Catalytic Cyclization/Silylation of Dienes Containing 1,1-Disubstituted Olefins Using Organolanthanide and Group 3 Organometallic Complexes

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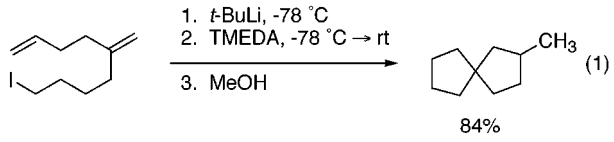
The catalytic cyclization/silylation reaction of hindered dienes has been investigated using the relatively unhindered complexes $Me_2Si(C_5H_3SiMe_3)_2YCH(TMS)_2$ and $[Cp^{TMS}{}_2LnMe]_2$ (Ln = Y, Lu). A wide variety of dienes and trienes bearing a number of functional groups were cyclized, affording silanes containing quaternary centers in a diastereoselective fashion and in good yield. The products can be oxidized using one of several different protocols, yielding alcohols for further functionalization.

Introduction

Organolanthanide and group 3 metallocene complexes have been the subject of extensive investigations[1] into their ability to mediate hydrogenation,[2] hydroamination,[3] hydroboration,[4] hydrostannylation,[5] and hydrosilylation reactions of olefins,[6] as well as cyclization[7] and cyclization/silylation reactions of polyunsaturated substrates.[6a,b,d,f,h,8] The reactivity of these catalysts is predominantly sterically driven, which allows exquisite selectivity in complicated, polyfunctional substrates. This same steric discrimination, however, has heretofore inhibited reaction with other than monosubstituted olefins.

Historically, cyclization/functionalization reactions of hindered olefins have been achieved by employing a variety of approaches. For example, investigations have been carried out utilizing stoichiometric anionic olefin insertion chemistry. Several structurally diverse systems have proven amenable to this protocol, including those incorporating hindered double bonds.[9] The common starting point for these reactions is an unsaturated alkyl halide. Lithium−halogen exchange or Grignard reagent formation affords an organometallic, and the presence of certain additives facilitates intramolecular olefin insertion. Although these methods allow the construction of interesting molecules (eq 1), the requirement of initiating the reaction at a halide center and the necessity of utilizing stoichiometric amounts of harsh organometallic reagents, intolerant of polar functional groups, detract from the overall value of the method.



To address these limitations, catalytic carbometalation systems were developed that operated on dienes, thus foregoing the requirement of a polar initiation point. Waymouth and Shaughnessy studied a dimethyl zirconocene/trimethylaluminum system capable of cyclizing 2-substituted 1,5-hexadienes (eq 2).[10] The catalytic cycle involved insertion of the least hindered olefin into the zirconium−methyl bond followed by cyclization, with subsequent trapping by trimethylaluminum. Oxidative workup directly afforded alcohol products bearing a methyl group as required by the catalytic system. Hindered 1,6-heptadienes could not be cyclized utilizing this

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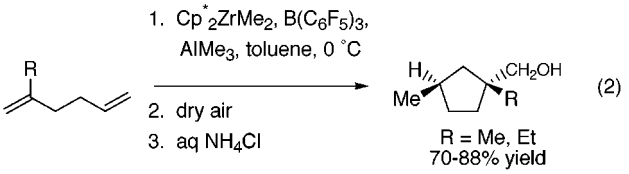
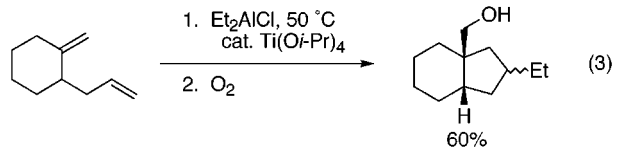
protocol, and only a small number of 2-substituted 1,5-dienes were investigated. In another report, Waymouth and co-workers found that a similar zirconocene catalytic system lacking a trapping agent could cyclopolymerize 2-methyl-1,5-hexadiene to provide a well-defined polymer.[11]



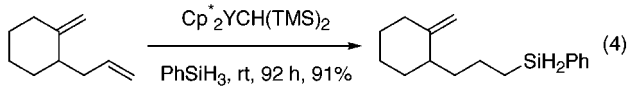
(2)

An operationally related catalytic carbometalation system was reported by Negishi and co-workers (eq 3).[12] They revealed that dialkylaluminum chloride in the presence of catalytic titanium(IV) isopropoxide mediated the cyclization of a number of diene systems. The organometallic products of the reaction were routinely oxidized to alcohols for analysis. A number of substrates were investigated, leading to a variety of monocyclic, spirocyclic, and bicyclic systems. All of the substrates studied, however, were hydrocarbons, leaving the question of functional group tolerability unanswered. The alkyl group installed in the reaction also limited the generality of the process.



(3)

Cyclization/silylation reactions catalyzed by organolanthanides or group 3 organometallics permit a number of interesting transformations that allow a rapid increase of molecular complexity in the transformation of simple polyunsaturated substrates to cyclized products.[6a,b,d,f,h,8] When presented with a suitable diene substrate, the highly reactive yet incredibly selective precatalyst, Cp*$_2$YMe·THF, is capable of selecting a single olefin site for initial insertion.[6b] The complex then inserts the remaining sterically available olefin, usually with high diastereoselectivity, before σ-bond metathesis[13] liberates the silane product. In this manner monocyclic[6b] and bicyclic systems[14] bearing a variety of substitution patterns have been generated. The utility of the silane products is extended by oxidation protocols that convert the carbon−silicon bond into an alcohol under acidic[15] or basic[16] conditions, allowing further functionalization. The silane products are stable, allowing the unmasking of an alcohol at a convenient time. The alcohol products formed upon oxidation in this manner are structurally complementary to those obtained by a carbometalation/oxidation protocol. Similar cyclization/silylation transformations have also been developed using triene, eneyne, and dieneyne substrates.[6f,14,17] By necessity, virtually all of the research in this area has focused on monosubstituted olefins because of the diminished reactivity of the "Cp*$_2$YH" catalyst with more highly hindered double bonds (eq 4).[6g] The goal of the current investigation was to extend the cyclization/silylation reaction to 1,1-disubstituted olefins, allowing the formation of quaternary centers in a stereoselective fashion.



(4)

One of the attractive features of organolanthanide and group 3 organometallic complexes is the ability to vary their reactivity by changing the metal or by altering the ligands on the metal. Larger metals and sterically less crowded ligand substitution surrounding the metal increase the open space about the catalytic center, thereby increasing access to more sterically demanding alkenes. Complexes incorporating metals with larger ionic radii have been explored in the hydrogenation and hydrosilylation of 1,1-disubstituted olefins.[6e] Thus, Cp*$_2$SmCH(TMS)$_2$ was utilized to increase reactivity toward a variety of more highly hindered olefins. This enhanced reactivity was attributed to the larger ionic radius of Sm^{3+} as compared to that of Y^{3+} (1.09 versus 1.02 Å).[18] Reactions times were long, however, and cyclization events involving disubstituted alkenes remained elusive.

Marks and co-workers probed another catalyst variation in a recent hydrogenation study.[2c] They prepared a silicon-bridged catalyst, Me$_2$Si(Me$_3$SiCp)[(−)-menthylCp]LnCH(TMS)$_2$, with decreased substitution on the Cp ligands that effected the efficient transformation of 2-methyl-1,5-hexadiene to 1,1-dimethylcyclopentane under a hydrogen atmosphere. Although encouraging, they did not attempt to terminate the process with silylation nor was the synthetic scope of the reaction explored.

Results and Discussion

The accepted catalytic cycle for the desired cyclization/silylation is pictured in Scheme 1.[6a,b] The precatalyst reacts with the silane via a σ-bond metathesis[13] reaction to generate an organolanthanide hydride, releasing the alkyl group. This hydride then inserts the least hindered olefin, placing the metal at the terminus of the carbon chain. The hydrocarbyl formed undergoes intramolecular olefin insertion (or multiple insertions) through a chair-like transition structure before reacting with the silane via σ-bond metathesis. This final step completes the catalytic cycle and liberates the desired product.

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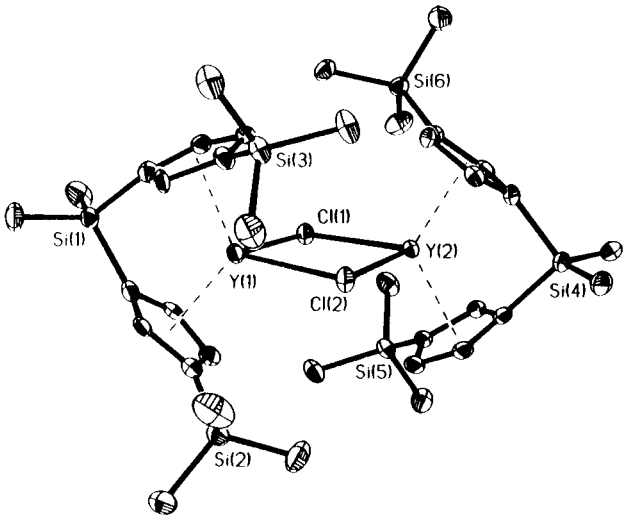
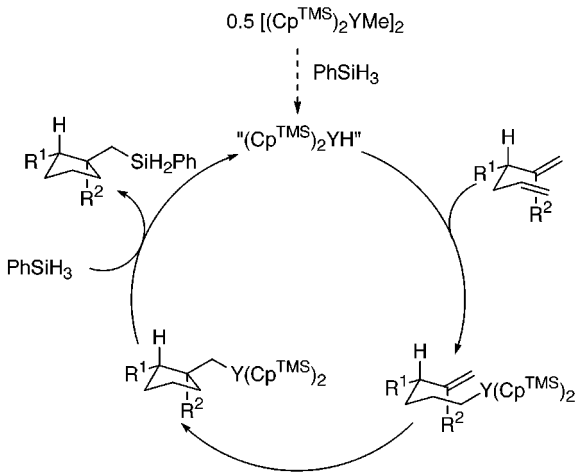


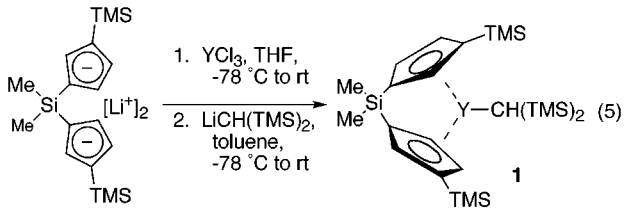
Figure 1. Perspective ORTEP drawing of the molecular structure of $[Me_2Si(C_5H_3SiMe_3)_2YCl]_2$.

