Do Bulky Aryl Groups Make Stable Silicon−Silicon Triple Bonds Synthetically Accessible?

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Received September 25, 2000

Summary: Effects of bulky aryl groups on silicon−silicon triple bonds have been investigated using density functional and ONIOM methods to make disilynes synthetically accessible and isolable in a stable form.

Since the first isolation of a stable disilene ($R_2Si{=}SiR_2$) in 1981,[1] a variety of synthetic methods have been developed for silicon−silicon double bonds.[2] However, stable disilynes ($RSi{\equiv}SiR$) are still unknown despite several attempts.[3] It has been repeatedly calculated that the parent $HSi{\equiv}SiH$ with a trans-bent structure is not the global minimum on the potential energy surface and undergoes facile isomerization to more stable 1,2-H shifted and bridged isomers.[4] Accordingly, mono- and dibridged structures have been detected and characterized using spectroscopic methods.[5] Upon substitution, these bridged structures are destabilized for steric reasons and tend to disappear from the potential energy surface of Si_2R_2 as R becomes bulkier.[6] Therefore, it is important to prevent the 1,2-R shift in $RSi{\equiv}SiR$ to maintain a disilyne structure.

It is an interesting subject whether disilynes can be synthesized as stable compounds when they are properly substituted. By providing theoretical insight into the nature of silicon−silicon triple bonding, we have recently investigated the effects of silyl substitution and found that bulky electropositive silyl groups such as $SiDep_3$ (Dep = 2,6-diethylphenyl) play an important role in making disilynes a viable synthetic target.[7] We now report the effects of bulky aryl groups. Geometries were optimized with density functional theory at the B3LYP level[8] using the Gaussian 98 program.[9] Because of the size of molecules, the 3-21G* basis set[10] was employed. The reliability of B3LYP/3-21G* calculations was calibrated in our previous study.[7]

Among aryl groups, 2,6-bis(2,4,6-triisopropylphenyl)-phenyl (denoted hereafter simply as Ar*) has served as a representative bulky substituent useful for the formation and stabilization of multiply bonded systems, as illustrated in several examples.[2c] By utilizing the bulky Ar* group, a formal lead analogue of alkynes, Ar*PbPbAr*, has very recently been synthesized.[11] A possible triple bond between gallium atoms has been also realized with the Ar* group in Na_2[Ar*GaGaAr*].[12]

The optimized structure of Ar*Si≡SiAr* is shown in Figure 1a, which has C_2 symmetry. The central Si−Si bond is well protected from the attack of reactive reagents by the two bulky Ar* groups. The Si−Si bond distance and Si−Si−C bond angle were 2.094 Å and 133.5°, respectively. It is noteworthy that the Si−Si distance is significantly shorter than the Si−Si double-bond distances (2.14−2.25 Å) determined up to now from the X-ray crystal structures of disilenes,[2] suggesting that Ar*Si≡SiAr* has triple-bond character between the two silicon atoms. This contrasts with the Ar*Pb-PbAr* case: the observed Pb−Pb distance of 3.188 is ca. 0.34 Å longer than the Pb−Pb single-bond distances in diplumbanes such as $Ph_3Pb{-}PbPh_3$ (2.844 Å).[11] In addition, it should be noted that the trans bending in Ar*Si≡SiAr* is ca. 40° smaller than that in Ar*PbPbAr*, where the Pb−Pb−C angle of 94.3° is close to 90°.[11]

The 1,2-Ar* shifted isomer $SiSiAr^*_2$ (shown in Figure 1b) was 12.9 kcal/mol more stable than Ar*Si≡SiAr*. As demonstrated for the M_2H_2 (M = Si, Ge, Sn, and Pb) series, the barrier for isomerization of $HM{\equiv}MH$ to MMH_2 is greatly decreased upon going from Si to Pb.[7b] Nevertheless, no isomerization (as well as dimerization)

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(1) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343.

