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Mechanistic Studies of the Reaction of Hydrosiloles with Nucleophiles. Crystal Structures of the Enantiomers of 1-Methyl-2-(dimethylsilyl)-2,3,4,5-tetraphenyl-1-silacyclo-3-pentene and 1-(Bis(trimethylsilyl)amino)-5-methyl-2,3,4,5-tetraphenyl-1-silacyclo-3-pentene

Seok-Bong Choi, Philip Boudjouk,* and Youlin Pan

Center for Main Group Chemistry, Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105

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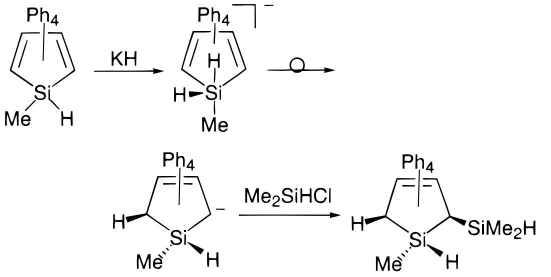
The X-ray crystal structure determination of the trapping products of 1-methyl-1,1-dihydrido-5-potassio-2,3,4,5-tetraphenyl-1-silacyclopentadiene silicate, $[Ph_4C_4SiMeH_2^-]\cdot[K^+]$ (**2**), with excess dimethylchlorosilane shows enantiomers of 1-methyl-2-(dimethylsilyl)-2,3,4,5-tetraphenyl-1-silacyclo-3-pentene (**5a1**, **5a2**) in a ratio of 1:1. The *trans* orientation of the H−Si−C−H linkage is confirmed by torsional angles of two hydrogens ($\angle HSiCH = 140.7°$). Structural characterization of the enantiomers of 1-(bis(trimethylsilyl)amino)-5-methyl-2,3,4,5-tetraphenyl-1-silacyclo-3-pentene (**10a**, **10b**), obtained as major products from the reaction of 1-(bis(trimethylsilyl)amino)-5-sodio-2,3,4,5-tetraphenyl-1-silacyclo-3-pentene (**9**) with excess MeI indicate the *cis* arrangement of the H−Si−C−H linkage ($\angle HSiCH = 29.8°$). All of the reaction products can be envisioned as resulting from a pathway involving pentacoordinate anionic intermediates that undergo pseudorotation, 1,2-hydride migration from silicon to carbon, and quenching with RX (RX = Me_2HSiCl, MeI).

Introduction

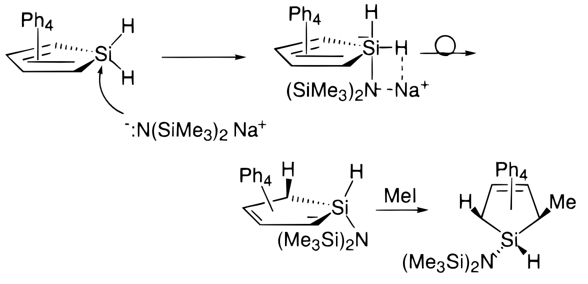
Deprotonation of hydrosiloles with nonnucleophilic bases has been examined intensively as a convenient route to aromatic silicon-containing species, silole anions.[1,2] However, substitution and/or subsequent hydride addition to the α-carbon atom has been the more common observation.[3]

In a previous report, we described the reaction of 1-hydro-1-methyl-Ph_4-silole (Ph_4-silole = 2,3,4,5-tetraphenyl-1-silacyclopentadiene) with potassium hydride, demonstrating that the primary product is the result of the addition of hydride ion to the silicon center to form a pentacoordinate silicon anion in which the two hydrogens are distinguishable.[4,5] It was also shown that the resulting carbanion reacts readily with electrophiles to give only one isomer of 1-methyl-2-(dimethylsilyl)-2,3,4,5-tetraphenyl-1-silacyclo-3-pentene (eq 1).



(1)

We also reported the reaction of 1,1-dihydro-(Ph_4-silole) with a nonnucleophilic base such as sodium bis(trimethylsilyl)amide in tetrahydrofuran (THF), illustrating that 1-(bis(trimethylsilyl)amino)-5-sodio-2,3,4,5-tetraphenyl-1-silacyclo-3-pentene, which is formed by hydride migration from silicon to carbon of the pentacoordinate anionic species 1-(bis(trimethylsilyl)amino)-1,1-dihydrido-Ph_4-silole silicate, $[Ph_4C_4Si((Me_3Si)_2N)H_2]\cdot[Na^+]$ (**9b**), is the dominant product (eq 2).[5]



(2)

Information about detailed reaction mechanisms, however, is sparse. We have continued our investigation

