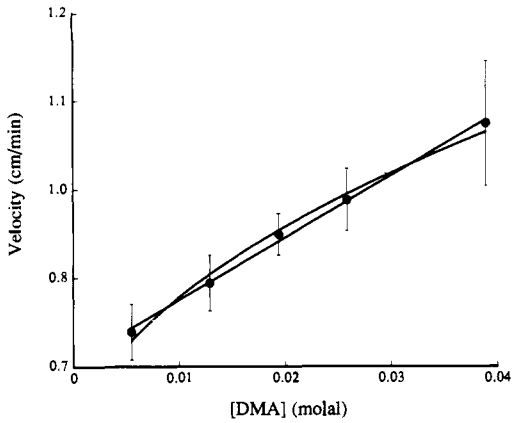

Figure 4. The front velocity as a function of the concentration of the promoter *N,N*-dimethylaniline (DMA) at a fixed initiator concentration, [benzoyl peroxide] = 0.041 *m*. The data were fit with a least-squares program to both a first-order (velocity = k_1[DMA] + constant) and a half-order dependence (velocity = k_2[DMA]$^{1/2}$ + constant). Higher concentrations of DMA were not possible because polymerization of the entire solution occurred at room temperature.

tration of initiator. It is not clear whether the front has first-order or half-order dependence on the promoter concentration. The advantage of a promoter is that it allows control over the front velocity without affecting the molecular weight distribution. However, if too much promoter is added, the entire solution polymerizes at room temperature.

Large density gradients are induced in the polymerizing solution by changes in chemical composition and temperature. Such gradients are known to cause free convection, which affects the traveling fronts.[20-22] Work will be forthcoming on convection and polymerization fronts.

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Direct Observation of an Azetidinium Imide Intermediate in $[\pi^2 + \sigma^2]$ Addition of 1,2,4-Triazoline-3,5-dione to Disilirane

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The interaction between σ-electron donor and π-electron acceptor has attracted continuing interest.[1,2] Cyclopropanes react with tetracyanoethylene to produce $[\pi^2 + \sigma^2]$ cycloaddition or ene reaction products, in which either diradicals or zwitterions have been postulated.[1c,d] However, no direct observation of the intermediate has been achieved. Our recent results that singlet oxygen inserts into the strained silicon-silicon σ bonds[3] in disilirane

Scheme I

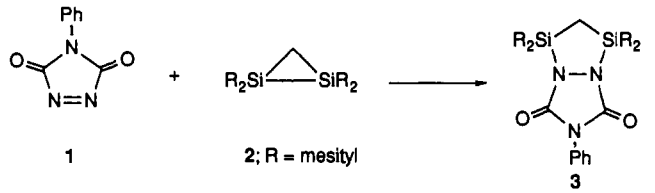


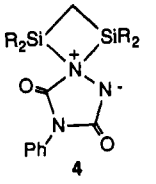
Table I. Coupling Constants (J^{13}_{C-1H} (Hz)) at the Methylene Carbons in 4 and Related Compounds

compd	^{13}C NMR (ppm)	$J_{^{13}C-^1H}$ (Hz)
2	4.05	137.65
5	21.40	128.60
4	5.81	127.18
6	17.50	124.50
3	8.24	119.67

derivatives, via peroxonium ion intermediates,[4] prompted us to investigate the reaction of disiliranes with 4-substituted 1,2,4-triazoline-3,5-dione (TAD). Recently, the aziridinium imide and azomethinimine intermediates in TAD addition to C=C π bonds[5] and C=N π bonds[6] have been characterized by NMR spectroscopy. We report here the first spectroscopic observation of an intermediate in $[\pi^2 + \sigma^2]$ addition of TAD to disilirane and assign its structure as an azetidinium imide.

When 4-phenyl-1,2,4-triazoline-3,5-dione (**1**) was added to a $CHCl_3$ solution of 1,1,2,2-tetramesityldisilirane (**2**)[4a] at room temperature in the dark, the red color of **1** rapidly disappeared. The crude reaction mixture was subjected to preparative HPLC, and recrystallization from hexane gave the corresponding adduct **3**[7] as a colorless crystal in 38% yield (69% yield by ^{1}H NMR). The spectra data are consistent with the 1,2,3,5-diazadisilolidine structure (Scheme I).

