The quest for a stable silyne, RSi≡CR′. The effect of bulky substituents [1]

Miriam Karni & Yitzhak Apeloig[1]

Department of Chemistry and the Lise Meitner-Minerva Center for Computational Quantum Chemistry,
Technion-Israel Institute of Technology, Haifa 32000, Israel
[1]*Author for correspondence (e-mail: chrapel@tx.technicon.ac.il)*

Abstract

The two major fundamental obstacles which so far have prevented the isolation of stable silynes, RSi≡CR′ (**1**), are: (a) the existence of more stable isomers, e.g., RR′C=Si: (**2**) and (b) their extremely facile (exothermic) dimerication. The steric and electronic effects of various substituents R and R′ (R = alkoxy, alkyl, aryl and silyl; R′ = alkyl and aryl groups) on the stability of RSi≡CR′ relative to the isomeric RR′C=Si: (ΔE(**1-2**)), and on the energy of dimerization to the corresponding 1,3-disilacyclobutadienes (ΔE(D)), were studied computationally using density functional theory (DFT) and the ONIOM method. The goal was to find a combination of substituents that will make RSi≡CR′ more stable than RR′C=Si: and which will also prevent its dimerization. For R = R′ = H, ΔE(**1-2**)) = 40.7 kcal/mol (i.e., **2** is lower in energy than **1**), and ΔE(D) = −104.0 kcal/mol. **1**, R = OH, R′ = *m*-Tbt ≡ 2,6-bis[bis(silyl)methyl]phenyl, is by 11.1 kcal/mol **more stable** than the isomeric silylidene **2**. However, the dimerization of **1**, R = OH, R′ = *m*-Tbt remains highly exothermic (by 101 kcal/mol). **1**, R = R′ = *m*-Tbt and **1**, R = (*t*-Bu)₃Si, R′ = *m*-Tbt, are by 5.8 and 2.0 kcal/mol, respectively, less stable than the corresponding **2**. However, the dimerization of **1**, R = (*t*-Bu)₃Si, = *m*-Tbt is exothermic by only 12 kcal/mol. For **1**, R = (*t*-Bu)₃Si, and R′ = Tbt′ ≡ 2,6-bis[bis(trimethylsilyl)methyl]phenyl, the corresponding 1,3-disilacyclobutadiene dimer **3**, dissociates spontaneously. Thus, (*t*-Bu₃Si)Si≡CTbt′ is predicted to be kinetically stable towards both, isomerization to (*t*-Bu₃Si)Tbt′C=Si: and dimerization to **3**, making it a viable synthetic target. The reported energies were calculated at B3LYP/6-31G**//B3LYP/3-21G*; good agreement is found between the DFT and the ONIOM results.

Following the landmark synthesis and isolation in 1981 of the first stable silene ($R_2Si=CR_2$)[2] and disilene (($R_2Si=SiR_2$)[3] many compounds with multiple bonds to silicon were isolated and their chemistry was studied extensively both experimentally and theoretically [4]. In contrast, until recently, HSi≡N was the only unequivocally detected silicon triply-bonded compound, although only as a transient in a matrix [5]. Other attempts to isolate RSi≡N resulted in RNSi [6]. $H_3CSi≡SiCH_3$ [7] and more recently RSi≡SiR, R = Tip₂C₆H₃ (Tip ≡ 2,4,6-triisopropylphenyl) [8] were proposed as transients, but conclusive evidence for their existence is not available. Recently we have shown experimetnally [9], following previous theor-
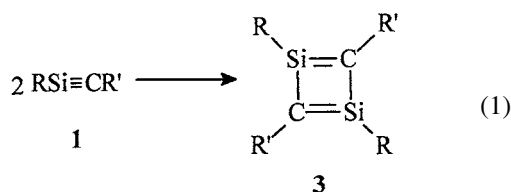
etical predictions [10], that FSi≡CH and ClSi≡CH exist in the gas phase. Yet, the isolation of a stable silyne in the condensed phase remains one of the 'holy grails' of silicon chemistry. In this paper we use quantum machanical calculations to predict specific silynes RSi≡CR′ which we believe are attractive candidates for synthesis and isolation.

