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Mechanism of Di-*tert*-Butylsilylene Transfer from a Silacyclopropane to an Alkene

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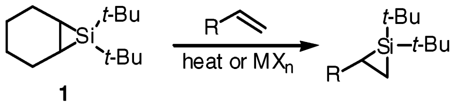
Abstract: Kinetic and thermodynamic studies of the reactions of cyclohexene silacyclopropane **1** and monosubstituted alkenes suggested a possible mechanism for di-*tert*-butylsilylene transfer. The kinetic order in cyclohexene silacyclopropane **1** and cyclohexene were determined to be 1 and −1, respectively. Saturation kinetic behavior in monosubstituted alkene concentration was observed. Competition experiments between substituted styrenes and a deficient amount of di-*tert*-butylsilylene from **1** correlated well with the Hammett equation and provided a ρ value of -0.666 ± 0.008, using σ_p constants. These data supported a two-step mechanism involving reversible di-*tert*-butylsilylene extrusion from **1**, followed by irreversible concerted electrophilic attack of the silylene on the monosubstituted alkene. Eyring activation parameters were found to be $\Delta H^{\ddagger} = 22.1 \pm 0.9$ kcal·mol^{-1} and $\Delta S^{\ddagger} = -15 \pm 2$ eu. Competition experiments between cycloalkenes and allylbenzene determined cycloalkenes to be more efficient silylene traps (k_{rel} =1.3, $\Delta\Delta G^{\ddagger} = 0.200$ kcal·mol^{-1}). A summary of the data resulted in a postulated reaction coordinate diagram. The mechanistic studies enabled rational modification of reaction conditions that improved the synthetic utility of silylene transfer. Removal of the volatile cyclohexene from the reaction mixture into an evacuated headspace led to the formation of previously inaccessible cyclohexene-derived silacyclopropanes.

Introduction

Insight into formation of silacyclopropanes is of particular interest because of the emerging synthetic utility of these strained-ring silanes.[1] Silacyclopropanes can be formed by thermolysis of a cyclic silane in the presence of an alkene,[2−8] a process that involves silylene intermediates.[9−13] Since the initial discovery by Seyferth and co-workers that hexamethylsilirane can generate silylene thermally,[6] other cyclic silanes, including cyclotrisilanes[2,5,14,15] and cyclohexene silacyclopropane **1**,[3,16] have been employed for silylene transfer. Our laboratory has shown that cyclohexene silacyclopropane **1** is an efficient source of silylene, providing silacyclopropanes from chiral, functionalized alkenes (eq 1).[17,18]

Through qualitative observations of silacyclopropane stability, the mechanism for thermal silylene transfer was postulated to involve the reversible extrusion of free silylene from a cyclic silane, followed by trapping of the intermediate silylene with an alkene.[2,4,8] Kinetic evidence that di-*tert*-butylsilylene formation is reversible, however, has not been obtained. If free di-*tert*-butylsilylene is formed from extrusion, its electronic nature has remained unknown. Additionally, little is known about the activation parameters of silylene transfer.[4b]



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(1)

To understand the fundamental reactivity of silacyclopropanes and their intermediates, we conducted a quantitative analysis of the thermal behavior of cyclohexene silacyclopropane **1** in the presence of an alkene. We believed that a mechanistic understanding of this reaction would guide improvements to silacyclopropane synthesis. Analysis of the kinetic behavior and

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(1) Franz, A. K.; Woerpel, K. A. *Acc. Chem. Res.* **2000**, *33*, 813−820.

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(5) Schäfer, A.; Weidenbruch, M.; Peters, K.; von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 302−303.

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(13) Silylenes can also be produced using photochemical methods. For recent examples, refer to: (a) Miyazawa, T.; Koshihara, S.; Liu, C.; Sakurai, H.; Kira, M. *J. Am. Chem. Soc.* **1999**, *121*, 3651−3656. (b) Gaspar, P. P.; Beatty, A. M.; Chen, T.; Haile, T.; Lei, D.; Winchester, W. R.; Braddock-Wilking, J.; Rath, N. P.; Klooster, W. T.; Koetzle, T. F.; Mason, S. A.; Albinati, A. *Organometallics* **1999**, *18*, 3921−3932. (c) Weidenbruch, M.; Meiners, F.; Saak, W. *Can. J. Chem.* **2000**, *78*, 1469−1473.

