The Trichlorovinylsilane/*tert*-Butyllithium Reagent—A Source for Transient Silenes?

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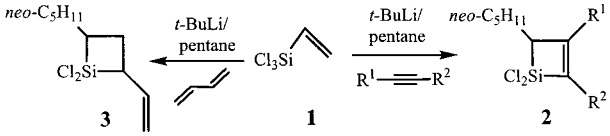
Summary: Quantum-mechanical calculations suggest that silenes are probably not involved as intermediates in the reaction of the trichlorovinylsilane/t-BuLi reagent with alkynes. Instead, the product **7** *is obtained via a carbometalation−elimination reaction.*

The reaction of trichlorovinylsilane (**1**) with *t*-BuLi in the presence of suitable scavengers provides a facile approach to silaheterocycles, i.e., **2** and **3** (eq 1), which serve as precursors to novel silicon-containing organic molecules with new, exciting properties.[1]



(1)

The formation of silaheterocycles in these reactions was generally rationalized by the intermediate formation of a silene, $Cl_2Si{=}C(H)CH_2Bu$-*t* (**4**), which is trapped to produce the final products;[2] e.g., it was assumed that the [4 + 2] cycloaddition products, produced in the reaction of transient **4** with reactive dienes, are formed via a Diels−Alder type reaction.[2a] The formation of the [2 + 2] cycloadducts **2** and **3** in the reaction of **1**/*t*-BuLi with alkynes and alkenes, respectively, was rationalized by the relaxation of the orbital symmetry requirements due to the highly polar nature of the Si=C bond in **4** (eq 1).[2b,3] However, despite considerable efforts all attempts to isolate or even to obtain spectroscopic evidence for the intermediacy of silenes, e.g., **4**, in reactions of type 1 were unsuccessful.[2−6]

Is silene **4** indeed an intermediate in the reaction of *t*-BuLi with **1**? The results of our quantum-mechanical calculations reported below do *not* support the intermediacy of **4**. Instead the calculations reveal the *existence of a competing alternative reaction path* leading to the observed cyclic products but *bypassing the silene*.

To gain a better understanding of the mechanism of reaction 1, we studied several theoretically possible reaction paths for a closely related *model reaction*, eq 2. The initial step of reaction 1 is most likely a carbometalation reaction of *t*-BuLi with **1**, yielding $Cl_3SiCH(Li)CH_2Bu$-*t* (**5**), as demonstrated recently for fluoroalkynylsilanes.[7] Reaction 2 models the experimentally known reactions of *t*-BuLi with trichlorovinylsilane (**1**) in the presence of disubstituted alkynes,[8] yielding the corresponding 1-silacyclobutenes in high yields[3a] (i.e., Cl_3SiCH_2Li (**6**) models **5** and acetylene models the disubstituted acetylenes).

$$\mathbf{6} + HC{\equiv}CH \rightarrow \mathbf{7} + LiCl \qquad (2)$$

The quantum-mechanical calculations were carried out using hybrid-density functional methods (DFT)[9a,b] with the B3LYP[9c,d] functional as well as at the MP4 level of ab initio theory.[10,11] The calculated structures

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(1) (a) An overview on the chemistry of the **1**/*t*-BuLi mixture is given in: Müller, T.; Ziche, W.; Auner, N. In *The Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2, Chapter 16. (b) Auner, N. *J. Prakt. Chem.* **1995**, *337*, 79. (c) Auner, N. *Z. Anorg. Allg. Chem.* **1988**, *558*, 55. (d) Pernisz, U.; Auner, N.; Backer, M. In *Silicones and Silicone-Modified Materials*; Clarson, S. J., Fitzgerald, J. J., Owen, M. J., Smith, S. D., Eds.; ACS Symposium Series 729; American Chemical Society: Washington, DC, 1998; Chapter 7. (e) Pernisz, U.; Auner, N. In *Organosilicon Chemistry IV, From Molecules to Materials*; Auner, N., Weis, J., Eds.; Wiley-VCH: Weinheim, Germany, 2000; p 505.

