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| 6. AUTHOR(S)<br>Dietmar Seyferth                                                                                                                                         |                                                             |                                                            |                                                                         |  |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)<br>Massachusetts Institute of Technology<br>Department of Chemistry<br>77 Massachusetts Avenue<br>Cambridge, MA 02139 |                                                             |                                                            | 8. PERFORMING ORGANIZATION<br>REPORT NUMBER<br><br>2 15<br>AFOSR-TR     |  |
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| 13. ABSTRACT (Maximum 200 words)<br><br>A three-year summary of the principal investigator's research on organosilicon chemistry directed toward ceramics synthesis.     |                                                             |                                                            |                                                                         |  |
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FINAL SCIENTIFIC REPORT  
Grant No. AF-AFOSR-89-0040

"Organosilicon Compounds and Polymers and Silicon Ceramics"

Principal Investigator: Professor Dietmar Seyferth

Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

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November 23, 1992

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**A. Period Covered and Personnel****1. Period Covered**

1 November 1988 - 30 September 1992

**2. Personnel**

(Personnel are listed whose salaries and/or research costs were covered totally or in part by this Grant.)

**a. Principal Investigator**

Dietmar Seyferth, Professor of Chemistry

**b. Postdoctoral Investigators**

Miklos Tasi (University of Veszprem)

Hee-Gweon Woo (University of California at San Diego)

Gregor Brodt (University of Heidelberg)

Herbert Plenio (University of Göttingen)

Lars Wesemann (University of Aachen)

Yoshiyuki Sugahara (Waseda University)

Marion Meyer (University of Bielefeld)

**c. Predoctoral Investigators**

C.A. Sobon (Ph.D.)

H.J. Tracy (Ph.D.)

J.L. Robison (Ph.D.)

D. Son

P. Czubarow

## B. Research Accomplishments

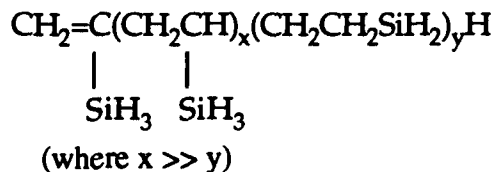
### 1. Polysilane Synthesis and Modification

Reaction of  $\text{CH}_3\text{SiHCl}_2$  with sodium in 7:1 (by volume) hexane/THF gives a liquid polysilane. Detailed NMR studies have established a constitution  $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y(\text{CH}_3\text{SiH}_2)_z]_n$ , where  $x + y + z = 1$ . The  $\text{CH}_3\text{SiH}_2$  units are the end groups. Conditions of the synthesis have been worked out such that  $x \sim 0.95$ , i.e., there is little crosslinking. Pyrolysis of this poly(methylsilane) (to  $1000^\circ\text{C}$  in argon) gives a low ( $\sim 20\%$ ) yield of ceramic residue that contains  $\sim 74$  wt % SiC and 26 wt % Si.

It was found that treatment with a catalytic quantity of a bis(cyclopentadienyl) Group IV compound (such as  $[\text{Cp}_2\text{ZrH}_2]_2$ ,  $\text{Cp}_2\text{ZrMe}_2$ ,  $\text{Cp}_2\text{ZrHCl}$  and  $\text{Cp}_2\text{TiMe}_2$ ) served to crosslink the poly(methylsilane) such that a high ( $> 70\%$ ) ceramic yield was obtained and the ceramic residue was near-stoichiometric SiC.

### 2. Poly(vinylsilane)

Vinyltrichlorosilane was polymerized using  $^{60}\text{Co}$   $\gamma$  radiation. The polymer yield was found to increase linearly with doses and about 40 Mrad was required for 50-60% yield. Vinyltriethoxysilane was much more readily polymerized. Reduction of poly(vinyltrichlorosilane) with  $\text{LiAlH}_4$  gave poly(vinylsilane). Detailed NMR studies indicated a constitution



This polymer may be crosslinked using transition metal catalysis and is then an excellent SiC precursor. Some Si-X conversion reactions of  $\text{PVSiCl}_3$  and  $\text{PVSiH}_3$  have been studied.

