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13. ABSTRACT (Maximum 200 words) This report summarizes the results of research in the following areas: 1-The completion of a project on di-t-butylsilylene. 2-A novel route to binary semiconducting materials composed from the elements tin, germanium, lead, sulfur, selenium, and tellurium. 3-A new method of making ternary composites using the elements mentioned in 2. 4-The development of convenient procedures for making gallium arsenide, gallium phosphide and indium phosphide. 5-Expansion of the chemistry of siliranes. 6-The synthesis of three stable aromatic species containing silicon. 8-The synthesis of the first stable adduct of dichlorosilane 9-The initial studies on the synthesis of silicon-based dendrimers. 10-The initial studies on the synthesis of doped silicon carbides. 11-The development of a new procedure for preparing very high molecular weight polysilanes.			
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Principal Investigator: Philip Boudjouk (AFOSR 91-0197)

ANNUAL TECHNICAL REPORT for April 1, 1993 - March 31, 1994

I. List of Objectives

The list of objectives parallels the outline in our research proposal (AFOSR No. 91-0197):

- 1- Conduct an in-depth study of the reactions and mechanisms of highly reactive species containing silicon with emphases on hindered silylenes, siliranes, intermediates with silicon to transition metal bonds and intermediates with silicon-chalcogen linkages;
- 2- Expand the number of catalytic processes involving silicon with particular emphasis on the hydrosilylation reaction; and,
- 3-Initiate a program focused on the syntheses and characterization of novel polymers based on silicon with emphases on dendrimers and transition metal containing polysilanes and polysiloxanes.

In the last 24 months we expanded one of the objectives in number 1 above which dealt with intermediates with silicon chalcogen linkages to include intermediates with atoms from Groups 13, 14, 15, and 16. In this third and final year of this grant we placed considerable emphasis on this chemistry because of its potential for generating materials with novel electronic and optoelectronic properties.

II. Status of Research Effort

We have made substantial progress in all three areas in the time period April 1, 1993 - March 31, 1994. Below is a summary of our status in each area.

A. Reactive Organosilanes

Our program in this area consists of six projects:

1. Hindered Silylenes

During the first year of this grant we essentially completed the program initiated under AFOSR 88-0060 in which our goal was to develop convenient synthetic pathways to divalent silicon containing reactive intermediates that featured large groups on the silicon atom, to explore the synthetic utility of these species and to establish at least the main features of the mechanisms important to the generation and reactivity of these reactive intermediates.

Our studies in this area led to several important discoveries, the most important of which are the development of a convenient, high yield synthesis of highly hindered silylenes and the elucidation of the α - elimination mechanism for difunctional silanes. Some of these results were outlined in last year's technical report and are detailed in publications (Nos. 59, 66, 73, 86 and 100 in the List of Publications and Ph. D. Thesis of Eric Black, North Dakota State University, 1992).

2. Group 14 - 16 Intermediates - Extensions to Groups 13 - 15

We succeeded in generating and characterizing reactive intermediates of the type, $R_2Si=E$, where $E = S$ and Se , by thermolysis or pyrolysis of six membered rings of the formula, $(R_2SiE)_3$. The results were

outlined each of the last two reports and are detailed in publications 56, 67, 70, 74 and 86 in the List of Publications.

When we replaced silicon with tin in cyclic systems of the type $(\text{Ph}_2\text{SnE})_3$, we obtained a very surprising and useful result. Phenyl groups attached to tin were easily removed by thermolysis leaving very pure samples of tin sulfide and tin selenide, respectively. For linear systems like $(\text{Ph}_3\text{Sn-E-SnPh}_3)$ we observed similar results, i.e., efficient production of SnE phase pure binaries, but we also obtained some evidence for the intermediacy of the highly reactive intermediates, $\text{Ph}_2\text{Sn=E}$. These results are summarized in the section below, Group 14 Chalcogenides

a. Group 14 Chalcogenides

1-Tin Sulfides and Selenides

We developed the chemistry of heavy atom analogs to ketones under our earlier grant (AFOSR 88-0060) and were interested to extend the work on $\text{R}_2\text{Si=S}$ and $\text{R}_2\text{Si=Se}$ to the tellurium, tin, germanium and lead analogues. To our surprise, we found that our low temperature pyrolysis techniques ($<400^\circ\text{C}$) led to high yields of very pure tin sulfide and tin selenide. Our samples are semiconductors. The findings are unique in that we discovered that phenyl groups attached to heavy atoms are facile migrators, even in the condensed phase at low temperatures, i.e., $<400^\circ\text{C}$, permitting phenylated tin chalcogens to serve as excellent precursors to Group 14-16 binary compounds. This work has recently been published (No. 77 in the List of Publications). We can now produce high quality SnS and SnSe in multigram quantities from readily available cyclic and linear compounds.

We have successfully extended our approach to tellurium and have prepared excellent samples of tin telluride from compounds as simple as $\text{Ph}_3\text{Sn-Te-SnPh}_3$ (this work is detailed in publication 90 on the List of Publications). We have also produced thin films of SnTe with surface areas of several square centimeters.