There are two major obstacles in the synthesis of triply-bonded silicon compounds, even as transients: (a) the existence of lower energy isomers [9–12] and (b) their expected high reactivity, e.g., towards dimerization. The parent silyne, **1**, R = R′ = H, is calculated to be by 35.0 kcal/mol less stable than the isomeric silylidene, **2**, and as the barrier for the

$1 \rightarrow 2$ isomerization is only 6.0 kcal/mol, **1** rearranges to **2** instantenously (i.e., obstacle (a)) [9–12]. Our previous study [10] showed how obstacle (a) can be overcome. Substitution of **1**, $R' = H$, with R = F, Cl and OH, reduces considerably or even inverts (for R = F) the silyne-silylidene energy difference. Furthermore, the barrier for the $1 \rightarrow 2$ isomerization increases to 24.9, 24.5, and 15.1 kcal/mol for R = F, OH, and Cl respectively, making these silynes kinetically stable [10]. Following these theoretical predictions Schwarz, Apeloig et al., provided recently the first firm evidence for the existence of RSi≡CH, R = F, Cl in the gas phase [9].

$$\underset{\textbf{1}}{\text{RSi}\equiv\text{CR}'} \quad \underset{\textbf{2}}{\text{RR}'\text{C}=\text{Si:}}$$
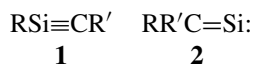
Obstacle (b) is more difficult to overcome due to the extreme high exothermicity of the dimerization of simple silynes to the corresponding 1,3-disilacyclobutadienes (Equation 1) or disilatetrahedrane.

$$2\ \underset{\textbf{1}}{\text{RSi}\equiv\text{CR'}} \longrightarrow \underset{\textbf{3}}{\begin{array}{c} \text{R}\diagdown \quad \diagup \text{R'} \\ \text{Si}=\text{C} \\ | \quad | \\ \text{C}=\text{Si} \\ \text{R'}\diagup \quad \diagdown \text{R} \end{array}} \qquad (1)$$

A possible strategy to overcome both obstacles is to use very bulky substituents, which will sterically destabilize **2** relative to **1** [13] and which may also prevent the dimerization [13c] of **1**. The central question is which set of substituents can achieve this goal leading to a clear theoretical prediction of a potentially stable silyne.

To design theoretically a possible stable silyne we evaluated computationally [14] the effects of various combinations of alkoxy, alkyl, aryl and silyl substituents, on the relative energy of **1** and **2** and on the dimerization energy of **1** to **3**. The discussion below is based on the results of density functional calculations at the B3LYP/6-31G**//B3LYP/3-21G* level of theory [14a,b] unless stated otherwise. For some of the smaller systems higher level calculations were carried out, supporting the general reliability of the B3LYP/6-31G**//B3LYP/3-21G* results, as was also found for disilynes [13]. The compounds with the most bulky substituents were calculated using the recently developed ONIOM method [14c,d].

Our starting point were hydroxy silynes, HOSi≡CR', because for $R' = H$, we found previously that $\Delta E(\textbf{1-2})$

is small, only 10.9 kcal/mol (i.e., **2** is lower in energy than **1**) [10]. Thus, hydroxy (or alkoxy) silynes are good candidates to overcome obstacle (a). The calculations show (Table 1) that for $R' = Me$, $\Delta E(\textbf{1-2})$ is reduced to 6.6 kcal/mol. A phenyl substituent at C has a larger effect (the effect is electronic in nature) reducing $\Delta E(\textbf{1-2})$ to −1.2 kcal/mol (i.e., **1** is more stable **2**). As expected bulky *ortho*-substituents on the phenyl ring decrease $\Delta E(\textbf{1-2})$ further i.e., to −7.6 kcal/mol and −11.1 kcal/mol for R = OH, $R' = $ Dip and R = OH, $R' = m$-Tbt [15] (Scheme 1), respectively. A t-BuO substituent at silicon has a minor effect on $\Delta E(\textbf{1-2})$ (Table 1). Thus, by combining the electronic effect of hydroxy substitution at silicon with the electronic and steric effects of m-Tbt substitution at C, $\Delta E(\textbf{1-2})$ is decreased by as much as **51.8 kcal/mol** relative to HSi≡CH, overcoming obstacle (a).

