

# Ab Initio and DFT Study of the $^{29}\text{Si}$ NMR Chemical Shifts in $\text{RSi}\equiv\text{SiR}$

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The syntheses of the first two disilynes were reported recently: the first by Wiberg and co-workers, who synthesized  $\text{RSi}\equiv\text{SiR}$  (**1**;  $\text{R} = \text{SiMe}(\text{Si}-t\text{-Bu}_3)_2$ ), and the second by Sekiguchi and co-workers, who synthesized  $\text{RSi}\equiv\text{SiR}$  (**2**;  $\text{R} = \text{Si}-i\text{-Pr}[\text{CH}(\text{SiMe}_3)_2]_2$ ), which was also characterized by X-ray crystallography and NMR spectroscopy. We report the first detailed quantum-mechanical study of the  $^{29}\text{Si}$  NMR chemical shifts of disilynes,  $\text{RSi}\equiv\text{SiR}$ , in particular those with  $\text{R} = \text{H}$ ,  $\text{CH}_3$ ,  $\text{SiH}_3$ ,  $\text{SiMe}(\text{SiH}_3)_2$ ,  $\text{SiMe}(\text{SiMe}_3)_2$ ,  $\text{SiMe}(\text{Si}-t\text{-Bu}_3)_2$  (**1**),  $\text{Si}-i\text{-Pr}[\text{CH}(\text{SiMe}_3)_2]_2$  (**2**). The main conclusions are as follows: (1) Small changes in geometry (i.e., in  $r(\text{Si}\equiv\text{Si})$ , in the  $\text{RSiSi}$  bond angle, and in the  $\text{RSiSiR}$  torsion angle) strongly affect the chemical shift. (2)  $\delta(^{29}\text{Si})$  values of the triply bonded silicon atoms in  $\text{RSi}\equiv\text{SiR}$  ( $\text{R} = \text{H}$ ,  $\text{SiH}_3$ ) are  $-26$  and  $68$  ppm, respectively (at MP2/6-311G(3d)//B3LYP/6-31G(d,p)), reflecting a significant effect of the silyl substituent. (3)  $\delta(^{29}\text{Si})$  values calculated using the HCTH407 GGA functional are in excellent agreement with those calculated at the MP2 and CCSD levels of theory for model disilynes and with experimental chemical shifts measured for disilenes. This is therefore our recommended method for calculating  $\delta(^{29}\text{Si})$  values of disilynes, especially with large substituents. A poorer agreement is observed when applying the commonly used hybrid B3LYP functional. (4) The calculated chemical shift of the triply bonded silicon atoms in **1** is in the range of  $88 \pm 5$  ppm, in good agreement with the observed chemical shift of the product obtained by Wiberg, supporting his assignment. (5) The calculated  $\delta(^{29}\text{Si})$  value in **2** is ca. 60 ppm, considerably upfield from the experimental chemical shift of 89.9 ppm (in solution), raising the possibility that the structure of **2** in solution is slightly different from that in the solid state.

## Introduction

One of the major challenges in contemporary organosilicon chemistry is the synthesis and isolation of triply bonded silicon compounds.<sup>1</sup> Until recently,  $\text{HSi}\equiv\text{N}$  was the only triply bonded silicon compound identified unequivocally, but it exists only as a transient in a matrix.<sup>2</sup> Attempts to isolate  $\text{RSi}\equiv\text{N}$  resulted in the isomeric  $\text{RNSi}$ .<sup>3</sup>  $\text{H}_3\text{CSi}\equiv\text{SiCH}_3$ <sup>4</sup> and  $\text{RSi}\equiv\text{SiR}$  ( $\text{R} = \text{Tip}_2\text{C}_6\text{H}_3$  ( $\text{Tip} \equiv 2,4,6\text{-triisopropylphenyl}$ ))<sup>5</sup> were proposed as transients, but conclusive evidence for their existence was not presented.

There are two major obstacles in the synthesis of triply bonded silicon compounds. The first is the fact

that usually the triply bonded isomer (e.g.,  $\text{HSi}\equiv\text{SiH}$  and  $\text{HC}\equiv\text{SiH}$ ), is less stable than its isomeric forms (e.g.,  $\text{H}_2\text{Si}=\text{Si}$ : and  $\text{H}_2\text{C}=\text{Si}$ :),<sup>6–10</sup> and the second is their extremely high reactivity (e.g., toward dimerization).<sup>9,10</sup> A theoretical study by Apeloig and Karni, which predicted that electronegative substituents stabilize the triply bonded isomer electronically relative to the si-

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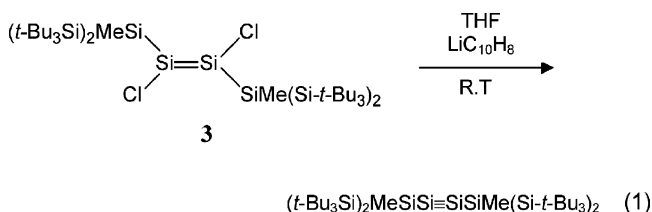
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lylidene isomer,<sup>11</sup> led to the first detection and unequivocal identification of  $\text{FSi}\equiv\text{CH}$  and  $\text{ClSi}\equiv\text{CH}$  in the gas phase.<sup>12</sup> Still, the isolation of stable silynes and disilynes in the condensed phase remained one of the major contemporary goals of organosilicon chemistry.

A series of computational papers by our two groups on the effects of bulky substituents on the stabilities of  $\text{RSi}\equiv\text{SiR}$ <sup>9</sup> and  $\text{RC}\equiv\text{SiR}$ <sup>10</sup> relative to their isomeric forms and to their dimerization products have shown that large substituents such as  $\text{Tbt} \equiv \text{C}_6\text{H}_2\text{-2,4,6-}[\text{CH}(\text{SiMe}_3)_2]_3$  and  $\text{Ar}^* \equiv \text{C}_6\text{H}_3\text{-2,6-(C}_6\text{H}_2\text{-2,4,6-}i\text{-Pr}_3)_2$  reverse the isomeric stability order so that these substituted disilynes and silynes are more stable than their silylidene isomers ( $\text{RR}'\text{M}=\text{Si}$ ,  $\text{M} = \text{C, Si}$ ).<sup>9,10</sup> Furthermore, these very bulky substituents also prevent dimerization reactions.<sup>9,10</sup> Similar substituent effects were calculated for the heavier congeners  $\text{RM}=\text{MR}$  ( $\text{M} = \text{Ge, Sn, Pb}$ ).<sup>13</sup> These theoretical predictions were confirmed by the successful isolation and characterization by X-ray crystallography of  $\text{Ar}'\text{GeGeAr}'$ ,<sup>15</sup>  $\text{Ar}'\text{SnSnAr}'$  ( $\text{Ar}' = \text{C}_6\text{H}_3\text{-2,6-(C}_6\text{H}_2\text{-2,4,6-}i\text{-Pr}_3)_2$ ),<sup>16</sup> and  $\text{Ar}^*\text{PbPbAr}^*$ .<sup>17</sup> However, on the basis of the  $\text{M}-\text{M}$  bond lengths and calculated bond orders it was concluded that the  $\text{M}-\text{M}$  bonds in  $\text{Ar}^*\text{MMAr}'$  ( $\text{M} = \text{Ge, Sn}$ )<sup>1a,15,16</sup> are not triple bonds but rather lie between the extremes of an hypothetical linear triply bonded compound and a singly bonded metallylene having an electron lone pair on each  $\text{M}$ . The  $\text{Pb}-\text{Pb}$  bond in  $\text{Ar}^*\text{PbPbAr}^*$  was concluded to be a single bond.<sup>1a,18</sup>

The first report that claimed the isolation of a disilyne,  $\text{RSi}\equiv\text{SiR}$  (**1**;  $\text{R} = \text{SiMe}(\text{Si-}t\text{-Bu}_3)_2$ ), in the condensed phase was published in 2002 by Wiberg and co-workers.<sup>19</sup> These authors synthesized and characterized by X-ray crystallography the stable disilene **3** and suggested that it undergoes dechlorination by  $\text{LiC}_{10}\text{H}_8$  to produce disilyne **1** (eq 1).



Unfortunately, attempts to obtain the crystal structure of the product isolated from reaction 1 failed, and the suggestion that it is disilyne **1** was based mainly on the observed  $\delta(^{29}\text{Si})$  NMR chemical shift at 91.5 ppm, on the observed mass spectrometry peaks of masses  $\text{M}(\text{1})^{+\bullet}$  and  $[\text{M}(\text{1}) + \text{O}_2]^{+\bullet}$ , and on trapping reactions.<sup>19</sup> Calculations that followed Wiberg's report confirmed that **1** is more stable than its  $\text{R}_2\text{Si}=\text{Si}$ : isomer by 30

kcal/mol and that its dimerization is endothermic,<sup>20a,b</sup> suggesting that **1** may indeed exist in the condensed phase.

Wiberg's experiments<sup>19</sup> were the trigger to our theoretical studies in an attempt to determine if the observed  $\delta(^{29}\text{Si})$  NMR signal indeed belongs to disilyne **1**. When our paper was in the hands of the reviewers,<sup>20c</sup> Sekiguchi and co-workers reported the ground-breaking synthesis, isolation, and characterization by X-ray crystallography and by NMR spectroscopy of the stable disilyne  $\text{RSi}\equiv\text{SiR}$  (**2**;  $\text{R} = \text{Si-}i\text{-Pr}[\text{CH}(\text{SiMe}_3)_2]_2$ ).<sup>21</sup> The measured (in  $d_6$ -benzene solution) chemical shift of the triply bonded silicon atoms in this compound is 89.9 ppm.<sup>21</sup> Despite this important experimental achievement, the knowledge of the factors which control the  $^{29}\text{Si}$  NMR chemical shifts of disilynes is scarce and Wiberg's assignment of the  $\delta(^{29}\text{Si})$  signal at 91.5 ppm to indicate a  $\text{Si}=\text{Si}$  triple bond remains uncertain and requires further experimental and computational support. Furthermore, as more attempts are being made to synthesize new triply bonded silicon compounds the theoretical understanding and the ability to predict the NMR chemical shifts of these compounds becomes even more important, allowing the experimentalists to base their identification of new compounds on reliable theoretical predictions.

In this paper, for the first time, we study computationally by quantum mechanical ab initio and DFT methods the  $^{29}\text{Si}$  NMR chemical shifts of a variety of substituted disilynes,  $\text{RSi}\equiv\text{SiR}$ , with  $\text{R} = \text{H, CH}_3, \text{SiH}_3, \text{SiMe}(\text{SiH}_3)_2, \text{SiMe}(\text{SiMe}_3)_2, \text{SiMe}(\text{Si-}t\text{-Bu}_3)_2$  (**1**),  $\text{Si-}i\text{-Pr}[\text{CH}(\text{SiMe}_3)_2]_2$  (**2**). Several theoretical methods are tested and compared. After submitting this paper, we became aware of a paper by Auer, Kaupp, and Strohmman which also studies the factors that affect the chemical shifts of several small disilynes. This paper is published immediately after our paper in this issue.

The results of our calculations support Wiberg's conclusion that the product of reaction 1 is indeed disilyne **1**.<sup>19</sup> Interestingly, there is a discrepancy of ca. 30 ppm between the calculated and experimental  $\delta(^{29}\text{Si})$  values of the triply bonded silicon atoms of **2**. Possible reasons for this discrepancy are discussed.

