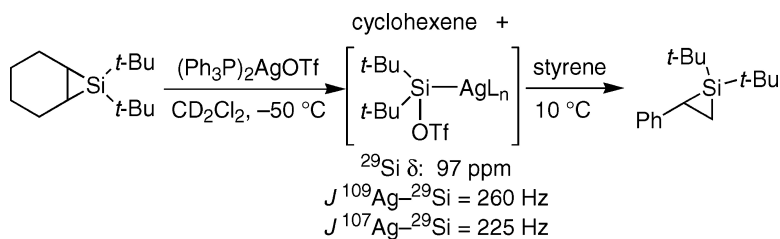


Mechanism of Silver-Mediated Di-*tert*-butylsilylene Transfer from a Silacyclopropane to an Alkene

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Mechanism of Silver-Mediated Di-*tert*-butylsilylene Transfer from a Silacyclopropane to an Alkene

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Abstract: Kinetic studies of the reactions of cyclohexene silacyclopropane **1** and monosubstituted alkenes in the presence of 5 mol % of $(\text{Ph}_3\text{P})_2\text{AgOTf}$ suggested a possible mechanism for silver-mediated di-*tert*-butylsilylene transfer. The kinetic order in cyclohexene silacyclopropane **1** was determined to be one. Inverse kinetic saturation behavior (rate inhibition) was observed in monosubstituted alkene and cyclohexene concentrations. Saturation kinetic behavior in catalyst concentration was observed. A reactive intermediate, a silylsilver complex, was observed using low temperature ^{29}Si NMR spectroscopy. Competition experiments between substituted styrenes and a deficient amount of **1** correlated well with the Hammett equation and provided a ρ value of -0.62 ± 0.02 using σ_p constants. These data support a mechanism involving reversible silver-promoted di-*tert*-butylsilylene extrusion from **1** followed by irreversible concerted electrophilic attack of the silylsilver intermediate on the alkene.

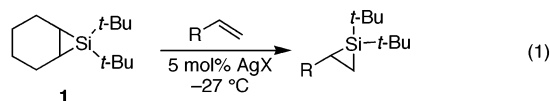
Introduction

The unique reactivity of silacyclopropanes^{1–6} has prompted interest in developing efficient methods for their construction.^{7,8} The syntheses of silacyclopropanes often rely on the transfer of silylene intermediates $(\text{R}_2\text{Si})^{9–24}$ to alkenes. For example, thermolysis of various cyclic silanes^{25–28} produces silylene intermediates that can be trapped by alkenes to form silacyclopropanes.^{29–32} Alternatively, the required silylene or silylenoid

intermediates can be generated through photolysis of cyclic silanes or trisilanes^{33,34} or the use of strong reductants (such as lithium or potassium) with dihalosilanes.^{26,28,35–38} We recently reported a mild method for silacyclopropane synthesis by silver-catalyzed silylene transfer at -27°C from cyclohexene sily-

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cyclopropane **1**^{31,39} to various chiral, functionalized alkenes (eq 1).⁴⁰ This reaction is stereospecific, stereoselective, and tolerant of various functional groups. Because silver-catalyzed silylene transfer has proven to be a mild method for the silacyclopropanation of alkenes, we believed that a detailed mechanistic understanding of this reaction would guide future improvements in silacyclopropane synthesis.



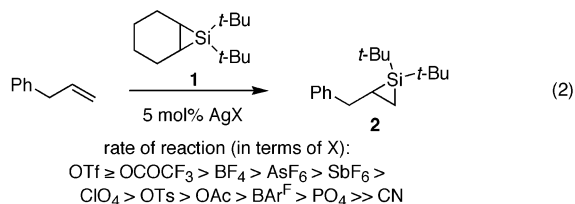
The mechanisms of analogous silver-promoted carbene transfer reactions remain poorly understood,^{41–43} although other metal-mediated carbene transfer reactions^{44–49} have been studied extensively. In general, silver-catalyzed reactions⁵⁰ provide different products from copper-catalyzed processes, because the silver-mediated reactions likely proceed by free carbenes, not metal carbenoids.^{51–55} By analogy, the silver-promoted silylene transfer could involve a free silylene intermediate, or it could proceed via a silver silylenoid species.^{56,57} Because of these ambiguities, we believed a quantitative study was needed to eliminate a mechanism involving free silylene as a reactive intermediate.

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To understand the fundamental reactivity of the intermediates in the silver-catalyzed formation of silacyclopropanes, we conducted a quantitative analysis of the behavior of cyclohexene silacyclopropane **1** in the presence of an alkene and a catalytic amount of a silver salt. Analysis of the kinetic behavior and the spectroscopic observation of a silylsilver intermediate led us to propose a mechanism likely involving reversible silver-catalyzed extrusion of di-*tert*-butylsilylenoid from silacyclopropane **1** followed by irreversible cyclization with an alkene. The electrophilicity of the silylsilver intermediate was established by the identification of a Hammett ρ value. These results and data from competition experiments permitted construction of a reasonable catalytic cycle to describe the silver-mediated silylene transfer from **1** to an alkene.

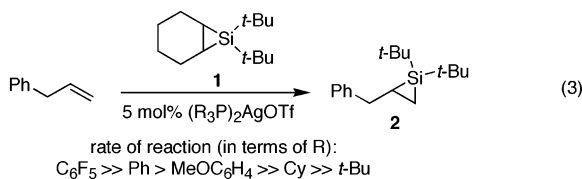
Results and Discussion

Influence of Catalyst on Reaction Rate. Insight into the mechanism of silver-promoted di-*tert*-butylsilylene transfer from cyclohexene silacyclopropane **1** to an alkene began with the optimization of experimental conditions. To facilitate kinetic analysis using ¹H NMR spectroscopy, a reproducible reaction that occurred at a moderate rate around 0 °C was sought. Extensive experimentation was required to identify the optimum silver salt to fulfill this requirement. Many silver salts promoted this reaction at low temperatures (≤ 25 °C, eq 2). The duration of the reaction time, however, was found to be dependent upon the counterion. The half-life of silylene transfer varied from 30 min at -35 °C employing 5 mol % of AgOTf or AgOCOCF₃ to greater than 8 h at 25 °C with 5 mol % of Ag₃PO₄.



During the screening of different silver salts, several challenges arose. Monitoring the progress of reactions using more-reactive silver salts such as AgOTf or AgOCOCF₃ was difficult. Agitation of the cold (-78 °C) reaction mixture before placement in a cold (-40 °C) NMR probe induced reaction up to 20%. The accumulation of Ag(0) as a mirror or precipitate as the reaction progressed represented an additional obstacle. The combination of these challenges led to irreproducible data.

The addition of ancillary ligands was postulated to address the aforementioned challenges by limiting the decomposition of the catalyst through the stabilization of reactive intermediates. The use of phosphine ligands allowed the rate of silylene transfer to be studied conveniently using ¹H NMR spectroscopy. The substituents on phosphine were varied to observe their impact on reaction rate (eq 3). Alkyl phosphines were found to inhibit the reaction. While no reaction was observed employing *t*-Bu₃P, silylene transfer took place using Cy₃P only at temperatures in excess of 60 °C. At this temperature, silylene transfer occurs thermally.²³ Aryl substituents on phosphine, conversely, facilitated silylene transfer at 25 °C without significant catalyst decomposition.



The electronic nature of the phosphine appears to control the rate of the reaction.⁵⁸ Steric effects can be discounted, because the fastest reaction occurs using (C₆F₅)₃P as the ancillary ligand, which is similar in size to Cy₃P.⁵⁹ Due to its increased solubility and the moderate rate of reaction at 10 °C, (Ph₃P)₂AgOTf was chosen as the catalyst to study the transfer of di-tert-butylsilylene from cyclohexene silacyclopropane **1** to an alkene.