Are alkoxy silynes such as **1**, R = t-BuO, $R' = m$-Tbt kinetically stable towards dimerization? Disappointingly, the calculations show that the dimerization energy of **1**, R = t-BuO, $R' = m$-Tbt to the corresponding 1,3-disilacyclobutadiene (Equation 1) is exothermic by 101 kcal/mol, very similar to the value for the parent HSi ≡ CH of 104.1 kcal/mol.
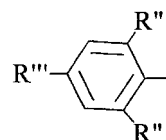
Dip: R" = $CH(CH_3)_2$ R''' = H;

***m*-Tbt**: R" = $CH(SiH_3)_2$, R''' = H;

Tbt': R" = $CH(SiMe_3)_2$, R''' = H;

Tbt: R" = R''' = $CH(SiMe_3)_2$

Scheme 1.

Since even large substituents did not reduce significantly the dimerization energies of alkoxy silynes, we turned to alkyl, aryl and silyl substituents, although the initial $\Delta E(\textbf{1-2})$ difference of 40.7 kcal/mol for HSi≡CH is by 29.8 kcal/mol larger than for HOSi≡CH. t-Bu and methyl substitution on C reduce $\Delta E(\textbf{1-2})$ to 30.4 kcal/mol, but, when attached to silicon, their effect is smaller (Table 1). Phenyl substitution at C has a larger effect than t-Bu and it reduces $\Delta E(\textbf{1-2})$ to 27.0 kcal/mol, but when attached to Si its effect is nearly zero (Table 1). The key observation from these calculations (Table 1) is that it is advantageous to attach an aryl substituent to the carbon atom of the silyne rather than to the silicon atom [17a]. Large *ortho*-substituents on the phelyl group e.g., R' =

Table 1. The effect of alkyl and aryl substituents on the energy differences between RSi≡CR′ (**1**) and RR′C=Si: (**2**), ΔE(**1-2**), (kcal mol^{-1}).

R(Si)	R′(C)	ΔE(1-2)[a]
R = OH, t-BuO		
H	H	40.7; (35.0)[b]
HO	H	10.9; (3.1)[b]
t-BuO	H	11.2
HO	Me	6.6; (1.6)[b]
t-BuO	Me	7.3
t-BuO	*t*-Bu	6.7
HO	Ph	−1.2
HO	Dip[c]	−7.6
HO	*m*-Tbt[c]	−11.1
t-BuO	*m*-Tbt	−9.7
R = alkyl, aryl		
H	Me	30.3; (28.6)[b]
Me	H	32.0; (27.5)[b]
H	*t*-Bu	30.4
t-Bu	H	36.7
H	Ph	27.0
Ph	H	40.0
H	Dip[c]	25.4
H	*m*-Tbt[c]	23.1
m-Tbt[c]	H	38.8
Me	Me	28.5; (24.4)[b]
t-Bu	*t*-Bu	18.9; (18.3)[d]
Ph	Ph	25.8
m-Tbt[c]	*t*-Bu	19.8
t-Bu	*m*-Tbt[c]	10.4; (9.6)[d]
***m*-Tbt**[c]	***m*-Tbt**[c]	**6.6; (5.8)**[d]
***t*-Bu₃Si**	***m*-Tbt**[c]	**2.0**[d]

[a] At B3LYP/6-31G**//B3LYP/3-21G*, unless stated otherwise;
[b] At QCISD(T)/6-31G**//QCISD/6-31G**;
[c] See Scheme 1 for definition;
[d] at ONIOM(B3LYP/6-31G**: HF/STO-3G) [16].

Table 2. Dimerization energies of RSi≡CR′ (**1**) to the corresponding 1,3-disilacyclobutadiene (**3**), ΔE(D), (kcal/mol).

