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Some Notable Discoveries in Organosilicon Chemistry: Proceedings of the History and Retrospective Session of the 34th Organosilicon Symposium (2001)

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**Some Notable Discoveries in
Organosilicon Chemistry**

**Proceedings of the History and
Retrospective Session of the
34th Organosilicon Symposium (2001)**

PREFACE

The 34th Organosilicon Symposium at White Plains, NY, in 2001 featured a **History and Retrospective Session**, during which invited speakers from academic and industrial laboratories recounted the path to some significant 20th century discoveries in organosilicon chemistry. Their stories, listed below, have now been compiled and made available in this depository.

- The Si=C Story: The Way it Happened, Adrian Brook (Univ. Toronto)
- The Discovery of Stable Disilenes and Silylenes, Robert West (Univ. Wisconsin)
- Yellow Fever: The Story Behind the Synthesis of Germasilenes, Kim Baines (Univ. Western Ontario)
- Direct Synthesis of Tris(dimethylamino)silane, William Herdle (OSi Specialties, formerly of Union Carbide Corp)
- Discovery of Tin and Phosphorus Effects on the Direct Synthesis of Methylchlorosilanes, Larry Wood (Dow Corning Corp)
- Discovery of Methylchlorosilylene (CH_3SiCl) as a Key Intermediate in the Direct Synthesis of Dimethyldichlorosilane, $((\text{CH}_3)_2\text{SiCl}_2)$, Kenrick Lewis (OSi Specialties, formerly of Union Carbide Corp)
- The First Platinum-Catalyzed Hydrosilylation With Supported Platinum Catalysts, George Wagner (Retired. Formerly of Union Carbide Corp)
- The Discovery of Silicone Surfactants for Polyurethane Foam, Bernard Kanner (Retired. Formerly of Union Carbide Corp)
- The Discovery of Silane Coupling Agents, Bernard Kanner (Retired. Formerly of Union Carbide Corp)

The idea for the History and Retrospective Session arose during a conversation between Dr. Bernard Kanner and me in late 2000. I was the Chairperson of the Organizing Committee of the 34th Organosilicon Symposium. In addition to the usual format comprising Plenary, Invited and Contributed Lectures, Poster presentations and a Banquet Lecture, I wanted to have a new event in the program. Bernie had recently completed a paper on the history of Union Carbide Silicones. Our discussion turned to the landmark XVth Organosilicon Symposium at Duke University in March 1981, during which announcements of isolable compounds with silicon – carbon and silicon – silicon double bonds were made. His and Bill Herdle's invention of the Direct Synthesis of tris(dimethylamino)silane was also disclosed publicly for the first time. It had been

twenty years since that symposium. I thought it would be exciting to learn how these discoveries and inventions occurred. The Organizing Committee concurred.

Accordingly, Professors Adrian Brook and Bob West were invited to present their stories on the synthesis of stable silenes ($\text{Si}=\text{C}$) and disilenes ($\text{Si}=\text{Si}$), respectively, and Dr. Bill Herdle to do so for the Direct Synthesis of tris(dimethylamino)silane. At the Xth International Symposium on Organosilicon Chemistry, Poznan, Poland, August 1993, I heard a lecture on stable germasilenes ($\text{Si}=\text{Ge}$) by then graduate student Jeff Cooke. So, it was fitting to include Professor Kim Baines among the invited lecturers. I considered that the narratives on silenes ($\text{Si}=\text{C}$), disilenes ($\text{Si}=\text{Si}$) and germasilenes ($\text{Si}=\text{Ge}$) would be particularly noteworthy since early twentieth century textbooks had taught that silicon was incapable of forming double bonds.

The Symposium Organizing Committee also agreed to invite Dr. Kanner to share the stories of the development of organofunctional silanes and silicone surfactants at Union Carbide and he, in turn, recommended that Dr. George Wagner be invited to relate how he came to invent platinum-catalyzed hydrosilylation. I telephoned Dr. Wagner and invited him to the symposium. He was in poor health and unable to travel. However, he agreed to prepare a manuscript that Dr. Kanner would read at the symposium.

The discovery of the potentiating effects of tin on rate and selectivity in the Rochow-Müller Direct Synthesis of methylchlorosilanes had been made independently by scientists at Dow Corning, GE Silicones and Union Carbide. Available information indicated that Dow Corning had been first. So, Larry Wood was invited to share how that happened. I told how the discovery of the intermediacy of methylchlorosilylene (CH_3SiCl) in the Direct Synthesis of methylchlorosilanes came about from collaboration between Prof. John Falconer's group at the University of Colorado (Boulder) and my team at Union Carbide in Tarrytown, NY.

It is my hope that readers of these accounts will feel and share the excitement of the original discoverers and inventors as they learn of these advancements in organosilicon chemistry.

Since 2001, I have made many unsuccessful attempts to find a permanent archive for the proceedings of the History and Retrospective Session. So, I am especially grateful that Kim Baines has arranged to have them deposited with the University of Western Ontario. My thanks to her and to Myra Gordon for their assistance in accomplishing this.

Kenrick M. Lewis
Momentive Performance Materials, Inc.
Tarrytown, NY
October 22, 2021

The Si=C Story: How It Happened

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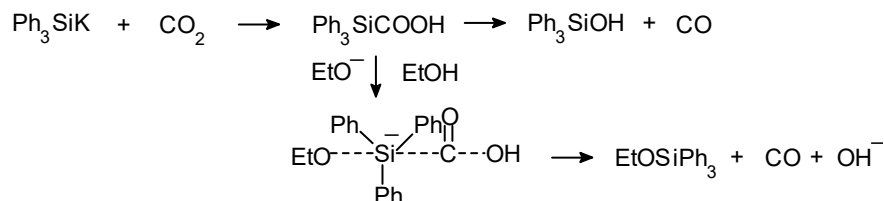
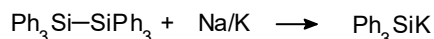


The Si=C Story: How It Happened

Adrian G. Brook, Department of Chemistry, University of Toronto, Toronto, ON M3S 3H6 Canada

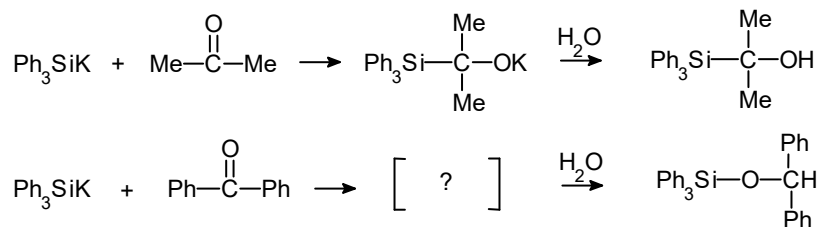


I first got involved with organosilicon chemistry in 1952, when I spent a year as post-doctoral fellow with Professor Henry Gilman at what is now known as Iowa State University. Gilman's group had just learned how to make triphenylsilylpotassium, the first organosilyl-metallic reagent and were investigating its properties. One of my contributions was to carbonate it to get pure triphenylsilanecarboxylic acid for the first time.

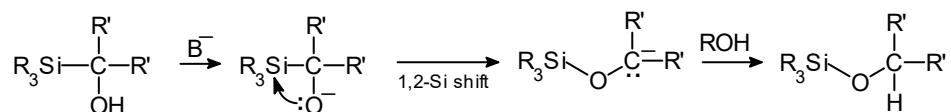


The acid showed unusual properties in that at its melting point it frothed vigorously, evolving carbon monoxide! In solution in a protic solvent such as ethanol containing a little base, it again evolved carbon monoxide vigorously at room temperature, strange behavior for a carboxylic acid.

It was also found that when the silylmetallic reagent was treated with simple carbonyl compounds such as acetone the expected alcohol was obtained, whereas treatment with an aromatic carbonyl compound gave the isomeric silyl ether.

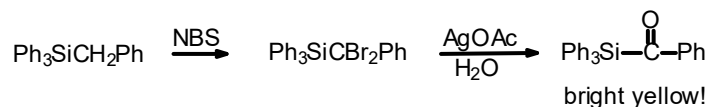


Over the years I investigated this behavior in detail and established that silylcarbinols underwent a base-catalyzed rearrangement to their isomeric silyl ethers, a process that became known as the Brook rearrangement.



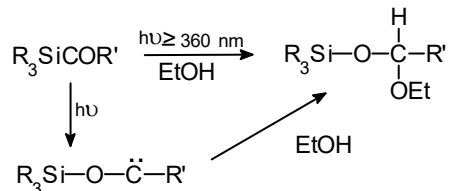
This was a second example of unusual behavior of a common functional group when it was adjacent to silicon.

A logical extension of this study was to make a ketone analog with the skeleton Si-CO-C, a species which we erroneously called silylketones for a while, but which are properly named acylsilanes.

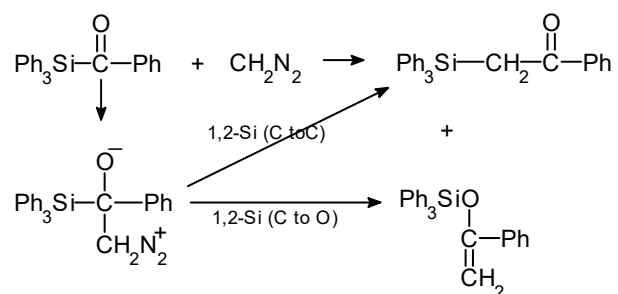


The first one we made, benzoyltriphenylsilane, was coloured yellow, although its carbon analog beta-benzpinacolone was colourless. That an organosilicon compound could be coloured was unheard of at the time, and I well remember Cecil Frye, during a visit to Dow Corning, trying to persuade me that I had a coloured impurity in my material. After all, silicon didn't form double bonds, so conjugation and resonance contributions were impossible, and hence silicon analogs of coloured carbon compounds wouldn't be coloured if silicon were part of the chromophoric system. Well acylsilanes can be coloured, due to interactions of silicon with the adjacent carbonyl group.

We spent a lot of time studying the spectroscopic and chemical properties of a variety of acylsilanes. One important reaction was their 1,2-photochemical isomerization to yield transient siloxycarbenes, Si-O-C:, using visible or near UV radiation: the siloxycarbenes were readily trapped by alcohols to yield mixed acetals.

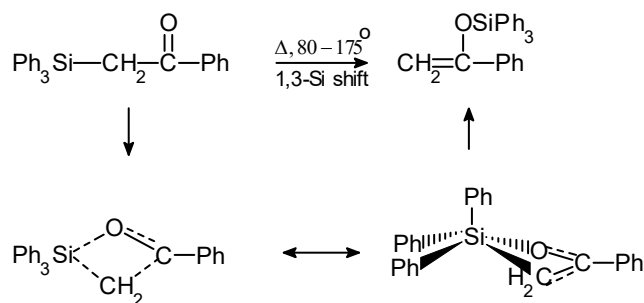


A second reaction of interest was with diazomethane where a mixture of two compounds was formed, an α -silylketone (or β -ketosilane), Si-C-CO-C, and also its siloxyalkene isomer, Si-O-C=C.



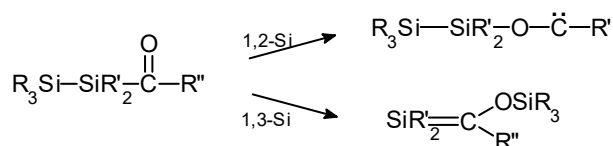
The β -ketosilane resulted from the relatively conventional C to C migration of the silyl group in an intermediary adduct, and the siloxyalkene arose from an analog of the Brook rearrangement, where the silyl group migrated 1,2 to oxygen.