Structure of [(Ph₃P)₂AgOTf]_n. The mechanistic study of silver-mediated silylene transfer commenced with structural determination of (Ph₃P)₂AgOTf. In the solid state, the catalyst exists as the dinuclear complex [(Ph₃P)₂AgOTf]₂, where the triflates serve as bridges between the two distorted tetrahedral silver atoms.⁶⁰ Silver phosphine complexes often exist as higher-order oligomers in the solid state. With counterions such as halides or perchlorate, infinite polymeric chains,⁶¹ or cubane structures^{62,63} are typically observed.

In solution, the silver phosphine complex used for catalysis exists as a dynamic species.^{60,64} IR spectroscopy of our catalyst in solution closely resembled its solid state (KBr pellet) spectrum: prominent S=O stretches at 1293 and 1096 cm⁻¹ indicated the ionic nature of the triflate counterion.⁶⁵ Analysis of (Ph₃P)₂AgOTf using variable temperature ³¹P NMR spectroscopy further illuminated the catalyst solution structure. At -40 °C, the ³¹P {¹H} NMR spectrum displayed two doublets at δ 12.4 ppm, corresponding to ³¹P-¹⁰⁷Ag and ³¹P-¹⁰⁹Ag coupling (*J* = 487.4 Hz and *J* = 560.0 Hz, respectively).⁶⁶ At temperatures above -20 °C,⁶⁷ the doublets at δ 12.4 ppm coalesced into broad peaks at δ 13.5 and 11.0 ppm, indicating the rapid exchange of triphenylphosphine between ¹⁰⁷Ag and ¹⁰⁹Ag atoms.⁶⁸ These studies reveal that at 10 °C, the temperature at which catalysis occurs, a molecule of free triphenylphosphine is rapidly exchanging with the silver phosphine complex.

Relative Reactivity of Silacyclopropanes with (Ph₃P)₂AgOTf. The reactivities of various silacyclopropanes in the

presence of styrene and a catalytic amount of (Ph₃P)₂AgOTf were examined to determine if cyclohexene silacyclopropane **1** is the most efficient source of di-tert-butylsilylene and if silylene transfer were reversible (eq 4, Table 1). Of the bicyclic silacyclopropanes examined, cyclohexene silacyclopropane **1** exhibited the highest reactivity, with a half-life of 1 h at 10 °C (entry 1). Decreasing or increasing the size of the cycloalkene portion of the silacyclopropane diminished the rate of reaction. Cyclopentene silacyclopropane **4** reacted slowly at 25 °C (*t*_{1/2} ≈ 25 h, entry 2), and cyclooctene silacyclopropane **5** required temperatures in excess of 60 °C to afford any styrene silacyclopropane **3** (entry 3). The different rates for silylene extrusion from silacyclopropanes **1**, **4**, and **5** were consistent with the thermal stabilities of **1**, **4**, and **5**. The cause for the different relative stabilities of cycloalkene silacyclopropanes, however, has not been determined.

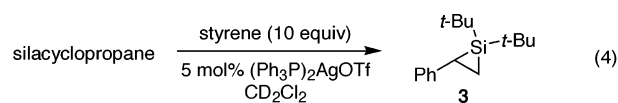


Table 1. Relative Reactivity of Silacyclopropanes

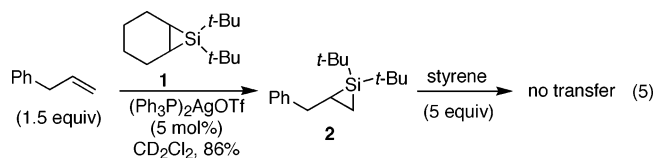
Entry	Silacyclopropane	Temp. (°C)	Reaction progress
1		10	<i>t</i> _{1/2} ~ 1 h
2		25	<i>t</i> _{1/2} ~ 25 h
3		60	48 h, 8% (5 , 70%)
4		60	no transfer

Monocyclic silacyclopropane **2** was determined to be stable to the reaction conditions. Exposure of silacyclopropane **2** to (Ph₃P)₂AgOTf and styrene afforded neither silacyclopropane **3** nor any decomposition products (entry 4). After 3 days at 60 °C, silacyclopropane **2** remained in over 90% of its starting concentration. The stability of benzyl silacyclopropane **2** towards any silver species produced from di-tert-butylsilylene transfer was also established. After silylene transfer from cyclohexene silacyclopropane **1** to allylbenzene (to form **2** in 86% yield), styrene was added (eq 5). Neither silylene transfer to styrene nor decomposition of **2** was observed. Because silacyclopropanes **2** and **5** are inert to silver-salt catalysis below 25 °C, silylene transfer to acyclic and likely most cyclic alkenes must be irreversible.

Examination of the Initial Rates of Di-tert-butylsilylene Transfer. A kinetic analysis of (Ph₃P)₂AgOTf-mediated di-tert-butylsilylene transfer from cyclohexene silacyclopropane **1** to an alkene was performed using the optimal experimental

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- (66) Elemental silver exists as a 48:52 mixture of two NMR active (*I* = 1/2) isotopes, ¹⁰⁷Ag and ¹⁰⁹Ag, with a gyromagnetic ratio of 1.15. Becker, E. D. *High-Resolution NMR: Theory and Chemical Applications*; Academic: San Diego, 1980; pp 281–291.
- (67) At low temperatures (below -40 °C), the disproportionation of (Ph₃P)₂AgOTf into (Ph₃P)₃AgOTf and Ph₃PAgOTf was observed in the resolution of small broad peaks upfield at 12.3 and 10.6 ppm. See Muetterties and Alegrianti⁶⁴ for further details.

- (68) The dissociation constants for silver triphenylphosphine complexes have been elucidated in DMSO, pyridine, and water and show a significant solvent effect resulting from the difference in Ag(I) solvation. In methylene chloride, the expected dissociation constant (*K*₂) is expected to be significantly smaller than the 8.91 × 10⁵ s⁻¹ reported in water. Refer to: (a) Ahrland, S.; Hultén, F.; Persson, I. *Acta Chem. Scand.* **1986**, *A40*, 595–600. (b) Ahrland, S.; Hultén, F. *Inorg. Chem.* **1987**, *26*, 1796–1798. (c) Di Bernardo, P.; Dolcetti, G.; Portanova, R.; Tolazzi, M.; Tomat, G.; Zanonato, P. *Inorg. Chem.* **1990**, *29*, 2859–2862.



conditions. To ensure the solubility of the silver salt over a range of temperatures, CD_2Cl_2 was selected as the solvent. Because of its high boiling point, low polarity, and distinct ^1H NMR spectrum, phenyltrimethylsilane was chosen as the internal standard. The selection of styrene as the di-*tert*-butylsilylene acceptor facilitated analysis using ^1H NMR spectroscopy. Several signals, including those of the *t*-Bu groups, were distinct for both the product and starting material. The kinetic order experiments were performed by the dropwise addition of a CD_2Cl_2 solution containing the silver catalyst and alkene to a cold (-78°C) CD_2Cl_2 solution of cyclohexene silacyclopropane **1**. Because of this procedure, the catalyst is assumed to exist at the outset of the reaction as the 18-electron alkene complex, $(\text{Ph}_3\text{P})_2\text{Ag}(\text{styrene})_2\text{OTf}$.⁶⁹ After agitation, the NMR tube containing the reaction mixture was placed in a cool (-20°C) NMR probe. The reaction progress was monitored at 10°C .⁷⁰

Insight into the mechanism of silver-mediated 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). Inverse saturation behavior was observed for both styrene and cyclohexene concentrations (Figure 2). Inhibition of the reaction by cyclohexene was more than four times more severe than styrene. Addition of 1 equiv of triphenylphosphine (relative to catalyst) caused immediate precipitation of a white solid, presumed to be $[(\text{Ph}_3\text{P})_3\text{AgOTf}]_n$, and the reaction was completely suppressed.

