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FINAL SCIENTIFIC REPORT
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"Organosilicon Compounds and Organosilicon
Polymer Intermediates"

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Studies of the highly reactive Si-C bonds of hexamethylsilacyclopropane and 1,1-dimethyl-3,4-bis(trimethylsilyl)-1-silacyclopropene and of the reactive Si-Si bond of octamethyl-1,2-disilacyclobutane completed. RP- and RAs-bridged ferrocenophanes were prepared and their reactions with organolithium reagents studied. Ferrocenylenephosphine polymers were prepared for use as ligands in catalysis studies. Their cobalt complexes are active hydroformylation catalysts. A novel and useful route to acylsilanes based on the carbon monoxide-derived acyllithium reagents has been developed. The hydrolysis of dichlorosilane, was found to give cyclic oligomers, with n equals 4 through 23, in decreasing amounts. Linear species also were prepared and studied. A study of the transition metal chemistry of cyclodiisopropylsilane was initiated with the ultimate objective of preparing transition metal silicides. A study of the reactivity of calcium disilicide derived 'reactive silicon' and 'silicon mono halides' was started.
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A. Period Covered and Personnel

1. Period Covered

1 October 1978 - 30 September 1982

2. Personnel*

a. Senior Investigator: Professor Dietmar Seyferth

b. Postdoctoral Investigators:

C. Prud'homme (Rhone-Poulenc, Lyon, France)

J. Escudie (University of Toulouse)

J. Pornet (University of Poitiers)

W.-L. Wang (Chenguang Chemical Industry Res. Inst.,
P.R.C.)

c. Predoctoral Investigators**

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E.W. Goldman (Ph.D.)

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R.M. Simon (Ph.D.)

R.M. Weinstein

T.G. Wood

Form with fields for "Name", "Title", "Address", "City", "State", "Zip", "Country", "Phone", "Fax", "E-mail", "Web", "Notes". A large handwritten "H" is visible below the form.

* Personal are listed whose salaries and/or research costs were covered totally or in part by this Grant.

** Those whose name is followed by (Ph.D.) obtained their Ph.D. degree during the grant period.

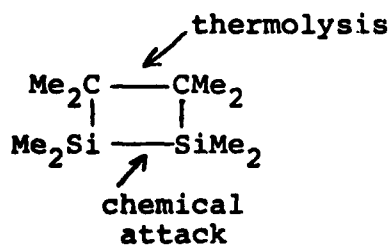
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MATTHEW J. R. [illegible]
Chief, Technical Information Division

B. Research Accomplishments

1. Silacyclopropanes, Silacyclopropenes and Octamethyl-1,2-disilacyclobutane

Our studies of the synthesis of strained, highly reactive small ring silacarbo-cyclic compounds are now essentially complete. Among the last reactions which we examined in the SiC_2 ring series were apparently free radical reactions with polyhalomethanes and Group IV organometallic hydrides and two-atom insertions (spontaneous as well as palladium-catalyzed) of acetylenes, activated olefins and carbonyl compounds. This work has been published in part, but some more full papers remain to be written.

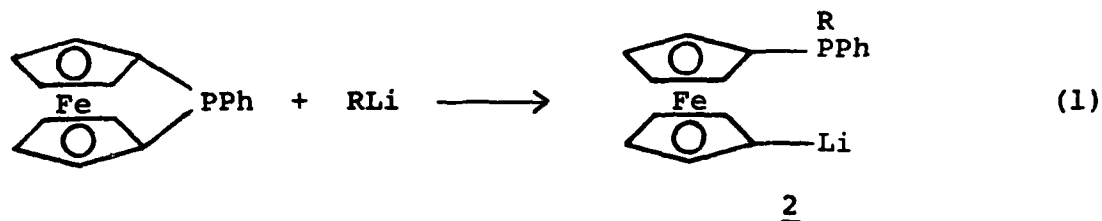
Our studies of the chemistry of octamethyl-1,2-disilacyclobutane have focused mainly on simple cleavage reactions with reagents such as halogens, acids, RLi , etc. and insertion reactions (O_2 , S_8 , Pd-catalyzed acetylene insertions). In all of these reactions it is the Si-Si bond which is the site of reactivity. However, in the thermolysis of octamethyl-1,2-disilacyclobutane it is the C-C bond which is ruptured.