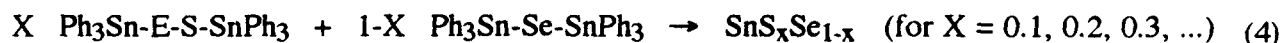
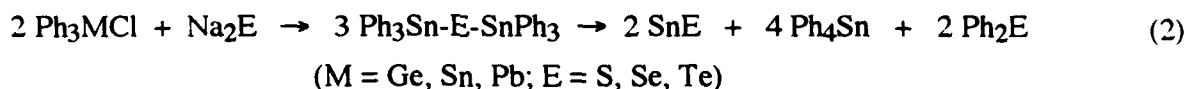
2-Germanium and Lead Analogs

Germanium, lead and tellurium binary compounds, because of their well known utility as infrared detectors, are target materials for us. On our way to these binaries we had to develop a useful synthesis of likely precursors to our desired lead sulfide and lead selenide. A paper describing much improved syntheses of key intermediates was recently published (No. 78 in the List of Publications). We have prepared samples of lead sulfide and lead selenide using our pyrolysis technique. However, unlike all other cases we have examined, the target product is contaminated with elemental metal. We are working towards developing conditions for producing PbS and PbSe as well as PbS_2 and PbSe_2 without the production of free lead. Progress on germanium has been slower mostly because of the expense of germanium starting materials.

3-Ternary Compounds of Groups 14 and 16

Potentially more exciting than the above is our new found ability to make **ternary** compounds such as $\text{SnS}_x\text{Se}_{1-x}$ with good control over x by a very simple technique: simply mix the ring systems $(\text{Ph}_2\text{SnS})_3$ and $(\text{Ph}_2\text{SnSe})_3$ and pyrolyze the mixture. Since this is a **condensed phase** pyrolysis, the

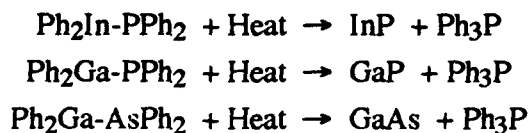
ratios will be preserved. For example, a 1:1 mixture of $(\text{Ph}_2\text{SnS})_3$ and $(\text{Ph}_2\text{SnSe})_3$ gave excellent yields of very pure $\text{SnS}_{0.5}\text{Se}_{0.5}$. This is definitely a **single phase** and not a mixture of SnS and SnSe as determined by x-ray diffraction. We have since extended this methodology to cover the full range of stoichiometries. Thus we have successfully prepared $\text{SnS}_x\text{Se}_{1-x}$ in which x is varied from 0.1 to 0.9 in increments of 0.1. Each of these solid solutions is being characterized by x-ray crystallography. We have also found that this approach applies to linear systems. That linear systems are excellent single source precursors to these materials is significant because linear structures are much easier to prepare. As an example, we can access tellurides very easily via the linear compounds (eqn 2), whereas we have been unable to prepare good quantities of ring systems containing tellurium. We also discovered that combinations involving lead are easily made from linear systems. Equations 1-4 summarize our results.



We are now applying this methodology to Group 13 - 15 and Group 13 - 16 combinations. We expect to prepare solid solutions of the following general types: $\text{GaAs}_x\text{P}_{1-x}$ and $\text{GaS}_x\text{Se}_{1-x}$. Further work will lead us to compositions from three different groups, examples of which are: $\text{GaAs}_x\text{S}_{1-x}$, $\text{GaSe}_x\text{P}_{1-x}$ and $\text{Ga}_x\text{In}_{1-x}\text{As}$. Our research on Group 13 - 15 combinations is discussed in the next section.

4-Extensions to Group 13-15

In April 1992 we opened a new line of investigation that is truly exciting and very promising for the development of new materials based on Group 13-15 elements, specifically, materials with novel electronic properties. In brief, we discovered that the aryl migration mechanism responsible for the facile generation of SnS and SnSe also provides an easy pathway to binaries such as InP and GaAs. Thus, we have produced these materials in very high purity and high yield by the following equations:



The gallium arsenide synthesis is particularly noteworthy because our material is highly crystalline, carbon free and eliminates the use of highly volatile, and thereby more toxic starting materials. We reported these results at the American Chemical Society Meeting in Chicago (August, 1993)

5-Proposed Research Effort in this Area for the Period 4/93 - 3/94 vs Results

Below is a brief outline of our efforts in this area for the period 4/93 - 3/94. Goals are restated from last year's report.

1. Goals: Group 14 - 16 binary semiconductors with band gaps of 1.1-1.3 eV that appear to have their best potential as photovoltaic devices. Results: Synthesis of very pure SnS, SnSe, GeS, and GeSe, all of which have band gaps in the 1.1-1.5 eV range. Soon to be published (no 87 on the Publication List) is our **standard preparation** of tin (II) sulfide and tin (II) selenide.

2. Goal: Group 14 - 16 binary semiconductors with narrow band gaps of 0.1 - 0.4 eV for potential use as IR detectors and switching devices. Results: Synthesis of very pure, SnTe, PbS, PbSe, PbTe. Measurements are not yet complete. Lead samples were difficult to prepare free of elemental lead. SnTe can be prepared in very high yield in a high state of purity.

