resultant solution was extracted with 10% NaOH (2 × 100 mL). The organic layer was dried with $MgSO_4$ and the solvent removed. Vacuum distillation gave 55 g (88%) of a colorless oil: bp 115 °C (0.25 mm); ^1H NMR ($CDCl_3$, δ) 6.65 (m, 3 H), 5.35 (br, 1 H), 3.78 (s, 3 H), 3.70 (s, 3 H), 1.65 (m, 9 H).

3,6-Dimethoxy-2-hydroxybenzaldehyde (22). 2,5-Dimethoxyphenol tetrahydropyranyl ether (**31**) (10.3 g, 43.09 mmol) was stirred in 500 mL of dry THF under argon for 10 min. The solution was then cooled to 0 °C, and 23.4 mL of *n*-butyllithium (2.03 M in hexane) was slowly added. The mixture was brought to room temperature, stirred for 2 h, and then cooled to −78 °C prior to addition of dry *N,N*-dimethylformamide (12.6 g, 172.4 mmol). The stirring was continued for 2 h while the solution was allowed to come to room temperature. Then, 40 mL of 6 N hydrochloric acid was carefully added and the mixture stirred vigorously for 1 h. The organic layer was removed to give a yellow oil that was passed through a flash column (fluorisil; hexane/ethyl acetate, 1:1) to give 6.0 g (79%) of the desired product as yellow needles: mp 67–69 °C; ^1H NMR ($CDCl_3$, δ) 12.18 (s, 1 H), 10.22 (s, 1 H), 7.01 (d, 1 H), 6.25 (d, 1 H), 3.83 (s, 6 H).

2-Acetoxy-3-methoxybenzaldehyde (33). A solution of 50 g (0.329 mol) of *o*-vanillin (**32**) in 50 mL of pyridine and 35 mL (0.340 mol) of acetic anhydride was stirred at room temperature for 24 h to give a white precipitate. The mixture was transferred to a flask containing 300 mL of 6 N HCl solution. The solids were collected by filtration, and the product was washed with additional (400 mL) 6 N HCl followed by distilled water. White crystals were obtained after recrystallization from methanol: 62 g (97%); mp 68–70 °C [lit.[8] mp 72–73 °C]; ^1H NMR ($CDCl_3$, δ) 10.12 (s, 1 H), 7.28 (m, 3 H), 3.86 (s, 3 H), 2.39 (s, 3 H).

2-Hydroxy-3-methoxy-6-bromobenzaldehyde (34). The aldehyde **33** (2.0 g, 10.3 mmol) was added in small portions to a solution of 4.0 g of KBr and 0.60 mL of bromine in 40 mL of distilled water. The mixture was stirred for 1 h and the resulting precipitate collected by filtration. The crude product (pinkish solid) was suspended in 50 mL of 6 N HCl and stirred for 3 h at room temperature. The yellow precipitate obtained was collected by filtration and recrystallized from methanol to give 1.9 g (68%) of yellow crystals: mp 116–117 °C [lit.[9] mp 105–108 °C]; ^1H NMR ($CDCl_3$, δ) 12.16 (s, 1 H), 10.29 (s, 1 H), 7.21 (d, J = 8.4 Hz, 1 H), 7.0 (d, J = 8.5 Hz, 1 H), 3.88 (s, 3 H).

3,6-Dimethoxy-2-hydroxybenzaldehyde (22). In a 500-mL three-necked flask, fitted with a condenser and an addition funnel, was added 38.4 g (0.713 mol) of sodium very slowly to 250 mL of absolute methanol. After all of the sodium was added, the mixture was stirred until hydrogen evolution ceased (15 min). Then, 25.0 g (0.108 mol) of **34** dissolved in 100 mL of dry DMF was added along with 2.0 g of copper(I) iodide. The mixture was refluxed for 4 h. After it was cooled to room temperature and filtered, the filtrate was transferred to an Erlenmeyer flask containing 300 g of ice and 100 mL of concentrated HCl. The yellow precipitate that formed was separated by filtration and recrystallized from boiling methanol to afford 14.2 g (72%) of fine yellow needles: mp 68–69 °C [lit.[10] mp 68–69 °C]; ^1H NMR ($CDCl_3$, δ) 12.16 (s, 1 H), 10.32 (s, 1 H), 7.0 (d, J = 8.8 Hz, 1 H), 6.25 (d, J = 9.4 Hz, 1 H), 3.80 (s, 3 H), 3.76 (s, 3 H).

3,6-Dimethoxy-1,2-benzenediol (35). A solution containing 3.60 g (19.8 mmol) of **22** in 100 mL of 2% NaOH was stirred at room temperature while 2.46 g (21.77 mmol) of 30% hydrogen peroxide in 30 mL of distilled water was added dropwise. After the addition was complete, the mixture was stirred for 90 min. The mixture was then transferred to an Erlenmeyer flask containing 250 mL of distilled water and 50 mL of concentrated HCl. The aqueous solution was extracted with dichloromethane (3 × 150 mL), and the organic layers were combined and dried with $MgSO_4$. Evaporation of the solvent gave a residue that was immediately filtered through silica gel (hexanes/ethyl acetate). Evaporation of the eluent afforded 2.6 g (79%) of a yellow solid: mp 105–106 °C [lit.[10] mp 105–106 °C]; ^1H NMR ($CDCl_3$, δ) 6.37 (s, 1 H), 5.65 (br, 1 H), 3.83 (s, 3 H).

3,6-Dimethoxy-1,2-benzoquinone (36). A mixture containing 2.65 g (15.6 mmol) of **35** and 3.91 g (12.3 mmol) of *o*-chloranil was stirred in 100 mL of anhydrous ether under argon at −22 °C for 2 h. The product was filtered and washed several times with cold ether to give 2.55 g (98%) of orthoquinone **36** as a dark purple solid: mp 120–122 °C; ^1H NMR ($CDCl_3$, δ) 5.87 (s, 1 H), 3.73 (s, 3 H); IR (KBr, cm^{-1}) 3070 (m), 2840 (m), 1670 (s), 1380 (s), 1340 (s), 1140 (s); MS, m/z 169 (Cl); exact mass calcd for $C_8H_8O_4$ 168.04220, found 168.04000.

Acknowledgment. We thank the National Institutes of Health (Grant CA-11890) for financial support of this work.

Registry No. **1**, 21086-65-7; **2**, 109765-47-1; **3**, 108213-18-9; **4**, 109765-48-2; **5**, 109765-49-3; **6**, 109765-50-6; **7**, 109765-51-7; **8**, 108214-15-9; **9**, 14382-91-3; **10**, 109765-52-8; **11**, 109765-53-9; **12**, 108232-95-7; **13**, 109765-54-0; **14**, 3997-18-0; **15**, 109765-55-1; **16**, 109765-56-2; **17**, 109765-57-3; **18**, 708-76-9; **19**, 109765-58-4; **20**, 109765-59-5; **21**, 108213-29-2; **22**, 64466-51-9; **23**, 109765-60-8; **24**, 65162-35-8; **25**, 109765-61-9; **26**, 109765-62-0; **27**, 109765-63-1; **28**, 109765-64-2; **29**, 93-02-7; **30**, 18113-18-3; **31**, 109765-65-3; **32**, 148-53-8; **33**, 7150-01-8; **34**, 20035-41-0; **35**, 109765-60-8; **36**, 108213-73-6.