## Theoretical Methods

Geometries of the small model systems were optimized using the hybrid density functional method B3LYP<sup>22</sup> with the 6-31G(d,p)<sup>23</sup> basis set. The large experimentally studied molecules

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RSi≡SiR (R = SiMe(Si-*t*-Bu<sub>3</sub>)<sub>2</sub>, Si-*i*-Pr[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and (*E*)-RClSi=SiClR (R = SiMe(Si-*t*-Bu<sub>3</sub>)<sub>2</sub>) were optimized at B3LYP/6-31G(d), B3LYP/6-311G(d)[Si]:3-21G[C,H],<sup>24</sup> and B3LYP/6-311G(d)[Si]:6-31G(d)[C,H].<sup>24</sup> For the calculation of the NMR chemical shifts we used the GIAO ansatz<sup>25</sup> with the B3LYP hybrid functional and with the BPW91,<sup>22d,26</sup> BP86,<sup>22d,27</sup> and HCTH407<sup>28</sup> general gradient approximation (GGA) functionals and the MP2<sup>29</sup> and CCSD<sup>30</sup> ab initio methods. These methods were accompanied by a variety of Pople's basis sets<sup>23</sup> augmented with d- and f-polarization functions as well as with diffuse functions on Si and C and p-polarization functions on H. Frequencies were calculated at B3LYP/6-31G(d,p) for the model systems in order to identify them as minima. The following basis set notations are used throughout the paper:<sup>24</sup> base1 = 6-31G(d); base2 = 6-31G(d,p); base3 = 6-311G(d)[Si]:6-31G(d)[C,H]; base4 = 6-311G(3d)[Si]:3-21G[C,H]; base5 = 6-311G(3d)[Si]:6-31G(d)[C,H].

Geometry optimizations, frequency calculations, and NMR calculations by the DFT and MP2 methods were performed with the Gaussian 98<sup>31a</sup> and Gaussian 03<sup>31b</sup> series of programs. TURBOMOLE was used for the NMR calculations of RSi≡SiR (R = SiMe(SiH<sub>3</sub>)<sub>2</sub>) at GIAO-MP2.<sup>32a</sup> The CCSD NMR values were calculated using ACESII.<sup>32b</sup>

## Results and Discussion

The discussion is divided into two parts: (I) an evaluation of the performance of various computational

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methods for calculating  $\delta(^{29}\text{Si})$  values of the triply bonded silicon atoms in disilynes and (II) analysis of the  $\delta(^{29}\text{Si})$  values of RSi≡SiR (R = H, CH<sub>3</sub>, SiH<sub>3</sub>, SiMe(SiH<sub>3</sub>)<sub>2</sub>, SiMe(SiMe<sub>3</sub>)<sub>2</sub>, SiMe(Si-*t*-Bu<sub>3</sub>)<sub>2</sub> (**1**), Si-*i*-Pr[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (**2**)) as a function of the geometry and the substituent R. Throughout the discussion  $\delta(^{29}\text{Si})$  refers to the chemical shift of the triply bonded silicon atoms, unless otherwise stated.

**I. Effect of the Computational Method on the Calculated Chemical Shielding ( $\sigma$ ) and Chemical Shift ( $\delta$ ).** As this is the first theoretical study of the NMR chemical shifts of triply bonded silicon compounds, a survey of the effect of various computational methods and of the type and size of the basis set on the calculated chemical shifts is important. Such a survey will help in finding a suitable functional for the calculation of chemical shifts of actual experimental molecules, which are usually too large for high-level NMR calculations (e.g., methods which explicitly include electron correlation) and, therefore, have to be calculated using DFT methods.

The calculated  $\delta(^{29}\text{Si})$  chemical shifts of RSi≡SiR (R = H (**4**), CH<sub>3</sub> (**5**), SiH<sub>3</sub> (**6**)) are given in Table 1. These values were calculated using the GIAO ansatz by the HF, B3LYP, BPW91, HCTH407, MP2, and CCSD methods with a wide variety of Pople-type basis sets, as indicated in Table 1, and with Si(CH<sub>3</sub>)<sub>4</sub> (TMS) as the reference compound; i.e.,  $\delta_{\text{A}}(^{29}\text{Si}) = \sigma_{\text{TMS}} - \sigma_{\text{A}}$ . The absolute  $\sigma(^{29}\text{Si})$  values of disilynes **4–6** and of TMS are given in Table 1S in the Supporting Information. The optimized geometry parameters (at B3LYP/6-31G(d,p)) of **4–6** are given in Table 1 (the Cartesian coordinates are given in the Supporting Information).

**(a) Effect of the Computational Method on the Isotropic Chemical Shielding  $\sigma$ .** The computational method that is used has a significant effect on the calculated chemical shielding of RSi≡SiR (Table 1S). The experience in the literature is that chemical shielding and chemical shifts are in general calculated more accurately with ab initio methods which include explicitly electron correlation, such as CCSD and MP2.<sup>33,34a</sup> As there were no experimental data available for disilynes, and as for large systems these methods are not practical, we decided to follow the computational experience gathered for other systems<sup>33</sup> and to search for density functional methods which can reproduce closely the calculated CCSD or MP2 values of triply bonded silicon atoms. We hope that this strategy will prove to be valid when more experimental data on disilynes will become available. Using the 6-311G(3d) basis set, the B3LYP  $\sigma(^{29}\text{Si})$  values are shifted downfield

(32) (a) TURBOMOLE: TURBOMOLE Version 5-6; The Quantum Chemistry Group, University of Karlsruhe, Germany. Direct MP2 NMR chemical shifts: Kollwitz, M.; Gauss, J.; Haser, M. *J. Chem. Phys.* **1998**, *108*, 8295. Direct RHF NMR chemical shifts: Haser, M.; Ahlrichs, R.; Baron, H. P.; Weis, P.; Horn, H. *Theor. Chim. Acta* **1992**, *83*, 455. Kollwitz, M.; Gauss, J. *Chem. Phys. Lett.* **1996**, *260*, 639. (b) ACESII version 0.3: Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1992**, *26*, 879.

(33) See for example: (a) Gauss, J.; Stanton, J. F. In *Calculation of NMR and EPR Parameters*; Kaupp, M., Bühl, M., Malkin, V. G., Eds.; Wiley-VCH: Weinheim, Germany, 2004; Chapter 8, p 124. (b) Auer, A. A.; Gauss, J.; Stanton, J. F. *J. Phys. Chem.* **2003**, *118*, 10407. (c) Gauss, J.; Stanton, J. F. *Adv. Chem. Phys.* **2002**, *123*, 355. (d) Schreckenbach, G.; Ziegler, T. *Theor. Chem. Acc.* **1998**, *99*, 71. (e) Cheeseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. *J. Chem. Phys.* **1996**, *104*, 5497.



**Table 1. Calculated Structures and  $\delta(^{29}\text{Si})$  Chemical Shifts<sup>a,b</sup> of the Triply Bonded Silicon Atoms in  $\text{RSi}\equiv\text{SiR}$** 

		$\delta(^{29}\text{Si})$ Chemical Shifts (ppm)		
		R		
method no. <sup>c</sup>	method	H	$\text{CH}_3$	$\text{SiH}_3^d$
	HF/6-31G(d)	7.2	32.8	128.4
	HF/6-311+G(2df,p)	−2.9	34.7	128.1
1	B3LYP/6-31G(d)	23.7	50.1	122.8 (−59.4)
2	B3LYP/6-311G(d)	9.2	49.4	117.1 (−93.9)
3	B3LYP/6-311G(2d)	0.3	39.9	110.3 (−96.7)
4	B3LYP/6-311+G(2df,p) <sup>e</sup>	0.4 [−195.1]	39.6 [−199.5]	113.0 [−51.1] (−96.5)
5	B3LYP/6-311G(3d)	−5.4	34.9	103.1 (−100.2)
7	BPW91/6-311G(d) <sup>f</sup>	24.9	47.2	110.5 (−54.0)
8	BPW91/6-311G(d) <sup>f</sup>	5.5	41.6	99.3 (−92.7)
9	BPW91/6-311G(2d) <sup>f</sup>	−2.5	33.0	93.6 (−94.0)
10	BPW91/6-311G(2df,p) <sup>f</sup>	−1.4	32.8	96.3 (−94.1)
11	BPW91/6-311G(3d) <sup>f</sup>	−8.7	27.3	86.0 (−98.2)
13	HCTH407/6-31G(d)	3.6	30.7	88.8 (−68.8)
14	HCTH407/6-311G(d)	−7.7	30.1	81.1 (−93.8)
15	HCTH407/6-311G(2d)	−15.6	21.6	74.8 (−95.9)
16	HCTH407/6-311+G(2df,p)	−14.8	22.2	78 (−96.2)
17	HCTH407/6-311G(3d)	−20.2	17.3	68.6 (−99.0)
20	MP2/6-31G(d)	−16.5	16.6	62.2 (−79.8)
21	MP2/6-311G(d)	−20.8	22.5	66.9 (−107.3)
22	MP2/6-311G(d,p)	−23.2	21.4	65.9 (−97.4)
23	MP2/6-311G(2d)	−24.7	16.8	70.0 (−109.0)
24	MP2/6-311G(2d,p)	−27.3	15.7	68.9 (−103.1)
25	MP2/6-311G(2df,p)	−27.7	13.1	66.9 (−109.2)
26	MP2/6-311+G(2df,p) <sup>e</sup>	−29.1 [−180.5]	12.8 [−179.3]	66.8 [−52.6] (−102.7)
27	MP2/6-311G(3d)	−26.0	15.0	67.6 (−110.1)
29	CCSD/6-31G(d)	−15.7	7.6	66.0 (−78.7)
30	CCSD/6-311G(d)	−16.6	15.1	72.5 (−99.1)
31	CCSD/6-311G(2d)	−17.5	11.8	75.7 (−105.8)
32	CCSD/6-311G(3d)	−19.1	10.1	73.0 (−106.9)
Geometry <sup>g,h</sup>				
		R		
		H	$\text{CH}_3$	$\text{SiH}_3^d$
$r(\text{Si}\equiv\text{Si}), \text{\AA}^e$		2.112 [1.974]	2.123 [1.976]	2.101 <sup>i</sup> [2.010]
$\theta, \text{deg}$		55.6	50.7	49.9 <sup>j</sup>

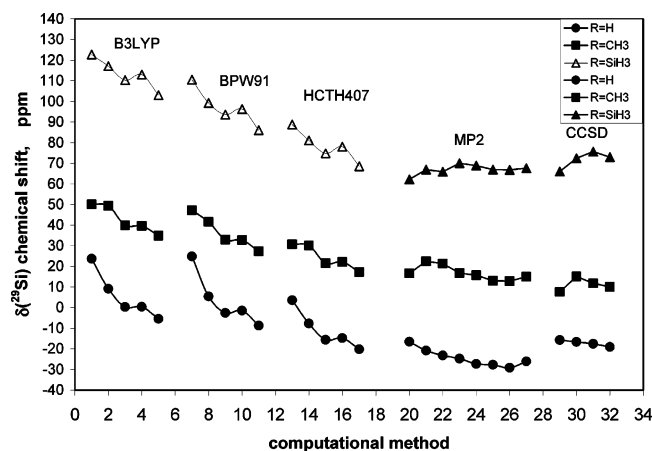
<sup>a</sup> Using the GIAO method with B3LYP/6-31G(d,p) optimized geometries. <sup>b</sup> Relative to the chemical shielding constants of TMS calculated at the same level. <sup>c</sup> The numbering refers to numbering of the theoretical method in Figure 1. <sup>d</sup>  $\delta(^{29}\text{Si})$  values of the  $\text{SiH}_3$  silicon atoms are given in parentheses. <sup>e</sup> The chemical shifts and the  $\text{Si}\equiv\text{Si}$  bond lengths of the constrained linear structures are given in brackets. <sup>f</sup> Almost identical values were obtained with the BP86 functional. <sup>g</sup> At B3LYP/6-31G(d,p). <sup>h</sup> The  $\text{SiSiSiSi}$  torsion angle is  $180^\circ$ . <sup>i</sup> At B3LYP/6-311+G(d,p),  $r(\text{Si}\equiv\text{Si})=2.096 \text{ \AA}$  and  $\theta = 50.0^\circ$ ;  $\delta(^{29}\text{Si})$  101.5 and 67.3 ppm at B3LYP/6-311G(3d) and HCTH407/6-311G(3d), respectively.

relative to the CCSD values by 58 (R = H), 69 (R =  $\text{CH}_3$ ), and 75 ppm (R =  $\text{SiH}_3$ ) (and by 61, 60, and 76 ppm, respectively, relative to the MP2 values). The largest differences between the B3LYP and the CCSD and MP2 values are found for the silyl-substituted disilyne **6**. The  $\sigma(^{29}\text{Si})$  values calculated with the BPW91 GGA functional are slightly closer to those calculated with the CCSD and MP2 methods (Table 1S). These differences decrease significantly when the HCTH407

functional is used, leading to downfield shifts of 33 (R = H), 42 (R =  $\text{CH}_3$ ), and 30 ppm (R =  $\text{SiH}_3$ ) relative to the CCSD values (and by 36, 32, and 31 ppm, respectively, relative to the MP2 values). The basis set also has a large effect on  $\sigma$ . With all computational methods (ab initio and DFT), the largest effect is caused by replacing a double-split basis set by a triple-split basis set; the MP2/6-311G(d) and CCSD/6-311G(d)  $\sigma$  values are shifted downfield (smaller  $\sigma$ ) by about 61 ppm for R = H and by 68–70 ppm for R =  $\text{CH}_3$ ,  $\text{SiH}_3$ , relative to those obtained at MP2/6-31G(d) and CCSD/6-31G(d) (a similar effect was observed also for  $\sigma(^{29}\text{Si})$  of TMS (Table 1S)<sup>34a</sup>). The effect of additional sets of d-polarization functions is small, and the effect of adding f-polarization functions and diffuse functions is negligible (Table 1S). Very similar trends are observed also with the B3LYP, BPW91, and HCTH407 DFT methods.