R	R′	ΔE(D)
H	H	−104.0[a]; −91.3[b]
t-Bu	*t*-Bu	−80.7[a]; −80.7[c]
Ph	Ph	−94.3[a]
t-Bu	*m*-Tbt[d]	−70.2[a]; −65.5[c]
m-Tbt[d]	*m*-Tbt[d]	−24.3[a]; −18.6[c]
t-Bu₃Si	*m*-Tbt[d]	−12.6[c]
***t*-Bu₃Si**	**Tbt′**[d]	**Dissociates**[e,f]

[a] At B3LYP/6-31G**//B3LYP/3-21G*;
[b] At QCISD(T)/6-31G**//QCISD/6-31G**;
[c] At ONIOM(B3LYP/6-31G**: HF/STO-3G) [16];
[d] See Scheme 1 for definition;
[e] At ONIOM(B3LYP/6-31G**: HF/3-21G*: Dreiding) [16];
[f] **3**, R = *t*-Bu₃Si, R′ = Tbt′ dissociates upon geometry optimization. An energy minimum could not be found.

Dip or R′ = *m*-Tbt (R = H) reduce ΔE(**1-2**) further to 25.4 and 23.1 kcal/mol, respectively, but the silylidene is still significantly more stable than the silyne. However, when both R and R′ are very large groups ΔE(**1-2**) decreases significantly (Table 1). Thus, ΔE(**1-2**) for R = *t*-Bu, R′ = *m*-Tbt is 10.4 kcal/mol [17b], for R = R′ = *m*-Tbt it is reduced to only 6.6 kcal/mol and for R = (*t*-Bu)₃Si [18], R′ = *m*-Tbt **ΔE(1-2) is only 2.0 kcal/mol** (at ONIOM(B3LYP/6-31G**: HF/STO-3G)) [19]. Taking into account the fact that the B3LYP/6-31G** level overestimates ΔE(**1-2**) by 1-8 kcal/mol relative to the more elaborate QCISD(T)/6-31G** level (Table 1), we conclude that (***m*-Tbt**)**Si≡C(***m*-Tbt**) and (***m*-Tbt**)₂**C=Si: have similar energies and *t*-Bu₃SiSi≡C(*m*-Tbt) is even more stable than its isomeric silylidene.**

Are these silynes also stable kinetically towards dimerization? A silyne can dimerize either to a 1,3-disilacyclobutadiene, **3** (Equation 1) or to a disilatetrahedrane, **4**. As **3**, R = R′ = H, is more stable than **4**, R = R′ = H, by 32.6 kcal/mol (29.5 kcal/mol at QCISD(T)/6-31G**//QCISD/6-31G**) we discuss here only the dimerization of **1** to **3**. The calculated dimerization energies (ΔE(D)) for representative silynes are given in Table 2.

