Organometallics 1993, *12*, 4607–4612 4607

Indenyl- and Fluorenylsilanes: Synthesis and Thermal Diastereomerization

You-Xian Chen,[1a] Marvin D. Rausch,[*,1a] and James C. W. Chien[*,1a,b]

Department of Chemistry, Department of Polymer Science and Engineering, Materials Research Laboratories, University of Massachusetts, Amherst, Massachusetts 01003

Received August 24, 1993[⊗]

Indenyl- and fluorenylmagnesium bromides were found to be particularly effective for the synthesis of L_xSiCl_{4-x} (L = Ind, Flu) and for their dimethyl and dimethoxy derivatives. The substitution of Si on indene occurs exclusively at the 1-position. Two diastereomers, the (*R,R*/*S,S*)-racemic and (*R,S*)-meso structures, were obtained and separated for $(Ind)_2SiX_2$ (X = Cl, OCH_3, CH_3). Thermal diastereomerization of racemic to meso structures has been shown to occur by the dynamic NMR method, and thermodynamic parameters have been determined. A possible mechanism involving intramolecular 1,3-metallotropic shifts for the diastereomerization process is proposed.

Introduction

There is intense research interest in group 4 metallocene compounds[1] because they are precursors to metallocenium catalysts[1,2] for olefin polymerization. The group 4 metallocene usually contains one or two cyclopentadienyl (Cp), indenyl (Ind), or fluorenyl (Flu) moieties. Stereospecific polymerization of propylene is attainable only with stereorigid complexes, whereas nonrigid complexes produce atactic polypropylene. Stereorigidity was shown to be simply achieved by linking the two hapto moieties, i.e., an *ansa*-metallocene compound. For example, the cations derived from ethylene-[2p] or (dimethylsilylene)bis(1-η^5-indenyl)dichlorozirconium,[2p,3] isopropylidene-[4] or neopentylidene(1-η^5-cyclopentadienyl)(1-η^5-fluorenyl)dichlorozirconium,[5] and ethylidene(1-η^5-2,3,4,5-tetramethylcyclopentadienyl)(1-η^5-indenyl)dichlorotitanium[6] produce polypropylenes of isotactic, syndiotactic, and isotactic-*b*-atactic structures, respectively.

For certain situations, it would be desirable to be able to vary substituents at the bridgehead atom of an *ansa*-metallocene compound. For instance, a ligand with a $Cl_2Si<$ linkage would enable its attachment to an inorganic oxide support.[7] A bridging group $R_2Si<$ where R is a long chain alkyl group would impart hydrocarbon solubility to the metallocene compound. Metallocenes linked by silacycloalkanes could be obtained by the reaction of a $Cl_2Si<$ bridged complex with $Li(CH_2)_nLi$.[7] For these reasons, the family of compounds with the general structure of L_xSiCl_{4-x}, where L = Cp, Ind, Flu, would be valuable intermediates for the synthesis of metallocene precursors for homogeneous Ziegler–Natta catalysts. A series of indenyl silanes was prepared by Sommer and Marans[8] as early as 1951, although their further synthetic utility was limited due to the lack of additional reactive atoms or groups on silicon.

Synthetic methods are available for alkylindene derivatives substituted at either the 1- or 3-positions; base-catalyzed tautomeric rearrangements from one to the other have been investigated.[9] Also, (trimethylsilyl)indenes have been shown to be fluxional molecules.[10-13] At temperatures above 150 °C, fluxional (metallotropic) rearrangements and isomerization (prototropic) reactions interconvert 1-, 2-, and 3-(trimethylsilyl)indenes. One purpose of the present study was to develop syntheses for pure isomers of L_xSiCl_{4-x} and to investigate their isomerization behavior for compounds **1**–**6**. The conversions of these new organosilicon compounds to the corresponding zirconocene or titanocene derivatives and their olefin polymerization behaviors will be published elsewhere.

[⊗] Abstract published in *Advance ACS Abstracts*, October 1, 1993.

(1) For recent reviews of metallocene polymerization catalysis see: (a) Keii, T., Soga, K., Eds. *Catalytic Olefin Polymerization*; Kodansha and Elsevier: Tokyo and New York, 1990. (b) Quirk, R. P. Ed. *Transition Metal Catalyzed Polymerizations Ziegler-Natta and Metathesis Polymerizations*; Cambridge Press: New York, 1988. (c) Kaminsky, W.; Sinn, H. Eds. *Olefin Polymerization*; Springer-Verlag: Berlin, 1988. (d) Keii, T.; Soga, K. *Catalytic Polymerization of Olefins*; Kodansha and Elsevier: Tokyo and New York, 1986.

(2) Chemical evidence for cationic intermediates has been reported: (a) Dyachkovskii, F. S.; Shilova, A. K.; Shilov, A. Y. *J. Polym. Sci., Part C* **1967**, 2333. (c) Dahman, K. H.; Hedden, D.; Burwell, R. L., Jr.; Marks, T. J. *Langmuir* **1988**, *4*, 1212. Modeling studies of cationic intermediates have been given: (c) Eisch, J. J.; Pietrowski, A. M.; Brownstein, S. K.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219. (d) Jordan, R. F.; La Pointe, R. F.; Bradley, P. K.; Baenziger, N. *Organometallics* **1989**, *8*, 2892 and references therein. (e) Bochmann, M.; Jaggar, A. J.; Nicholls, J. C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 780 and references therein. (f) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728. (g) Taube, R.; Krukowa, L. *J. Organomet. Chem.* **1988**, *347*, C9. (h) Pellecchia, C.; Proto, A.; Longo, P.; Zambelli, A. *Makromol. Chem. Rapid Commun.* **1991**, *12*, 663. (i) Zambelli, A.; Longo, P.; Grassi, A. *Macromolecules* **1989**, *22*, 2186. (j) Turner, H. W. Eur. Pat. Appl. A1 0277004, 1988. Spectroscopic evidence for cationic intermediates can be found: (k) Long, W. P. *J. Am. Chem. Soc.* **1959**, *81*, 5312. (l) Gassman, P. G.; Callstrom, M. R. *J. Am. Chem. Soc.* **1987**, *109*, 7875. (m) Sishta, C.; Hathorn, R. M.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 1112. High polymerization activity by metallocenium ions has been shown for ethylene: (n) Yang, X.; Stern, C. L.; Marks, T. *J. Am. Chem. Soc.* **1991**, *113*, 3623. And also for propylene with stereospecificity: (o) Chien, J. C. W.; Tsai, W.-M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570.