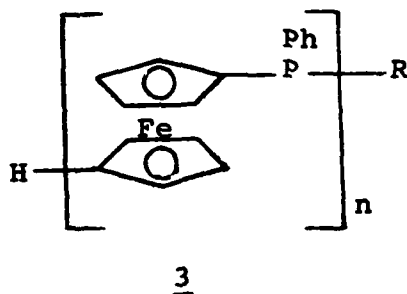
2. Ferrocenophanes

Most of our work in this area was devoted to the synthesis and chemistry of 1. In particular, we have been interested in the

ring-opening of 1 by RLi (eq 1). Further reactions of 2 were



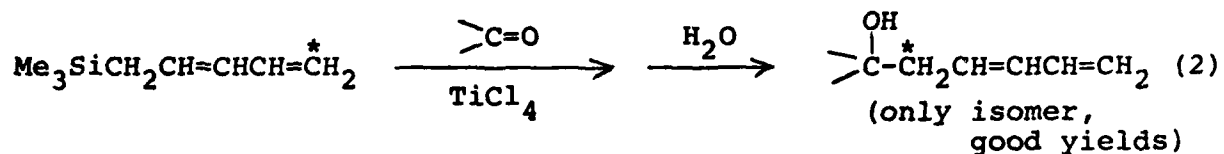
studied, including its reaction with 1 to give oligomers of type 3. The lower members (R=Ph, n=2-5) could be isolated as



pure species by HPLC. A polymer of molecular weight $\sim 160,000$ was prepared by reaction of 1,1'-dilithioferrocene with PhPCl_2 . Both the lower oligomers and the polymer form complexes with transition metals. The Co carbonyl derivatives are active hydroformylation catalysts.

3. Pentadienylsilanes

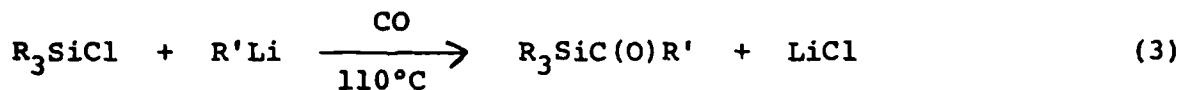
$\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$ has been added to the arsenal of the synthetic chemist as a useful source of the $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}_2-$ group (eq 2). Results of reactions with C-methyl-substituted



pentadienylsilanes showed that an $\text{S}_{\text{E}}2'$ type mechanism is involved.

4. Acylsilanes

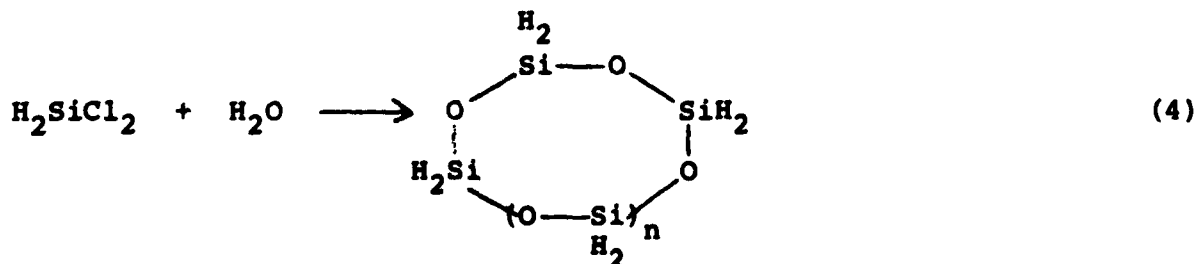
A useful, direct synthesis of acylsilanes has been developed (eq 3). This reaction proceeds via the in situ genera-



tion and subsequent trapping of the elusive RC(O)Li reagent. Application of RC(O)Li reagents to organic synthesis are now being pursued under a PRF grant.

5. Hydrolysis of Dichlorosilane

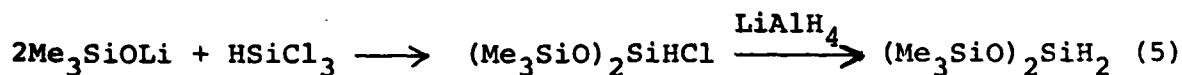
We have found conditions for the hydrolysis of dichlorosilane which produce a high yield of volatile cyclic products (eq 4). By gas chromatography and gas chromatography/mass



spectroscopy we can identify all cyclics from $n=1$ to $n=23$ in the distillate. The residue appears to contain (by NMR) still higher cyclics. These can be converted to an elastomer by the action of H_2SO_4 .