ΔE(D) of PhSi≡CPh is −94.3 kcal/mol, only slightly smaller than that of the parent HSi≡CH (Table 2). However, with bulkier substituents ΔE(D) drops substantially i.e., to only −24.3 kcal/mol (−18.6, ONIOM(B3LYP/6-31G**: HF/STO-3G)) for (*m*-Tbt)Si≡C(*m*-Tbt), and to −12.6 kcal/mol (ONIOM(B3LYP/6-31G**: HF/STO-3G for *t*-Bu₃SiSi≡C (*m*-Tbt) [20]. In **3**, R = *t*-Bu₃Si, R′ = *m*-Tbt, the significant steric congestion around the 4-membered ring (Figure 1b) enforces a considerable elongation of two ring Si-C bonds (to 1.947 Å compared to 1.784 Å in **3**, R = R′ = H) and of the exocyclic Si-Si(*t*-Bu)₃ bonds (to 2.583 Å compared to 2.411 Å in *t*-Bu₃SiSi≡C (*m*-Tbt)). When the H₃Si groups of *m*-Tbt are replaced by Me₃Si groups, used experimentally (i.e., Tbt′, Scheme 1), **3**, R = *t*-Bu₃Si, R′ = Tbt′ is not a minimum on the potential energy surface and it dissociates upon geometry optimization. Despite various attempts an energy minimum corresponding to **3**, R = R = *t*-Bu₃Si, R′ = Tbt′ could not be found. Thus, **1**,
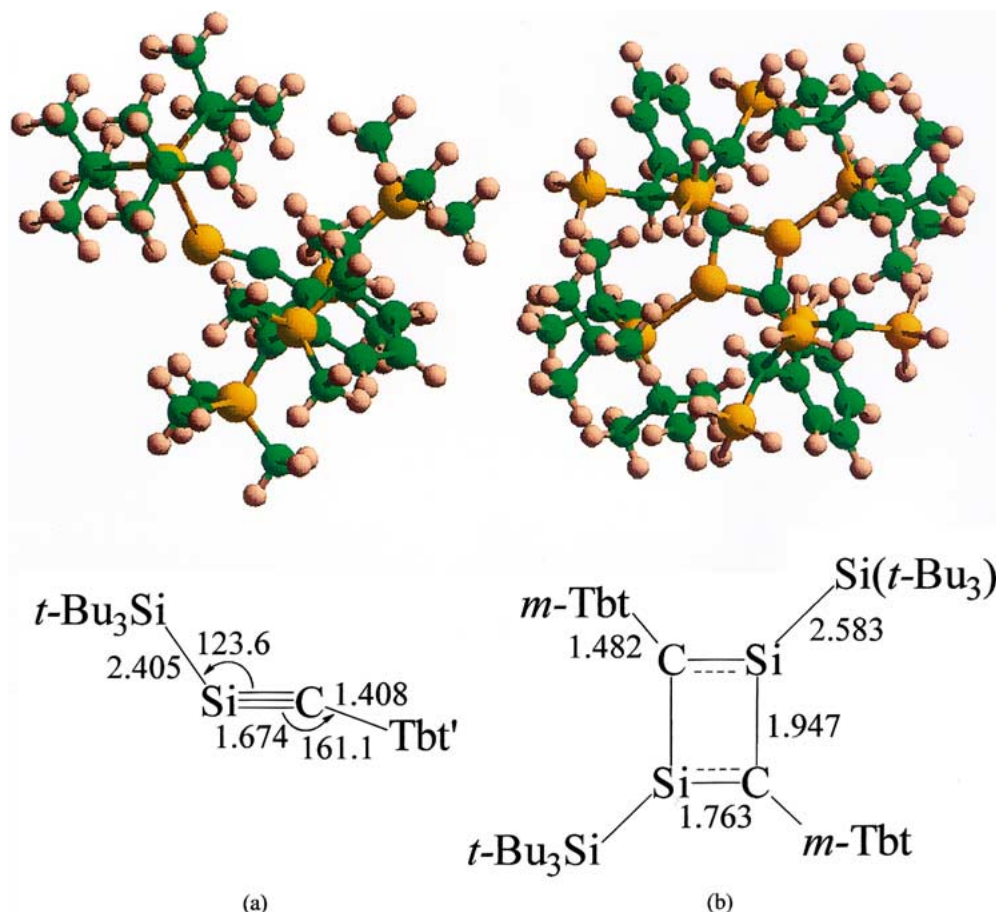
Figure 1. Optimized geometries at ONIOM(B3LYP/6-31G**: HF/STO-3G) [16] of: (a) t-Bu$_3$SiSi ≡ CTbt$'$ and (b) **3**, R = t-Bu$_3$Si; R$'$ = m-Tbt. Bond lengths in Å, bond angles in degrees. Color index: Si – orange, C – green, H – light brown.

R = t-Bu$_3$Si, R$'$ = Tbt$'$ (Figure 1a), if generated, is predicted not to dimerize to **3**. We thus conclude, that **t-Bu$_3$SiSi≡CTbt$'$ (or t-Bu$_3$SiSi≡CTbt) will resist dimerization as well as isomerization to the corresponding silylidenes, and these silynes are therefore attractive candidates for synthesis and isolation** [21]. Substituents which are larger than Tbt, such as C$_6$H$_3$-2,6-Trip$_2$ (Trip = C$_6$H$_2$-2,4,6-i-Pr$_3$) which was used in the synthesis of stable salts of digallyne [22a], digermyne [22b], distannyne [22b] and of neutral PBbPbR [22c], or CAr$_3$, (Es(CPh$_3$) = 4.91 compared to Es(t-Bu) of 1.43) [23], are also attractive substituents for stabilizing the silyne.

t-Bu$_3$SiSi≡CTbt$'$ is calculated to have a C ≡ Si bond length of 1.674 Å (similar to that in PhSi≡CPh of 1.676 Å), shorter than a C=Si double bond (ca. 1.70 Å) [24]. Despite the severe steric repulsions between the bulky substituents, t-Bu$_3$SiSi≡Ctbt$'$ is not linear (similarly to all other silynes [10]), exhibiting a stronger bending at Si (∠SiSi≡C = 123.6 °) than at C (∠CC≡Si = 161.1 °), but it is not twisted around the C≡Si bond (∠SiSiCC = 179 °).

