Triple Bonds to Silicon. Substituent Effects on the Thermodynamic and Kinetic Stabilities of Silynes Relative to Their Isomeric Silylidenes and Silavinylidenes

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Summary: Substituent effects on the potential energy surface (PES) of RHSiC (R = H, CH_3, SiH_3, F, OH) were studied by ab initio molecular orbital methods. The unimolecular and kinetic stability of silaacetylenes is strongly dependent on the substituent, pointing to FSi≡CH and R′OSi≡CH as viable candidates for experimental observation.

The first stable compounds with double bonds to silicon were synthesized in 1981, and since then they have been studied extensively both experimentally[1] and theoretically.[2] In contrast, stable compounds containing triply-bonded silicon compounds are still unknown, except for HSi≡N which was characterized spectroscopically at 10 K.[3a,b] Evidence for the involvement of the "synthetic equivalent" on $CH_3Si{\equiv}SiCH_3$ was presented recently by West et al., but the existence of a Si≡Si bond could not be shown unequivocally.[4]

One of the major obstacles to the synthesis of triply-bonded silicon compounds even as transients results from the existence of more stable isomers, e.g., for Si_2H_2 the dibridged, monobridged, and $H_2Si{=}Si{:}$ isomers are more stable than HSi≡SiH.[5] This contrasts with C_2H_2 where acetylene is the global minimum, $H_2C{=}C{:}$ is by 43 kcal/mol higher in energy, and the H-bridged species are not minima on the potential energy surface (PES).[6]

For the parent H_2CSi, structures **1**−**4** (R = H) were studied computationally.[7−11] At the HF level only **3** (R = H) and **4** (R = H) are minima on the PES, but at correlated levels the *trans-bent*-silyne **2** (R = H) is also in a shallow minimum.[7d,9,10] The linear silyne **1** (R = H) is not a minimum on the PES.[7d,e,8−10] The global minimum is $H_2C{=}Si{:}$, being by 86.8 and 39.2 kcal/mol (at CCSD(T)/TZ2P(fd)[10]) more stable than **4** (R = H) and **2** (R = H), respectively. Relatively small barriers separate **4** (R = H) from **2** (R = H) (2.7 kcal/mol at CCSD(T)/TZ2P(fd))[10] and **2** (R = H) from **3** (R = H) (ca. 5.0 kcal/mol at QCISD(T)/6-311++G(3df,3dp)[9] and CCSD(T)/TZ2P(f,d)[10]), predicting that the half-life of HSi≡CH is ca. 10^{-8} s, suggesting that it might be observed spectroscopically.[9] However so far only $H_2C{=}Si{:}$ was detected.[11,12]

H−C≡Si−R

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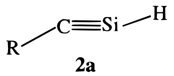

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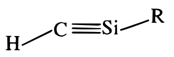

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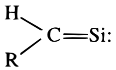

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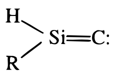

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Can substitution reverse the order of stability of **2** and **3** making the silaacetylene **2** the global minimum? Or alternatively, can substitution increase the barrier for the **2** → **3** interconversion, making silynes a viable synthetic target? To answer these questions we have calculated[13] at a highly correlated level the PES of several monosubstituted RHSiC systems **2**−**4**, with R = CH_3, SiH_3, F, and OH,[14] and *these calculations point to a possible strategy for the synthesis of persistent silynes.*

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[13] The calculations were carried out using the Gaussian 92 package of programs. Gaussian 92: Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Goperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN 92/DFT*, Revision G; Gaussian Inc.: Pittsburgh, 1992.