### 3. Borasilazanes

Treatment of the polysilazane obtained by ammonolysis of  $\text{CH}_3\text{SiHCl}_2$ ,  $[(\text{CH}_3\text{SiH}_2\text{NH})_a(\text{CH}_3\text{SiN})_b]_n$ , with  $\text{H}_3\text{B} \cdot \text{SMe}_2$  resulted in evolution of hydrogen and formation of a network polymer composed of borazine rings linked by polysilazane bridges.

Various Si/B ratios were investigated. High ratios gave liquid products; use of increasing amounts of  $\text{BH}_3 \cdot \text{SMe}_2$  gave solids. Pyrolysis in an atmosphere of ammonia gave borosilicon nitride in high ceramic yield.  $\text{BH}_3 \cdot \text{NHMe}_2$  and  $\text{BH}_3 \cdot \text{THF}$  could be used in place of  $\text{BH}_3 \cdot \text{SMe}_2$ . It is noteworthy that such incorporation of boron had as a consequence that  $\text{Si}_3\text{N}_4$  had not segregated and crystallized by  $1500^\circ\text{C}$ .

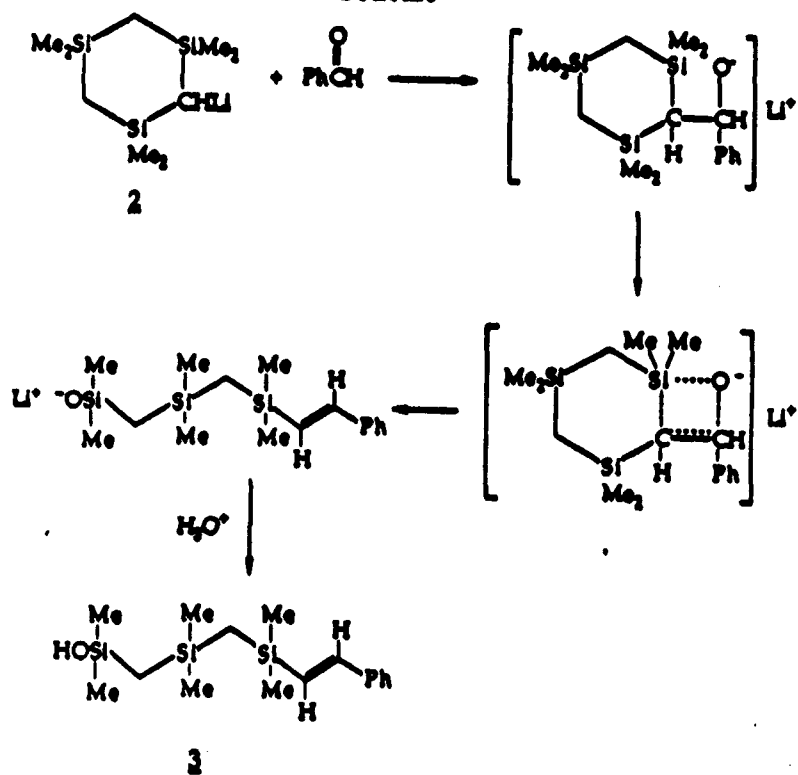
#### 4. An Approach to Ceramic Blends

The biscyclopentadienyldimethyl derivatives of Ti, Zr and Hf react with the  $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y]_n$  polysilanes to give, under appropriate conditions, soluble hybrid polymers that contain silicon and the other metal. Pyrolysis of these new polymers leaves a ceramic residue that contains SiC and TiC (or ZrC or HfC) plus substantial amounts of free carbon. The problem of excess C can be dealt with in two ways: (1) by pyrolyzing in a stream of ammonia, which results in removal of carbon, but converts the transition metal carbide to the nitride, so that SiC/MN blends result; (2) by adding sufficient metal powder to the polymer, so that the excess carbon will react to form the metal carbide. This results in C-free SiC/MC composites.