Scheme 1



In an attempt to build on the study of Marks and coworkers, a bridged complex $[Me_2Si(Me_3SiCp)_2YCH(TMS)_2$, (**1**)] was prepared via a one-pot procedure (eq 5). Characterization of the alkyl complex by NMR showed an excess of resonance peaks, undoubtedly because of hindered rotation about the carbon−metal bond.[19] The NMR spectra of the complex exhibited temperature-dependent phenomena, but coalesence could not be achieved. All attempts at obtaining crystalline material suitable for X-ray analysis failed. The yttrocene chloride intermediate (**2**, Figure 1) could be isolated, however, and proved more amenable to structural elucidation. The NMR spectra of this material was consistent with a structure in which the cyclopentadienyl ligands were bound in a chelating mode. The X-ray structure of this dimer showed that the desired ligand array had been prepared and was attached to the metal in a manner analogous to that previously observed for similar complexes.[2c]

Alkyl complex **1** was used to effect the cyclization/silylation of a variety of hindered dienes (Table 1). This initial complex proved to be catalytically active at high temperatures over the long reaction periods required for the reactions to proceed to completion. It is also notable



(5)

that the Lewis acidic complex did not isomerize the alkene substrates under the rigorous reaction conditions. Utilizing this protocol, 1,1-disubstituted alkenes participated efficiently in the reactions. Alkyl chlorides could be tolerated (entry 2), and quaternary centers were generated with essentially complete stereochemical control (entries 3−5). Products possessing a variety of structural motifs could be accessed, including spirocyclic systems (entry 6). Although initial success was achieved in cyclizing these more highly substituted alkenes, the elevated temperatures and long reaction times required prompted us to search for other, more reactive, catalyst systems.

After a variety of potential complexes with larger metals and/or less hindered ligands were prepared and tested, the known[20] and easily prepared[21] metallocenes $[Cp^{TMS}{}_2LnMe]_2$ (Ln = Y, Lu) were selected as the precatalysts of choice. In each case they provided the desired cyclic products under milder conditions and in higher yields than complex **1**. These organometallic complexes also exhibit attenuated air sensitivity when compared with other organolanthanide alkyl complexes. In fact, hydrosilylation reactions using this precatalyst have been performed on the benchtop[22] using standard techniques for handling air-sensitive reagents.[23]

This metal/ligand/silane system proved to be extremely versatile and adaptable to various substrate demands. The ability to "tune" the reaction conditions for optimum selectivity was illustrated in the reaction of 2-methyl-1,5-hexadiene (eq 6). Cyclization of this diene with $[(Cp^{TMS})_2YMe]_2$ in the presence of phenylsilane led to high yields of cyclized products **4a** and **4b** with 9:1 selectivity in the initial olefin insertion step. When a precatalyst with a slightly smaller metal was used, $[(Cp^{TMS})_2LuMe]_2$, the initial olefin insertion occurred exclusively at the monosubstituted alkene.[24] In this case, however, the cyclized product was contaminated with substantial amounts of uncyclized material **4c**. To remedy this situation, the silane was switched to the more hindered methylphenylsilane. The additional alkyl group on the silane slowed the σ-bond metathesis termination step enough to allow complete cyclization prior to silylation. This series of reactions effectively demonstrates how both

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(20) (a) Ballard, D. G. H.; Courtis, A.; Holton, J.; McMeeking, J.; Pearce, R. *J. Chem. Soc., Chem. Commun.* **1978**, 994. (b) Boskoboynikov, A. Z.; Parshina, I. N.; Shestakova, A. K.; Butin, K. P.; Beletskaya, I. P.; Kuz'mina, L. G.; Howard, J. A. K. *Organometallics* **1997**, *16*, 4041.

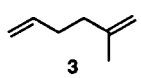
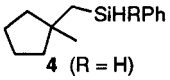
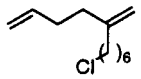
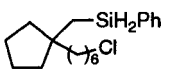
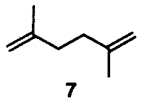
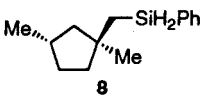
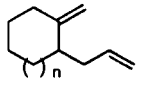
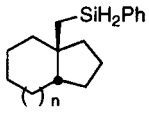
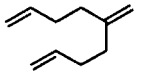
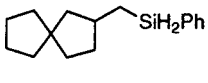
(21) Prepared by a modification of the procedure given in ref 20b: KCp^{TMS} (6 mmol) and $LnCl_3$ (3 mmol) were heated at reflux in THF for 4 h. The solvent was removed in vacuo and replaced with Et_2O. MeLi (2.15 mL of a 1.4 M solution in Et_2O, 3 mmol) was added at −78 °C, and the reaction was warmed to room temperature. After the solution was stirred for 4 h, the solvent was removed and the solids were extracted with hexanes. Decantation and crystallization from hexanes yielded the desired organometallics.

(22) Markus Keitsch, unpublished results.

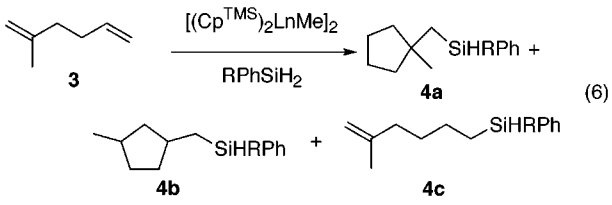
(23) Brown, H. C. *Organic Syntheses via Boranes*; Wiley: New York, 1975.

(24) The ionic radii of Lu^{3+} and Y^{3+} are 0.97 and 1.02 Å respectively. See ref 18.

Table 1. Cyclization/Silylation Reactions Catalyzed by $Me_2Si(C_5H_3SiMe_3)_2YCH(TMS)_2$ (1)

entry	substrate	products	conditions temp, time, isolated yield
1	 **3**	 **4** (R = H)	90 °C, 12 h, 76%
2	 **5**	 **6**	110 °C, 2 h, 66%
3	 **7**	 **8**	90 °C, 48 h, 58%
4	 **10** n = 0	 **11**	90 °C, 14 h, 58%
5	**12** n = 1	**13**	90 °C, 24 h, 79%
6	 **17**	 **18**	90 °C, 24 h, 68%

the catalyst and the silane can be simultaneously adjusted to effect desired outcomes in reactions of interest.

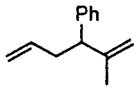
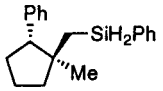
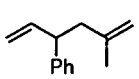
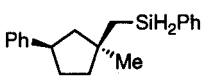
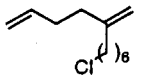
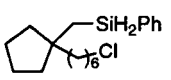
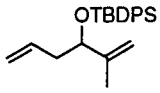
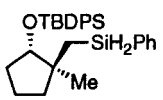
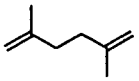
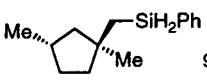
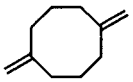
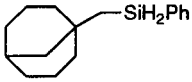
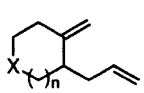
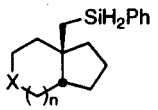
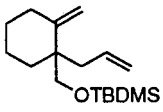
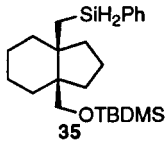


(6)

Ln = Y, R = H; **4a** = 86%, **4b** = 9%, **4c** = 0
Ln = Lu, R = H; **4a** = 63%, **4b** = 0, **4c** = 5%
Ln = Lu, R = Me; **4a** = 80%, **4b** = 0, **4c** = 0

The utility of a successful catalytic system would be enhanced if it tolerated a wide variety of common organic functional groups (or their protected versions), as well as a number of substitution patterns. To assess these factors, several diene substrates were prepared by standard literature methods. The effects of varying substituents and substitution patterns in cyclizations of 1,5-dienes are displayed in Table 2. Entries 1 and 4 demonstrate the high diastereoselectivity possible in the formation of a quaternary center with this transformation. In each of these cases a single product isomer was generated, the stereochemistry of which is best rationalized by a chairlike transition structure (see Scheme 1) that places the allylic substituent in an equatorial orientation. The stereochemistry of the product was confirmed by NOE difference spectroscopy. Substrate **21** (entry 2), in which the substituent is one carbon closer to the unhindered olefin, provided an inseparable mixture of diastereomers and regioisomers. The erosion of diastereoselectivity has previously been noted in the cyclization of 4-substituted heptadienes with an organoyttrium complex.[6b] The minor regioisomeric product comes from insertion of the disubstituted olefin first followed by ring

Table 2. Cyclization/Silylation Reactions Catalyzed by $[(Cp^{TMS})_2YMe]_2$

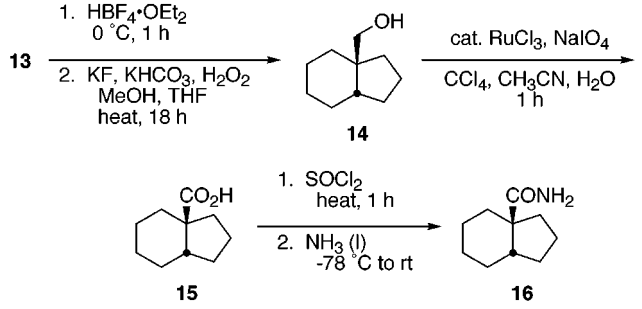
entry	substrate	products	conditions temp, time, isolated yield
1	 **19**	 **20**	rt, 12 h, 92%
2	 **21**	 **22**	rt, 12 h, 95%[a]
3	 **5**	 **6**	rt, 1 h, 79%
4	 **24**	 **25**	rt, 16 h, 74%
5	 **7**	 **8**	90 °C, 12 h, 92%
6	 **26**	 **27**	rt, 20 h, 49%
7	 **10** n = 0, X = CH_2	 **11**	rt, 1 h, 73%
8	**12** n = 1, X = CH_2	**13**	rt, 1 h, 95%
9	**28** n = 1, X = NBn	**29**	rt, 20 h, 77%
10	**30** n = 1, X = O	**31**	90 °C, 24 h, 57%
11	**32** n = 1, X = $C(SCH_2)_2$	**33**	rt, 8 h, 98%
12	 **34**	 **35**	rt, 16 h, 70%

closure and silylation. This occurs because the presence of substitution allylic to the monosubstituted olefin sterically shields it, making the insertion of the disubstituted olefin somewhat competitive. The identity of the major isomer was elucidated by oxidation of the silane products to the corresponding alcohols followed by chromatographic separation and NOE analysis of the major alcohol **23**.