**(b) Effect of the Computational Method on  $\delta(^{29}\text{Si})$ .** Comparison of the chemical shifts of  $\text{RSi}\equiv\text{SiR}$  calculated using DFT methods with those calculated using MP2 and CCSD methods (with the 6-311G(3d) basis set), the latter believed to be more reliable,<sup>33</sup> shows (Table 1, Figure 1) that the B3LYP  $\delta(^{29}\text{Si})$  values are shifted downfield by 14 (R = H), 25 (R =  $\text{CH}_3$ ), and 30

(34) (a) The agreement between calculated and measured  $^{29}\text{Si}$  chemical shielding constants of TMS ( $\sigma_{\text{TMS}}$ ) is highly dependent on the computational method and on the basis set. Excellent agreement was achieved using the MP2 and CCSD methods with a triple-split basis set; e.g., with 6-311G(3d),  $\sigma(^{29}\text{Si})$  361 (MP2) and 366 ppm (CCSD) (Table 1S) compared to the experimental value of  $368 \pm 10 \text{ ppm}$ .<sup>34b</sup> Increasing the basis sets has a minor effect (Table 1S).  $\sigma(^{29}\text{Si})$  values calculated using DFT methods with a triple-split basis set are in poorer agreement with experiment.<sup>34c</sup> With the smaller 6-31G(d) basis set,  $\sigma(^{29}\text{Si})$  values of 441 (MP2), 443 (CCSD), 415 (B3LYP), 405 (BPW91) and 404 ppm (HCTH407) were calculated. These values are shifted considerably upfield relative to the experimental value. Because TMS serves as the reference compound, the accuracy of its calculated chemical shielding constants may have a significant effect on the agreement between the calculated and measured chemical shifts.<sup>34d</sup> (b) Jameson, C. J.; Jameson, A. K. *Chem. Phys. Lett.* **1988**, *149*, 300. (c) Heine, T.; Goursot, A.; Seifert, G.; Weber, J. *J. Phys. Chem.* **2001**, *105*, 620. (d) Baldrige, K. K.; Siegel, J. S. *J. Phys. Chem. A* **1999**, *103*, 4038.



**Figure 1.** Calculated  $\delta(^{29}\text{Si})$  values of  $\text{Si}^1$  in  $\text{RSi}^1\equiv\text{Si}^1\text{R}$  ( $\text{R} = \text{H}, \text{CH}_3$  and  $\text{SiH}_3$ ) at various theoretical levels. The numbering of the theoretical method on the abscissa refers to the method numbering defined in Table 1.

ppm ( $\text{R} = \text{SiH}_3$ ) relative to those calculated with the CCSD method (by 21, 20, and 36 ppm, respectively, relative to MP2). These differences are significantly smaller than the corresponding differences in the  $\sigma(^{29}\text{Si})$  values (see above), due to the fact that the effects of the computational method on  $\sigma(^{29}\text{Si})$  of the disilyne and of TMS are similar. Smaller differences are observed when the BPW91 functional is used (Table 1).<sup>35</sup> Using density functional theory with the HCTH407 functional, an excellent agreement with the chemical shifts calculated with the CCSD and MP2 methods is obtained, the difference being only a few ppm; e.g.,  $\delta(^{29}\text{Si})$  of  $\text{H}_3\text{SiSi}\equiv\text{SiSiH}_3$  calculated at HCTH407/6-311G(3d) differs from that calculated at CCSD/6-311G(3d) by only 4.4 ppm (1 ppm relative to the MP2 value, Table 1).<sup>36</sup>

The large effect on  $\sigma(^{29}\text{Si})$  of triple- $\zeta$  vs double- $\zeta$  basis sets (Table 1S), is significantly smaller for  $\delta(^{29}\text{Si})$  (Figure 1, Table 1) due to the very similar effects of the basis set on  $\sigma(^{29}\text{Si})$  in  $\text{RSi}\equiv\text{SiR}$  and in TMS.<sup>34</sup> At MP2 and CCSD expanding the basis set has a relatively small effect on  $\delta(^{29}\text{Si})$ , the largest change in  $\delta(^{29}\text{Si})$  being ca. 10 ppm for  $\text{H}_3\text{SiSi}\equiv\text{SiH}_3$ . For the three DFT methods that were tested, i.e., B3LYP, BPW91, and HCTH407, the effect on  $\delta(^{29}\text{Si})$  of both double- $\zeta$  vs triple- $\zeta$  basis sets and of additional augmented sets of d-polarization functions is somewhat more pronounced (Table 1, Figure 1). The effect of diffuse functions and augmented f-polarization functions is negligible. Thus, with these DFT methods the recommended level of calculation consists of a triple- $\zeta$  type basis set augmented with three sets of d-polarization functions.

The calculated chemical shifts of the  $\alpha$ -silyl silicon atoms ( $\delta(^{29}\text{Si}^2)$  in  $\text{H}_3\text{Si}^2\text{Si}^1\equiv\text{Si}^1\text{Si}^2\text{H}_3$ ) are very similar

**Table 2.** Calculated and Experimental  $\delta(^{29}\text{Si})$  Chemical Shifts of the Doubly Bonded Silicon Atoms in  $\text{RR}'\text{Si}=\text{SiR}'$

R, R'	$\delta(^{29}\text{Si})$ , ppm		
	calcd		exptl
	B3LYP <sup>a</sup>	HCTH407 <sup>a</sup>	
R = R' = Si- <i>i</i> -Pr <sub>3</sub>			
X-ray coordinates <sup>b</sup>	203.4	167.3	154.5 (soln) <sup>c</sup>
optimized structure <sup>d</sup>	199.8	162.7	164 (solid state) <sup>e</sup>
R = R' = SiMe <sub>2</sub> - <i>t</i> -Bu			
X-ray coordinates <sup>b</sup>	175.0	145.1	142.1 (soln) <sup>c</sup>
optimized structure <sup>d</sup>	180.2	149.3	
R = <i>t</i> -Bu, R' = Mes <sup>f</sup>			
( <i>E</i> isomer)			
X-ray coordinates <sup>b</sup>	96.9	83.7	90.3 (soln) <sup>c</sup>
optimized structure <sup>d</sup>	95.8	81.6	86.1 (solid state) <sup>e</sup>
R = R' = Mes <sup>f</sup>			
optimized structure <sup>d</sup>	70.5	60.7	63.2 (soln) <sup>e</sup> 63.3 (solid state) <sup>e</sup>

<sup>a</sup> Using base 5, experimental X-ray geometries and fully optimized structures as specified. <sup>b</sup> Imported from the Cambridge Data Base. <sup>c</sup> Reference 40. <sup>d</sup> Optimized at B3LYP/base3. <sup>e</sup> Reference 39a. <sup>f</sup> Mes = 2,4,6-trimethylphenyl.

with all DFT methods used here, being −100.2 (B3LYP), −98.2 (BPW91), and −99.0 (HCTH407) ppm (using the 6-311G(3d) basis set), in good agreement with the MP2 (−110.1 ppm) and CCSD (−106.9 ppm) values.  $\delta(^{29}\text{Si}^2)$  is affected more significantly by increasing the basis set from a double-split to a triple-split type than is  $\delta(^{29}\text{Si}^1)$ .

To gain more confidence in the reliability of the HCTH407 functional for calculating  $\delta(^{29}\text{Si})$  of low-coordination silicon atoms in large real molecules, we have tested its performance for calculating  $\delta(^{29}\text{Si})$  chemical shifts of doubly bonded silicon atoms in disilenes, for which more experimental data are available. The calculated  $\delta(^{29}\text{Si}^1)$  chemical shifts (using the 6-311G(3d) basis set) for the model disilene ( $\text{H}_3\text{Si})_2\text{Si}^1=\text{Si}^1(\text{SiH}_3)_2$  (optimized at B3LYP/6-31G(d,p)) are (in ppm) 121.7 (MP2), 119.4 (HCTH407), and 147.1 (B3LYP), respectively. There is again an excellent agreement between the MP2 and HCTH407 chemical shifts, while the B3LYP  $\delta(^{29}\text{Si}^1)$  value is shifted downfield by ca. 30 ppm, similarly to the trend found in  $\delta(^{29}\text{Si})$  for silyl-substituted disilynes (Table 1). We next compared the performance of the HCTH407 functional to that of the B3LYP functional for a series of four experimentally studied disilenes,  $\text{RR}'\text{Si}=\text{SiRR}'$ , for which both the X-ray structures and the NMR spectra, both in solution and in the solid state, were measured, so that we can be confident that the molecular structures in solution and in the solid state are not different. The NMR calculations used both the experimentally derived X-ray coordinates and the computationally optimized structures. The calculated and experimental chemical shifts are given in Table 2.

Table 2 shows for the four disilenes an excellent agreement between the experimental chemical shifts and the HCTH407 calculated values, when using either the X-ray coordinates or the calculated structures. This excellent agreement strongly supports the predictive power of the HCTH407 functional. In contrast, the B3LYP calculated chemical shifts for the silyl-substituted disilenes are considerably shifted downfield relative to the experimental values (and relative to the HCTH407 values), reflecting the poorer performance of B3LYP for these molecules.<sup>37,38</sup> For alkyl- and aryl-

(35) The superiority of GGA functionals over hybrid functionals for the calculation of chemical shielding constants of light main-group atoms (e.g., C, O, N) was demonstrated by: Teale, A. M.; Tozer, D. J. *Chem. Phys. Lett.* **2004**, *383*, 109.

(36) The excellent agreement of the HCTH407 calculated chemical shifts with those calculated at CCSD and MP2 may result from the fact that its parameterization involved not only a wide variety of energetic and geometric data but also near-exact potentials derived from Brueckner doubles ab initio calculations through the Zhao–Morrison–Parr procedure. The source of error in the NMR calculations using the hybrid B3LYP functional, especially for molecules having a small HOMO–LUMO gap, is likely to result from the nonmultiplicative potential exhibited by the Hartree–Fock method. Martin, J. M. L. Private communication. Boese, A. D. Private communication.