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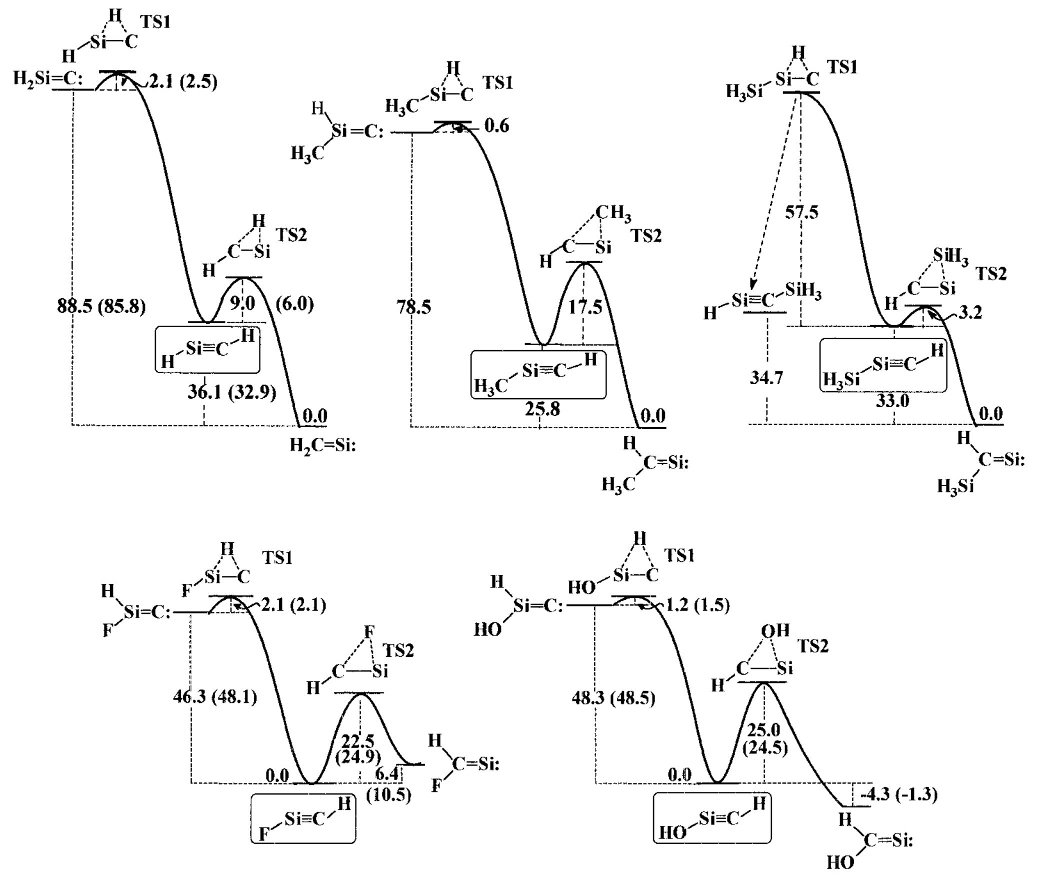

Figure 1. Potential energy surfaces for RHCSi, R = H, CH_3, SiH_3, F, and OH. Energies are in kcal/mol, calculated at MP4SDTQ/6-31G(d,p)//MP2/6-31G(d,p) + ZPE; the values in parentheses are at QCISD(T)/6-31G(d,p)//QCISD/6-31G(d,p) + ZPE (ZPE calculated numerically).

The geometries of all stationary points were fully optimized and characterized by their Hessian matrices at MP2/6-31G(d,p) and for R = F and OH also at QCISD/6-31G(d,p).[13] The optimized geometries of **2a**,**b**, **3**, and **4** and of the transition structures separating **2b** from **4** (TS1) and from **3** (TS2) for R = H, CH_3, SiH_3, OH, and F are given in Table 1 of the Supporting Information. Single point energies at these optimized geometries were calculated at MP4SDTQ/6-31G(d,p)//MP2/6-31G-(d,p) and at QCISD(T)/6-31G(d,p)//QCISD/6-31G(d,p) (Tables 2 and 3, Supporting Information).

The PES of H_2SiC was restudied in detail (including geometry optimizations at MP2/6-31G(2d,p), MP2/6-31G(2df,p), and MP2/6-311G(d,p)), and the results (Table 4, Supporting Information) indicate that addition of a second set of d or f polarization functions or further splitting of the valence shell all have a minor effect on the relative energies of the **2**−**4** (R = H) isomers and on the barriers for their interconversion. The reasonably good agreement between the experimental[11] and the calculated harmonic vibrational frequencies[15] of $H_2C{=}Si$: (Table 5, Supporting Information) lends confidence in the reliability of the computational methods that are used in this study.

The calculated PES for RHCSi, R = H, CH_3, SiH_3, F, and OH, at MP4SDTQ/6-31G(d,p)//MP2/6-31G(d,p) and at QCISD(T)/6-31G(d,p)//QCISD/6-31G(d,p) are shown in Figure 1.[16,17] The "classical" linear silynes **1** are not minima on the PES for all systems. Their two imaginary frequencies lead to the corresponding *trans-bent*-silyne minima, whose energies relative to the other isomers change significantly with substitution.