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[1] (a) Gilman, M.; Steudel, W. *Chem. Ind.* **1959**, 1094. (b) Rühlmann, K. *Z. Chem.* **1965**, *5*, 354. (c) Hagen, V.; Rühlmann, K. *Z. Chem.* **1967**, *7*, 462. (d) Corriu, R. J. P.; Guérin, C. *J. Chem. Soc., Chem. Commun.* **1980**, 168. (e) Corriu, R. J. P.; Guérin, C.; Kolani, B. *Bull. Soc. Chim. Fr.* **1985**, 973. (f) Dubac, J.; Guerin, C.; Meunier, P. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, Part 3, Chapter 34, pp 1961−2036.

[2] (a) Lambert, J. B.; Schulz, W. J., Jr. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 16, p 1007. (b) Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215. (c) Colomer, E.; Corriu, R. J. P.; Lheureux, M. *Chem. Rev.* **1990**, *90*, 265. (d) Freeman, W. P.; Tilley, T. D. *J. Am. Chem. Soc.* **1994**, *116*, 8428. (e) Grüntzmacher, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 295.

[3] (a) Curtis, M. D. *J. Am. Chem. Soc.* **1969**, *91*, 6011. (b) Jutzi, P.; Karl, A. *J. Organomet. Chem.* **1981**, 214, 289. (c) Dubac, J.; Iloughmane, H.; Laporterie, A.; Roques, C. *Tetrahedron Lett.* **1985**, *26*, 1315. (d) Beteille, J.-P.; Laporterie, A.; Dubac, J. *Organometallics* **1989**, *8*, 1799.

10.1021/om990225m CCC: $18.00

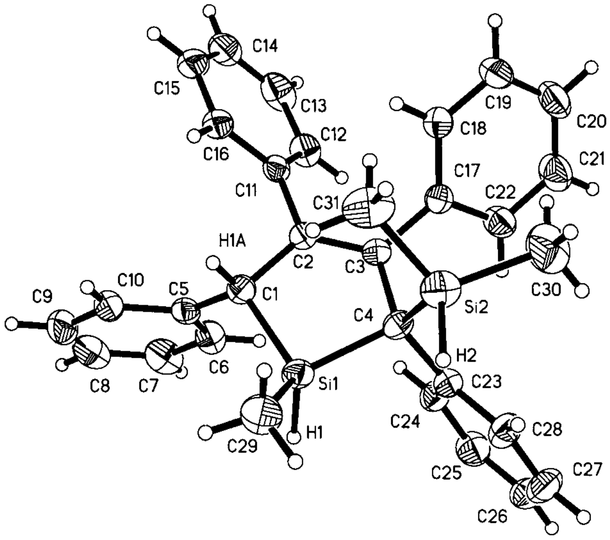
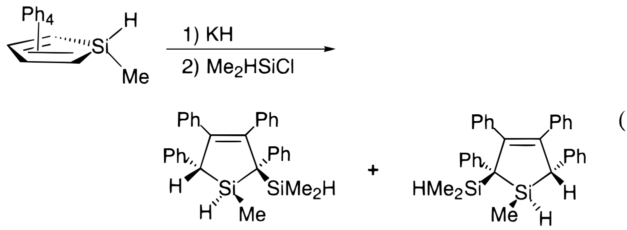


Figure 1. Thermal ellipsoid diagram of **5a**.

to elucidate mechanistic details. Recently we were able to obtain crystal structures of quenching products from the above reactions. The crystal structures of the enantiomers of 1-methyl-2-(dimethylsilyl)-2,3,4,5-tetraphenyl-1-silacyclo-3-pentene (**5a1**, **5a2**) and 1-(bis(trimethylsilyl)amino)-5-methyl-2,3,4,5-tetraphenyl-1-silacyclo-3-pentene (**10a**, **10b**) are reported here. We also present mechanisms for their formation.

Results

The reaction of 1-hydro-1-methyl-(Ph_4-silole) (**1**) with potassium hydride in THF gives a dark red solution. The 1-methyl-1,1-dihydrido-(Ph_4-silole) silicate $[Ph_4C_4SiMeH_2]\cdot[K^+]$ (**2**) and 1-methyl-5-potassio-2,3,4,5-tetraphenyl-1-silacyclo-3-pentene (**4**) have been characterized from this solution by ^1H, ^{13}C, and ^{29}Si NMR studies.[4a] Treatment of the solution of these anions with dimethylchlorosilane gives C-substituted products, the enantiomers of 1-methyl-2-(dimethylsilyl)-2,3,4,5-tetraphenyl-1-silacyclo-3-pentene (**5**) in a 1:1 ratio (eq 3).