**Table 3.** Calculated<sup>a</sup> and Measured (in Parentheses)  $\delta(\text{M})$  Values (ppm) of  $\text{RH}_3\text{M}$ ,  $\text{R}_2\text{M}=\text{MR}_2$ , and  $\text{RM}\equiv\text{MR}$  (M = C, Si; R = H,  $\text{CH}_3$ ,  $\text{SiH}_3$ )

R	$\text{RH}_3\text{M}$		$\text{R}_2\text{M}=\text{MR}_2$		$\text{RM}\equiv\text{MR}$	
	M = C	M = Si	M = C	M = Si	M = C	M = Si
H	-5.1 (-2.3) <sup>b</sup>	-117.9 (-93.1) <sup>c</sup>	120.9 (123.3) <sup>b</sup>	65.9 <sup>d</sup>	70.3 (71.9) <sup>e</sup>	-26.0
$\text{CH}_3$	9.1 (6.5) <sup>b</sup>	-80.4 (-65.2) <sup>b</sup>	127.3 <sup>f</sup> (123.5) <sup>g</sup>	96.1 <sup>d</sup>	78.8 (74.8) <sup>e</sup>	15.0
$\text{SiH}_3$	-10.4 (-14.3) <sup>b</sup>	-122.6 (-103.1) <sup>c</sup>	185.0 <sup>h</sup> (195.3) <sup>i</sup>	147.5 <sup>d</sup> (154.5) <sup>j,k</sup>	112.8 (113.7) <sup>l</sup>	67.6

<sup>a</sup> At MP2/6-311G(3d) unless stated otherwise. <sup>b</sup> References cited in: Kutzelnigg, W.; Fleischer, U.; Schindler, M. in *NMR—Basic Principles and Progress*; Springer-Verlag: Heidelberg, Germany, 1990; Vol. 23, p 165. <sup>c</sup> Hahn, J. Z. *Naturforsch.* **1980**, *35b*, 282. <sup>d</sup> At B3LYP/6-311+G(3df,p).<sup>39a</sup> <sup>e</sup> Reference 41a. <sup>f</sup> At MP2/6-311+G(2df,p).<sup>39b</sup> <sup>g</sup> SDBS No. 4816; <http://www.aist.go.jp>. <sup>h</sup> At B3LYP/6-311G(3d)//B3LYP/6-311G(d,p). <sup>i</sup> R =  $\text{Me}_3\text{Si}$ : Sakurai, H.; Nakadaira, Y.; Kira, M.; Tobita, H. *Tetrahedron Lett.* **1980**, *21*, 3077. <sup>j</sup> R = Si-*i*-Pr.<sup>40</sup> <sup>k</sup> 162.7 ppm at HCTH407/base5//B3LYP/base3. <sup>l</sup> R =  $\text{Me}_3\text{Si}$ : Han, S.; Kass, S. R. *J. Chem. Soc. Perkin Trans. 1* **1999**, 1553.

substituted disilenes, the chemical shifts calculated at both HCTH407 and B3LYP are in very good agreement with experiment.

In conclusion, we find, based on the calculated chemical shift values of real experimental disilenes and of the model disilene, that both the MP2 and HCTH407 methods are more reliable than the B3LYP method for calculating <sup>29</sup>Si NMR chemical shifts of disilenes (especially for those substituted by silyl groups). This conclusion adds support to our belief in the superiority of MP2 and HCTH407 methods over the B3LYP method also for calculating chemical shifts of disilynes.

As calculations of chemical shifts using CCSD or MP2 are limited to relatively small molecules due to the prohibitively long CPU time and large disk space demands of such calculations, we have used the B3LYP, BPW91, and HCTH407 DFT methods for calculating the chemical shifts of the large disilynes **1** and **2** that were studied experimentally. According to the conclusions reached above, the B3LYP and BPW91 chemical shifts will be corrected according to MP2 chemical shifts calculated for smaller model systems. The HCTH407 chemical shifts require no correction.

**II. NMR Chemical Shifts of Substituted Disilynes.** (a)  $\delta(^{29}\text{Si})$  of  $\text{RSi}\equiv\text{SiR}$  (R = H,  $\text{CH}_3$ ,  $\text{SiH}_3$ ). What is the chemical shift of a triply bonded silicon atom? Do the <sup>29</sup>Si chemical shifts of organosilicon compounds follow a trend similar to the general trend observed for hydrocarbons; i.e.,  $\delta(^{13}\text{C}(\text{sp}^3)) < \delta(^{13}\text{C}(\text{sp})) < \delta(^{13}\text{C}(\text{sp}^2))$  (e.g.,  $\delta(^{13}\text{C}) = -2.3$  ( $\text{CH}_4$ ), 71.9 ( $\text{HC}\equiv\text{CH}$ ), and 123.3 ( $\text{H}_2\text{C}=\text{CH}_2$ ) ppm; Table 3, measured values)? Our calculations show that  $\delta(^{29}\text{Si})$  values of organosilicon compounds follow a similar trend; thus,  $\delta(^{29}\text{Si}) = -117.9$  ( $\text{SiH}_4$ ),  $< -26.0$  ( $\text{HSi}\equiv\text{SiH}$ )  $< 65.9$  ( $\text{H}_2\text{Si}=\text{SiH}_2$ ) ppm (Table 3, calculated values). Substituents have a significant effect on the chemical shift, but the general trend outlined above is maintained also for the substituted silicon compounds (Table 3).

**(i) Substituent Effects.** The average  $\delta(^{29}\text{Si}^1)$  values (in ppm), calculated at MP2 and CCSD (using several

basis sets) for  $\text{RSi}^1\equiv\text{Si}^1\text{R}$ , are  $-23 \pm 4$  (R = H),  $15 \pm 4$  (R =  $\text{CH}_3$ ), and  $69 \pm 3$  (R =  $\text{SiH}_3$ ) (Table 1). These values show that silyl substitution induces a substantial shift of  $\delta(^{29}\text{Si}^1)$  to lower field (higher  $\delta$  values). Silyl substitution causes a similar downfield shift in  $\delta(^{13}\text{C})$  of acetylene as well as for the doubly bonded Si and C atoms in disilene and ethylene, as shown in Table 3 (see also Table 2). This observation is in contrast with the simplistic expectation from the relative electronegativities of silyl vs methyl (more electronegative), which is followed in saturated hydrocarbons and silanes, where electropositive substituents (e.g., silyl) cause shifts to higher fields (Table 3).

What are the reasons for the large downfield shift of the chemical shifts of doubly and triply bonded atoms which are substituted by silyl groups? The answer lies in the fact that the chemical shifts of low-coordinated atoms in unsaturated compounds are mainly determined by the paramagnetic contribution to the chemical shielding,  $\sigma^p$ .<sup>41</sup> The paramagnetic contribution results from paramagnetic currents that are induced by the applied magnetic field via coupling of occupied and virtual orbitals. These induced currents induce a local magnetic field that enhances the applied magnetic field, thus causing downfield shifts. The paramagnetic contribution,  $\sigma^p$ , is determined by the Ramsey formula,<sup>42a,b</sup> which may be expressed by a double sum over occupied and vacant MOs, with orbital energies  $\epsilon_k$  and  $\epsilon_a$ , respectively<sup>42c</sup> (eq 2;  $u$  and  $v$  represent the Cartesian

$$\sigma_{N,uv}^p = \frac{2}{c^2} \sum_k \sum_a \frac{\langle \varphi_k | l_{O,u} | \varphi_a \rangle \cdot \langle \varphi_a | l_{N,v} \cdot r_N^{-3} | \varphi_k \rangle}{\epsilon_k - \epsilon_a} \quad (2)$$

components,  $l_O$  is the angular momentum operator that represents the interaction of the external magnetic field with the electrons, and  $l_{N,v} \cdot r_N^{-3}$  corresponds to the interaction of the electrons with the nuclear magnetic dipole field). According to eq 2,  $\sigma^p$  is inversely propor-

(37) (a) One of the reasons for the poor performance of traditional GGAs or hybrid schemes in the calculation of NMR properties is related to the deficiencies of these methods in correctly calculating the energy differences between the occupied and virtual orbitals. To solve this problem, level-shift methods were developed.<sup>38b,c</sup> (b) Malkin, V. G.; Malkina, O. L.; Salahub, D. R. *Chem. Phys. Lett.* **1993**, *204*, 80. Malkin, V. G.; Malkina, O. L.; Casida, M. E.; Salahub, D. R. *J. Am. Chem. Soc.* **1994**, *116*, 5898. (c) Magyarfalvi, G.; Pulay, P. *J. Chem. Phys.* **2003**, *119*, 1350.

(38) For studies that report improved functionals for NMR calculations see: (a) Keal, T. W.; Tozer, Helgaker, T. *Chem. Phys. Lett.* **2004**, *391*, 374. (b) Keal, T. W.; Tozer, D. J. *J. Chem. Phys.* **2004**, *121*, 5654. (c) Arbuznikov, A. V.; Kaupp, M. *Chem. Phys. Lett.* **2004**, *386*, 8. (d) Hieringer, W.; Della Seta, F.; Görling, A. *Chem. Phys. Lett.* **2004**, *386*, 115. (e) Reference 35. (f) Wilson, P. J.; Amos, R. D.; Handy, N. C. *Mol. Phys.* **1999**, *97*, 757, and the references cited therein.

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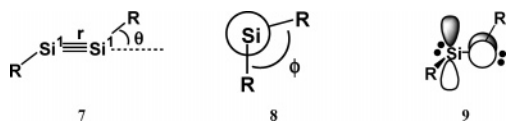
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tional to the energy difference between the occupied and virtual orbitals that are coupled by the external magnetic field. The smaller this difference, the larger the shift to lower field. In doubly bonded systems (e.g., ethylenes and disilenes) the main contribution to  $\sigma^p$  is attributed to the coupling between the  $\sigma$  and  $\pi^*$  orbitals and the changes in the chemical shifts of these compounds were found to be strongly affected by the energy differences of these two orbitals.<sup>39,41,43a,b</sup> We now find<sup>43a,c</sup> that, also in disilynes, the large downfield shift caused by silyl substitution is related to the smaller  $\sigma$ – $\pi^*$  energy difference in H<sub>3</sub>SiSi≡SiSiH<sub>3</sub> (10.6 eV; HF/6-31G(d,p)) relative to that in HSi≡SiH (12.3 eV).

$\beta$ -silyl substituents, e.g., in (H<sub>3</sub>Si)<sub>2</sub>MeSiSi≡SiSiMe(SiH<sub>3</sub>)<sub>2</sub>, cause an additional downfield shift of  $\delta(^{29}\text{Si})$  to 88.4 ppm (MP2/base5) relative to 67.6 ppm in H<sub>3</sub>SiSi≡SiSiH<sub>3</sub>.

**(ii) Geometry Effects.** The optimized geometry parameters of RSi≡SiR (R = H, CH<sub>3</sub>, SiH<sub>3</sub>) are given in Table 1. Disilynes are *trans-bent* as shown in **7**, in



contrast to the analogous acetylenes, which are linear. The linear RSi≡SiR are not minima on the potential energy surface (PES).<sup>44,45</sup> The computational prediction that disilynes are *trans-bent*<sup>44,45</sup> was recently confirmed by the X-ray structure of RSi≡SiR (R = Si-*i*-Pr[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>), which shows a RSiSi angle of 137.4°. The calculated central Si–Si bond length in H<sub>3</sub>SiSi≡SiSiH<sub>3</sub> is ca. 2.10 Å, slightly longer than in the linear (non-minimum) structure, but it is shorter than that of the Si=Si bond in R<sub>2</sub>Si=SiR<sub>2</sub> (R = SiH<sub>3</sub>; 2.17 Å). Methyl substitution lengthens the Si=Si bond, while silyl substitution causes a slight shortening. The *trans*-bending angle  $\theta$  is 56° in HSi≡SiH, and it decreases slightly to ca. 50° in the dimethyl- and disilyl-substituted disilynes (Table 1). In RSi≡SiR (R = H, CH<sub>3</sub>, SiH<sub>3</sub>) the torsion angle  $\phi$  (see **8**)<sup>46</sup> is 180.0°; i.e., the Si≡Si atoms and the atoms attached to them are in the same plane.

Below we discuss the dependence of the  $\delta(^{29}\text{Si})$  value of RSi≡SiR on the RSiSi bending angle ( $\theta$ ), the RSiSi torsion angle ( $\phi$ )<sup>46</sup>, and the bond length  $r(\text{Si}=\text{Si})$ . The discussion is for R = SiH<sub>3</sub>, but the trends and the main conclusions drawn for R = SiH<sub>3</sub> apply also to R = H and to R = CH<sub>3</sub>.