3. Goals: Group 14 - 16 ternary materials. For example, $\text{Sn}_x\text{Pb}_{1-x}\text{S}$ and $\text{Sn}_x\text{Pb}_{1-x}\text{Se}$ have the best characteristics for solar cells of the entire group 14 - 16 binary or ternary class.

Our goal is develop new synthetic methodologies for

- 1) known useful combinations of Group 14 - 16 elements (examples in I, II, III above) and,
- 2) new combinations of these elements with potentially improved electronic properties

(Example, our prep of the $\text{SnS}_x\text{Se}_{1-x}$ series).

Results: 1-Successful preparations of small samples of SnGeS, SnGeSe and SnGeTe ternaries.

2-Successful synthesis of precursors for lead analogues to the above ternaries.

3-Complete crystallographic characterization of all 10 combinations of $\text{SnS}_x\text{Se}_{1-x}$.

4-Successful upscaling of synthesis of binaries and ternaries to multigram quantities.

5-Successful preliminary studies on preparations of $\text{PbS}_x\text{Se}_{1-x}$, $\text{GeS}_x\text{Se}_{1-x}$ and $\text{PbTe}_x\text{Se}_{1-x}$.

6-Successful preliminary studies on preparations of $\text{Pb}_x\text{Ge}_{1-x}\text{S}$.

4. Goal: Investigate benzyl groups as cooperative fragments in the pyrolysis of organometallics.

This project has been very successful. We have discovered that benzyl groups are far more efficient as leaving groups in fragmentation reactions than the traditional t-butyl groups employed by most workers in the field. High yields of the target binaries are obtained with remarkably low levels of carbon contamination. This is not a rearrangement mechanism as is the phenyl substituted models but a classic homolytic cleavage. The equation below summarizes our findings. More detailed information on this work is in our Annual Technical Report for Grant No. F49620-92-0431. This is a highly promising route, probably better than our phenyl methodology, to main group metal chalcogenides and we will continue to explore this chemistry.



3. Siliranes and Silirenes

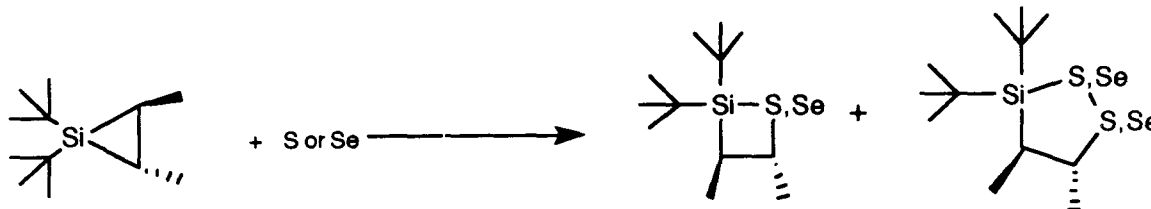
One of the most useful reactions of our silylene generation reaction is its reaction with olefins to yield siliranes in high yield. We have developed the chemistry of 1,1-di-t-butylsiliranes in some detail. That

work is published or in press with three more papers soon to be submitted (publications 66, 67, 73, 86, 88, and 100 on the List of Publications). Among those articles is one in press for *Inorganic Syntheses* which gives the details of a **standard preparation** of 1,1-di-*tert*-butyl-2,3-dimethylsilirane (No 88) and the synthesis of the first silirane with only hydrogen substituents on the carbon atoms (No 73). The latter paper resolved an important bonding question in strained rings containing silicon.

a. Insertion reactions

The high strain in the silirane ring was exploited for synthetic purposes. We prepared the first examples of the novel four membered ring systems in Figure 1 simply by exposing the silirane to sulfur or

Figure 1



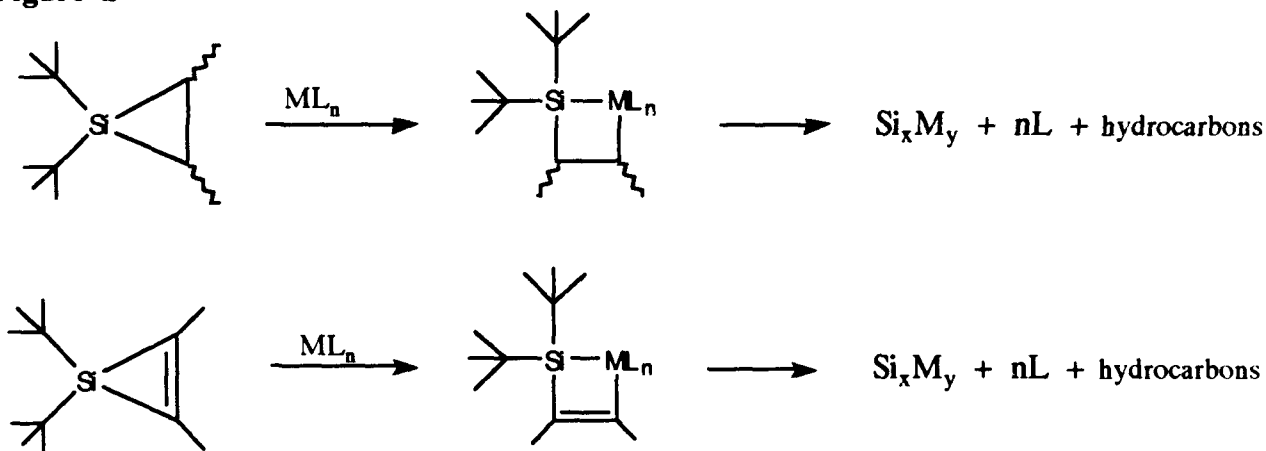
selenium at room temperature. We also found that salts accelerate the reaction and affect the stereochemistry of insertion. These are the first examples of these ring systems. These studies have been accepted for publication (Nos. 67, 74, and 86 on the List of Publications). Publication 86 is a very detailed study of the synthesis, mechanisms and structures of these molecules. The work includes two crystal structures, extensive 2-D nmr work and rate studies pertinent to the reactions of these systems.