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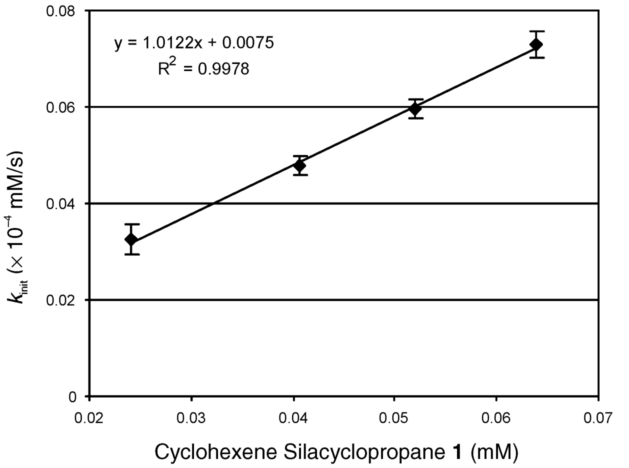
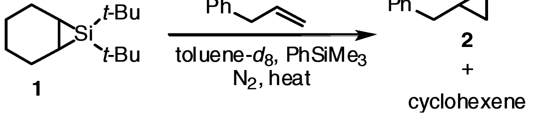


Figure 1. Determination of kinetic order for cyclohexene silacyclopropane **1**, 60 °C.

Eyring activation parameters suggested the formation of di-*tert*-butylsilylene as the reactive intermediate. The electrophilicity of the di-*tert*-butylsilylene intermediate was established by the identification of a Hammett ρ value. These results and data from competition experiments permit construction of a reaction coordinate diagram for thermal silylene transfer from **1**. Finally, the mechanistic study culminated in the rational modification of reaction parameters to allow synthesis of previously inaccessible cyclohexene-derived silacyclopropanes.

Results and Discussion

Initial experiments between cyclohexene silacyclopropane **1** and an alkene focused on optimizing the conditions for measuring kinetic parameters (eq 2). Allylbenzene was chosen as the di-*tert*-butylsilylene acceptor to facilitate analysis using ^{1}H NMR spectroscopy. Several signals, including diagnostic *t*-Bu and Bn signals of both the product and starting material, were distinct. In addition, the similar dielectric constant of allylbenzene ($\epsilon = 2.63$)[19] as compared to toluene ($\epsilon = 2.38$)[19] would ensure that the polarity of the solvent would remain unchanged at high concentrations of alkene. Because of its high boiling point, low polarity, and distinct ^{1}H NMR spectrum, phenyltrimethylsilane was chosen as the internal standard. For all experiments, the components were heated in a valved NMR tube under a headspace of nitrogen at ambient pressure.



(2)

Insight into the mechanism of thermal silylene transfer was obtained through an examination of the initial rates under pseudo-first-order reaction conditions. The kinetic order was determined to be one in cyclohexene silacyclopropane **1** concentration (Figure 1) and negative one in the concentration of cyclohexene.[20] Inhibition of silylene transfer by cyclohexene prohibits a bimolecular reaction mechanism between **1** and allylbenzene. Saturation dependence in allylbenzene concentration was observed (Figure 2), confirming the formation of an intermediate.