(3) Tsai, W.-M.; Rausch, M. D.; Chien, J. C. W. *Appl. Organomet. Chem.* **1993**, *7*, 71.

(4) Ewen, J. A.; Elder, M. J.; Jones, R. L.; Haspeslagh, L.; Atwood, J. L.; Bott, S. G.; Robinson, K. *Makromol. Chem., Macromol. Symp.* **1991**, *48*/*49*, 253.

(5) Fierro, R.; Chien, J. C. W.; Rausch, M. D. *Organometallics*, submitted for publication.

(6) (a) Mallin, D. T.; Rausch, M. D.; Lin, Y.-G.; Dong, S.-H.; Chien, J. C. W. *J. Am. Chem. Soc.* **1990**, *112*, 2030. (b) Llinas, G. H.; Dong, S.-H.; Mallin, D. T.; Rausch, M. D.; Lin, Y.-G.; Winter, H. H.; Chien, J. C. W. *Macromolecules* **1992**, *25*, 1242. (c) Chien, J. C. W.; Llinas, G. H.; Rausch, M. D.; Lin, Y.-G.; Winter, H. H.; Atwood, J. L.; Bott, S. G. *J. Am. Chem. Soc.* **1991**, *113*, 8569; *J. Polym. Sci., Part A* **1992**, *30*, 2601.

(7) Tsai, W.-M.; Chen, Y.-X.; Chien, J. C. W.; Rausch, M. D. Unpublished results.

(8) Sommer, L. H.; Marans, N. S. *J. Am. Chem. Soc.* **1951**, *73*, 5135.

(9) Weidler, A. M. *Acta Chem. Scand.* **1963**, *17*, 2724.

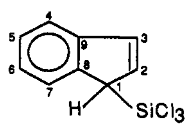
(10) Rakita, P. E.; Davison, A. *Inorg. Chem.* **1969**, *5*, 1164.

(11) Larrabee, R. B.; Dowden, B. F. *Tetrahedron Lett.* **1970**, *12*, 915.

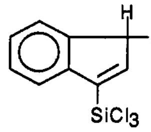
(12) Davison, A.; Rakita, P. E. *J. Organomet. Chem.* **1970**, *23*, 407.

(13) Luzikov, Yu. N.; Sergeyev, N. M.; Ustynyuk, Yu. A. *J. Organomet. Chem.* **1974**, *65*, 303.

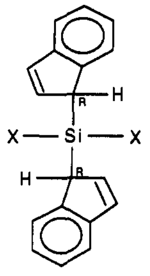
0276-7333/93/2312-4607$04.00/0



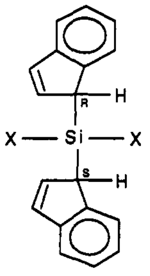
1 a



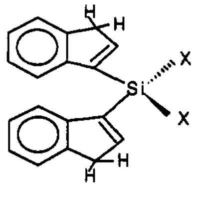
1 b



(R,R/S,S)



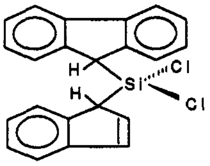
(R,S)



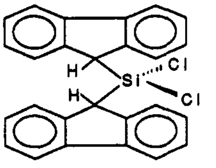
2 a, X = Cl
3 a, X = OCH3
4 a, X = CH3

2 b, X = Cl
3 b, X = OCH3
4 b, X = CH3

2 c, X = Cl
3 c, X = OCH3
4 c, X = CH3



5



6

Results and Discussion

Synthesis of 1-Indenyltrichlorosilane (1). Indenyllithium proved to be too active a reagent to be used in conjunction with $SiCl_4$ to synthesize the individual compounds $(Ind)_xSiCl_{4-x}$. A mixture of 1, 2, and triindenylmonochlorosilane (7) always resulted regardless of the ratio of the reactants, solvents (THF, diethyl ether, or hexane), temperatures (−78 °C to refluxing), and other experimental conditions.

We subsequently found that indenylmagnesium bromide (8) is a much milder reagent, and its reaction with $SiCl_4$ can be influenced by the proper choice of solvent. When *n*-hexane is the medium, 1 is the major product. This is true even when the amount of 8 used is twice that of $SiCl_4$. To achieve the best yield of 1, a 20% excess of $SiCl_4$ was employed in the synthesis. Therefore, excess $SiCl_4$ is present to convert 2, a minor product, into 1 via a disproportionation reaction. The yield of 1, after purification by vacuum distillation, was 80%.

The ^1H NMR spectrum of this new compound 1 contains three sets of peaks at 4.02, 6.65, and 7.18 ppm from TMS in a 1:1:1 intensity ratio. They can be assigned to the H-1, H-2, and H-3 protons of **1a**, respectively. On the other hand, structure **1b**, if formed, would exhibit one olefin and two aliphatic protons with different splitting patterns and coupling constants. The ^{13}C NMR spectrum of the product exhibits two resonances at 144.89 and 139.05 ppm for C-8 and C-9 quaternary carbons of structure **1a**, respectively. Structure **1b** would possess three quaternary carbons in this region. Both NMR results therefore confirmed that isomer **1a** was formed in the synthesis.