The <sup>29</sup>Si chemical shift is extremely sensitive to the bending angle  $\theta$ . A linear correlation was found between  $\delta(^{29}\text{Si})$  and  $\cos^2\theta$  ( $R^2 = 0.990$ ,  $0.991$ , and  $0.994$  at B3LYP, HCTH407, and MP2, respectively; Figure 2a),

suggesting that a relation exists between the chemical shift and the overlap between the two Si<sup>1</sup>(3p<sub>z</sub>) orbitals that form the  $\sigma(\text{Si}^1\text{--Si}^1)$  MO.<sup>47a</sup> The reduced orbital overlap when  $\theta$  increases raises the energy of the  $\sigma(\text{Si}^1\text{--Si}^1)$  orbital, resulting in a smaller  $\sigma$ – $\pi^*$  energy gap, causing according to eq 2 an increase in the paramagnetic contribution to the chemical shielding and thus to a downfield shift of  $\delta(^{29}\text{Si})$  relative to the linear structure ( $\theta = 0^\circ$ ).<sup>41–43</sup> The effect of bending is linear in  $\cos^2\theta$  and thus quadratic in  $\theta$ ,<sup>47b</sup> causing a rapid increase in  $\delta$  as the deviation from linearity increases. A smaller bending angle (e.g., due to steric repulsion) will cause the opposite effect; i.e., in H<sub>3</sub>SiSi≡SiSiH<sub>3</sub> decreasing  $\theta$  from the optimized value of 50° to 40°, which requires only about 1 kcal/mol, causes a significant upfield shift of ca. 37 ppm (B3LYP/6-311+G(2df,p); 30 ppm at MP2/6-311+G(2df,p), Figure 2a). In line with this correlation, in the hypothetical linear RSi≡SiR,  $\delta(^{29}\text{Si})$  values are considerably upfield relative to those of the optimized *trans*-bent structures: i.e., for linear RSi≡SiR,  $\delta(^{29}\text{Si})$  (ppm) = –180.5 (R = H), –179.3 (R = CH<sub>3</sub>), and –52.6 (R = SiH<sub>3</sub>), relative to –29.1, 12.8, and 66.8 in the corresponding *trans*-bent disilynes (at MP2/6-311+G(2df,p)). These extremely large difference in  $\delta(^{29}\text{Si})$  are consistent with the decrease in the  $\sigma$ – $\pi^*$  energy gap (eq 2) upon bending: e.g., from 12.5 eV for linear H<sub>3</sub>SiSi≡SiSiH<sub>3</sub> to 10.6 eV (HF/6-31G(d,p))<sup>48</sup> for the optimized *trans*-bent structure.

The Si≡Si bond length ( $r$ ) and the torsion angle about the Si≡Si bond,  $\phi$  (see **8**) also affect significantly the chemical shift of the triply bonded silicon atoms, as shown in Figures 2b,c, although to a smaller extent than the bending angle  $\theta$ . A linear correlation exists between  $\delta(^{29}\text{Si})$  and  $\cos^2\phi$  ( $R^2 = 0.9998$  and  $0.9995$  for B3LYP and HCTH407, respectively)<sup>49</sup> (Figure 2b). The effect of twisting on  $\delta$  is small in the vicinity of the optimized bent-planar structure; i.e., for  $\phi = 170^\circ$   $\delta(^{29}\text{Si})$  is shifted downfield by only 6 ppm.<sup>50</sup> However, as the effect of twisting is quadratic in  $\phi$ ,<sup>47b</sup> its size increases rapidly as the deviation from planarity increases ( $\phi$  decreases; Figure 2b), and for  $\phi = 90^\circ$ ,  $\delta(^{29}\text{Si})$  is as high as 378 ppm (at B3LYP/6-311+G(2df,p)). This is, probably due to the buildup of a bis(silylene) character (**9**) upon twisting.

A linear correlation exists between  $\delta(^{29}\text{Si})$  and the Si≡Si bond distance ( $r$ ) (Figure 2c). Elongation of

(47) (a) It is known that orbital overlap is related to  $\cos^2\theta$ : Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 2371. (b) The linear correlation of  $\delta(^{29}\text{Si})$  with  $\cos^2\theta$  and  $\cos^2\phi$  also implies a quadratic correlation with  $\theta$  and  $\phi$ , respectively:  $\delta(^{29}\text{Si}) = 0.028\theta^2 + 1.47\theta - 26.33$ ,  $R^2 = 0.998$ ;  $\delta(^{29}\text{Si}) = 0.056\phi^2 - 20.4\phi + 1961.8$ ,  $R^2 = 0.999$ ;  $\theta$  and  $\phi$  in degrees (B3LYP/6-311+G(2df,p)).

(48) The differences in the  $\sigma$ – $\pi^*$  energy gaps between the linear and bent structures are very similar when using HF, B3LYP, and HCTH407 methods: i.e., for H<sub>3</sub>SiSi≡SiSiH<sub>3</sub> they are 2.10, 1.85, and 1.75 eV, respectively.

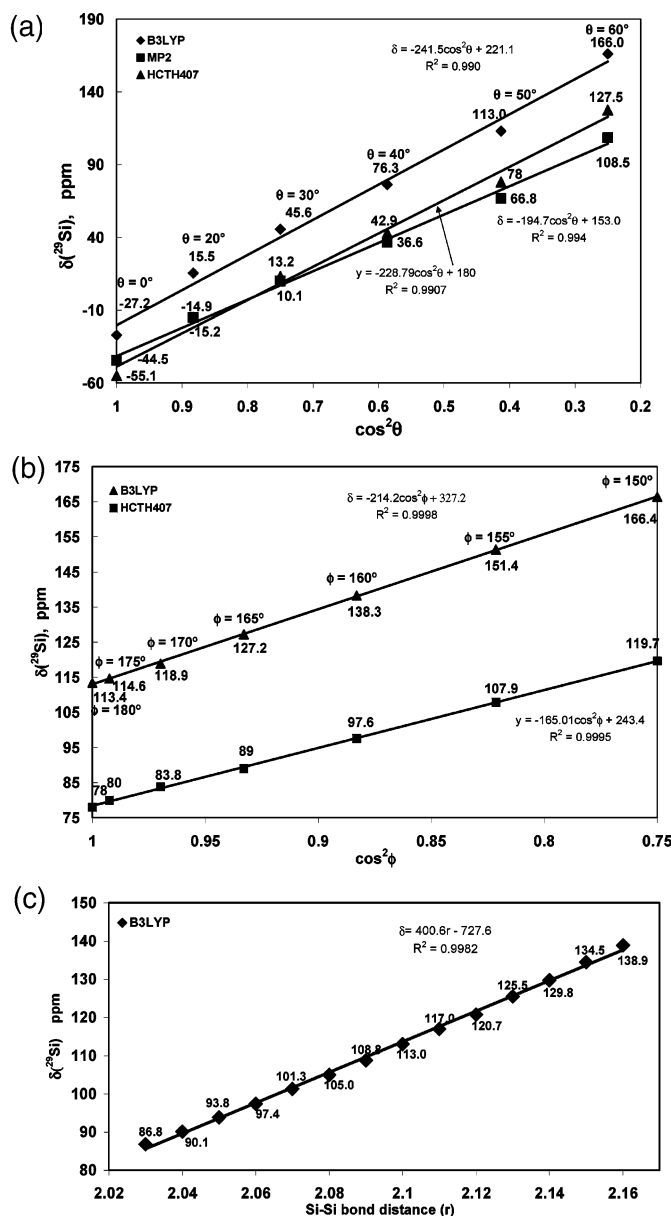
(49) Oddly, the MP2 line correlating  $\delta(^{29}\text{Si})$  and  $\cos^2\phi$  has a *positive* slope, i.e., the chemical shift *decreases* (shifts to higher field) upon twisting ( $\phi$  decreases). In the bent-planar structure the chemical shifts calculated at MP2 and CCSD are very similar (Table 1), while for a SiSiSiSi dihedral angle of 165°,  $\delta(^{29}\text{Si})$  at MP2/6-311+G(2df,p) is –42.8 ppm compared to +87.2 ppm at CCSD/6-311G(d) and 91.4 ppm at HCTH407/6-311G(d) (89.0 ppm at HCTH407/6-311+G(2df,p)). Furthermore, an unreasonably large anisotropy of 3029 ppm was calculated at MP2 for the twisted disilyne, compared to 813 and 793 ppm at CCSD and HCTH407, respectively. These results raise questions regarding the reliability of the MP2 method for calculating NMR chemical shifts of disilynes in which the SiSiSiSi backbone deviates from planarity.

(43) (a) Karni, M.; Apeloig, Y. The 6th World Congress of Theoretically Oriented Chemists (WATOC'02), Lugano, Switzerland, August 4–9, 2002; Abstract C62. Karni, M.; Apeloig, Y. *Theory and Application of Computational Chemistry* (TACC) 2004, Gyeongju, Korea, February 15–20, 2004; Abstract C47. (b) Auer, D.; Strohmman, C.; Arbuznikov, A. V.; Kaupp, M. *Organometallics* **2003**, *22*, 2442. (c) See also the paper by Kaupp and coworkers immediately following our paper in this issue.

(44) Colegrove, B. T.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1991**, *113*, 1557.

(45) Apeloig, Y.; Karni, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 2001; Vol. 3, Chapter 1, pp 1–163.

(46)  $\phi$  is the dihedral angle XSiSiX, and X is the atom directly attached to the triply bonded Si atom.



**Figure 2.** Calculated  $\delta(^{29}\text{Si})$  values of  $\text{H}_3\text{SiSi}^1\equiv\text{Si}^1\text{SiH}_3$  vs the following geometric parameters: (a)  $\cos^2\theta$  ( $\phi$  and  $r$  are kept at the values of the fully optimized structures); (b)  $\cos^2\phi$  ( $\theta$  and  $r$  are kept at the values of the fully optimized structure); (c)  $\text{Si}^1\equiv\text{Si}^1$  bond length ( $\theta$  and  $\phi$  are kept at the values of the fully optimized structures). All values were calculated using the 6-311+G(2df,p) basis set with the B3LYP/6-31G(d,p) geometry.

$r(\text{Si}\equiv\text{Si})$  by 0.05 Å, which requires only 1 kcal/mol, causes a 26 ppm downfield shift in  $\delta(^{29}\text{Si})$  (Figure 2c).

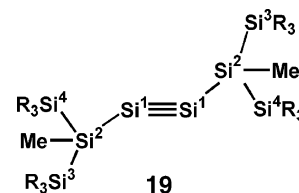
Similar effects on  $\delta(^{29}\text{Si})$ , though somewhat smaller in magnitude, were calculated for the bending, twisting, and Si=Si bond elongation in disilenes.<sup>39a</sup>

A very important insight of the calculations is the realization that the potential energy surface (PES) of the studied disilynes, with regard to bending, twisting, and bond elongation, is very soft. Thus, within a range of ca. 3 kcal/mol a very large spectrum of geometries can be reached. As demonstrated above, even small changes in the disilyne geometry cause significant changes in  $\delta(^{29}\text{Si})$ , making the determination of the precise geometry of the molecule of interest crucial for predicting accurately its NMR spectrum. This point is important

to realize, because the large substituents used experimentally<sup>19,21</sup> may cause substantial geometry changes and deformations (see below). Thus, to obtain a reliable computational prediction of the NMR chemical shifts of newly synthesized disilynes, the calculated geometry has to be very close to the actual experimental geometry. The requirement of an accurate geometry on one hand, and of a high computational level for the calculation of the NMR chemical shifts on the other, is a computational challenge. Thus, accurate calculation of NMR chemical shifts requires a careful combination of accurate geometry calculations for the large experimental molecules using density functional methods on one hand with accurate NMR calculations (e.g., at MP2, CCSD) for small model molecules which serve for evaluation and correction of the DFT chemical shifts<sup>33</sup> on the other.

**(b) Calculated Structures and  $\delta(^{29}\text{Si})$  Values of  $\text{RSi}\equiv\text{SiR}$  ( $\text{R} = \text{SiMe}(\text{SiH}_3)_2$ ,  $\text{SiMe}(\text{SiMe}_3)_2$ ).** These molecules, on which relatively accurate calculations can still be performed, serve as models for the larger experimental disilyne **1**, for which such calculations are not practical.

