

Disilenes: Synthesis, Structure and Reactivity

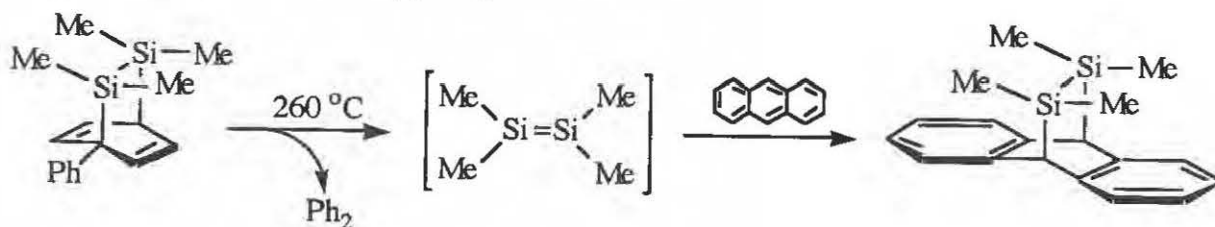
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Early reports of unsaturated disilicon species were incorrect, as proposed species with the formula R_2Si were shown to consist of cyclic oligomers [1]. The nonoccurrence of disilene compounds was explained in terms of the 'double bond rule', which suggested that multiple bonds between elements of the second or third row were inherently unstable due to the large radii of the elements, and the resultant poor $p\pi$ - $p\pi$ overlap [2].

Solid evidence for the existence of transient disilenes began to emerge in the 1970's. For example, in 1972, Roark and Peddle showed that cothermolysis of anthracene and a disilabicyclooctadiene afforded the 9,10-adduct of anthracene [3]. It was proposed that this reaction proceeded via retro-Diels-Alder fragmentation to form a transient disilene, $Me_2Si=SiMe_2$, which was trapped by anthracene.



Studies of photolytically produced silylenes, R_2Si , led to the discovery of the first isolable disilene, tetramesityldisilene (mesityl = 2,4,6-trimethylphenyl) [4]. The bulky mesityl substituents blocked polymerization to oligosilanes.

Since the discovery of kinetically stabilized disilenes, several methods of synthesis have been reported with the isolation of stable species dependent on the steric bulk of the substituents. These methods include photolysis of linear and cyclic trisilanes [4,5], controlled-potential electrolysis of $R_4Si_2Cl_2$ [6], ultrasound promoted dehalogenation of $R_4Si_2Cl_2$ with lithium metal [6], reductive coupling of R_2SiCl_2 with lithium naphthalenide [7] and photo-induced retro-Diels-Alder reactions [8].

The availability of thermally stable disilenes has permitted detailed studies of the physical properties of the silicon-silicon double bond. The X-ray crystal structures of several disilenes place the average silicon-silicon double bond distance between 2.14 and 2.16 Å, approximately 0.20 Å shorter than the average silicon-silicon single bond distance [9]. For comparison, the decrease in bond length from alkanes to alkenes is about 0.18 Å. For many disilenes, deviations from strict planar geometry about the silicon-silicon bond is observed, due in part to steric effects. Ab initio calculations also suggest that $Si=Si$ bonds are flexible toward distortion [10]. Many of these compounds are thermochromic, which presumably results from flexibility in the molecular structure upon changing temperature.

Disilenes show absorption of light around 400 nm. The energy of this π to π^* transition is about half that of the corresponding alkenes. Also, cyclic voltammetry of disilenes shows that oxidation occurs at less positive potentials and reduction at less negative potentials than similarly substituted alkenes [11]. The $Si=Si$ double bond has been shown to be highly anisotropic and ^{29}Si NMR measurements show that silicon atoms in disilenes are deshielded by about 80 ppm vs. disilanes [12]. This follows the trend observed for alkenes vs. alkanes. Furthermore, studies of unsymmetrically substituted disilenes show that the Si-Si coupling constants (about 155 Hz) are much larger than typical silanes (about 85 Hz) [13]. This increase is consistent with greater s character in the $Si=Si$ interaction.

The reaction chemistry of disilenes is extensive despite their steric bulk. Reactions with hydrogen halides, halogens, and alcohols result in 1,2-addition. Aldehydes, ketones, and some terminal alkynes react to give [2+2] cycloaddition products [14]. Reactions leading to 3,4, and 5+ membered ring systems are observed with a variety of reagents [15].

Of recent interest are reactions producing three-membered heterocyclopropane-like structures, including η^2 -transition metal complexes. Disilenes react with elemental sulfur, selenium, and tellurium to produce three-membered Si_2E rings and with N_2O to produce Si_2O rings. Interestingly, the Si-Si distance in these compounds increases from 2.23 Å to 2.34 Å, in proceeding from oxygen to tellurium. Only the latter contains a Si-Si bond which approaches that of a typical silane, 2.35 Å. Furthermore, the Si_2R_4 fragment remains nearly planar as observed by the sum of the angles around the silicon atoms. This information suggests the possibility of residual multiple bonding between the silicon atoms. This view is further supported by Si-Si one bond coupling constants of 99 Hz for unsymmetrically substituted oxadisiliranes [16].

In 1986, the first evidence for metal complexes of η^2 -disilenes was reported [17]. Although thermally unstable, these mercury(II) trifluoroacetate complexes exhibited spectroscopic properties consistent with HgSi_2 rings. Stable η^2 -disilene platinum complexes have been prepared by addition of Pt(0) sources to R_4Si_2 and by elimination of dihydrogen from $\text{R}_2(\text{H})\text{Si}-\text{Si}(\text{H})\text{R}_2$ [18]. Elimination of halides from $\text{R}_2(\text{X})\text{Si}-\text{Si}(\text{X})\text{R}_2$ has been applied to the synthesis of η^2 -disilene complexes of tungsten and molybdenum which have been characterized structurally by X-ray crystallography [19].

In little over a decade, disilenes have evolved from transient intermediates to isolable, characterizable compounds with extensive reaction chemistry [20].

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