Success in this area leads us to believe that other insertion reactions will work. We were particularly hopeful that we would be able to insert metal fragments into the silirane, or perhaps silirene, ring system to produce 1,2-silametallocyclobutanes and 1,2-silametallocyclobutenes.

b. Silametallacyclobutanes and Silametallacyclobutenes

During this last year of the grant we have made no substantial progress on this difficult project. We prepared key starting materials to conduct the essential experiments discussed in our original proposal.

Figure 2

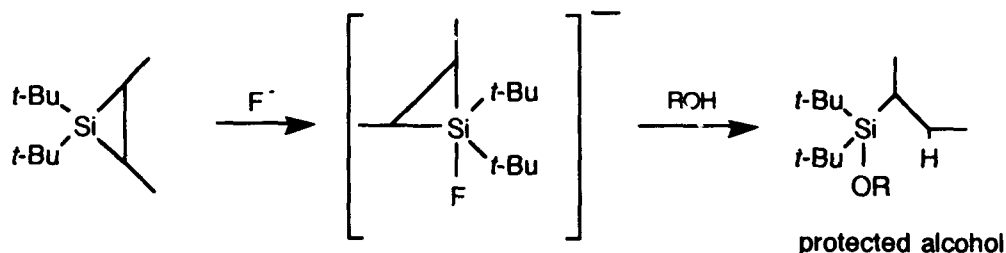


However, we have been unsuccessful in our attempts to isolate characterizable materials from our efforts to insert metal fragments into our siliranes. These insertion compounds, if prepared, may be very useful precursors metal silicides (Figure 2).

c. Ring opening reactions

We found an unexpected and potentially useful result: siliranes are efficient precursors to exceptional protecting groups for alcohols. We have completed a study of the ability of siliranes to form protected ethers and amines (No. 98 on the Publication List). The protected ethers are easily prepared (No. 66 on the Publication List) by heating the silirane with an alcohol and potassium fluoride (Figure 3).

Figure 3



These ethers are stable to acid, base, reducing agents and oxidizing agents. As an example, ethers protected with the *tert*-Bu₂(i-Bu)Si group are resistant to concentrated acid for over 24 hours!

In the last year we have tested a broad variety of reagents and conditions in efforts to remove the silyl group from the oxygen. We were not successful. The net result is that we have developed an extraordinarily stable protecting group that will be useful for cases where the active site of a drug is NOT the protected function. One example that stands out would be the protection of digitalis, a well-known heart drug. In this case, the role of the oxygen protecting group is to fix stereochemistry to maintain activity. We will obtain a sample of digitalis, put on our silyl group and have the drug tested for activity. Another important agent requiring protection is aziridine, an important antitumor drug. We will followup on these cases in the coming year. They are low effort tasks requiring little time after we secure good drug samples.

4. Reactive Intermediates with Trivalent Silicon

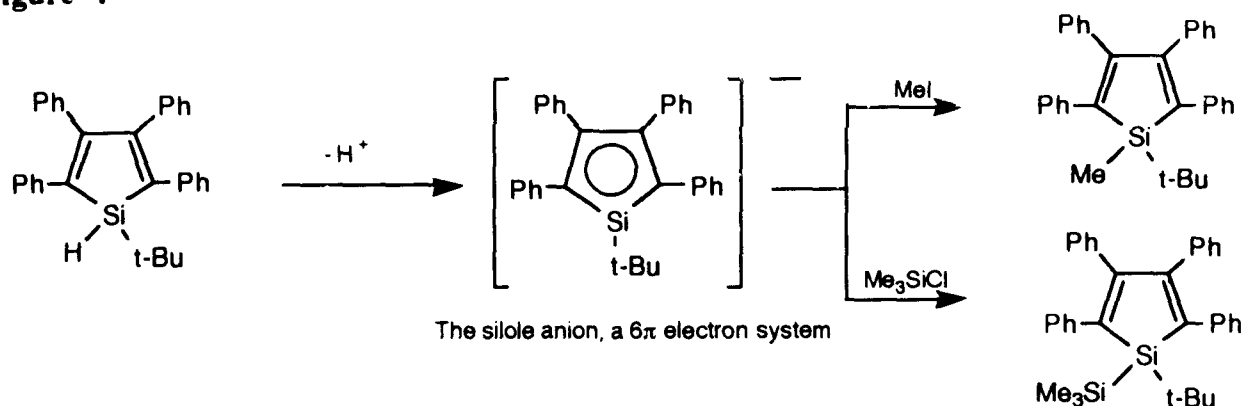
There is a great deal of interest in reactive intermediates in which silicon is in the trivalent state. The two systems we have investigated are silyl cations and the particular case of aromatic silyl anions. We have demonstrated that silyl hydrides will undergo hydride abstraction in presence of nitriles to form coordinated silyl cations:



We have reported on this work (Publications 79 and 83 in the List of Publications). The latter paper describes one of the most detailed studies to date on coordinated silyl cations.

A stable species in which silicon is part of an aromatic system has been an important target for synthetic chemists for several decades. Species stable at 10°K have been detected but no room temperature species has been characterized. We have generated such a

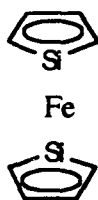
Figure 4



compound. It is stable for weeks in solution and we have been able to determine some of its reaction chemistry (Figure 4). We attribute the stabilization to two causes: aromaticity of the 6π electron silole ring and the bulk of the four phenyl groups on the carbon atoms in the ring.

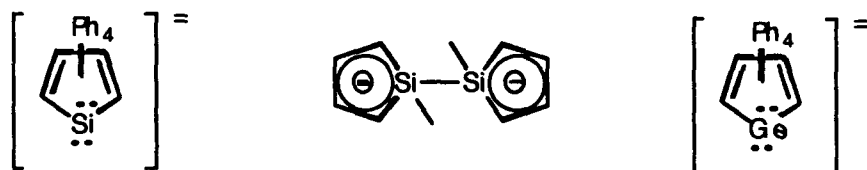
The highly delocalized structure is justified by the Si-29 chemical shift which is 30 ppm downfield from the neutral silane and 60 ppm downfield from other silyl anions. We reported this discovery at the Organosilicon Symposium in March of 1993 and at the Chicago ACS meeting in August of 1993. The details of the synthesis and characterization have been published in the Journal of the American Chemical Society (No 84 in the Publication List). This work solves a problem in organosilicon chemistry that is at least three decades old and establishes a base for an entirely new area of research. Fundamentally, the impact will be large and long lasting. The question, "Will silicon form stable aromatic compounds?" has now been answered: YES!

Presently we are investigating the synthesis of sandwich compounds with transition metals such as that depicted below:



We have been working on sandwich compounds of silicon but to no avail. This is still an important project for us.

We have been successful in extending the series of aromatic compounds containing silicon to two novel species, the silole dianion and the disilafulvalene dianion:



These are remarkably stable species and we have been able to fully characterize them by NMR spectroscopy. Our preliminary results were reported at the Silicon Symposium in Troy NY in March of 1994 (Poster No 23) and are currently in press (No. 89 on the Publication List). We have extended this work to germanium and successfully characterized the germole dianion (No 93 on the Publication List).

5. Disilabetweenanenes

We report no significant progress on this project.

6. Silylene Complexes of Metallocenes

No progress. We have not succeeded in preparing intermediates we consider essential to a successful investigation of the proposed intermediates (pg 4 of original proposal).

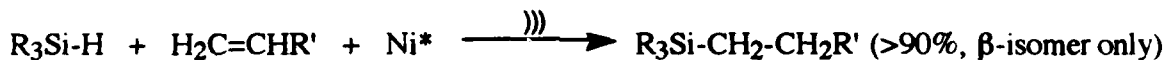
B. Catalytic Processes

1. Nickel Catalyzed Hydrosilation Reactions

The major driving force behind this project is our discovery that activated nickel, produced by the ultrasound promoted reduction of nickel halides by alkali metals, will replace platinum as a catalyst for hydrosilylation. This is the first example of efficient catalysis of hydrosilylation by an abundant metal.

a. Simple olefins

These reactions are characterized by high yields, short reaction times and mild conditions. The terminal,



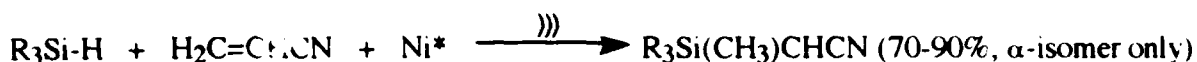
or β , isomer is the exclusive product in all of the non functional olefins we examined. We were surprised to find out that, in the absence of olefins, the nickel will catalyze reductive coupling of silanes to form disilanes, trisilanes and tetrasilanes. These results open the door for more studies using common metals to catalyze these critical reactions. Our results are summarized in publications 71, 72 and 75 in the List of Publications. Our recent efforts focused on controlling regio and stereochemistry of the addition reaction to simple olefins as well as improving the current low reaction efficiency with internal olefins. We are also spending considerable effort in preparing a soluble, homogeneous analog to the nickel surface.