We conclude that silynes bearing suitable bulky substituents are attractive synthetic targets. Our theoretical predictions await experimental testing which hopefully will lead to the synthesis of the first stable silyne.

Note added in proofs

While this paper was in press, Wiberg and coworkers reported possible synthesis and identification (by NMR and MASS spectometry) of R*Si≡SiR*, R* = Me(t-Bu$_3$Si)$_2$Si. The assignment of the ^{29}Si chemical shift is being checked now computationally [25b,c].

Acknowledgement

References

1. Reported in part at the 12th International Symposium on Organosilicon Chemistry, May 23–28, 1999, Sendai, Japan; Book of Abstracts, p. 197 and at the 5th World Congress of Theoretically Oriented Chemists, WATOC'99, August, 1–6, 1999, London, U.K.; Book of Abstracts, p. 367.

2. Brook, A.G., Abdesaken, F., Gutekunst, B., Gutekunst, R. & Kallury, K. 1981 *J. Chem. Soc., Chem. Commun.*, 191.

3. West, R., Fink, M.J. & Michl, J. 1981 *Science* **214**, 1343.

4. For comprehensive reviews, see: (a) *The Chemistry of Organic Silicon Compounds*, ed. S. Patai & Z. Rappoport. Wiley, New York, 1989. E.g., Apeloig, Y., p. 57; Raabe, G. & Michl, J., p. 1015; (b) *The Chemistry of Organic Silicon Compouns*, Vol. 2, ed. Z. Rappoport & Y. Apeloig. Wiley, New York, 1998. E.g., Sakurai, H., p. 827; Müller, T., Ziche, W. & Auner, N., p. 857; Tokitoh, N. & Okazaki, R., p. 1063; (c) Brook, A.G. & Brook, M.A. 1996 *Adv. Organomet. Chem.* **39**, 71; (d) Driess, M. 1996 *Adv. Organomet. Chem.* **39**, 193; (e) Okazaki, R. & West, R. 1996 *Adv. Organomet. Chem.* **39**, 232.

5. Maier, G. & Glatthaar, J. 1994 *Angew. Chem., Int. Ed. Eng.* **33**, 473.

6. The nature of the Si-N bond in RNSi compounds has still to be determined. (a) Bock, H. & Dammel, R. 1985 *Angew. Chem., Int. Ed. Engl.* **24**, 111; (b) Elhanine, M., Farrenq, R. & Guelachvili, G. 1991 *J. Chem. Phys.* **94**, 2529; (c) Bogey, M., Demuynck, C., Destombes, J.L. & Walters, A. 1991 *Astron. Astrophys.* **244**, 247; (d) Radziswski, J.G., Littmann, D., Balaji, V., Fabry, L., Gross, G. & Michl, J. 1993 *Organometallics* **12**, 4816; (e) Goldberg, N., Iraqi, M., Hrusak, J. & Schwarz, H. 1993 *Int. J. Mass Spectrum. Ion Processes* **125**, 267.

7. Sekiguchi, A., Zigler, S.S., West, R. & Michl, J. 1986 *J. Am. Chem. Soc.* **108**, 4241.

8. Pietschnig, R., West, R. & Powell, D.R. 2000 *Organometallics* **19**, 2724.

9. Karni, M., Apeloig, Y., Schröder, D., Zummack, W., Rabezzana, R. & Schwarz, H. 1999 *Angew. Chem., Int. Ed.* **38**, 332.

10. Apeloig, Y. & Karni, M. 1997 *Organometallics* **16**, 310.

11. (a) Gordon, M.S. & Pople, J.A. 1981 *J. Am. Chem. Soc.* **103**, 2945; (b) Gordon, M.S. 1982 *J. Am. Chem. Soc.* **104**, 4352; (c) Hopkinson, A.C., Lien, M.H. & Csizmadia, I.G. 1983 *Chem. Phys. Lett.* **95**, 232; (d) Hoffman, M.R., Yoshioka, Y. & Schaefer III, H.F. 1983 *J. Am. Chem. Soc.* **105**, 1084; (e) Luke, B.T., Pople, J.A., Krogh-Jespersen, M.-B., Apeloig, Y., Karni, M., Chandrasekhar, J. & Schleyer, P.v.R. 1980 *J. Am. Chem. Soc.*, 108, 270; (f) Colgrove, B.T. & Schaefer III, H.F. 1990 *J. Phys. Chem.* **94**, 5593; (g) Grev, R. & Schaefer III, H.F. 1992