The analogy between the reactivity of $^1O_2$ and that of TAD suggests the intermediacy of an azetidinium imide **4**. Addition



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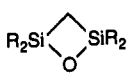

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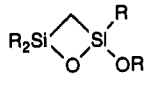

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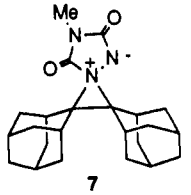

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of **1** to **2** was monitored by low-temperature ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy in deuteriochloroform. After standing at room temperature for 60 s, a mixture of disilirane **2** and 1.2 equiv of **1** in a Pyrex NMR tube was rapidly cooled down to -78 °C, and the spectra were recorded at -55 °C. A series of new resonances in the ^{13}C NMR spectrum appeared at δ 157.29 (s), 150.70 (s),

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(7) **3**: mp 293-295 °C; IR (CCl_4) 1746, 1690 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.44 (m, 5 H), 6.78 (s, 8 H), 2.31 (12 H, s), 2.12 (s, 24 H), 1.70 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.65 (s), 143.22 (s), 140.22 (s), 130.92 (s), 129.50 (d), 129.09 (d), 128.30 (s), 128.25 (d), 125.98 (d), 23.67 (q), 21.26 (q), 8.26 (t); ^{29}Si NMR (78 MHz, $CDCl_3$) δ -12.87; exact mass calcd for $C_{45}H_{51}N_3O_2Si_2$ 721.3515, found 721.3518.

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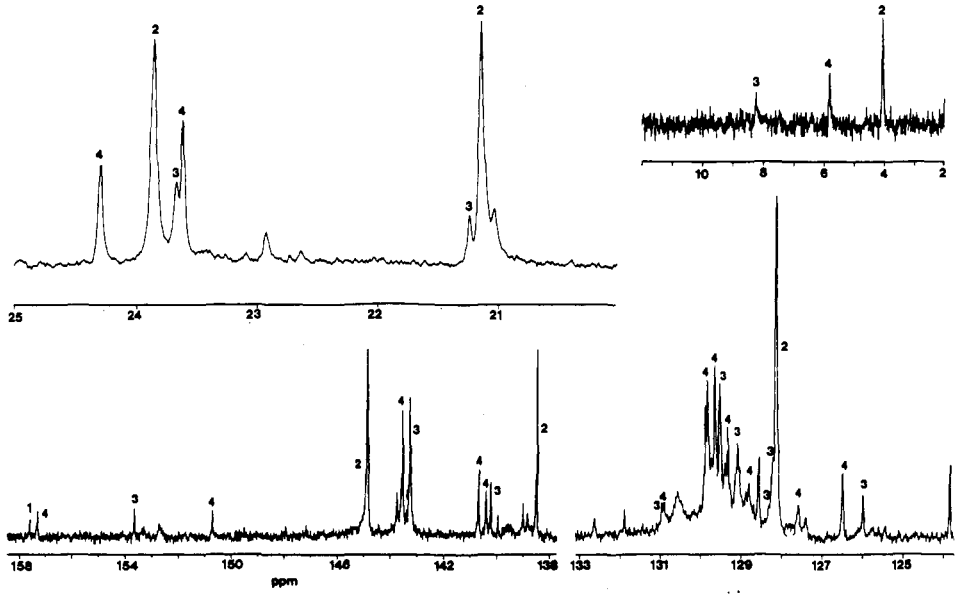

Figure 1. ^{13}C NMR spectrum (125 MHz) at −55 °C in $CDCl_3$, after mixing of **1** with **2** at 25 °C for 60 s.

143.53 (s), 140.68 (s), 140.39 (s), 130.91 (s), 129.81 (d), 129.63 (d), 129.32 (d), 128.79 (s), 127.58 (d), 126.48 (d), 24.30 (q), 23.61 (q), and 5.81 (t) together with those of **2** and **3** (Figure 1). The ratio of these species was approximately 7:4:2 for **2**, the intermediate, and **3**, respectively, by comparison of the peak heights of the methylene carbons in the spectrum. The ^1H NMR spectrum, however, showed a complex multiplet, and only one resonance assignable for a methyl group of the intermediate was observed, at δ 2.03. These new peaks gradually decreased at −55 °C with a concomitant increase of those of **3**. Warming up to −30 °C resulted in their complete disappearance within 20 min. Meanwhile, disilirane **2** did not react with **1** at temperatures below −20 °C. The appearance of two carbonyl carbon resonances at δ 157.29 and 150.70 suggested the unsymmetrical structure of the TAD moiety. The nonequivalence of the methylene hydrogens and the mesityl groups might be indicative of a cyclic structure of the intermediate. There should be four methyl groups, and all the mesitylene ring carbons should be doubled. The H,C COSY[8] and H,H COSY NMR measurements unfortunately gave unclear results for the existence of two differing methylene hydrogens. Although two resonances are missed due to the overlapping, 10 aromatic (mesityl and phenyl) ring carbon resonances appeared. In the ^{13}C DEPT NMR spectrum of the intermediate, besides the two methyl signals at δ 24.30 and 23.61, one more resonance at δ 21.13[9] was assigned to the intermediate (Figure 2). These spectroscopic features support the nonequivalence. The ^{13}C–^1H coupled spectrum shows a 127.18-Hz coupling constant for the hydrogen attached to the methylene carbon. The value lies between those obtained for **5**[4a] and **6**,[4a] implying the existence of a four-membered (Table I). In the ^{29}Si NMR spectrum a new signal at δ 3.05, assigned for the intermediate, was observed, together with those of **2** and **3**. Furthermore, FT-IR monitoring of the reaction mixture at room temperature confirmed the presence of a thermally labile intermediate, which exhibited two carbonyl absorption bands, at 1777 and 1669 cm^{-1}. These absorptions are consistent with those of the aziridinium imide **7** (1790 and 1670 cm^{-1}) reported by Nelsen and Kapp.[5a] These NMR and IR data reveal that azetidinium imide structure **4**[10,11] best

