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Communication

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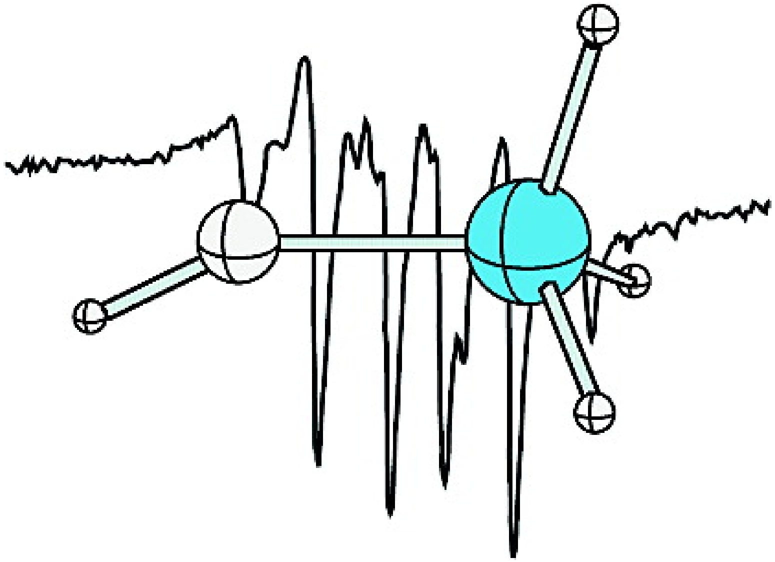

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COMMUNICATIONS

$H-C-SiH_3$: Direct Generation and Spectroscopic Identification of Ethylidene's Cousin

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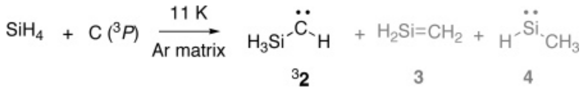
Ethylidene (**1**, $H-C-CH_3$, methylcarbene) has thus far escaped direct spectroscopic identification because the barrier for the C−H shift to ethylene is very small ($\Delta H^{\ddagger} = 1-2$ kcal mol^{-1}).[1] The photochemical or thermal generation of **1** from diazoethane or diazirine invariably gives the singlet state, although the triplet is the electronic ground state ($\Delta E_{ST} = 4-5$ kcal mol^{-1}).[2] As the rate for intersystem crossing is expected to be smaller than the rate for the H-shift, the triplet state seems virtually inaccessible by the common carbene preparation routes.[3] The existence of singlet ethylidene as a diazo decomposition product has been inferred by trapping **1** with CO to give methylketene in CO-containing matrices at 10 K[4] or perdeuterated **1** (deuteration decreases the rate of rearrangement) with pyridine to yield ethylidene-d_4-pyridine ylide (in several aprotic solvents).[5]

The present communication reports the direct generation as well as spectroscopic and computational characterization of the silicon-substituted analogue of **1**, namely, silaethylidene $H-C-SiH_3$ (**2**) in its triplet ground state (^{3}**2**). Structure **2** can also be viewed as a small, monosubstituted methylene derivative, for which condensed phase infrared spectra are virtually nonexistent.[6,7]

Our novel strategy for the preparation of ^{3}**2** avoids the decomposition of diazo or other precursors. Instead, we generate ^{3}**2** directly through the reaction of ground-state triplet carbon atoms with SiH_4 (Scheme 1). The carbon atoms are prepared by laser ablation of a rotating graphite disk in a closed-cycle helium refrigerator system. Matrix samples were prepared by co-deposition of the products of the laser ablated graphite plume with an SiH_4/Ar gas mixture on the surface of a cold window (10−12 K); complete experimental details are described elsewhere.[8] The analogous preparation of ^{3}**2** through the reaction of silicon atoms with methane does *not* give ^{3}**2** through photochemical rearrangement of triplet silaethylene ^{3}**3** because the triplet surface is energetically inaccessible;[9] much more stable silylene **4** is formed instead.