J. Chem. Phys. **97**, 7990; (h) Jursic, B.S. 1999 *J. Mol. Struct.*, 459, 221.

12. (a) Nguyen, M.T., Sengupta, D. & Vanquickborne, L.G. 1995 *Chem. Phys. Lett.* **244**, 83; (b) Stegmann, R. & Frenking, G. 1996 *J. Comp. Chem.* **17**, 781.

13. We have already pointed out this possibility in Ref. 10; Recent theoretical studies have shown that with very bulky substituents, **disilynes (RSi ≡ SiR)** are more stable than their isomeric silylidene (RR′Si = Si:) [13a,b] and that they can also be stabilized towards dimerization [13c]. (a) Kobayashi, K. & Nagase, S. 1997 *Organometallics* **16**, 2489; (b) Nagase, S., Kobayashi, K. & Takagi, N. 2000 *J. Organomet. Chem.* **611**, 264; (c) Kobayashi, N., Takagi, N. & Nagase, S. 2001 *Organometallics* **20**, 234; (d) Takagi, N. % Nagase, S. 2001 *Chemistry Lett.* 966.

14. (a) The calculations were performed using the Gaussian 98 package of programs: *Gaussian 98, Revision A.7*, Gausian, Inc., Pittsburgh PA, 1998; (b) Structures were optimized and frequencies and zero point vibrational energies were calculated using the hybrid-density functional method, with the B3LYP functional and the 3-21G* basis set (B3LYP/3-21G*). Single point energies at these geometries were calculated at B3LYP/6-31G**. B3LYP/6-31G**//B3LYP/3-21G* was the most elaborate level which we could use for the entire set of molecules. For small and medium size systems the reaction energies calculated at B3LYP/6-31G**//B3LYP/6-31G** are very similar to those calculated using B3LYP/3-21G* geometries, giving confidence in the B3LYP/3-21G* geometries used for the larger systems. For some of the small systems, we have also used configuration interaction calculations at the QCISD(T)//6-31G**//QCISD/6-31G** level, and these energies served to calibrate the energies calculated for the larger systems. References to the computational methods and basis sets are given in Ref. 14a; (c) The isomerization and dimerization emergies of silynes substituted with very bulky substituents were calculated with the ONIOM method [14d]. The ONIOM method can be described as an extrapolation scheme where different levels of theory are applied to different parts of the molecule; e.g., in ONIOM(B3LYP/6-31G**: HF/STO-3G), the electronic active inner-layer ('model') is optimized at the B3LYP/6-31G** level, while the entire molecule ('real'), i.e., inner-layer + outer-layer, is calculated at the lower HF/STO-3G level; (d) Daprich, S., Komáromi, I., Byun, K.S., Morokuma, K. & Frisch, M.J. 1999 *J. Mol. Struct.* **461–462**, 1.

15. *m*-Tbt models the significantly larger Tbt group (Scheme 1) which was used successfully in the recent synthesis of several stable doubly-bonded silicon and germanium compounds. See: (a) Suzuki, H., Tokitoh, N., Okazaki, R., Nagase, S. & Goto, M. 1998 *J. Am. Chem. Soc.* **120**, 11096; (b) Wakita, K., Tokitoh, N., Okazaki, R., Nagase, S., Schleyer, P.v.R. & Jiao, H. 1999 *J. Am. Chem. Soc.* **121**, 11336; (c) Tokitoh, N., Kishikawa, K. & Okazaki, R. 1999 *Phosphorous, Sulfur Silicon Relet. Elem.* **150–151**, 137; (d) Tokitoh, N. 1999 *Pure Appl. Chem.* **71**, 495.