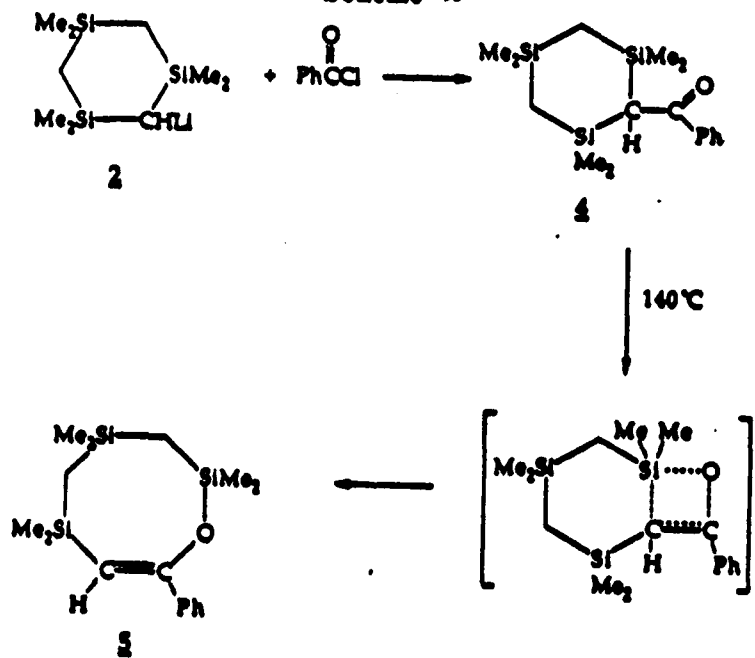
#### 5. Chemistry of Cyclic Polycarbosilanes

The structure of the lithium derivative of 1,1,3,3-tetramethyl-1,3-disilacyclobutane has been determined by X-ray diffraction (Fig. 1). The reactions of 2-lithio-1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane with benzaldehyde, benzoyl chloride and benzonitrile have been studied. (Schemes 1, 2 and 3).