**(i) Structures.** Three rotamers of each of the two disilynes (**10–12** for  $\text{R} = \text{SiMe}(\text{SiH}_3)_2$  and **13–15** for  $\text{R} = \text{SiMe}(\text{SiMe}_3)_2$ ), which differ from each other by rotation around the  $\text{Si}^1\text{—Si}^2$  bonds, were studied. The fully optimized structures of **10–15**, constrained to  $C_i$  (**10**, **13**) and  $C_2$  (**11**, **12**, **14**, **15**) symmetry,<sup>51a</sup> are given in Table 4 (see **19** for atom numbering). There is a close



similarity in the structures of the two disilynes (i.e., **10** and **13**, **11** and **14**, **12** and **15**), indicating that the larger  $\text{SiMe}(\text{SiMe}_3)_2$  substituents in **13–15** have a small effect on the structural parameters. The  $C_i$  structures (**10** and **13**) have a planar  $\text{SiSiSiSi}$  skeleton (due to the  $C_i$  symmetry constraint), while the  $C_2$  conformations have a twisted  $\text{SiSiSiSi}$  backbone. Structures **11** and **14** show a larger deviation from planarity ( $\phi = 153.1$  and  $149.3^\circ$ , respectively) than **12** and **15** ( $\phi = 164.2$  and  $169.8^\circ$ , respectively), which also results in a slightly elongated  $\text{Si}^1\equiv\text{Si}^1$  bond of 2.11 Å in **11** and **14** relative to ca. 2.10 Å in **10** and **13** ( $C_i$  symmetry) and in **12** and **15** ( $C_2$  symmetry). The bending angle  $\theta$  in all six structures is in the range of  $46\text{--}50^\circ$ .

For each of the disilynes, the three rotamers differ in energy by less than 0.6 kcal/mol. Calculations show that PES for rotation around the  $\text{Si}^1\text{—Si}^2$  bond in **19** ( $\text{R} = \text{H}$ ; keeping  $C_2$  symmetry)<sup>51b</sup> is very flat; the highest point is the planar conformation with  $\angle\text{MeSi}^2\text{Si}^1\text{Si}^1 = 0.0^\circ$ , being only 1.7 kcal/mol above the value for the fully optimized structure (**11**). The  $\text{Si}^2\text{Si}^1\text{Si}^1\text{Si}^2$  skeleton,

(50) The energy required for this twist is only  $\sim 0.1$  kcal/mol.

(51) (a) We limit our discussion only to structures with a symmetry which maintains identical chemical shifts for the two SiR fragments. (b) Freezing the  $\text{MeSi}^2\text{Si}^1\text{Si}^1$  dihedral angles (Me refers to the C atom in the methyl group) at 0.0, 30.0, 60.0, 90.0, 120.0, 150.0, and 180.0° and optimizing all other geometric parameters.



**Table 4. Optimized Structural Parameters<sup>a</sup> of RSi≡SiR (R = SiR'<sub>3</sub>)<sup>b</sup> and Relative Energies (ΔE, kcal/mol) of Rotamers**

rotamer, method <sup>c</sup>	<i>r</i> (Si <sup>1</sup> –Si <sup>1</sup> )	<i>r</i> (Si <sup>1</sup> –Si <sup>2</sup> )	<i>r</i> (Si <sup>2</sup> –Si <sup>3</sup> )	<i>r</i> (Si <sup>2</sup> –Si <sup>4</sup> )	θ <sup>d</sup>	φ(Si <sup>2</sup> Si <sup>1</sup> Si <sup>1</sup> Si <sup>2</sup> ) <sup>e</sup>	∠MeSi <sup>2</sup> Si <sup>1</sup> Si <sup>1</sup> <sup>f</sup>	ΔE
R = SiH <sub>3</sub> (C <sub>2h</sub> )								
B3LYP/base2	2.101	2.358			49.9	180.0		
MP2/base2	2.105	2.341			50.6	180.0		
R = SiMe(SiH <sub>3</sub> ) <sub>2</sub> <sup>g</sup>								
<i>C<sub>i</sub></i> ( <b>10</b> ) <sup>h</sup>	2.104	2.364	2.361	2.361	49.6	180.0	–169.8	0.0
<i>C<sub>2</sub></i> ( <b>11</b> ) <sup>i</sup>	2.114	2.363	2.362	2.362	51.9	153.1	150.3	0.3
<i>C<sub>2</sub></i> ( <b>12</b> ) <sup>j</sup>	2.108	2.360	2.361	2.364	49.7	–164.2	–123.5	0.0
R = SiMe(SiMe <sub>3</sub> ) <sub>2</sub>								
<i>C<sub>i</sub></i> ( <b>13</b> )								
B3LYP/base2 <sup>k</sup>	2.103	2.369	2.379	2.380	47.2	180.0	–179.0	0.2
B3LYP/base3	2.098	2.369	2.382	2.382	46.6	180.0	–173.7	
<i>C<sub>2</sub></i>								
( <b>14</b> ) B3LYP/base2 <sup>l</sup>	2.111	2.367	2.378	2.382	48.6	149.3	156.7	0.0
( <b>15</b> ) B3LYP/base2 <sup>m</sup>	2.104	2.367	2.380	2.380	45.9	169.8	108.0	0.6
R = SiMe(Si- <i>t</i> -Bu <sub>3</sub> ) <sub>2</sub> ( <b>1</b> ) <sup>n</sup>								
<i>C<sub>i</sub></i> ( <b>16</b> )	2.099	2.427	2.588	2.591	34.1	180.0	–171.0	1.8
<i>C<sub>2</sub></i> ( <b>17</b> )	2.093	2.406	2.574	2.591	35.0	178.2	153.4	0.0
<i>C<sub>2</sub></i> ( <b>18</b> )	2.100	2.407	2.586	2.586	41.4	163.1	–8.4	0.0
R = Si- <i>i</i> -Pr[CH(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> ( <b>2</b> ) <sup>n</sup>								
<i>C<sub>i</sub></i> ( <b>21</b> )	2.088	2.406			44.0	180.0	2.6 <sup>o</sup>	0.0
<i>C<sub>2</sub></i> ( <b>22</b> )	2.091	2.412			43.6	177.7	–32.0 <sup>o</sup>	0.06
<i>C<sub>2</sub></i> ( <b>23</b> )	2.081	2.412			37.4	–157.9	140.9 <sup>o</sup>	2.4
exptl <sup>p</sup>	2.062	2.369			42.6	–179.4	–31.7 <sup>o</sup>	

<sup>a</sup> Fully optimized at the indicated symmetry point group. Bond lengths are given in Å and bond angles in degrees. <sup>b</sup> Atom numbering according to **19**. <sup>c</sup> The basis set designations are given in Theoretical Methods. <sup>d</sup> For the definition, see **7**. <sup>e</sup> For the definition, see **8**. <sup>f</sup> Me stands for the C atom in the methyl group. <sup>g</sup> Optimized at B3LYP/base2. <sup>h</sup> One negative eigenvalue (–6.3 cm<sup>–1</sup>). <sup>i</sup> No negative eigenvalues. <sup>j</sup> One negative eigenvalue (–11.1 cm<sup>–1</sup>). <sup>k</sup> One negative eigenvalue (–10 cm<sup>–1</sup>). <sup>l</sup> One negative eigenvalue (–9 cm<sup>–1</sup>). <sup>m</sup> No negative eigenvalues. <sup>n</sup> Optimized at B3LYP/base3. <sup>o</sup> ∠*i*-PrSi<sup>2</sup>Si<sup>1</sup>Si<sup>1</sup>. <sup>p</sup> Reference 21.

which is planar for ∠MeSi<sup>2</sup>Si<sup>1</sup>Si<sup>1</sup> = 0.0 and 180.0°, is twisted in all other rotation angles.

(ii) **δ(<sup>29</sup>Si) NMR Chemical Shifts.** The chemical shifts of both disilynes calculated using the B3LYP, BPW91, and HCTH407 DFT methods with triple-ζ basis sets are presented in Table 5. Chemical shifts using the MP2 method were calculated only for **10**, which has a planar silicon backbone.<sup>49</sup> As discussed previously for RSi≡SiR (R = SiH<sub>3</sub>), also for **10**–**15**, the chemical shift values calculated at B3LYP and BPW91 are shifted to low field relative to those calculated at HCTH407 (and also relative to the MP2 value of **10**). Furthermore, δ(<sup>29</sup>Si<sup>1</sup>) of **10** calculated at HCTH407 is in excellent agreement with the MP2 value, and therefore, we discuss below only the chemical shifts calculated at HCTH407.

We find three distinct δ(<sup>29</sup>Si<sup>1</sup>) values, each associated with one of the three structures that were located upon full geometry optimization for each of the disilynes. Thus, δ(<sup>29</sup>Si<sup>1</sup>) of the planar *C<sub>i</sub>* structures **10** and **13** are 86.9 and 87.1 ppm, respectively, those of the twisted *C<sub>2</sub>* structures **12** and **15** are at 109.9 and 107.5 ppm, respectively, and δ(<sup>29</sup>Si<sup>1</sup>) of the more strongly twisted structures **11** and **14** (which also have a longer Si<sup>1</sup>≡Si<sup>1</sup> bond) are shifted downfield significantly to 141.7 and 138.4 ppm, respectively. These very large changes in δ(<sup>29</sup>Si<sup>1</sup>) as a function of the Si<sup>2</sup>Si<sup>1</sup>Si<sup>1</sup>Si<sup>2</sup> torsion angle, spanning over 50 ppm, are in agreement with the dependence of δ(<sup>29</sup>Si) on the torsion angle φ and on *r*(Si<sup>1</sup>–Si<sup>1</sup>) shown in Figures 2b,c.

(c) **Calculated Structure and δ(<sup>29</sup>Si) Values of (t-Bu<sub>3</sub>Si)<sub>2</sub>MeSiSi≡SiSiMe(Si-*t*-Bu<sub>3</sub>)<sub>2</sub> (**1**). (i) Structures.** Carrying out full geometry optimization at the B3LYP method (constrained to the indicated symmetry

point groups),<sup>51a,52a</sup> we have located several local minima structures of **1** which are related to each other by rotation around the Si<sup>1</sup>–Si<sup>2</sup> bond. Geometric parameters (using base3) of the three lowest energy structures of **1** having *C<sub>i</sub>* (**16**) and *C<sub>2</sub>* (**17**, **18**) symmetry that were located are given in Table 4.<sup>52b</sup>

The two *C<sub>2</sub>* rotamers **17** and **18** (Chart 1; the dark and open circles represent R<sub>3</sub>Si and Me substituents, respectively) differ significantly in the MeSi<sup>2</sup>Si<sup>1</sup>Si<sup>1</sup> dihedral angle,<sup>51b</sup> being 153 and –8°, respectively (Table 4). Furthermore, **17** has an essentially planar Si<sup>2</sup>Si<sup>1</sup>Si<sup>1</sup>Si<sup>2</sup> backbone (φ = 178°), while **18** is considerably twisted (φ = 163°), leading in **18** to a slightly longer Si<sup>1</sup>≡Si<sup>1</sup> bond of 2.10 Å (Table 4). The bending angle θ is larger in **18** (41°) than in **17** (35°). Despite these structural differences, **17** and **18** have identical energies (at B3LYP/base3). The *C<sub>i</sub>* conformer (**16**) has a planar SiSiSiSi backbone (due to symmetry constraints) and is 1.8 kcal/mol higher in energy than **17** and **18**.

A schematic presentation of the optimized structure of **18** is shown in Figure 3, and we believe that it (or the structure of **17**) will correspond closely to that of **1** when it will be determined experimentally.