(3)

trans (**5a1**) : *trans* (**5a2**)
1 : 1

Table 1. Crystal Data and Structure Refinement for 5a and 10a

	5a	**10a**
empirical formula	$C_{31}H_{32}Si_2$	$C_{35}H_{43}NSi_3$
fw	460.75	561.97
temp, K	298(2)	298(2)
cryst syst	monoclinic	triclinic
space group	$C2/c$	$P\bar{1}$
a, Å	30.6342(17)	9.8100(5)
b, Å	10.5466(5)	10.7711(6)
c, Å	20.6134(13)	18.0967(10)
α, deg	90.00	75.9630(10)
β, deg	125.076(2)	83.1880(10)
γ, deg	90.00	63.8640(10)
V, Å^3; Z	5450.4(5); 8	1665.25(16); 2
density (calcd), Mg/m^3	1.123	1.121
abs coeff, mm^{-1}	0.146	0.166
F(000)	1968	604
cryst size, mm^3	0.50 × 0.50 × 0.60	0.50 × 0.60 × 0.35
θ range, deg	1.62−28.34	1.16−28.29
index ranges	$-40 \le h \le 40$	$-12 \le h \le 12$
	$-13 \le k \le 10$	$-14 \le k \le 13$
	$-27 \le l \le 26$	$-21 \le l \le 23$
no. of rflns collected	15564	9872
no. of indep rflns	6247 (R(int) = 0.0550)	7172 (R(int) = 0.0446)
no. of data/restraints/ params	6247/0/306	7172/0/356
goodness of fit on F^2	1.054	1.102
final R indices ($I > 2\sigma(I)$)	R1 = 0.0452	R1 = 0.0490
	wR2 = 0.1231	wR2 = 0.1268
largest diff peak and hole, e Å^{-3}	0.250 and −0.332	0.252 and −0.260

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $C_{31}H_{32}Si_2$ (5a)

Si(1)−C(29)	1.8639(19)	Si(1)−C(1)	1.8847(15)
Si(1)−C(4)	1.9153(15)	Si(2)−C(30)	1.868(2)
Si(2)−C(31)	1.864(2)	Si(2)−C(4)	1.9084(15)
Si(1)−H(1)	1.417	C(1)−H(1A)	0.980
C(1)−C(5)	1.505(2)	C(1)−C(2)	1.5312(19)
C(2)−C(3)	1.3480(19)	C(2)−C(11)	1.4912(19)
C(3)−C(17)	1.4989(19)	C(3)−C(4)	1.5473(18)
C(4)−C(23)	1.526(2)		
C(29)−Si(1)−C(1)	114.31(8)	C(29)−Si(1)−C(4)	119.41(8)
C(1)−Si(1)−C(4)	96.35(6)	C(30)−Si(2)−C(31)	110.54(13)
C(30)−Si(2)−C(4)	114.21(9)	C(31)−Si(2)−C(4)	108.35(8)
C(5)−C(1)−C(2)	113.80(12)	C(5)−C(1)−Si(1)	114.91(10)
C(2)−C(1)−Si(1)	103.10(9)	C(3)−C(2)−C(11)	125.07(12)
C(3)−C(2)−C(1)	118.95(12)	C(11)−C(2)−C(1)	115.93(12)
C(2)−C(3)−C(17)	122.57(12)	C(2)−C(3)−C(4)	118.65(12)
C(17)−C(3)−C(4)	118.00(12)	C(23)−C(4)−C(3)	115.13(12)
C(23)−C(4)−Si(2)	115.02(10)	C(3)−C(4)−Si(2)	107.64(9)
C(23)−C(4)−Si(1)	106.16(10)	C(3)−C(4)−Si(1)	101.75(9)
Si(2)−C(4)−Si(1)	110.29(7)	C(6)−C(5)−C(10)	117.78(16)
C(29)−Si(1)−H(1)	106.1	Si(1)−C(1)−H(1A)	108.2
C(2)−C(1)−H(1A)	108.2	C(5)−C(1)−H(1A)	108.2
C(1)−Si(1)−H(1)	111.0	C(4)−Si(1)−H(1)	109.5
H(1)−Si(1)−C(1)−H(1A)			140.7

The X-ray structure of 1-methyl-2-(dimethylsilyl)-2,3,4,5-tetraphenyl-1-silacyclo-3-pentene is shown in Figure 1, and the crystallographic data and selected bond lengths and bond angles are listed in Tables 1 and 2, respectively. We found enantiomers **5a1** and **5a2** in the crystal packing diagram in a ratio of 1:1. The *trans* orientation of the H−Si−C−H linkage is confirmed by torsional angles of two hydrogens (∠H(1)−Si(1)−C(1)−H(1A) = 140.7°). This torsional angle value is consistent with the previously reported coupling constant $^3J_{H-H}$ = 4.4 Hz.[4a]