The cyclization protocol was extended to dienes where both double bonds were disubstituted. Symmetrical diene **7** reacted to afford a single product (entry 5). The stereochemistry was as expected and proven by conversion to the alcohol **9** and comparison to literature data.[10]

The issue of minimum catalyst loading necessary to convert substrates efficiently to products is an important one and has been addressed in the current study on a reasonably large-scale reaction. In a typical experiment,

Scheme 2



approximately 0.5 mmol of substrate was exposed to 5 mol % of the precatalyst, a convenient amount to weigh. To determine the minimum catalyst loading possible, the amount of **7** was increased while using very small amounts of the catalyst. On a 20 mmol scale with as little as 0.5 mol % catalyst, the reaction proceeded smoothly (in virtually the same reaction time as small-scale reactions loaded at 5 mol %) to provide good yields (~80%) of the desired product.

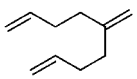
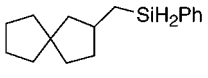
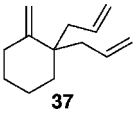
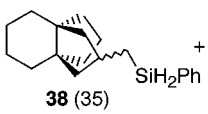
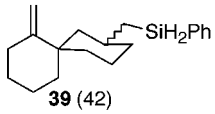
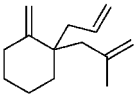
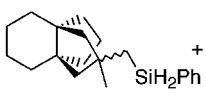
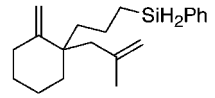
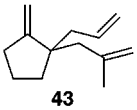
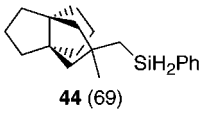
A transannular cyclization was conducted to provide bridged bicyclic product **27** (entry 6). The yield of this transformation was reduced by the isomerization of one exocyclic double bond into the ring, preventing cyclization. Several other metallocene complexes were used in attempts to accomplish this transformation, but in each case the yield of the desired bridgehead bicyclic product was very low. For example, the yield of the bicyclo[3.3.1] system was <10% using complex **1** under all conditions attempted.

A number of bicyclic products were generated by the ring closure of pendant alkenyl side chains onto an existing ring. A wide variety of α-allyl methylenecycloalkanes were found to cyclize efficiently to form bicyclo[3.3.0] and bicyclo[4.3.0] systems (entries 7−12). The stereochemistry of the ring juncture in one of these examples was determined by the conversion of silane **13** to the corresponding carboxamide **16** and comparison with literature data for this reported compound (Scheme 2).[25] The generation of cis-fused products complements the formation of *trans*-bicyclo[3.3.0] systems developed previously using similar group 3 metallocene complexes.[14]

Heteroatoms were generally tolerated, although reaction times were lengthened because of Lewis base coordination to the metal center. In the extreme case of unhindered ether **30** (entry 10), heating was required to obtain complete reaction in a reasonable time. This depression of catalytic turnover has previously been observed in olefin hydrogenation.[2a,e] The effect of Lewis bases on catalytic activity is not ubiquitous, however, as $Cp^*_2YMe\cdot THF$ is more efficient as a precatalyst for diene cyclization/silylation than the ether-free complex $Cp^*_2YCH(TMS)_2$.[6b]

The intramolecular insertion of multiple double bonds before the trapping event has been effectively exploited for monosubstituted diene systems. In properly designed substrates, single diastereomers of complex bicyclic silanes were obtained.[14] To investigate the possibility of multiple olefin insertions exploiting the current catalyst's capabilities, several triene substrates were prepared (Table 3). In substrate **17**, the complex initially inserted one of the monosubstituted olefins before cyclizing onto the 1,1-disubstituted olefin (entry 1). This first ring-forming step is selective for the formation of the five-membered ring, and the intermediate monocyclic hydrocarbyl is persistent enough to form another ring in a spirocyclic fashion before the trapping event to afford the observed product **18** in good yield.

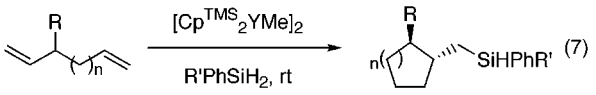
Table 3. Cyclization/Silylation Reactions Involving Multiple Bond Insertions

entry	substrate	products (% isolated yield)
1	 **17**	 **18** (88)
2	 **37**	 **38** (35) +  **39** (42)
3	 **40**	 **41** (75) +  **42** (14)
4	 **43**	 **44** (69)

Entries 2−4 explore another scenario for multiple insertions, building additional rings onto an existing structure. In each of these cases the reaction begins with the insertion of the least hindered double bond. In substrate **37** the initial hydrocarbyl intermediate formed then has a choice of inserting the 1,1-disubstituted olefin to form a five-membered ring or the less hindered monosubstituted double bond to form a six-membered ring. As outlined in Table 3, the hindered cyclization was competitive, and a mixture of propellane (**38**) and uncharacterized isomers assumed to be spirocyclic (**39**) was obtained. To make the first cyclization event more selective, substrate **40** was prepared in which the complex must choose between insertion of two 1,1-disubstituted olefins: one forming a cyclopentane, the other a cyclohexane. The observed products indicate that the subsequent cyclization passed through the five-ring manifold, with a small amount of material being trapped before any cyclization events occur. Products **38** and **41** were composed of inseparable mixtures of diastereomers, epimeric at the silane-bearing substituent. Substrate **43** was designed to eliminate this mixture, as it cyclized to symmetrical propellane **44** in good yield.

The cyclization of bis(monosubstituted) dienes was also explored to assess the generality of the current catalytic system. Five- and six-membered rings were formed in this manner. However, methylphenylsilane was required in cyclohexane generation to slow the trapping event relative to intramolecular insertion (eq 7). In experiments combining 1,6-heptadiene and phenylsilane, the linear disilylated product dominated. Also interesting was the successful cyclization of 3-substituted 1,6-heptadienes, a substitution pattern found to be problematic in an earlier study with a different catalyst.[6b] The allylic substitution was sufficient to direct the complex to the less hindered olefin for initial insertion. In the cyclization of **49**, the product derived from initial insertion of the allylically substituted olefin was detected, eroding the yield of **50**. The trans stereochemistry of products **50** and

53 was determined by the oxidation of the silanes to known alcohols **51** and **54**, respectively.[26,27]



45 R = H, n = 1, R' = H
47 R = H, n = 2, R' = Me
49 R = Ph, n = 2, R' = Me
52 R = OTBDPS, n = 2, R' = Me

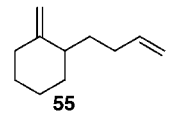
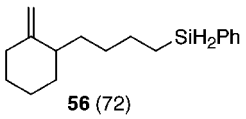
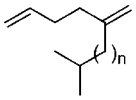
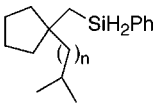
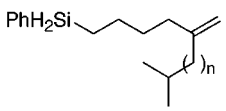
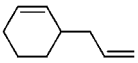
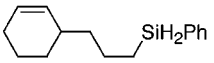
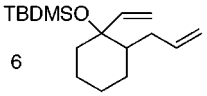
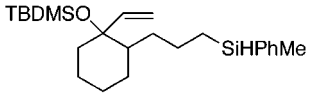
46 (98%, 4 h)
48 (86%, 12 h)
50 (56%, 12 h)
53 (71%, 2 d)

The present limitations of this protocol are shown in Table 4. Substrate **55** was designed to provide a bicyclo[4.4.0] product. Monocyclic products such as **56** were obtained rapidly and in good yield under all conditions attempted, including those where $PhMeSiH_2$ was utilized as a terminating agent (entry 1). This result mirrors the dimethylzirconocene results of Waymouth discussed earlier, where hindered cyclohexane formation was not observed.[10] It was also discovered that isopropyl substitution on the hindered olefin prevented cyclization (entry 2). The insertion of one methylene unit between the double bond and the branch point allowed approximately half of the material to cyclize (entry 3), while two methylene units allowed the cyclized product to be isolated in good yield (entry 4). 3-Allylcyclohexene (**64**) was prepared in hopes that the catalyst would form a bicyclo[4.3.0] product, but uncyclized monosilylated product was obtained exclusively. Substrate **66** contained a quaternary vinyl group that was previously found not to cyclize using other catalysts.[14] We exposed this to the current reaction conditions with the expectation that the less hindered catalyst would provide a different result. The material obtained, however, was spectroscopically identical to the product previously generated (entry 6).

Conclusions

The cyclization/silylation of dienes has been extended to 1,1-disubstituted olefins by the development of $[(Cp^{TMS})_2LnMe]_2$ complexes as precatalysts. This class of organometallics demonstrated enhanced reactivity toward more highly hindered alkenes, and thus catalyst loadings as low as 0.5 mol % can be utilized on large-scale reactions. Despite their high reactivity, the complexes described herein exhibit surprising stability to air. They are thus much easier to handle than previously developed catalysts from the same family. A variety of monocyclic, bicyclic, spirocyclic, and propellane products were generated efficiently, diastereoselectively, and under mild conditions. Importantly, quaternary stereocenters were created with virtually complete stereochemical control. The cyclized silanes were synthesized by an atom economical process,[28] and this, plus the fact that reactions are performed in hydrocarbon solvents, facilitates isolation of the desired products. The silane moiety generated is stable, allowing unmasking to the corresponding alcohol at a convenient time. These alcohols are complementary to those derived from analogous carbometalation/cyclization procedures.

Table 4. Substrates Providing Predominantly Uncyclized Products

entry	substrate	products (% isolated yield)[a]		
1	 **55**	 **56** (72)		
2	 **57** n = 0	 (0)	+ 	**58** (84)
3	**59** n = 1	**60** (52)		**61** (36)
4	**62** n = 2	**63** (84)		(0)
5	 **64**	 **65** (93)		
6	 **66**	 **67** (88)[b]		

[a] $PhSiH_3$ was used as the trapping reagent except as noted. [b] $MePhSiH_2$ was used as the trapping reagent.

Experimental Section

All experiments involving the organometallic complexes were performed with careful exclusion of oxygen and moisture in flame-dried Schlenk-type glassware interfaced to a vacuum-argon double manifold,[29] or in a nitrogen-filled Vacuum Atmospheres glovebox. The cyclohexane and benzene-d_6 used as solvents in the catalytic reactions were distilled from Na/benzophenone under argon and stored in the glovebox. All substrates were distilled and degassed before use. 2-Methyl-1,5-hexadiene, 2,5-dimethyl-1,5-hexadiene, 1,5-hexadiene, 1,6-heptadiene, and phenylsilane were purchased from Aldrich. Methylphenylsilane was purchased from United Chemical Technologies. Substrates **12**,[6g] **26**,[30] **64**,[31] and **66**[14] were prepared according to literature methods.