(2) For recent reviews, see: (a) Okazaki, R.; West, R. *Adv. Organomet. Chem*. **1996**, *39*, 231. (b) Weidenbruch, M. *Eur. J. Inorg. Chem*. **1999**, 373. (c) Power, P. P. *Chem. Rev*. **1999**, *99*, 3463.

(3) For the proposal of transient existence of disilynes as possible intermediates, see: (a) Sekiguchi, A.; Zigler, S. S.; West, R. *J. Am. Chem. Soc.* **1986**, *108*, 4241. (b) Sekiguchi, A.; Gillete, G. R.; West, R. *Organometallics* **1988**, *7*, 1226. (c) Pietschnig, R.; West, R.; Powell, D. R. *Organometallics* **2000**, *19*, 2724.

(4) For example, see: (a) Colegrove, B. T.; Schaefer, H. F., III. *J. Phys. Chem*. **1990**, *94*, 5593. (b) Grev, R. S.; Schaefer, H. F., III. *J. Chem. Phys*. **1992**, *97*, 7990. (c) Huhn, M. M.; Amos, R. D.; Kobayashi, R.; Handy, N. C. *J. Chem. Phys*. **1993**, *98*, 7107. (d) Grev, R. S. *Adv. Organomet. Chem*. **1991**, *33*, 125.

(5) (a) Bogey, M.; Bolvin, H.; Demuynck, C.; Destombes, J.-L. *Phys. Rev. Lett*. **1991**, *66*, 413. (b) Cordonnier, M.; Bogey, M.; Demuynck, C.; Destombes, J.-L. *J. Chem. Phys*. **1992**, *97*, 7984. (c) Bogey, M.; Bolvin, H.; Cordonnier, M.; Demuynck, C.; Destombes, J.-L.; Császár, A. G. *J. Chem. Phys*. **1994**, *100*, 8614. (d) Maier, G.; Reisenauer, H. P.; Meudt, A.; Egenolf, H. *Chem. Ber. Recl*. **1997**, *130*, 1043.

(6) Takagi, N.; Nagase, S. To be submitted for publication.

(7) (a) Kobayashi, K.; Nagase, S. *Organometallics* **1997**, *16*, 2489. (b) Nagase, S.; Kobayashi, K.; Takagi, N. *J. Organomet. Chem*. **2000**, *611*, 263.

(8) (a) Becke, A. D. *Phys. Rev*. **1988**, *A38*, 3098. (b) Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev*. **1988**, *B37*, 785.

(9) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(10) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039.

(11) Pu, L.; Twamley, B.; Power, P. P. *J. Am. Chem. Soc.* **2000**, *122*, 3524.

(12) (a) Su, J.; Li, X.-W.; Crittendon, R. C.; Robinson, G. H. *J. Am. Chem. Soc.* **1997**, *119*, 5471. (b) Robinson, G. H. *Acc. Chem. Res*. **1999**, *32*, 773.