Scheme 1



The EPR spectrum clearly identifies **2** as a triplet (Figure 1). The zero-field splitting parameters, *E* and *D*, are 0.0 and 0.632 cm^{-1}, respectively; a hyperfine structure is observable [$A_{\alpha\perp} = 2.38$ mT and $A_{\beta\perp} = 1.38$ mT]. These data are consistent with a (time-averaged, vide infra) quasi-linear $H-C-Si$ moiety, in agreement with earlier findings on $H-Si(CH_3)_3$ and $H-SiH(CH_3)_2$.[10] The sizable *D* value indicates that the spin is localized on one center, as expected for a triplet carbene. Owing to the much reduced hyperfine deuterium coupling, the spectrum of the perdeuterated isotopolog is not resolved.

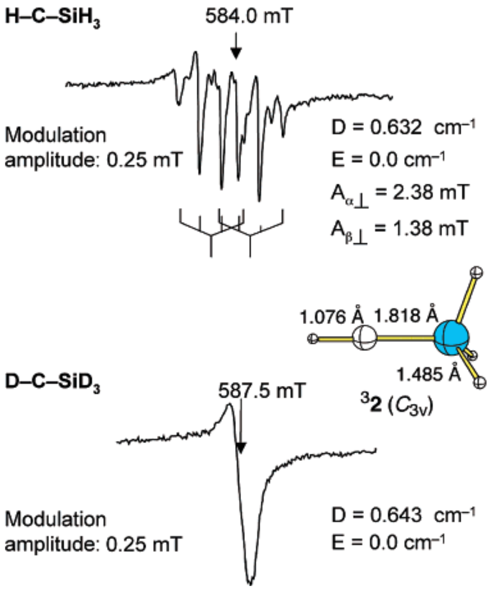
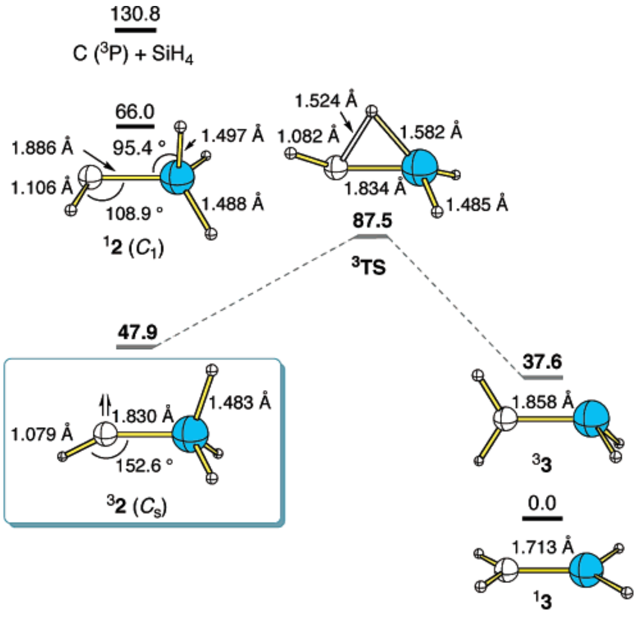


Figure 1. EPR spectrum (*x*-band, 9.44 GHz, xy_2-line) of **2** and its perdeuterated isotopolog (bottom) at 11 K. A full overview ESR spectrum is given in the Supporting Information.

Scheme 2. Complete Basis Set CCSD(T) Relative Energetics (kcal mol^{-1}) on the $HCSiH_3$ PES



To characterize ^{3}**2** further, we optimized all species in Scheme 2 using high-level coupled-cluster theory [CCSD(T)][11] with a high-quality cc-pVTZ basis set.[12] Focal-point (fp) extrapolations[13] to the

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Table 1. Comparison of Theoretical [CCSD(T)/cc-pVTZ], Harmonic (ω), and Fundamental (ν) Vibrational Frequencies (in cm^{-1}) to Experimental Bands (Ar matrix, 11 K) for ^{3}**2** (C_{3v} and C_s) and Its Perdeuterated Isotopolog. Relative IR Absorption Intensities (I_{rel}) Are Included from MP2/cc-pVTZ Computations (Overview IR Spectra Are Given in the Supporting Information)