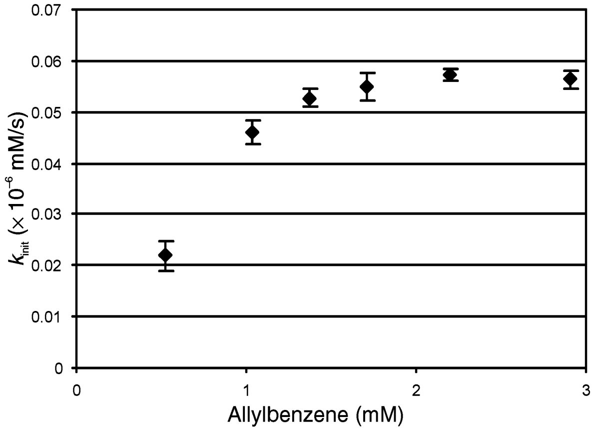
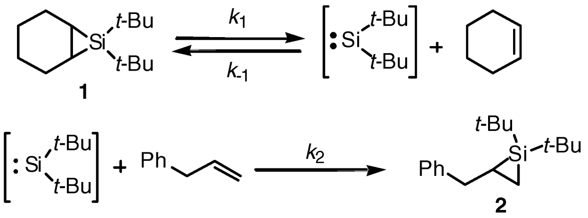


Figure 2. Saturation kinetic behavior observed for allylbenzene, 60 °C.

Scheme 1. Mechanism of Di-*tert*-Butylsilylene Transfer



Inhibition by cyclohexene and saturation with allylbenzene established that **1** is reversibly converted to an intermediate that can be intercepted by allylbenzene. Because the data is not consistent with a bimolecular step, this reactive intermediate must not contain either cyclohexene or allylbenzene, and the intermediate is postulated to be di-*tert*-butylsilylene (Scheme 1). Because di-*tert*-butylsilylene was never observed using NMR spectroscopy, it was treated as a steady-state intermediate for derivation of the experimentally determined rate law (eq 3). The saturation kinetic behavior observed indicates the silylene intermediate reacts at similar rates with cyclohexene (k_{-1}) and allylbenzene (k_2). At 30 equiv of allylbenzene, k_{-1}[cyclohexene] no longer impacted the rate, simplifying the rate law to d[**2**]/dt = k_1[**1**], in which the extrusion of silylene was rate-limiting. If k_{-1} was significantly larger than k_2, a pre-equilibrium would be established and the kinetic order in allylbenzene would have been one throughout all allylbenzene concentrations. This mechanistic analysis quantitatively confirms the aforementioned conclusions of Belzner,[2] Gaspar,[4b] and Seyferth[8] that extrusion of a silylene species from a cyclic silane is reversible.

$$\frac{d[\mathbf{2}]}{dt} = \frac{k_1 k_2[\mathbf{1}][\text{allylbenzene}]}{k_{-1}[\text{cyclohexene}] + k_2[\text{allylbenzene}]} \tag{3}$$

A series of competition experiments between various para-substituted styrenes (*p*-OMe, *p*-Me, *p*-F, *p*-Cl, and *p*-CF$_3$) and a deficient amount of **1** provided insight into the electronic nature of the transition state for cycloaddition (eq 4). Higher reactivity was observed with more electron-rich styrenes. The rate difference in formation of substituted styrene silacyclopropanes correlated linearly with the Hammett equation using σ_p

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(19) Wohlfarth, C. In *CRC Handbook of Chemistry and Physics*, 83rd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL; 2003, pp 6.153−6.173.

(20) Refer to the Supporting Information for tabular and graphical presentation of the kinetic data.

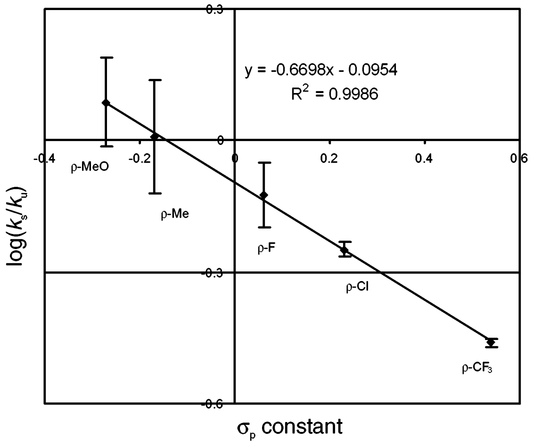
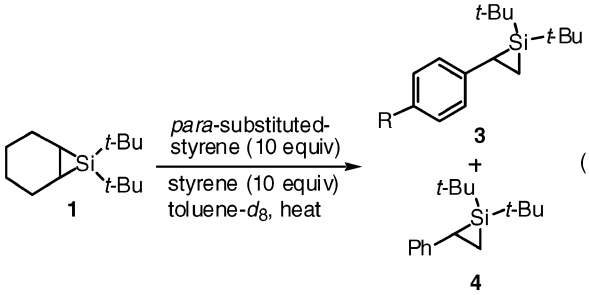