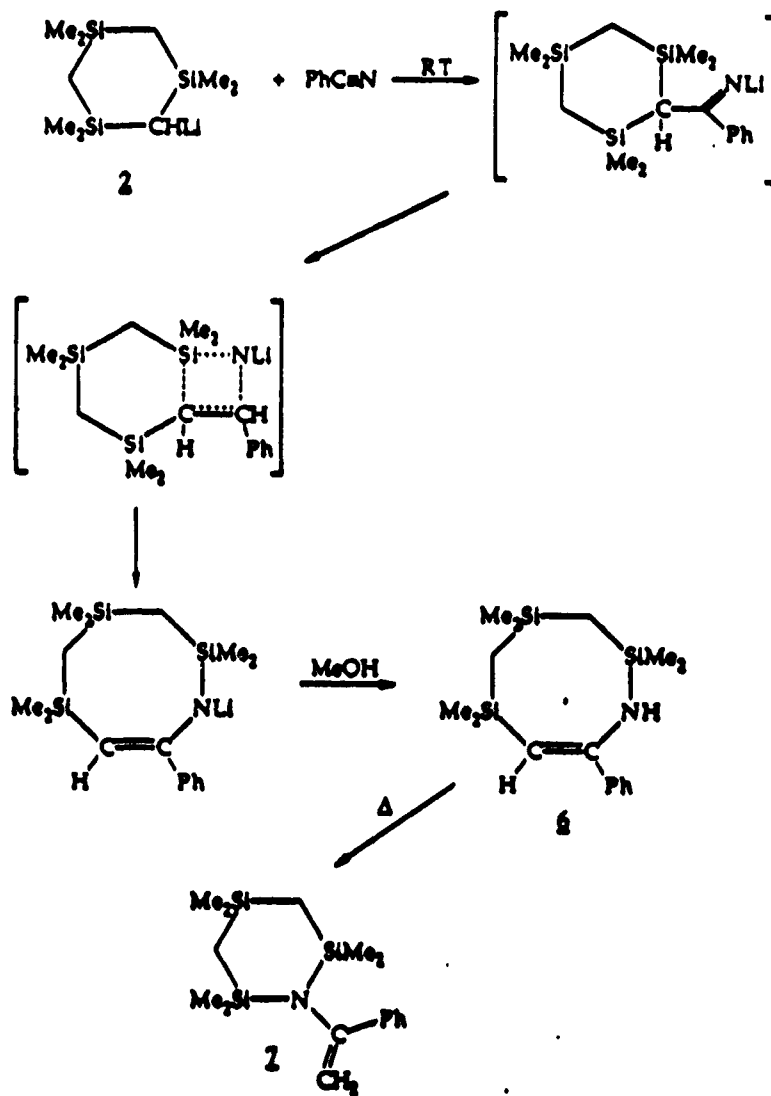
Scheme 1



Scheme 2



# Scheme 3



### C. Publication List

1. Synthese und Reaktivität von Alkynyl-substituierten Titanocen-Komplexen.  
*Z. Naturforsch.*, **45b**, 212 (1990).  
H. Lang and D. Seyferth.
2. Borasilazane Polymeric Precursors for Borosilicon Nitride.  
*J. Am. Ceram. Soc.*, **73**, 2131 (1990).  
D. Seyferth and H. Plenio.
3. Synthesis and Reactivity of 2-Lithio-1,1,3,3-tetramethyl-1,3-disilacyclobutane. Strain-Assisted Ring-Opening Processes.  
*Organometallics*, **9**, 2677 (1990).  
D. Seyferth, J.L. Robison and J. Mercer.
4. A New Procedure for "Up-Grading" the Nicalon Polycarbosilane and Related Si-H Containing Organosilicon Polymers.  
*New J. Chem.*, **14**, 545 (1990).  
D. Seyferth, C.A. Sobon and J. Borm.
5. Pyrolysis of Metallocene Complexes,  $(\eta\text{-C}_5\text{H}_4\text{R})_2\text{MR}'_2$ : An Organometallic Route to Metal Carbide (MC) Materials (M = Ti, Zr, Hf)  
*Appl. Organomet. Chem.*, **4** (1990) 599.  
D. Seyferth and H. Lang.
6. 4-ansa-Metallocene Complexes: Synthesis of 1,1,4,4-Tetramethyl-1,4-disilabutylene-Bridged Titanocene, Zirconocene and Hafnocene Derivatives.  
*Organometallics*, **10**, 347 (1991).  
D. Seyferth and H. Lang.
7. Preparation of Preceramic Polymers via the Metalation of Poly(dimethylsilene).  
*Organometallics*, **10** (1991) 551.  
D. Seyferth and H. Lang.
8. Structure of the 2-Lithio-1,1,3,3-tetramethyl-1,3-disilacyclobutane-N,N,N',N'-Tetramethylethylenediamine Adduct.  
*Organometallics*, **10**, 3385 (1991).  
J.L. Robison, W.M. Davis and D. Seyferth.
9. Chemical Modification of Preceramic Polymers: Some Examples from Silicon Chemistry.  
*Polymer Preprints*, **32**, No. 3, 581 (1991).  
D. Seyferth, H. Lang, H.J. Tracy, C. Sobon, and J. Borm.

10. Functionalization and Further Crosslinking of the Nicalon Polycarbosilane Based on Its Metalation with the n-Butyllithium-Potassium t-Butoxide Reagent.  
*Appl. Organomet. Chem.*, **5**, 463 (1991).  
D. Seyferth and H. Lang.
11. Chemical Modification of Preceramic Polymers: Their Reactions with Transition Metal Complexes and Transition Metal Powders.  
*J. Inorg. Organomet. Polym.*, **2**, 59 (1992).  
D. Seyferth, H. Lang, C.A. Sobon, J. Borm, H.J. Tracy and N. Bryson.
12. Near-Stoichiometric Silicon Carbide from an Economical Polysilane Precursor.  
*J. Am. Ceram. Soc.*, **75**, 1300 (1992).  
D. Seyferth, T.G. Wood, H.J. Tracy and J.L. Robison.
13. Reactions of 2-Lithio-1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane with Benzaldehyde, Benzoyl Chloride, and Benzonitrile.  
*Organometallics*, **11**, 3464 (1992).  
D. Seyferth and J. L. Robison.
14. Synthesis of Some Organosilicon Polymers and Their Pyrolytic Conversion to Ceramics.  
in "Silicon-Based Polymer Science - A Comprehensive Resource", Advances in Chemistry Series 224, J.M. Zeigler and F.W.G. Fearon, editors, American Chemical Society, Washington, DC, 1990, pp. 565-591.  
D. Seyferth.
15. Silicon Ceramics with a Dash of Boron.  
in "Frontiers of Organosilicon Chemistry", A.R. Bassindale and P.P. Gaspar, editors, Royal Society of Chemistry, Cambridge, 1991, pp. 15-27.  
D. Seyferth, H. Plenio, W.S. Rees, Jr. and K. Büchner.
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in "Materials: Today and Tomorrow", M.-C. H. Lutz, R. Ouliac and J.-P. Pradel, editors, Société Rhône-Poulenc Recherches, Paris, 1991, pp. 29-56.  
D. Seyferth.
17. Synthesis and Useful Reactions of Organosilicon Polymeric Precursors for Ceramics.  
in Materials Research Society Symposium Proceedings, Vol. 249, W.E. Rhine, T.M. Shaw, R.J. Gottschall and Y. Chen, editors, Materials Research Society, Pittsburgh, 1992, pp. 3-14.  
D. Seyferth, C. Strohmman, H.J. Tracy, J.L. Robison.