(8) Lambooy, J. F. *J. Am. Chem. Soc.* **1954**, *76*, 133.
(9) Brink, M. *Acta Univ. Lund., Sect. 2* **1967**, *36*, 12.
(10) Rene, L.; Blanco, L.; Royer, R.; Cavier, R.; Lemoine, J. *Eur. J. Med. Chem. Chim. Ther.* **1977**, *12*, 385.
(11) Lechner, J.; Wessley, P. *Monatsh. Chem.* **1932**, *60*, 160.

Metalation Reactions of 1-Silacyclo-3-pentenes

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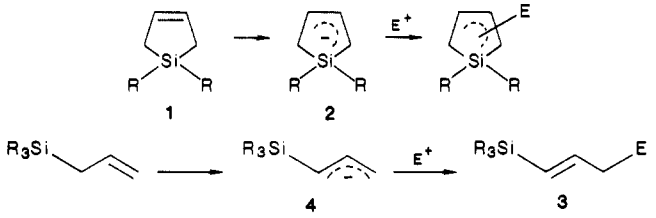
The metalation of a series of 1-silacyclo-3-pentenes was studied. The reaction depends critically on the substituent at the silicon. 1,1-Bis(4-*tert*-butylphenyl)-1-silacyclo-3-pentene was metalated cleanly to give the anion derived from proton abstraction on the cyclopentenyl ring. The regioselectivity of the reaction of the 1-silacyclopentenyl anion with electrophiles was examined and found to be influenced by the steric size of the electrophile.

The α-silylallyl anion, derived from the metalation of allylsilanes, has found considerable application[1] in organic synthesis; however, the corresponding anion **2** derived from the metalation of 1-silacyclo-3-pentene **1** so far has not been studied. The anion **2** is potentially useful in synthesis since it is a polymetallic reagent with multiple reactive sites at carbons 1, 3, and 4. Reaction of these sites with electrophiles can give variously substituted siloles that may serve as functionalized masked dienes.[2] Another point

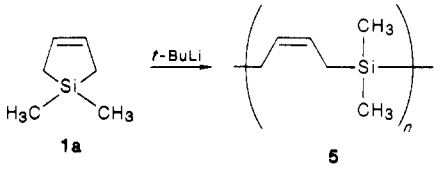
(1) (a) Lau, P. W. K.; Chan, T. H. *Tetrahedron Lett.* **1978**, *18*, 2383. (b) Chan, T. H.; Koumaglo, K. *J. Organomet. Chem.* **1985**, *285*, 109.

0022-3263/87/1952-4489$01.50/0

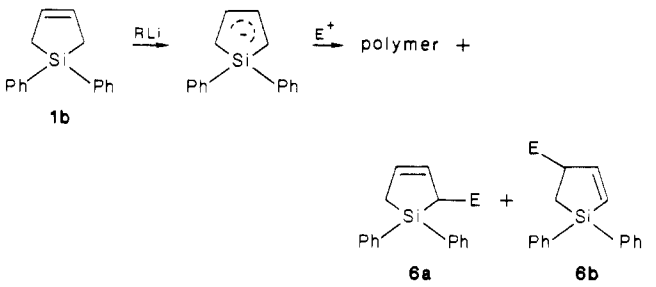
Scheme I



Scheme II



Scheme III



of interest is the regioselectivity of the reaction of **2** with electrophiles. The α-silylallyl anion is known to react with electrophiles with γ-selectivity, giving stereoselectively the (*E*)-vinylsilane **3**.[3] This is presumably due to the transoid stereochemistry of **4**. Because of the cyclopentyl structure, the anion **2** has to adopt a cisoid stereochemistry. This stereochemical change may modify the regioselection of the reaction of the anion with electrophiles (Scheme I).

Results and Discussion

We found that metalation of **1a** with *tert*-butyllithium, with or without HMPA, gave a viscous, nonvolatile, polymeric product. From the relatively clean ^{1}H NMR spectrum, structure **5** was assigned. Efforts to trap the intermediate anion, if it were formed, with electrophiles did not lead to any isolable, low molecular weight product (Scheme II).

Reaction of 1,1-diphenyl-1-silacyclo-3-pentene (**1b**) with *n*-butyllithium also gave a polymer as the product. With *sec*-butyllithium as the metalating agent and iodomethane as the alkylating agent, the reaction gave, in addition to the polymer, a small but isolable yield (8%) of the alkylated products **6a** and **6b** (E = CH_3) in a ratio of 4.7:1. When bromomethane or methyl trifluoromethanesulfonate was used as the electrophile, the ratio of **6a** to **6b** became 8.8:1 and 3.1:1, respectively. Finally, when *tert*-butyllithium was used as the metalating agent, the yield of **6** improved slightly but the polymer remained as the predominant product. Variation of solvent (THF, ether, DME, hexanes), temperature (−78 °C to room temperature), reaction time (5 min to 2 h), concentration, additives (TMEDA, HMPA), and metalating agent (organolithium or magnesium reagents) either gave the unreacted starting material or gave a polymer, with the yield of **6** below 25% at best (Scheme III).

Scheme IV

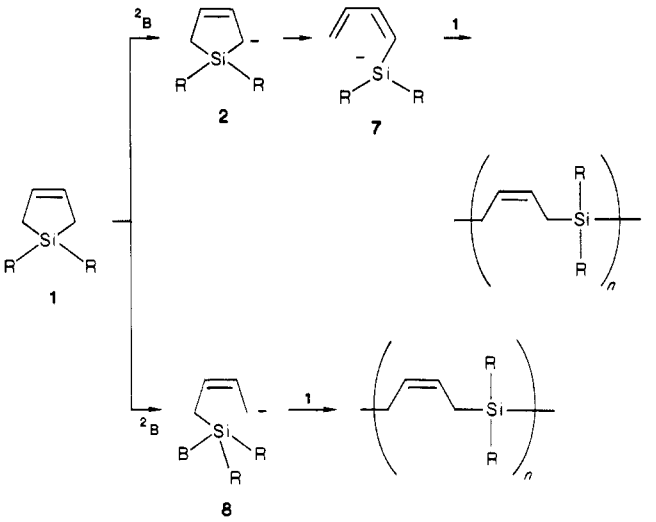
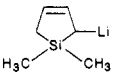
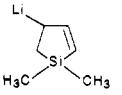
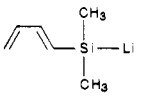
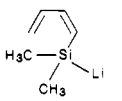


Table I. Calculated Heats of Formation from AMPAC by the AM1 Hamiltonian[5]

structure	no.	ΔH, kcal
	**2a**	−79.0
	**2b**	−78.2
	**7a**	−61.3
	**7b**	−58.4

It was clear that we had to address the problem of polymerization. Two possible pathways can be envisaged for the formation of the polymer. In the first case, the anion **2** was formed, but it was unstable and decomposed by a ring-opening process to give the silyl anion **7**, which then polymerized. A similar polymerization process was proposed for the metalation of sulfolenes.[4] Alternatively, the anion **2** was not formed at all, but the silacyclopentene ring suffered nucleophilic ring opening to give the anion **8**, which reacted further to give the polymer (Scheme IV). Semiempirical calculations using the AM1 Hamiltonian[5] showed that the anion **2a** is more stable than the ring-opened anions **7a** and **7b** by 17.7 and 20.6 kcal, respectively (Table I). These calculations tend to disfavor the first pathway. Furthermore, supporting evidence for the formation of **8** was found when we reacted **1b** with *tert*-butyllithium/potassium *tert*-butoxide as the proton-ab-

(2) Expulsion of silicon by thermolysis has precedence elsewhere in literature. See: Manuel, G.; Bertrand, G.; Weber, W. P.; Kazoura, S. A. *Organometallics* **1984**, *3*, 1340.