Figure 3. Linear correlation of log(k_{rel}) with σ_{para} constants using the Hammett equation.

constants[21] to result in a ρ value of -0.666 ± 0.008 at 87 °C (Figure 3). The magnitude and sign of the ρ value were validated through examination of temperatures within ±30 °C that did not reveal an isokinetic point. The ρ values at 55 and 120 °C were found to be -0.57 and -0.79, respectively.[22] The linear relationship observed between temperature and ρ value[22] allowed estimation of the isokinetic temperature to be -110 °C. Because the reaction was carried out at temperatures substantially above the isokinetic point (and therefore entropy controlled), the apparent ρ value should be evaluated cautiously. The reaction was affected, however, in a linear fashion by the electronic nature of the para-substituent on styrene: the rate of silylene addition was accelerated by electron-donating groups and retarded by electron-withdrawing substituents.



(4)

The small negative ρ value provided insight into the electronic nature of the cycloaddition. The negative value revealed the nucleophile to be the alkene and established the electrophilicity of di-*tert*-butylsilylene.[23] Stepwise reactions that involved charged intermediates, such as the hydration and bromination of styrene, were typified by large negative ρ values (hydration,[24] $\rho = -4$; bromination,[25] $\rho = -4.3$). The small negative ρ value suggested that a concerted electrophilic attack of free di-*tert*-butylsilylene on the acceptor alkene involves the formation of a slightly polar transition state. This reaction mechanism agreed with gas-phase studies[26] and ab initio calculations[27] describing the reaction of silylene with ethylene in which the reaction proceeded by an initial electrophilic phase resulting from the interaction of the silylene LUMO with the π-electrons of the alkene. A similar small negative ρ value (-0.619 obtained using σ^+ constants) was observed in the concerted, electrophilic cyclopropanation of substituted styrenes with phenyl(bromodichloromethyl)mercury-derived dichlorocarbene.[28]

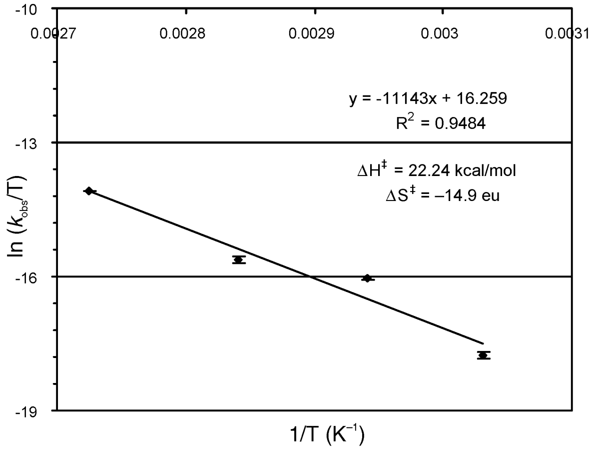


Figure 4. Plot of ln(k_{obs}/T) vs 1/T for the reaction of cyclohexene silacyclopropane **1** and allylbenzene.