16. The 'real' system is the entire molecule and it is calculated in the lower level of theory. For the two layer ONIOM calculations the inner layer, i.e., the 'model' was chosen as follows: for *t*-BuSi≡C (*m*-Tbt), the 'model' is $H_3CSi≡CPh$; for *t*-Bu$_3$SiSi≡C(*m*-Tbt) it is $H_3SiSi≡CPh$; for (*m*-Tbt)Si≡C(*m*-Tbt) the 'model' is PhSi≡CPh. For the corresponding dimers, **3**, the 'model' was chosen as the dimer of the 'model' system of the corresponding silynes, e.g., for **3**, R = *t*-Bu$_3$Si, R′ = m-Tbt, the model is **3**, R = SiH$_3$, R′ = Ph. For **3**, R = *t*-Bu$_3$Si, R′ = Tbt′ a three layer ONIOM was used: the most inner layer

is **3**, R = R′ = H calculated at B3LYP/6-31G**; the second, 'intermediate model' is **3**, R = H_3Si; R′ = Ph, Calculated at HF/3-21G* and the 'real' system, **3**, R = t-Bu_3Si, R′ = Tbt′, was calculated using the Dreiding force field implemented in G98 [14a].

17. (a) For all alkyl and aryl substituents, ΔE(**1-2**) is smaller when the alkyl substituent is attached to the Si-end of the silyne and the aryl to the C-end of the silyne. (b) ΔE(**1-2**) for R = m-Tbt, R′ = t-Bu is higher, 19.8 kcal/mol [17a].

18. This substituent was used successfully in the synthesis of a stable tetrasilatetrahedrane: Wiberg, N., Finger, C.M.M. & Polborn, K. 1993 *Angew. Chem. Int. Ed. Engl.* **32**, 1054.

19. The large effects of R = R′ = m-Tbt and R = t-Bu_3Si, R′ = m-Tbt on ΔE (**1-2**) (Table 1), result from a cooperative effect: **stabilization** of the silyne by the aryl group and **destabilization** of the silylidene by the steric repulsions between R and R′ which amounts (according to isodesmic Equation 2) to ca. 8.2 kcal/mol (11.7 kcal/mol, ONOIM) for R = R′ = m-Tbt and to 17.8 kcal/mol (ONOIM) for R = t-Bu_3Si; R′ = m-Tbt,
$$RR′C = Si: + H_2C = Si: \longrightarrow RHC = Si: + R′HC = Si: \quad (2)$$

20. The right reliability of the ONIOM(B3LYP/6-31G**:HF/STO-3G) calculations is clearly evident from the data in Tables 1 and 2, i.e., the differences between the ONIOM and B3LYP/6-31G** results for ΔE(**1-2**) and ΔE(D) are small. This applies also to the calculated geometries of the dimers. A detailed comparision between the ONIOM and B3LYP calculations will be presented elsewhere.

21. Our study cannot however, exclude the possibility that other reactions such as insertions [8], or H-abstraction would complicate the isolation of the silyne. We are currently studying computationally these reactions.

22. (a) Su, J., Li, X.-W., Critterdon, C. & Robinson, G.H. 1997 *J. Am. Chem. Soc.* **119**, 5471; (b) Pu, L., Senge, M.O., Olmstead, M.M. & Power, P.P. 1998 *J. Am. Chem. Soc.* **120**, 12682; (c) Pu, L., Twamley, B. & Power, P.P. 2000 *J. Am. Chem. Soc.* **122**, 3524.

23. White, D.P., Antony, J.C. & Oyefeso, A.O. 1999 *J. Org. Chem.* **64**, 7707.

24. A detailed VB analysis confirms that the bond in the trans-bent HSi $\equiv$ CH is a genuine triple bond; see: Danovich, D., Ogliaro, F., Karni, M., Apeloig, Y., Cooper, D.L. & Shaik, S. 2001 *Angew. Chem. Int. Ed.* **113**, 4146.

25. (a) Wiberg, N., Niedermayer, W., Fisscher, G., Nöth, H. & Suter, M. 2002 *Eur. J. Inorg. Chem.* 1066; (b) Takagi, N. & Nagase, S. submitted, *Eur. J. Inorg. Chem.* (c) Karni, M. & Apeloig, Y., reported at the 6th World Congress of Theoretically Oriented Chemists, WATOC '02, August, 4–9, 2002, Lugano, Switzerland (oral contribution No. 97).