The silole ring is slightly bent with the Si(1) atom 0.2324 Å out of the plane of the four carbon atoms. The Si(1)−C(4) distance (1.9153 Å) is slightly longer than the Si(1)−C(1) distance (1.8847 Å), perhaps indicating steric hindrance between methyl and dimethylsilyl groups, which is consistent with ^1H and ^{13}C NMR studies in our previous paper.[4a]

Stirring 1,1-dihydro-(Ph_4-silole) (**6**) with sodium bis(trimethylsilyl)amide in THF at −25 °C for 4 h and then

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[4] (a) Hong, J.-H.; Boudjouk, P. *Organometallics* **1995**, *14*, 574. Other dihydrosiliconates have been reported: (b) Becker, B.; Corriu, R. J. P.; Guérin, C.; Henner, B.; Wang, Q. *J. Organomet. Chem.* **1989**, *368*, C25. (c) Corriu, R. J. P.; Guérin, C.; Henner, B.; Wang, Q. *Organometallics* **1991**, *10*, 3574. (d) Corriu, R.; Guérin, C.; Henner, B.; Wang, Q. *Inorg. Chim. Acta* **1992**, *198−200*, 705.

[5] Pan, Y.; Hong, J.-H.; Choi, S.-B.; Boudjouk, P. *Organometallics* **1997**, *16*, 1445.

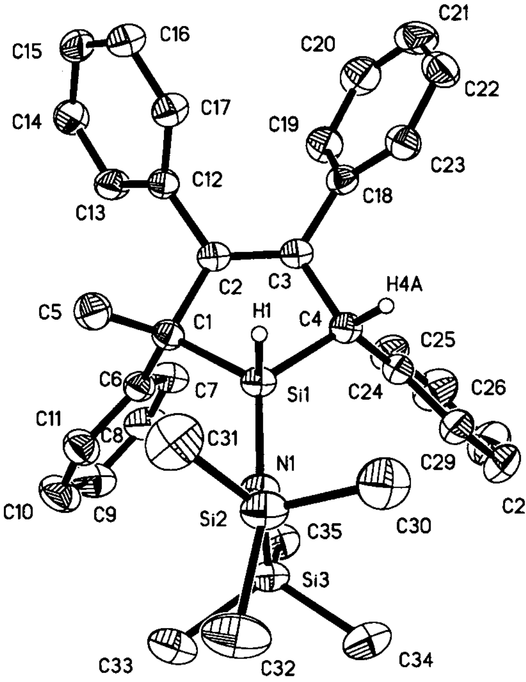
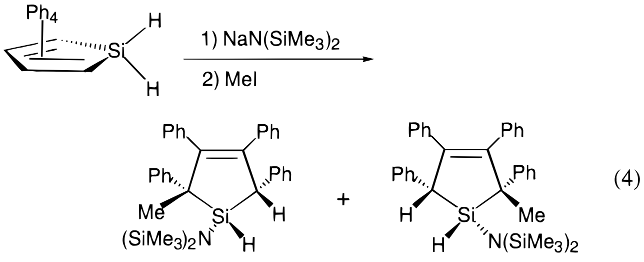


Figure 2. Thermal ellipsoid diagram of **10a**.

at room temperature for 2 h produced a deep violet solution.[6] We found the enantiomers of 1-(bis(trimethylsilyl)amino)-5-methyl-2,3,4,5-tetraphenyl-1-silacyclo-3-pentene (**10a**, **10b**) in a ratio of 1:1 as the major products after quenching with excess methyl iodide (eq 4).



(4)

cis (**10a**) : *cis* (**10b**)
1 : 1

The hydrogens in the H−Si−C−H linkage are in a *cis* arrangement with a small torsional angle (∠H(1)−Si(1)−C(4)−H(4a) = 29.8°). The ORTEP view of **10a** is given in Figure 2, and the crystallographic data and selected bond lengths and bond angles are listed in Tables 1 and 3, respectively.

The coordination about the ring silicon in **10** is a slightly distorted tetrahedron with a Si(1)−N(1) distance of 1.7251 Å, which is shorter than Si(2)−N(1) (1.7726 Å) and Si(3)−N(1) (1.7657 Å). The silole ring is significantly bent with the Si(1) atom 0.6221 Å out of the plane of the four carbon atoms, causing a small bond angle on C(1) and C(4) (∠Si(1)−C(1)−C(2) = 96.96°, ∠Si(1)−C(4)−C(3) = 97.99°).