$[Me_2Si(Me_3SiCp)_2YCH(TMS)_2]$ (1). $Me_2Si(Me_3SiCp)_2Li_2$ (0.861 g, 2.5 mmol) and YCl_3 (0.490 g, 2.5 mmol) were weighed into a Schlenk flask and cooled to −78 °C, and 75 mL of THF was added. The mixture was allowed to warm to room temperature and stirred for 12 h. After cooling, the solvent was removed in vacuo and replaced with Et_2O. Next, the mixture was cooled to −78 °C, and $LiCH(TMS)_2$ (0.415 g, 2.5 mmol) was added slowly. The mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed in vacuo and the residue extracted with hexanes. The supernatant was decanted and concentrated for crystallization at −30 °C. A light tan solid (1.11 g, 1.92 mmol, 77%) was obtained whose NMR was complex and exhibited temperature dependent phenomena. All attempts at obtaining crystals suitable for X-ray analysis failed.

$[Me_2Si(Me_3SiCp)_2YCl]_2$ (2). A Schlenk flask was charged with 35 mL of THF and cooled to −78 °C before $Me_2Si(Me_3SiCp)_2Li_2$ (0.344 g, 1.0 mmol) and YCl_3 (0.195 g, 1.0 mmol) were added slowly. The mixture was warmed to reflux and stirred for 6 h. After cooling, the solvent was removed in vacuo and the solid residue extracted with 50 mL of hexanes. The supernatant was decanted, concentrated slightly, and cooled overnight for crystallization. The white crystals generated (0.090 g, 0.10 mmol, 20%) were dried and submitted for X-ray

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analysis: ^{1}H NMR (400 MHz, C_6D_6) δ 7.00 (t, J = 2.2 Hz, 2H), 6.62 (t, J = 2.0 Hz, 2H), 6.33 (t, J = 2.2 Hz, 2H), 0.78 (s, 3H), 0.42 (s, 3H), 0.36 (s, 18H); ^{13}C NMR (100 MHz, C_6D_6) δ 135.37, 123.92, 121.92, 120.86, 120.43, 0.14, −2.35, −6.00.

Cyclizations Using 1 as the Precatalyst: 1-Methyl-1-[(phenylsilyl)methyl]cyclopentane (4, R = H) (General Procedure for Cyclization/Silylation Using 1). The precatalyst (5 mg, 8.6 μmol) was dissolved in cyclohexane (0.5 mL) in the glovebox. Next, 2-methyl-1,5-hexadiene was added (26 mg, 0.27 mmol) followed by phenylsilane (32 mg, 0.29 mmol). This solution was transferred to a tube with a Teflon screw valve which was sealed, and the tube was removed from the glovebox. This tube was heated to 90 °C with stirring for 12 h. After cooling, the reaction vessel was opened to the air and the contents were filtered through a small plug of Florisil. The filtrate was concentrated and purified by flash chromatography followed by Kugelrohr distillation to yield a colorless oil (42 mg, 76%): ot 50 °C/0.05 mmHg; R_f 0.59 (hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.55 (m, 2H), 7.37−7.31 (m, 3H), 4.33 (t, J = 4.1 Hz, 2H), 1.65−1.59 (m, 4H), 1.59−1.40 (m, 4H), 1.15 (t, J = 4.1 Hz, 2H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 133.5, 129.4, 127.9, 41.8, 41.2, 28.1, 24.8, 24.2; IR (neat) 3068, 2951, 2870, 2135 cm^{-1}; HRMS calcd for $C_{13}H_{20}Si$ 204.1334, found 204.1349; LRMS (EI$^+$) m/z 204 (2), 189 (7), 126 (78), 107 (100), 105 (51), 97 (34). Anal. Calcd for $C_{13}H_{20}Si$: C, 76.40; H, 9.86. Found: C, 76.26; H, 9.85.

1-(6-Chlorohexyl)-1-[(phenylsilyl)methyl]cyclopentane (6) was prepared from **5** according to the general experimental procedure for cyclization/silylation using **1**. The reaction was found to be complete by GC analysis after 2 h at 110 °C. Workup and purification by Kugelrohr distillation afforded the title compound in 66% yield: ot 130 °C/0.05 mmHg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.54 (m, 2H), 7.39−7.30 (m, 3H), 4.29 (t, J = 4.1 Hz, 2H), 3.50 (t, J = 6.8 Hz, 2H), 1.78−1.67 (m, 2H), 1.64−1.53 (m, 4H), 1.45−1.32 (m, 8H), 1.30−1.16 (m, 4H), 1.11 (t, J = 4.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 133.4, 129.4, 127.9, 45.2, 44.3, 41.0, 40.1, 32.6, 29.6, 26.9, 24.9, 24.3, 21.5; IR (neat) 3067.7, 2932.0, 2132.8 cm^{-1}; LRMS (EI$^+$) m/z 308 (1), 189 (100), 161 (80), 107 (92), 105 (72). Anal. Calcd for $C_{18}H_{29}ClSi$: C, 70.20; H, 9.49. Found: C, 70.46; H, 9.73.

(1*R,3*R**)-1,3-Dimethyl-1-[(phenylsilyl)methyl]cyclopentane (8)** was prepared from **7** according to the general experimental procedure for cyclization/silylation using **1**. The reaction was found to be complete by GC analysis after 48 h at 90 °C. Workup and purification by Kugelrohr distillation afforded the title compound in 58% yield: ot 58 °C/0.01 mmHg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.54 (m, 2H), 7.38−7.30 (m, 3H), 4.31 (t, J = 4.1 Hz, 2H), 2.09−2.03 (m, 1H), 1.84−1.72 (m, 2H), 1.51−1.48 (m, 2H), 1.24−1.16 (m, 1H), 1.14 (t, J = 4.1 Hz, 2H), 1.10 (s, 3H), 1.03−0.99 (m, 1H), 0.96 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 133.4, 129.3, 127.9, 50.8, 42.3, 41.4, 34.0, 33.8, 30.3, 25.4, 21.4; IR (neat) 3068.5, 2949.4, 2866.5, 2135.1, 1455.4 cm^{-1}; LRMS (EI$^+$) m/z 218 (4), 203 (33), 189 (36), 147 (62), 140 (70), 107 (79), 105 (74), 97 (91), 81 (100). Anal. Calcd for $C_{14}H_{22}Si$: C, 76.99; H, 10.15. Found: C, 76.82; H, 10.30.

1-[(Phenylsilyl)methyl]-*cis*-bicyclo[3.3.0]octane (11) was prepared from **10** according to the general experimental procedure for cyclization/silylation using **1**. The reaction was found to be complete by GC analysis after 14 h at 90 °C. Workup and purification by Kugelrohr distillation afforded the title compound in 58% yield: ot 70 °C/0.05 mmHg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58−7.55 (m, 2H), 7.39−7.32 (m, 3H), 4.33 (t, J = 4.17 Hz, 2H), 2.03−1.97 (m, 1H), 1.82−1.75 (m, 2H), 1.59−1.46 (m, 8H), 1.26−1.20 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.19, 133.46, 129.33, 127.91, 52.44, 51.87, 41.63, 34.34, 25.88, 25.39; IR (neat) 3067.8, 2940.3, 2859.9, 2133.4 cm^{-1}; LRMS (EI$^+$) m/z 230 (9), 173 (8), 152 (100), 123 (36), 121 (27), 107 (74), 105 (38). Anal. Calcd for $C_{15}H_{22}Si$: C, 78.19; H, 9.62. Found: C, 78.16; H, 9.58.

1-[(Phenylsilyl)methyl]-*cis*-bicyclo[4.3.0]nonane (13) was prepared from **12** according to the general experimental procedure for cyclization/silylation using **1**. The reaction was found to be complete by GC analysis after 24 h at 90 °C. Workup and purification by flash chromatography followed by Kugelrohr distillation afforded the title compound in 79% yield: ot 75 °C/0.05 mmHg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58−7.55 (m, 2H), 7.39−7.31 (m, 3H), 4.34−4.27 (m, 2H), 1.70−1.49 (m, 7H), 1.45−1.31 (m, 9H), 1.02−0.96 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 133.6, 129.3, 127.9, 46.5, 42.6, 38.2, 32.6, 28.2, 25.8, 22.1, 21.9, 21.2, 20.5; IR (neat) 3068, 3051, 3000, 2923, 2132 cm^{-1}; HRMS calcd for $C_{16}H_{24}Si$ 244.1647, found 244.1645; LRMS (EI$^+$) m/z 244 (7), 166 (100), 137 (20), 123 (24), 121 (54), 107 (96). Anal. Calcd for $C_{16}H_{24}Si$: C, 78.61; H, 9.90. Found: C, 78.84; H, 9.98.

2-[(Phenylsilyl)methyl]spiro[4.4]nonane (18) was prepared from **17** according to the general experimental procedure for cyclization/silylation using **1**. The reaction was found to be complete by GC analysis after 24 h at 90 °C. Workup and purification by flash chromatography followed by Kugelrohr distillation afforded the title compound in 68% yield: ot 90 °C/0.05 mmHg; R_f 0.53 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.55 (m, 2H), 7.40−7.32 (m, 3H), 4.28 (t, J = 4.0 Hz, 2H), 2.11−2.00 (m, 1H), 1.90−1.82 (m, 1H), 1.73 (dd, J = 12.3, 7.2 Hz, 1H), 1.60−1.50 (m, 5H), 1.48−1.34 (m, 5H), 1.29−1.19 (m, 1H), 1.13 (dd, J = 12.3, 9.9 Hz, 1H), 1.07−1.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.20, 133.02, 129.42, 127.92, 50.66, 48.99, 40.38, 40.14, 38.86, 36.09, 34.96, 24.39, 24.36, 17.66; IR (neat) 3067.7, 2940.0, 2855.8, 2132.5 cm^{-1}; LRMS (EI$^+$) m/z 244 (3), 187 (11), 166 (97), 137 (35), 124 (79), 121 (90), 107 (100), 105 (49). Anal. Calcd for $C_{16}H_{24}Si$: C, 78.62; H, 9.90. Found: C, 78.29; H, 9.76.