10.1021/om000824p CCC: $20.00
Publication on Web 12/15/2000

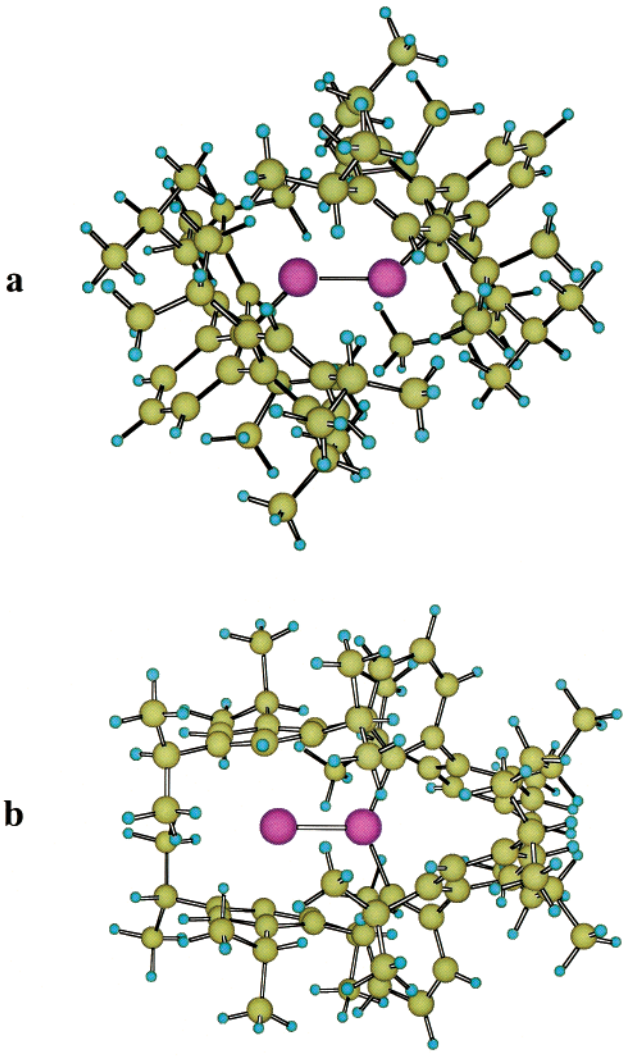

Figure 1. Optimized structures of Ar*Si≡SiAr* (a) and SiSiAr*$_2$ (b) at the B3LYP/3-21G* level. Silicon atoms are denoted as red-purple circles.

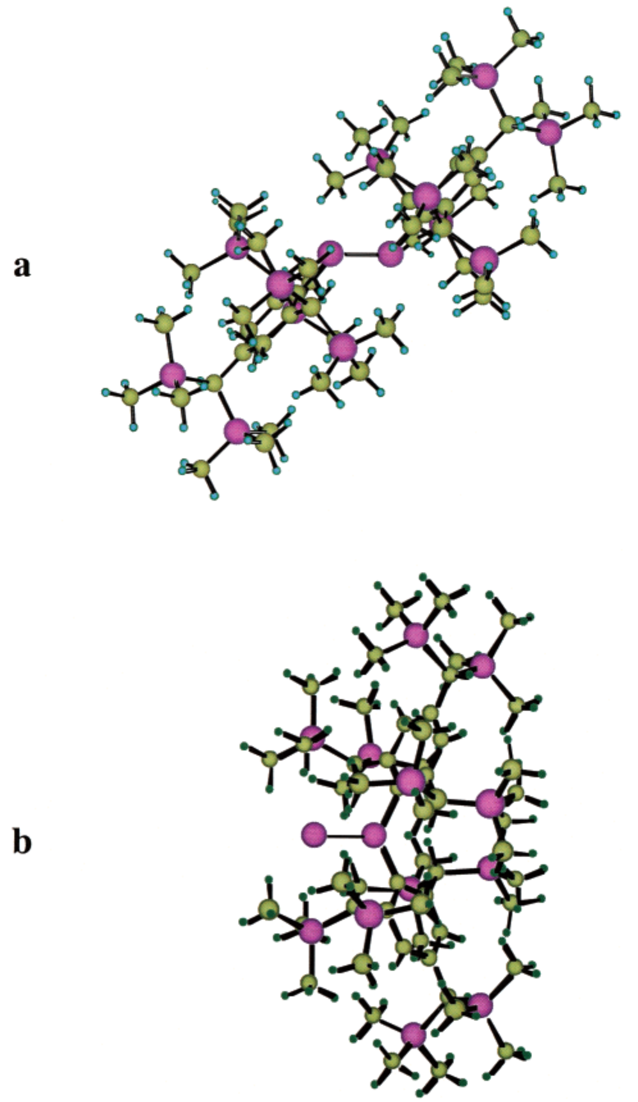

Figure 2. Optimized structures of TbtSi≡SiTbt (a) and SiSiTbt$_2$ (b) at the B3LYP/3-21G* level. Silicon atoms are denoted as red-purple circles.

has been reported for Ar*PbPbAr*.[11] These facts suggest that the isomerization of Ar*Si≡SiAr* to SiSiAr*$_2$ is hindered by a sizable barrier owing to the shifting group of vast bulk, though we did not attempt to locate the transition state because of the size of the system.