(2) (a) Auner, N. *J. Organomet. Chem.* **1988**, *353*, 275. (b) Auner, N.; Heikenwälder, C.-R.; Wagner, C. *Organometallics* **1993**, *12*, 4135.

(3) (a) Auner, N.; Seidenschwarz, C.; Herdtweck, E. *Angew. Chem.* **1991**, *102*, 1172; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1151. (b) Sewald, N.; Ziche, W.; Wolff, A.; Auner, N. *Organometallics* **1993**, *12*, 4123.

(4) (a) Auner, N. Habilitationschrift, Münster, Germany, 1988. (b) However, recently Couret et al. reported on the synthesis of the sterically protected kinetically stable $Mes_2Si{=}CHCH_2Bu$-*t* (Mes = 2,4,6-$Me_3C_6H_2$) by the reaction of $Mes_2FSiCH{=}CH_2$ with *t*-BuLi: Delpon-Lacaze, G.; Couret, C. *J. Organomet. Chem.* **1994**, *480*, C14. Delpon-Lacaze, G.; de Battisti, C.; Couret, C. *J. Organomet. Chem.* **1996**, *514*, 59.

(5) Mixing chlorosilane **1** with *t*-BuLi at −78 °C using *n*-pentane or toluene-d_8 as solvent in a NMR tube showed only signals of the starting materials. Raising the temperature to −20 °C caused LiCl elimination and broadening of the signals in the ^1H, ^{13}C, and ^{29}Si NMR spectra. In a temperature range of −10 to 20 °C the spectra showed the formation of a complex product mixture, and assignment of any of the signals to the lithiated compound **5** or to silene **4** was not possible. The addition of *t*-BuLi to **1** in THF-d_8 at −78 °C caused an immediate change of the color to orange-red, and the NMR signals, including that of the ^7Li nucleus, became very broad. No LiCl elimination could be observed, even after prolonged time at room temperature. Removal of the solvent resulted in LiCl elimination (or crystalization) and the formation of disilacyclobutane $(Cl_2SiCH(CH_2Bu$-*t*$))_2$, the formal dimer of **4**.

(6) Furthermore, when it is treated with *t*-BuLi, **1** behaves differently from vinylchlorosilanes which have other substituents at silicon; e.g., $(H_3C)_2ClSiCH{=}CH_2$/*t*-BuLi does not react with alkynes.[3] The "$Cl_2Si{=}CHCH_2Bu$-*t*" equivalent also produces a much higher [2 + 2]/[4 + 2] product ratio than other silenes.[1a]

(7) Trommer, M.; Miracle, G. E.; Eichler, B. E.; Powell, D. R.; West, R. *Organometallics* **1997**, *16*, 5737.

(8) Since the experimental systems included only disubstituted acetylenes,[3a] we ignore in the calculations the reaction path **6** + $HC{\equiv}CH \rightarrow Cl_3SiCH_3 + LiC{\equiv}CH$, which with $HC{\equiv}CH$ (or with monosubstituted acetylenes) is energetically more favorable than the process shown in reaction 2.