The β -ketosilanes had no unusual spectroscopic properties, but were found to undergo a thermal rearrangement under very mild conditions involving a 1,3-silyl carbon-to-oxygen migration, with retention of configuration at a chiral silicon centre, to yield siloxyalkenes.

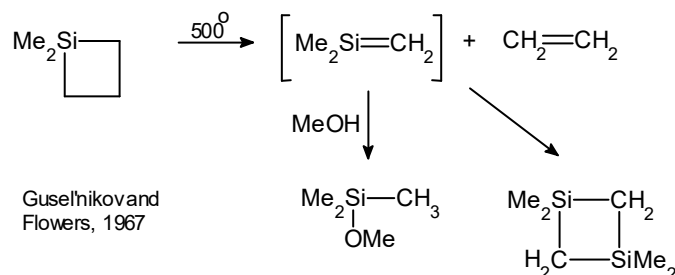


Recent findings by Kira¹ suggest that this rearrangement involves a distorted square pyramidal intermediate.

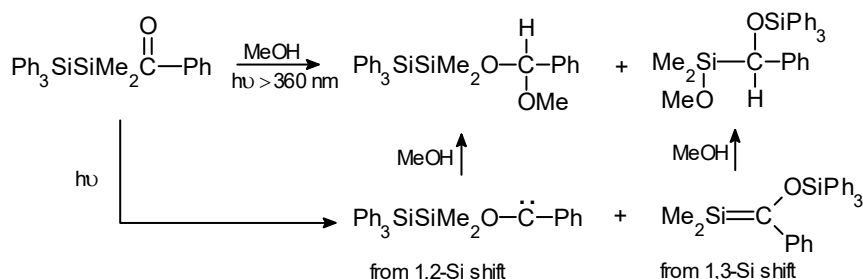
This result led us to wonder what would happen if an acyldisilane was photolyzed or thermolyzed.



Would a 1,2-C to O silyl shift occur (as with a simple acyldisilane) involving the adjacent α silicon atom to give a disilyloxy carbene, or would a 1,3-C to O silyl shift involving the β silicon atom occur (like a β -ketosilane) to give a compound containing a silicon-carbon double bond? This latter possibility was of great interest. The work of Gusel'nikov and Flowers² had recently shown convincingly that a silene was formed when dimethylsilacyclobutane was heated at about 500°C, the first compelling evidence that a silicon-carbon double bond could form.



We hoped our approach to silenes using acyldisilanes, if it worked, would be a much milder method for the generation of silenes which might make their study easier. And it did work. When each of several acyldisilanes were photolyzed with long wavelength radiation in ethanol solution, mixtures of the ethanol-trapped disilyloxy carbene and ethanol-trapped silene were isolated. Some of this work was carried out by one of my graduate students under the supervision of my post-doc and colleague Alan Bassindale while I was absent on sabbatical leave.



predicted that by following what now appears to be a logical sequence of studies, we would end up with stable silenes. Subsequent work in our laboratory has revealed much about the chemical behavior of the silicon-carbon double bond, including the fact that it is stable enough for geometrical isomers of suitably substituted compounds to exist, and numerous other chemists have subsequently created other examples of stable silenes.

References:

1. Takahashi, M.; Kira, M. *J. Am. Chem. Soc.* **1999**, *121*, 8597.
2. Gusel'nikov, L. E.; Flowers, M. C., *Chem. Commun.* **1967**, 864.
3. Brook, A. G. *et al.*, *Chem. Commun.* **1981**, 191.
4. Brook, A. G. *et al.*, *J. Am. Chem. Soc.* **1982**, *104*, 5667.
5. Nyburg, S.C.; Brook, A. G. *et al.*, *Acta Crystallographica*, **1985**, *C41*, 1632.

The Discovery of Stable Disilenes and Silylenes

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The Discovery of Stable Disilenes and Silylenes

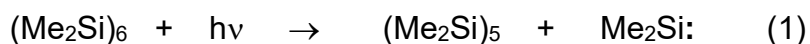
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Before 1981, the overwhelming view was that compounds containing multiple bonds to silicon and other heavier elements were bound to be unstable. This conventional wisdom was enshrined in the “double bond rule”, appearing in many textbooks, stating that elements outside the first row of the periodic table would not form double bonds. This generalization arose as a result of the numerous unsuccessful attempts to synthesize such compounds. For example, the pioneer organosilicon chemist, F. S. Kipping, labored mightily to make Si=C, Si=Si and Si=O compounds, but always obtained singly-bonded products, and eventually concluded that multiple bonds to silicon were not possible.¹ Nevertheless his term “silicone”, originally applied to the hoped-for Si=O containing molecule, was carried over to the actual products, the siloxane polymers.

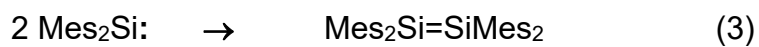
In 1981, at the 15th Organosilicon Symposium in Durham NC, the first stable Si=C and Si=Si compounds were announced and displayed, in back-to-back papers.^{2,3} These discoveries, together with the nearly simultaneous publication of a P=P compound by Yoshifuji,⁴ decisively overturned the double bond rule, and led to a paradigm shift. An entirely new area of chemistry was thus opened up for exploration. Stable compounds containing the following kinds of multiple bonds to silicon are now known: Si=C, Si=Si, Si=N, Si=P, Si=As, Si=Ge, Si=S, Si=Se, and Si=Te. Additional multiply bonded compounds have been isolated for Ge, Sn, Pb, As, Sb, B, Al, Ga and In. Indeed, in 1996 an entire volume of *Advances in Organometallic Chemistry* was devoted to multiply bonded compounds of the heavier elements was published, in which many of these classes of compounds are described.⁵

The events leading up to the discovery of disilenes have been recounted in an earlier review.⁶ In 1977, Josef Michl and I embarked on a collaborative effort, involving our experience with organosilicon compounds and his expertise in matrix isolation of unstable species. A graduate student, Tim Drahnak, traveled from Wisconsin to Utah to take part in this research. Initially he attempted to make tetramethyldisilene by dehalogenation of Me₂XSi-SiXMe₂ compounds, but these experiments failed dismally. He then turned his attention to organosilylenes, R₂Si:. Although these were well known as transient intermediates in organosilicon chemistry they had not been observed directly. Photochemical generation of dimethylsilylene from a cyclic polysilane in argon matrix at ~10 K was immediately successful (Equation 1)⁷, making possible the first



spectroscopic investigation of this important intermediate.⁸ Soon, we found that organosilylenes could also be isolated in a hydrocarbon matrix at liquid nitrogen temperature, making them much easier to generate.⁹

This research was continued by Mark Fink, who made a variety of silylenes, all brightly colored in the hydrocarbon matrix. Upon melting of the matrix these decomposed, eventually forming colorless polymers. In some cases, however, a yellow color persisted for a time in solution during the warmup. Eventually we investigated dimesitylsilylene, made by photolysis of the corresponding trisilane (equation 2). The silylene, bright blue in the matrix, gave way to a yellow solution *which persisted up to room temperature*. Evaporation of the solvent gave the stable Si=Si compound, tetramesityldisilene (equation 3).¹⁰



The four mesityl groups provide the steric hindrance needed to stabilize the Si=Si double bond against polymerization. The numerous disilenes later synthesized are all similarly stabilized by bulky substituents.¹¹

Disilenes are yellow to red, brightly colored solids. Their color results from the $\pi-\pi^*$ excitation of the electrons in the Si=Si double bond. Compared with alkenes, the Si=Si double bond HOMO lies at higher energy and the LUMO at lower energy, making the transition energy only about half that of C=C (Figure 1). Disilenes are thus simultaneously more electron rich and more electron deficient than alkenes. As a result, they have an exceptionally versatile reactivity, which has given rise to a rich and beautiful chemistry.¹¹

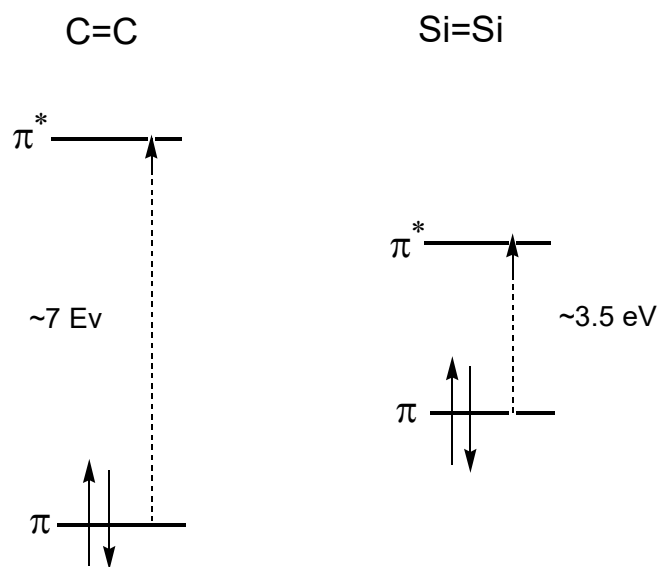
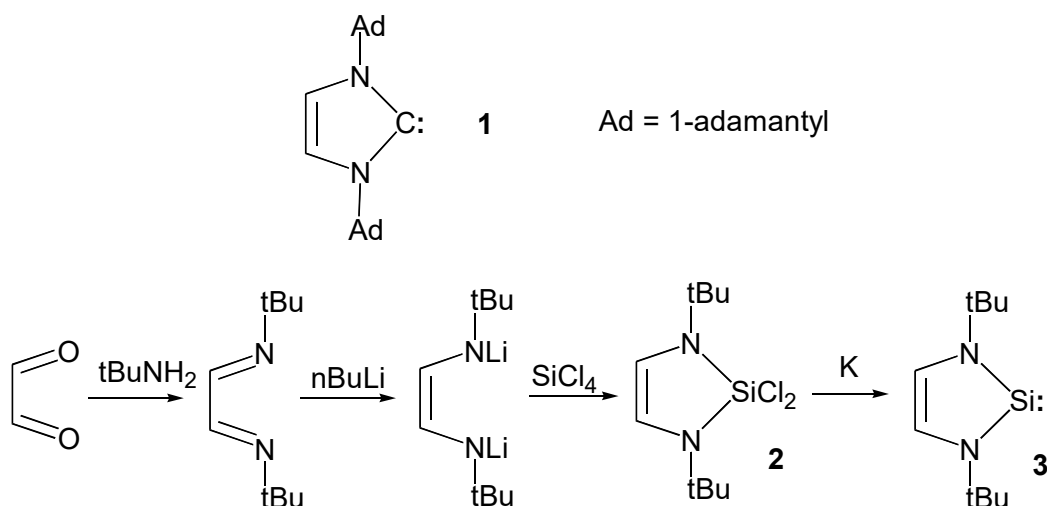


Figure 1. $\pi-\pi^*$ excitation energies for double bonds

Disilenes are dimers of silylenes, $R_2Si:$, which are the silicon counterparts to the carbenes of organic chemistry. Like carbenes, most silylenes are extremely reactive and unstable species. However, in 1994, Arduengo and coworkers published the synthesis of a stable carbene, **1**.¹² This striking finding left silicon as the only element in group 14 lacking a stable divalent, dicoordinate species, since divalent germanium, tin and lead compounds had long been known. At this time Dr. Michael Denk came to our laboratories at Wisconsin from Munich, and we decided to tackle this problem.