Inhibition of the reaction rate through the addition of triphenylphosphine and the rate differences between aryl and alkyl phosphines (vide supra) suggest that the ancillary ligand must initially dissociate (Scheme 1). The addition of triphenylphosphine may only have generated insoluble silver oligomeric complexes. Alternatively, increasing the phosphine concentration could suppress reaction by decreasing the amount of monophosphine complex **6**. The rate acceleration observed with the perfluorinated aryl phosphine silver complex could reflect the lability of this electron poor ligand.⁵⁸ In contrast, the electron-rich ancillary ligand, tricyclohexylphosphine, could have slowed the rate of silylene transfer because of its potent coordination.

Inhibition of the reaction rate by alkene implicates a mechanism in which dissociation of a molecule of alkene must occur before reaction of the catalyst with cyclohexene silacyclopropane **1** (Scheme 1). Given silver's affinity for alkenes,^{71–75} increasing the concentration of either styrene or cyclohexene would have

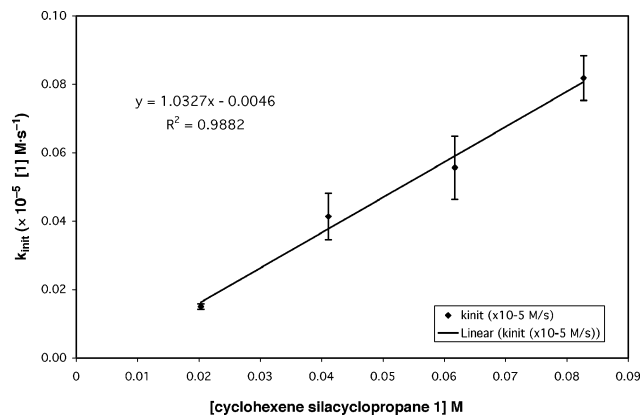


Figure 1. Determination of kinetic order in [cyclohexene silacyclopropane **1**].

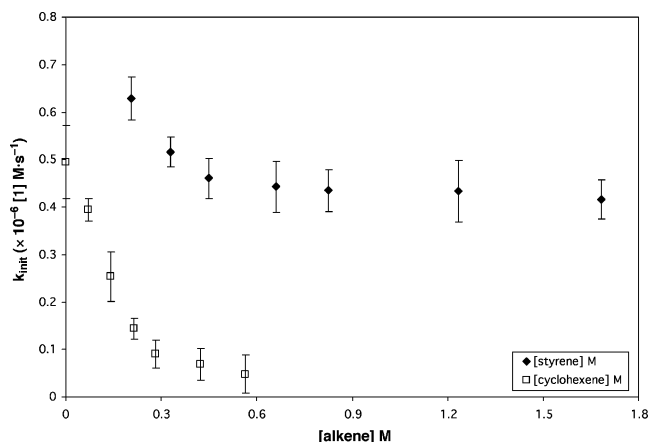
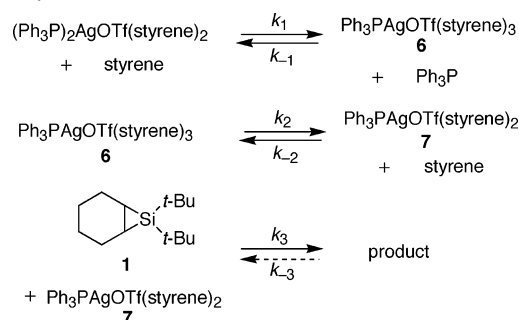


Figure 2. Determination of kinetic order in [styrene] and [cyclohexene].

Scheme 1. Mechanistic Origin of Rate Suppression by Alkene and Phosphine Concentration



a deleterious effect on reaction rate by decreasing the amount of free, reactive catalyst (**7**). The proposal that an alkene must dissociate from silver is also consistent with the relative magnitude of inhibition by addition of different alkenes. The observation that silylene transfer is inhibited four times more by cyclohexene than by styrene correlates well with the known four-fold lower dissociation constants for disubstituted alkenes versus monosubstituted alkenes.⁷⁴ The suppressed rate could originate, additionally, from faster trapping of an intermediate by cyclohexene than by styrene, as has been observed for *t*-Bu₂Si.²³

Determination of kinetic order concluded with the observation of saturation behavior in $(\text{Ph}_3\text{P})_2\text{AgOTf}$ concentration (Figure 3). Saturation behavior occurs when the concentration of catalyst, $(\text{Ph}_3\text{P})_2\text{Ag}(\text{styrene})_2\text{OTf}$, appears in both the numerator and the denominator of the rate expression. To satisfy this

(69) Typically when olefin ligands are present, the Ag^+ ion is tetrahedrally coordinated. See: (a) Baenziger, N. C.; Haight, H. L.; Alexander, R.; Doyle, J. R. *Inorg. Chem.* **1966**, *5*, 1399–1400. (b) Gray, D.; Wies, R. A.; Closson, W. D. *Tetrahedron Lett.* **1968**, *9*, 5639–5641. (c) Rodesiler, P. F.; Hall Griffith, E. A.; Amma, B. L. *J. Am. Chem. Soc.* **1972**, *94*, 761–766. (d) Mak, T. C. W.; Ho, W. C.; Huang, N. Z. *J. Organomet. Chem.* **1983**, *251*, 413–421.

(70) Refer to the experimental and Supporting Information sections for further details.

(71) Keller, R. N. *Chem. Rev.* **1941**, *28*, 229–267.

(72) Fueno, T.; Okuyama, T.; Deguchi, T.; Furukawa, J. *J. Am. Chem. Soc.* **1965**, *87*, 170–174.

(73) Parker, R. G.; Roberts, J. D. *J. Am. Chem. Soc.* **1970**, *92*, 743.

(74) Wilcox, C. F., Jr.; Gaal, W. *J. Am. Chem. Soc.* **1971**, *93*, 2453–2459.

(75) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889–1897.

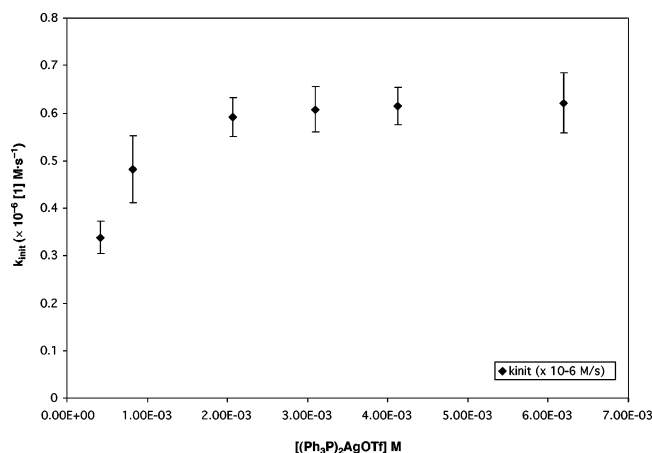
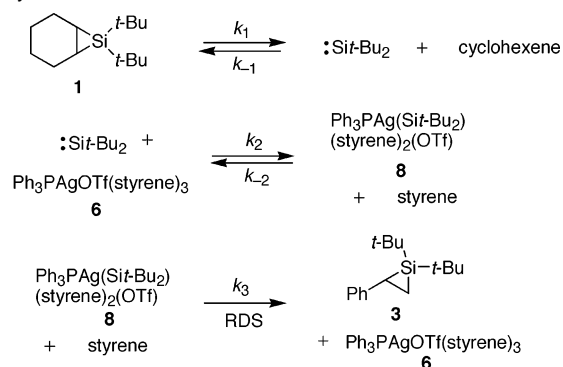


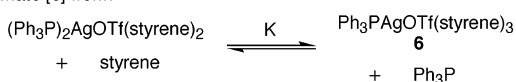
Figure 3. Determination of kinetic order in [(Ph₃P)₂AgOTf].