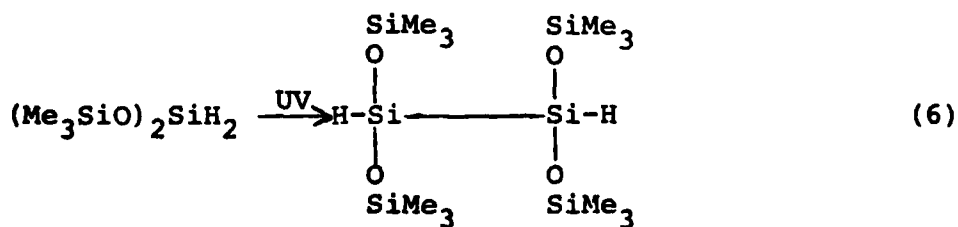
It will be of interest to convert these cyclics to a linear $\{H_2SiO\}_n$ polysiloxane. Such a material might prove to be a precursor for SiO_2 fibers via oxidative pyrolysis.

We have prepared $Me_3SiOSiH_2OSiMe_3$, 4, by the cohydrolysis of H_2SiCl_2 , by the reaction of Me_3SiOLi with H_2SiCl_2 and also by the route shown in eq 5.



5

We have begun a study of the chemistry of 4 and 5. An interesting reaction which we found is that shown in eq 6.



6

The yield of 6 was moderate and higher oligomers also were formed.

Cohydrolysis of Me_2RSiCl ($R=H, Me$) and H_2SiCl_2 was used to prepare lower members of the series $Me_2RSiO\{H_2SiO\}_nSiMe_2R$.

6. Silicon-Transition Metal Complexes

The pyrolysis of compounds containing Si-transition metal bonds is a potential route to transition metal silicides, and the object of one of our new projects is to explore this possibility. Our current research is involved in examining the transition metal chemistry of 7. Both insertions of low valent, coordinatively



7

unsaturated species (L_2Pd , L_2Pt , $\text{Fe}(\text{CO})_2$, etc.) and reactions of 7 catalyzed by such species (e.g., acetylene insertion) are of immediate interest.

7. Highly-reactive Elemental Silicon

It is known that the extraction of calcium (generally as CaCl_2 or CaBr_2) from CaSi_2 leaves highly reactive sheets of silicon which, according to limited studies (Kautsky, Bonitz, Hengge), show high reactivity toward reagents toward which normal bulk silicon is unreactive. We have started our work in this area with a study of the halogenation of CaSi_2 with Cl_2 , BrCl and ICl . When the best procedure has been developed, we will proceed with our reactivity/synthetic studies. We also are looking at the preparation of $(\text{SiCl})_n$ obtainable by further chlorination of this reactive silicon.

C. Publication List

Published

1. Reactions of Siliranes with Elemental Sulfur and with t-Butyl Mercaptan. Preparation of the 2,3-Dithia-1-Silacyclopentane Ring System.
J. Organometal. Chem., 164, 305 (1979).
D. Seyferth, D.P. Duncan and C.K. Haas.
2. Unusual Lithium Transfer Reactions in Lithium-Substituted Organosilicon Compounds. Reinvestigation of the Reaction of 1,8-Dilithionaphthalene with Trimethylchlorosilane.
J. Organometal. Chem., 170, C29 (1979).
R.J. Wroczynski, M.W. Baum, D.Kost, K. Mislow, S.C. Vick and D. Seyferth.
3. [1]Ferrocenophanes with Phosphorus and Arsenic as the Bridging Atoms: Synthesis and Some Reactions. A New Route to Ferrocenyllithium Reagents.
J. Organometal. Chem., 185, C1 (1980).
D. Seyferth and H.P. Withers, Jr.
4. The Elusive Germa- and Stanna-cyclopropanes. Attempted Preparation by the Reaction of 1,3-Dihalides with Magnesium.
J. Organometal. Chem., 185, 307 (1980).
D. Seyferth, M. Massol, J. Barrau and S. Monteverdi.
5. The Reaction of the Trimethylchlorosilane/Magnesium Reagent with gem-Dibromocyclopropanes.
J. Organometal. Chem., 187, 1 (1980).
D. Seyferth and D.P. Duncan.
6. A Gas Kinetic Study of the Pyrolysis of Octamethyl-1,2-disilacyclobutane.
J. Organometal. Chem., 187, 297 (1980).
I.M.T. Davidson, N.A. Ostah, D. Seyferth and D.P. Duncan.
7. Tetramethylcyclopropyllithium: Stability in Diethyl Ether and Reactions with Trimethylchlorosilane and Trimethyltin Chloride.
Synth. React. Inorg. Metal-Org. Chem., 10, 137 (1980).
D. Seyferth and D.D. Dagani
8. 2,4-Pentadienyltrimethylsilane: a Useful Pentadienylation Reagent.
J. Org. Chem., 45, 1721 (1980).
D. Seyferth and J. Pornet.
9. Hexamethylsilirane: Ring Cleavage by Germanium and Tin Hydrides.
J. Organometal. Chem., 198, C51 (1980).
D. Seyferth, J. Escudie, M.L. Shannon and J. Satgé.