To further test the effect of bulky aryl groups, TbtSi≡SiTbt (Tbt = 2,4,6-tris(bis(trimethylsilyl)methyl)phenyl) was investigated. This disilyne is interesting, since it bears a structural resemblance to TbtSb=SbTbt and TbtBi=BiTbt isolated recently as stable doubly bonded compounds.[13] The optimized C_i structure of TbtSi≡SiTbt is shown in Figure 2a. The Si−Si distance and Si−Si−C angle were calculated to be 2.121 Å and 130.9°, respectively. This distance and trans bending are 0.027 Å longer and 2.6° larger than those of Ar*Si≡SiAr*, respectively; they are 0.049 Å longer and 10.1° larger than those of Dep$_3$SiSi≡SiSiDep$_3$[7] because of the electronegative character of the Tbt group.[14] However, it should be noted that the two bulky Tbt groups help to destabilize the 1,2-Tbt shifted isomer SiSiTbt$_2$, since they crowd much more around one end of the Si−Si bond (Figure 2b).[15] Thus, TbtSi≡SiTbt is 19 kcal/mol more stable than SiSiTbt$_2$. This energy difference is sufficiently large to prevent the 1,2-Tbt shift in TbtSi≡SiTbt.

The energy required for breaking the central Si−Si bond in TbtSi≡SiTbt was 52 kcal/mol. This binding

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(13) (a) Tokitoh, N.; Arai, Y.; Okazaki, R.; Nagase, S. *Science* **1997**, *277*, 78. (b) Tokitoh, N.; Arai, Y.; Sasamori, T.; Okazaki, R.; Nagase, S.; Uekusa, H.; Ohashi, Y. *J. Am. Chem. Soc.* **1998**, *120*, 433. For the synthesis by using the Ar* group, see: (c) Twamley, B.; Sofield, C. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1999**, *121*, 3357.

(14) The doublet−quartet energy difference of the SiR part in RSi≡SiR decreases as R becomes electropositive. This energy closeness leads to the decreased trans bending and shorter Si−Si distance.[7] The energy difference of 50 kcal/mol for R = Tbt (electronegative) is larger than that of 29 kcal/mol for R = SiDep$_3$ (electropositive) at the B3LYP/3-21G* level. Thus, Tbt is unfavorable as an electronic effect but favorable as a sterically crowding group. On the other hand, the electropositive SiDep$_3$ decreases the size difference between valence s and p orbitals on the Si atoms in RSi≡SiR and makes efficient hybridization facile. As a result, Dep$_3$SiSi≡SiSiDep$_3$ has a shorter Si−Si distance (2.072 Å) than HSi≡SiH (2.093 Å), the former being 16.1° less trans bent than the latter with an Si−Si−C angle of 124.9°, despite the bulkiness of SiDep$_3$. Since the doublet−quartet energy difference of 9 kcal/mol for R = Si(t-Bu)$_3$ is smaller than that for R = SiDep$_3$, the Si−Si distance of 2.068 Å in (t-Bu)$_3$SiSi≡SiSi(t-Bu)$_3$ is still shorter than that in Dep$_3$SiSi≡SiSiDep$_3$.[7]

(15) In contrast, in the SiSiAr*$_2$ isomer the left Si atom can interact weakly in an attractive way with the 2,4,6-triisopropylphenyl on each Ar* as a result of the sterically crowded space.

energy is smaller than that of 62 kcal/mol calculated for $HSi\equiv SiH$ because of a steric repulsion between Tbt groups. However, the still large binding energy suggests that $TbtSi\equiv SiTbt$ does not dissociate to two SiTbt fragments even in solution, unlike the heavier (Sn, Pb, and some Ge) analogues of alkenes.[2] The same is also expected for $Ar^*Si\equiv SiAr^*$, whose binding energy is 39 kcal/mol despite the bulky Ar* group.