The activation parameters of di-*tert*-butylsilylene extrusion from **1** were identified.[4b] A correlation between the observed rate and temperature was obtained between 55 and 95 °C (Figure 4). Saturation by allylbenzene was chosen to simplify the rate law ($d[\mathbf{2}]/dt = k_1[\mathbf{1}]$). Under saturation conditions, the extrusion of di-*tert*-butylsilylene from cyclohexene silacyclopropane **1** could be described using Eyring activation parameters ($\Delta H^\ddagger = 22.1 \pm 0.9$ kcal·mol^{-1}, $\Delta S^\ddagger = -15 \pm 2$ eu). The negative $\Delta S^\ddagger$ value was unexpected for a unimolecular reaction in which one particle becomes two.[29] Since the synchronous fission of two bonds in a three-membered ring is forbidden,[30] the loss of entropy in the transition state could result from an asynchronous cheletropic elimination of di-*tert*-butylsilylene which would require extensive organization by the silacyclopropane **1**.[31,32] Because the reaction involved a polarized transition state (vide supra) between a silylene and an alkene, an additional entropic penalty would result from solvent reorganization. The displacement of several solvent molecules by the disassociation of the sterically large di-*tert*-butylsilylene could also account for the negative entropy. Alternatively, a di-*tert*-butylsilylene−Lewis base complex[33] (with either cyclohexene or toluene[34] serving as the Lewis base) could be involved.

The $\Delta\Delta G^\ddagger$ between cycloaddition onto cyclohexene and allylbenzene was estimated by comparison of the relative rates of di-*tert*-butylsilylene trapping by cyclopentene and cyclooctene

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(21) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−195.

(22) Please refer to the Supporting Information.

(23) The apparent electrophilicity of *t*-Bu_2Si contrasts with the observed nucleophilicity ($\rho = +0.85 \pm 0.2$) of Ar_2Si (Ar = 2-(Me_2NCH_2)C_6H_4) observed by Belzner and co-workers in ref 14.

(24) Schubert, W. M.; Lamm, B.; Keefe, J. R. *J. Am. Chem. Soc.* **1964**, *86*, 4727−4729.

(25) Dubois, J. E.; Schwarcz, A. *Tetrahedron Lett.* **1964**, *5*, 2167−2173.

(26) Baggott, J. E.; Blitz, M. A.; Frey, H. M.; Lightfoot, P. D.; Walsh, R. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 515−526.

(27) Anwari, F.; Gordon, M. S. *Isr. J. Chem.* **1983**, *23*, 129−132.

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(29) For two examples of positive $\Delta S^\ddagger$ parameters resulting from one molecule becoming two, refer to: (a) $\Delta S^\ddagger = 3.5$ eu (retro-Diels−Alder); Beno, B. R.; Wilsey, S.; Houk, K. N. *J. Am. Chem. Soc.* **1999**, *121*, 4816−4826. (b) $\Delta S^\ddagger = 11.9$ eu (S_N1); Hinkle, R. J.; McNeil, A. J.; Thomas, Q. A.; Andrews, M. N. *J. Am. Chem. Soc.* **1999**, *121*, 7437−7438.

(30) Hoffmann, R. W. *J. Am. Chem. Soc.* **1968**, *90*, 1475−1485.

(31) For a general discussion of cheletropic reactions, refer to Woodward, R. B.; Hoffmann, R. W. *The Conservation of Orbital Symmetry*; VCH: Weinheim, Germany, 1970; pp 152−163.

(32) Recently, a $\Delta S^\ddagger$ term of -7.6 eu was observed for the cheletropic decomposition of a nitrosoamine in heptane by Shustov, G. V.; Rauk, A. *J. Org. Chem.* **2000**, *65*, 3612−3619.