Scheme 2. Possible Mechanism To Satisfy Saturation Behavior of Catalyst



$$\frac{d[\text{pdt}]}{dt} = \frac{Kk_1k_2k_3[\text{Ag}(\text{styrene})_2][1][\text{styrene}]}{(k_{-1}k_{-2} + k_{-1}k_3)[\text{cyclohexene}][\text{Ph}_3\text{P}] + Kk_2k_3[\text{Ag}(\text{styrene})_2][\text{styrene}]} \quad (6)$$

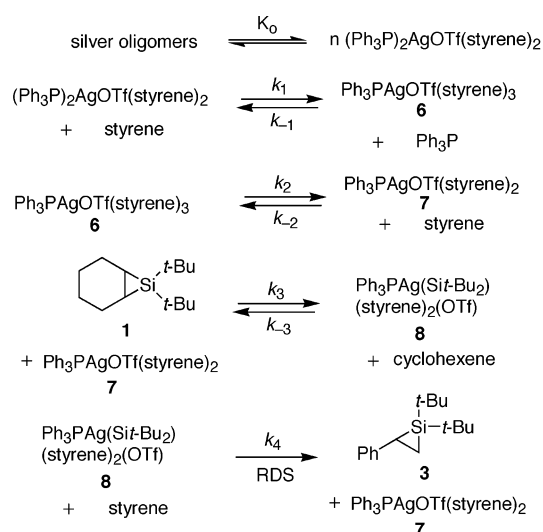
Estimate [6] from:



requirement, a reversible step must precede participation of a molecule of catalyst in the mechanism. If unreactive silver catalyst oligomers accumulated at higher concentrations, this nonlinear behavior could result from a kinetic order less than one (but greater than zero). All experiments, however, were performed significantly below concentrations where silver phosphine complexes have been reported to be monomeric.^{60,64,76}

Mechanisms Consistent with the Kinetic Behavior. Several mechanisms satisfy the rate expression constraints imposed by the observed saturation behavior (Schemes 2 and 3).⁷⁷ In the first mechanism (Scheme 2, eq 6), cyclohexene silacyclopropane **1** extrudes di-tert-butylsilylene, which is rapidly trapped with catalyst. Silylsilver complex **9** then reacts with a molecule of styrene to afford the product styrene silacyclopropane. This mechanism has several liabilities. First, it violates the principle of microscopic reversibility, since silver only participates in the

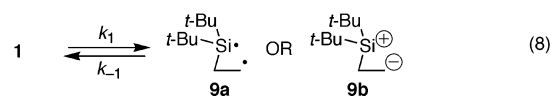
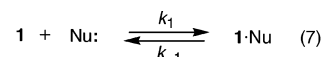
Scheme 3. Oligomerization as Explanation for Saturation Behavior in Silver Concentration



$$\frac{d[\text{pdt}]}{dt} = \frac{k_1k_2k_3k_4(K_0)^{1/n}[\text{Ag}_n]^{1/n}[1][\text{styrene}]}{(k_{-1}k_{-2}k_{-3}[\text{cyclohexene}] + k_{-1}k_{-2}k_4[\text{styrene}])[\text{Ph}_3\text{P}] + (k_{-1}k_3k_4[\text{Ph}_3\text{P}] + k_2k_3k_4)[1]} \quad (9)$$

formation of and not the ring-opening of silacyclopanes. Second, similar activation parameters to thermal silylene transfer²³ would be expected to describe this mechanism, but they are different (vide infra).

Other mechanisms involving the preactivation of cyclohexene silacyclopropane **1** before reaction with the silver catalyst also appear to be inconsistent with our observations (eq 7). While the formation of the siliconate of **1** should increase the lability of di-tert-butylsilylene, coordination by triflate or alkene would lead to kinetic orders in catalyst or alkene that are greater than one. Unique activation parameters would be observed if the siliconate is formed with solvent, but these parameters are consistent in two different solvents (vide infra). In an additional mechanism, the cleavage of a C–Si bond before reaction with catalyst could occur (eq 8). The silver-catalyzed silylene transfer, however, is stereospecific,⁴⁰ and a Hammett ρ value inconsistent with the stepwise extrusion of silylenoid was observed (vide infra). The activation of cyclohexene silacyclopropane **1** does not appear to occur before reaction with catalyst.



A mechanism that involves the sequestering of the silver catalyst as a silver oligomer appears to be most consistent with the observed data (Scheme 3). In this mechanism, increasing the concentration of silver serves only to favor the equilibrium toward an unreactive oligomeric reservoir. Upon dissociation, ligand exchange of triphenylphosphine with a molecule of styrene occurs to form **6**. To liberate a coordination site and thus allow reaction with cyclohexene silacyclopropane **1**, styrene dissociates from the monophosphine catalyst. These two elementary steps explain the inhibition by alkene and phosphine. Silver then mediates the reversible extrusion of di-tert-butyl-

(76) Bachman, R. E.; Andretta, D. F. *Inorg. Chem.* **1998**, *37*, 5657–5663.

(77) Another conceivable reaction mechanism in which free silylene reacts with a molecule of (Ph₃P)₂Ag(styrene)₂OTf to produce product would exhibit a rate law inconsistent with the kinetic data (zero order in styrene concentration would be predicted). For more details and analyses of other less-likely mechanisms refer to the Supporting Information.