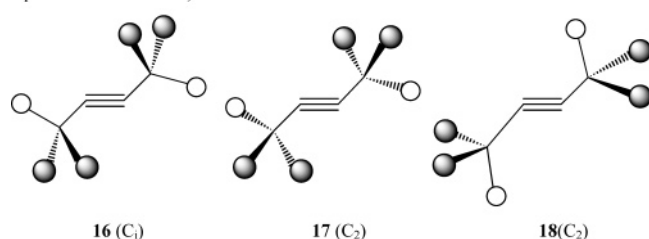
A major difference between the calculated structures of **16**–**18** and those of the smaller models **10**–**15** is the bending angle θ, which is ca. 50° in the smaller models, 34–35° in **16** and **17**, and 41° in **18**; i.e., the heavily

(52) (a) The *C<sub>2h</sub>* conformer which is 7.4 kcal/mol higher in energy is not discussed here. (b) Similar structural parameters were also obtained at B3LYP/3-21G, B3LYP/base1, and B3LYP/6-311G(d)[Si]: 3-21G[C,H]. The chemical shifts of **1** were calculated using also the optimized structures at the levels of theory mentioned above. As the optimized structures and the calculated chemical shifts at the various optimization levels are similar, we show in Table 5 only the chemical shifts calculated at the B3LYP/base3 geometry.

**Table 5.** Calculated  $\delta(^{29}\text{Si})$  Values (ppm) of  $\text{RSi}\equiv\text{SiR}$ 

rotamer, method <sup>a</sup>	$\delta(^{29}\text{Si})^b$				$\delta(^{29}\text{Si})$ corrected <sup>b,c</sup>	
	Si <sup>1</sup>	Si <sup>2</sup>	Si <sup>3</sup>	Si <sup>4</sup>	Si <sup>1</sup>	Si <sup>2</sup>
R = SiMe(SiH <sub>3</sub> ) <sub>2</sub>						
<b>C<sub>i</sub> (10)</b>						
B3LYP/base5//B3LYP/base2	123.5	−47.4	−96.1	−99.6		
BPW91/base5//B3LYP/base2	103.8	−51.1	−98.1	−102.0		
HCTH407/base5//B3LYP/base2	<b>86.9</b>	−50.0	−95.8	−99.7		
MP2/base4//B3LYP/base2	<b>88.4<sup>d</sup></b>	−63.4	−106.0	−109.4		
<b>C<sub>2</sub> (11)</b>						
B3LYP/6-311G(3d)//B3LYP/base2	190.1	−50.0	−91.1	−100.7	155.0	
HCTH407/6-311G(3d)//B3LYP/base2	<b>141.7</b>	−51.3	−90.1	−101.2		
<b>C<sub>2</sub> (12)</b>						
B3LYP/base5//B3LYP/base2	150.3	−48.8	−103.6	−90.4	115.2	
HCTH407/base5//B3LYP/base2	<b>109.9</b>	−50.5	−104.3	−89.5		
R = SiMe(SiMe <sub>3</sub> ) <sub>2</sub>						
<b>C<sub>i</sub> (13)</b>						
B3LYP/base5//B3LYP/base3	127.5	−37.3	−10.0	−9.1	92.4	−53.3
BPW91/base5//B3LYP/base3	105.3	−39.7	−10.7	−9.4	89.9	−52.0
HCTH407/base5//B3LYP/base2	90.3	−41.4	−10.3	−10.2		−54.8
HCTH407/base5//B3LYP/base3	<b>87.1</b>	−41.4	−10.9	−10.0		−54.8
<b>C<sub>2</sub> (14)</b>						
B3LYP/base5//B3LYP/base2	188.7	−38.6	−10.1	−8.7	153.6	−54.6
HCTH407/base5//B3LYP/base2	<b>138.4</b>	−42.0	−10.6	−8.6		−55.4
<b>C<sub>2</sub> (15)</b>						
B3LYP/base5//B3LYP/base2	149.7	−33.1	−8.7	−6.2	114.6	−49.1
HCTH407/base5//B3LYP/base2	<b>107.5</b>	−37.2	−9.1	−6.3		−50.6
R = SiMe(Si- <i>t</i> -Bu <sub>3</sub> ) <sub>2</sub> (1)						
<b>C<sub>i</sub> (16)</b>						
B3LYP/base5//B3LYP/base3	120.8	−24.2	35.3	39.4	<b>85.7</b>	−40.2
BPW91/base5//B3LYP/base3	103.0	−30.0	38.3	39.5	<b>87.9</b>	−42.3
HCTH407/base5//B3LYP/base3	<b>83.1</b>	−28.5	34.7	35.9		−41.9
<b>C<sub>2</sub> (17)</b>						
B3LYP/base5//B3LYP/base3	129.9	−32.2	35.4	42.6	<b>94.8</b>	−48.2
BPW91/base5//B3LYP/base3	109.8	−39.6	33.9	42.4	<b>94.4</b>	−51.9
HCTH407/base5//B3LYP/base3	<b>90.0</b>	−37.0	30.8	38.2		−50.4
<b>C<sub>2</sub> (18)</b>						
B3LYP/base5//B3LYP/base3	123.9	−26.7	37.4	39.3	<b>88.8</b>	−42.7
BPW91/base5//B3LYP/base3	99.3	−33.1	36.7	39.0	<b>83.9</b>	−45.4
HCTH407/base5//B3LYP/base4	<b>82.3</b>	−31.2	33.3	35.3		−44.6
exptl <sup>e</sup>	<b>91.5</b>	−57.0	<b>43.4</b>			
R = Si- <i>i</i> -Pr[CH(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> (2)						
<b>C<sub>i</sub> (21)</b>						
B3LYP/base5//B3LYP/base3	102.4	27.8				
HCTH407/base5//B3LYP/base3	65.4	23.3				
<b>C<sub>2</sub> (22)</b>						
B3LYP/base5//B3LYP/base3	98.4	26.4				
HCTH407/base5//B3LYP/base3	61.9	22.0				
<b>C<sub>2</sub> (23)</b>						
B3LYP/base5//B3LYP/base3	133.6	22.9				
HCTH407/base5//B3LYP/base3	93.5	19.1				
X-ray Coordinates						
B3LYP/base5	91.7	16.5				
HCTH407/base5	56.9	13.1				
exptl <sup>f</sup>	<b>89.9</b>	<b>20.7</b>				

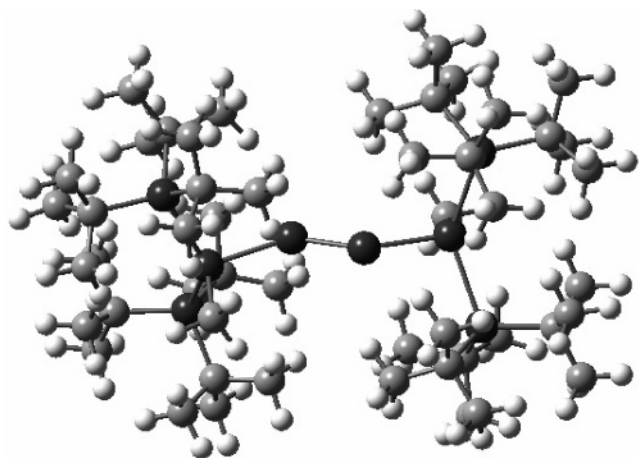
<sup>a</sup> The basis set designations are given in Theoretical Methods. <sup>b</sup> Atom numbering according to **19**. <sup>c</sup> Corrected according to the MP2 values of **10** using the formula:  $\text{MP2/base5 (corrected; target molecule)} = \text{B3LYP or BPW91/base5 (target molecule)} - \text{B3LYP or BPW91/base5(model (10))} + \text{MP2/base4(model (10))}$ . <sup>d</sup> 77.7 and 81.0 ppm at MP2/6-31G(d) and MP2/6-311G(d), respectively. <sup>e</sup> Reference 19. <sup>f</sup> Reference 21.

**Chart 1**

substituted disilynes are less strongly bent. Another significant difference is found in the  $\beta\text{-Si}^2\text{-Si}^3$  and

$\beta\text{-Si}^2\text{-Si}^4$  bond lengths, which are ca. 2.59 Å in **16–18** (R = SiMe(Si-*t*-Bu<sub>3</sub>)<sub>2</sub>) and 2.36–2.38 Å in the smaller  $\text{RSi}\equiv\text{SiR}$  (R = SiMe(SiH<sub>3</sub>)<sub>2</sub>, SiMe(SiMe<sub>3</sub>)<sub>2</sub>) (Table 4). A similarly long  $\beta\text{-Si-Si}$  bond of 2.55 Å was measured by X-ray crystallography in **3**.<sup>19</sup> These geometrical differences can be attributed to the large steric repulsion caused by the “mega-silyl” SiMe(Si-*t*-Bu<sub>3</sub>)<sub>2</sub> substituent.

As discussed above, such differences in geometry may significantly affect  $\delta(^{29}\text{Si})$ , and therefore, a reliable theoretical prediction of the chemical shifts of **1** has to be based on an actual calculation of **1**, as predictions based on the calculated geometry of smaller model systems may lead to erroneous calculated chemical



**Figure 3.** Stick and ball representation of the optimized structure (B3LYP/base3) of RSi≡SiR (**18**; R = SiMe(Si-*t*-Bu)<sub>2</sub>): (black balls) silicon atoms; (dark gray balls) carbon atoms; (light gray balls) hydrogens.

shifts. For a large molecule such as **1**, calculation of the geometry and of the chemical shifts can be carried out only by DFT methods.

(ii) <sup>29</sup>Si NMR Chemical Shift. The NMR chemical shifts of **1** that were calculated using B3LYP/base5, BPW91/base5, and HCTH407/base5 are presented in Table 5.<sup>52b</sup> As in other cases, the B3LYP and BPW91 chemical shift values are shifted downfield relative to the HCTH407/base5 values. When the B3LYP and BPW91 values are corrected according to the calculated MP2 values of **10**,<sup>53</sup> they are quite similar to the HCTH407 values (Table 5). As we believe that the HCTH407 functionals are more reliable than those calculated at either B3LYP or BPW91 (see above), we will focus our following discussion on the chemical shifts calculated using the HCTH407 functional.

δ(<sup>29</sup>Si) chemical shifts of **1** in conformations **16–18** (using geometries optimized at B3LYP/base3) are 83.1, 90.0, and 82.3 ppm at HCTH407/base5. The differences in the calculated chemical shifts of these three structures are relatively small, despite their very different structural parameters. The chemical shifts of the singly bonded silicon atoms (Si<sup>2</sup>), in **16–18** (Table 5) and in the model disilynes **6** (Table 1) and **10–15** (Table 5), are hardly affected by the choice of the DFT functional, in contrast to the significant dependence on the DFT method of δ(<sup>29</sup>Si) of the triply bonded silicon atoms.

What is the theoretically predicted chemical shift of the triply bonded silicon atoms in **1**? Taking into consideration the calculated values given in Table 5 as well as the expected fast rotation, on the NMR time scale, about the Si<sup>1</sup>–Si<sup>2</sup> bonds (the calculated rotation barrier is 2.6 kcal/mol), a single averaged NMR chemical shift for **1** at 88.0 ± 5 ppm is predicted. This calculated value is in excellent agreement with the experimentally measured chemical shift of 91.5 ppm.

In view of the good agreement between the calculated and experimental chemical shifts of the triply bonded Si atoms of **1** (and also of the α-Si atoms<sup>54</sup>) and the fact that the predicted <sup>29</sup>Si NMR spectra of possible iso-

mers<sup>55</sup> or of its precursor **3** (eq 1)<sup>56</sup> are very different from those of **1**, we strongly support Wiberg's conclusion<sup>19</sup> that the product isolated from reaction 1 is indeed RSi≡SiR (R = SiMe(Si-*t*-Bu)<sub>2</sub> (**1**)).