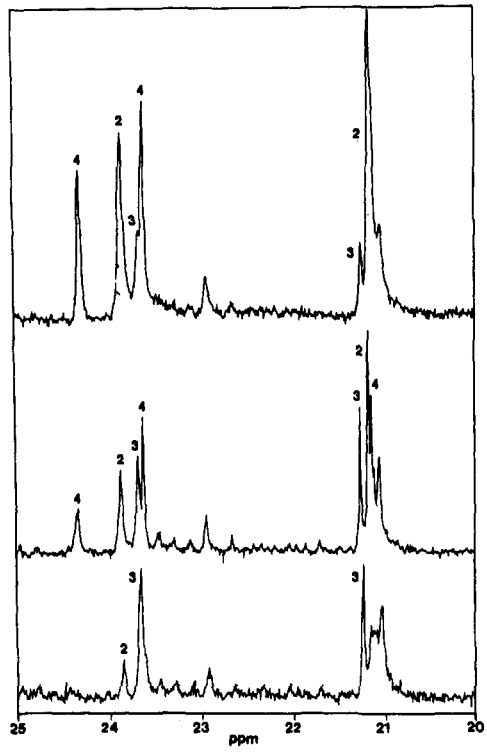

Figure 2. ^{13}C DEPT NMR spectrum (125 MHz) at −55 °C in $CDCl_3$. Top: After mixing of **1** with **2** at 25 °C for 60 s. Middle: After mixing of **1** with **2** at 25 °C for 120 s. Bottom: After warming up to 25 °C and standing for 5 min.

represents the structure for the intermediate, which cyclizes to **3** as in the case of singlet oxygenation of **2**.[4,12]

(8) In the H,C COSY spectrum of the intermediate, the methylene carbon resonance at δ 5.81 showed the cross peak to the weak broad proton resonance at δ 1.85–1.95.

(9) The fourth peak assigned to the intermediate is still missed due to overlapping by those of **2** and **3**.

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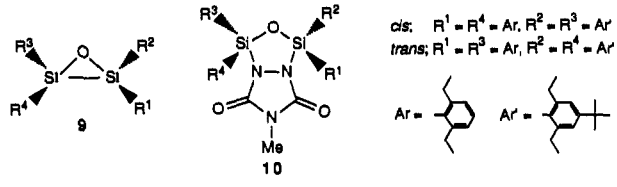
(11) The intermediacy of a cyclic adduct (**4**) might be supported also by the observation that stereospecific cycloadditions of 4-methyl-1,2,4-triazoline-3,5-dione (**8**) to two stereoisomeric **9** affording **10** took place. The details of the stereochemical study on the cycloaddition of **8** to **9** will be published elsewhere.



Acknowledgment. This work was supported by the Ministry of Education, Science and Culture in Japan and in part by a grant from ICI Japan Technical Centre.

Supplementary Material Available: ^1H and ^{13}C NMR spectra of **2** and **3** and ^1H, ^{13}C, and ^{29}Si NMR, H,C COSY NMR, and FT-IR spectra of the intermediate **4** (9 pages). Ordering information is given on any current masthead page.

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X-ray Absorption Spectroscopic Study of the Reductive Activation of *Thiocapsa roseopersicina* Hydrogenase

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Hydrogenases (H_2ases) are enzymes that catalyze the reversible oxidation of H_2.[1,2] In addition to containing Fe,S clusters, the majority of H_2ases also contain a Ni complex[3] that is redox-active[4] and involves S-donor ligands.[5] The H_2ase isolated from the purple photosynthetic bacterium *Thiocapsa roseopersicina* is a typical Fe,Ni H_2ase.[6] The presence of Ni in Fe,Ni H_2ases is often revealed by $S = {}^1/_2$ EPR signals in the oxidized and catalytically inactive forms of the enzyme (forms A and B), as well as in a reduced and active form (form C).[4,6b] These signals have been assigned to formally Ni(III) and/or Ni(I) centers because of the similarity of the EPR spectra to those of Ni(III) and Ni(I) coordination complexes[4a,b] and the observation of ^{61}Ni hyperfine interactions in spectra obtained from isotopically labeled preparations.[4a,b] These EPR signals have provided the principal spectroscopic probe of the Ni site and have been used to demonstrate the redox activity of the site,[4] the binding of CO (a competitive inhibitor) to Ni,[7] and the interaction of the site with H_2.[8] We report here the results of the first X-ray spectroscopic study of the structural changes in the Ni site accompanying reductive activation of a H_2ase. These studies reveal that the reductive activation of the enzyme is not accompanied by a change in the charge on the Ni or by a major reorganization of the Ni ligand environment.