The NMR spectra of **1a** remained unchanged between −20 and +100 °C. There was no indication for change in either structure or fluxional behavior. The latter was not expected until above 150 °C[10–13] if trichlorosilyl derivative **1a** behaves like (trimethylsilyl)indene.

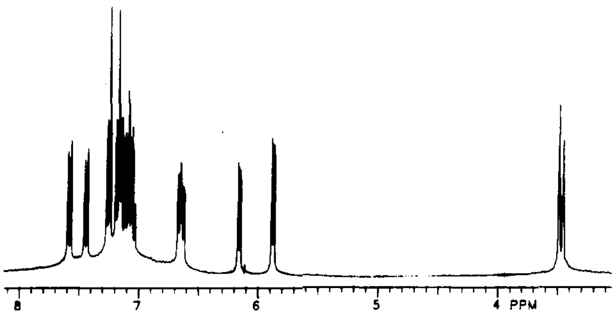


Figure 1. ^1H NMR (C_6D_6) spectrum of a mixture of two diastereomers **2a** and **2b**.

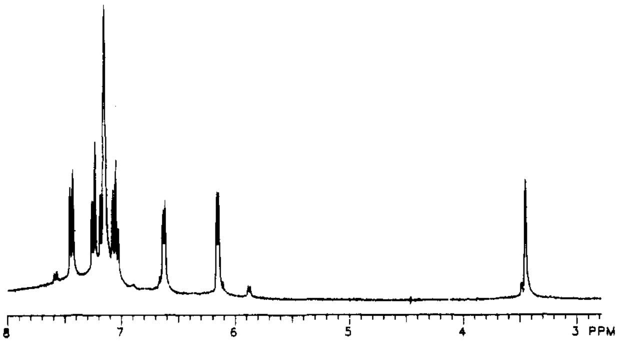


Figure 2. ^1H NMR (C_6D_6) spectrum of (*R,R*/*S,S*)-racemic **2a**.

Synthesis of Bis(1-indenyl)dichlorosilane (2). The Grignard reagent 8 was also used to synthesize 2. Reaction of 8 with $SiCl_4$ in THF produced a mixture of silanes (vide supra). However, this reaction when carried out in diethyl ether as the solvent afforded the desired product. The yield of 2 after purification was better than 60%. The ^1H NMR spectrum (Figure 1) of 2 in C_6D_6 shows a mixture of two diastereomers (**2a** and **2b**). The pure (*R,R*/*S,S*)-racemic **2a** was obtained as white crystals by fractional recrystallization from pentane at low temperatures. The ^1H NMR spectrum (Figure 2) of **2a** in C_6D_6 exhibits the following resonances: δ 7.44 (d, ^3J = 7.52 Hz), 7.25 (d, ^3J = 7.50 Hz), 7.15 (t, ^3J = 7.51 Hz), and 7.06 (t, ^3J = 7.51 Hz) ppm represent four sets of peaks of an ABCD spin system for a total of eight aromatic hydrogens (H4–7); H-1, H-2, and H-3 form an ABX spin system, with δ 6.65–6.62 (dd, J_{AB} = 5.37 Hz, J_{AX} = 1.96 Hz, 2H) for H-3, δ 6.18–6.15 (dd, J_{BA} = 5.37 Hz, J_{BX} = 1.96 Hz, 2H) for H-2, and δ 3.45 (s, 2H) for H-1.

The ^{13}C NMR spectrum of **2a** shows nine types of carbons: two quaternary aromatic carbons, δ 144.71 and 140.24 for C-8 and C-9, respectively; four aromatic methine (CH) groups, δ 132.62, 130.91, 126.53, and 124.72 for C-4, C-5, C-6, and C-7; two olefin CH groups in the C-5 ring at δ 123.82 and 121.52 for C-3 and C-2; and one saturated carbon at δ 46.66 for C-1. Both the ^1H NMR and ^{13}C NMR spectra are therefore consistent with 1-indenyl substitution but inconsistent with the 3-substituted derivative **2c**.

Figure 2 contains additional weak peaks indicative of another isomer, meso structure **2b**, and a thermal diastereomerization between **2a** and **2b** is discussed below.

Synthesis of Bis(1-indenyl)dimethoxysilane (3) and Bis(1-indenyl)dimethylsilane (4). Compound 3 was prepared by the reaction of 2 with methanol in pyridine. The proton NMR spectrum of a mixture of two diastereomers (**3a** and **3b**) contains two sets of resonances having

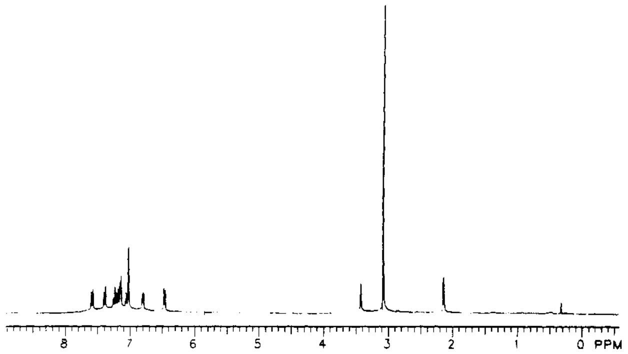


Figure 3. ^{1}H NMR (C_7D_8) spectrum of **3a** (δ 2.15, 7.05 ppm for toluene).

hyperfine structures very similar to the **2a** and **2b** resonances in Figure 1. The pure (*R,R/S,S*)-racemic **3a** was obtained from fractional recrystallization, and the ^{1}H NMR spectrum of **3a** shows one singlet at 3.09 ppm for two enantiotopic CH_3O groups (Figure 3). On the other hand, the (*R,S*)-meso type of diastereomer **3b** exhibits two singlets at 2.90 and 3.35 ppm, respectively, for two types of CH_3O groups because they are diastereotopic.