The synthesis was straightforward as far as the precursor molecule, the dichlorosilane **2**. The final step was formidably difficult, however. Finally, after almost 40 unsuccessful tries, Denk found that the chlorines of **2** could be removed cleanly by molten potassium metal in refluxing THF! Under these remarkably vigorous conditions, the stable silylene **3** is obtained in up to 80% yield.^{13,14}

Compared with most silylenes, which react or polymerize just above 77 K, the stability of **3** is astounding. It can be purified by sublimation at 90 °C, and survives unchanged after heating in toluene at 150 °C for four months. **3** finally decomposes at its melting point, 220 °C.



What can account for the remarkable stability of **3**? In part, this must result from electron donation by nitrogen, filling the vacant p orbital on silicon. But in addition, **3** contains six pi-electrons, and so may gain stabilization by aromatic electron delocalization. A great deal of evidence, both experimental and theoretical, has accumulated for such aromaticity.¹⁴ And, although several other silylenes have now been isolated, the truly stable silylenes all have a delocalized, aromatic structure. The silylene isostructural with **3** but lacking a double bond, and so unable to benefit from aromaticity, is far less robust than **3**.¹⁵

The stable silylenes react as nucleophiles, and like the disilenes, provide ways of synthesizing many new kinds of silicon compounds.¹⁶ Silylenes are isolobal with phosphines, and can take their place in metal complexes. Complexes of stable silylenes with Fe, Ru, Ni, Pt, Cr, Mo and W have been synthesized.^{14,17} The catalytic properties of such silylene complexes will surely be explored in the years to come. Meanwhile, compound **3** itself has been shown to be a powerful catalyst for the polymerization of olefins.^{16,18} The mechanism of polymerization is now being investigated. Stable silylenes, providing a large-scale source of reactive, divalent silicon, seem likely to have great importance in organosilicon chemistry in the future.

Acknowledgment: Research on disilenes and silylenes at Wisconsin has been supported by the National Science Foundation, and by the Sponsors of the Organosilicon Research Center.

References:

1. Kipping, F. S. *Proc. Roy. Soc. (London)* **1937**, A159, 139.
2. Brook, A. G., Abstracts of the XVth Organosilicon Symposium, Durham, NC, March 27-28, 1981.
3. West, R.; Fink, M. J.; Michl, J. Abstracts of the XVth Organosilicon Symposium, Durham, NC, March 27-28, 1981
4. Yoshifuji, M. *J. Am. Chem. Soc.* **1981** *103*, 4587.
5. Stone, F. G. A.; West, R., Eds. *Adv. Organometal. Chem.* **1996**, 39.
6. Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.
7. Drahnak, T.J.; Michl, J.; West, R. *J. Am. Chem. Soc.* **1979**, *101*, 5427.
8. Raabe, G.; Vancik, H.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 671.
9. Michalczyk, M. J.; Fink, M. J.; DeYoung, D. J.; Carlson, C. W.; Welsh, K. M.; R. West, R. *Silicon, Germanium, Tin and Lead Compounds* **1986**, *9*, 75.
10. West, R.; Fink, M. J.; Michl, J. *Science (Washington DC)* **1981**, *214*, 1343.
11. Okazaki, R.; West, R. *Adv. Organometal. Chem.* **1996**, *39*, 232.
12. Arduengo III, A. J.; Harlow, R. L.; Kline, M. J. *J. Am. Chem. Soc.* **1991**, *113*, 361.
13. Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. R.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691.
14. Haaf, M.; Schmedake, T. A.; West, R. *Acc. Chem. Res.* **2000**, *33*, 704.
15. Haaf, M.; Schmedake, T. A.; Paradise, B. J.; West, R. *Can. J. Chem.* **2000**, *78*, 1526.
16. Haaf, M.; Denk, M.; Schmeidl, A.; Powell, D. R.; West, R. *J. Am. Chem. Soc.* **1998**, *120*, 12714.
17. Haaf, M.; Schmedake, T. A.; West R. *J. Organometal. Chem.*, in press.
18. West, R.; Haaf, M.; Moser, D.F. unpublished research.

Yellow Fever: The Discovery of Germasilenes, A Personal Retrospective

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Yellow Fever: The Discovery of Germasilenes, A Personal Retrospective

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After graduating with an honors BSc degree from St. Mary's University in Halifax, Nova Scotia, I remember thinking to myself that, really, I didn't know a damn thing. This was not a criticism of my teachers, rather a compliment; they inspired me to learn more; however, I was daunted at the prospect of trying to master something like organic synthesis. After looking around at different universities and research programs, I was intrigued by the field of organosilicon chemistry. Here was a relatively new area of research, silenes that I felt I would be able to handle. I joined Adrian Brook's research group as a graduate student in the fall of 1982. The discovery of the first solid, stable silene had taken place in the previous year¹ and the synthesis of the first solid, stable disilene had recently been accomplished in Robert West's research group.² The five years that followed were heady times. It seemed like every time I picked up a new issue of a journal in the library, I was reading about some new and exciting aspect of the chemistry of doubly-bonded silicon and germanium compounds. In 1988, when I joined the faculty at the University of Western Ontario, I was well aware of, not only what had been accomplished, but also of what had not. Examples of compounds containing two different heavier Group 14 elements, either transient or stable, were conspicuously absent. In my first grant application to the Natural Sciences and Engineering Research Council of Canada, I proposed to synthesize a germasilene, a compound containing a double bond between a silicon and a germanium atom, from a disilagermirane, a three-membered ring compound containing two silicon atoms and a germanium atom. This was an afterthought to the main proposal which focused on the synthesis of a polysila[2.2.2]propellane.

This retrospective is not only about science but also about people doing science. I recall the day I met Jeff Cooke. He came into my office wanting to learn more about a 4th year undergraduate research project I had proposed concerning the synthesis of a disilagermirane and its photolysis to a silagermene (to be done in 5 months!). His enthusiasm for the project was matched only by mine. He spent his final undergraduate year valiantly trying to make the wrong molecule. I spent some of that time writing a research proposal to the Petroleum Research Foundation. In the course of writing that proposal, I realized that, by a simple thermodynamic argument, our target molecule should be a siladigermirane, not a disilagermirane. In the fall of 1989, Jeff started his graduate work on the synthesis of the siladigermirane. Not wanting to put all our eggs in one basket, in addition to the infamous [2.2.2] project (which never went anywhere), I had a graduate student, Babu Joseph, working on the synthesis of a germasilene via a β -elimination. If the truth be told, I believed the elimination route would ultimately be the successful route; however, Jeff continued with the three-membered ring approach.

Since the mesityl group had proven ideal in the synthesis of the disilene, it seemed a natural choice as a substituent in our studies. The chances of synthesizing a siladigermirane by the reaction of two equivalents of a dichlorogermene and one of a dichlorosilane seemed slim, and thus, we focused our efforts on the reductive cyclization of $(\text{Mes}_2\text{GeCl})_2$ and $\text{Mes}_2\text{SiCl}_2$. On Oct. 18, 1990,

Jeff isolated a “brown goo” (Lab Notebook, Vol. 1, pg 185) and dissolved it in hexanes. A colourless solid crystallized from the solution. After recrystallization from hexanes/methanol, the ^1H nmr spectrum of the solid revealed a broad hump at 2.3 ppm, characteristic of the ^1H nmr spectrum of hexakis(2,6-dimethylphenyl)cyclotrisilane synthesized by Satoru Masamune.³ This could be it! Because of the large hump, we thought we should examine the effects of temperature on the appearance of the spectrum. So on Nov. 20, 1990, we booked the old Varian XL-300 and together we ran variable temperature ^1H nmr spectra of the colourless solid. We took the temperature, stepwise, up to 110 °C. Of course, I was looking for two signals in a clean 1:2 ratio to resolve out of the hump. This is not what we observed; the spectrum was more complicated than I expected. A bit disappointed, I removed the sample from the probe (still at high temperature) and as it was taken out...WOW! It was yellow!!!! Of course, I was well aware that tetramesityldisilene was yellow. Intuitively, I knew the germasilene would be yellow. What excitement! That moment, I knew we could do it. It was only a matter of time now. Although, Jeff’s lab notebook does not reflect the excitement of the evening, an excerpt from his monthly report, even though written in the dispassionate passive voice of the chemist, gives an indication of our feelings:

“In addition, the sample retrieved from the nmr was yellow. This gave the idea that the system was thermally labile, maybe decomposing to the bright yellow disilene, digermene or (gasp) silagermene.” (J.A. Cooke, Monthly Report, November 1990)

Wataru Ando had recently published a communication in *Chem. Commun.* regarding the thermolysis of hexamesitylcyclotrigermane to give the yellow tetramesityldigermene.⁴ Everything fit. It made perfect sense to me that the siladigermirane may also thermolyze to give a yellow germasilene. Although, it was possible that the yellow colour was due to the digermene, I am, and was then, an optimist. This moment was particularly important for me. Not only did I now instinctively realize that the chemistry worked, but this was chemistry that *I* had conceived independently. I realized that I would “make it” as an academic. Of course, no one gets anywhere on a gut feeling, optimism, and a yellow colour; we had to demonstrate that indeed the germasilene was formed.

Although our original intention was to examine the photolysis of the siladigermirane, we turned our efforts towards examining the thermolysis of the siladigermirane in the presence of the quintessential dimetallene trapping agent, methanol. The very first thermolysis experiment gave, remarkably, only three products (and, significantly, not four). Again, the results were amply described in the November 1990 Monthly Report by Jeff.

“A small (0.01 g) sample [of the siladigermirane] was thermolyzed in the presence of methanol, in order to trap out any reactive silylenes, germylenes or any doubly-bonded species. This was met with much more success than anticipated: it appeared to thermolyze cleanly to three products (JC2–8-1), two appearing to be trapped doubly-bonded species, one a trapped divalent species. Separation by the Chromatotron confirmed this while the mass spectra helped pin down their identities. The first species was identified as $\text{Mes}_2\text{GeHSiMes}_2\text{OMe}$ (specs JC2-10-1, JC2-10-1MS), resulting from addition of methanol to (holy cow) $\text{Mes}_2\text{Ge}=\text{SiMes}_2$. The

second, $\text{Mes}_2\text{GeHGeMes}_2\text{OMe}$ from $\text{Mes}_2\text{Ge}=\text{GeMes}_2$, specs JC2-13-2B, JC2-13-

2BMS. The third was identified as Mes₂GeHOME, a trapped germylene, specs JC2-13-2C, JC2-13-2CMS.”

My biggest fear (and the reason why I thought the elimination route would be more successful) was that the cleavage of the ring would not be regioselective. The formation of the methanol adduct of the digermene suggested that the thermolysis of the siladigermirane was not regioselective. However, the methanol adduct of dimesitylsilylene was conspicuously absent. To make a long story short, we discovered that the siladigermirane was contaminated with some cyclotrigermane and this was the source of the digermene. The corollary of this is that the reaction was completely regioselective!! Another cause for celebration!

Shortly after, in April 1991, we began experiments designed to isolate the germasilene. The idea was to perform the thermolysis in the presence of triethylsilane, a “selective trapping reagent for metallylenes” (PRF application, Oct. 1989). I believed the separation of the germasilene and the silylgermane “should not present a significant problem” (*ibid*). In some ways, ignorance is bliss. I assumed, at the time, that germylenes would react in much the same way as silylenes: rapidly with Et₃SiH. I did not lose one iota of sleep worrying about whether or not the germylene would react with the silane. Upon thermolysis of the siladigermirane in the presence of Et₃SiH, once again, a bright yellow colour was formed. Once again, we were very excited. Imagine our disappointment when, after continued thermolysis, the colour significantly faded. Mes₂GeH(SiEt₃) was readily identified in the product mixture; however, the identity of the other products remained a mystery for quite some time (until November 1991). The significance of the facile trapping of a germylene by a silane was completely lost on me until Professor Peter Gaspar came for a visit in the spring of 1992. Although we were most impressed by our abilities to generate a germasilene, he appeared to be equally impressed by our ability to trap a germylene, in high yield, with a silane. Had I been diligent, and read all the available literature, I probably would not have even attempted to trap the germylene with a silane.

