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Torsional Strain as a Determinant for the Polymerizability of Cyclic Olefins: The Ring-Opening Metathesis Polymerization of 1,1,2,2-Tetramethyl-1,2-disilacyclopent-3-ene[†,‡]

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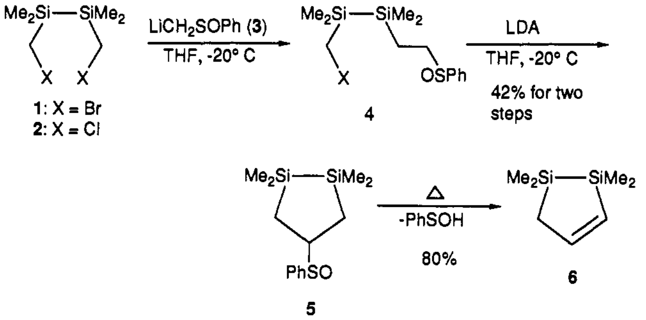
Polymers with backbones partially composed of silicon atoms (i.e., polycarbosilanes) are important materials for a range of potential applications that include microlithography and the production of high temperature ceramics,[1] and in this regard, the ring-opening metathesis polymerization (ROMP)[2] of carbocyclic alkenyl silanes would appear to offer an attractive route to new, well-defined, polycarbosilane structural classes. To date, however, only 1,1-disubstituted 1-silacyclopent-3-enes have been evaluated for ROMP, and in this case, owing to a fairly small (negative) free energy change associated with the opening of this five-membered ring, secondary metathesis reactions, such as cyclic oligomer formation and depolymerization via chain back-biting, can occur predominantly depending upon reaction conditions.[3] Herein, we extend the evaluation of carbocyclic alkenyl silanes for ROMP to include the previously unknown 1,2-disilacyclopent-3-ene ring system and show that when only a small amount of *ring strain* that arises from bond angle deformations is present in a cyclic monomer, the relief of *torsional strain* induced by nonbonded interactions between substituents on adjacent endocyclic centers can be a strong force which drives the ROMP process irreversibly forward. Accordingly, this latter type of strain energy may also be regarded as being yet another important determinant to be used in the design or selection of other organic/organometallic compounds that are suitable for ROMP.

As Scheme I shows, the successful construction of the 1,2-disilacyclopent-3-ene framework was achieved in a direct manner by implementing a synthetic strategy that utilizes sulfoxide elimination as a method to introduce the requisite unsaturation under mild conditions. Thus, reaction of either of the known 1,2-bis(halomethyl)-1,1,2,2-tetramethyldisilanes (**1** and **2**, X = Br and Cl, respectively),[4] with the carbanion of methylphenyl sulfoxide (**3**) in tetrahydrofuran (THF) at –20 °C, first provided the acyclic disilane adduct **4**, which was then cyclized, without isolation, to the crystalline, air-stable 1,2-disilacyclopentane derivative **5** via the addition of 1 equiv of lithium diisopropylamide (LDA) at the same temperature (42% overall yield).[5] In keeping with the prior report that a silicon atom at the β-position will facilitate sulfoxide elimination,[6] this process occurred cleanly for **5** to produce 1,1,2,2-tetramethyl-1,2-disilacyclopent-3-ene (**6**) in solution between 60 °C and 70 °C as monitored by ^{1}H NMR spectroscopy. On a larger scale, simply heating **5** in a Kugelrohr bulb-to-bulb distillation apparatus to 130 °C under reduced pressure (60 Torr), collecting the evolved product in a bulb cooled to –78 °C, and then redistilling this material conveniently provided pure **6** (bp 84 °C, 70 Torr) in 80% yield (Scheme I).[7]