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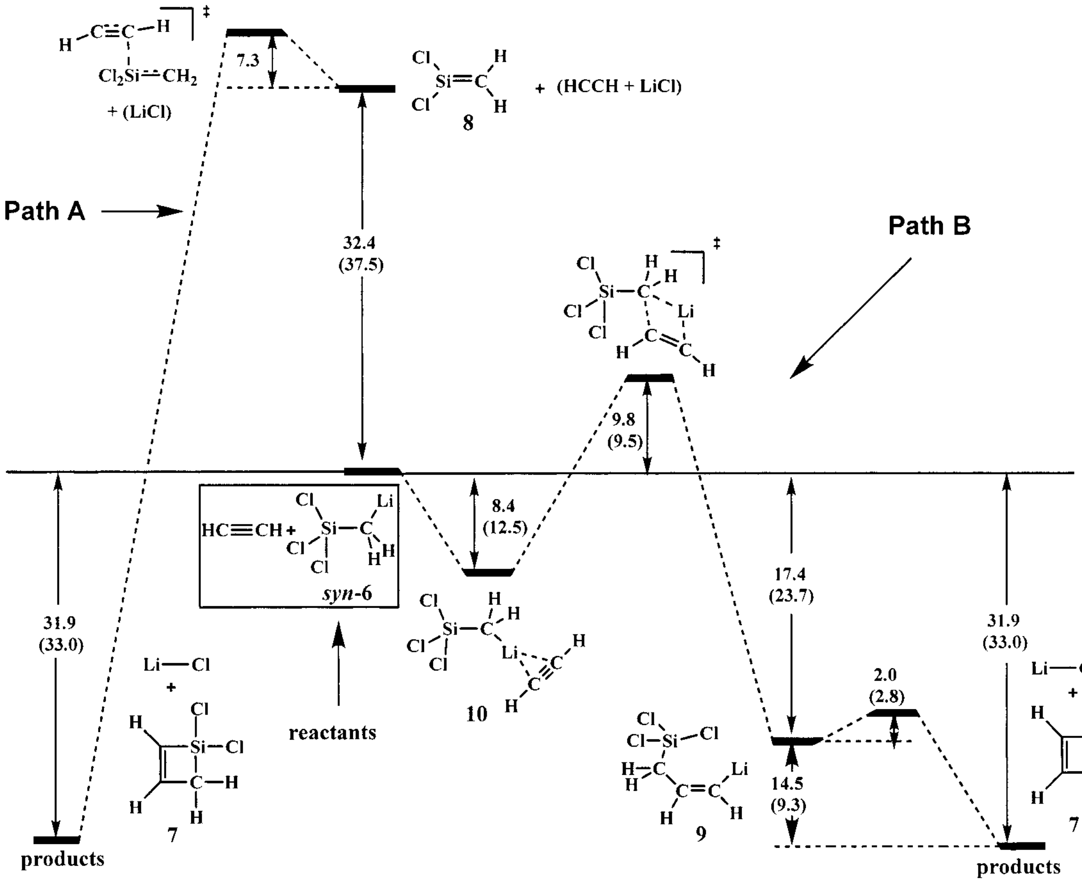
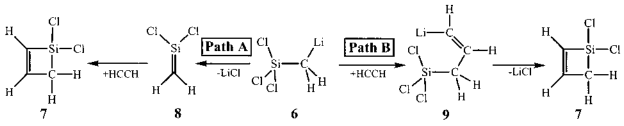


Figure 1. Calculated relative energies (kcal mol^{-1}) of reaction pathways A and B for the reaction of **6** with acetylene (Scheme 1), at the levels of theory B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) + ZPE and MP4/6-31+G(d)//B3LYP/6-311+G-(d,p) + ZPE (values given in parentheses). In path A the biradical intermediates which exist between **TS(8/7)** and the products[15] are not shown.

Scheme 1



of all compounds of interest and their relative and absolute energies are reported in the Supporting Information. For the discussion we use the B3LYP/6-311+G-(d,p)//B3LYP/6-311+G(d,p) energies (corrected for unscaled zero-point energy differences (ZPE)).[12] We note that the MP4(SDTQ)/6-31+G(d)//B3LYP/6-311+G(d,p) results are very similar (see Figure 1), and thus the level of theory used does not affect our major conclusions.

Two reaction paths leading from the initially formed (α-silylmethyl)lithium **6** to the product **7** were studied (Scheme 1): (1) path A, which involves in the first step elimination of LiCl to produce 1,1-dichlorosilene **8**, followed by a [2 + 2] cycloaddition of acetylene, producing silacyclobutane **7**; (2) path B, which involves a nucleophilic addition of **6** to acetylene, yielding the (γ-silylalkenyl)lithium **9**[8] (i.e., carbometalation).[13] **9** undergoes an intramolecular 1,4-LiCl elimination coupled with ring closure to produce **7**. The calculated energies of both reaction paths are shown in Figure 1.

Reaction 2 is exothermic by 31.9 kcal mol^{-1}. The calculations reveal, however, a dramatic difference between reaction pathways A and B. Path A involves very high reaction barriers, while along path B the calculated reaction barriers are small (Figure 1). Thus, elimination of LiCl from **6** and generation of 1,1-dichlorosilene (**8**) is endothermic by 32.4 kcal mol^{-1}.[14]

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(9) (a) Parr, R. G.; Yang W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989. (b) Koch, W.; Holthausen M. C. *A Chemist's Guide to Density Functional Theory*; Wiley-VCH: Weinheim, Germany, 2000. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (d) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(10) (a) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986. (b) Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91.