Cyclizations using [Cp$^{TMS}_2$LnMe]$_2$ as the Precatalyst: 1-Methyl-1-[(methylphenylsilyl)methyl]cyclopentane (4, R = Me) (Representative Procedure for the NMR Cyclization/Silylation Reaction Using [Cp$^{TMS}_2$LnMe]$_2$). In a nitrogen filled glovebox 0.077 g (0.63 mmol) of methylphenylsilane was added to 0.010 g (4.3 mol %) of the precatalyst [Cp$^{TMS}_2$LuMe]$_2$ dissolved in 0.7 mL of C_6D_6. Next, 0.048 g (0.50 mmol) of 2-methyl-1,5-hexadiene was added and the solution was transferred to a Teflon-valved NMR tube before being heated to 80 °C. The progress of the reaction was checked periodically by NMR, and the reaction was found to be complete after 12 h. The reaction mixture was next diluted with hexanes and filtered through a plug of Florisil. The solution was concentrated by rotary evaporation and purified by Kugelrohr distillation to yield 0.087 g (0.40 mmol, 80% yield) of **4** as a colorless oil: ot 70 °C/0.03 mmHg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54−7.51 (m, 2H), 7.35−7.31 (m, 3H), 4.45 (hextet, J = 3.8 Hz, 1H), 1.64−1.52 (m, 4H), 1.42−1.36 (m, 4H), 1.12 (dd, J = 14.8, 3.0 Hz, 1H), 1.00 (s, 3H), 0.99 (dd, J = 14.6, 4.2 Hz, 1H), 0.34 (d, J = 3.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.92, 134.26, 128.98, 127.78, 42.22, 42.21, 41.54, 28.65, 28.32, 24.14, 24.08, −3.36; IR (neat) 3068.0, 2952.3, 2870.4, 2118.8 cm^{-1}; HRMS calcd for $C_{14}H_{22}Si$ 218.1491, found 218.1525; LRMS (EI$^+$) m/z 218 (1), 203 (2), 161 (8), 140 (23), 121 (100). Anal. Calcd for $C_{14}H_{22}Si$: C, 76.99; H, 10.15. Found: C, 77.13; H, 10.29.

(1*R,2*R**)-1-Methyl-2-phenyl-1-[(phenylsilyl)methyl]-cyclopentane (20) (Representative Procedure for the Catalytic Cyclization/Silylation Reaction Using [Cp$^{TMS}_2$-YMe]$_2$ as the Precatalyst).** In a nitrogen-filled glovebox 0.066 g (0.61 mmol) of phenylsilane was added to 0.005 g (2.7 mol %) of the precatalyst [Cp$^{TMS}_2$YMe]$_2$ dissolved in 0.5 mL of cyclohexane. Next, 0.083 g (0.48 mmol) of 3-phenyl-2-methyl-1,5-hexadiene (**19**) was added and the solution was stirred at ambient temperature. Small aliquots were removed periodically for GC analysis, and the reaction was found to be complete after 12 h. After being removed from the glovebox, the reaction mixture was diluted with hexanes and filtered through a plug of Florisil. The solution was concentrated by rotary evaporation and purified by flash chromatography followed by Kugelrohr distillation to yield 0.124 g (0.44 mmol, 92% yield) of **20** as a colorless oil: ot 105 °C/0.01 mmHg; R_f 0.34 (hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55−7.51 (m, 2H), 7.39−7.31 (m, 3H), 7.29−7.25 (m, 2H), 7.22−7.19 (m, 3H), 4.35 (td, J = 5.9, 2.8 Hz, 1H), 4.31 (td, J = 5.9, 2.8 Hz, 1H), 2.79−2.75 (m, 1H), 2.10−1.98 (m, 2H), 1.84−1.64 (m, 4H), 1.18−1.13 (m, 1H), 1.04−1.00 (m, 1H), 0.76 (s, 3H); ^{13}C NMR

(125 MHz, $CDCl_3$) δ 141.32, 135.22, 133.25, 129.41, 128.95, 127.93, 127.70, 126.12, 58.33, 44.50, 40.58, 29.44, 24.13, 22.50, 21.26; IR (neat) 3066.7, 3025.9, 2955.4, 2873.0, 2134.2, 1601.0 cm^{-1}; HRMS calcd for $C_{19}H_{24}Si$ 280.1647, found 280.1649; LRMS (EI^+) *m/z* 280 (21), 238 (9), 202 (30), 189 (21), 183 (22), 147 (36), 107 (100), 105 (69), 91 (71).

(1*R,2*S**)-1-Methyl-3-phenyl-3-[(phenylsilyl)methyl]-cyclopentane (22)** was prepared from **21** according to the general experimental procedure for cyclization/silylation using $[Cp^{TMS}_2YMe]_2$ as the precatalyst. The reaction was found to be complete by GC analysis after 12 h at room temperature. Workup and purification by flash chromatography followed by Kugelrohr distillation afforded the title compound in 95% yield: ot 120 °C/0.05 mmHg; R_f 0.45 (hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.57−7.53 (m, 2H), 7.38−7.33 (m, 3H), 7.28−7.25 (m, 2H), 7.20−7.18 (m, 2H), 7.16−7.13 (m, 1H), 4.37−7.32 (m, 2H), 3.22−3.15 (m, 1H), 2.19−2.10 (m, 1H), 1.96−1.92 (m, 1H), 1.77−1.69 (m, 2H), 1.64−1.58 (m, 2H), 1.27−1.25 (m, 2H), 1.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.45, 135.22, 133.19, 129.44, 128.27, 127.97, 127.03, 125.71, 51.16, 44.53, 41.92, 41.42, 33.68, 29.12, 26.45; IR (neat) 3066.9, 3025.3, 2949.0, 2866.2, 2133.7, 1601.9 cm^{-1}; LRMS (EI^+) *m/z* 280 (4), 202 (22), 107 (100), 91 (57). Anal. Calcd for $C_{19}H_{24}Si$: C, 81.36; H, 8.62. Found: C, 81.48; H, 8.81.

(1*R,2*S**)-1-Methyl-3-phenyl-1-cyclopentanemethanol (23) (Representative Procedure for the Oxidation of Silanes).**[15b] The silane **22** (0.0598 g, 0.213 mmol) was dissolved in $CHCl_3$ (3 mL) and cooled to 0 °C before the addition of $HBF_4{\cdot}OEt_2$ (0.100 g, 0.62 mmol) via pipet. The mixture was next stirred for 1 h before the volitiles were removed in vacuo. The residue was dissolved in 3 mL of 1:1 MeOH:THF, and KF (0.062 g, 1.07 mmol), $KHCO_3$ (0.128 g, 1.28 mmol), and 0.5 mL of 30% H_2O_2 were added. The mixture was next heated at reflux for 12 h, during which a white precipitate formed. After cooling, the mixture was concentrated in vacuo and transferred onto 10 mL of saturated aqueous NaCl. The aqueous layer was extracted (3×) with 50 mL portions of Et_2O. The combined organic layers were dried over Na_2SO_4 and concentrated to yield a colorless oil. Purification by flash chromatography yielded a small amount of the major isomer pure along with a larger fraction consisting of a mixture of isomers (total yield: 0.0295 g, 0.139 mmol, 65%). The major isomer was subjected to NOE analysis to determine the stereochemistry: R_f 0.36 (20% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.28−7.22 (m, 4H), 7.18−7.14 (m, 1H), 3.47 and 3.45 (AB-system, J_{AB} = 10.42 Hz, 2H), 3.19 (tt, J = 11.1, 7.1 Hz, 1H), 2.14−2.07 (m, 1H), 1.82−1.76 (m, 2H), 1.73−1.64 (m, 1H), 1.60−1.55 (m, 1H), 1.46−1.40 (m, 2H), 1.11 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.43, 128.26, 127.00, 125.86, 71.97, 44.76, 44.68, 43.75, 36.02, 34.08, 25.30; IR (neat) 3354.1, 3082.8, 3060.3, 3026.4, 2947.9, 2865.7, 1601.9 cm^{-1}; HRMS calcd for $C_{13}H_{18}O$ 190.1358, found 190.1385; LRMS (EI^+) *m/z* 190 (32), 172 (14), 159 (50), 91 (100). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.98; H, 9.57.

1-(6-Chlorohexyl)-1-[(phenylsilyl)methyl]cyclopentane (6) was prepared from **5** according to the general experimental procedure for cyclization/silylation using $[Cp^{TMS}_2YMe]_2$ as the precatalyst. The reaction was found to be complete by GC analysis after 1 h at room temperature. Workup and purification by Kugelrohr distillation afforded the title compound in 79% yield. The spectra of this material were identical to those reported for cyclization using **1** as the precatalyst.

(1*R,2*R**)-2-(*tert*-Butyldiphenylsilyloxy)-1-methyl-1-[(phenylsilyl)methyl]cyclopentane (25)** was prepared from **24** according to the general experimental procedure for cyclization/silylation using $[Cp^{TMS}_2YMe]_2$ as the precatalyst. The reaction was found to be complete by GC analysis after 16 h at room temperature. Workup and purification by flash chromatography afforded the title compound in 74% yield: ^1H NMR (500 MHz, $CDCl_3$) δ 7.74−7.66 (m, 4H), 7.50−7.48 (m, 2H), 7.43−7.32 (m, 9H), 4.30−4.23 (m, 2H), 3.79 (t, J = 6.9 Hz, 1H), 1.65−1.48 (m, 4H), 1.42−1.30 (m, 2H), 1.18 (ddd, J = 14.6, 5.7, 3.0 Hz, 1H), 1.10 (s, 3H), 1.09 (s, 9H), 0.75 (ddd, J = 14.6, 5.5, 2.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.02, 135.97, 135.16, 134.95, 134.33, 129.49, 129.40, 127.87, 127.46, 127.35, 83.48, 44.45, 36.59, 31.74, 27.11, 22.32, 21.15, 19.43, 19.22; IR (neat) 3069.3, 3049.3, 2998.1, 2958.9, 2134.9, 1589.4 cm^{-1}; HRMS calcd for $C_{25}H_{29}OSi_2$ (M − *t*-Bu) 401.1757, found 401.1761; LRMS (EI^+) *m/z* 401 (21), 305 (100), 227 (60), 199 (58), 107 (27), 105 (24). Anal. Calcd for $C_{29}H_{38}OSi_2$: C, 75.92; H, 8.35. Found: C, 76.06; H, 8.73.