Scheme I



The observed inertness of the 4-(phenylsulfoxy)-1,2-disilacyclopentane derivative **5** and the 1,2-disilacyclopent-3-ene derivative **6** toward air oxidation is quite remarkable in light of previous reports of the extreme air-sensitivity of 1,1,2,2-tetramethyl-1,2-disilacyclopentane[8] and 1,1,2,2-tetramethyl-1,2-disilacyclohex-4-ene.[9] Hence, to obtain an insight into the origin of this unusual stability of **5** and **6** as well as to identify any consequences of strain in the 1,2-disilacyclopentane ring system, a crystallographic analysis of the related compound 4-(phenylsulfonyl)-1,1,2,2-tetramethyl-1,2-disilacyclopentane (**7**), which is also inert toward air-oxidation, was performed.[10] As Figure 1 shows, the crystal structure of **7** reveals few bond length or bond angle distortions; the most notable of these being the small endocyclic Si–Si–C bond angles of 93.2° which would appear to be significantly distorted from the idealized tetrahedral value of 109°28′.[5] However, from theoretical studies on cyclic systems, it has been shown that silicon in fact has a preference for and can form angles of near 90° with little cost in terms of ring strain.[11] Of greater importance, then, is the significant torsional strain that should be present in **7** due to the envelope conformation of the five-membered ring that enforces a complete eclipsing of the four methyl groups on the adjacent silicon atoms. Evidence that this conformation is rigidly held even in solution to temperatures of at least 110 °C is provided by variable-temperature ^{1}H NMR spectroscopy. Thus, for **7**, and presumably for **5** and **6** as well, it can be concluded that the origin of this compound's inertness toward air-oxidation is a result of a steric barrier against oxygen atom insertion that is reinforced by fixation of the methyl groups in a fully eclipsed arrangement, and once enough conformational mobility about the Si–Si bond is allowed, the magnitude of this property is greatly diminished.[12]

Concerning the ease of polymerization of the 1,2-disilacyclopent-3-ene derivative **6**, on the basis of ring strain considerations

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[†] Performed in part at Carnegie Mellon University, Pittsburgh, PA 1988–1989.

[‡] Dedicated to Professors Satoru Masamune and Robert West on the occasion of their 65th birthdays.

[§] CMU undergraduate, 1985–1989.

(1) (a) Zeldin, M.; Wynne, K. J.; Allcock, H. R., Eds. *Inorganic and Organometallic Polymers*; ACS Symposium Series 360; American Chemical Society: Washington, D.C., 1988. (b) Zeigler, J. M.; Fearon, F. W. G., Eds. *Silicon-Based Polymer Science*; Advances in Chemistry Series 224; American Chemical Society: Washington, D.C., 1990.

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(3) (a) Lammens, H.; Sartori, G.; Siffert, J.; Sprecher, N. *J. Polym. Sci. B, Polym. Lett.* **1971**, *9*, 341. (b) Finkel'shtein, E. S.; Portnykh, E. P.; Ushakov, N. V.; Vdovin, V. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, *3*, 641. (c) Stonich, D. A.; Weber, W. P. *Polym. Bull.* **1991**, *25*, 629. (d) Wang, L.; Ko, Y.-H.; Weber, W. P. *Macromolecules* **1992**, *25*, 2828. (e) Anhaus, J. T.; Gibson, V. C.; Clegg, W.; Collingwood, S. P. *Organometallics* **1993**, *12*, 1780.

(4) For X = Br, see: Tamao, K.; Kumada, M. *J. Organomet. Chem.* **1971**, *30*, 329. For X = Cl, see: Kobayashi, T.; Pannell, K. H. *Organometallics* **1990**, *9*, 2201.

(5) Further details are provided in the supplementary material.

(6) Fleming, I.; Perry, D. A. *Tetrahedron Lett.* **1981**, *22*, 5095.

(7) For **6**: ^{1}H NMR (300 MHz, benzene-d_6) δ 0.10 (s, 6H), 0.19 (s, 6H), 1.55 (dd, 2H, J = 2.0 Hz, J = 3.8 Hz), 6.16 (dt, 1H, J = 2.0 Hz, J = 11.3 Hz), 6.89 (dt, 1H, J = 3.8 Hz, J = 11.3 Hz); ^{13}C NMR (75 MHz, benzene-d_6) δ (proton-coupled) –4.13 (q), –3.54 (q), 23.92 (t), 134.86 (d), 149.91 (d); UV (hexane) λ_{max} 200 nm (ϵ_{max} 8896); IR (neat) $\nu_{C=C}$ 1559 cm^{-1}. Anal. Calcd for $C_7H_{16}Si_2$: C, 53.77; H, 10.31. Found: C, 53.43, H, 10.18.

(8) Tamao, K.; Kumada, M.; Takahashi, T. *J. Organomet. Chem.* **1975**, *94*, 367.