In time, we figured out that the germasilene was rearranging to a silylgermylene, which was also trapped by the silane. To prevent this, we proposed to photolyze the siladigermirane *in the cold* to prevent the rearrangement. On January 17, 1992, a solution of the siladigermirane and triethylsilane was irradiated in a dry ice/ethanol bath for 9 hours to give a “persistent yellow-green” solution. A ²⁹Si nmr spectrum of the solution was then recorded at room temperature. The spectrum was messy: we could clearly see triethylsilane, some unreacted siladigermirane, the trapped germylene, the trapped silylgermylene....and there at 68.6 ppm was what we thought was our germasilene. Double WOW! Upon further consideration, we realized that we should record the spectrum at -70 °C and not room temperature. (If only we could do everything right the first time!) If the solution was kept cold we might be able to reduce the amount of rearranged product and, by using less starting material and longer photolysis times, we could reduce the amount of unreacted siladigermirane. Also, we noted that we had referenced the spectrum incorrectly. We repeated the experiment, this time recording the ²⁹Si nmr spectrum of the photolysis solution at -70 °C. Now, much to our surprise, we observed *two* signals in the downfield region of the spectrum, one at 80.6 ppm and one at 63.1 ppm. We were happy nonetheless! We were puzzled as to why there were two signals in the downfield region of the spectrum, and the number 63.1 seemed vaguely familiar. It didn't take long to realize that this was the chemical shift of the silicon in tetramesityldisilene. And furthermore, after synthesizing numerous silylgermanes and examining trends in the ²⁹Si nmr

chemical shifts in comparison to disilanes, we knew that substitution of a silicon for germanium would result in a downfield shift. A shift to 80.6 ppm seemed perfect. Thus, after 3 ½ years, we had direct evidence for the germasilene!! Another happy night in the basement of the chemistry building. Of course, our spectroscopic work was eventually backed up with trapping experiments.

Upon reflection, I am forced to ask myself why it took us almost 14 months from the time we had the three-membered ring to the time we actually saw direct evidence for the germasilene. There are many reasons. Going back over his notebook, I realized that every other week Jeff was making more starting materials. We also had to unambiguously identify the ring. Finally, as a young assistant professor, I was anxious to publish and give a definitive “yes” to the Chair, G. Michael Bancroft, who would often casually ask me “Got a publication yet?” and to my colleague, Rob Lipson, who asked me the same question every week. Since I realized that, even if we never obtained a stable germasilene, the thermolysis experiments with methanol and triethylsilane were publishable results, Jeff spent many hours repeating the experiments and purifying and unambiguously identifying the products. After painstakingly preparing the manuscript and checking the data not once but twice and thrice (I wanted that first publication to be perfect!), we submitted a manuscript concerning the synthesis of the siladigermirane and the thermolysis of the ring in the presence of methanol to *Organometallics*.⁵ Reviewer B remarked “an excellent piece of work”; however, I was a tad mortified when I received the manuscript back from Dietmar Seyferth. I assume in an effort to help a fledgling faculty member, he took it upon himself to thoroughly edit the manuscript. We had made some mistakes including leaving out a few key words (like methanol!). I want to thank him now for those efforts. (Neither reviewer B nor Dietmar noticed that we had also made a mistake in the numbering of the compounds. Arghh!)

Over the years, some colleagues have commented “But you never obtained a solid, stable germasilene”. That is true. I would love to have a crystal structure of a germasilene. There are two comments I can make. Early in the game, we realized that the crystal structure of a germasilene with identical substituents on each end of the double bond would, in all probability, be disordered, and thus, we decided to wait until we had a germasilene with different substituents at the ends (and we have made efforts in that direction). Perhaps more importantly, we have no doubt about the identity of tetramesitylgermasilene. We are confident in our spectroscopic and reactivity data. With such a new and exciting molecule in hand, we were eager to explore its chemistry and that is what we focused on in the years following the discovery of the first stable germasilene.

The synthesis of the germasilene was the chemistry on which my tenure decision was based, and thus, is dear to my heart. Last year, I was promoted to Professor. Now I’ve “made it” I can only hope that the next dozen years will be as fun and exciting as the first! I cannot end without thanking Jeff Cooke for all his efforts and his humour and without acknowledging the NSERC and UWO for financial support.

References:

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1. Brook, A.G.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R.K.M.R. *J. Chem. Soc., Chem. Commun.* **1981**, 191.
 2. West, R.; Fink, M.J.; Michl, J. *Science* **1981**, *214*, 1343.
 3. Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J.F. *J. Am. Chem. Soc.* **1982**, *104*, 1150.
 4. Ando, W; Tsumuraya T. *J. Chem. Soc. Chem. Commun.* **1989**, 770.
 5. Baines, K.M.; Cooke, J.A. *Organometallics* **1991**, *10*, 3420.

Direct Synthesis of Tris(dimethylamino)silane

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In late 1974, taking advantage of the recent development of more active forms of copper-activated silicon masses at Union Carbide, Bernard Kanner proposed that a newly hired chemist be assigned to investigate direct reactions of silicon with organic compounds other than the halides and alcohols that were then known to react. When William Herdle arrived for work in Tarrytown in late 1975 with a Ph. D. in organic chemistry, he (perhaps naively) accepted Kanner's proposal that dimethylamine ought to react in a copper-catalyzed high-temperature gas-solid reaction. Upon learning some small part of the enormous body of knowledge about fluidized bed reactors and building a quartz laboratory reactor with the assistance of Jeff Mui, Herdle set out to demonstrate that reaction. The first experiments were conducted using active mass prepared at the Sistersville plant and shipped to Tarrytown. This mass was reactive toward methyl chloride, but when subjected to dimethylamine at conditions similar to those used for the methyl chloride reaction, it produced entirely products of dimethylamine cracking. Herdle discovered that if the mass was reacted first with HCl or methyl chloride to re-activate it, and then with dimethylamine, small amounts of aminosilanes were produced in addition to the cracking products. Soon he learned that at lower temperatures, around 250°C, the dimethylamine reaction could be made to proceed smoothly and to produce almost entirely tris(dimethylamino)silane, later referred to internally as "tris".

A patent was easily obtained, particularly in view of prior literature references claiming that the dimethylamine reaction with silicon could not be made to proceed. However, it was never exploited commercially, despite the considerable efforts of subsequent researchers working under Kanner to develop a general route to silanes from "tris", replacing trichlorosilane in most cases.



Discovery of Tin and Phosphorus Effects on the Direct Synthesis of Methylchlorosilanes

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Concurrent with the commercialization of the copper catalyzed Direct Process Reaction of methyl chloride with silicon, research efforts got underway not only to explore what new products could be made and sold, but how to make those products more economically. While the direct process reaction was a significant improvement over the Grignard process, the yields to desirable products were dismal when compared to today's standards. Much of this poor performance was due to the quality of silicon and copper raw materials used by the industry. Initial process development work was done with ferrosilicon and with copper whose purity was only 95-96%. Much of the focus at the time was on just getting the silicon to react, and there was much effort to discover better initiation parameters such as HCl addition and temperature. The progress in the field was hampered by a lack of a fundamental understanding of the chemistry of the reaction, and much of the improvements made were simply finding a better source of copper and a better source of silicon with minor tweaks in the process. At the same time, changing the commercial reactor design complicated the picture as the fluidized bed reactor replaced the tumbling bed reactor. In addition, the desirable product from the reaction has not been consistent. While MeSiCl_3 has always been undesirable, at times it was advantageous to suffer an increase in the MeSiCl_3 produced and a decrease in the Me_2SiCl_2 in order to maximize the MeHSiCl_2 . As can be expected, this led to much confusion when identifying what a "good" run was compared to a "bad" run, and contributed not a little to confusion in the ongoing research efforts.

As with practically all the other additives evaluated, tin and phosphorus have been seen as positive by some researchers and negative by others. This is undoubtedly due to the changing picture as to the quality of the silicon raw material and the copper catalyst. Few of the silicon and copper impurities were suspected to have the kind of impact on the Direct Process reaction, at the levels they were present, as is observed today.

Of tin and phosphorus, tin was the first observed to affect the Direct Process reaction significantly. At Dow Corning, Robert Rownd first recorded the effect of tin in 1950, as he began studying the effects of additives to an experimental fluidized bed reactor. Then he reported the characteristic reduction of SiH-containing chlorosilanes such as MeHSiCl_2 and HSiCl_3 , though this was considered somewhat as a negative, as it was desirable to maximize MeHSiCl_2 at that time. Dow Corning was obviously not alone in the search for beneficial additives as, in 1951, Hoshino and Kojima, of the Tokyo Institute of Technology, received a patent on the use of tin(II) chloride as a treatment of silicon to increase the yields of Me_2SiCl_2 . Throughout the 50s and 60s, experiments were conducted in laboratory scale reactors by Don Vallender and David Thomas to determine the optimum levels of tin to add depending on the desirable product distribution at the time. Since the effect of tin was so significant at such low levels, it was suspected that there was likely an interaction between tin and other impurities/additives that could be capitalized upon. Subsequently, Ken Moorhead continued designed

experimental studies in the 1970s using stirred bed reactors, and included tin in his study of the effect of various additives to the Direct Process reaction. The importance of tin to both reactivity and product distribution was confirmed.

During these development efforts, the characteristic effect of tin increasing the Direct Process Residue was observed as well as the negative impact that too much tin has on silicon conversion. The levels of added tin have changed little since the commercial reactors have been optimized for the production of Me_2SiCl_2 . However, the reason that a few tens of ppm of tin can have such a large impact on the reactivity and product distribution is still not understood.

Like tin, phosphorus has been investigated since the early 1950s. When first added as phosphorus trichloride to the Direct Process Tumbler reactors, little effect was observed. Phosphorus has been reported by other researchers since that time to be both a promoter and a poison to the Direct Process reaction. The different conclusions concerning the effect of phosphorus on the Direct Process reaction were likely due to the varying techniques used to add phosphorus to the reaction contact mass, as well as other additives/impurities present in the silicon raw material and copper catalyst.

The effort at Dow Corning which led to the conclusive discovery that phosphorus could be used to improve the product distribution from the Direct Process reaction began as a program to control the species in the metallurgical grade silicon with the goal of increasing the efficiency of the reaction with methyl chloride. A new silicon refining technology was found by a team of Dr. Roland Halm, Ollie Wilding, and Regie Zapp to produce silicon that gave better performance in the Direct Process than silicon refined by the conventional techniques of chlorine or oxygen gas blowing. Dr. Robert Smith was called upon to identify differences in the silicon refined by the different techniques to see if the cause of the improvements could be discovered. Though it was at the limits of the DC arc emission analytical technique he was using, he was able to identify an increase in phosphorus in the silicon refined by the new technology as compared to that refined by the conventional technology. Phosphorus had been unknowingly added to the silicon. This led to the discovery that a processing aid in the new technology had tricalcium phosphate added to it as an anti-caking additive.

A hypothesis was developed to explain how phosphorus could be present in the silicon metal. The vapor pressure of elemental phosphorus indicated that it was not possible for it to exist in solution at the levels indicated. It was proposed that a phosphorus compound was formed from the reduction of the tricalcium phosphate by the molten silicon metal which had a vapor pressure low enough that at molten silicon temperatures it could remain in the silicon at concentrations above 100 ppm. Thermodynamic calculations indicated that the reduction of tricalcium phosphate by silicon to calcium phosphide (Ca_3P_2) was possible. Calcium phosphide has a boiling point of 1540 °C.