Although bis(1-indenyl)dimethylsilane (**4**) was synthesized by Sommer et al. in 1951 (as a liquid)[8] and then by Marechal et al. in 1968 (as a solid),[14] the yields were very low and the structures were not well characterized. We found that two 1-substituted diastereomers **4a** and **4b** and the 3-substituted isomer **4c** were formed when dichlorodimethylsilane reacted with either indenyllithium or Grignard reagent 8. Yields were up to 56.0% from (Ind)Li, and 47.0% from (Ind)MgBr. The pure (*R,R/S,S*)-racemic **4a** was obtained as white crystals after fractional recrystallization in diethyl ether at −20 °C, and the ^{1}H NMR spectrum (C_6D_6) shows one singlet at −0.43 ppm for two enantiotopic CH_3 groups. Likewise, the (*R,S*)-meso type of diastereomer **4b** which remained in the mother liquor exhibits two diastereotopic CH_3 groups at −0.21 and −0.58 ppm, respectively.

Thermal Diastereomerization. ^{1}H NMR spectra were recorded for **2a** from −21 to +110 °C in $CDCl_3$ for low temperatures and in toluene-d_8 for higher temperatures. There were no observable spectral changes between −21 and +40 °C. Beginning at 50 °C there appeared additional resonances indicating formation of a second diastereomer **2b**. The spectral intensities of the latter increase with increasing temperature. At 100 °C, the two diastereomers were present in about equal amounts (Figure 4). Above 110 °C the peaks attributed to the two diastereomers begin to coalesce, and the coalescence is reversed upon cooling. Similar NMR changes occurred for samples initially containing both **2a** and **2b**. Due to limitations of our spectrometer and the complexity caused by the occurrence of the fluxional process at high temperatures, the study of the complete range of coalescence was not feasible. The above study shows that molecule **2** is not fluxional up to 110 °C, which is consistent with the previous observation for (trimethylsilyl)indene that the onset of changes in the NMR spectrum due to the fluxional migration occurs at ≥150 °C.[10-13]

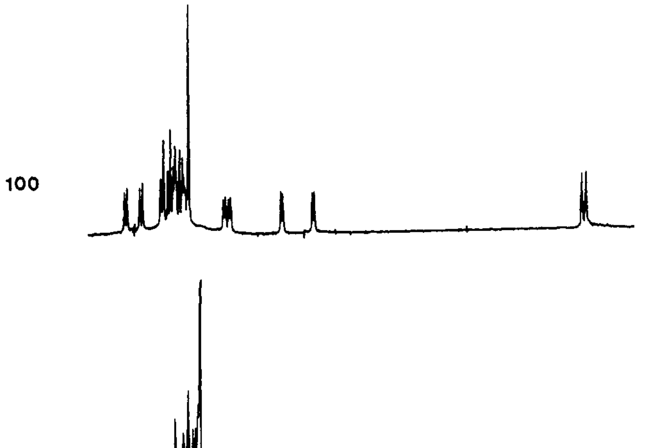


Figure 4. VT ^{1}H NMR (C_7D_8) spectra of the conversion process of diastereomer **2a** → **2b**.

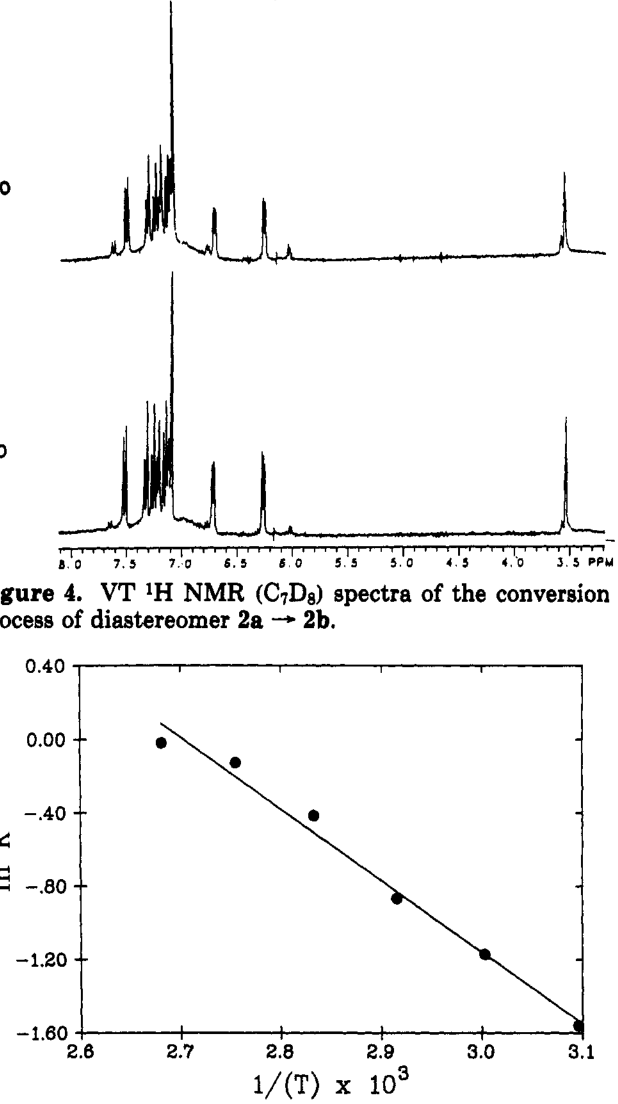


Figure 5. Variation in the equilibrium constant K with temperature for the diastereomerization of **2a** → **2b**.