Silyl has a very small effect on the relative stabilities of the RHSiC isomers: **3** remains the global minimum, and the silynes **2a**,**b** are by 34.7 and 33.0 kcal/mol less stable than the corresponding silylidene. A methyl causes a somewhat larger effect, but the silylidene **3** is still by 28.6 and 25.8 kcal/mol more stable than **2a**,**b**, respectively. However, the kinetic stability of **2b** is quite strongly affected by these substituents. Thus, for R = CH_3 the barrier for the **2b** → **3** isomerization increases by 8.5 kcal/mol (relative to R = H) to 17.5 kcal/mol, making $CH_3Si{\equiv}CH$ *relatively stable kinetically if it were produced*. On the other hand, for R = SiH_3, the **2b** → **3** barrier decreases to only 3.2 kcal/mol and the data in Figure 1 suggest that at higher computational levels it will be smaller or will even disappear, questioning the possible existence of **2b**, R = SiH_3. In contrast, the effect of F and OH on the relative stabilities of $RSi{\equiv}CH$ (**2b**) and $RHC{=}Si$: (**3**) is very large. F actually *reverses the stability order* and $FSi{\equiv}CH$ (**2b**) *is the global minimum* on the PES, being by 6.4 kcal/mol (10.5

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(14) For previous lower level HF studies on the effect of substituents on RR′SiC: see the following. (a) For Li, Me, and F at HF/6-31G*//3-21G (stationary points were not characterized), see ref 7c. (b) For $CSiF_2$ at HF/6-31G*//3-21G, see ref 7b.

(15) The best experimental−theoretical agreement is obtained using the MP2/6-31G(2df,p) optimized geometries. However as the relative energies of **2**−**4** (R = H) are hardly affected by increasing the basis set, we assume that MP4SDTQ/6-31G(d,p)//MP2/6-31G(d,p) calculations can be used for estimating reliably the relative energies of the various stationary points on the RHSiC PES.

(16) Relative energies in the text are given at the MP4SDTQ/6-31G**//MP2/6-31G** + ZPE level unless otherwise stated.

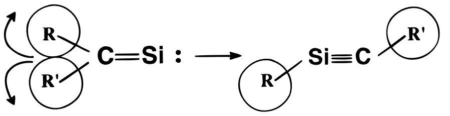
(17) For all systems the effect of entropy on the relative energies of the isomers is very small, and Δ*G* is therefore very similar to the relative energies given in Figure 1.

kcal/mol at QCISD(T)/6-31G**//QCISD/6-31G** + ZPE) more stable than HFC=Si:! For R = OH, **3** is still more stable than **2b**, but by *only 4.3 kcal/mol* (1.3 kcal/mol at QCISD(T)/6-31G**//QCISD/6-31G** + ZPE). These large effects are best understood in terms of the R−Si vs R−C bond energies, where the very strong Si−F and Si−O bonds (bond dissociation energies: Si−F = 152 kcal/mol, Si−O = 129 kcal/mol,[18] C−F = 110 kcal/mol, C−O = 92.2[19]) override the large intrinsic preference of $H_2C{=}Si$: over $HSi{\equiv}CH$. The strong Si−F and Si−O bonds also dictate the higher stability of $RSi{\equiv}CH$ relative to $HSi{\equiv}CR$ (by 33.4 and 23.4 kcal/mol for R = F and OH, respectively).

F and OH substitution also dramatically stabilizes *kinetically* the silynes **2b**. Thus, the barrier for the isomerization of **2b** to **3** (Figure 1) increases from only 9.0 kcal/mol for R = H to 22.5 and 25.0 kcal/mol for R = F and OH respectively (24.9 and 24.5 kcal/mol, respectively, at QCISD(T)/6-31G(d,p)//QCISD/6-31G(d,p) + ZPE). Consequently we predict that if $FSi{\equiv}CH$, and $HOSi{\equiv}CH$ will be generated (e.g., in a matrix), their rearrangement to the corresponding $RHC{=}Si$: isomers will be slow even at relatively high temperatures.[20] The same should apply to systems such as $FSi{\equiv}CR$ or $R''OSi{\equiv}CR'$, where R, R′, or R″ = alkyl or aryl.