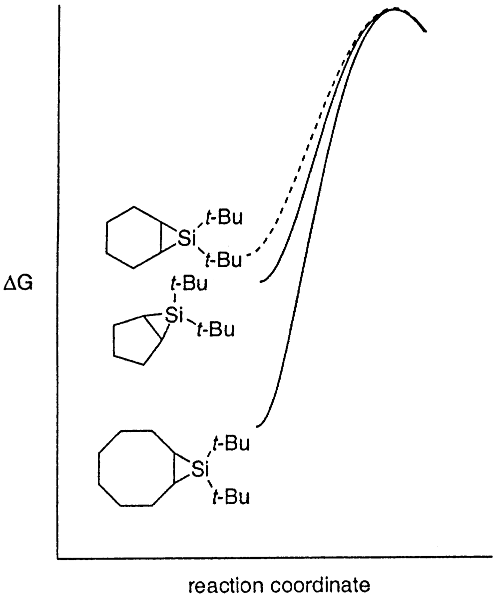
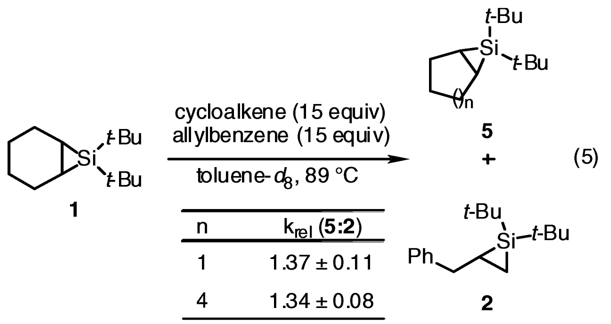
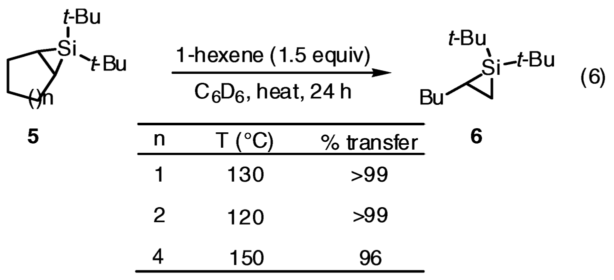


Figure 5. Correlation of cycloalkene trapping efficiency to estimate the cyclohexene silacyclopropane silylene extrusion thermodynamic profile.

versus allylbenzene (eq 5). Competition experiments were performed using 15 equiv of each alkene. Both cyclopentene and cyclooctene were equally reactive (within experimental error) and more efficient than allylbenzene in trapping silylene (cyclopentene, $k_{\mathrm{rel}} = 1.37 \pm 0.11$; cyclooctene $k_{\mathrm{rel}} = 1.34 \pm 0.08$). Because cyclopentene- and cyclooctene-derived silacyclopropanes differ in thermodynamic stability (eq 6), the similar k_{rel} values indicate that the transition state for extrusion must be product-like (t-Bu$_2$Si:), and the observed k_{rel} of 1.3 should extend to describe cycloaddition of di-*tert*-butylsilylene with cyclohexene (Figure 5).



n	k_{rel} (5:2)
1	1.37 ± 0.11
4	1.34 ± 0.08



n	T (°C)	% transfer
1	130	>99
2	120	>99
4	150	96

The thermodynamic and kinetic data can be represented as a reaction coordinate diagram to describe di-*tert*-butylsilylene transfer from cyclohexene silacyclopropane **1** to allylbenzene (eq 7; Figure 6). The difference in ground-state energies ($\Delta G°$) can be estimated to be ≥4.8 kcal, since the reaction goes to >99% completion. Since cyclic alkenes are more reactive than acyclic alkenes ($k_{\mathrm{rel}} = 1.3$), the transition state for extrusion is marginally lower in energy than cycloaddition of silylene onto allylbenzene by 200 cal·mol^{-1}. The kinetic data did not provide insight into the relative energies of the silylene–alkene complexes and free silylene.

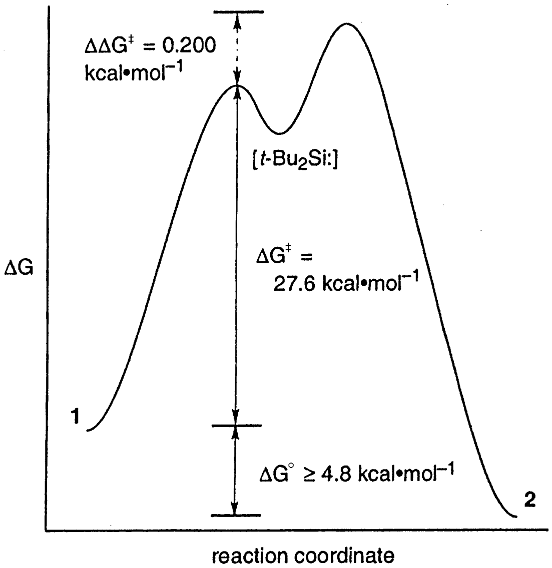
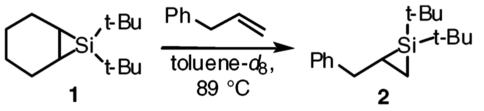


Figure 6. Reaction coordinate diagram describing silylene transfer from **1** to allylbenzene.