Scheme 4. Behavior for Silylsilver Complex 8

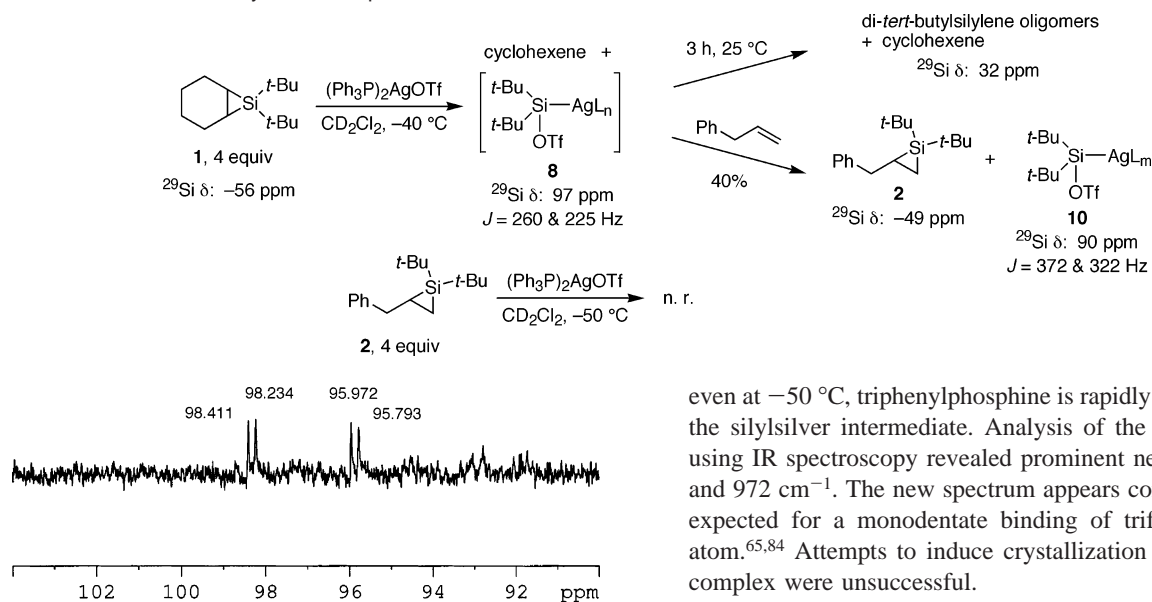


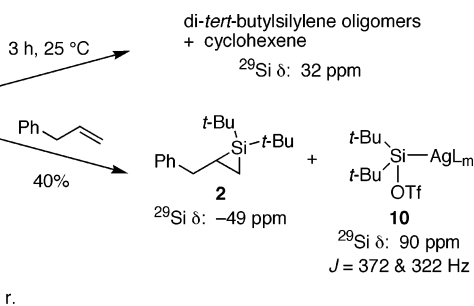
Figure 4. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectroscopic evidence for silylsilver complex **8**.

silylene from **1** to form silylsilver complex **8**, which then reacts with an additional molecule of alkene to form the product, styrene silacyclopropane **3**. The resultant rate expression (eq 9) indicates that saturation behavior in cyclohexene silacyclopropane **1** should be observed. Because only a small range of concentrations was examined for **1**, it is possible that saturation never was reached.

Identification and Analysis of a Silylsilver Intermediate.

Silylsilver complex **8** was identified as a reactive intermediate using low-temperature NMR and IR spectroscopy. For these experiments, the reaction between $(\text{Ph}_3\text{P})_2\text{AgOTf}$ (1 equiv) and cyclohexene silacyclopropane **1** (2 equiv) was analyzed at $-40\text{ }^\circ\text{C}$ (Scheme 4). Free cyclohexene was observed in the ^1H NMR spectrum,⁷⁸ and analysis of the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum revealed the appearance of two new doublets situated at δ 97 ppm (Figure 4). The observed 1.155:1 ratio between the coupling constants ($J = 259.9$ and 224.9 Hz) implicates $^{107}\text{Ag}-^{29}\text{Si}$ and $^{109}\text{Ag}-^{29}\text{Si}$ coupling, since their relative gyromagnetic ratio is 1.15.⁶⁶ The downfield location of this silicon species is consistent with a Lewis base-stabilized metal silylenoid.^{79,80} Recently, the silicon atom of the silylgold complex, $\text{Ph}_3\text{PAu}-\text{SiCp}^*_2\text{Cl}$,^{56e} was reported to appear at δ 77.6 ppm.⁸¹ In contrast to the silylgold species, no $^{31}\text{P}-^{29}\text{Si}$ coupling was observed in either the ^{29}Si or $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of our silver intermediate.^{82,83} The lack of phosphorus coupling indicates that

- (78) The absence of a diagnostic δ ppm shift in the ^1H NMR spectrum of cyclohexene in the presence of silylsilver complex **8** (relative to cyclohexene without silver) did not provide evidence for the coordination of cyclohexene to silver.
- (79) Lewis base stabilized silylenoid complexes have been reported to appear at ^{29}Si δ 88.6 ppm for $(\text{Et}_3\text{P})_2\text{Pt}(\text{Si}(\text{t-Bu})_2(\text{OEt}_2))$ by Mitchell, G. P.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 7635–7636 or ^{29}Si δ 56.0 ppm for $\text{Fp}-\text{SiMe}_2\text{Ot-Bu}$ by Sharma, H. K.; Pannell, K. H. *Organometallics* **2001**, *20*, 7–9.
- (80) Neutral metal silylenoids appear further downfield: ^{29}Si δ 367 ppm for $(\text{Cy}_3\text{P})_2\text{Pt}=\text{SiMe}_2$ by Feldman, J. D.; Mitchell, G. P.; Nolte, J.-O.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 11184–11185 and ^{29}Si δ 241 ppm for $[\text{PhB}(\text{CH}_2\text{PPh}_2)_3\text{Ir}(\text{H})_2(=\text{SiMe}_2)]^+$ by Peters, J. C.; Feldman, J. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1999**, *121*, 9871–9872.
- (81) Exposure of 1 equiv of Ph_3PAuCl to 2 equiv of cyclohexene silacyclopropane **1** led to the appearance of a broad peak between 80 and 82 ppm in the ^{29}Si NMR spectrum attributable to the formation of $\text{Ph}_3\text{PAu}-\text{Si}(\text{t-Bu})_2(\text{Cl})$.



even at $-50\text{ }^\circ\text{C}$, triphenylphosphine is rapidly exchanging from the silylsilver intermediate. Analysis of the reaction mixture using IR spectroscopy revealed prominent new peaks at 1204 and 972 cm^{-1} . The new spectrum appears consistent with that expected for a monodentate binding of triflate to a silicon atom.^{65,84} Attempts to induce crystallization of the silylsilver complex were unsuccessful.

The behavior of the reactive silver intermediate was analyzed qualitatively (Scheme 4). Warming silylsilver complex **8** to above $-20\text{ }^\circ\text{C}$ resulted in the disappearance of the distinctive ^{29}Si NMR doublets and the accumulation of oligomeric silicon products.⁸⁵ The silylsilver complex appeared to be catalytically active. The addition of allylbenzene (4 equiv) to the intermediate resulted in complete consumption of cyclohexene silacyclopropane **1** and formation of product silacyclopropane **2**. Furthermore, analysis of the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum revealed the disappearance of the peaks associated with silylsilver complex **8** and the appearance of a new set of two doublets situated at δ 90 ppm. The observed ratio of 1.155:1 between the coupling constants ($J = 372.5$ and 322.4 Hz) is consistent with the gyromagnetic ratio expected for $^{109}\text{Ag}-^{29}\text{Si}$ and $^{107}\text{Ag}-^{29}\text{Si}$ coupling.⁶⁶ A different ligand environment around silver (cyclohexene replaced with allylbenzene) could account for the variation of chemical shift and coupling constants between **8** and **10**. Since exposure of silacyclopropane **2** to $(\text{Ph}_3\text{P})_2\text{AgOTf}$ did not yield **8**, **10**, or allylbenzene, formation of silylsilver complex **8** from cyclohexene silacyclopropane **1** is unique. Unfortunately, monitoring the rate of formation of silver intermediate **8** using spectroscopic techniques was not successful.