The ratio of the integrated intensities of the ^{1}H NMR peaks in toluene-d_8 at δ 7.65 (or 3.58) to those at δ 7.52 (or 3.55) were measured quantitatively. At a given temperature, the sample was allowed to reach thermal equilibrium in the probe for *ca.* 15 min before recording and integrating the spectrum. The equilibrium constant, $K = [\mathbf{2b}]/[\mathbf{2a}]$, is plotted in the Arrhenius dependence of ln K versus $1/T$ (K) (Figure 5). The slope gives $\Delta H = 7.7$ kcal/mol. At 50 °C $\Delta G = 1.0$ kcal/mol.

A similar diastereomerization process for **3a** to **3b** was observed in the temperature range from 40 to 70 °C. From

---

(14) Marechal, E.; Tortal, J. P. *C. R. Acad. Sci. Paris* **1968**, *267*, 467.

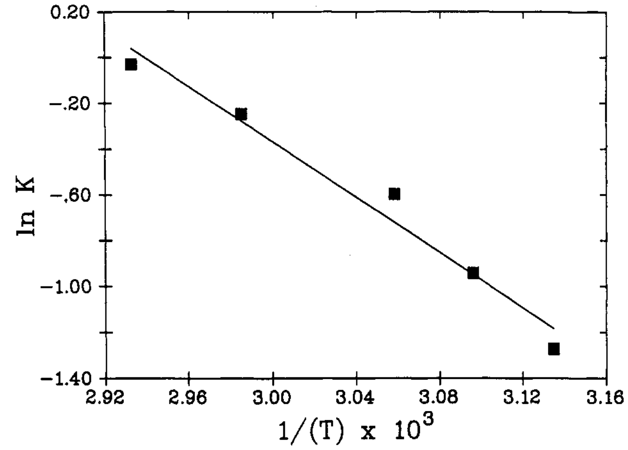


Figure 6. Variation in the equilibrium constant K with temperature for the diastereomerization of **3a** → **3b**.

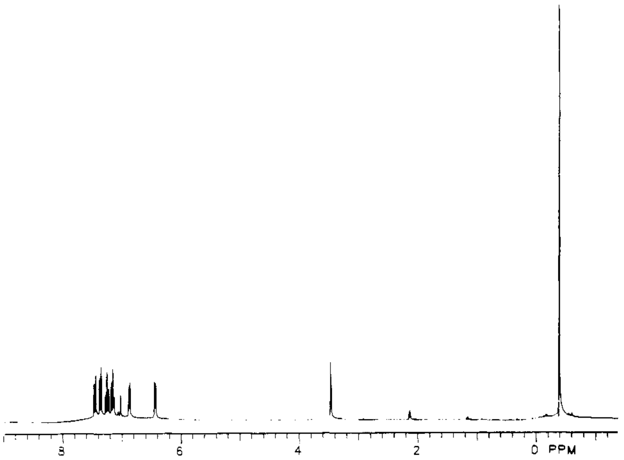


Figure 7. ^1H NMR (C_7D_8) spectrum of **4** at 20 °C (**4a** only).

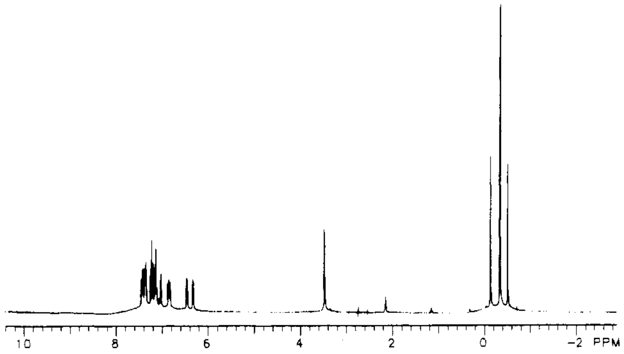


Figure 8. ^1H NMR (C_7D_8) spectrum of **4** at 54 °C (**4a** and **4b**).

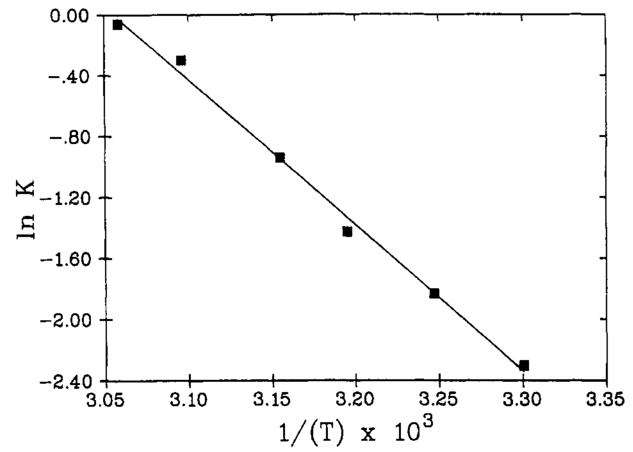
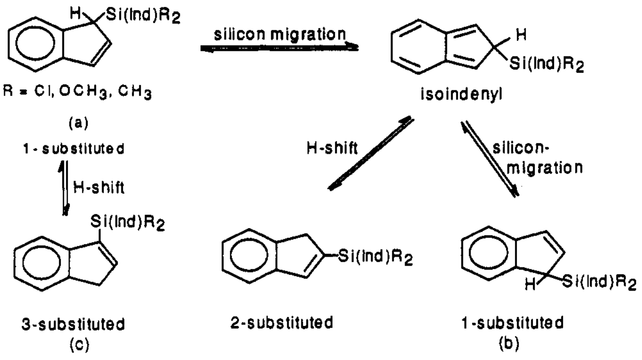


Figure 9. Variation in the equilibrium constant K with temperature for the diastereomerization of **4a** → **4b**.