10. Hexamethylsilirane. I. Preparation, Characterization and Thermal Decomposition.
J. Organometal. Chem., 201, 179 (1980).
D. Seyferth, D.C. Annarelli, S.C. Vick and D.P. Duncan
11. η^5 -Pentadienyltricarbonylmanganese, an "Open" Analog of Cymantrene.
J. Organometal. Chem., 208, 189 (1981).
D. Seyferth, E.W. Goldman, and J. Porner.
12. Hexamethylsilirane. II. Ring-Opening Reactions with Some Simple Reagents.
J. Organometal. Chem., 225, 177 (1982).
D. Seyferth, D.C. Annarelli, M.L. Shannon, J. Escudie, and D.P. Duncan.
13. Bis(iodomethyl)mercury as a CH_2 Transfer Reagent.
J. Indian Chem. Soc., 59, 111 (1982).
D. Seyferth, C.K. Haas and D. Dagani.
14. Phosphorus- and Arsenic-Bridged [1]Ferrocenophanes. I. Synthesis and Characterization.
Organometallics 1, 1275 (1982).
D. Seyferth and H.P. Withers, Jr.
15. Phosphorus- and Arsenic-Bridged [1]Ferrocenophanes. II. Synthesis of Poly(1,1'-ferrocenylenephénylphosphine): Oligomers and Polymers.
Organometallics 1, 1283 (1982).
H.P. Withers, Jr., D. Seyferth, J.D. Fellman, P.E. Garrou, and S. Martin.
16. Hexamethylsilirane. III. Dimethylsilylene Transfer Chemistry.
Organometallics 1, 1288 (1982).
D. Seyferth, D.C. Annarelli and D.P. Duncan
17. High-Yield Acyl Anion Trapping Reactions: A Synthesis of Acyltrimethylsilanes.
J. Am. Chem. Soc., 104, 5534, (1982).
D. Seyferth and R.M. Weinstein.
18. A Useful Dienemethylation Reagent: (2,4-Pentadienyl)trimethylsilane.
Organometallics, 1, 1651 (1982).
D. Seyferth, J. Porner and R.M. Weinstein.

D. Lectures Presented on AFOSR Research during Grant Period

Baltimore ACS Section
Cleveland ACS Section Organic/Inorganic Topical Group
Case Western Reserve University
Bell Laboratories, Murray Hill, NJ
University of Houston
Paul Sabatier University, Toulouse
University of Bordeaux
University of Nice
University of Aix-Marseille III
Silicone Products Dept., GE, Waterford, NY
University of Georgia
State University of NY, Buffalo
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University of North Dakota
Union Carbide, Tarrytown, NY
Naval Research Laboratory, Washington, D.C.
Purdue University
Union Carbide, Sistersville, W.VA.
Texas A&M University
University of New Hampshire
Corporate R&O Center, GE, Schenectady, NY
Dow Corning Corp.
Louisiana State University
Kipping Award Symposium, Midland, MI

E. Special Recognition of (in part) AFOSR-Sponsored Research

- a) Dr. honoris causa, University of Aix-Marseille III.
- b) ACS Award for Distinguished Service in the Advancement of Inorganic Chemistry.
- c) Robert T. Haslam and Bradley Dewey Professorship in Chemistry at M.I.T.
- d) Proctor and Gamble Lecturer, Technical University of Munich.
- e) George A. Abbott Lectureship in Chemistry, University of North Dakota.
- f) Harold A. Iddles Lecturer, University of New Hampshire.