Another major difficulty in preparing disilynes is ascribed to the facile dimerization that leads to tetrasilatetrahedranes or tetrasilacyclobutadienes (Si_4R_4).[16] Accordingly, it has recently been verified from preliminary experiments that tetrasilatetrahedranes are readily obtained when R is as bulky as Si(t-Bu)$_3$.[17] In this context, it is interesting that the first synthesis of a tetrasilatetrahedrane was performed with Si(t-Bu)$_3$ groups.[18] To test if $TbtSi\equiv SiTbt$ is stable to dimerization, calculations were carried out using the recently developed two-layered ONIOM (B3LYP/3-21G*:AM1) method.[19] This method can well reproduce the full B3LYP/3-21G* calculations, when the first layer at the B3LYP/3-21G* level is large.[19b] For example, the Si−Si distance and Si−Si−C angle of 2.112 Å and 131.9° in $TbtSi\equiv SiTbt$ calculated with the ONIOM method agree well with the values of 2.121 Å and 130.9° at the full B3LYP/3-21G* level, respectively. The energy difference of 19 kcal/mol favoring $TbtSi\equiv SiTbt$ over $SiSiTbt_2$ calculated with the ONIOM method agrees perfectly with the full B3LYP value of 19 kcal/mol, while the binding energy of 50 kcal/mol (ONIOM) for $TbtSi\equiv SiTbt$ differs little from that of 52 kcal/mol (full B3LYP).

Calculations with the ONIOM method predict that the dimerization of $TbtSi\equiv SiTbt$ to tetrasilatetrahedrane (Figure 3a) and tetrasilacyclobutadiene (Figure 3b) structures is endothermic by 58 and 42 kcal/mol, respectively. This confirms that $TbtSi\equiv SiTbt$ is stable to dimerization.[20] When the Me groups in Tbt ($=C_6H_2$-2,4,6-$\{CH(SiMe_3)_2\}_3$) are replaced by H atoms, dimerization to tetrasilatetrahedrane becomes exothermic by 66 kcal/mol (ONIOM and full B3LYP).[21] Upon the replacement, the 1,2-shifted isomer becomes 7 kcal/mol (full B3LYP) more stable than the disilyne structure. It should be also noted that the structure of $Ar^*Si\equiv SiAr^*$ is considerably twisted around the Si−Si bond when the i-Pr groups in Ar* ($= C_6H_3$-2,4,6-i-$Pr_3C_6H_2$) are replaced by H atoms.[22] These results indicate that it is very important to prepare carefully substituent groups as well as precursors[23] in order to make disilyne structures stable thermodynamically and kinetically.