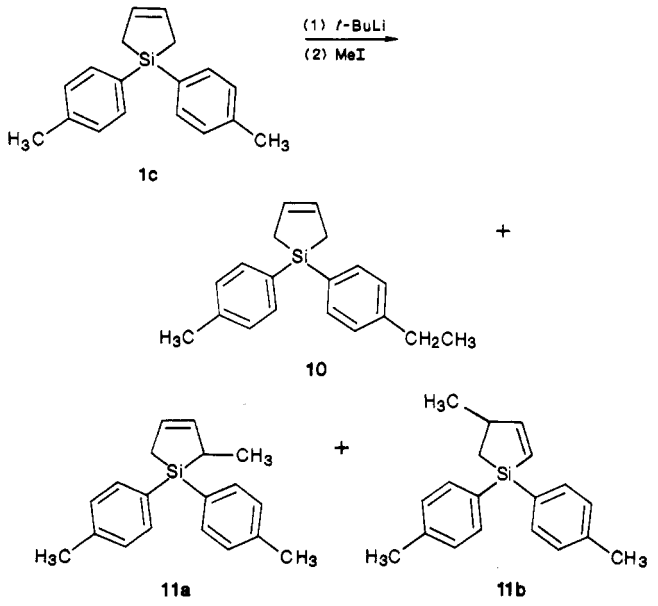
(3) (a) Corriu, R. J. P.; Lanneau, G. F.; Masse, J. P.; Samate, D. *J. Organomet. Chem.* **1977**, *127*, 281. (b) Koumaglo, K.; Chan, T. H. *Tetrahedron Lett.* **1984**, *25*, 717.

(4) (a) Krug, R. C.; Rigney, J. A.; Tichelaar, G. R. *J. Org. Chem.* **1962**, *27*, 1305. (b) Kloosteriziel, H.; van Drunen, J. A.; Galama, P. *J. Chem. Soc. D* **1969**, 885.

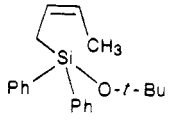
(5) Structures were preminimized with MODEL[6a] before calculating ΔH in the AMPAC by the AM1 Hamiltonian[6b] parameterized for silicon.[6c] The programs used are available from Indiana University's Quantum Chemistry Program Exchange.

(6) (a) MODEL is a graphics interactive version of the MM2 molecular mechanics program. See: Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. (b) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. (c) Dewar, M. J. S.; Friedheim, J.; Grady, G.; Healy, E. F.; Stewart, J. J. P. *Organometallics* **1986**, *5*, 375.

Scheme V



stracting system. Compound **9** was obtained as the product, confirming the susceptibility of **1** to nucleophilic attack.



It seemed to us that either pathway could be suppressed by introducing an electron-donating group[7] on the phenyl substituent attached to silicon in **1b**. Accordingly, 1,1-bis(4-methylphenyl)-1-silacyclo-3-pentene (**1c**) was synthesized from dichlorobis(4-methylphenyl)silane, (*Z*)-1,4-dibromo-2-butene, and magnesium. Reaction of **1c** with *t*-BuLi/HMPA[8] in THF at −78 °C generated a red solution. Quenching of the reaction mixture with iodomethane gave, on workup, the alkylated product as a mixture of isomers **10** and **11** and a dialkylated product, detected only by low- and high-resolution GC–MS (see the Experimental Section) (Scheme V). A polymer was hardly formed in the reaction as evident from the ^{1}H NMR of the crude product mixture. It appeared, therefore, that introduction of the *p*-methyl group on the phenyl ring did suppress the polymer-forming reaction. On the other hand, proton abstraction at the benzylic methyl group had become a significant competing reaction, presumably due to stabilization of the intermediate anion by silicon, since the ratio of **10** to **11** was about 3.3:1 as determined by GC analysis. Allowing the reaction mixture to equilibrate at −78 °C for 17 h before quenching with iodomethane gave again **10** and **11**, but with a ratio of 6:1. This suggested that benzylic anion formation was favored kinetically as well as thermodynamically.

(7) Others have shown that silicon does not significantly participate in pπ–pπ or pπ–dπ conjugation; therefore, we chose a substituent that donates electrons to silicon by induction rather than through resonance. See: (a) Buncel, E.; Venkatachalam, T. K.; Edlund, V.; Eliasson, B. *J. Chem. Soc., Chem. Commun.* **1984**, 1476. (b) Buncel, E.; Venkatachalam, T. K.; Eliasson, B.; Edlund, V. *J. Am. Chem. Soc.* **1985**, *107*, 303. (c) Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467. (d) Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M. B.; Apeloig, Y.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 260.

(8) No metalation reaction occurs without the use of HMPA. This may imply that **1c** is less acidic than **1b**, as expected.

Scheme VI

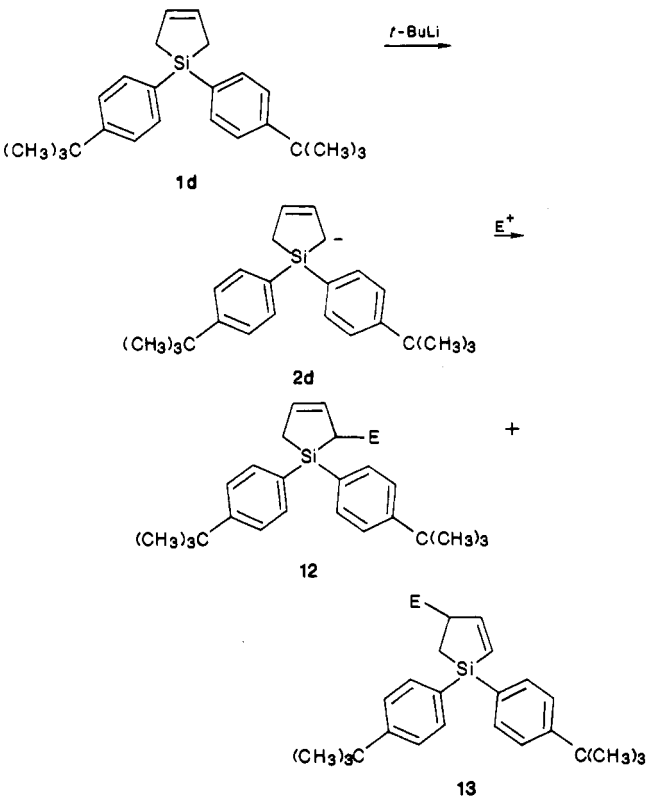


Table II. Yields and Ratios of Compounds 12 and 13 Obtained When Anion 2d Is Reacted with Various Electrophiles

electrophile	products 12 and 13	12:13[a]	% yield
D_2O	**a**, E = D	>99:1	62
CH_3Br	**b**, E = Me	8.7:1	69
CH_3I		3.9:1	77
CH_3CH_2Br	**c**, E = Et	1:1.2	63
CH_3CH_2I		1:1.2	64
CH_2CHCH_2Br	**d**, E = allyl	1:1.8[b]	66
$CH_3(CH_2)_2Br$	**e**, E = propyl	1:1.8	66
$CH_3(CH_2)_2I$		1:1.6	57
$CH_3(CH_2)_3Cl$	**f**, E = butyl	1:1.3	57
$CH_3(CH_2)_3Br$		1:1.6	71
$CH_3(CH_2)_3I$		1:1.4	70
$CH_3(CH_2)_7Cl$	**g**, E = octyl	1:1.0	57
$CH_3(CH_2)_7Br$		1:1.1	68
$CH_3(CH_2)_8Br$	**h**, E = nonyl	1:1.2	57
$CH_3(CH_2)_9I$	**i**, E = decyl	1:1.1	55
$C_6H_5CH_2Br$	**j**, E = benzyl	1:1.5[b]	56
$(CH_3)_3SiCl$	**k**, E = Me_3Si	1:1.2	71
$(CH_3)_3SiBr$		1:1.2[b]	44
$(CH_3)_3SiOSO_2CF_3$		1.3:1[b]	
$(CH_3CH_2)_3SiBr$	**l**, E = $SiEt_3$	1:1.5	57
$[CH_3(CH_2)_2]_3SiCl$	**m**, E = $Si(Pr)_3$	1.4:1	59
$[(CH_3)_2CH]_3SiOSO_2CF_3$	**n**, E = $Si(i\text{-}Pr)_3$	1:1.3	71
$CH_3(CH_2)_2CHO$	**o**, E = $CHOH(CH_2)_2CH_3$	1:1.0[b]	65
C_6H_5CHO	**p**, E = CHOHPh	1:1.4	42

[a] Ratios were obtained from the ^{1}H NMR spectra except where indicated otherwise. [b] The ratio of **12** to **13** was obtained by GC.