- (82) At $-60\text{ }^\circ\text{C}$, the peaks present in $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum sharpened, and the area of the doublet at 6.23 ppm was noticeably smaller. Examination of the NMR tube, however, revealed the formation of extensive precipitation. Further analysis at this (or lower) temperatures was hampered by the insolubility of the intermediates.
- (83) In addition to a large singlet at δ -1.95 ppm, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum also exhibited smaller peaks at δ 6.23 ppm ($d, J = 248$ Hz) and 4.52 ppm. The identity of the doublet at δ 6.23 ppm could be $(\text{Ph}_3\text{P})_4\text{AgOTf}$ (data consistent with the report of Laguna et al.⁶⁰). Since there were no other identifiable peaks in the ^{29}Si NMR spectrum, the smaller broad singlet at δ 4.52 could either be another product that does not contain silicon or evidence of the formation of an oligomeric silicon phosphine compound.
- (84) A 0.4 M solution of $\text{t-BuMe}_2\text{SiOTf}$ in CH_2Cl_2 exhibited an IR spectrum with peaks at 1390, 1247, 1212, 1154, and 970 cm^{-1} . Refer to the Supporting Information for an overlay of the silylsilver intermediate and $\text{t-BuMe}_2\text{SiOTf}$ IR spectra.
- (85) While the isolation of any distinct products was not possible, no spectroscopic evidence for the formation of any Si-H products was observed. For references on various oligomeric silicon products resulting from the decomposition of silylenes refer to: (a) Masamune, S.; Murakami, S.; Tobita, H. *Organometallics* **1983**, *2*, 1464–1466. (b) Watanabe, H.; Muraoka, T.; Kageyama, M.; Yochizumi, K.; Nagai, Y. *Organometallics* **1984**, *3*, 141–147. (c) Kyushin, S.; Sakurai, H.; Matsumoto, H. *J. Organomet. Chem.* **1995**, *499*, 235–240.

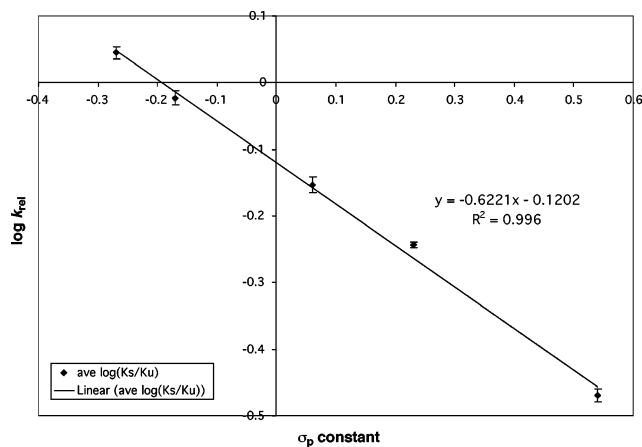


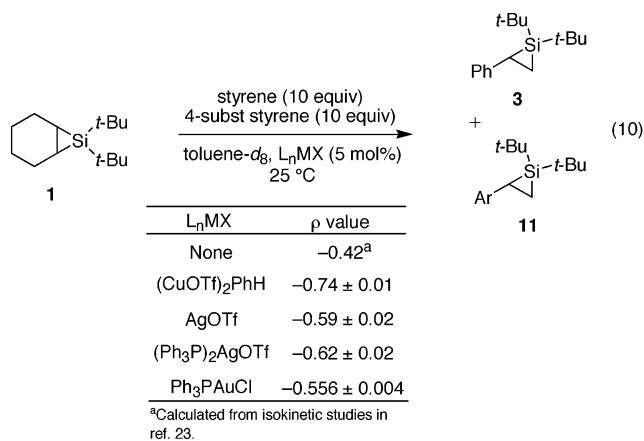
Figure 5. Linear correlation of k_{rel} with the Hammett equation using σ_p constants.

Competition Experiments between *para*-Substituted Styrenes. A series of competition experiments between various *para*-substituted styrenes (*p*-OMe, *p*-Me, *p*-F, *p*-Cl, and *p*-CF₃) and a deficient amount of **1** in the presence of 5 mol % of (Ph₃P)₂AgOTf provided insight into the electronic nature of the transition state for metal-mediated cycloaddition. Electron-rich styrenes were found to be more reactive. The rate difference for formation of substituted styrene silacyclopropanes correlated linearly with the Hammett equation using σ_p ⁸⁶ constants to result in a ρ value of -0.62 ± 0.02 at 25 °C (Figure 5). The negative value reveals the nucleophile to be the alkene source and establishes the electrophilicity of the silylsilver intermediate. The magnitude of the ρ value suggests a concerted reaction in which a small partial positive charge is generated on the benzylic carbon in the transition state.⁸⁷

The magnitude and sign of the Hammett ρ value were validated through examination of temperatures within 30 °C that did not reveal an isokinetic point. The ρ value at 8 °C and -8 °C were found to be -0.71 and -0.79 , respectively. The linear relationship observed between temperature and ρ value allowed estimation of the isokinetic temperature to be 129 °C. The isokinetic relationship observed in silver-mediated silylene transfer is opposite to what was observed for the metal-free, thermal reaction.²³ Silver-mediated silylene transfer is therefore under enthalpic control, whereas thermal silylene transfer is entropically driven. Enthalpic control of cyclization requires a relatively large ΔH^\ddagger (vide infra) and implicates formation of a stable reactive intermediate, which is consistent with the proposal that the observed silylsilver complex (vide supra) is an intermediate prior to cyclization.

In addition to (Ph₃P)₂AgOTf, other salts, including (CuOTf)₂·PhH, AgOTf, and Ph₃PAuCl, were examined as catalysts (eq 10). In each case, a unique negative Hammett ρ value was obtained. The different values indicate that neither counterion nor phosphine is responsible for cyclization. The values are also different in magnitude from the ρ value (-0.415) calculated from the thermal, metal-free isokinetic studies,²³ eliminating cyclization involving free silylene as a possible mechanism. The

sign and magnitude of the ρ -values, however, are all similar, indicating that the values are not describing styrene dissociating from a metal-alkene complex. If such were the case, work by Roberts⁷³ and Kochi⁷⁵ would predict a change in the ρ -value sign when copper was substituted for silver as the silylene transfer catalyst.⁸⁸ In these reports, a silver-alkene complex was described as having less electron density on the alkene (as compared to the free alkene),^{89,90} a copper-alkene complex has increased electron density,⁷⁵ and a gold-alkene complex a mixture (electron density on one carbon increased, the other reduced).^{91,92}

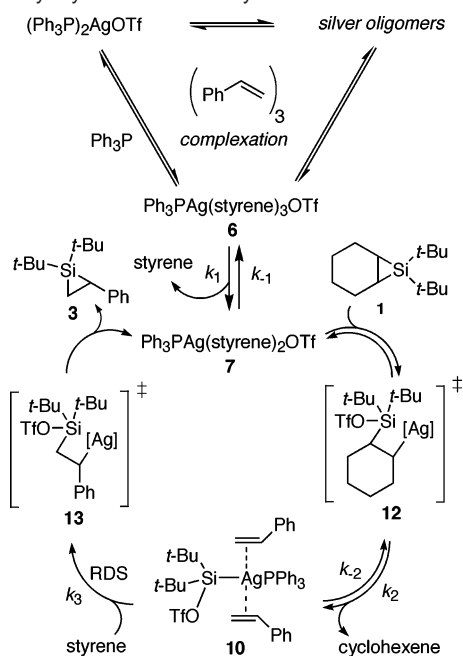


The reduction of electron density on the alkene in a silver-alkene complex is also inconsistent with it acting as the nucleophile in the mechanism. While the presence of an electron-donating ancillary ligand impacts the electron density of metal-olefin complex,^{93–96} we observed little variation in the ¹H NMR spectra of the vinylic protons of styrene when it was exposed to various concentrations of (Ph₃P)₂AgOTf.⁹⁷ While the lack of diagnostic ¹H NMR spectroscopic shifts prevented a definitive conclusion on the nucleophilicity of the phosphine silver-alkene complex, they did establish that the alkene portion of the (Ph₃P)₂Ag(styrene)₂OTf complex does not contain significantly more electron density (i.e., is not more nucleophilic) than uncomplexed styrene.