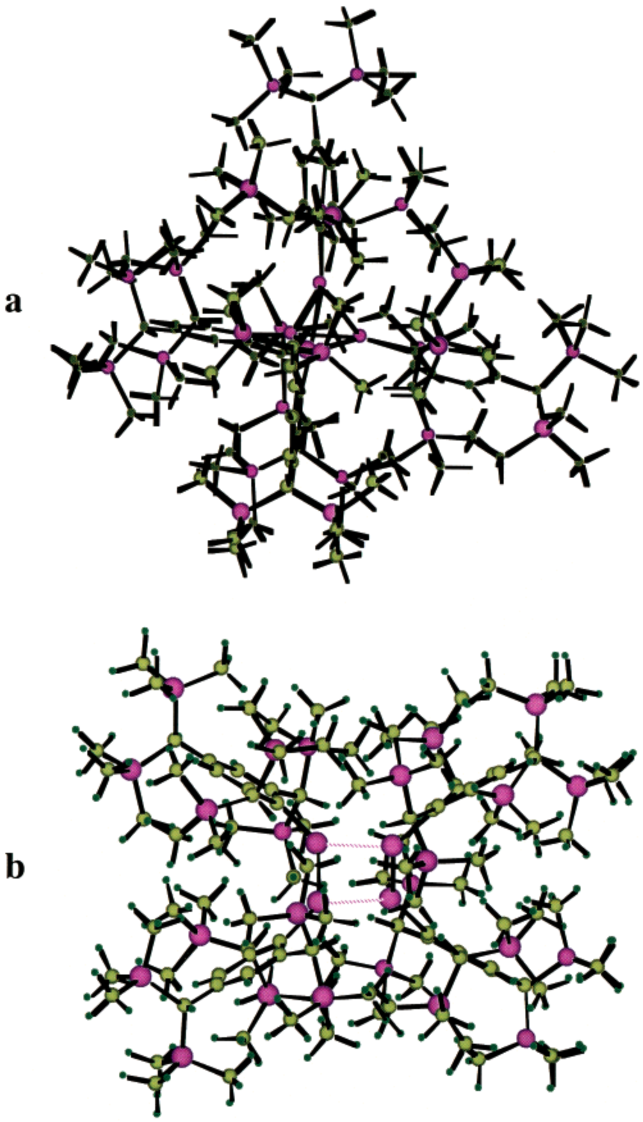

Figure 3. Tbt-substituted tetrasilatetrahedrane (a) and tetrasilacyclobutadiene (b) optimized with the ONIOM method. Silicon atoms are denoted as red-purple circles.

We conclude that disilynes bearing suitable aryl groups are interesting synthetic targets worthy of experimental testing. It is expected that disilynes will be soon synthesized and isolated as stable triply bonded compounds, opening a new area of silicon chemistry.

Acknowledgment. This work was supported in part by a Grant-in-Aid from the Ministry of Education, Science, Sports and Culture of Japan.

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(16) The dimerization of $RM\equiv MR$ becomes less facile upon going from M = Si to M = Pb (Takagi, N.; Nagase, S. Unpublished results).

(17) Sekiguchi, A. Private communication.

(18) Wiberg, N.; Finger, C. M. M.; Polborn, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1054. For the synthesis of a tetragermatetrahedrane derivative with Si(t-Bu)$_3$ groups, see: Wiberg, N.; Hochmuth, W.; Nöth, H.; Appel, A.; Schmidt-Amelunxen, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1333. For the unsuccessful synthesis of the tin analogue, see: Wiberg, N.; Lerner, H.-W.; Nöth, H.; Ponikwar, W. *Angew. Chem., Int. Ed.* **1999**, *38*, 1103.

(19) (a) Dapprich, S.; Komáromi, I.; Byun, K. S.; Morokuma, K.; Frisch, M. J. *J. Mol. Struct. (THEOCHEM)* **1999**, *461/462*, 1. (b) In the two-layer ONIOM (B3LYP/3-21G*:AM1) method, the inner layer (in which only the $SiMe_3$ groups in Tbt were replaced by H atoms) was calculated at the B3LYP/3-21G* level and the rest was treated as the outer layer with the semiempirical AM1 method (for AM1, see: Dewar, M. J. S.; Jie, C. X. *Organometallics* **1987**, *6*, 1486).

(20) The dimerization of (t-Bu)$_3SiSi\equiv SiSi$(t-Bu)$_3$ to a tetrahedrane structure is exothermic by 78 kcal/mol (ONIOM) and 80 kcal/mol (full B3LYP). This is because the strain in the tetrahedrane framework is released to a considerable extent, owing to the electropositive Si(t-Bu)$_3$ groups. For silyl-substituent effects on the strain energies of polyhedral silicon compounds, see: (a) Nagase, S. *Acc. Chem. Res.* **1995**, *28*, 469. (b) Sekiguchi, A.; Nagase, S. In *The Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Chapter 3, pp 119−154.

(21) Since a total of 72 Me groups are involved in the dimerization of $TbtSi\equiv SiTbt$, the global energy difference of 124 kcal/mol is formally ascribed to a contribution of 1.7 kcal/mol per Me group.

(22) It is also interesting that the i-Pr groups in Ar* play an important role in the synthesis of $Na_2[Ar^*GaGaAr^*]$.[12b] The same type of synthetic procedure using Me groups instead of i-Pr leads to a three-membered gallium ring, not $Na_2[Ar^*GaGaAr^*]$.

(23) For recent undesirable results from the reduction of terphenyltrifluorosilanes, see ref 3c.