Obviously, benzylic anion formation can be overcome by using a substituent with no benzylic hydrogen. Thus, 1,1-bis(4-*tert*-butylphenyl)-1-silacyclo-3-pentene (**1d**) was prepared similarly from dichlorobis(4-*tert*-butylphenyl)-silane. Compound **1d** could indeed be metalated cleanly with *t*-BuLi/HMPA in THF at −78 °C (Scheme VI).

The results of the reaction of anion **2d** with various electrophiles are summarized in Table II. It is interesting to note that **2d** reacted with D_2O to give only the α-product

12a. Similarly, bromomethane gave regioselectively the α-product (**12b:13b** = 8.7:1). The regioselectivity decreased with iodomethane as the electrophile (**12b:13b** = 3.9:1). With other alkyl halides, γ-alkylation was favored slightly. The nature of the leaving group (Cl, Br, I, or triflate) did not seem to affect the regioselection[9] greatly, neither did the reactivity of the electrophile. For example, benzyl bromide showed the same regioselection as bromobutane. Reaction of **2d** with aldehydes showed slight γ-preference. The same appeared to be true for silylation as well. A tentative interpretation of the results is that regioselection is controlled mainly by the steric size of the approaching electrophile. The smaller electrophiles, such as D_2O or halomethanes, favored α-selection. For the larger electrophiles, γ-reaction became competitive or preferred.

In conclusion, we have demonstrated that by manipulation of the substituents on silicon it was possible to direct the metalation reaction on silacyclopentene. The regioselection of the reaction of the anion with various electrophiles appeared to be controlled by the steric size of the approaching electrophile.

Experimental Section

General Methods. Materials were obtained from commercial suppliers unless noted otherwise. Tetrahydrofuran and hexanes were distilled from sodium–benzophenone ketyl, and ether was prepared from lithium aluminum hydride immediately prior to use. Dimethoxyethane was distilled from sodium and stored over sodium wire. Potassium *tert*-butoxide was resublimed before use. Anhydrous magnesium bromide was prepared according to literature procedure.[10] *tert*-Butyllithium, *sec*-butyllithium, and *n*-butyllithium were titrated periodically according to literature procedure.[11] Hexamethylphosphoramide (HMPA) and tetramethylethylenediamine (TMEDA) were distilled from calcium hydride and stored over 3Å molecular sieves. Melting points (mp), determined on a Gallenkamp block, and boiling points (bp) are uncorrected. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel 60 F_{254}. Compound visualization was effected with iodine vapor or with ceric acid mist. Flash chromatography[12] was done with Merck silica gel 60 (230–400 mesh ASTM) with 10% carbon tetrachloride (CCl_4) in hexanes as the eluent unless indicated otherwise. Capillary gas chromatography analysis was done with a Hewlett-Packard 5890A series instrument fitted with a 25 m × 0.2 mm high-performance column (cross-linked methylsilicone, film thickness (0.33 μM)). Infrared (IR) spectra were obtained on a Perkin-Elmer Model 297 spectrophotometer and are reported in reciprocal centimeters. ^{1}H NMR spectra were recorded on Varian FT, XL-200, or XL-300 instruments and Varian CW, T-60, or T-60A instruments. All NMR spectra were determined with $CDCl_3$ as the solvent and $CDCl_3$ or tetramethylsilane (TMS) as the internal standard. Chemical shifts are expressed in parts per million (ppm). Significant ^{1}H NMR data are tabulated in the following order: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), number of protons, coupling constants in hertz. Decoupling experiments were performed to unambiguously assign selected spectra. Low- and high-resolution mass spectra (MS) were obtained with the Du Pont 21-492B and the ZAB 2F HS mass spectrometers (EI, 70 eV; CI, NH_3) and are reported as m/z (relative intensity in percent). Other mass spectra were obtained on a Finnigan Mat series 700 ion trap detector coupled to a Varian series 3500 capillary (30 m × 0.25 mm, methylsilcone with 5% phenylsilicone, 0.25 μm) gas chromatograph or a Hewlett-Packard 5980A GC–MS fitted with a packed column (6% OV-101, 2 m × 6 mm). Metalations were performed on a 100-mg scale by using standard syringe–septum cap techniques under inert atmosphere for work with moisture-sensitive reagents. "Standard workup" will refer to evaporation of THF from the reaction mixture under reduced pressure, treatment of the residue with ammonium chloride (NH_4Cl) solution, extraction of the aqueous phase four times with methylene chloride (CH_2Cl_2), washing the combined organic fractions with brine, drying the organic extract over magnesium sulfate ($MgSO_4$), and concentrating it with a rotary evaporator.

1,1-Diphenyl-1-silacyclo-3-pentene (1b), 1,1-Dimethyl-1-silacyclo-3-pentene (1a),[13] and (*Z*)-1,4-Dibromo-2-butene (14).[14] These compounds were prepared by previously reported methods and have spectral and physical properties in complete agreement with literature values.

Dichlorobis(4-methylphenyl)silane (15). This compound was prepared by following a general procedure from the literature.[15] A 500-mL, 3-neck, round-bottom flask fitted with a double condenser, 250-mL dropping funnel, magnetic stirring bar, and a rubber septum was charged with magnesium powder (14.6 g, 600 mmol, 50 mesh, 99+%, Aldrich) and ether (150 mL). The funnel was charged with 4-bromotoluene (102 g, 600 mmol) and ether (150 mL), and the mixture was added dropwise over 1 h to the magnesium ethereal solution. After this, the mixture was refluxed for 0.5 h. A 1-L, 3-neck, round-bottom flask fitted with a mechanical stirrer, condenser, and a rubber septum was charged with silicon tetrachloride (44.2 g, 260 mmol) and ether (130 mL) and was cooled to 10 °C. The freshly prepared Grignard reagent was transferred dropwise from its reaction flask to the silicon tetrachloride ethereal solution via a double-ended needle. After this addition, the reaction was stirred for 2 h at 10 °C and then at ambient temperature overnight. The magnesium salt was filtered from the reaction mixture and rinsed with ether. The filtrate was stripped of solvent, and hexanes were added to the residue. The solution was filtered, and the solvent was removed again. The crude product was distilled under vacuum to yield 30.0 g (41%) of **15**: bp 140–144 °C (0.25 mm); IR (film) 1600, 1120, 800; ^{1}H NMR 7.6–7.0 (m, 8 H), 2.3 (s, 6 H); MS 284 (34, M + 4), 282 (72, M + 2), 280 (74, M$^+$), 229 (46), 191 (51), 182 (100), 91 (65).

