

## 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.<sup>1</sup> 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 15<sup>th</sup> Organosilicon Symposium in Durham NC, the first stable Si=C and Si=Si compounds were announced and displayed, in back-to-back papers.<sup>2,3</sup> These discoveries, together with the nearly simultaneous publication of a P=P compound by Yoshifuji,<sup>4</sup> 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.<sup>5</sup>

The events leading up to the discovery of disilenes have been recounted in an earlier review.<sup>6</sup> 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 Me<sub>2</sub>XSi-SiXMe<sub>2</sub> compounds, but these experiments failed dismally. He

then turned his attention to organosilylenes, R<sub>2</sub>Si:. 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)<sup>7</sup>, making possible the first



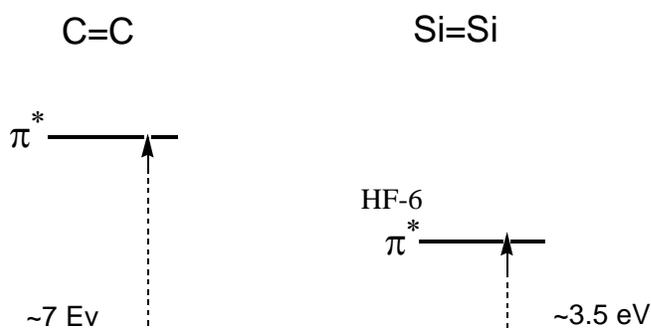
spectroscopic investigation of this important intermediate.<sup>8</sup> Soon, we found that organosilylenes could also be isolated in a hydrocarbon matrix at liquid nitrogen temperature, making them much easier to generate.<sup>9</sup>

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).<sup>10</sup>



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.<sup>11</sup>

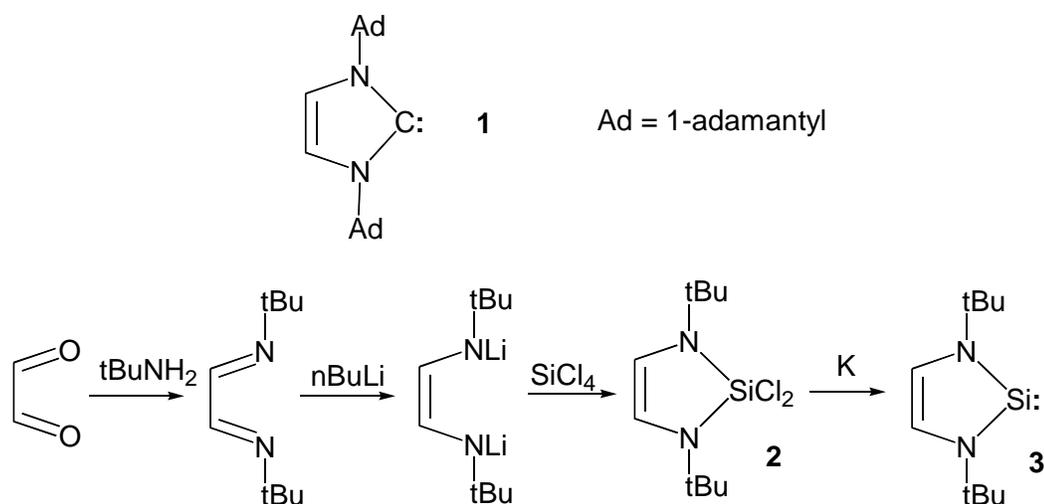
Disilenes are yellow to red, brightly colored solids. Their color results from the  $\pi-\pi^*$  excitation of the electrons in the Si=Si double bond. Compared with alkenes, the Si=Si double bond HOMO lies at higher energy and the LUMO at lower energy, making the transition energy only about half that 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.<sup>11</sup>



Disilenes are dimers of silylenes,  $R_2Si_2$ , 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**.<sup>12</sup> 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.<sup>13,14</sup>

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.<sup>14</sup> 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**.<sup>15</sup>

The stable silylenes react as nucleophiles, and like the disilenes, provide ways of synthesizing many new kinds of silicon compounds.<sup>16</sup> 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.<sup>14,17</sup> 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.<sup>16,18</sup> 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.

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