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $C_{35}H_{43}NSi_3$ (10a)

Si(1)−N(1)	1.7251(15)	Si(1)−C(4)	1.9001(19)
Si(1)−C(1)	1.9085(18)	Si(2)−N(1)	1.7726(15)
Si(1)−H(1)	1.369	C(4)−H(4A)	0.980
C(1)−C(6)	1.523(3)	Si(3)−N(1)	1.7657(16)
C(1)−C(2)	1.542(2)	C(1)−C(5)	1.545(3)
C(2)−C(3)	1.343(3)	C(3)−C(4)	1.531(2)
N(1)−Si(1)−C(4)	124.61(8)	N(1)−Si(1)−C(1)	122.54(8)
C(4)−Si(1)−C(1)	97.25(8)	Si(1)−N(1)−Si(3)	127.22(9)
Si(1)−N(1)−Si(2)	113.17(9)	Si(3)−N(1)−Si(2)	119.22(8)
C(6)−C(1)−C(2)	113.95(14)	C(6)−C(1)−C(5)	111.04(16)
C(2)−C(1)−C(5)	109.80(15)	C(6)−C(1)−Si(1)	115.54(12)
C(2)−C(1)−Si(1)	96.96(11)	C(5)−C(1)−Si(1)	108.69(13)
C(2)−C(3)−C(4)	119.16(15)	C(3)−C(2)−C(1)	119.90(15)
C(28)−C(29)−C(24)	121.3(2)	C(3)−C(4)−Si(1)	97.99(12)
N(1)−Si(1)−H(1)	106.3	C(4)−Si(1)−H(1)	99.6
Si(1)−C(4)−H(4A)	105.3	C(1)−Si(1)−H(1)	102.7
C(24)−C(4)−H(4A)	105.3	C(3)−C(4)−H(4A)	105.3
H(1)−Si(1)−C(4)−H(4a)	29.8		

Discussion

A mechanism is proposed that accounts for the *trans* arrangement of the H−Si−C−H linkages in **5a1** and **5a2** (Scheme 1). The first step is nucleophilic attack of hydride at silicon at the least hindered triangular face ($Me-C_1-H^2$) of **1**.[6] In the NMR, two distinct hydrogens attached to silicon were detected.[4a] This observation can be explained by structure **2** or by a discriminating influence of the potassium ion in **3a**.

The pseudorotation of **2** leading to **3a** can be explained in terms of geometries available to the intermediates formed. The C−Si−C angles in all known siloles are near 90°;[2b] thus, the trigonal-bipyramidal geometry of **2** in which the silole ring is in the equatorial plane would be substantially distorted from the ideal equatorial bond angles of 120°. Thus, rearrangement to **3a**, in which the silole ring is part axial and equatorial with bond angles much closer to 90°, is reasonable. That only **3a** is generated and not **3b1** and **3b2** is surprising and is possibly attributable to the difference in electronegativities between carbon and hydrogen. The more electronegative groups generally prefer axial sites in five-coordinate silanes.[7]

The subsequent hydride migration in **3a** from silicon to an adjacent ring carbon leads to the enantiomeric carbanions **4a1** and **4a2**, which have been observed by NMR.[4a] Quanching of **4a1** and **4a2** with dimethylchlorosilane leads to the enantiomers **5a1** and **5a2**.

The same mechanism can also account for the *cis* arrangement of the H−Si−C−H linkage in the silacyclopent-3-enes **10a** and **10b** (Scheme 2). The pentavalent intermediate **7**, however, has both hydrogens in axial positions. Pseudorotation of **7**, which can only produce **8a** and **8b**, allows for reduction of strain. The preference for the *cis* arrangement of the H−Si−C−H linkage in **9a** and **9b** has been reported[4a] and can be explained by subsequent hydride migration in **8a** and **8b** from silicon to adjacent ring carbons leading to the formation of carbanions **9a** and **9b**. Subsequent methylation leads to the enantiomers **10a** and **10b**.

It is noteworthy that we observed no inversion of carbanions **4** and **9**, as demonstrated in the structures of **5a** and **10**. High barriers to inversion may arise from the carbanions being in a small ring and close to large substituents.

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(6) (a) Corriu, R. J. P.; Guérin, C. *J. Organomet. Chem.* **1980**, *198*, 231. (b) Corriu, R. J. P.; Guérin, C. *Adv. Organomet. Chem.* **1982**, *20*, 265. (c) Corriu, R. J. P.; Guérin, C.; Moreau, J. J. E. *Top. Stereochem.* **1984**, *15*, 43.