Dichlorobis(4-*tert*-butylphenyl)silane (16). By the same procedure described for the preparation of **15**, 1-bromo-4-*tert*-butylbenzene (50.0 g, 235 mmol) was treated with magnesium and silicon tetrachloride to give 12.1 g (32%) of **16** after distillation: bp 162–170 °C (0.05 mm); mp 69–79 °C; IR (KBr) 1590, 1080, 810; ^{1}H NMR 7.5–7.1 (m, 8 H), 1.2 (s, 18 H); MS 368 (1, M + 4), 366 (7, M + 2), 364 (18, M$^+$), 349 (52), 251 (100).

1,1-Bis(4-methylphenyl)-1-silacyclo-3-pentene (1c). This compound was prepared by following a general procedure from the literature.[13] A 1-L, 3-neck, round-bottom flask fitted with a double condenser, two 150-mL dropping funnels, and a magnetic stirring bar was charged with magnesium powder (10.4 g, 428 mmol, 50 mesh, 99+%, Aldrich) and ether (140 mL). One funnel was charged with freshly distilled **14** (23.0 g, 107 mmol) and ether (120 mL), and the other was charged with compound **15** (30 g, 107 mmol) and ether (110 mL). About one-fourth of the ethereal solution of **14** was added to the reaction flask. Once the Grignard reaction was well under way, the solutions contained in both funnels were added dropwise, simultaneously. Subsequently, heat was applied to maintain reflux for at least 48 h. The magnesium salt was filtered, and the ether was evaporated from the filtrate under reduced pressure. Hexanes were added to the residue, the solution was then filtered, and the solvent was evaporated again. Standard workup of the residue afforded 27.9 g of crude product whose ^{1}H NMR looked perfectly clean. Purification by distillation decomposed a substantial amount of product to yield only 9.0 g (32%) of **1c**: bp 154–156 °C (0.3 mm); IR (film) 1600, 1100, 790; ^{1}H NMR 7.5–7.1 (m, 8 H), 6.00 (s, 2 H), 2.34 (s, 6 H), 1.80 (s, 4 H); MS 266 (18, M + 2), 265 (40, M + 1), 264 (83, M$^+$), 236 (30), 210 (100), 195 (56), 172 (86), 119 (54); exact mass for $C_{24}H_{32}Si$, calcd 264.133, found 264.135.

(9) For a discussion on the regioselectivity of ambident anions in reactions with electrophiles of varying reactivity, see: Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: London, 1976; p 40.
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(13) For a general procedure on the preparation of silacyclopentenes, see: Manuel, G.; Mazerolles, P.; Florence, J. C. *J. Organometal. Chem.* **1971**, *30*, 5.
(14) Feigenbaum, A.; Lehn, J. M. *Bull. Soc. Chim. Fr.* **1973**, 198.
(15) Kuroda, K.; Ishikawa, N. *Nippon Kagaku Zasshi* **1969**, *90*, 322.

1,1-Bis(4-*tert*-butylphenyl)-1-silacyclo-3-pentene (1d). By the same procedure described for the preparation of **1c**, compound **14** was treated with magnesium and **16** (12.0 g, 33 mmol) to afford 7.0 g (61%) of **1d** after flash chromatography (10% benzene in hexanes). Compound **1d** was further purified by recrystallization from hot absolute ethanol: mp 95–96 °C; IR (KBr) 1590, 1080, 800; ^{1}H NMR 7.6–7.3 (m, 8 H), 6.00 (s, 2 H), 1.82 (s, 4 H), 1.31 (s, 18 H); MS 350 (9, M + 2), 349 (39, M + 1), 348 (100, M$^+$), 333 (63), 320 (47), 294 (53), 279 (69), 237 (58), 214 (91), 145 (47), 57 (84); exact mass for $C_{24}H_{32}Si$, calcd 348.227, found 348.218.

General Procedure for the Preparation of Compounds 12a–p and 13a–p. To a dried 25-mL round-bottom flask were added THF (8 mL) and HMPA (0.25 mL, 1.4 mmol). The solution was stirred at −78 °C, and *t*-BuLi (1.30 mL, 1.4 mmol, 1.1 M in pentane)[16] was added. A solution of **1d** (0.100 g, 0.29 mmol) in THF (2 mL) was added dropwise (inverse addition) to give a dark reaction mixture. The mixture was stirred for 0.5 h and quenched with an excess of electrophile to give a colorless solution. The mixture was allowed to warm to ambient temperature overnight. After standard workup, the crude product was purified by flash chromatography to yield a mixture of products **12** and **13**.

1,1-Bis(4-*tert*-butylphenyl)-2-deuterio-1-silacyclo-3-pentene (12a): ^{1}H NMR 7.6–7.3 (m, 8 H), 6.00 (s, 2 H), 1.82 (s, 3 H), 1.32 (s, 18 H); MS 351 (11, M + 2), 350 (51, M + 1), 349 (100, M$^+$, 95% deuterium incorporation), 348 (5), 334 (74), 321 (36), 294 (80), 279 (62), 237 (35), 215 (71), 160 (88), 146 (44), 132 (43), 57 (78).

1,1-Bis(4-*tert*-butylphenyl)-2-methyl-1-silacyclo-3-pentene (12b) and 1,1-bis(4-*tert*-butylphenyl)-4-methyl-1-silacyclo-2-pentene (13b): ^{1}H NMR 7.6–7.3 (m, 16 H), 6.91 (dd, 1 Hγ, J = 2.3, 10), 6.16 (dd, 1 Hγ, J = 2.2, 10), 5.97 (m, 1 Hα), 5.86 (m, 1 Hα), 2.95 (m, 1 Hγ), 2.24 (m, 1 Hα), 2.00 (dm, 1 Hα, J = 20), 1.77 (dm 1 Hα, J = 20), 1.31 (s, 36 H), 1.17 (d, 3 Hγ, J = 7.4), 1.03 (d, 3 Hα, J = 7.4), 0.77 (dd, 1 Hγ, J = 5.4, 16); GC–MS (**12b**) 362 (8, M$^+$), 305 (4), 279 (11), 229 (7), 57 (100); GC–MS (**13b**) 362 (10, M$^+$), 320 (33), 305 (20), 263 (8), 229 (6), 109 (3), 57 (100); exact mass for $C_{25}H_{34}Si$, calcd 362.243, found 362.243.

1,1-Bis(4-*tert*-butylphenyl)-2-ethyl-1-silacyclo-3-pentene (12c) and 1,1-bis(4-*tert*-butylphenyl)-4-ethyl-1-silacyclo-2-pentene (13c): ^{1}H NMR 7.6–7.3 (m, 16 H), 6.97 (dd, 1 Hγ, J = 2.2, 10), 6.19 (dd, 1 Hγ, J = 2.6, 10), 5.99 (m, 2 Hα), 2.78 (m, 1 Hγ), 2.10 (m, 1 Hα), 1.95 (dm, 1 Hα, J = 20), 1.75 (dm, 1 Hα, J = 20), 1.6–1.2 (m, 5 H), 1.32 (s, 36 H), 0.97 (t, 3 Hγ, J = 7), 0.87 (t, 3 Hα, J = 7), 0.77 (dd, 1 Hγ, J = 5.4, 16); GC–MS (**12c**) 376 (8, M$^+$), 348 (11), 295 (17), 279 (10), 241 (10), 185 (6), 57 (100); GC–MS (**13c**) 376 (10, M$^+$), 320 (26), 305 (7), 242 (13), 185 (3), 109 (5), 57 (100).