The mechanistic insight gained in this study was applied toward the development of methodology to improve the construction of silacyclopropanes. Because the thermodynamic driving force to transfer di-*tert*-butylsilylene from **1** to substituted cyclohexenes was missing, statistical mixture of products were obtained by using the previously reported methods.[17] The reversibility of the extrusion from **1** could be exploited to access these desirable silacyclopropanes. If cyclohexene could be removed from the reaction mixture, the formation of functionalized cyclohexene-derived silacyclopropanes could be achieved. Cyclohexene could be effectively removed from the reaction mixture using an evacuated headspace and toluene solvent because the lowest-boiling component of the reaction is cyclohexene. Rational modification of reaction conditions provided functionalized silacyclopropanes **8** and **10** (eqs 8 and 9).

Conclusion

A quantitative analysis of the thermal behavior of cyclohexene silacyclopropane **1** in the presence of an alkene improved our understanding of the fundamental reactivity of silacyclopropanes. The kinetic behavior confirmed that the formation of di-

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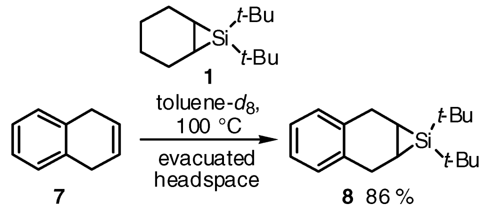
(33) For leading references to the coordination of Lewis bases with silylenes, refer to: (a) Steele, K. P.; Weber, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 2, 6095–6097. (b) Weidenbruch, M.; Piel, H.; Lesch, A.; Peters, K.; von Schnering, H. G. *J. Organomet. Chem.* **1993**, *454*, 35–43. (c) Bott, S. G.; Marshall, P.; Wagenseller, P. E.; Wang, Y.; Conlin, R. T. *J. Organomet. Chem.* **1995**, *499*, 11–16. (d) Takeda, N.; Suzuki, H.; Tokitoh, N.; Okazaki, R.; Nagase, S. *J. Am. Chem. Soc.* **1997**, *119*, 1456–1457. (e) Belzner, J.; Ihmels, H. *Adv. Organomet. Chem.* **1999**, *43*, 1–42. (f) Bharatam, P. V.; Moudgil, R.; Kaur, D. *Organometallics* **2002**, *21*, 3683–3690.

(34) The reviewers are gratefully acknowledged for this insight.



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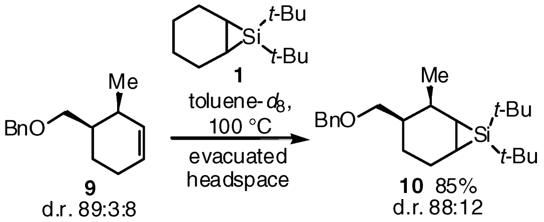

(9)

tert-silylene is reversible and established that the rate of cycloaddition with cyclohexene and allylbenzene is similar. The observed small, negative Hammett ρ value suggested that cycloaddition occurs through a concerted, electrophilic attack of di-*tert*-butylsilylene on the alkene. Determination of the Eyring activation parameter $\Delta S^{\ddagger}$ to be -15 eu suggested that the silylene transition state may consist of an alkene−silylene complex. Mechanistic insight guided the rational modification of reaction conditions to permit construction of previously inaccessible cyclohexene-derived silacyclopropanes.