**18. Polycarbosilanes as Silicon Carbide Precursors**

in "Ultrastructure Processing of Advanced Materials" (Proceedings of the Fourth International Conference on Ultrastructure Processing of Ceramics, Glasses and Composites, February 20-24, 1989, Tucson, AZ), D.R. Uhlmann and D.R. Ulrich, editors, Wiley, New York, 1992, pp. 667-673.

D. Seyferth and H. Lang.

**D. Patents**

**1. Preceramic Organosilicon-Metal Carbonyl Polymers.**

U.S. Patent 5,070,116 (December 3, 1991).

D. Seyferth, C.A. Sobon and J. Borm.

**E. Lectures Given by the Principal Investigator During the Grant Period**

**1989**

University of Tsukuba (Japan)

National Chemical Laboratory for Industry (Tsukuba, Japan)

Mitsubishi Petrochemical Company (Tsukuba)

University of Tokyo

Tonen Corp.

Chisso Chemical Co.

New York Academy of Sciences

State University of New York at Albany (Henry G. Kuivila Lecturer)

Syracuse University

ACS Short Course on Inorganic Polymers (Philadelphia)

Hercules, Inc.

University of Heidelberg

Technical University of München

University of München

University of Würzburg

BASF (Ludwigshafen, Germany)

EUCHEM Königstein Conference on Applications of Organometallic Chemistry (invited lecture)

Ethyl Corp. (Baton Rouge)

First International Ceramic Science and Technology Congress (Anaheim, CA; invited lecture)

## 1990

GTE (Waltham Labs)

University of Texas at El Paso

Case Western Reserve University

MIT Industrial Liaison Symposium on Multifunctional Polymers

International Symposium on Organosilicon Chemistry Directed Towards Materials Science (Tohoku University; invited speaker)

Chisso Corp. (Minamata, Japan)

Japan Fine Ceramics Center (Nagoya, Japan)

Showa Denko Co. (Tokyo, Japan)

Sumitomo Chemical Co. (Tsukuba, Japan)

Florida State University

Rhône-Poulenc Co. (St. Fons, France)

University of Toulouse (France)

ACS Short Course on Inorganic Polymers (Chicago)

Technical University of Berlin

Akzo Research Labs in Arnhem

Akzo Research Labs at Obernburg

IX International Symposium of Organosilicon Chemistry (Edinburgh; invited speaker)

XIVth International Conference on Organometallic Chemistry (Detroit; invited speaker)

Central Research and Development Department, du Pont (Wilmington, DE)

Alcoa Technical Center

XIX Congreso Latinoamericano de Química (Buenos Aires; invited speaker)

## 1991

University of California at San Diego

University of Western Ontario (3M University Lecturer)

Japan-US Joint Seminar on Inorganic and Organometallic Polymers (Nagoya, Japan; invited speaker)

Kanegafuchi Chemical Co. (Kobe, Japan)

Toyota Central R&D Laboratories (Nagakute, Japan)

X Congreso Nacional de la Academia Mexicana de Quimica Inorganica (Zacatecas, Mexico; invited speaker)