1,1-Bis(4-*tert*-butylphenyl)-2-(2-propenyl)-1-silacyclo-3-pentene (12d) and 1,1-bis(4-*tert*-butylphenyl)-4-(2-propenyl)-1-silacyclo-2-pentene (13d): ^{1}H NMR 7.6–7.3 (m, 16 H), 6.96 (dd, 1 Hγ, J = 2.2, 10), 6.22 (dd, 1 Hγ, 2.2, 10), 6.1–5.6 (m, 4 H), 5.2–4.7 (m, 4 H), 2.94 (m, 1 Hγ), 2.4–1.4 (m, 8 H), 1.32 (s, 36 H), 0.88 (dd, 1 Hγ, J = 5.4, 16); GC–MS (**12d**) 388 (1, M$^+$), 347 (2), 295 (3), 254 (25), 120 (3), 57 (100); GC–MS (**13d**) 388 (1, M$^+$), 347 (4), 255 (12), 57 (100).

1,1-Bis(4-*tert*-butylphenyl)-2-propyl-1-silacyclo-3-pentene (12e) and 1,1-bis(4-*tert*-butylphenyl)-4-propyl-1-silacyclo-2-pentene (13e): ^{1}H NMR 7.6–7.3 (m, 16 H), 6.96 (dd, 1 Hγ, J = 2.2, 10), 6.18 (dd, 1 Hγ, J = 2.4, 10), 5.97 (m, 2 Hα), 2.85 (m, 1 Hγ), 2.17 (m, 1 Hα), 1.95 (dm, 1 Hα, J = 20), 1.74 (dm, 1 Hα, J = 20), 1.6–0.8 (m, 10 H), 1.32 (s, 36 H), 0.92 (t, 3 Hγ, J = 7), 0.74 (t, 3 Hα, J = 7); GC–MS (**12e**) 390 (9, M$^+$), 362 (6), 295 (18), 279 (8), 256 (9), 214 (4), 57 (92), 28 (100); GC–MS (**13e**) 390 (6, M$^+$), 347 (3), 321 (14), 305 (5), 257 (12), 214 (12), 57 (100).

1,1-Bis(4-*tert*-butylphenyl)-2-butyl-1-silacyclo-3-pentene (12f) and 1,1-bis(4-*tert*-butylphenyl)-4-butyl-1-silacyclo-2-pentene (13f): ^{1}H NMR 7.7–7.3 (m, 16 H), 6.96 (dd, 1 Hγ, J = 2.2, 10), 6.18 (dd, 1 Hγ, J = 2.2, 10), 5.97 (m, 2 Hα), 2.85 (m, 1 Hγ), 2.18 (m, 1 Hα), 2.00 (dm, 1 Hα, J = 20), 1.79 (dm, 1 Hα, J = 20), 1.6–0.6 (m, 20 H), 1.35 (s, 36 H); GC–MS (**12f**) 404 (2, M$^+$), 376 (4), 347 (2), 295 (14), 270 (4), 228 (2), 214 (2), 51 (21), 28 (100); GC–MS (**13f**) 404 (3, M$^+$), 376 (1), 347 (2), 320 (13), 305 (4), 295 (3), 270 (8), 214 (8), 136 (3), 57 (39), 28 (100).

(16) Optimum yields were obtained when the concentration of *tert*-butyllithium in pentane was not higher than 1.1 M.

1,1-Bis(4-*tert*-butylphenyl)-2-octyl-1-silacyclo-3-pentene (12g) and 1,1-bis(4-*tert*-butylphenyl)-4-octyl-1-silacyclo-2-pentene (13g): ^{1}H NMR 7.7–7.3 (m, 16 H), 6.96 (dd, 1 Hγ, J = 2.2, 10), 6.18 (dd, 1 Hγ, J = 2.2, 10), 5.96 (m, 2 Hα), 2.82 (m, 1 Hγ), 2.15 (m, 1 Hα), 1.97 (dm, 1 Hα, J = 20), 1.72 (dm, 1 Hα, J = 20), 1.6–0.7 (m, 36 H), 1.30 (s, 36 H); GC–MS (**12g**) 460 (4, M$^+$), 432 (2), 347 (1), 326 (4), 295 (14), 228 (2), 57 (18), 28 (100); GC–MS (**13g**) 460 (2, M$^+$), 347 (2), 326 (4), 320 (9), 305 (3), 214 (8), 192 (3), 57 (20), 28 (100).

1,1-Bis(4-*tert*-butylphenyl)-2-nonyl-1-silacyclo-3-pentene (12h) and 1,1-bis(4-*tert*-butylphenyl)-4-nonyl-1-silacyclo-2-pentene (13h): ^{1}H NMR 7.7–7.3 (m, 16 H), 6.96 (dd, 1 Hγ, J = 2.2, 10), 6.18 (dd, 1 Hγ, J = 2.2, 10), 5.96 (m, 2 Hα), 2.83 (m, 1 Hγ), 2.16 (m, 1 Hα), 1.95 (dm, 1 Hα, J = 20), 1.72 (dm, 1 Hα, J = 20), 1.6–0.7 (m, 40 H), 1.30 (s, 36 H); GC–MS (**12h**) 474 (10, M$^+$), 428 (6), 340 (5), 295 (29), 228 (4), 57 (100); GC–MS (**13h**) 474 (3, M$^+$), 428 (4), 320 (12), 214 (8), 57 (100).

1,1-Bis(4-*tert*-butylphenyl)-2-decyl-1-silacyclo-3-pentene (12i) and 1,1-bis(4-*tert*-butylphenyl)-4-decyl-1-silacyclo-2-pentene (13i): ^{1}H NMR 7.7–7.3 (m, 16 H), 6.96 (dd, 1 Hγ, J = 2.2, 10), 6.18 (dd, 1 Hγ, J = 2.2, 10), 5.96 (m, 2 Hα), 2.87 (m, 1 Hγ), 2.19 (m, 1 Hα), 2.00 (dm, 1 Hα, J = 20), 1.79 (dm, 1 Hα, J = 20), 1.6–0.7 (m, 44 H), 1.30 (s, 36 H); GC–MS (**12i**) 488 (7, M$^+$), 460 (4), 428 (5), 355 (5), 295 (10), 57 (100); GC–MS (**13i**) 488 (3, M$^+$), 427 (5), 355 (4), 320 (3), 220 (2), 57 (100).

2-Benzyl-1,1-bis(4-*tert*-butylphenyl)-1-silacyclo-3-pentene (12j) and 4-Benzyl-1,1-bis(4-*tert*-butylphenyl)-1-silacyclo-2-pentene (13j). Isomers **12j** and **13j** were separated by flash chromatography in this case: ^{1}H NMR (**12j**) 7.39 (m, 8 H), 7.3–6.9 (m, 5 H), 6.02 (m, 1 H), 5.83 (m, 1 H), 2.8–2.4 (m, 3 H), 2.01 (dm, 1 H, J = 19), 1.80 (dm, 1 H, J = 19), 1.33 (s, 9 H), 1.32 (s, 9 H); ^{1}H NMR (**13j**) 7.5–7.1 (m, 13 H), 6.96 (dd, 1 H, J = 2.2, 10), 6.24 (dd, 1 H, J = 2.4, 10), 3.16 (m, 1 H), 2.86 (dd, 1 H, J = 6.7, 13), 2.66 (dd, 1 H, J = 8.5, 13), 1.39 (dd, 1 H, J = 8, 16), 1.32 (s, 9 H), 1.30 (s, 9 H), 0.87 (dd, 1 H, J = 5.4, 16); MS (**12j**) 439 (6, M + 1), 438 (26, M$^+$), 347 (65), 304 (36), 295 (83), 213 (27), 180 (54), 131 (42), 91 (86), 57 (100); exact mass for $C_{31}H_{38}Si$, calcd 438.274, found 438.274; MS (**13j**) 438 (1, M$^+$), 436 (7), 347 (100), 319 (14), 213 (33), 161 (13), 91 (37), 57 (69).