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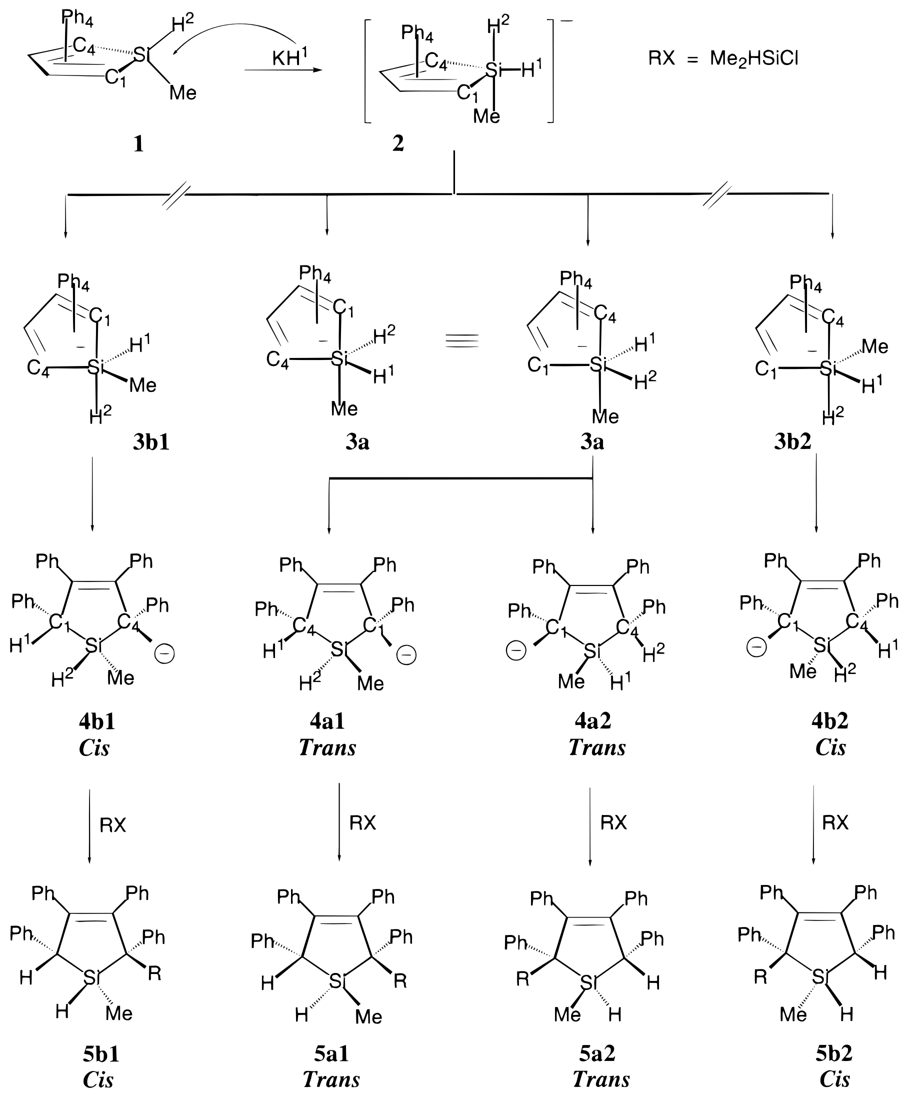
Scheme 1. Possible Mechanism for Formation of Enantiomers 5a1 and 5a2 from Reaction of 1-Methyl-1-hydro-2,3,4,5-tetraphenylcyclopentadiene with Potassium Hydride



Conclusions

Nucleophilic addition to hydrosiloles followed by pseudorotation and 1,2-hydride migration is the pathway proposed to explain the formation of the product enantiomers. The *trans* orientation of the H−Si−C−H linkage in the racemic mixture of 1-methyl-2-(dimethylsilyl)-2,3,4,5-tetraphenyl-1-silacyclo-3-pentene (**5a1**, **5a2**) and the *cis* arrangement of the H−Si−C−H linkage in the racemic mixture of 1-(bis(trimethylsilyl)-amino)-5-methyl-2,3,4,5-tetraphenyl-1-silacyclo-3-pentene (**10a**, **10b**) have been confirmed by crystallographic studies.

Experimental Section

General Procedures. All reactions were performed under an inert argon atmosphere using standard Schlenk techniques. Air-sensitive reagents were transferred in an argon-filled glovebox. THF and DME were freshly distilled under nitrogen from sodium/benzophenone ketyl immediately prior to use. Hexane and pentane were stirred over sulfuric acid, distilled from calcium hydride, and stored over 4 Å molecular sieves. IR spectra were recorded on a Mattson 2020 Galaxy FT-IR instrument. MS data were obtained on a Hewlett-Packard 5988A GC-MS system equipped with a methyl silicon capillary column. NMR spectra were obtained on JEOL GSX270 and GSX400 spectrometers.