Institute of Materials Science, University of Connecticut

Ethyl Corporation (Baton Rouge)

Rhône-Poulenc Co. (St. Fons, France)

University of Montpellier (France)

Fourth Chemical Congress of North America, New York (invited speaker, symposium on preceramic and inorganic hybrid materials)

European Ceramic Society Second Conference (Augsburg; invited speaker)

European Research Conference on New Perspectives in Organometallic and Coordination Chemistry (Kreuth, Germany)

Akzo Chemical Division (Dobbs Ferry, New York)

Fall Materials Research Society Meeting, Symposium on Synthesis and Processing of Ceramics: Scientific Issues (Boston; invited speaker)

## 1992

University of South Florida

XXV Silicon Symposium (Los Angeles; invited speaker)

Washington University (St. Louis)

University of Missouri at St. Louis

Monsanto Corporate Research Laboratories (St. Louis)

Flamel Technologies (Venissieux, France)

École Polytechnique, Palaiseau (France)

Münchener Silicontage (Munich; invited speaker)

204th National ACS Meeting, Symposium on Materials Chemistry (Washington, DC; invited speaker)

University of Toulouse (France)

ACS Short Course on Inorganic Polymers (Philadelphia)

## COMPLETED PROJECT SUMMARY

1. TITLE: Organosilicon Compounds and Polymers and Silicon Ceramics
2. PRINCIPAL INVESTIGATOR: Prof. Dietmar Seyferth  
Dept. of Chemistry, Room 4-382  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139
3. INCLUSIVE DATES: 1 November 1988 - 30 September 1992
4. GRANT NO.: AF-AFOSR-89-0040
5. COST AND FY SOURCE:
6. SENIOR RESEARCH PERSONNEL: Miklos Tasi  
Hee-Gweon Woo  
Gregor Brodt  
Herbert Plenio  
Lars Wesemann  
Yoshiyuki Sugahara  
Marion Meyer
7. JUNIOR RESEARCH PERSONNEL: C.A. Sobon  
H.J. Tracy  
J.L. Robinson  
D. Son  
P. Czubarow
8. PUBLICATIONS:

"Synthese und Reaktivität von Alkynyl-substituierten Titanocen-Komplexen," H. Lang and D. Seyferth. *Z. Naturforsch.*, **45b**, 212 (1990).

Borasilazane Polymeric Precursors for Borosilicon Nitride," D. Seyferth and H. Plenio. *J. Am. Ceram. Soc.*, **73**, 2131 (1990).

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"A New Procedure for "Up-Grading" the Nicalon Polycarbosilane and Related Si-H Containing Organosilicon Polymers," D. Seyferth, C.A. Sobon and J. Borm. *New J. Chem.*, **14**, 545 (1990).

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"Preparation of Preceramic Polymers via the Metalation of Poly(dimethylsilene)," D. Seyferth and H. Lang. *Organometallics*, **10** (1991) 551.

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## 9. ABSTRACT AND OBJECTIVES AND ACCOMPLISHMENTS

Research is described in the following areas: (1) synthesis and modification of a poly(methylsilane) by treatment with catalytic quantities of a Group 4 metallocene derivative so that pyrolysis of the modified polysilane (in argon) gives near stoichiometric SiC. (2) Synthesis of poly(vinylsilane),  $[\text{CH}_2\text{CH}(\text{SiH}_3)]_n$ , and its use as a precursor for SiC. (3) Synthesis of a class of borasilazanes. These are excellent precursors for

borosilicon nitride when their pyrolysis is effected in a stream of ammonia. (4) A procedure for the preparation of SiC/MC ( $M = \text{Ti, Zr, Hf}$ ) composites based on modification of poly(methylsilane) by reaction with stoichiometric amounts of  $\text{Cp}_2\text{MMe}_2$  and pyrolysis of the resulting polymers. Addition of a sufficient amount of the metal powder  $M$  to polymer serves to react with excess carbon formed in pyrolysis of the polymer, giving additional MC. (e) Studies on the chemistry and structure of cyclic polycarbosilanes,  $[\text{Me}_2\text{SiCH}_2]_n$  ( $n = 2,3$ ).