1,1-Bis(4-*tert*-butylphenyl)-2-(trimethylsilyl)-1-silacyclo-3-pentene (12k) and 1,1-bis(4-*tert*-butylphenyl)-4-(trimethylsilyl)-1-silacyclo-2-pentene (13k): ^{1}H NMR 7.6–7.3 (m, 16 H), 7.08 (dd, 1 Hγ, J = 2.4, 10), 6.14 (dd, 1 Hγ, J = 2.7, 10), 5.99 (s, 2 Hα), 2.28 (m, 1 Hγ), 2.05 (dm, 1 Hα, J = 19), 1.68 (dm, 1 Hα, J = 19), 1.54 (s, 1 Hα), 1.5–1.2 (m, 1 Hγ), 1.36 (s, 36 H), 1.05 (dd, 1 Hγ, J = 5.4, 16), 0.00 (s, 9 Hγ), −1.80 (s, 9 Hα); GC–MS (**12k**) 420 (1, M$^+$), 407 (100), 349 (4), 309 (4), 287 (14), 57 (21); GC–MS (**13k**) 420 (2, M$^+$), 405 (49), 349 (6), 309 (11), 287 (96), 231 (7), 57 (100).

1,1-Bis(4-*tert*-butylphenyl)-2-(triethylsilyl)-1-silacyclo-3-pentene (12l) and 1,1-bis(4-*tert*-butylphenyl)-4-(triethylsilyl)-1-silacyclo-2-pentene (13l): ^{1}H NMR 7.7–7.3 (m, 16 H), 7.14 (dd, 1 Hγ, J = 2.3, 10), 6.15 (dd, 1 Hγ, J = 2.8, 10), 6.02 (m, 1 Hα), 5.97 (m, 1 Hα), 2.45 (m, 1 Hγ), 2.10 (dm, 1 Hα, J = 20), 1.70 (m, 1 Hα), 1.7–1.3 (m, 2 H), 1.36 (s, 36 H), 1.13 (dd, 1 Hγ, J = 5.4, 16), 0.98 (t, 9 Hγ, J = 8), 0.88 (t, 9 Hα, J = 8), 0.62 (q, 6 Hγ, J = 8), 0.38 (q, 6 Hα, J = 8); GC–MS (**12l**) 462 (1, M$^+$), 433 (54), 329 (18), 115 (6), 57 (100); GC–MS (**13l**) 462 (1, M$^+$), 433 (32), 377 (4), 329 (46), 301 (7), 272 (3), 115 (6), 57 (100).

1,1-Bis(4-*tert*-butylphenyl)-2-(tri-*n*-propylsilyl)-1-silacyclo-3-pentene (12m) and 1,1-bis(4-*tert*-butylphenyl)-4-(tri-*n*-propylsilyl)-1-silacyclo-2-pentene (13m): ^{1}H NMR 7.6–7.3 (m, 16 H), 7.12 (dd, 1 Hγ, J = 2.5, 10), 6.13 (dd, 1 Hγ, J = 2.6, 10), 5.97 (m, 2 Hα), 2.40 (m, 1 Hγ), 2.07 (dm, 1 Hα, J = 20), 1.7–1.6 (m, 2 Hα), 1.5–0.2 (m, 44 H), 1.35 (s, 36 H); GC–MS (**12m**) 504 (2, M$^+$), 462 (100), 416 (13), 371 (39), 327 (25), 323 (27), 283 (9), 251 (10), 101 (3), 57 (37); GC–MS (**13m**) 504 (2, M$^+$), 461 (84), 418 (11), 371 (47), 328 (53), 285 (20), 250 (11), 115 (9), 57 (100).

1,1-Bis(4-*tert*-butylphenyl)-2-(triisopropylsilyl)-1-silacyclo-3-pentene (12n) and 1,1-bis(4-*tert*-butylphenyl)-4-(triisopropylsilyl)-1-silacyclo-2-pentene (13n): ^{1}H NMR 7.7–7.3 (m, 16 H), 7.21 (dd, 1 Hγ, J = 2.6, 10), 6.13 (dd, 1 Hγ, J = 3.3, 10), 6.08 (m, 1 Hα), 5.87 (m, 1 Hα), 2.56 (m, 1 Hγ), 2.12 (dm, 1 Hα, J = 20), 1.89 (dd, 1 Hα, J = 2.8, 5.4), 1.66 (dm, 1 Hα, J = 20), 1.6–0.7 (m, 44 H), 1.35 (s, 36 H); GC–MS (**12n**) 504 (1,

M^+), 461 (71), 419 (3), 371 (21), 329 (8), 271 (5), 57 (100); GC–MS (**13n**) 504 (1, M^+), 461 (74), 405 (5), 371 (66), 329 (11), 273 (4), 157 (8), 115 (18), 57 (100).

1,1-Bis(4-*tert*-butylphenyl)-2-(1-hydroxybutyl)-1-silacyclo-3-pentene (12o) and 1,1-Bis(4-*tert*-butylphenyl)-4-(1-hydroxybutyl)-1-silacyclo-2-pentene (13o). The same procedure was followed except another quench with water, at −78 °C, was made 15 min later. Regioisomers **12o** and **13o** were separated by flash chromatography in this case: ^{1}H NMR (**12o**) 7.6–7.2 (m, 8 H), 5.97 (m, 2 H), 3.35 (br, 1 H), 2.5–0.7 (m, 11 H), 1.30 (s, 18 H); ^{1}H NMR (**13o**) 7.6–7.3 (m, 8 H), 6.93 (dd, 1 H, J = 1.5, 6.6), 6.38 (dd, 1 H, J = 1.6, 6.6), 3.83 (br, 1 H), 3.00 (m, 1 H), 1.6–0.8 (m, 10 H), 1.32 (s, 18 H); ^{1}H NMR (detected diastereomer of **13o**) 7.13 (dd, 1 H, J = 1.6), 3.59 (br, 1 H); GC–MS (**12o**) 403 (11, $M^+ + H^+ - H_2O$), 333 (4), 311 (10), 273 (11), 269 (14), 214 (7), 153 (17), 111 (4), 57 (100); GC–MS (**13o**) 403 (6, $M^+ + H^+ - H_2O$), 320 (5), 311 (10), 273 (14), 269 (17), 214 (10), 153 (11), 57 (100).

2-(α-Hydroxybenzyl)-1,1-bis(4-*tert*-butylphenyl)-1-silacyclo-3-pentene (12p) and 4-(α-Hydroxybenzyl)-1,1-bis(4-*tert*-butylphenyl)-1-silacyclo-2-pentene (13p). The same procedure was followed except another quench with water, at −78 °C, was made 15 min later: ^{1}H NMR 7.5–7.2 (m, 26 H), 7.16 (dd, 1 Hγ, J = 2.2, 10), 6.80 (dd, 1 Hγ, J = 2.2, 10), 6.37 (m, 2 Hα), 4.73 (d, 1 H, J = 5.8), 4.59 (d, 1 H, J = 6.0), 3.28 (m, 1 Hγ), 2.0–1.6 (br, 2 H, exchangeable with D_2O), 2.0–0.8 (m, 5 H), 1.33 (s, 36 H); MS 436 (20, $M^+ - H_2O$), 400 (15), 347 (30), 319 (13), 266 (11), 214 (100), 161 (18), 107 (52), 57 (98); exact mass for $C_{31}H_{38}OSi$ ($M^+ + H^+ - H_2O$), calcd 437.266, found 437.266.