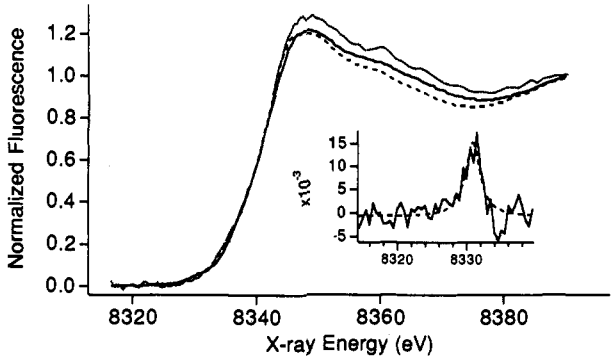

Figure 1. Ni K-edge spectra of *T. roseopersicina* hydrogenase poised in forms A (dashed line), B (solid line), and C (dotted line). Insert: The base line corrected 1s → 3d transition observed for form B (solid line) and a Lorentzian fit (dashed line).

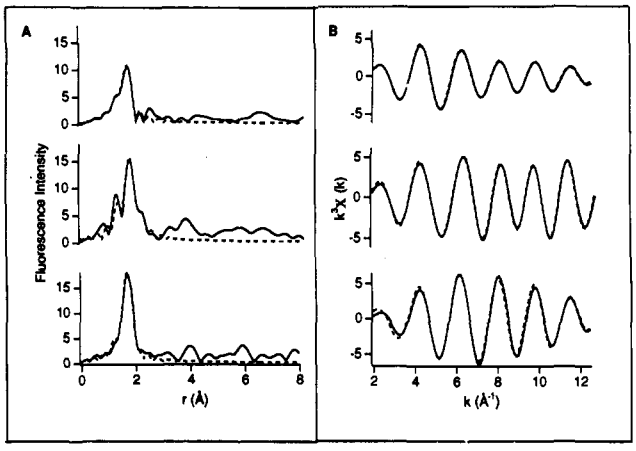

Figure 2. Ni K-edge EXAFS spectra obtained from *T. roseopersicina* hydrogenase poised in forms A (top), B (middle), and C (bottom). (A) Fourier transformed EXAFS spectra (uncorrected for phase shift, solid lines) and first coordination sphere fits (dashed lines). (B) Fourier filtered first coordination sphere EXAFS spectra (back-transform window = 1.1-2.3 Å, solid lines) and fits (dashed lines). Fits shown: Form A, (3) Ni-N 1.99 Å, $(10^3)\Delta\sigma^2 = 11.8$ Å^2; (2) Ni-S 2.20 Å, $(10^3)\Delta\sigma^2 = 0.2$ Å^2; (1) Ni-S 2.40 Å, $(10^3)\Delta\sigma^2 = 2.5$ Å^2, $R = 0.10$. Form B, (2) Ni-N 1.93 Å, $(10^3)\Delta\sigma^2 = -2.7$ Å^2; (3) Ni-S 2.24 Å, $(10^3)\Delta\sigma^2 = -1.3$ Å^2; (1) Ni-S 2.50 Å, $(10^3)\Delta\sigma^2 = -2.9$ Å^2, $R = 0.24$. Form C, (3) N 2.06 Å, $(10^3)\Delta\sigma^2 = -6.4$ Å^2; (2) Ni-S 2.21 Å, $(10^3)\Delta\sigma^2 = 1.6$ Å^2, $R = 0.34$.

T. roseopersicina was cultured and the H_2ase isolated and assayed as previously described.[5b,9] The enzyme was poised in forms A and B by using a minor modification of the procedure described by van der Zwaan et al.[7] X-ray absorption spectra were obtained on frozen solutions (77 K) prepared in 20 mM Tris·HCl (pH 8) buffer containing 20% glycerol that had Ni concentrations of 0.8 mM. X-ray fluorescence data were collected at beam line X9A at the National Synchrotron Light Source (2.53 GeV, ca. 110-200 mA) employing a monochromator and Si[111] crystals (resolution ca. 1 eV) and a 13-element Ge X-ray fluorescence detector. Energy calibrations were performed by using Ni foil

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