(11) (a) Calculations were performed using the Gaussian 94 program: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision B.1–E.1; Gaussian, Inc.: Pittsburgh, PA, 1995. (b) The geometries of all species were fully optimized using the B3LYP[9c,d] method and the polarized 6-311+G(d,p) basis set.[11a]

(12) For reactions involving biradical intermediates, B3LYP energies are expected to be more reliable than MP4 energies; see: Goldstein, E.; Beno, B.; Houk, K. N. *J. Am. Chem. Soc.* **1996**, *118*, 6036.

(13) Similar additions of alkyllithium to alkynes have been reported; see: (a) Wakefield, B. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 7, p 2. (b) Knochel, P. In *Comprehensive Organic Synthesis*; Trost, B., Fleming, I., Eds.; Pergamon: New York, 1991; Vol. 4, p 865. (c) Marek, I.; Normant, J. F. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P., Eds.; Wiley-VCH: Weinheim, Germany, 1998; p 271.

(14) We could not locate the TS for this process. Apparently, the reverse reaction proceeds without a barrier.

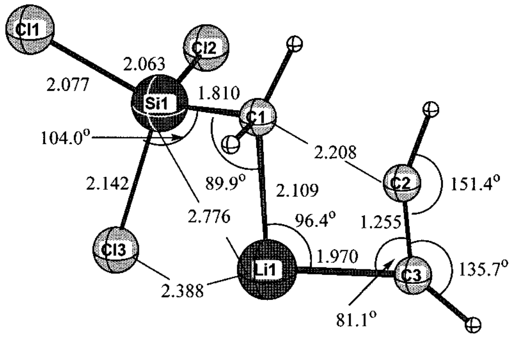

Figure 2. Calculated geometry at the B3LYP/6-311+G-(d,p) level of the transition state connecting **10** and **9**, **TS-(10/9)**. Bond lengths are given in Å and bond angles in deg.

The subsequent [2 + 2] cycloaddition of **8** to acetylene involves an additional energy barrier of 7.3 kcal mol^{-1}, and it proceeds via a rate-determining C−Si bond formation and biradical intermediates[12,15] (not shown in Figure 1). Thus, the overall barrier for the formation of **7** along path A is 39.7 kcal mol^{-1}.

Along reaction path B the energy barriers are much smaller. The first step involves the barrierless exothermic (by 8.4 kcal mol^{-1}) complexation of acetylene to the lithium atom of **6** to yield **10**. The second step, the highest point along path B, involves the formation of a new C−C bond via a concerted carbometalation of the complexed acetylene (i.e., **10** → **9**). However, surprisingly, the carbometalation transition state (**TS**(**10**/**9**)) is only 9.8 kcal mol^{-1} higher in energy than the reactants and only 18.2 kcal mol^{-1} higher in energy than **10**. The final step, the elimination of LiCl from **9**, is exothermic by 14.5 kcal mol^{-1}, and involves a barrier of only 2.0 kcal mol^{-1}.

The calculated geometry of **TS(10/9)** (Figure 2) shows that while the new C^1-C^2 bond is only weakly developed ($r(C^1-C^2) = 2.208$ Å vs 1.525 Å in **9**), the acetylene moiety is already significantly distorted (the HC^3C^2 and HC^2C^3 bond angles are 135.7 and 151.4°, respectively, while in **10** they are nearly linear) and the acetylenic $r(C^2-C^3)$ of 1.255 Å is intermediate between a triple and a double bond (1.202 Å in **10**, 1.344 Å in **9**). The forming C^3-Li bond is significantly shortened (1.970 Å) and the C^1-Li bond is somewhat elongated (2.109 Å) compared to **10** (2.388 and 2.068 Å, respectively).