Our observations are not consistent with a mechanism involving free silylene. The reduction in reaction temperature from the addition of catalyst implicates silver involvement in silylene extrusion. The identification of the silylsilver reactive intermediate suggests that silylene is shuttled from cyclohexene

(86) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165–195.
 (87) Stepwise reactions that involve charged intermediates, such as the hydration and bromination of styrene, are typified by large negative ρ values. For example: hydration $\rho = -4$ (by Schubert, W. M.; Lamm, B.; Keefe, J. R. *J. Am. Chem. Soc.* **1964**, *86*, 4727–4729) and bromination $\rho = -4.3$ (by Dubois, J. E.; Schwarcz, A. *Tetrahedron Lett.* **1964**, *5*, 2167–2173).

(88) The shielding or deshielding of vinylic protons ($\Delta\delta$ ppm) between an alkene and a metal-alkene complex was used to generalize the amount of π electron density present on the alkene moiety.
 (89) Quinn, H. W.; McIntyre, J. S.; Peterson, D. J. *Can. J. Chem.* **1965**, *43*, 2896–2910.
 (90) Quinn, H. W.; VanGilder, R. L. *Can. J. Chem.* **1969**, *47*, 4691–4694.
 (91) Hüttel, R.; Reinheimer, H. *Chem. Ber.* **1966**, *99*, 2778–2781.
 (92) Hüttel, R.; Reinheimer, H.; Nowak, K. *Chem. Ber.* **1968**, *101*, 3761–3776.
 (93) Solodar, J.; Petrovich, J. P. *Inorg. Chem.* **1971**, *10*, 395–397.
 (94) For the Dewar-Chatt model of metal-olefin bonding, see: (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71–C79. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939–2947.
 (95) Bennett, M. A.; Kneen, W. R.; Nyholm, R. S. *Inorg. Chem.* **1968**, *7*, 552–556.
 (96) Electron-rich 2,2'-bipyridine ancillary ligands on copper(I) alkene complexes augmented the electron density present on the bound alkene (relative to free alkene) through increased π back-donation in the copper(I)-ethylene bonding. See: Munakata, M.; Kitagawa, S.; Kosome, S.; Asahara, A. *Inorg. Chem.* **1986**, *25*, 2622–2627.
 (97) In contrast to $\Delta\delta$ of 0.90, 0.62, and 0.33 ppm reported in Quinn and VanGilder⁹⁰ for AgOTf-*tert*-butylethylene, we observed $\Delta\delta$ of 0.019, 0.015, and 0.015 ppm for (Ph₃P)₂Ag(styrene)_nOTf.

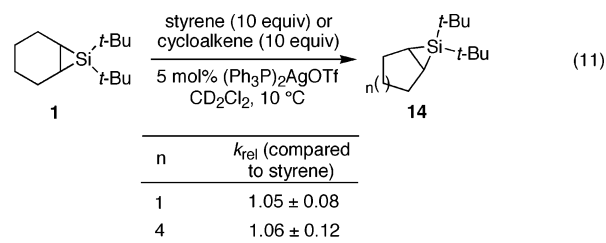
Scheme 5. Catalytic Cycle To Describe Silver-Catalyzed Transfer of Di-*tert*-butylsilylene from **1** to Styrene

to styrene without dissociation from silver. Since silver is involved in extrusion it must also be involved in cyclization. The Hammett ρ value describing the silver-promoted transfer of silylene is different than the ρ value estimated for 25 °C from the thermal transfer of silylene. Additionally, the identification that the silver-catalyzed cyclization of silylene is under enthalpic control is different from the entropic control of thermal silylene transfer. Enthalpic control is not consistent with free silylene as an intermediate prior to cyclization.

Derivation of a Catalytic Cycle. Analysis of the experimental data in its entirety allows construction of a catalytic cycle that describes the silver-mediated di-*tert*-butylsilylene transfer from cyclohexene silacyclopropane **1** to styrene (Scheme 5). The solid $[(\text{Ph}_3\text{P})_2\text{AgOTf}]_2$ first dissociates into the monomeric species followed by coordination of styrene. Presumably, a third molecule of styrene replaces a triphenylphosphine ligand to generate the active catalyst **6**. At any point in the saturation of silver's coordination sphere with styrene, oligomerization is believed to be a competing pathway. A molecule of styrene, subsequently, is exchanged for silacyclopropane **1**. Because of silver's affinity for alkenes and from the observation of inverse saturation behavior in alkene concentration, k_{-1} is greater than the rate of silylene extrusion (k_2). Upon coordination of **1**, silver-mediated β -silyl elimination⁹⁸ (i.e., migratory insertion/deinsertion) occurs to yield cyclohexene and the silylsilver complex **10** that was observed spectroscopically. Based on low-temperature NMR spectroscopic experiments, the first three mechanistic steps (phosphine dissociation, styrene dissociation, and silver-mediated silylene extrusion from **1**) are significantly more rapid than electrophilic attack of the silylsilver complex. From kinetic order experiments, the rate-determining step appears to

be the concerted, electrophilic cyclization of the silylsilver complex **10** with a molecule of alkene. Because a silylsilver complex can be observed and the cyclization is enthalpically driven (vide supra), a considerable ΔG^\ddagger is implicated for cyclization and extrusion. Since the progress of the reaction can be followed using NMR spectroscopy without evidence of a paramagnetic species, transition structure **12**, formed via transmetalation, is postulated. Rate-determining cyclization then occurs rapidly to form product silacyclopropane **3** and regenerate the silver-alkene catalyst.

The difference in rate between cycloaddition onto cyclohexene and styrene (k_3 and k_{-2}) was estimated by comparison of the initial rates of silylsilver complex trapping by cyclopentene and cyclooctene versus styrene (eq 11). Competition experiments were performed using 10 equiv of alkene (below saturation behavior). Both cyclopentene and cyclooctene were equally reactive (within experimental error) and slightly more efficient than styrene in consuming cyclohexene silacyclopropane **1**. Since the difference in mono- versus disubstituted alkene dissociation from Ag^+ has been reported to be four,⁷⁴ the k_{rel} value of 1.1 may reflect the difference between cyclization of silylsilver complex **10** onto a cyclic alkene and styrene.



Determination of Activation Parameters. The activation parameters of silver-mediated di-*tert*-butylsilylene transfer from cyclohexene silacyclopropane **1** to styrene were determined in both toluene- d_8 and CD_2Cl_2 . Unfortunately, neither the extrusion nor cyclization mechanistic step could be isolated for analysis through the manipulation of reagent concentrations. For the activation parameters to represent the entire mechanism, and not alkene dissociation from the silver-alkene complex, an alkene concentration below saturation behavior (5 equiv) was chosen for investigation. A correlation between the observed rate and temperature was obtained between 10 °C and 30 °C (Figures 6 and 7).⁹⁹ In toluene- d_8 , Arrhenius and Eyring activation parameters were determined to be: $E_a = 30 \pm 1 \text{ kcal}\cdot\text{mol}^{-1}$, $A = 1.25 \times 10^{19} \text{ s}^{-1}$ and $\Delta H^\ddagger = 30 \pm 1 \text{ kcal}\cdot\text{mol}^{-1}$, and $\Delta S^\ddagger = 27 \pm 7 \text{ eu}$.^{100,101} Similar activation parameters were observed in CD_2Cl_2 : (Arrhenius) $E_a = 31 \pm 1 \text{ kcal}\cdot\text{mol}^{-1}$, $A = 1.26 \times 10^{20} \text{ s}^{-1}$ and (Eyring) $\Delta H^\ddagger = 30 \pm 1 \text{ kcal}\cdot\text{mol}^{-1}$, and $\Delta S^\ddagger = 31 \pm 7 \text{ eu}$. The similar magnitude of the activation parameters obtained in CD_2Cl_2 and toluene- d_8 suggest the

(99) Since a limited temperature range (40 °C) was used to determine the activation parameters, caution should be used in drawing firm conclusions from them.