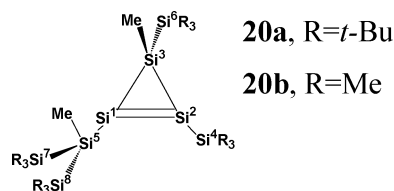
(d) Calculated Chemical Shifts of *i*-Pr-(Me<sub>3</sub>Si)<sub>2</sub>CH<sub>2</sub>SiSi≡SiSi(CH(SiMe<sub>3</sub>)<sub>2</sub>)<sub>2</sub>*i*-Pr (**2**). Three fully optimized structures of **2**, within the constraints of C<sub>i</sub> symmetry (**21**) and C<sub>2</sub> (**22** and **23**) symmetry, which are related by rotation around the Si<sup>1</sup>–Si<sup>2</sup> bond were located,<sup>51a</sup> and their structures are given in Table 4.<sup>57</sup> **21** and **22**, which have identical energies, have a planar SiSiSiSi backbone (Table 4) and their structural parameters are in good agreement with the experimental structure of **2**. In **23**, which is 2.3 kcal/mol less stable than **21** and **22**, the *i*-PrSi<sup>2</sup>Si<sup>1</sup>Si<sup>1</sup> (*i*-Pr stands for the C atom in the *i*-Pr group) torsion angle is 141° (compared to –32° in **22** and in the experimental structure of **2**). Its SiSiSiSi skeleton is not planar, but it is twisted around the Si≡Si bond with a SiSi≡SiSi torsion angle of 158° and the bending angle θ is 37°, slightly smaller than in **22**. All three optimized structures (**21–23**) have Si≡Si and Si–SiR bonds slightly longer than those observed in the X-ray structure of **2** (Table 4).<sup>21,57</sup>

The NMR chemical shifts of structures **21–23** were calculated at B3LYP/base5 and at HCTH407/base5 using the B3LYP/base3 optimized geometries as well as the experimental X-ray coordinates. The calculated and experimental<sup>21</sup> δ(<sup>29</sup>Si<sup>1</sup>) and δ(<sup>29</sup>Si<sup>2</sup>) values are presented

(54) Two weak NMR signals at –57 and 43.4 ppm were also observed experimentally. They were assigned to the Si<sup>2</sup> and Si-*t*-Bu atoms, respectively. The calculated chemical shifts of Si<sup>2</sup> (averaged over all conformations) is –45 ± 5 ppm, and those for Si<sup>3</sup> and Si<sup>4</sup> are 35 ± 3 and 39 ± 3 ppm, respectively, in relatively good agreement with those measured experimentally.

(55) The chemical shifts of several possible isomers of **1** were calculated for related smaller model systems. However, their calculated NMR chemical shifts were not consistent with that of **1**; for example: (a) Wiberg suggested that **1** isomerizes to trisilylcyclopropene **20a** upon heating.<sup>19b</sup> The calculated (HCTH407/base5//B3LYP/base3) δ(<sup>29</sup>Si) signals of **20b** (a model of **20a**), which is 13.1 kcal/mol (B3LYP/base3) more stable than disilyne **15**, are 97.1, 94.9, –75.4, –3.7, –59.4, –14.2, –9.7, and –9.0 ppm for Si<sup>1</sup>–Si<sup>8</sup>, respectively. Although the chemical shifts of the doubly bonded silicon atoms in **20b** are close to those calculated for the triply bonded silicon atoms in RSi≡SiR, R = SiMe(SiMe<sub>3</sub>)<sub>2</sub> (**13**, **15**), the full NMR spectrum of **20b** is predicted to be very different. (b) Isomerization of **1** to the silylidene R<sub>2</sub>Si<sup>1</sup>=Si<sup>2</sup>: is unlikely, as it is 31 kcal/mol less stable than **1** (B3LYP/base3).<sup>20a</sup> In any case, δ(<sup>29</sup>Si<sup>1</sup>) and δ(<sup>29</sup>Si<sup>2</sup>) in R<sub>2</sub>Si<sup>1</sup>=Si<sup>2</sup> are calculated to be 216.7 and 1047.3 ppm, respectively, very different from those of **1**.

(56) The geometry of **3** was optimized at the planar C<sub>2h</sub> symmetry and at C<sub>i</sub> symmetry, using the B3LYP/3-21G(d), B3LYP/6-31G(d), and B3LYP/6-311G(d)[Si, Cl]:3-21G[C, H] levels of theory. The optimized C<sub>2h</sub> and C<sub>i</sub> structures are nearly identical with the experimental<sup>19</sup> structure of **3**. The calculated δ(<sup>29</sup>Si) values of the doubly bonded silicon atoms in **3** (C<sub>2h</sub>) are as follows (in ppm): 180 (B3LYP/6-311G(3d)[Si, Cl]:3-21G[C, H]), 163 (after MP2 correction)<sup>53</sup> and 172 (HCTH407/6-311G(3d)[Si, Cl]:6-31G(d)[C, H]//B3LYP/6-311G(d)[Si, Cl]:6-31G(d)[C, H]). All of these values are shifted downfield considerably relative to **1**. The calculated chemical shift of **3** awaits experimental verification.



(57) The structure of **2** was optimized at B3LYP using the following basis sets for the silicon atoms: 3-21G(d), 6-31G(d), 6-311G(2d), 6-311G(2df), 6-311G(3d), 6-311G(3df), and 6-311+G(3df); 6-31G(d) was used for C and H. Interestingly, the best agreement with the experimental structure is obtained at B3LYP/3-21G(d); e.g., r(Si≡Si) = 2.072 Å (3-21G(d)), 2.091 Å (6-311G(d)), 2.062 Å (experimental). The optimized structures at all other levels are very similar. For detailed structures see Table 2S in the Supporting Information.

(53) Using the following additivity scheme: MP2/base5 (corrected; target molecule) = B3LYP or BPW91/base5 (target molecule) – B3LYP or BPW91/base5 (model) + MP2/base4 (model).



in Table 5. The  $\delta(^{29}\text{Si}^1)$  values calculated at HCTH407, for **2** (using its experimental X-ray coordinates) and for the optimized structures **21** and **22**, are in the range of 57–65 ppm. These values are shifted upfield by ca. 25–35 ppm compared to the measured value in  $d_6$ -benzene solution of 89.9 ppm (Table 5).<sup>58</sup> The  $\delta(^{29}\text{Si}^1)$  value of **23**, which has a twisted skeleton, is 93.5 ppm (at HCTH407/base5), shifted downfield (relative to that of **21** and **22** and to the calculated  $\delta(^{29}\text{Si}^1)$  of **2** using its experimental structure) as expected from its twisted structure (Figure 2b). This value is close to the experimental chemical shift, but it is based on a geometry which is very different from that observed experimentally.<sup>59</sup>  $\delta(^{29}\text{Si})$  values of the  $\alpha$ -silicons ( $\text{Si}^2$ ) and  $\delta(^{29}\text{Si}-\text{Me}_3)$  in **21–23** are in good agreement with the experimental values (Table 5).<sup>60</sup>

What is the reason for the significant disagreement of 25–35 ppm in the  $\delta(^{29}\text{Si}^1)$  value of **2** between theory and experiment? We may question the reliability of the HCTH407 results, but the excellent experimental–computational agreement for disilenes (Table 2) and the good agreement between the chemical shifts calculated at HCTH407 and those calculated at MP2 and CCSD for model disilenes and disilynes (Table 1, Table 5)<sup>58</sup> leads us to believe that the HCTH407 computational results are reliable. However, the possibility of a small computational error cannot be ruled out. A second possibility is that, due to the very flat PES for rotation around the  $\text{Si}^1-\text{Si}^2$  bond and other structural deformations (see above), in solution **2** has a highly dynamic structure spanning over conformations with highly twisted structures, causing on the average a downfield shift in  $\delta(^{29}\text{Si}^1)$ . Before drawing more definite conclusions as to the reasons for the computational–experimental discrepancy, more experiments, e.g., solid-state NMR and dynamic solution NMR studies of **2**, as well as a computational study of solvent effects on the chemical shifts of disilynes are recommended. We hope that this paper will stimulate such studies.

## Conclusions

The chemical shifts of the triply bonded silicon atoms in disilynes are shifted to higher fields (lower  $\delta(^{29}\text{Si})$  values) relative to analogous doubly bonded silicon atoms in disilenes. In  $\text{RSi}=\text{SiR}$ , silyl substitution shifts  $\delta(^{29}\text{Si})$  of the triply bonded silicon atoms considerably

to lower fields relative to  $\text{R} = \text{H}$ ,  $\text{CH}_3$ , similarly to their effect in disilenes. Small geometry changes in the  $\text{RSi}=\text{Si}$  bending angle, rotating of the R substituents about the  $\text{Si}=\text{Si}$  bond, and changes in the  $\text{Si}=\text{Si}$  bond length cause significant changes in  $\delta(^{29}\text{Si})$ .

The calculated chemical shifts strongly depend on the theoretical method. At the DFT B3LYP level  $\delta(^{29}\text{Si})$  is shifted to lower fields (higher  $\delta(^{29}\text{Si})$  values) relative to those calculated at the ab initio MP2 or CCSD levels. This is especially pronounced for silyl-substituted disilynes. Excellent agreement with the MP2 and CCSD  $\delta(^{29}\text{Si})$  values of  $\text{RSi}=\text{SiR}$  as well as with the experimental  $\delta(^{29}\text{Si})$  values measured for disilenes is obtained with the HCTH407 GGA functional. The size of the basis set has a large effect on the calculated chemical shifts with all the tested DFT methods but has a relatively small effect at MP2 and CCSD. On the basis of our study, the recommended method for calculating the chemical shifts of triply bonded silicon atoms in large disilynes is DFT with the HCTH407 functional and a triple- $\zeta$  basis set augmented with three sets of d-polarization functions.

The calculated  $\delta(^{29}\text{Si})$  chemical shift of the triply bonded silicon atoms in  $(t\text{-Bu}_3\text{Si})_2\text{MeSiSi}=\text{SiSiMe}(\text{Si}t\text{-Bu}_3)_2$  (**1**) is  $88 \pm 5$  ppm, in very good agreement with the experimentally observed chemical shift of 91.5 ppm, strongly supporting the assignment of the product obtained in reaction 1 to disilyne **1**.<sup>19</sup> The calculated  $\delta(^{29}\text{Si}^1)$  values (at HCTH407/base5) for  $i\text{-Pr}(\text{Me}_3\text{Si})_2\text{-CH}_2\text{SiSi}^1=\text{Si}^1\text{Si}(\text{CH}(\text{SiMe}_3)_2)_2i\text{-Pr}$  (**2**) are ca. 60 ppm, shifted by 30 ppm to higher field relative to the experimental value (in solution) of 89.9 ppm.<sup>21</sup> One obvious reason for this experimental–theoretical discrepancy might be a failure of the HCTH407 method for **2**. Another, more interesting possibility is that the discrepancy is due to different structures of **2** in solution and in the solid state. This intriguing possibility awaits experimental testing.

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**Supporting Information Available:** Table 1S, giving calculated  $\sigma(^{29}\text{Si})$  (ppm) chemical shielding constants of TMS and of the triply bonded silicon atoms in  $\text{RSi}=\text{SiR}$ , Table 2S, giving optimized geometries of structures **21** and **22** using B3LYP with various basis sets, and Table 3S, giving Cartesian coordinates and total energies of all structures discussed in this paper. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(58)  $\delta(^{29}\text{Si}^1)$  in  $\text{Me}_3\text{SiSi}^1=\text{Si}^1\text{SiMe}_3$  ( $C_2$  symmetry), which models **2**, is 85.5 ppm at HCTH407/6-311G(3d), in excellent agreement with the value of 86.3 ppm calculated at MP2/6-311G(3d). The corresponding B3LYP/6-311G(3d) chemical shift is very different: 120.8 ppm. These results support our prediction that the HCTH407 functional produces reliable NMR chemical shifts for disilynes.

(59)  $\delta(^{29}\text{Si}^1)$  values calculated for **2** with the B3LYP method (which we believe to be less accurate for NMR calculations of disilynes than the HCTH407 functional) are much closer to the experimental value, being 91.7 ppm (**2** using the X-ray coordinates), 102.4 ppm (**21**), and 98.4 ppm (**22**). We believe that this agreement might be fortuitous.

(60) The experimental NMR signal for  $\text{Si-Me}_3$  are at 0.0 and  $-0.3$  ppm, and the calculated (HCTH407/base5)  $\delta(^{29}\text{Si-Me}_3)$  chemical shifts in **22** are  $-0.6$ ,  $0.5$ ,  $0.3$ , and  $0.0$  ppm.