(1*R,3*R**)-1,3-Dimethyl-1-[(phenylsilyl)methyl]cyclopentane (8)** was prepared from **7** according to the general experimental procedure for NMR cyclization/silylation using $[Cp^{TMS}_2YMe]_2$ as the precatalyst. The reaction was found to be complete by NMR after 12 h at 90 °C. Workup and purification by Kugelrohr distillation afforded the title compound in 92% yield. The spectra of this material were identical to those reported for cyclization using **1** as the precatalyst.

(1*R,3*R**)-1,3-Dimethyl-1-cyclopentanemethanol (9)** was prepared from **8** according to the general procedure for silane oxidation. The spectra of the material obtained were similar to the data reported in the literature for the title compound.[10]

1-[(Phenylsilyl)methyl]bicyclo[3.3.1]nonane (27) was prepared from **26** according to the general experimental procedure for cyclization/silylation using $[Cp^{TMS}_2YMe]_2$ as the precatalyst. The reaction was found to be complete by GC analysis after 20 h at room temperature. Workup and purification by flash chromatography followed by Kugelrohr distillation afforded the title compound in 49% yield: ot 100 °C/0.05 mmHg; ^1H NMR (500 MHz, $CDCl_3$) δ 7.56−7.54 (m, 2H), 7.36−7.30 (m, 3H), 4.33 (t, J = 4.3 Hz, 2H), 1.93−1.88 (m, 3H), 1.70 (dd, J = 13.4, 6.0 Hz, 2H), 1.64−1.49 (m, 6H), 1.42−1.36 (m, 4H), 0.93 (t, J = 4.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.21, 133.68, 129.28, 127.89, 43.50, 39.06, 32.10, 30.77, 29.68, 29.55, 22.87; IR (neat) 3067.6, 2987.1, 2898.3, 2843.6, 2133.4 cm^{-1}; LRMS (EI^+) *m/z* 244 (6), 201 (91), 173 (81), 166 (93), 107 (100). Anal. Calcd for $C_{16}H_{24}Si$: C, 78.62; H, 9.90. Found: C, 78.99; H, 10.14.

1-[(Phenylsilyl)methyl]-*cis*-bicyclo[3.3.0]octane (11) was prepared from **10** according to the general experimental procedure for cyclization/silylation using $[Cp^{TMS}_2YMe]_2$ as the precatalyst. The reaction was found to be complete by GC analysis after 1 h at room temperature. Workup and purification by Kugelrohr distillation afforded the title compound in 73% yield. The spectra of this material were identical to those reported for cyclization using **1** as the precatalyst.

1-[(Phenylsilyl)methyl]-*cis*-bicyclo[4.3.0]nonane (13) was prepared from **12** according to the general experimental procedure for cyclization/silylation using $[Cp^{TMS}_2LuMe]_2$ as the precatalyst. The reaction was found to be complete by GC analysis after 1 h at room temperature. Workup and purification by flash chromatography followed by Kugelrohr distillation afforded the title compound in 95% yield. The spectra of this material were identical to those reported for cyclization using **1** as the precatalyst.

***cis*-Bicyclo[4.3.0]nonane-1-methanol (14).** Silane **13** was oxidized to the title compound using the general oxidation procedure given above. The alcohol obtained was purified by flash chromatography: R_f 0.36 (20% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 3.53 (d, J = 10.7 Hz, 1H), 3.31 (d, J = 10.7 Hz, 1H), 1.75−1.22 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.8, 45.8, 39.8, 33.1, 29.2, 28.6, 26.8, 22.6, 21.9, 20.7; IR (neat) 3333, 2925, 2858 cm^{-1}; HRMS calcd for $C_{10}H_{16}$ (M − H_2O) 136.1252, found 136.1257; LRMS (EI^+) *m/z* 136 (4), 123 (81), 81 (95), 31 (100).

***cis*-Bicyclo[4.3.0]nonane-1-carboxylic Acid (15).** Alcohol **14** was converted to the corresponding carboxylic acid using a literature procedure for RuO_4 oxidation:[32] ^1H NMR (400 MHz, $CDCl_3$) δ 12.4−11.6 (br s, 1H), 2.47−2.41 (m, 1H), 1.97−1.80 (m, 2H), 1.76−1.56 (m, 6H), 1.52−1.30 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.5, 52.1, 41.0, 36.1, 29.5, 28.2, 25.8, 23.0, 21.4, 21.2; IR (neat) 3200−2700, 1694 cm^{-1}; HRMS calcd for $C_{10}H_{16}O_2$ 168.1150, found 168.1152; LRMS (EI^+) *m/z* 168 (19), 150 (11), 123 (90), 113 (56), 81 (100).

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***cis*-Bicyclo[4.3.0]nonane-1-carboxamide (16).** Carboxylic acid **15** was converted to the primary carboxamide via a literature procedure.[25] The melting point of the white solid obtained closely matched the literature values (109−110 °C,[25] 114−115 °C[33]): mp 110−111.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (br s, 1H), 5.66 (br s, 1H), 2.31−2.30 (m, 1H), 1.83−1.15 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 52.4, 40.9, 36.5, 30.6, 28.2, 26.0, 22.9, 21.4, 21.1; IR (neat) 3434, 3354, 3198, 2926, 2870, 1644, 1613 cm^{-1}; HRMS calcd for $C_{10}H_{17}NO$ 167.1310, found 167.1302; LRMS (EI$^+$) *m*/*z* 167 (19), 150 (6), 123 (54), 112 (52), 81 (100).

4-Aza-4-benzyl-1-[(phenylsilyl)methyl]-*cis*-bicyclo[4.3.0]-nonane (29) was prepared from **28** according to the general experimental procedure for cyclization/silylation using [Cp^{TMS}_2-YMe]$_2$ as the precatalyst. The reaction was found to be complete by GC analysis after 20 h at room temperature. Workup and purification by flash chromatography followed by Kugelrohr distillation afforded the title compound in 77% yield: ot 160 °C/0.01 mmHg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56−7.54 (m, 2H), 7.38−7.26 (m, 7H), 7.24−7.19 (m, 1H), 4.32−4.28 (m, 2H), 3.47 (d, J = 13.3 Hz, 1H), 3.41 (d, J = 13.3 Hz, 1H), 2.40−2.36 (m, 1H), 2.31−2.23 (m, 3H), 1.75−1.58 (m, 7H), 1.48−1.41 (m, 2H), 1.31−1.26 (m, 1H), 1.06−1.01 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.16, 135.19, 133.24, 129.42, 128.82, 128.08, 127.95, 126.71, 63.22, 53.62, 50.02, 47.11, 41.18, 37.02, 32.85, 27.45, 21.04, 20.63; IR (neat) 3065.8, 3024.6, 2951.3, 2873.6, 2797.0, 2759.9, 2132.9 cm^{-1}; LRMS (EI$^+$) *m*/*z* 335 (3), 334 (4), 257 (5), 244 (18), 228 (11), 153 (15), 107 (30), 91 (100). Anal. Calcd for $C_{22}H_{29}NSi$: C, 78.74; H, 8.71. Found: C, 78.95; H, 8.81.

1-[(Phenylsilyl)methyl]-4-oxa-*cis*-bicyclo[4.3.0]nonane (31) was prepared from **30** according to the general experimental procedure for cyclization/silylation using [Cp^{TMS}_2-YMe]$_2$ as the precatalyst. The reaction was found to be complete by GC analysis after 24 h at 90 °C. Workup and purification by flash chromatography followed by Kugelrohr distillation afforded the title compound in 57% yield: ot 110 °C/0.05 mmHg; R_f 0.40 (5% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58−7.54 (m, 2H), 7.41−7.31 (m, 3H), 4.35−4.31 (m, 2H), 3.68−3.50 (m, 3H), 3.47−3.42 (m, 1H), 1.78−1.61 (m, 7H), 1.59−1.33 (m, 3H), 1.12−1.04 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.16, 132.83, 129.56, 128.03, 66.69, 64.12, 46.58, 40.53, 37.64, 32.54, 25.99, 20.73, 20.59; IR (neat) 3067.7, 2951.6, 2873.2, 2133.0 cm^{-1}; LRMS (EI$^+$) *m*/*z* 246 (4), 245 (15), 169 (22), 168 (14), 140 (19), 123 (27), 107 (100), 105 (66). Anal. Calcd for $C_{15}H_{22}OSi$: C, 73.11; H, 9.00. Found: C, 73.34; H, 8.81.

6-[(Phenylsilyl)methyl]-*cis*-bicyclo[4.3.0]nonan-3-one, dithioethane acetal (33) was prepared from **32** according to the general experimental procedure for cyclization/silylation using [Cp^{TMS}_2YMe]$_2$ as the precatalyst. The reaction was found to be complete by GC analysis after 8 h at room temperature. Workup and purification by flash chromatography afforded the title compound in 98% yield. The product was contaminated with 9% uncyclized hydrosilylated product that could not be removed chromatographically: R_f 0.30 (5% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56−7.54 (m, 2H), 7.38−7.31 (m, 3H), 4.35 (t, J = 4.4 Hz, 2H), 3.30−3.24 (m, 4H), 2.04−1.65 (m, 11H), 1.36−1.29 (m, 2H), 1.13−1.05 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.20, 133.10, 129.44, 127.97, 68.24, 46.84, 44.81, 42.54, 38.64, 38.25, 38.08, 33.88, 33.08, 29.88, 23.58, 20.50; IR (neat) 3066.4, 2922.6, 2874.5, 2133.7 cm^{-1}; HRMS calcd for $C_{18}H_{26}S_2Si$ 334.1245, found 334.1237; LRMS (EI$^+$) *m*/*z* 334 (46), 306 (8), 273 (42), 257 (20), 240 (20), 197 (80), 107 (100). Anal. Calcd for $C_{18}H_{26}S_2Si$: C, 64.61; H, 7.83. Found: C, 64.51; H, 7.98.