Alloying experiments were subsequently carried out in a laboratory furnace to test this hypothesis via the addition of calcium phosphide to molten silicon. These experiments were successful in obtaining the dramatic improvement in the Direct Process selectivity that had been observed earlier. It was then proposed that this phosphorus species might also improve the

selectivity of the Direct Process reaction simply by adding it directly to the ground silicon used in the reaction instead of going through the alloying step.

Evaluation of the addition of calcium phosphide to the Direct Process reaction contact mass in the Vibrating Bed Reactors (VBRs) demonstrated that the improvement in selectivity towards Me_2SiCl_2 could be achieved by its addition as a powder as well as by being alloyed into the silicon. It was observed as well to have a negative impact on silicon conversion.

Because of the negative effect on silicon conversion and the handling difficulties of Ca_3P_2 , experimentation was shifted to identifying alternative phosphorus compounds, which would give similar beneficial effects. Numerous compounds were evaluated. Oxygen containing compounds of phosphorus were found to be ineffective or detrimental to the reaction. A number of metal phosphides was identified which give the desired selectivity enhancement and copper phosphide was chosen for application on the commercial scale.

One may ask what those factors were that have impeded progress in the identification of the “best” catalyst package for the Direct Process reaction. One of the chief of these factors has been the inability to see signals above the noise of the process. In the commercial processes the fluid bed reactors are still not run in a consistent manner. Not only are these reactors run differently in different companies, but they are run differently in the different sites within a company, the different fluid beds of a site, and even differently by the different operators of a single reactor. The variability caused by these differences many times mask the differences caused by different silicons being reacted and the different catalytic packages being added. Improvements in the consistency of operation of the reactors are being made, and this has resulted in new signals above the noise. This same problem affects laboratory experimentation. The variability of results seen in the laboratory reactors, whether they be Fixed Bed Reactors, Vibrating Bed Reactors, Stirred Bed Reactors, or Fluid Bed Reactors have, in many cases, been worse than that observed in commercial scale reactors. Dow Corning has been fortunate to have essentially one person running the laboratory scale reactors for the past 20 years. This has given us the opportunity to achieve a degree of precision that has allowed us to see signals not seen before. It could well be said that the discovery of the benefits of phosphorus addition could have been delayed for a number of years if we had not the precision in the running of our laboratory reactors which we then did. It is my belief that the next step change improvement in the operation of the FBRs will be as a result of operating the reactors, both commercial and laboratory, in a more consistent and repeatable fashion.

**Discovery of Methylchlorosilylene (CH_3SiCl) as a
Key Intermediate in the Direct Synthesis of
Dimethyldichlorosilane, ($(\text{CH}_3)_2\text{SiCl}_2$)**

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My intention, in this memoir, is to document the events leading to discovery of methylchlorosilylene (silylenoid) as a key intermediate in the Rochow-Müller Direct Synthesis of dimethyldichlorosilane. In particular, I want to discuss the influence of various factors and individuals and pay tribute to mentors and contributors.



When, in January 1979, I transferred from the Linde Research Department of Union Carbide to the Exploratory and Basic Group of Silicones R&D, one of my first assignments was to identify and develop exploitable concepts and phenomena to improve the performance of the Rochow-Müller Direct Synthesis of methylchlorosilanes. Dr. Bernie Kanner, my Group Manager, had told me that there was much that was still unknown about the reaction, despite almost forty years of commercial practice at that point. I was excited by the fact the Direct Synthesis is a copper-catalyzed reaction. My fascination with copper chemistry had started during my senior year at the University of Alberta (Edmonton) with a lecture by Prof. Robert Jordan on the physiological role of copper enzymes and copper proteins. It continued through graduate school at the University of Massachusetts (Amherst), where I had studied the corrosion chemistry of the copper intrauterine device (IUD) during my doctoral research. In the Linde Research Department, use of chelation technology to recover copper and other metals from industrial wastes and hydrometallurgical solutions was one of my projects. Now, in Silicones R&D, I was going to study the catalysis of the Direct Synthesis with emphasis on the role of copper.

My review of the published literature had revealed that the role of copper in the catalysis had not been elucidated. Prevailing ideas about the mechanism of the Rochow-Müller Direct Synthesis of dimethyldichlorosilane had originated from the research of Voorhoeve and coworkers, and van den Berg and coworkers in The Netherlands, Bazant and coworkers in Czechoslovakia and from Golubtsov, Lobusevich and coworkers in The USSR. Voorhoeve's monograph, *Organohalosilanes: Precursors to Silicones*, was the primary authoritative source of published information. The tenets of the prevailing hypothesis were

1. Cu_3Si (η phase) is the active catalyst leading to selective formation of $(\text{CH}_3)_2\text{SiCl}_2$.
2. The polarity of the metal – silicon bond in metal silicides determines or influences product selectivity.
3. The Cu – Si bond energy (46 kcal/mole) is greater than the Si – Si bond energy (42 kcal/mole).
4. Promoters, particularly zinc, cadmium and antimony, enhance catalytic activity and selectivity when used in small (< 1 weight percent) amounts.

5. Neither methyl chloride adsorption nor copper diffusion is the rate-limiting step of the reaction.
6. Methyl chloride is dissociatively chemisorbed on the catalytic surface.
7. The reaction follows Langmuir-Hinshelwood kinetics.
8. $(\text{CH}_3)_2\text{SiCl}_2$ is formed from a surface intermediate with dimethylsilyl groups.

At the conclusion of his Plenary Lecture at the International Symposium on Organosilicon Chemistry in 1969, Bazant acknowledged the difficulty of mechanistic research on a reaction as complex as the Rochow-Müller Direct Synthesis of methylchlorosilanes (see *Pure & Applied Chem.* **1969** *19*, 473 – 488). This is a copper-catalyzed, gas – solid reaction, not the familiar reaction of gaseous reactants over a heterogeneous catalyst. Bazant's remarks inspired the surface-chemical investigations, which we initiated in 1980. Our objectives were

- To understand the significance of bonding, thermochemical and morphological changes accompanying alloy formation in the Cu-Si binary and Cu-Si-Zn ternary systems.
- To determine surface compositions in these systems in the temperature range ($280^\circ - 350^\circ\text{C}$) in which selectivity to dimethyldichlorosilane is high.
- To characterize the valence states of Cu, Zn and Si in these systems *in vacuo* and following methyl chloride chemisorption.
- To elucidate structure and composition of the surface intermediates and active sites following chemisorption.
- To assess state-of-the-art mechanistic proposals and make new ones consistent with the surface analytical results.
- To exploit findings that will improve the performance of our commercial reactors.

Although our research was begun independently, it soon became a joint effort with that of Prof. John Falconer's group at the University of Colorado (Boulder). John's group used Auger Electron Spectroscopy (AES) and Temperature Programmed Desorption/ Mass Spectrometry (TPD/MS) and we, at Tarrytown, employed X-Ray Photoelectron Spectroscopy (XPS) and Mass Spectrometry. Early on, John and his collaborators (Timothy Frank and Keith Kester) and Don McLeod and I both discovered the surface enrichment of silicon which occurs on copper - silicon alloys and solid solutions and the enhancement of this enrichment by zinc, a known promoter of selectivity to dimethyldichlorosilane. Lead, a well-known poison of the reaction, inhibited the surface enrichment of silicon. High tin concentrations also suppress silicon surface enrichment. Tin-induced zinc surface enrichment provided evidence of interactive effects of zinc and tin on the catalytic surface. Whereas both zinc and tin were evaporated from the surface above about 450 K at 10^{-10} torr, lead was retained. The Boulder team showed that silicon surface enrichment was predicted by the empirical rule of Burton and Machlin. Their results were published in *Applied Surface Science* **1982 – 83**, *14*, 359. We showed that the thermodynamics of silicon enrichment was in agreement with the comprehensive model of Wynblatt and Ku, but it was 1987 before we were permitted to publish our results (*Catalysis 1987*; J. W. Ward, Ed.; pp 415 – 434).

In the meantime, we had calculated the Cu-Si bond energy to be 30.6 ± 2.4 kcal/mole, that is, less than the Si-Si bond energy of 53 kcal/mole. An independent quantum mechanical

calculation by Chou, *et al.* (*J. Am. Chem. Soc.* **1987**, *109*, 1880) found 30.7 kcal/mole as the Cu-Si bond energy. The reduced energy of Cu-Si bonds compared to Si-Si bonds is consistent with copper catalysis and the fact that it is the alloyed silicon, which is reactive. The composition of the catalyst surface at reaction temperatures is 40 - 55 atom % Si and not the 25 atom % expected from the formula, Cu₃Si. In fact, it emerged that Voorhoeve and other researchers had associated Cu₃Si with high catalytic effectiveness because of the accident of its faster nucleation when reacted copper-silicon masses had been cooled to room temperature for x-ray diffraction measurements. Calculation of Auger Parameters and application of various electronegativity scales allowed Don McLeod and me to conclude that, while both copper and silicon are formally zerovalent in Cu₃Si prior to exposure to methyl chloride, the Cu^{δ+} - Si^{δ-} bond is polarized with a partial positive charge on copper and a partial negative charge on silicon. These results had challenged and vanquished some of the key tenets of the prevailing hypothesis.

Chemisorption studies with methyl chloride disclosed that there was a desorbable intermediate leaving the catalytic surface above 160°C at 10⁻⁹ torr. Based on the simultaneous decrease of silicon, carbon and chlorine intensities in the XPS spectra, I concluded that this intermediate contained these three elements. Moreover, with a Si 2p binding energy of 102.8 eV, this species had a silicon valence between those of elemental silicon (Si 2p = 99.3 eV) and tetravalent silicon (Si 2p = 103.4 eV), and was most probably divalent. We did not yet have a mass spectrometer attached to our high vacuum reaction chamber. So we had no data on the masses of the desorbates. We acquired one later.

At that time, there were only two literature references to the silylene, CH₃SiCl, even though the early eighties was the era in which silylene chemistry was one of the hot organosilicon chemistry topics. Tom Barton's group (*J. Am. Chem. Soc.* **1977**, *99*, 5199 - 5200), Morey Ring's group, (*Inorg. Chem.* **1973**, *12*, 2968 - 2972) and much later, G. Maier's group (*Chem. Ber.* **1984**, *117*, 2369 - 2381; *J. Organomet. Chem.* **1989**, *366*, 25 - 38) and Heinecke, *et al.* (*J. Anal. Appl. Pyrol.* **1994**, *28*, 93 - 105) demonstrated the intermediacy of CH₃SiCl in gas phase trapping experiments. Others before me, for example Rochow, *et al.*, (*J. Am. Chem. Soc.* **1952**, *74*, 5545 - 5546), Hertwig (*Z. Naturforsch.* **1951**, *6B*, 337 - 338) and Schenk, *et al.*, (*Z. Anorg. Allg. Chem.* **1964**, *334*, 57 - 65), had suggested that silylenes might be intermediates in the Direct Synthesis, but no experimental verification of these suggestions had been undertaken under Direct Synthesis conditions. I wanted more proof before I proclaimed so revolutionary an idea as an unknown (or unpublished) silylene as a key intermediate in a mechanism, which had been so rife with controversy. At the 1966 International Symposium on Organosilicon Chemistry, Prof. Bazant responded to critical comments on his proposed mechanism by asking the questioners, "were you there and did you see what the active sites and activated complexes looked like?" I wanted to avoid that type of contention.