Regarding the coupling of hydrosilanes: this is a reaction with potentially enormous impact. Polysilanes have secured an important niche in high performance specialty polymers. Unfortunately, the current preferred synthesis is stoichiometric and very expensive. A cheap recyclable catalyst that facilitates the formation of silicon-silicon bonds would greatly enhance the commercial potential of polysilanes.

b. Functionalized olefins

As pointed out in each of the last two reports, functionalized olefins combined with functionalized silanes are key building blocks in the synthesis of polymers. During the course of this last year we have been studying the mechanism of the successful hydrosilylation of acrylonitrile in the α position when nickel is the catalyst. We are now in the midst of detailed rate studies in an effort to elucidate the rate

determining step and the key intermediates. Preliminary evidence supports the formation of an nickel-olefin complex and silicon hydride oxidative addition to nickel as key steps.



c. Surface studies

The high reactivity of the nickel prompted us to examine the surface of the metal using Scanning Electron Microscopy. We observed that ultrasound produced unusual deformations on the surface of the metal in the form of craters. These craters have not been observed on metal surfaces before and suggest that the ultrasound is causing a plastic deformation of the surface (the craters have smooth edges) perhaps resulting from a localized effect of the imploding cavities generated by the ultrasonic waves. We have recently summarized these observations for the Royal Society (No 85 in the Publication List).

In addition to the SEM studies we have investigated the species formed on the surface of the metal using Raman spectroscopy. We observed carbonyl species on the surface and were surprised to find both bridging and terminal carbonyls. The most amazing fact uncovered here is that the Ni-carbonyl linkages are essential to the hydrosilylation and reductive coupling reactions. Our preliminary results have been published (Nos. 71, 72 and 75 in the Publication List).

The necessary next step is a thorough study of the surface using High Energy X-Ray Dispersion Techniques which allow qualitative and quantitative determination of the surface composition. We will follow this with a surface study using Atomic Force Microscopy/Scanning Tunneling Microscopy.

2. Platinum-on-Carbon Catalyzed Hydrosilylation of Alkynes

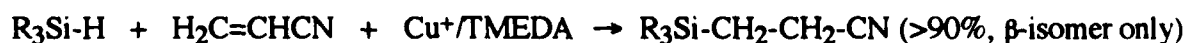
We have completed the **first** broad-based study of the effect of platinum on carbon on the hydrosilylation of alkynes. Remarkably, this reaction has not been investigated in detail. In brief, we found that inexpensive platinum on carbon is as effective as the far more expensive Karstedt's catalyst that is most commonly used. We presented our results at the American Chemical Society meeting in August of 1993 and a full manuscript is very near completion (No. 96 in the Publication List). This work is the subject of a thesis (M.S. Thesis, Brian J. Hauck, North Dakota State University, 1994)

3. Amine-Based Catalysts for Hydrosilylation

Our studies in this area have focused mostly on the use of copper salts in combination with diamines as catalysts for hydrosilylation of functionalized olefins. This work was begun under AFOSR 88-0060.

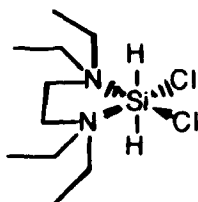
a. Nitriles

The hydrosilylation of acrylonitrile is a commercially important reaction and we have devoted considerable effort to the optimization of the reaction and a study of its mechanism. Our catalyst system is unique because it promotes the **exclusive** formation of the β isomer, the most useful silyl derivative of acrylonitrile.



In our mechanistic work we have demonstrated 1) the necessity of diamines to the reaction (simple amines are far less effective); 2) diamines catalyze by a different mechanism than simple monoamines, the former proceed through five and perhaps six coordinate siliconates, and that 3) for the latter, the monoamines, the trichlorosilyl anion is essential to the hydrosilylation. The last point has been inferred from previous work but we have now demonstrated it clearly using Si-29 NMR spectroscopy.

This past year we succeeded in isolating, for the first time, the diamine complex of dichlorosilane:



This result is quite significant because this crystalline, thermally stable, slightly water sensitive complex is far easier and safer to handle than the uncomplexed dichlorosilane, H_2SiCl_2 , which is a flammable gas that can explode on contact with moist air. Our complex can be weighed in a glove bag and will decompose slowly in air to form siloxane polymers and free diamine. We have obtained the crystal structure of this complex and we have submitted this synthesis to *Inorganic Syntheses* (No. 92 in the Publication List) for evaluation as a standard preparation of this compound. The Editorial Board has recommended acceptance and the procedure is now being checked in an independent laboratory.

We have further studied this complex and found that it performs all of the important reactions that the uncomplexed dichlorosilane does. Thus we have "tamed" dichlorosilane to the point where it can be handled by relatively novice lab workers. The complexing diamine can be recovered from all reactions. This investigation led to the synthesis and isolation of several novel complexed silanes in addition to a thorough study of the hydrosilylation of acrylonitrile and methyl acrylate catalyzed by copper complexes. These studies are summarized in a thesis (Ph. D. Thesis, Steven D. Kloos, North Dakota State University, 1994) and a full manuscript that is in preparation.

b. Acrylates

We were happily surprised to find out that this catalyst system applies very well to acrylates. Only one product (again the β isomer) is obtained in most cases and the total hydrosilylation is in very high yield.