Scheme I



the slope of a plot of ln K vs $1/T$ (K) (Figure 6), we obtained ΔH = 12.0 kcal/mol and ΔG = 0.6 kcal/mol at 50 °C.

Likewise, **4a** isomerizes to its diastereomer **4b** beginning at 30 °C and reaches the equilibrium with **4b** at 54 °C (Figures 7 and 8).

The slope of a plot of ln K vs $1/T$ (K) (Figure 9) corresponds to ΔH = 18.9 kcal/mol and ΔG = 0.2 kcal/mol at 50 °C.

Several types of processes were considered to account for the VT NMR results: they are prototropic isomerization, fluxional migration, and 1,3-silyl migration.[15]

The fluxional migration and prototropic isomerization processes usually occur at ≥150 °C.[10-13,16] In order to confirm this conclusion, on heating at 200 °C in the absence of air for 6 h, **2a** and **4a** each afforded a mixture of all types of isomers: 1-substituted indene (two diastereomers), 2-substituted indene, and 3-substituted indene, indicating fluxional rearrangements and prototropic isomerizations had occurred. The generally accepted mechanism may be written as in Scheme I.

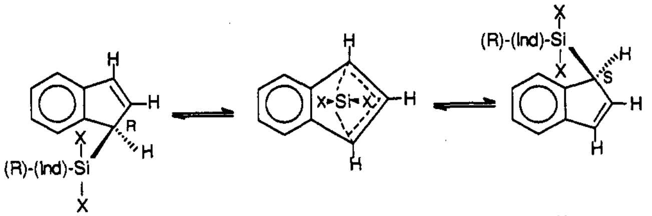
On the other hand, on warming to 100 °C, **2a**, **3a**, and **4a** did not produce any trace of prototropic isomerization products, **2c**, **3c**, and **4c**, nor any other fluxional migration products. There was only isomerization of the compounds to their corresponding diastereomers, **2b**, **3b**, and **4b**. Obviously, this diastereomerization process should undergo a lower energy pathway. A plausible mechanism for this process involves the concerted intramolecular 1,3-metallotropic shift (Scheme II). A suprafacial shift of the silyl group gives equilibration of the enantiamorphous structures **9a** and **9b** and thus reverses the configuration at the asymmetric carbon atom. The relative order of migratory aptitude (**4a** > **3a** > **2a**) according to energetic considerations (vide supra) may indicate steric effects on the diastereomerization rather than involving electronic effects, which supports the transition state proposed in Scheme II.

---

[15] (a) Photochemical 1,3-silyl migration in allylsilanes has been reported: Kira, M.; Taki, T.; Sakurai, H. *J. Org. Chem.* **1989**, *54*, 5647. (b) Because of inversion of the chiral carbon configuration in the process and as a result of singlets for the two methyl groups in both **3a** and **4a** at room temperature, conformational exchange would not account for the VT spectral changes. Additionally, a molecular mechanics calculation on molecule **2a** indicates that the highest rotational barrier between the two indenyl rings is *ca.* 4.8 kcal/mol. This result means that if there is conformational exchange, the conformers will not be frozen out down to -70 °C.

[16] Andrews, M. N.; Rakita, P. E.; Taylor, G. A. *Inorg. Chim. Acta* **1975**, *13*, 191.

Scheme II



9a (R,R)

X = CH_3, OCH_3, Cl

(an indenyl group directly above Si omitted for clarity)

9b (R,S)

Experimental Section

All reactions with organometallic reagents were carried out in an inert atmosphere (argon) using Schlenk techniques. Solvents were dried and distilled under argon prior to use. NMR spectra were measured on a Varian XL-300 NMR spectrometer with variable-temperature probes. Temperature calibrations were made with ethylene glycol, and spectra were recorded in solutions of chloroform-*d*, benzene-d_6, or toluene-d_8. The program used to perform the molecular mechanics calculation was Allinger's MM2.[17] All calculations were carried out using the CAChe Modeling software system (2.7 version, 1991).

Elemental analyses were performed by the Microanalytical Laboratory at the University of Massachusetts, Amherst. Melting points are uncorrected. Unless otherwise indicated, all chemicals were purchased from Aldrich.

(1-Indenyl)trichlorosilane (1a). A 500-mL Schlenk flask was charged with 11.0 g (50.0 mmol) of indenylmagnesium bromide, synthesized by a modification of a published procedure in 96.0% yield,[18] and 300 mL of hexane. A solution of silicon tetrachloride (8.00 mL, 11.9 g, 70.0 mmol) and 50 mL of hexane was added dropwise at room temperature. After the addition was complete, the reaction mixture was heated at reflux with stirring for 12 h. The resulting suspension solution was filtered through a Celite plug and then washed with two portions of dry hexane. The solvent was removed and the residual oil was distilled at 1.1 mmHg to give 10.0 g (80.1% yield) of **1a**, bp 82.0 °C, d_4^{20} = 1.472, $n^{20}{}_D$ = 1.5734, air and moisture sensitive.

^1H NMR ($CDCl_3$): δ 7.76 (d, ^3J = 7.50 Hz, 1H, H-4), 7.56 (d, ^3J = 7.50 Hz, 1H, H-7), 7.42 (t, ^3J = 7.50 Hz, 1H, H-5), 7.34 (t, ^3J = 7.50 Hz, 1H, H-6), 7.18 (dd, J_{AB} = 5.18 Hz, J_{AX} = 1.36 Hz, 1H, H-3), 6.65 (dd, J_{BA} = 5.18 Hz, J_{BX} = 1.82 Hz, 1H, H-2), 4.02 (s, 1H, H-1). ^1H NMR (C_6D_6): δ 7.58 (d), 7.22 (d), 7.18 (t), 7.08 (t), 6.79 (dd), 6.23 (dd), 3.41 (s). ^{13}C NMR ($CDCl_3$): δ 144.89, 139.05 (C-8, C-9), 134.78, 129.59, 127.27, 125.41 (C-4, C-5, C-6, C-7), 124.05, 121.89 (C-3, C-2), 49.01 (C-1). Anal. Calcd for $C_9H_7Cl_3Si$ (248.60): C, 43.31; H, 2.83; Cl, 42.61. Found: C, 43.16; H, 2.87; Cl, 42.49.