So it was that in the summer of 1982 that I journeyed to Boulder to share results with Prof. Falconer and review the status of his research. In our first conversation, he said that a desorbate of mass 78 was consistently observed following methyl chloride chemisorption on the silicon-enriched surfaces of copper - silicon catalysts. This species was more abundant than could be accounted for by the mass spectral fragmentation of dimethyldichlorosilane and other methylchlorosilanes. He could not explain its formation. You can well imagine my joy at having independent confirmation of the intermediacy of CH₃SiCl (methylchlorosilylene, mass

78) in the Direct Synthesis as I wrote down, for John's benefit, the silylene insertion reactions that made up my proposed mechanism. We had just successfully challenged another of the basic tenets of Voorhoeve's monograph on the Direct Synthesis. The Klebansky-Vikhtengol'ts-Voorhoeve mechanism proposed a dimethylsilyl $((\text{CH}_3)_2\text{Si})$ intermediate as the surface species leading to $(\text{CH}_3)_2\text{SiCl}_2$. Later, Timothy Frank showed that the intensity ratio of mass 78/mass 80 ($\text{CH}_3\text{Si}^{35}\text{Cl}/\text{CH}_3\text{Si}^{37}\text{Cl}$) was 0.3 and temperature independent as required by the natural isotopic distribution of chlorine.

As often happens in research, serendipity was to intervene, not once but three times. First, Keith Kester, who had done his doctoral research on the Direct Synthesis of dimethyldichlorogermane with Prof. Rochow at Harvard, was one of John's colleagues and collaborators. He made us aware of results, published only in his dissertation, that $(\text{CH}_3)_2\text{GeCl}_2$ adsorbed on germanium can decompose to CH_3GeCl , (methylchloro-germylene) and CH_3Cl (methyl chloride) under the influence of radio-frequency fields. This information became significant when we sought to obtain reference XPS and AES/TPD spectra for $(\text{CH}_3)_2\text{SiCl}_2$ on copper – silicon alloys. The data were indistinguishable from those of methyl chloride on the alloys. In addition, mass 78 and mass 50 (CH_3Cl), both of which are weak in the mass spectrum of $(\text{CH}_3)_2\text{SiCl}_2$, were quite prominent. Thus, both the Boulder and Tarrytown groups demonstrated that CH_3SiCl and CH_3Cl are formed when $(\text{CH}_3)_2\text{SiCl}_2$ is chemisorbed on copper-silicon surfaces.

John visited Tarrytown in November 1982 and we both presented seminars on the discoveries and status of the research to the R&D staff. Later, there was a brainstorming session in Bernie's office on what additional confirmatory experiments on the intermediacy of CH_3SiCl in $(\text{CH}_3)_2\text{SiCl}_2$ formation could be undertaken, how CH_3SiCl might be trapped in laboratory reactors and how this new knowledge might be exploited commercially. Ethylene, acetylene and 1,3-butadiene were suggested as trapping agents, but I was concerned about extensive carbon formation in my fluidized bed reactor. My preferred trapping agents were H_2 and an Si-H monomer like $(\text{CH}_3)_3\text{SiH}$. A 6 – 15 fold increase in the intensity of the mass 78 peak had been observed in XPS/MS experiments when $\text{CH}_3\text{Cl} - \text{H}_2$ mixtures had been used for chemisorption. It had been reported in the literature that the insertion of silylenes into H_2 and into Si-H bonds proceeded with near zero activation energy. Furthermore, based on the findings of DeCooker, *et al.*, (*J. Organomet. Chem.* **1975**, *99*, 371 – 377), I was already studying the effects of H_2 on product selectivity, especially in the absence of zinc and other promoters.

Our fluidized bed reactions confirmed that selectivity to $\text{CH}_3\text{SiHCl}_2$ and $(\text{CH}_3)_2\text{SiHCl}$ is increased by the use of $\text{CH}_3\text{Cl} - \text{H}_2$ in the absence of promoters like zinc, antimony and tin. There was no evidence of $\text{CH}_3\text{SiH}_2\text{Cl}$ until one day in May 1984, when the methyl chloride supply from the cylinder was insufficient to fluidize the bed. Thereafter, CH_3SiCl trapping with H_2 was done with the fluid bed reactor operated as a fixed bed. GC/MS, GC/FTIR and ^{29}Si NMR data and comparison of these results with those of an authentic sample confirmed the presence of $\text{CH}_3\text{SiH}_2\text{Cl}$ in the reaction product. Gas circulation in the fluidized bed had increased the probability of the redistribution reactions, which consume $\text{CH}_3\text{SiH}_2\text{Cl}$. This was a good illustration that batch or plug-flow reactors provide better selectivity to early intermediates in reaction pathways. However, the serendipitous decrease of the methyl chloride flow had

allowed Rudy Cameron and me to trap CH_3SiCl in a large laboratory reactor as well as accomplish the Direct Synthesis of $\text{CH}_3\text{SiH}_2\text{Cl}$.

Jeff Larned and I performed fluidized bed experiments with $\text{CH}_3\text{Cl} - \text{H}_2$ and periodic injections of methylchlorosilanes, particularly CH_3SiCl_3 . The objective was to trap CH_3SiCl as the disilane ($\text{CH}_3\text{Cl}_2\text{SiSiCl}_2\text{CH}_3$). The disilane was not detected. Instead, the rate of formation of the methylchlorohydrosilanes increased 2 - 5 fold. We had earlier expended a great deal of effort to find promoters for this Direct Synthesis (*see US 4,973,725*). Serendipity had intervened for a third time. We pursued its lead and never got back to investigating the effect of injecting methylchlorosilanes or Si-H monomers into the fixed bed Direct Reaction with $\text{CH}_3\text{Cl} - \text{H}_2$. Based on our results and those of Michael Clarke and Ian Davidson, the Ono group and Gerhard Roewer's group with 1,3-butadiene, I am confident that the silylene (silylenoid) intermediates will someday be trapped as disilanes.

The surface-chemical studies, silylene trapping experiments and other studies conducted by various groups from 1980 to the present permit an updated understanding of the course of the Rochow - Müller Direct Synthesis.

- The active catalytic surface is a solid solution containing 40 - 55 atom percent Si along with Cu, Zn and Sn.
- Zn is a structural promoter (affecting energy of activation) and Sn and P are textural promoters (affecting number of active sites)
- M - Si bond polarities do not correlate with product selectivity
- Cu - Si bond energy (~ 31 kcal/mole) < Si - Si bond energy (~ 53 kcal/mole)
- Surface precursor of $(\text{CH}_3)_2\text{SiCl}_2$ is CH_3SiCl . Other silanes (except $\text{Si}(\text{CH}_3)_4$ and SiCl_4) and the disilanes also originate from silylene intermediates
- The divalent silicon intermediate mechanism is also applicable to other Direct Syntheses of silanes.

Experimental evidence in support of these ideas has been published in *Catalyzed Direct Reactions of Silicon* (K. M. Lewis; D. G. Rethwisch, Eds.; Elsevier, 1993). Nonetheless, very many questions about the atomic and molecular events of the reaction still remain unanswered. Some of these are

- What is the structure of the active site leading to selective formation of $(\text{CH}_3)_2\text{SiCl}_2$?
- Why is the reaction so much more sensitive to Sb, Sn and P than to Zn?
- Do silylenes (for example, RSiX , R = H, CH₃, X = Cl, Br, OCH₃, N(CH₃)₂) disproportionate ($2\text{RSiX} \leftrightarrow \text{R}_2\text{Si} + \text{SiX}_2$) under Direct Synthesis conditions, and how significant is this reaction in product selectivity?
- Why are the Direct Reactions with HCl, ROH and $(\text{CH}_3)_2\text{NH}$, which are selective for the trifunctional silanes, inhibited by promoters of $(\text{CH}_3)_2\text{SiCl}_2$ formation?

Throughout the telling of this story I have mentioned the names of my assistants, collaborators and mentors. I want to acknowledge their contributions to the successes we have had and to thank them for their support, their assistance and their inspiration. Others I want to

recognize include the members of the analytical group and the Library staff at Tarrytown, Cynthia Vail, my secretary, and my wife for putting up with my work habits. Bernie Kanner stands out as an influential mentor. One day in 1983, following the methylchlorosilylene and silicon, zinc and tin surface-enrichment discoveries, I reminded him of my question to him during our initial meeting in January 1979. The question was whether there were enough challenging problems in silicon chemistry yet to be solved to keep researchers interested and productive. At that time, silicon's position in the periodic table and the existence of inorganic polymers called silicones were about the limits of my knowledge of silicon chemistry. Bernie had replied that he and others like Don Bailey and Bela Prokai, had had very productive careers up to that point and that he was looking forward to making many more contributions before his retirement. He also said that there was still much that was not known about the Direct Synthesis of methylchlorosilanes, a copper-catalyzed reaction.

Now, in 1983, in response to my reminder, Bernie said that when H. C. Brown, (Bernie's Ph.D. adviser at Purdue University and later a Nobel Laureate), began to realize the potential of hydroboration he remarked that he felt like a guy who had fallen into a pit full of gold nuggets. He was too busy filling his pockets to stop to query how they got there, or how he was going to climb out so fully laden. Bernie was saying that organosilicon chemistry had provided a similar gold mine for us. I shall add that for me copper also glitters.

**The First Platinum-Catalyzed Hydrosilylation
with Supported Platinum Catalysts**

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The First Platinum-Catalyzed Hydrosilylation with Supported Platinum Catalysts

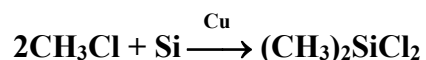
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The subject of this presentation is the reaction of silicon-hydrogen (Si-H) bonded compounds with unsaturated organics, either C=C or C≡C, using a heterogeneous Pt catalyst. This reaction was first carried out in the Linde Laboratory of Union Carbide and Carbon Corporation at Tonawanda, New York, in 1946. The original patent (US 2,632,013) was filed October 9, 1946. Additional related inventions are disclosed in US Patents 2,637,738; 2,657,114 and 2,851,473.

In 1944, I was moved from the automotive group at Linde to a silicon chemistry group. I was head of the group—five chemists. We were to establish a business based on organosilicon chemicals. The logic was that Union Carbide wanted to expand its chemical business. Already it was a powerhouse in organic chemicals, number two in the nation, DuPont being number one. Several companies had built businesses based on inorganic chemicals. We saw a large undeveloped area in organometallic chemistry. At that time, there were about 92 elements in the Periodic Table. Which metal should we attach organics to? For some time, this small group of five chemists had wandered all over the Periodic Table—chromium, vanadium, and uranium. For various reasons, it was decided that we should stick to silicon. For one thing, it is near carbon in the Periodic Table and should be compatible with it chemically.

Silicon metal was readily available from another division of Union Carbide. But how to attach carbon to silicon, i.e. how do you make a C-Si bond? The Grignard Reaction had been used in universities to do this, but it was too expensive for commercial use. Eugene Rochow, at General Electric Company, had recently discovered and patented the Direct Synthesis method:



This was a great invention, but it made only a few silicon compounds. While reading, thinking, and studying this problem, one day in early 1946 in the Linde library, it occurred to me like a flash that an SiH bond should react with C=C and C≡C bonds to make Si-C bonds. I talked ideas over with my supervisor, Dr. C. O. Strother. Bond energy calculations indicated that such reactions should be thermodynamically favorable and strongly exothermic. I must have been excited with the idea because I followed the rules to a T: I wrote up an idea record, had it witnessed, and signed it.