This work has recently been published (No. 82 in the Publication List). Recent work has allowed us to characterize, by NMR spectroscopy, the Cu-acrylate complex formed as the intermediate.

C. New Materials From Silicon-Based Dendrimers

One of the new areas we are exploring is the synthesis and characterization of novel polymers with silicon-containing backbones. Among the classes we are investigating is the **starburst** or **dendrimer**

class, We are in the initial stages in this work and we have successfully prepared several "kernels" of our dendrimer (or "star") using one of our hydrosilylation techniques.

The key building blocks we now have in hand are:

1) $[(CH_2=CH)_3Si]_3SiCH_2CH_2)_4Si$. The terminal vinyl groups will now serve as functionalities for such reactions as additional hydrosilylation, complexation to metals or conversion to other functionalities.

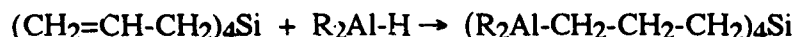
2) $(C_8H_{17}CH=CHC_{12}H_{24}O)_4Si$. internal double bond available for functionalization, Si-O bond supplies strength and flexibility.

Potential uses: high performance lubricants, preceramics with control over Si/C ratios; conductive thin films; high volume-low mass applications.

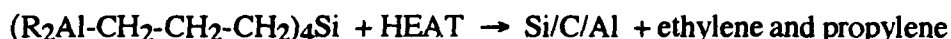
Results in the April 1993 - March 1994 time period: The unit in 1) has been extended one more generation but in yields of less than 5%. The compound in 2) above is undergoing testing for lubricity, thermal stability and resistance to oxidation.

D. Precursors to Doped SiC Materials

Using smaller highly symmetrically substituted silanes we have discovered a simple way to make silicon carbide doped with a variety of metals. For example, when the tetraallyl silane below is treated with a hydroalumination reagent we obtain an aluminum-incorporated precursor to aluminum doped silicon carbide:



Simple heating of this compound gave a gray-black material containing only trace hydrogen but significant silicon, carbon and aluminum:



Hydrometallation with boron and tin was successful but failed with iron and chromium. The boron and tin cases gave Si/B/C and Si/Sn/C powders respectively when heated. These powders have yet to be fully characterized.

E. Improved Synthesis of Polysilanes Using Ultrasound

During the course of our studies to make functionalized polysilanes we found it worthwhile to examine new methods of preparing polysilanes. In brief, we have discovered that by using **pulsed** ultrasonic waves from a high intensity ultrasonic horn that we can prepare polysilanes consistently with **molecular weights in excess of one million!** There are only a few reports in the literature describing polysilanes with such high molecular weights. These have been very difficult to reproduce. Our methodology has the advantage of simplicity and consistency.

III. List of Publications

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94. "Phenylated Group 13/15 Compounds: Synthesis, Characterization and Pyrolysis. A Convenient Route to Group 13/15 Phase Pure Binaries", P. Boudjouk and Y. Pan, *Chem. Mater.*, to be submitted.
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96. "Hydrosilylation of Alkynes Catalyzed by Platinum on Carbon", P. Boudjouk, B. Hauck and B.-H. Han, *Organometallics*, to be submitted.
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99. "Unexpected Reactions of 1,4-Dithio-1,2,3,4-tetraphenyl-1,3-butadiene. Synthesis and Structure of 1,1-Dichloro-2,3,4,5-tetraphenyl-7-(dichlorovinylsilyl)-1-silacyclohepta-2,3-diene", Y. Pan and P. Boudjouk, to be submitted.
100. "The α -Elimination Route to Silylenes. Alkali Metal Reduction of Highly Hindered Dihalosilanes", P. Boudjouk, E. Black, U. Samaraweera, R. Kumarathasan and I. Stoenescu, to be submitted.

IV. List of Professional Personnel (4/1/93 - 3/31/94)

Senior Personnel	Philip Boudjouk, Principal Investigator	
Postdoctoral Associates	Jang-Hwan Hong Youlin Pan Vivian McGrath	
Graduate Assistants	David Garlie Duane Simonson Timothy Splinter Brian Hauck Steven Kloos	Seok-Bong Choi Beon-Kyu Kim Dean Seidler Scott Payne
Undergraduate Assistants	Ioanna Stoenescu Christopher Meyer Bill Korinec	

V. Interactions

A. Papers presented at meetings, conferences and seminars

1. Papers/Posters (presenter underlined)

SYNTHESIS AND CHARACTERIZATION OF 2,3,4,5-TETRAPHENYL-1-SILACYCLOPENTADIENIDE SILOLE DIANIONS. Jang-Hwan Hong, Philip Boudjouk*, and Stephen Castellino, Silicon Symposium-March 1994 Troy P-23

"EFFECTS OF PULSING SONICATION ON POLYSILANE SYNTHESIS", D. Garlie, K. Matsukawa and P. Boudjouk, Silicon Symposium-March 1994 Troy, P-18:

Division of Inorganic Chemistry, 206th ACS National Meeting Chicago, 8/22/93 - 8/27/93.