Bis(1-indenyl)dichlorosilane (2). A 500-mL round-bottom flask was equipped with a reflux condenser, a magnetic stirring bar, and a dropping funnel. Indenylmagnesium bromide (11.0 g, 50.0 mmol) was added to the flask followed by 200 mL of diethyl ether. Stirring was begun and silicon tetrachloride (4.25 g, 2.87 mL, 25.0 mmol) in 100 mL of diethyl ether was added dropwise at -20 °C. After the addition was complete, the reaction mixture was warmed to room temperature and then heated at reflux with stirring for 12 h. The solvent was removed in vacuo, and 300 mL of hexane was added. The resulting thick precipitate was stirred for 2 h, filtered through a Celite plug, and then washed with two portions of dry hexane. The solvent of the filtrate was removed to produce a sticky orange oil which was then dried under vacuum for 2 h. Dry pentane (20 mL) was added, and the precipitate was filtered out as a white solid. The crude product was purified by recrystallization from diethyl ether and pentane, affording 5.10 g (61.9% yield) of white crystals, mp 82–84 °C, air and moisture sensitive. NMR showed this product to be a mixture of two diastereomers.

^1H NMR (C_6D_6): δ 7.58 (d, *J* = 7.60 Hz, 2H, H-4, **2b**), 7.44 (d, *J* = 7.60 Hz, 2H, H-4, **2a**), 7.26–7.03 (m, 12H, H-5, H-6, H-7, **2a** and **2b**), 6.67–6.65 (dd, $J_{A'B'}$ = 5.34 Hz, $J_{A'X'}$ = 1.36 Hz, 2H, H-3, **2b**), 6.64–6.62 (dd, J_{AB} = 5.34 Hz, J_{AX} = 1.36 Hz, 2H, H-3, **2a**), 6.17–6.15 (dd, J_{BA} = 5.34 Hz, J_{BX} = 1.36 Hz, 2H, H-2, **2a**), 5.89–5.87 (dd, $J_{B'A'}$ = 5.34 Hz, $J_{B'X'}$ = 1.36 Hz, 2H, H-2, **2b**), 3.48 (s, 2H, H-1, **2b**), 3.45 (s, 2H, H-1, **2a**). ^1H NMR ($CDCl_3$) (the splitting patterns and coupling constants are almost the same as those in C_6D_6): δ 7.65 (d, 2H), 7.55 (d, 2H), 7.48–7.19 (m, 6H), 6.98 (dd, 2H), 6.90 (dd, 2H), 6.38 (dd, 2H), 6.09 (dd, 2H), 3.80 (s, 2H), 3.75 (s, 2H).

Fractional recrystallization from pentane at -20 °C gave the pure (*R,R/S,S*)-racemic **2a** as white crystals, mp 98.0–98.5 °C. Anal. Calcd for $C_{18}H_{14}Cl_2Si$ (329.303): C, 65.66; H, 4.29; Cl, 21.53. Found: C, 65.67; H, 4.43; Cl, 21.41.

^1H NMR (C_6D_6): δ 7.44 (d, ^3J = 7.60 Hz, 2H, H-4), 7.25 (d, ^3J = 7.57 Hz, 2H, H-7), 7.15 (t, ^3J = 7.15 Hz, 2H, H-5), 7.06 (t, ^3J = 7.51 Hz, 2H, H-6), 6.65–6.62 (dd, J_{AB} = 5.37 Hz, J_{AX} = 1.96 Hz, 2H, H-3), 6.18–6.15 (dd, J_{BA} = 5.37 Hz, J_{BX} = 1.96 Hz, 2H, H-2), 3.45 (s, 2H, H-1). ^{13}C NMR ($CDCl_3$): δ 144.71, 140.24 (C-8, C-9), 132.62, 130.91, 126.53, 124.72 (C-4, C-5, C-6, C-7), 123.87, 121.52 (C-3, C-2), 46.66 (C-1). The (*R,S*)-meso type of diastereomer **2b** was enriched in the mother liquor as a sticky orange oil after removal of the recrystallization solvent. For ^1H NMR data, see above.

Bis(1-indenyl)dimethoxysilane (3). A 250-mL Schlenk flask was charged with 2.00 g (6.10 mmol) of bis(1-indenyl)dichlorosilane (containing two diastereomers) and 100 mL of hexane. A solution of methanol (0.50 g, 15.6 mmol) and pyridine (*ca.* 2 g) was added dropwise. After the addition was complete, the reaction mixture was stirred for 1 h and then extracted with 100 mL of diethyl ether. The organic extracts were washed repeatedly with 100 mL of water and then dried over anhydrous sodium sulfate. The yellow oil remaining after removal of the solvent was characterized by NMR as a mixture of two diastereomers and then recrystallized from methylene chloride and a methanol mixture several times to afford 1.30 g of **3a** (67.0%) as white crystals, mp 78.0–79.0 °C. Anal. Calcd for $C_{20}H_{20}SiO_2$ (320.46): C, 74.96; H, 6.29. Found: C, 74.56; H, 6.17.