The calculated $Si{\equiv}C$ bond lengths of $RSi{\equiv}CH$ (**2b**) are 1.632 Å (R = H), 1.651 Å (R = F), and 1.658 Å (R = OH) at MP2/6-31G(d,p) and 1.673 Å (R = H), 1.692 Å (R = F), and 1.685 Å (R = OH) at QCISD/6-31G(d,p).[21] These distances are significantly shorter than r(Si=C) in the corresponding $RHSi{=}CH_2$, i.e., 1.714 Å (R = H), 1.695 Å (R = F), and 1.700 Å (R=OH) at MP2/6-31G(d,p) (although they are longer than those calculated for the corresponding linear silynes **1** of 1.609, 1.586, and 1.590 Å, respectively (MP2/6-31G(d,p))), indicating the presence of a $Si{\equiv}C$ bond. The calculated $Si{\equiv}C$ harmonic stretching frequencies of **2b** (Table 6 of the Supporting Information), which are 1224 cm^{-1} (R = H), 1218 cm^{-1} (R = F), and 1200 cm^{-1} (R = OH) (1012, 1082, and 1068 cm^{-1} for the corresponding silenes, respectively), and the natural resonance theory (NRT)[22a] and Wiberg's[22b] bond orders (in natural atomic orbital basis) also support the presence of a $Si{\equiv}C$ triple bond in **2b**; i.e., for trans-bent $HSi{\equiv}CH$, $FSi{\equiv}CH$, and $HOSi{\equiv}CH$ the NRT and Wiberg's (in parentheses) bond orders are 2.93 (2.51), 2.80 (2.39), and 2.76 (2.33),[22c] respectively (very similar values were calculated for the corresponding linear **1**), compared to 2.01 (1.65), 1.93 (1.54), and 1.90 (1.52) in the corresponding silenes.

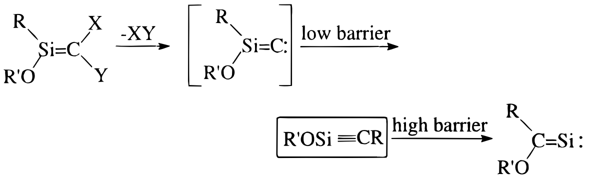
Bulky substituents are expected to destabilize $RR'C{=}Si$: relative to $RSi{\equiv}CR'$ as shown schematically in eq 1. In addition, the presence of very bulky substituents at both ends of the silyne may protect the triple bond from intermolecular reactions such as dimerization. How large are such steric effects?



(1)

Calculations (using BLYP/6-31G(d,p)//BLYP/6-31G(d,p)) of the (**2**−**3**) energy difference (ΔE) show that ΔE is reduced from 21.2 kcal/mol for R = R′ = Me to 13.9 kcal/mol for R = R′ = *t*-Bu. The effect of R = OMe, R′ = *t*-Bu is much smaller; ΔE is reduced by only 1.3 kcal/mol relative to R = OMe, R′ = Me. However, the initial ΔE for $HC{\equiv}SiOH$ is small (Figure 1). Bulkier substituents such as *t*-Bu$(CH_3)_2C$ and 2,4,6-tri-*tert*-butylphenyl or 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl][23,24] will reduce ΔE further and may even reverse the stability order making alkoxy-, alkyl- or arylsilynes with bulky substituents attractive candidates for detection and isolation.

A possible promising strategy, suggested by the calculations for the synthesis of a relatively stable alkoxysilyne, is based on the high energy of the alkoxysilavinylidene (**4**, R = R′ = H) and the low barrier for its rearrangement,[20b] suggesting that if a silavinylidene is generated (photochemically or thermally), it would rearrange spontaneously to the more stable silyne which should survive (e.g., in a matrix) as it is separated by a significant barrier from further rearrangements (eq 2).



(2)

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Supporting Information Available: Tables 1−6, listing optimized geometrical parameters of the stationary points on the RHSiC PES, absolute energies for stationary points on the RHSiC PES, relative energies of stationary points on the PES of RHCSi, relative energies of H_2SiC isomers and the barriers for their interconversion, calculated harmonic and experimental fundamental vibrational frequencies of $H_2C{=}Si$:, and harmonic vibrational frequencies for RSiCH and $RHC{=}Si$: (at MP2/6-31G(d,p)) (10 pages). Ordering information is given on any current masthead page.

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[20] (a) H-rearrangements converting $RSi{\equiv}CH$ to $HRSi{=}C$: have very high barriers (ca. 50 kcal/mol), and therefore they are not viable disappearance channels for the silynes (Figure 1). (b) $FHSi{=}C$: and $(HO)HSi{=}C$: are predicted to rearrange rapidly to $FSi{\equiv}CH$ and $HOSi{\equiv}CH$, respectively (Figure 1).

[21] The longer bond lengths calculated at QCISD/6-31G(d,p) reflect the contribution of biradical configurations to the wavefunction. On the basis of the best available calculations for **2** (R = H) (at CCSD(T)/TZ2P), it was recently suggested[10] that the correct $Si{\equiv}C$ bond length is 1.65−1.66 Å, a value which is intermediate between our MP2 and QCISD values.

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[23] For R = R′ = Ph, Δ is relatively high (18.9 kcal/mol) because the phenyl rings in **3** can rotate to minimize their steric interactions. However, bulky ortho-substituents may change this situation.

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