{CH}_2$ ,<sup>23</sup> respectively, the presence of these two isobutene- $d_1$  and - $d_0$  isotopologues could not be directly confirmed in the GC/EI-MS spectrum of isobutene isotopologues. However, isotubene- $d_0$  was identified in the difference spectrum between this GC/EI-MS spectrum and that of  $(\text{CH}_3)_2\text{C}=\text{CD}_2$ .<sup>23</sup>

Neopentanes- $d_1$ , - $d_2$ , and - $d_3$  were directly identified in the GC/MS peak of the neopentane isotopologues by their *tert*-butyl cations  $(\text{H}_3\text{C})_2(\text{H}_2\text{DC})\text{C}^+$ ,  $(\text{H}_3\text{C})_2(\text{HD}_2\text{C})\text{C}^+$ , and  $(\text{H}_3\text{C})_2(\text{D}_3\text{C})\text{C}^+$  at mass 58, 59, and 60, respectively (see earlier discussion on EI-MS). No quantitative analysis was performed; such analysis will not be accurate because of the partial GC separation of these isotopologues.

## References and Footnotes

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## Vita

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