Inor 384. SYNTHESIS AND CHARACTERIZATION OF BIS(1-LITHIO-2,3,4,5-TETRAPHENYL-1-SILACYCLOPENTADIENIDE), A SILICON ANALOG TO THE FULVALENE DIANION. Jang-Hwan Hong and Philip Boudjouk

Inor 92. HYDROMETALLATED POLYMERS AS PRECURSORS TO $(M_{13,15})_x(SiC)_y$. Timothy A. Splinter and Philip Boudjouk

Inor 93. GROUP 13/15 COMPOUNDS WITH PHENYL SUBSTITUENTS. Youlin Pan and Philip Boudjouk

Inor 94. EFFECTS OF PULSING SONIFICATION ON THE SYNTHESIS OF POLYSILANES. Kimihiro Matsukawa and Philip Boudjouk

Inor 95. SYNTHESIS AND CHARACTERIZATION OF 2,3,4,5-TETRAPHENYL-1-GERMACYCLOPENTADIENIDE GERMOLÉ DIANIONS. Jang-Hwan Hong and Philip Boudjouk

Inor 96. RING OPENING REACTIONS OF BULKY SILIRANES. SYNTHESIS OF HIGHLY HINDERED SILYL ETHERS AND SILYL AMINES. Ioana Stoenescu, Rajkumar Kumarathasan and Philip Boudjouk

Inor 166. A MECHANISTIC INVESTIGATION OF THE SYNTHESIS OF GROUP 14-16 SEMICONDUCTOR MATERIALS FROM ORGANOMETALLIC PRECURSORS. Dean J. Seidler and Philip Boudjouk

Inor 382. MECHANISTIC AND REACTIVITY STUDY OF THE COPPER-TMEDA HYDROSILYLATION CATALYST. Steven D. Kloos and Philip Boudjouk

Inor 383. HYDROSILYLATION OF ALKYNES CATALYZED BY PLATINUM ON CARBON. Brian J. Hauck, Byung-Hee Han and Philip Boudjouk

Invited Lectures (expenses paid)

JAPAN 1993

"Sonochemistry: Applications of Ultrasonic Waves in Organic Synthesis", Osaka University, Oct. 13.

"Sonochemistry: Applications of Ultrasonic Waves in Catalysis and Polymer Synthesis", sponsored by the Polymer Division of the Japanese Chemical Society. Osaka Municipal Technical Institute, Oct. 14.

"New Catalytic Processes for the Synthesis of Organosilanes", University of Hiroshima, October 15.

"Hypovalent Reactive Intermediates Containing Silicon", Tohoku University, October 18.

"Platinum-Catalyzed Hydrosilylations of Alkynes", Dow Corning Corp. in Odawara, October 19.

KOREA 1993

"Simple and Efficient Routes to Semiconductor Materials from Organometallic Reagents", Chungnam National University, October 21.

"New Catalytic Processes for the Synthesis of Organosilanes", Korean Advanced Institute for Science and Technology, October 26. (Daejeon)

"Simple and Efficient Routes to Semiconductor Materials from Organometallic Reagents", Konju National University, October 27.

"New Catalytic Processes for the Synthesis of Organosilanes", Korean Institute of Science and Technology, October 29. (Seoul)

Plenary Lecture (expenses paid)

"HYPOVALENT REACTIVE INTERMEDIATES CONTAINING SILICON", Philip Boudjouk;
Korean Chemical Society-Wonkwang University -October 22-23, 1993

B. Consultative and advisory functions

The Principal Investigator has been working with Dow Corning Corporation regarding commercial applications of his research in silicon chemistry.

C. New discoveries, inventions or patent disclosures

We have discovered the first stable aromatic species containing silicon and prepared two additional members of that series. We have developed a highly efficient and convenient procedure for preparing binary semiconductors such as tin selenide and gallium arsenide as well as ternary materials such as $\text{SnS}_x\text{Se}_{1-x}$. We have prepared the first complex of dichlorosilane, an important building block in silicon chemistry. We have developed a procedure for preparing polysilanes with molecular weights in excess of 1 million.

Patent disclosures on the complex of dichlorosilane and the efficient preparation of Groups 13-15, 14-16 and 13-16 binaries and ternaries will be filed in the Fall of 1994.

D. Additional information

The research conducted under this grant continues to generate interest from US, Australian, Asian and European firms. In particular, several companies have expressed interest in our work the areas of catalysis of organosilanes and the use of ultrasonic waves to promote chemical reactions. Our research was briefly highlighted in the Australian engineering publication, *Engineering World*, in June of 1992.

At the 206th National Meeting of the American Chemical Society in Chicago in August of 1993, our group presented nine papers. That was the largest number of papers presented by one research group (all divisions) at that meeting.

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