I tried the reaction in the lab using a platinum catalyst with the following reactants:



Catalyst = none, reaction Temp. = 350°C.

Catalyst = Pt, Pt on silica, Pt on asbestos, reaction Temp. = 100°C.

Olefins: styrene, butadiene, 1-alkenes to octene-1, allylchloride, $\text{CF}_2=\text{CH}_2$, vinyl chloride, cyclohexene, trichloroethylene, acetylene,

Other Silanes : $(\text{EtO})_3\text{SiH}$, Cl_2SiH_2 , $\text{CH}_2=\text{CHSiCl}_2\text{H}$; the latter to oils and orientable fibers

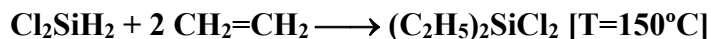
The reaction was vigorous and complete and occurred at 100°-200°C lower than the uncatalyzed reaction. As indicated above, most of the innumerable C=C and C≡C bonded compounds I tried reacted. By substituting different alkenes for the ethylene, I could change the result from ethyltrichlorosilane to other alkyltrichlorosilanes, and of even greater interest, to organofunctional alkylchlorosilanes.

By substituting acetylene, I could produce vinyltrichlorosilane. In large scale preparation,



a continuous-flow reactor reduced the subsequent product of the reaction, vinyltrichlorosilane, with another trichlorosilane to produce $\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{SiCl}_3$. An even better method would be a continuous flow over a fixed catalyst bed to avoid $\text{Cl}_3\text{SiC}_2\text{H}_4\text{SiCl}_3$.

However, acrylonitrile ($\text{CH}_2=\text{CHCN}$) was a special case. Its hydrosilylation required a special basic catalyst (as worked out by Dr. V. B. Jex) to give $\text{CNC}_2\text{H}_2\text{SiCl}_3$, which was later converted to either the amino or the carboxy silane. The γ -aminopropyltriethoxysilane and its analogs were found by one of the glass companies to be the best coupling agent for epoxy resins and were eventually used around the world for this purpose.



Catalysts: Pt on charcoal (40 m²/g), on alpha Al₂O₃, on asbestos, on silica gel, or on gamma Al₂O₃ (500 m²/g).

0.2g gamma Al₂O₃ containing 0.05% Pt (= 0.1 mg Pt) gave 90% conversion of 100 ml SiH₂Cl₂ in 0.8 hr.

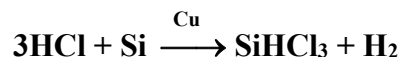
As is shown in US 2,851,473 (filed December 23, 1955), platinum on gamma alumina is a superior catalyst for heterogeneous hydrosilylation. In general, the high-surface-area catalysts were best. Note that 0.1 mg of Pt dispersed on gamma Al₂O₃ (~500 m²/g) gave good conversion in 0.8 hr. It is difficult to imagine a better catalyst. For the homogeneous catalyst users, it is helpful to remember that silicon oxyhydride, the hydrolyzable product of SiHCl₃, is a strong

reducing agent. It quickly removes Ag^+ from aqueous solutions as Ag^0 . Other SiH hydrolyzates are probably good reducing agents. Aqueous solutions of Pt compounds added to SiH compounds could easily form some metallic Pt.

The extreme activity of Pt-on- γ -alumina catalysts always intrigued me. The usual mechanism of adsorption and desorption of catalyst and product did not seem possible. How could so many molecules adsorb on such a tiny amount of catalyst in such a short time? Yet, the reaction rate increased with the surface area of the catalyst, as an adsorption mechanism would suggest.

My original thought was that the catalyst let loose into the solution free radicals, such as $\cdot\text{SiCl}_3$, and subsequent events proceeded by a chain reaction. To test this, we built a pressure reactor with a sapphire head through which ultraviolet light shined continuously. Using trichlorosilane and ethylene, we obtained no reaction. Later Dr. Leo Sommer of Penn. State reacted an alkene (pentene, I believe) with an SiH compound using a peroxide free radical generator and got a very poor yield.

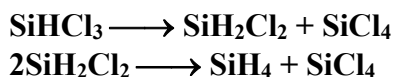
Trichlorosilane is readily prepared from silicon:



So now we had the basis of an organosilicon business—a way to make a variety of compounds. The heterogeneously catalyzed hydrosilylation reaction was the key to the mission of our small group of Linde researchers, who were funded by Corporation dollars, not Linde's, to find and exploit a route to a business based on organometallics. Initially, there were no uses for the compounds. So two new groups were started at Linde—a research group to find uses for the compounds and an engineering group to learn how to scale up the laboratory operations to plant size. It was an exciting time. We, the research group, converted the Cl-containing compounds to benign liquids, oils, and polymers. This vast group of chemicals was all unknown in nature and new to man.

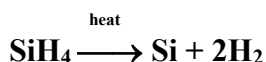
According to Petrov, et al. (Synthesis of Organosilicon Monomers, Consultants Bureau, 1964, p 389), the platinum-catalyzed hydrosilylation also provided a new avenue for investigators in the field and greatly expanded synthetic possibilities. The reaction allowed the preparation of a host of previously unknown organosilicon compounds; a new Beilstein was created for these compounds. Union Carbide had faith that uses would be found for them, just as uses were found for other organic fine chemicals when vinyl resins wound up in men's belts, ethylene glycol in auto radiators, etc, etc. These new organosilicon compounds had unusual properties: They were much more resistant to heat than organics, they were not wetted by water, and they had other unusual surface properties. In 1940, sales of these compounds were zero. Today, over \$2 billion worth of organosilicon compounds are sold in the USA every year.

Along the way, as part of making new organosilicon compounds, I gained insights into the problem of silicon purification. I studied the chemistry of SiH compounds and learned how to go from SiHCl_3 (trichlorosilane) to SiH_4 (monosilane) by a series of so-called disproportionation reactions, such as:



Both of the above happen in sequence, but rapidly. Normally the reactions do not run to completion; all the compounds exist together, in equilibrium. But if you run the reactions in a still and remove the low-boiling compound, they run to completion. Don Bailey and I patented the first reaction.

SiH_4 is a gas that can be purified further by distillation. Pure SiH_4 is easily converted to pure Si by heat:



Furthermore, C. E. Erickson and I learned how to recycle the SiCl_4 to SiHCl_3 , which can then be fed back into the beginning of the process:



We patented this reaction. It consumes metallurgical grade silicon, which is readily available. So the overall process trades impure silicon for pure silicon. Because purifying silicon was incidental to my job of hunting for useful organosilicon compounds, I didn't make a big deal of these discoveries, but I kept Linde informed via internal reports. Much later, Don Bailey put this knowledge to good use when he served as a design consultant for the silicon plant that was built in 1984 in Moses Lake, Washington. Today, that plant makes, by the above reactions, most of the world's premium (99.99999999 percent pure) silicon.

Our work on disproportionation reactions was part of a search for a route to SiH_2Cl_2 . This is a difunctional molecule necessary for making R_2SiCl_2 , the difunctional monomer needed to make silicone oils and rubber. Our intention was R=ethyl (from ethylene via Pt-catalyzed hydrosilylation), the lowest-carbon-containing silicones available by this route. This would put us in competition with dimethyl silicones, which were the basis for the silicone business of our competitors—Dow-Corning and General Electric.

Much research went into successfully determining how to make oils and rubber out of diethyl silicones. We isolated the cyclic compounds $(\text{Et}_2\text{SiO})_x$ from $x=3$ to 7 and determined their polymerization characteristics. Research was far-ranging. But because of their high-temperature instability relative to the dimethyl silicones, the diethyl silicones were turned down, as a business venture, by the business people in charge of the silicones project at UCC.

All told, I have about 35 US patents related to silicon chemistry. The most important and useful, in my estimation, is that for preparing compounds with silicon-carbon bonds. Making pure Si available to the semiconductor industry by providing chlorosilanes as industrial chemicals was gravy from this. In 1960, I received the Schoellkopf Medal from the American Chemical Society (Western New York Section) for my "pioneering contributions to the technology of polyalkylene oxide lubricants and organosilicon monomers and polymers."

The early books on the history of silicones, one from Dow-Corning and one from General Electric, afforded little space, outside of a footnote, to the heterogeneously-catalyzed, SiH – Olefin reaction. But these authors wrote silicone history from the viewpoints of their laboratories. The full history of silicones at Union Carbide still remains to be told.

Mr. P. W. Shafer and Mr. W. G. Whitehead contributed to the experimental work reported here. Mr. Shafer could build or fix anything mechanical, and Mr. Whitehead always wanted one more experiment for verification.

The Discovery of Silicone Surfactants for Polyurethane Foam

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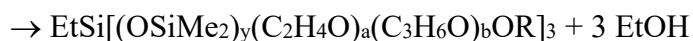
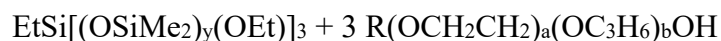
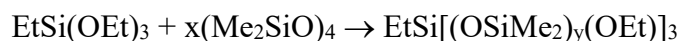
The Discovery of Silicone Surfactants for Polyurethane Foam

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By 1953, Don Bailey's research interests had shifted to the synthesis of new types of silicone-organic copolymers initially directed to the preparation of silicone fibers. Initially, he sought to introduce chain-stiffening groups into the siloxane backbone. The synthesis routes employed presented considerable difficulties and progress was discouragingly slow. His effort then shifted to the incorporation of polyether blocks. In the course of introducing dipropylene glycol units into the silicone chain, he made the observation that Si-O-C and Si-O-Si bonds reacted equivalently using base-catalyzed equilibration conditions. This led to a convenient synthesis of alkoxy-endblocked silicones. The alkoxy-endblocked silicones were then reacted with a series of hydroxyl terminated polyethers (UCONs), which were Union Carbide products. These included polymers made from ethylene and propylene oxides as well as mixtures of the two oxides.

These were the first known copolymers of silicones with polyethers and had both linear and branched structures:



These, and many other structural and compositional variations, were synthesized by Bailey and F. M. O'Connor (See for example, U.S. Patent 2,834,748, issued May 13, 1958 and U.S. Patent 2,917,480, issued December 15, 1959). These new copolymers, of course, proved to be of no interest as silicone fibers, but the latter objective was quickly shelved when it appeared that these novel copolymers might have many other interesting possibilities.

Tom Welch (later a Director of R&D for Silicones), who came to Linde with an extensive background in rubber technology, was seeking improved tire mold release agents, and was aware of the lubricating properties of UCON fluids. He was the first to use the new copolymers for mold release at Dunlop Tire in Buffalo. Other uses envisioned for these copolymers included antifoams, lubricants, hydraulic fluids, brake fluids and textile treatment. The metal-on-metal lubricating properties of these copolymers were markedly superior to pure polydimethylsiloxanes.

These intriguing early results led to a period of intense examination of the potential utility of these compounds in a number of applications. This effort continued for more than two years, but did not lead to the successful marketing of any new products. It was recognized early

on that a possible drawback of copolymers prepared by the transesterification was their limited hydrolytic stability, especially in the presence of acids or bases.

To overcome this problem, hydrolytically stable copolymers were prepared via the platinum-catalyzed hydrosilation of polydimethylsiloxane polymers containing methylhydrogen-siloxane units with allyl-endblocked polyethers. By this time, interest in silicone-polyether copolymers was beginning to wane, however, as none of the potential new applications had yet proved to be commercially attractive. For this reason, the filing of patents on the new non-hydrolyzable copolymers was not actively pursued. However, other developments were then underway which were soon to change the entire future of siliconopolyether copolymers.