description	ω (C_{3v})	ω (C_s) (I_{rel})	ν (C_s)	expt.
		$HCSiH_3$		
CH str. (a_1)	3298	3255 (0.01)	3142	
SiH_3 str. (a_1)	2235	2250 (0.41)	2177	
SiH_3 str. (e)	2232	2226 (0.53)	2139	2139.1
		2225 (0.31)	2138	
SiH_3 def. (a_1)	959	955 (1.00)	943	
SiH_3 def. (e)	958	958 (0.25)	938	929.1
		958 (0.24)	938	
SiC str. (a_1)	813	799 (0.13)	789	789.8
SiH_3 rock (e)	646	659 (0.21)	648	631.3
		645 (0.20)	634	
HCSi bend (e)	301i	395 (0.10)		
		118 (0.13)		
		$DCSiD_3$		
CD str. (a_1)	2436	2401 (0.05)	2341	
SiD_3 str. (e)	1612	1622 (0.61)	1577	
		1608 (0.65)	1563	1563.0
SiD_3 str. (a_1)	1590	1588 (0.31)	1552	
SiC str. (a_1)	796	786 (1.00)	777	784.8
SiD_3 def. (a_1)	689	683 (0.50)	676	
SiD_3 def. (e)	688	688 (0.31)	676	
		688 (0.29)	676	
SiD_3 rock (e)	486	509 (0.26)	504	
		492 (0.24)	487	472.4
DCSi bend (e)	230i	293 (0.10)		
		88 (0.14)		

complete basis set CCSD(T) limit then pinpointed the relevant energetics on the $HCSiH_3$ surface. While ^{3}**2** exhibits a C_s equilibrium structure with a H−C−Si angle of 152.6°, a C_{3v} transition state with a linear carbene moiety lies only 0.24 kcal mol^{-1} higher (fp limit). This barrier can be surmounted readily by zero-point vibrations. In addition to harmonic vibrational frequencies for ^{3}**2**(C_{3v}) and ^{3}**2**(C_s), C_{3v} anharmonicities were determined by applying second-order vibrational perturbation theory (VPT2)[14] to a CCSD(T)/cc-pVTZ complete quartic force field computed from a grid of 2062 tightly converged energy points. The final CCSD(T)/cc-pVTZ predictions [$\nu(C_s)$ in Table 1] for the vibrational spectrum of ^{3}**2** were obtained by appending the C_{3v} anharmonicities to the harmonic frequencies of the bent (C_s) structure. The agreement with the experimental IR fundamentals is remarkable, generally within 10 cm^{-1} and *without* any empirical scaling of the theoretical frequencies.

As there is apparently no energetically feasible path for rearrangement of the more stable **4** (Scheme 1 and Supporting Information) back to ^{3}**2**, the latter must form in the reaction of the carbon atoms with silane, and the Si−H shift barrier for rearrangement of ^{3}**2** to the triplet silene (^{3}**3**) must be large (Scheme 2). Indeed, the computed barrier for this unfavorable three center−three electron hydrogen shift is 39.6 kcal mol^{-1}, retarding the rearrangement to ^{3}**3** at the experimental conditions.

The computed ΔE_{ST} for **2** is 18.1 kcal mol^{-1} and thus about twice as large as that of methylene. Hence, the SiH_3 substituent preferentially stabilizes the triplet, while a methyl group (as in **1**) favors the singlet state.[2] The difference in stabilization energies, as derived from the differences in ΔE_{ST} of **2** versus **1**, amounts to about 15 kcal mol^{-1}. This highlights the triplet stabilizing power of electropositive elements attached to carbene centers, whereby σ-electron donation[15] outweighs singlet hyperconjugation. The latter is evident from the C_1 structure of ^{1}**2**, in which one Si−H bond is bent (∠C−Si−H = 95.4°) toward the empty p-orbital on carbon and is lengthened by 0.009 Å compared to the remaining Si−H bonds (Scheme 2).[7]

We have shown that triplet silaethylidene ^{3}**2**, which is indefinitely stable under low-temperature matrix isolation conditions, is accessible through the direct reaction of atomic ground-state triplet carbon atoms with silane. The structures and IR spectra of ^{3}**2** and its perdeuterated isotopolog were unequivocally assigned through matching of experimental and high-level computational data.

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Supporting Information Available: Experimental setup and spectra, tables of electronic total energies, Cartesian coordinates, and vibrational frequencies of all optimized species; internal coordinate quadratic force field of ^{3}**2** and analysis of the normal modes of vibration of the parent and deuterated isotopologs. This material is available free of charge via the Internet at http://pubs.acs.org.

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