(9) Birkofer, L.; Weniger, W. *Chem. Ber.* **1973**, *106*, 3595.

(10) Compound **7** was prepared in one step (59% yield) by the addition of the dianion of methylphenyl sulfone to **1** (or **2**) in THF at –78 °C.[5]

(11) (a) Boatz, J. A.; Gordon, M. S.; Hilderbrandt, R. J. *J. Am. Chem. Soc.* **1988**, *110*, 352. (b) Nagase, S. *Polyhedron* **1991**, *10*, 1299.

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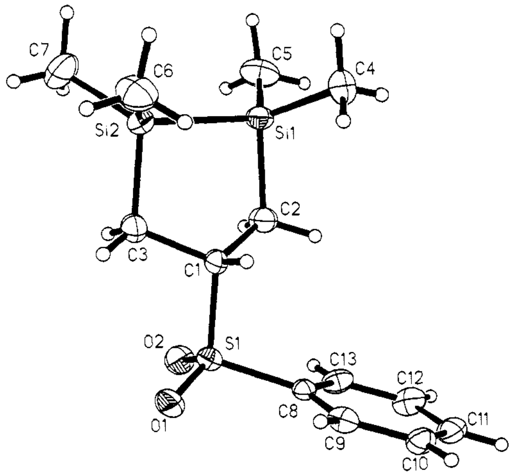
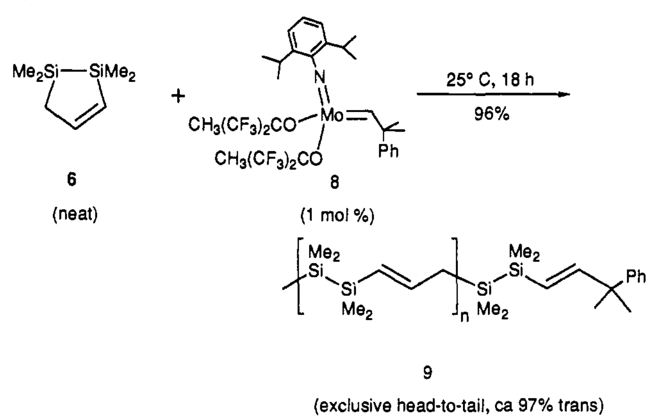


Figure 1. ORTEP representation of the molecular structure of **7**. Selected bond lengths (Å) and bond angles (deg): Si_1–Si_2 2.336(1), Si_1–C_2 1.905(3), Si_2–C_3 1.913(3), C_1–C_2 1.537(3), C_1–C_3 1.534(4); Si_2–Si_1–C_2 93.2(1), Si_1–Si_2–C_3 93.2(1), C_2–C_1–C_3 112.2(2), Si_1–C_2–C_1 108.9(2), Si_2–C_3–C_1 108.4(2).

Scheme II



alone, it could be argued that this compound would not be a good candidate for ROMP since it should be even less strained than either cyclopentene or 1-silacyclopent-3-ene. However, contrary to this expectation, we found that by employing Schrock's well-defined molybdenum imido alkylidene complex **8**[13] as the catalyst (1 mol %), the ROMP of **6** (neat) proceeded exceedingly well (96% yield) in both the highly stereoselective and the regioselective manner depicted in Scheme II to produce the new polycarbosilane material **9**.[14] Interestingly, upon dissolution of an aliquot of the crude polymer reaction mixture still containing active metathesis species into benzene-d_6, ^1H NMR spectroscopy showed that virtually no depolymerization of **9** occurs with very little, if any, linear or cyclic oligomers being present (Figure 2). In addition, the relatively narrow line widths observed in both the ^1H and the ^{13}C NMR spectra of **9** strongly suggest that the polymer backbone of this material is conformationally well-defined.[15] Taken together, these results can be rationalized on the basis that the relief of the torsional strain associated with eclipsing methyl groups drives the ROMP of **6** irreversibly forward and that in the polymer **9** these same nonbonded interactions between adjacent silicon substituents, as well as the *trans* geometry of the olefinic linkage, strongly dictate backbone conformation. The possibility of torsional strain being the major determinant governing the polymerizability of a cyclic olefin by ROMP implies that, in the future, this type of strain energy can be used as a design criterion in selecting new classes of potential ROMP monomers.[16]