(1*R,2*R**)-6-[(*tert*-Butyldimethylsilyloxy)methyl]-1-[(phenylsilyl)methyl]bicyclo[4.3.0]nonane (35)** was prepared from **34** according to the general experimental procedure for cyclization/silylation using [Cp^{TMS}_2YMe]$_2$ as the precatalyst. The reaction was found to be complete by GC analysis after 16 h at room temperature. Workup and purification by flash chromatography followed by Kugelrohr distillation afforded the title compound in 70% yield. The material isolated was contaminated with 10% uncyclized hydrosilylated material that could not be removed chromatographically. Pure cyclized diol could be obtained after oxidation as described below: R_f 0.52 (hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57−7.53 (m, 2H), 7.38−7.32 (m, 3H), 4.33−4.26 (m, 2H), 3.39 (d, J = 9.5 Hz, 1H), 3.32 (d, J = 9.5 Hz, 1H), 1.68−1.61 (m, 6H), 1.48−1.34 (m, 5H), 1.30−1.20 (m, 4H), 0.98−0.89 (m, 1H), 0.86 (s, 9H), −0.01 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.21, 133.68, 129.35, 127.91, 68.70, 48.97, 44.54, 38.08, 34.39, 30.29, 28.23, 25.91, 22.13, 21.79, 21.59, 19.37, 18.21, 15.75, −5.54, −5.55; IR (neat) 2927.5, 2857.1, 2134.5 cm^{-1}; HRMS calcd for $C_{19}H_{31}OSi_2$ (M − *t*-Bu) 331.1913, found 331.1890; LRMS (EI$^+$) *m*/*z* 331 (14), 235 (23), 181 (100), 107 (66), 105 (48). Anal. Calcd for $C_{23}H_{40}OSi_2$: C, 71.06; H, 10.37. Found: C, 71.14; H, 10.66.

1,6-Bis(hydroxymethyl)-*cis*-bicyclo[4.3.0]nonane (36). To obtain material free of contamination, **34** was subjected to catalytic cyclization/silylation according to the general procedure. After workup the crude material was oxidized according to the general procedure given for the preparation of **23**. Analogous workup and purification by flash chromatography yielded the title compounds as a white solid in 58% yield: mp 207−208 °C (lit.[34] mp 203 °C); R_f 0.44 (75% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.60−3.51 (m, 4H), 2.69 (br s, 2H), 1.70−1.62 (m, 2H), 1.60−1.55 (m, 4H), 1.53−1.48 (m, 2H), 1.47−1.43 (m, 4H), 1.35−1.31 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 67.90, 47.38, 32.35, 30.63, 22.04, 18.74; IR (neat) 3267.8 br, 2931.9 cm^{-1}; HRMS calcd for $C_{11}H_{18}O$ (M − H_2O) 166.1358, found 166.1358; LRMS (EI$^+$) *m*/*z* 166 (2), 153 (10), 135 (100), 121 (24).

2-[(Phenylsilyl)methyl]spiro[4.4]nonane (18) was prepared from **17** according to the general experimental procedure for cyclization/silylation using [Cp^{TMS}_2YMe]$_2$ as the precatalyst. The reaction was found to be complete by GC analysis after 1 h at room temperature. Workup and purification by flash chromatography followed by Kugelrohr distillation afforded the title compound in 88% yield. The spectra of this material were identical to those reported for cyclization using **1** as the precatalyst.

8-[(Phenylsilyl)methyl]tricyclo[4.3.3.0]dodecane (38) was prepared from **37** according to the general experimental procedure for cyclization/silylation using [Cp^{TMS}_2YMe]$_2$ as the precatalyst. The reaction was found to be complete by GC analysis after 1 h at room temperature. Workup and purification by flash chromatography followed by Kugelrohr distillation afforded the title compound in 35% yield. A 42% yield of uncharacterized isomers assumed to be spiro[5.5]dodecane product **39** from the cyclization of the terminal olefins was also isolated: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56−7.54 (m, 2H), 7.39−7.32 (m, 3H), 4.26 (t, J = 4.0 Hz, 2H), 2.23−2.16 (m, 1H), 1.68 (dd, J = 13.0, 8.0 Hz, 2H), 1.57−1.26 (m, 16H), 1.08−1.05 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.19, 132.98, 129.42, 127.92, 50.86, 47.46, 39.60, 32.71, 32.29, 22.50, 20.21, 18.53; IR (neat) 3067.9, 2926.0, 2857.5, 2132.2 cm^{-1}; HRMS calcd for $C_{19}H_{28}Si$ 284.1960, found 284.1951; LRMS (EI$^+$) *m*/*z* 284 (2), 241 (13), 206 (100), 107 (87). Anal. Calcd for $C_{19}H_{28}Si$: C, 80.21; H, 9.92. Found: C, 80.42; H, 10.32.

8-Methyl-8-[(phenylsilyl)methyl]tricyclo[4.3.3.0]dodecane (41) was prepared from **40** according to the general experimental procedure for cyclization/silylation using [Cp^{TMS}_2-YMe]$_2$ as the precatalyst. The reaction was found to be complete by GC analysis after 1 h at room temperature. Workup and purification by flash chromatography afforded the title compound in 75% yield. A monocyclic hydrosilylated product whose spectal data are described below was also isolated in 14% yield: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57−7.55 (m, 2H), 7.36−7.32 (m, 3H), 4.31 (t, J = 4.2 Hz, 2H), 1.77−1.52 (m, 10H), 1.46−1.28 (m, 10H), 1.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.20, 133.49, 129.33, 127.92, 54.38, 52.52,

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39.25, 37.92, 33.86, 32.73, 31.58, 22.04, 20.89; IR (neat) 3067.9, 2925.5, 2857.5, 2134.2 cm^{-1}; HRMS calcd for $C_{20}H_{30}Si$ 298.2117, found 298.2099; LRMS (EI^+) *m/z* 298 (8), 283 (16), 220 (100), 107 (81).

2-Methallyl-1-methylene-2-[3-(phenylsilyl)propyl]cyclohexane (42): minor product isolated in the preparation of **41**; ^1H NMR (500 MHz, $CDCl_3$) δ 7.65−7.51 (m, 2H), 7.37−7.31 (m, 3H), 4.79−4.73 (m, 2H), 4.55−4.54 (m, 2H), 4.27 (t, J = 3.8 Hz, 2H), 2.46 (d, J = 13.4 Hz, 1H), 2.22−2.18 (m, 1H), 2.12−2.07 (m, 1H), 1.94 (d, J = 13.4 Hz, 1H), 1.69 (s, 3H), 1.56−1.23 (m, 10H), 0.92−0.87 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.52, 143.63, 135.16, 132.76, 129.46, 127.93, 114.01, 107.94, 43.13, 42.34, 38.40, 38.10, 33.79, 28.43, 25.09, 21.84, 19.02, 10.63; IR (neat) 3069.0, 2931.6, 2854.6, 2131.6, 1635.4 cm^{-1}; HRMS calcd for $C_{20}H_{30}Si$ 298.2117, found 298.2112; LRMS (EI^+) *m/z* 298 (1), 283 (6), 243 (8), 149 (25), 107 (100), 105 (54).

7-Methyl-7-[(phenylsilyl)methyl]tricyclo[3.3.3.0]undecane (44) was prepared from **43** according to the general experimental procedure for cyclization/silylation using $[Cp^{TMS}{}_2YMe]_2$ as the precatalyst. The reaction was found to be complete by GC analysis after 3 h at room temperature. Workup and purification by flash chromatography afforded the title compound in 69% yield: R_f 0.61 (hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.56−7.53 (m, 2H), 7.37−7.31 (m, 3H), 4.30 (t, J = 4.2 Hz, 2H), 1.71−1.40 (m, 14H), 1.29−1.24 (m, 2H), 1.18 (t, J = 4.2 Hz, 2H), 1.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.21, 133.43, 129.35, 127.92, 62.20, 55.81, 43.35, 42.61, 41.98, 29.86, 27.48, 25.24, 24.91; IR (neat) 3068.0, 2936.1, 2865.3, 2134.3 cm^{-1}; HRMS calcd for $C_{19}H_{28}Si$ 284.1960, found 284.1937; LRMS (EI^+) *m/z* 284 (10), 269 (13), 206 (100), 191 (34), 122 (98), 107 (97), 105 (46).

1-[(Phenylsilyl)methyl]cyclopentane (46) was prepared from **45** according to the general experimental procedure for cyclization/silylation using $[Cp^{TMS}{}_2YMe]_2$ as the precatalyst. The reaction was found to be complete by GC analysis after 4 h at room temperature. Workup and purification by Kugelrohr distillation afforded the title compound in 98% yield. The material obtained was spectroscopically identical to that reported in the literature.[6b]

[(Methylphenylsilyl)methyl]cyclohexane (48) was prepared from **47** according to the general experimental procedure for cyclization/silylation except using methylphenylsilane as the trapping reagent. The reaction was found to be complete by GC analysis after 12 h at room temperature. Workup and purification by Kugelrohr distillation afforded the title compound in 86% yield. The material obtained was spectroscopically identical to that reported in the literature.[6b]

(1*R,2*R**)-1-[(Methylphenylsilyl)methyl]-2-phenylcyclohexane (50)** was prepared from **49** according to the general experimental procedure for cyclization/silylation except using methylphenylsilane as the trapping reagent. The reaction was found to be complete by GC analysis after 12 h at room temperature. Workup and purification by flash chromatography followed by Kugelrohr distillation afforded the title compound in 56% yield as a mixture of diastereomers due to the stereocenter at silicon. The purity and identity of the major product were determined by oxidation to the alcohol as described below: R_f 0.35 (7.5% C_6H_6/hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.55−7.21 (m, 7H), 7.17−7.14 (m, 1H), 7.10−7.04 (m, 2H), 4.30−4.28 (m, 1H), 2.20−2.14 (m, 1H), 2.01−1.99 (m, 1H), 1.80−1.60 (m, 4H), 1.52−1.23 (m, 3H), 1.12−0.98 (m, 1H), 0.89−0.72 (m, 1H), 0.54−0.32 (m, 1H), 0.21−0.17 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.62, 136.96, 134.31, 134.23, 129.00, 128.27, 127.70, 125.80, 53.73, 39.22, 36.12, 35.20, 26.89, 26.84, 19.08, −5.18; IR (neat) 3066.6, 3024.7, 2920.8, 2851.6, 2113.2, 1601.5 cm^{-1}; HRMS calcd for $C_{20}H_{26}Si$ 294.1804, found 294.1786; LRMS (EI^+) *m/z* 294 (3), 279 (10), 216 (38), 121 (100).

***trans*-2-Phenylcyclohexanemethanol (51).** Substrate **49** was cyclized according to the general procedure for cyclization/silylation given above. The crude material isolated was subjected to the general oxidation conditions to give the title compound in 53% over two steps. The NMR spectra and melting point closely match literature values: mp 48−49 °C (lit.[26] mp 50−51 °C). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.29; H, 9.72. 4-Phenyl-1-cyclohexanemethanol was also isolated in 26% yield. This product was identified by NMR and HRMS.