1,1-Diphenyl-2-methyl-1-silacyclo-3-pentene (6a) and 1,1-Diphenyl-3-methyl-1-silacyclo-2-pentene (6b). By the same procedure, compound **1b** was metalated and subsequently quenched with a methylating agent: ^{1}H NMR 7.7–7.3 (m, 20 H), 6.98 (dd, 1 Hγ, J = 1.6, 6.4), 6.19 (dd, 1 Hγ, J = 1.6, 6.4), 6.00 (m, 1 Hα), 5.90 (m, 1 Hα), 2.98 (m, 1 Hγ), 2.25 (m, 1 Hα), 2.00 (dm, 1 Hα, J = 20), 1.80 (dm, 1 Hα, J = 20), 1.19 (d, 3 Hγ, J = 7), 1.02 (d, 3 Hα, J = 7), 0.77 (dd, 1 Hγ, J = 5.3, 16); GC–MS (isomers could not be resolved) 250 (73, M^+), 235 (25), 222 (15), 208 (11), 181 (100), 172 (40), 157 (9), 109 (13).

1-(4-Ethylphenyl)-1-(4-methylphenyl)-1-silacyclo-3-pentene (10), 1,1-Bis(4-methylphenyl)-2-methyl-1-silacyclo-3-pentene (11a), and 1,1-Bis(4-methylphenyl)-3-methyl-1-silacyclo-2-pentene (11b). By the same procedure, 0.144 g of compound **1c** was metalated and then quenched with iodomethane. Products **10** and **11** (0.041 g) were isolated after flash chromatography (25% benzene in hexanes): ^{1}H NMR (**10**) 7.6–7.4 (m, 4 H), 7.3–7.1 (m, 4 H), 6.01 (s, 2 H), 2.64 (q, 2 H, J = 7.6), 2.35 (s, 3 H), 1.81 (s, 4 H), 1.24 (t, 3 H, J = 7.6); ^{1}H NMR (**11a**) 5.7 (m, 1 H), 1.00 (d, 3 H, J = 7.6); ^{1}H NMR (**11b**) 6.15 (dd, 1 H, J = 2, 10), 1.2 (d, 1 H, J = 7); GC–MS (**10**) 278 (100, M^+), 250 (53), 209 (18), 186 (29), 172 (60), 119 (27), 105 (28); GC–MS (**11**, regioisomers could not be resolved) 278 (100, M^+), 263 (21), 250 (23), 186 (44), 145 (9), 119 (46); exact mass for $C_{19}H_{22}Si$, calcd 278.149, found 278.149. A dialkylated product was also observed: GC–MS 292 (97, M^+), 264 (57), 186 (100), 133 (31), 105 (56); exact mass for $C_{20}H_{24}Si$, calcd 292.165, found 292.165.

Poly(dimethylsilylbut-2-ene) (5). To a round-bottom flask containing THF (3 mL) at −78 °C was added *t*-BuLi (0.72 mL, 1.0 mmol, 1.4 M in pentane). To this solution was added **1a** (0.102 g, 0.91 mmol) dissolved in THF (1 mL). The yellow solution was stirred for 1 h and then quenched with an excess of bromomethane (1 mL). After standard workup the crude product was purified by flash chromatography (acetone) to give 0.061 g of **5**: ^{1}H NMR 5.31 (t, 2 H, J = 6.5), 1.42 (d, 4 H, J = 6.5), 0.03 (s, 6 H).

4-(*tert*-Butoxydiphenylsilyl)but-2-ene (9). To a round-bottom flask containing *t*-BuOK (0.048 g, 0.43 mmol) and THF (1 mL) at −78 °C was added *t*-BuLi (0.31 mL, 0.43 mmol, 1.4 M). The colorless solution was stirred for 0.5 h before a solution of **1b** in THF (1 mL) was added to it. The mixture was allowed to warm to ambient temperature and then was stirred for 3 h before quenching with an excess of bromomethane (1 mL). After standard workup and flask chromatography (25% benzene in hexanes), 0.035 g of **9** was obtained: ^{1}H NMR 7.7–7.6 (m, 10 H), 5.6–5.3 (m, 2 H), 2.12 (d, 2 H, J = 8), 1.38 (d, 3 H, J = 6), 1.25 (s, 9 H); GC–MS 310 (9, M^+), 282 (49), 255 (100), 199 (43), 177 (27), 105 (18), 77 (17), 55 (6); exact mass for $C_{20}H_{26}OSi$, calcd 310.175, found 310.175.

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Registry No. **1a**, 16054-12-9; **1b**, 34106-93-9; **1c**, 109959-50-4; **1d**, 109927-96-0; **2a**, 109928-33-8; **2b**, 109928-34-9; **5**, 31672-73-8; **6a**, 109959-51-5; **6b**, 109928-28-1; **7a**, 109928-35-0; **7b**, 109928-36-1; **9**, 109928-32-7; **10**, 109928-29-2; **11a**, 109928-30-5; **11b**, 109928-31-6; **12a**, 109927-97-1; **12b**, 109927-98-2; **12c**, 109927-99-3; **12d**, 109928-00-9; **12e**, 109928-01-0; **12f**, 109928-02-1; **12g**, 109928-03-2; **12h**, 109928-04-3; **12i**, 109928-05-4; **12j**, 109928-06-5; **12k**, 109928-07-6; **12l**, 109928-08-7; **12m**, 109928-09-8; **12n**, 109928-10-1; **12o**, 109928-11-2; **12p**, 109928-12-3; **13b**, 109928-13-4; **13c**, 109928-14-5; **13d**, 109928-15-6; **13e**, 109928-16-7; **13f**, 109928-17-8; **13g**, 109928-18-9; **13h**, 109928-19-0; **13i**, 109928-20-3; **13j**, 109928-21-4; **13k**, 109928-22-5; **13l**, 109928-23-6; **13m**, 109928-24-7; **13n**, 109928-25-8; **13o**, 109928-26-9; **13p**, 109928-27-0; **14**, 18866-73-4; **15**, 18414-38-5; **16**, 88794-44-9; D_2O, 7789-20-0; CH_3Br, 74-83-9; CH_3I, 74-88-4; CH_3CH_2Br, 74-96-4; CH_3CH_2I, 75-03-6; CH_2CHCH_2Br, 106-95-6; $CH_3(CH_2)_2Br$, 106-94-5; $CH_3(CH_2)_2I$, 107-08-4; $CH_3(CH_2)_3Cl$, 109-69-3; $CH_3(CH_2)_3Br$, 109-65-9; $CH_3(CH_2)_3I$, 542-69-8; $CH_3(CH_2)_7Cl$, 111-85-3; $CH_3(CH_2)_7Br$, 111-83-1; $CH_3(CH_2)_8Br$, 693-58-3; $CH_3(CH_2)_9I$, 2050-77-3; $C_6H_5CH_2Br$, 100-39-0; $(CH_3)_3SiCl$, 75-77-4; $(CH_3)_3SiBr$, 2857-97-8; $(CH_3)_3SiOSO_2CF_3$, 27607-77-8; $(CH_3CH_2)_3SiBr$, 1112-48-7; $[CH_3(CH_2)_2]_3SiCl$, 995-25-5; $[(CH_3)_2CH]_3SiOSO_2CF_3$, 80522-42-5; $CH_3(CH_2)_2CHO$, 123-72-8; C_6H_5CHO, 100-52-7; $CH_3C_6H_4$-*p*-Br, 28807-97-8; $SiCl_4$, 10026-04-7; *t*-BuC_6H_4-*p*-Br, 3972-65-4.