Details of the synthesis of **5a** and **10a** and analytical data (NMR, IR, mass, and elemental analysis) have been published.[4a,5]

Synthesis of 1-Methyl-2-(dimethylsilyl)-2,3,4,5-tetraphenyl-1-silacyclo-3-pentene (5a). 1-Methyl-(Ph_4-silole)[8] (2.50 g, 5.50 mmol) and KH (0.27 g, 6.73 mmol, 1.22 equiv) were placed in a 100 mL flask with DME (60 mL). After the mixture was stirred at −20 °C for 40 min, the greenish yellow slurry turned bright red and finally dark purple. Stirring was continued for 8 h at −20 °C. Filtration of the mixture under nitrogen produced a deep violet solution. This solution was added to an excess of Me_2SiHCl (1.20 mL, 11.0 mmol) in DME at room temperature. Stirring for an additional 3 h produced a yellow-green solution. After solvent and Me_2SiHCl were removed under reduced pressure, the residual solid was extracted with hexane. Several recrystallizations in hexane gave **5a** as colorless crystals: yield 71%; mp 132−133 °C. ^1H NMR ($CDCl_3$; solvent reference, 7.27 ppm): 0.21 (d, 3H, $SiMe_2$, $^3J_{Me-H} = 3.66$ Hz), 0.33 (d, 3H, $SiMe_2$, $^3J_{Me-H} = 3.66$ Hz), 0.60 (d, 3H, SiMe, $^3J_{Me-H} = 3.66$ Hz), 3.86 (d, 1H, CH, $^3J_{H-H} = 4.40$ Hz), 4.03 (quint, 1H, SiH), 4.49 (sept, 1H, SiH, $^3J_{Me-H} = 3.66$ Hz), and 6.9−7.8 ppm (brd m, 20 H, Ph). ^{13}C NMR ($CDCl_3$; solvent reference 77.00 ppm): −4.26 (SiMe), −4.63, −4.71

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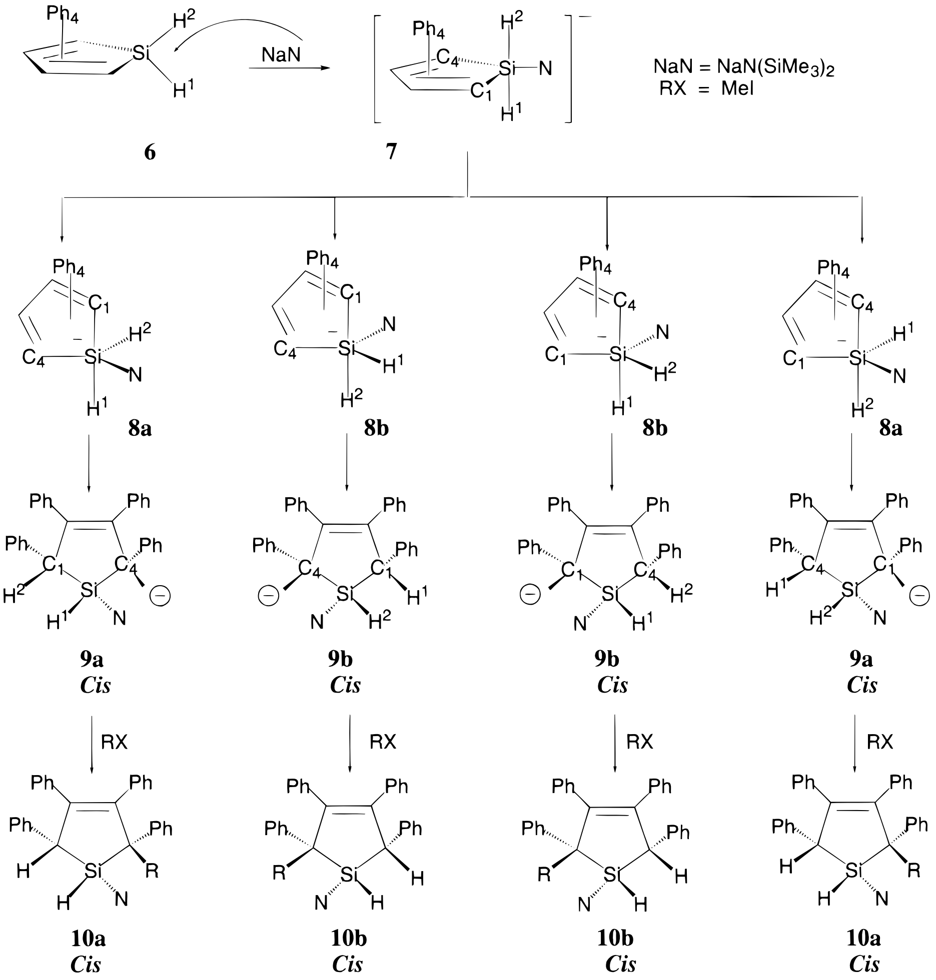
(8) Boudjouk, P.; Sooriyakumaran, R.; Han, B.-H. *J. Org. Chem.* **1986**, *51*, 2818.