Thus, reaction path B is 29.9 kcal mol^{-1} more favorable than reaction path A, which proceeds via a 1,1-dichlorosilene (**8**).[16] In conclusion, according to the calculations, the reaction of *t*-BuLi with vinyltrichlorosilane in the presence of alkynes[8] proceeds via path B, which *does not involve a silene as an intermediate.*

Are these theoretical conclusions, which apply directly only to the isolated reactants in the gas phase, relevant also to the reactions which were carried out in pentane or toluene solutions?[1−5] First, in solution the energy gained in the formation of **10** can be rapidly distributed to the environment and the complex can reach its vibronic ground state. However even if this effect is included, the overall activation barrier along path B, i.e., **10** → **9**, of 18.2 kcal mol^{-1} is still 21.5 kcal mol^{-1} lower than that along path A.[16] Previous theoretical studies of reactions of monomeric and dimeric RLi compounds with unsaturated compounds support the conclusion that in such reactions solvent effects are not significant on going from the gas phase to pentane solution.[17] In particular, formation of strong complexes between the reaction intermediates and solvent molecules can be excluded.[17] Another factor is the known tendency of organolithium compounds (and LiCl) to form aggregates in nonpolar solvents.[18] The calculated dimerization energy of **6** is indeed substantial, 25.5 kcal mol^{-1}. However, also this factor is not expected to alter our major conclusion, because both reaction paths A and B are retarded to a similar extent by the formation of aggregates of **6**.[19]

In conclusion, quantum-mechanical calculations suggest that a "trichlorovinylsilane/*t*-BuLi mixture" is *not* necessarily a source of 1,1-dichloroneopentylsilene (**4**), in its reactions with alkynes (and by analogy also with dienes). A competing reaction path which is lower in energy exists, and it involves nucleophilic addition of the initially formed lithiated species to the alkyne (carbometalation).[20] The balance between the two reaction paths may change as a function of the substituents at silicon, the halogen, the alkyllithium reagent used, the solvent, and the reaction conditions. Additional theoretical calculations as well as new experimental efforts to detect the intermediates in these reactions are in progress.

Acknowledgment. This paper is dedicated to Professor Ruben Pauncz, a pioneer in quantum chemistry, on the occasion of his 80th birthday. We thank Prof. I. Marek (Technion) and Prof. K. N. Houk (UCLA) for many helpful discussions. This research was supported by the German-Israeli Foundation for Scientific Research and Development (GIF), the Minerva Foundation in Munich, and the Fund for Promotion of Research (Technion). T.M. thanks the DFG for a scholarship.

Supporting Information Available: Tables giving total energies (hartrees) and *xyz* coordinates for all calculated compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] The concerted cycloaddition requires 12.5 kcal mol^{-1}, and the barrier for the biradical pathway with initial C−C bond formation requires 18.1 kcal mol^{-1}. Detailed discussion will be presented elsewhere.

[16] Entropy has a minor effect on the two reaction paths.

[17] See, for example: (a) Kaufmann, E.; Schleyer, P. v. R.; Houk, K. N.; Wu, Y. D. *J. Am. Chem. Soc.* **1985**, *107*, 5560. (b) Houk, K. N.; Schleyer, P. v. R.; Kaufmann, E.; Clark, T. *J. Am. Chem. Soc.* **1985**, *107*, 2821. (c) Stork, G.; Polt, R. L.; Li, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1988**, *110*, 8360. (d) Nakamura, E.; Miyachi, Y.; Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1992**, *114*, 6686. (e) Nakamura, M.; Nakamura, E.; Koga, N.; Morokuma, K. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1789.

[18] (a) Wardrell, J. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 1, p 43. (b) Spase, A.-M., Schleyer, P. v. R., Eds. *Lithium Chemistry*; Wiley: New York, 1995.

[19] Aggregation of LiCl may lower the energy barrier along path A (i.e. for the step **6** → **8**), but again the available data indicate that the change will not be sufficiently large to favor path A over path B.

[20] We use a simple theoretical "gas-phase"-type model to describe a complex process in solution and our conclusions are therefore subject to uncertainty, especially regarding factors not included in the computational model. However, the calculations point clearly to the existence of a favorable pathway bypassing the silene.