

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 dichlorogermane 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) siladigermirane." (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, germynes 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 $\text{Mes}_2\text{GeHOME}$, 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 cyclotri-germane 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 germynes would react in much the same way as silylenes: rapidly with Et_3SiH . 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 Et_3SiH , 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. $\text{Mes}_2\text{GeH}(\text{SiEt}_3)$ 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 ^{29}Si 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 $-70\text{ }^\circ\text{C}$ 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 ^{29}Si nmr spectrum of the photolysis solution at $-70\text{ }^\circ\text{C}$. 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 ^{29}Si 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.

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