Scheme 2. Possible Mechanism for Formation of Enantiomers 10a and 10b from Reaction of 1,1-Dihydro-2,3,4,5-tetraphenylcyclopentadiene with Sodium Bis(trimethylsilyl)amide



(SiMe$_2$), 39.85 (*t*-CH), 43.33 (CSiMe$_2$H), 124.22, 124.28, 125.91, 126.65, 127.21, 127.34, 127.90, 128.11, 128.42, 129.01, 130.17, 130.96, 139.92, 141.48, 142.32, 143.49, 144.81, and 146.76 ppm. ^{29}Si NMR(CDCl$_3$, external TMS reference): −15.61 (HSiMe$_2$) and 28.45 ppm (HSiMe). MS (M$^+$, relative abundance): *m*/*z* 461 (M$^+$ + 1, 5), 460 (M$^+$, 13), 400 (M$^+$ − 60, 100), 197 (48), 121 (74), and 59 (50). Anal. Calcd for $C_{34}H_{32}Si_2$: C, 80.81; H, 7.00, Found: C, 81.13; H, 6.94.

Synthesis of 1-(Bis(trimethylsilyl)amino)-2-methyl-2,3,4,5-tetraphenyl-1-silacyclo-3-pentene (10a). 1,1-Dihydro-(Ph$_4$-silole)[5] (0.77 g, 2 mmol) was dissolved in THF (35 mL) and cooled to −78 °C. To this solution was added Na[N(SiMe$_3$)$_2$] (2.0 mL, 2 mmol) in THF, and a deep violet color developed immediately. After it was stirred at −78 °C for 2 h, this violet solution was added by cannulation to excess MeI (0.50 mL, 8 mmol) in THF (10 mL) at room temperature. The mixture was stirred at room temperature for 30 min, and a yellow solution was formed. The volatiles were slowly evaporated under reduced pressure, and pentane (20 mL) was added to the resultant residue. After filtration, pentane (ca. 15 mL) was removed from the solution, and 20 mL of MeOH was added to cause the formation of white solid **10a**: yield 0.38 g, 34%; mp 177−178 °C. ^{1}H NMR (CDCl$_3$; solvent reference 7.27 ppm): −0.18 (s, 18H), 1.38 (s, 3H), 4.13 (d, 1H, $^3J_{H-H} = 4.6$ Hz), 4.88 (d, 1H, $^3J_{H-H} = 4.6$ Hz), and 7.08−7.75 ppm (m, 20H). ^{13}C{^{1}H} NMR (CDCl$_3$; solvent reference 77.00 ppm): 4.01, 25.31, 41.17, 42.67, 124.22, 124.94, 126.26, 126.44, 127.42, 127.60, 127.84, 128.11, 128.32, 128.40, 129.82, 130.54, 139.50, 140.66, 140.79, 141.18, 146.74, and 146.86 ppm. ^{29}Si NMR: −2.49, 5.81. MS (EI, 70 eV): *m*/*z* 561 (M$^+$, 8), 546 (M$^+$ − CH$_3$, 6), 483 (M$^+$ − C$_6$H$_6$, 8), and 250 (100). IR (KBr, cm^{-1}): ν(Si−H) 2150 (vs, br). Anal. Calcd for $C_{35}H_{43}NSi_3$: C, 74.80; H, 7.71. Found: C, 74.78; H, 7.48.

X-ray Structure Determination. X-ray-quality crystals of **5a** were grown from a concentrated hexane solution of **5a**. Crystals of **10a** were obtained from a concentrated pentane and methanol solution of **10a**. A single crystal of **5a** or **10a** was mounted in a thin-walled glass capillary tube and sealed under nitrogen. Details on machine parameters, crystal data, data collection and refinement are given in Tables 1−3.

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Supporting Information Available: Tables of bond distances and angles, hydrogen atom coordinates, and anisotropic thermal parameters for **5a** and **10a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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