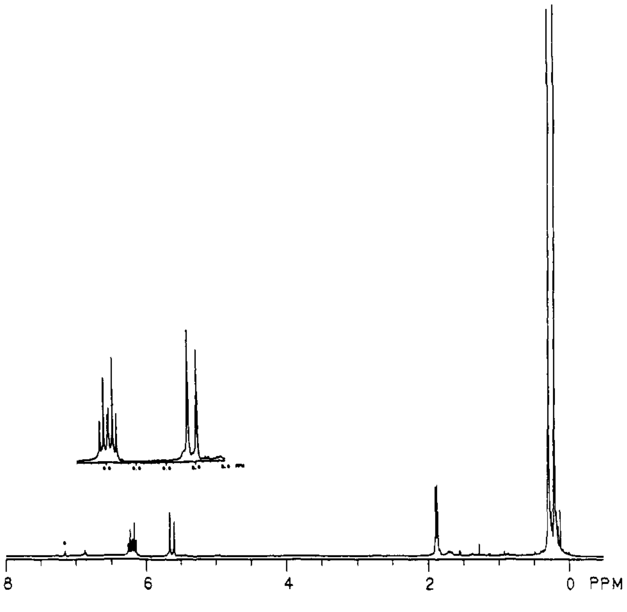


Figure 2. ^1H NMR (300 MHz, benzene-d_6) spectrum of a crude aliquot of the reaction mixture of **6** and **8** (1 mol%) taken after 18 h at 25 °C. Solvent peaks are marked with an asterisk.

As a final note, the polycarbosilane **9** possesses interesting properties which include air-stability, solubility in a range of solvents, and a large transparency window (λ_{max} 204 and 236 nm), and in keeping with observations of the photosensitive nature of vinyldisilanes[17] and of other materials which incorporates the vinyldisilanyl group within the polymer backbone,[18] **9** and its solutions photodegrade when exposed to 254-nm irradiation from a low-pressure Hg lamp. If the ROMP of **6** proceeds in a "living" fashion,[19] then it may be possible to fine-tune the physical properties of poly(1,2-disilapent-3-enes) such as **9** either through the optimization of molecular weight values or by forming block copolymers to produce new classes of materials that are of technological importance. Accordingly, further studies relating to the ROMP of **6** and other 1,2-disilacyclopent-3-ene derivatives are now in progress.

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Supplementary Material Available: Detailed information concerning the synthesis and characterization of all new compounds including listings of atomic coordinates and temperature factors, bond lengths, bond angles, and anisotropic temperature factors for the crystallographic analysis of **7** (12 pages). Ordering information is given on any current masthead page.

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(12) Oxidation of **7** can be accomplished with 1 equiv of *m*-chloroperbenzoic acid in toluene at room temperature to provide the corresponding 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane derivative in 97% yield.[5]

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(14) For **9**: ^1H NMR (300 MHz, benzene-d_6) δ 0.20 (s, 6H), 0.29 (s, 6H), 1.88 (dd, 2H, $J = 1.2$ Hz, $J = 7.8$ Hz), 5.63 (dt, 1H, $J = 1.2$ Hz, $J = 18.3$ Hz), 6.20 (dt, 1H, $J = 7.8$ Hz, $J = 18.3$ Hz); ^{13}C NMR (75 MHz, benzene-d_6) δ –0.48, –3.03, 27.19, 126.21 (*trans*), 126.52 (*cis*), 144.31 (*cis*), 144.60 (*trans*);[9] UV (hexane) λ_{max} 204, 236 nm; IR (neat) $\nu_{C=C}$ 1597, $\delta_{CH\,trans}$ 982 cm^{-1}. Anal. Calcd for $C_7H_{16}Si_2$: C, 53.77; H, 10.31. Found: C, 52.65, H, 10.30. GPC (methylene chloride, polystyrene molecular weight standards): M_w/M_n = 14 420/10 128 = 1.42.

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(16) Related to this work is the recent observation of another influence of substituents, the Thorpe–Ingold effect, which strongly directs metathesis cyclization rather than polymerization of certain classes of α,ω-dienes using the same catalyst **8**. See: Forbes, M. D. E.; Patton, J. T.; Myers, T. L.; Maynard, H. D.; Smith, D. W., Jr.; Schulz, G. R.; Wagener, K. B. *J. Am. Chem. Soc.* **1992**, *114*, 10978.

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