Experimental Section

General Comments Concerning the Procedure. Unless otherwise noted, all reagents were commercially obtained and, where appropriate, purified prior to use. Toluene-d_8 was distilled from CaH_2 and degassed prior to use. All reagents and cyclohexene di-*tert*-butylsilacyclopropane **1** were stored in an Innovative Technologies nitrogen atmosphere drybox.

The apparatuses (volumetric flasks and valved NMR tubes) were washed with a solution of 2:1 HCl (12 N):HNO_3 (16 N), rinsed with water and acetone, washed with ammonium hydroxide, and rinsed with water and acetone. The valved NMR tubes were dried at 130 °C. Each experiment was set up in the nitrogen atmosphere drybox and was carried out in triplicate (three at a time). The reaction mixture was heated to the desired temperature either in the NMR probe (kinetic order in allylbenzene and **1**) or using a 1000 mL oil bath. The reaction progress over the first half-life (or, when appropriate, five half-lives) was monitored periodically using ^{1}H NMR spectroscopy. The concentrations of the reactants and products were obtained through comparison of the area of the standard ($PhSiMe_3$ peak at 0.19 ppm, area = 1.0000) and the area of the *t*-Bu peaks of the silacyclopropanes **1** and **2** (**1**, 1.00 and 1.19 ppm; **2**, 1.06 and 0.98 ppm). The data obtained were fit to the best straight line using a least-squares program. For tabular and graphical representation of the data, refer to the Supporting Information.

The general procedure is illustrated for the reaction of cyclohexene silacyclopropane **1** with excess allylbenzene. To a solution of cyclohexene silacyclopropane **1** (0.200 mL of a 0.4455 M solution in toluene-d_8, 0.0891 mmol) in 0.600 mL of a 0.02346 M solution of $PhSiMe_3$ in toluene-d_8 (contained in a 2 mL volumetric flask) was added allylbenzene (0.275 mL, 2.07 mmol). The resulting solution was diluted to 2 mL with additional 0.02346 M solution of $PhSiMe_3$ in toluene-d_8. The reaction mixture was then divided among three valved NMR tubes (0.600 mL in each). Initial ^{1}H NMR spectra were obtained, and the temperature of the reaction mixture was regulated to 80 ± 1 °C. Periodically, the reaction mixture was rapidly cooled to 0 °C, and the reaction progress was measured relative to the internal standard of $PhSiMe_3$ at ambient temperature using ^{1}H NMR spectroscopy.

General Procedure for the Construction of the Cyclohexene-Derived Silacyclopropanes 8 and 10. The general procedure is illustrated for the reaction of cyclohexene silacyclopropane **1** with 1, 4-dihydronaphthalene. To a solution of 1,4-dihydronaphthalene (25.0 mg, 0.192 mmol) in 0.300 mL of a 0.02346 M solution of $PhSiMe_3$ in toluene-d_8 (contained in a medium wall NMR tube) was added 0.200 mL of a 0.4455 M solution of cyclohexene silacyclopropane **1** in toluene-d_8. The reaction mixture was degassed and sealed under vacuum. After an initial ^{1}H NMR spectrum was obtained, the reaction mixture was warmed to 100 °C for 16 h and monitored periodically using ^{1}H and ^{29}Si NMR spectroscopy. The ^{29}Si NMR spectrum was obtained to verify the formation of product silacyclopropane (δ -44.15 ppm). The yield of the reaction was determined by comparison of peaks associated with the product silacyclopropane **8** (diagnostic *t*-Bu peaks at δ 1.144 and 0.943 ppm) with the internal standard $PhSiMe_3$ (*t*-Bu peak at δ 0.19 ppm, area set to be one). The same procedure was followed with cyclohexene **9** to provide silacyclopropane **10** in 85% yield. Diagnostic peaks: *t*-Bu peaks at δ 1.16 and 0.99 ppm; ^{29}Si NMR peak at δ -54.7 ppm.

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Supporting Information Available: Experimental procedures, tabular, graphical, and mathematical derivations of kinetic and thermodynamic parameters, and spectroscopic data for the products (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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