(1*R,2*R**)-1-*tert*-Butyldiphenylsiloxy-2-[(methylphenylsilyl)methyl]cyclohexane (53)** was prepared from **52** according to the general experimental procedure for cyclization/silylation except using methylphenylsilane as the trapping reagent. The reaction was found to be complete by GC analysis after 2 d at room temperature. Workup and purification by flash chromatography afforded the title compound in 71% yield as a mixture of diastereomers due to the stereocenter at silicon. The purity and identity of the major product were determined by oxidizing the product to the diol as described below: R_f 0.35 (10% C_6H_6/hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.68−7.63 (m, 4H), 7.50−7.29 (m, 11H), 4.34−4.33 (m, 1H), 3.31−3.27 (m, 1H), 1.85−1.82 (m, 1H), 1.69−1.41 (m, 5H), 1.29−1.12 (m, 3H), 1.09−1.02 (m, 9H), 0.91−0.84 (m, 1H), 0.46−0.39 (m, 1H), 0.28−0.25 (m, 3H); IR (neat) 3069.1, 2929.7, 2114.1 cm^{-1}; HRMS calcd for $C_{26}H_{31}OSi_2$ (M − *t*-Bu) 415.1913, found 415.1948; LRMS (EI^+) *m/z* 415 (22), 375 (56), 319 (100). Anal. Calcd for $C_{30}H_{40}OSi_2$: C, 76.21; H, 8.53. Found: C, 76.32; H, 8.81.

***trans*-2-(Hydroxymethyl)cyclohexanol (54).** To obtain material free of additional stereocenters, diene **52** was cyclized according to the general cyclization/silylation protocol. The crude silane obtained was subjected to the oxidation procedure and purified by flash chromatography to give a colorless oil in 51% yield for the two steps. The material obtained was spectroscopically consistent with literature data for the trans compound.[27]

1-Methylene-2-[4-(phenylsilyl)butyl]cyclohexane (56) was prepared from **55** according to the general experimental procedure for cyclization/silylation using $[Cp^{TMS}{}_2YMe]_2$ as the precatalyst. The reaction was found to be complete by GC analysis after 1 h at room temperature. Workup and purification by flash chromatography followed by Kugelrohr distillation afforded the title compound in 72% yield: ot 110 °C/0.1 mmHg; ^1H NMR (500 MHz, $CDCl_3$) δ 7.56−7.54 (m, 2H), 7.39−7.32 (m, 3H), 4.61 (d, J = 0.9 Hz, 1H), 4.52 (s, 1H), 4.26 (t, J = 3.7 Hz, 2H), 2.21−2.16 (m, 1H), 2.00−1.94 (m, 2H), 1.74−1.68 (m, 1H), 1.66−1.50 (m, 3H), 1.49−1.16 (m, 8H), 0.95−0.91 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.16, 135.19, 132.75, 129.46, 127.94, 105.33, 42.99, 34.76, 33.85, 31.70, 30.68, 28.86, 25.29, 24.24, 10.04; IR (neat) 3068.0, 2925.5, 2853.2, 2131.5, 1644.1 cm^{-1}; HRMS calcd for $C_{17}H_{26}Si$ 258.1804, found 258.1813; LRMS (EI^+) *m/z* 258 (6), 180 (30), 161 (46), 107 (100), 105 (47), 96 (96).

2-Isopropyl-6-(phenylsilyl)-1-hexene (58) was prepared from **57** according to the general experimental procedure for cyclization/silylation except using $[Cp^{TMS}{}_2LuMe]_2$ as the precatalyst. The reaction was found to be complete by GC analysis after 1 h at room temperature. Workup and purification by flash chromatography followed by Kugelrohr distillation afforded the title compound in 84% yield: ot 65 °C/0.05 mmHg; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57−7.55 (m, 2H), 7.40−7.32 (m, 3H), 4.71 (s, 1H), 4.64 (s, 1H), 4.29−4.27 (m, 2H), 2.20 (heptet, J = 6.7 Hz, 1H), 2.02−1.98 (m, 2H), 1.51−1.43 (m, 4H), 1.00 (d, J = 6.7 Hz, 6H), 0.98−0.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.98, 135.20, 132.69, 129.49, 127.96, 106.16, 34.02, 33.69, 31.34, 24.99, 21.86, 9.98; IR (neat) 3069.0, 3052.0, 2960.7, 2926.8, 2132.4, 1641.2 cm^{-1}; HRMS calcd for $C_{15}H_{23}Si$ (M − H) 231.1569, found 231.1547; LRMS (EI^+) *m/z* 231 (1), 217 (3), 189 (45), 161 (47), 148 (36), 133 (20), 120 (63), 107 (100), 105 (68).

1-(2-Methylpropyl)-1-[(phenylsilyl)methyl]cyclopentane (60) was prepared from **59** according to the general experimental procedure for cyclization/silylation using $[Cp^{TMS}{}_2YMe]_2$ as the precatalyst. The reaction was found to be complete by GC analysis after 1 h at room temperature. Workup and purification by flash chromatography followed by Kugelrohr distillation afforded the title compound in 52% yield. A 36% yield of uncyclized hydrosilylated product was also isolated as described below: ot 80 °C/0.01 mmHg; R_f 0.55 (hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.75−7.55 (m, 2H),

7.38−7.32 (m, 3H), 4.31 (t, J = 4.2 Hz, 2H), 1.71 (nonlet, J = 6.5 Hz, 1H), 1.64−1.57 (m, 4H), 1.52−1.42 (m, 4H), 1.35 (d, J = 6.0 Hz, 2H), 1.14 (t, J = 4.2 Hz, 2H), 0.90 (d, J = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.21, 133.47, 129.36, 127.93, 49.79, 44.86, 40.90, 25.31, 24.82, 23.91, 21.00; IR (neat) 3068.0, 2952.3, 2869.8, 2135.4 cm^{-1}; HRMS calcd for $C_{16}H_{25}Si$ (M − H) 245.1726, found 245.1726; LRMS (EI$^+$) m/z 246 (1), 189 (76), 168 (10), 161 (56), 147 (19), 107 (100), 105 (48).

7-Methyl-5-methylene-1-(phenylsilyl)octane (61): minor product isolated from the preparation of **60**; ot 70 °C/0.01 mmHg; R_f 0.38 (hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57−7.55 (m, 2H), 7.37−7.33 (m, 3H), 4.70−4.65 (m, 2H), 4.28 (t, J = 3.7 Hz, 2H), 1.97−1.94 (m, 2H), 1.85 (d, J = 7.2 Hz, 2H), 1.73 (nonlet, J = 6.7 Hz, 1H), 1.51−1.42 (m, 4H), 0.98−1.93 (m, 2H), 0.85 (d, J = 6.6 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.67, 135.19, 132.69, 129.49, 127.95, 110.01, 45.91, 35.31, 30.88, 25.97, 24.89, 22.50, 9.95; IR (neat) 3068.6, 2952.8, 2925.4, 2867.2, 2132.4, 1642.0 cm^{-1}; HRMS calcd for $C_{16}H_{25}Si$ (M − H) 245.1726, found 245.1699; LRMS (EI$^+$) m/z 246 (1), 203 (15), 161 (40), 107 (100), 105 (40), 81 (17), 67 (13), 53 (20), 43 (73), 41 (53).

1-(3-Methylbutyl)-1-[(phenylsilyl)methyl]cyclopentane (63) was prepared from **62** according to the general experimental procedure for cyclization/silylation using $[Cp^{TMS}{}_2YMe]_2$ as the precatalyst. The reaction was found to be complete by GC analysis after 1 h at room temperature. Workup and purification by flash chromatography followed by Kugelrohr distillation afforded the title compound in 84% yield: ot 80 °C/0.01 mmHg; R_f 0.56 (hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57−7.54 (m, 2H), 7.36−7.31 (m, 3H), 4.30 (t, J = 4.3 Hz, 2H), 1.63−1.56 (m, 4H), 1.45−1.42 (m, 5H), 1.40−1.32 (m, 2H), 1.15−1.10 (m, 4H), 0.84 (d, J = 6.6 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.21, 133.50, 129.35, 127.91, 44.22, 40.15, 38.74, 34.17, 28.75, 24.32, 22.71, 21.46; IR (neat) 3068.0, 3051.4, 2951.8, 2868.4, 2134.8 cm^{-1}; LRMS (EI$^+$) m/z 260 (1), 189 (74), 161 (47), 107 (100). Anal. Calcd for $C_{17}H_{28}Si$: C, 78.38; H, 10.83. Found: C, 78.46; H, 11.04.

3-[3-(Phenylsilyl)propyl]cyclohexene (65) was prepared from **64** according to the general experimental procedure for cyclization/silylation except using $[Cp^{TMS}{}_2LuMe]_2$ as the precatalyst. The reaction was found to be complete by GC analysis after 1 h at room temperature. Workup and purification by flash chromatography followed by Kugelrohr distillation afforded the title compound in 93% yield: ot 70 °C/0.05 mmHg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58−7.55 (m, 2H), 7.40−7.33 (m, 3H), 5.65−5.62 (m, 1H), 5.54−5.52 (m, 1H), 4.29−4.27 (m, 2H), 2.05−2.02 (m, 1H), 1.97−1.93 (m, 2H), 1.78−1.67 (m, 2H), 1.54−1.29 (m, 5H), 1.20−1.14 (m, 1H), 0.95−0.90 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.19, 132.70, 132.05, 129.47, 127.94, 126.78, 39.58, 34.86, 28.98, 25.38, 22.46, 21.48, 10.20; IR (neat) 3068.0, 3016.1, 2922.7, 2856.2, 2131.6, 1648.0 cm^{-1}; HRMS calcd for $C_{15}H_{22}Si$ 230.1491, found 230.1482; LRMS (EI$^+$) m/z 230 (2), 187 (8), 173 (14), 152 (81), 107 (100), 105 (67). Anal. Calcd for $C_{15}H_{22}Si$: C, 78.19; H, 9.62. Found: C, 78.53; H, 9.57.

1-*tert*-Butyldimethylsiloxy-2-[3-(methylphenylsilyl)propyl]-1-vinylcyclohexane (67). Substrate **66** was cyclized according to the general procedure for NMR silylation given above. The reaction was found to be complete after 4 h at room temperature. Analogous workup and purification yielded 88% of the title compound. The NMR spectra closely match literature data.[14]

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Supporting Information Available: Experimental details and characterization for substrates **5**, **10**, **17**, **19**, **21**, **24**, **28**, **30**, **32**, **34**, **37**, **40**, **43**, **49**, **52**, **55**, **57**, **59**, and **62** and their precursors, NMR spectra for compounds without reported elemental analyses, and details of the X-ray stucture determination of **2** (151 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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