Polyurethanes, the reaction products of isocyanates with diols, had been discovered in Germany during World War II. The commercial exploitation of polyurethanes developed rapidly in the late 1940's, especially for polyurethane foam. Foamed polyurethane elastomers were made via a two step, so-called, prepolymer process. In the first step, an excess of an aromatic diisocyanate, such as toluene diisocyanate, was reacted with a hydroxyl-terminated polyester forming a viscous isocyanate-terminated prepolymer. In the second step, sufficient water was added to react with the excess isocyanate, forming urea, generating carbon dioxide, thus foaming the final polymer. The resulting foamed elastomer was of relatively low density, while retaining attractive physical properties; making it economically attractive for a number of applications.

The polyurethane foam prepared in this was inherently self-stabilizing because of its high viscosity. However, it was found that the addition of a small amount of a low molecular weight polydimethylsilicone oil considerably improved the foam cell uniformity. It was later established that the soluble low molecular weight polydimethylsilicone acted as a surfactant by lowering the surface tension of the reacting urethane mass. As interest in the commercial prospects of polyurethanes grew, efforts were underway in a number of laboratories, including DuPont, Mobay and UCC Chemicals. This took the direction of streamlining the foaming process and employing less expensive intermediates, thereby improving its overall economics. The main avenues of research involved substitution of the cheaper hydroxyl-terminated polyoxypropylenes for the polyester component and simultaneously reacting the isocyanate with the polyol and water all at once (known as the "one-shot" process).

Two problems had to be overcome before this process could be commercialized. The reactions between the isocyanate, polyols and water proved to be unacceptably slow. Effective catalysts had to be found. It was now also necessary to find a more effective foam stabilizer than the silicone oil that worked for the prepolymer process. As the viscosity of the "one-shot" polyurethane foam mixture was far lower than the prepolymer system, it was inherently much less stable and collapsed completely in the absence of an appropriate stabilizer.

At UC Chemicals Co. at South Charleston, West Virginia, the effort to solve these problems was headed by Fritz Hostettler and Eugene F. Cox. They made the important discovery that certain tin compounds, initially organotin compounds and, subsequently, stannous compounds, in combination with a variety of tertiary amines were excellent catalysts for the new process. They also had unexpected synergistic interactions for the "one-shot" process. The remaining problem, stabilization of the reaction mass, proved to be far more difficult of solution.

Hostettler and Cox had tried more than 100 surfactant candidates, including many polydimethylsilicones and a wide range of organics without success. It was far from clear that a solution lay ahead. At this point fortune intervened in an unexpected fashion.

At Silicones R&D in Tonawanda, Tony Pater was one of several investigators in the Development group who were trying to develop commercial applications for the silicone - polyether copolymers that had been made by Bailey and O'Connor. After more than two years of active investigation, although optimism still remained, a real commercial winner was yet to be identified. Three of the Bailey-O'Connor copolymer candidates had been scaled up in the pilot plant to facilitate these efforts. The three candidates were fairly closely related, differing mainly in the polyether component. These experimental compositions were identified as X-520, X-521 and X-522. In X-521 and X-522, the polyethers were based on all oxyethylene and oxypropylene units, respectively. Only in the case of X-520, (Later, L-520), did the polyether block contain both oxyethylene and oxypropylene units (50 % by weight of each component).

As part of an effort to interest other laboratories in evaluating these new compositions, Tony had scheduled a visit to the South Charleston Chemicals laboratories in the latter part of 1956. Before an R&D audience, Tony reviewed the extensive efforts at Linde to synthesize, characterize and commercialize the silicone-polyether copolymers. The South Charleston Chemicals R&D were invited to assist in this effort. Fritz Hostettler happened to be present at this review. Samples of the new copolymers were requested, and when they arrived in the early part of 1957, they were quickly evaluated in the "one-shot" South Charleston, prototype polyurethane system. Within the first few experiments, a new industry was essentially established. It was quickly observed that while X-521 and X-522 did not prevent foam collapse, X-520 was an excellent foam stabilizer for one-shot polyurethane foam.

Chance, as it does in so many important discoveries, had played a vital role. The timing of the development of the "one-shot" polyurethane foam system and the synthesis of the first silicone-polyether block copolymers could hardly have been better orchestrated. The selection of the three copolymer candidate compositions for scale up so as to include X-520 (L-520) which was to be one of the surfactant mainstays for the Polyurethane Industry for the next four decades, was indeed fortuitous. A great many other structural and compositional variations which had also been synthesized had failed to stabilize the one-shot polyurethane foam system.

With these discoveries and their subsequent confirmation in a number of other industrial laboratories, the commercialization of the "one-shot" polyurethane systems was assured. The development of appropriate foam formulations, foaming equipment and full scale testing required an additional couple of years. Significant sales of L-520 surfactant then began in the late 1950's. Of all the developments and discoveries that made the "one-shot" polyurethane foam process possible, it is generally recognized that the stabilization of the foam by L-520 was the most important. Don Bailey was to become a recipient of the Schoellkopf Award in 1968 for his pioneering work on L-520 and other silicone-polyether copolymers.

The Discovery of Silane Coupling Agents

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The Discovery of Silane Coupling Agents

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Discovery of the hydrosilation process led Bailey and others to explore the chemistry of reactive organosilanes. This began with the already available vinyltriethoxysilane. The peroxide-catalyzed polymerization led only to low molecular weight polymers, which did not merit further interest. At this time Bailey's research shifted to the synthesis of other organofunctional silanes and silicones capable of undergoing a variety of organic reactions. Shortly thereafter, commercial developments outside of Linde Silicones would soon greatly accelerate this work.



In the late 1940's, reinforced polymers had attracted considerable interest by the military because of their potential use in military aircraft. Glass fabric reinforced polyester laminates, in particular, were being evaluated as spacers for self-sealing gasoline tanks and as non-shattering structural components such as wings. These laminates were based on unsaturated polyesters and approximated the flexural strength of equivalent weights of structural steel. They were also lighter and stronger than equivalent thicknesses of structural aluminum alloys.

The critical deficiency of these laminates, which effectively prevented their commercial use, was the great loss in physical strength they exhibited on extended exposure to water vapor or liquid water. The loss in strength typically amounted to a catastrophic 60%! This was true whether one used desized glass or starch-oil sized glass, which was all that was available at the time. Some modest improvement was noted when a novel sizing agent, chromium methacrylate chloride, was used. The initial flexural strength was slightly increased and the loss on humid aging was decreased modestly to around 40%. This loss in physical strength was still unacceptably high for the use of these laminates in aircraft.

In an attempt to solve this problem, the Air Force granted a contract to the Bjorksten Research Laboratory in Madison, Wisconsin in late 1949 or early 1950 to develop a superior sizing agent for glass cloth polyester laminates. Success was achieved shortly thereafter.

The breakthrough results achieved by the Bjorksten Labs was reported in a paper presented at the Spring Meeting of the Reinforced Plastics Division of the SPI at Chicago in late February-March, 1951. They reported that vinyltrichlorosilane or its admixture with an allyl alcohol derivative not only raised the initial strength of the laminate by 15 to 25%, it also dramatically reduced the loss on humid aging from 10 to 0%. The resulting laminates were now stronger after humid aging than dry chromium methacrylate chloride sized laminates. These striking results attracted great attention and resulted in a special meeting organized by the Materials Laboratory of the Wright Air Development Center held later in March of the same year.

Following a presentation by Dr. Bjorksten of the results at his laboratory, Dr. Robert Steinman of the Garan Chemical Co., of Los Angeles, reported virtually the same results using

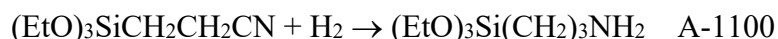
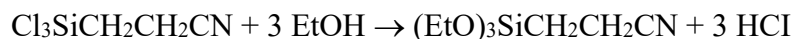
an undisclosed chemical in aqueous solution which was later identified as vinyltriethoxysilane. This was clearly superior to the use of vinyltrichlorosilane as it avoided HCl formation. At the same time, the Owens-Corning fiberglass representatives present at the meeting indicated that they also had a promising laboratory process for this same purpose. Further, plant trials were expected very shortly that they anticipated would be competitive with the Bjorksten and Garan processes. Some months later it was learned that the new Owens-Corning treatment, called Finish 136, was based on a product supplied by the Cowles Chemical Company. The product was made from vinyltrichlorosilane, which was converted to a water-soluble sodium salt which could be directly applied to glass from aqueous solution.

Thus, the discovery, which was the basis for the coupling agent, or, as it was later known as the organofunctional silane business, was made almost simultaneously in 3 different labs. It appears that the Bjorksten labs were first, closely followed by Garan and Owens-Corning. It also appears that all three treatment processes were based on samples of vinyltrichlorosilane or its ester obtained from Linde.

Members of Linde Silicones attended both of these meetings and the decision was quickly made to enter this promising field. Based on laboratory work carried out by Murray Jellinek, aided by Dave Braun and Sarah Camiolo, new vinylsilane esters products were introduced to the market by early 1953.

The rapid commercial acceptance of the vinylsilane coupling agents stirred renewed interest in George Wagner's Research group. The vinylsilanes were believed to bond with the silanol bonds on the glass surface and the vinyl functionality would then react chemically with the unsaturation in the polyester. The overall result would be a chemical bond between the glass surface and the polyesters. This made for improved reinforcement or increased laminate strength, while preventing water from degrading this interaction. Wagner believed that the availability of silanes with new types of organic functionality would greatly broaden the commercial utility of silane sizing agents.

To carry out this work, George asked Vic Jex, a recent addition to the Research group to synthesize a silane containing an amine functionality via a new route. Bailey had previously prepared amino functional silanes via the reaction of chloroalkylsilane esters with ammonia. However, this route resulted in extensive salt formation along with some undesirable side reactions. The new process involved the hydrosilation of acrylonitrile with trichlorosilane, followed by esterification and hydrogenation:



Unfortunately, the first step, which involved platinum catalysis, could not be made to go. This was one of the very few cases of hydrosilation for which platinum catalysis was ineffective. Perhaps fortuitously, Dr. Jex, as part of his graduate thesis, had investigated the base-catalyzed

cyanoethylation of sugar molecules. As it turned out, the tertiary amine-catalyzed cyanoethylation of trichlorosilane was the critical step in the synthesis of the amino functional silane. The product, gamma-aminopropyltriethoxysilane, received the commercial designation of A-1100.

Not too long afterwards, an Owens-Corning representative was brought to Dr. Wagner's office by Dr. Jellinek. There, he inquired whether a sizing agent suitable for use with epoxy resins might be available. He was promptly given the A-1100 sample that had been prepared by Vic Jex. Subsequent tests at Owens-Corning proved the effectiveness of A-1100 for epoxy resins. With the rapid industrial acceptance of the Linde Silicones vinyl- and aminoalkylsilane coupling agents in the 1950's, Linde became the leading supplier of silane coupling agents, a position that UCC Silicones and its successors have maintained until the present time.

As a postscript, for his "...pioneering contributions to the technology of organosilicon monomers and of polyalkylene oxide lubricants" George Wagner was to receive the Schoelkopf Award from the Western New York Chapter of the ACS on May 19, 1960. Several years before that, Dr. Wagner had left Linde Silicones to assume greater responsibilities, initially within Linde, and subsequently for other Divisions within UCC.

Presenters and Some Attendees

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Barry Arkles



Kim Baines



Adrian Brook



Adrian Brook and Bob West



Joyce Corey and Dietmar Seyferth



Bill Herdle



Roald Hoffman and Ken Lewis



Bernard Kanner



Bernard Kanner with George Wagner Photos



Ken Lewis



Bob West



Larry Wood



George Wagner