(100) The uncertainties in the activation parameters were calculated from the error propagation formulas derived by Girolami and Binsch. See: (a) Morse, P. M.; Spencer, M. D.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 1646–1655. (b) Steigel, A.; Sauer, J.; Kleier, D. A.; Binsch, G. *J. Am. Chem. Soc.* **1972**, *94*, 2770–2779.

(101) The systematic uncertainties δk_{sys} were estimated based on subjective judgments of the sensitivities of the NMR integration, ca. 5% (Morse et al.^{100a}). The total uncertainties δk were calculated from $\delta k = [\delta k_{\text{ran}}]^2 + \delta k_{\text{sys}}^2]^{1/2}$. See: Li, L.; Hung, M.; Xue, Z. *J. Am. Chem. Soc.* **1995**, *117*, 12746–12750.

(98) For reports of β -silyl elimination see: (a) Randolph, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 3366–3374. (b) Wakatsuki, Y.; Yamazaki, H.; Nakano, M.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 703–704. (c) Marciniac, B.; Pietraszuk, C. *J. Chem. Soc., Chem. Commun.* **1995**, 2003–2004. (d) Marciniac, B.; Kownacki, I.; Kubicki, M. *Organometallics* **2002**, *21*, 3263–3270.

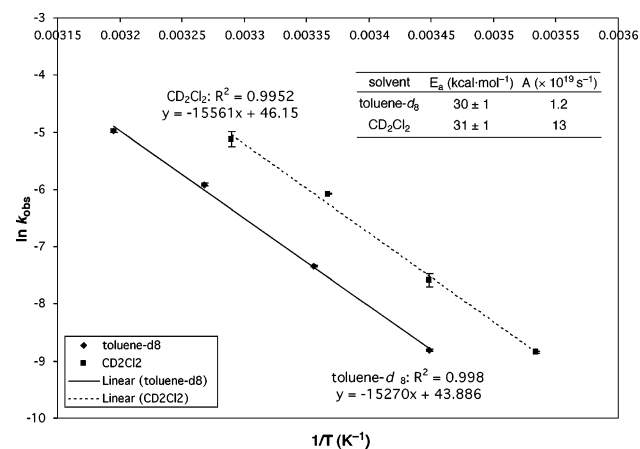


Figure 6. Linear Arrhenius correlation between rate and temperature.

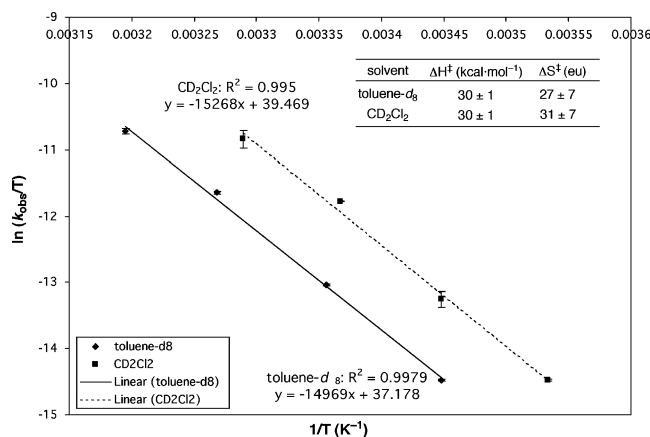


Figure 7. Linear Eyring correlation between rate and temperature.

mechanism of silver-mediated silylene transfer does not involve participation of a solvent.

The large, positive entropy of activation parameter could reflect several aspects of the mechanism. A significant portion of its value is the dissociation of the silver oligomer into the reactive monomer **6**. Additionally, the dissociation of a molecule of styrene from the silver·alkene complex **7** (step 1) and the loss of cyclohexene from the transition state **12** (step 2) may also contribute to the entropy of activation parameter. The magnitude of the entropy of activation term may also indicate that in the rate-determining step (step 3), a fragmentation occurs (such as loss of an alkene from the [Ag] complex).

Conclusion

A quantitative analysis of the behavior of cyclohexene silacyclopropane **1** upon exposure to an alkene and a catalytic amount of (Ph₃P)₂AgOTf improved our understanding of the fundamental reactivity of silacyclopropanes. Qualitative observations established the unique reactivity of **1** and the irreversibility of silver-mediated silylene transfer from **1** to cyclic and acyclic alkenes. A mechanism involving free silylene cyclization was eliminated through kinetic studies and spectroscopic observation of a catalytically active silylsilver intermediate. Kinetic order experiments implicated a mechanism in which silver mediates silylene extrusion from silacyclopropane **1**. The data were summarized into a plausible catalytic cycle that accommodated the inhibition of reaction rate in alkene concen-

tration and observed saturation behavior in catalyst concentration. The observed small, negative Hammett ρ value suggested that rate-determining cycloaddition occurs through a concerted, electrophilic attack of a silylsilver species on the alkene. Similar activation parameters obtained in toluene and methylene chloride suggested the generality of the mechanism across different solvents. We believe that the mechanistic insight gained in this study will guide future rational modifications to improve both the construction and synthetic utility of 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 CaH₂ and degassed prior to use. Deuterated methylene chloride was dried over activated molecular sieves and degassed before use. All reagents and cyclohexene di-*tert*-butylsilacyclopropane **1** were stored in an Innovative Technologies nitrogen atmosphere drybox.

The apparatuses (volumetric flasks and NMR tubes) were washed with a solution of 2:1 HCl (12 N): HNO₃ (16 N), rinsed with water and acetone, washed with ammonium hydroxide, and rinsed with water and acetone. The 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 reagents were added, dropwise, to a cold solution of cyclohexene silacyclopropane **1**. After agitation, the NMR tube containing the reaction mixture was placed in a cold (below the temperature for kinetic analysis) NMR spectrometer. The reaction mixture was warmed to the desired temperature in the NMR spectrometer. The reaction progress over the first half-life (or, when appropriate, five half-lives) was monitored periodically using ¹H NMR spectroscopy. The concentrations of the reactants and products were obtained through comparison of the area of the standard (PhSiMe₃ peak at 0.19 ppm, area = 1.0000) and the area of the *t*-Bu peaks of the silacyclopropanes **1** and **3** (**1**, 1.00 and 1.19 ppm; **3**, 1.06 and 0.83 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 styrene in the presence of 5 mol % of (Ph₃P)₂AgOTf. To a cool (−78 °C) solution of cyclohexene silacyclopropane **1** (0.065 mL of a 0.4455 M solution in CD₂Cl₂, 0.02895 mmol) in 0.200 mL of a 0.023246 M solution of PhSiMe₃ in CD₂Cl₂ (contained in a thin wall NMR tube) was added a solution containing styrene (0.065 mL, 2.07 mmol) and (Ph₃P)₂AgOTf (0.050 mL of a 0.02896 M solution in CD₂Cl₂) in 0.250 mL of a 0.023246 M solution of PhSiMe₃ in CD₂Cl₂. After thermal equilibration to −78 °C, the resulting solution was shaken 5 times. The reaction mixture was re-cooled to −78 °C, and then it was placed in a cool (−20 °C) NMR spectrometer. An initial ¹H NMR spectrum was obtained, and the temperature of the experiment was regulated to 10 °C. Periodically the reaction progress was measured relative to the internal standard of PhSiMe₃ using ¹H NMR spectroscopy.

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Supporting Information Available: Experimental procedures, tabular, graphical, 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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