^1H NMR ($CDCl_3$): δ 7.50 (d, ^3J = 7.51 Hz, 2H, H-4), 7.47 (d, ^3J = 7.51 Hz, 2H, H-7), 7.25 (t, ^3J = 7.50 Hz, 2H, H-5), 7.19 (t, ^3J = 7.50 Hz, 2H, H-6), 6.91 (dd, J_{AB} = 5.40 Hz, J_{AX} = 1.36 Hz, 2H, H-3), 6.50 (dd, J_{BA} = 5.40 Hz, J_{BX} = 1.36 Hz, 2H, H-2), 3.50 (s, 2H, H-1), 3.26 (s, 6H, $2CH_3O$).

The (*R,S*)-meso diastereomer **3b** was enriched in the mother liquor as a sticky orange oil after removal of the solvent, and ^1H NMR indicated two types of diastereotopic CH_3O groups instead of one type in the case of the (*R,R/S,S*) isomer.

^1H NMR ($CDCl_3$): δ 7.58 (d, ^3J = 7.51 Hz, 2H, H-4), 7.47 (d, ^3J = 7.51 Hz, 2H, H-7), 7.25 (t, ^3J = 7.50 Hz, 2H, H-5), 7.15 (t, ^3J = 7.50 Hz, 2H, H-6), 6.91 (dd, J_{AB} = 5.40 Hz, J_{AX} = 1.36 Hz, 2H, H-3), 6.20 (dd, J_{BA} = 5.40 Hz, J_{BX} = 1.36 Hz, 2H, H-2), 3.55 (s, 2H, H-1), 3.39 (s, 3H, CH_3O), 2.93 (s, 3H, CH_3O).

Bis(1-indenyl)dimethylsilane (4). A modification to the published procedure[14] was used to prepare the title compound. A mixture of two 1-substituted diastereomers **4a** and **4b** and one 3-substituted isomer **4c** was obtained after the workup process in 56.0% yield from (Ind)Li, 47.0% yield from (Ind)MgBr. Fractional recrystallization from ethyl ether at -20 °C afforded the pure (*R,R/S,S*)-racemic **4a** as white crystals in 25.0% yield from (Ind)Li, 14.0% yield from (Ind)MgBr, mp 86.0–87.0 °C.

^1H NMR (C_6D_6, Bruker/IBM 200 AC NMR): δ 7.46 (d, ^3J = 8.00 Hz, 2H, H-4), 7.35 (d, ^3J = 8.00 Hz, 2H, H-7), 7.25 (t, ^3J = 8.00 Hz, 2H, H-5), 7.13 (t, ^3J = 8.00 Hz, 2H, H-6), 6.86–6.83 (dd, J_{AB} = 6.00 Hz, J_{AX} = 1.20 Hz, 2H, H-3), 6.42–6.39 (dd, J_{BA} = 6.00 Hz, J_{BX} = 1.20 Hz, 2H, H-2), 3.47 (s, 2H, H-1), -0.43 (s, 6H, $2CH_3$).

The (*R,S*)-meso diastereomer **4b** and the 3-substituted isomer **4c** were collected from mother solutions as a sticky orange oil after removal of the solvent.

---

[17] (a) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. (b) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, DC, 1982.

[18] Smith, D.; Atwood, J. L. *Inorg. Synth.* **1976**, *16*, 137.

^{1}H NMR (C_6D_6) of **4b**: δ 7.46 (d, ^3J = 8.00 Hz, 2H, H-4), 7.35 (d, ^3J = 8.00 Hz, 2H, H-7), 7.25 (t, ^3J = 8.00 Hz, 2H, H-5), 7.13 (t, ^3J = 8.00 Hz, 2H, H-6), 6.88–6.84 (dd, J_{AB} = 6.00 Hz, J_{AX} = 1.20 Hz, 2H, H-3), 6.29–6.25 (dd, J_{BA} = 6.00 Hz, J_{BX} = 1.20 Hz, 2H, H-2), 3.47 (s, 2H, H-1), –0.21 (s, 3H, CH_3). –0.58 (s, 3H, CH_3). ^{1}H NMR (C_6D_6) of **4c**: δ 7.46 (d, ^3J = 8.00 Hz, 2H, H-4), 7.35 (d, ^3J = 8.00 Hz, 2H, H-7), 7.25 (t, ^3J = 8.00 Hz, 2H, H-5), 7.13 (t, ^3J = 8.00 Hz, 2H, H-6), 6.52 (t, ^3J = 5.22 Hz, 2H, H-2), 3.36 (s, 2H, H-1), –0.10 (d, J = 2.88 Hz, 3H, CH_3), –0.22 (d, J = 2.88 Hz, 3H, CH_3).

(9-Fluorenyl)(1-indenyl)dichlorosilane (5). (1-Indenyl)trichlorosilane (3.00 g, 12.0 mmol), 9-fluorenylmagnesium bromide, prepared in 93.0% yield according to a literature method[19] (3.24 g, 12.0 mmol), and 200 mL of diethyl ether were reacted and worked up as described for the synthesis of bis(1-indenyl)dichlorosilane to produce 2.07 g of **5** (45.5% yield) as a sticky orange oil. Anal. Calcd for $C_{22}H_{16}Cl_2Si$ (379.36): C, 69.65; H, 4.25. Found: C, 70.29; H, 4.46.

^{1}H NMR ($CDCl_3$): δ 7.80–7.05 (m, 12H, aromatic H), 6.59 (dd, J_{AB} = 5.37 Hz, J_{AX} = 1.96 Hz, 1H, H-3 (Ind)), 5.68 (dd, J_{BA} = 5.77 Hz, J_{BX} = 1.96 Hz, 1H, H-2 (Ind)), 4.03 (s, 1H, H-9 (Flu)), 3.41 (s, 1H, H-1 (Ind)).

Bis(9-fluorenyl)dichlorosilane (6). 9-Fluorenylmagnesium bromide (13.5 g, 50.0 mmol), silicon tetrachloride (4.25 g, 2.86 mL, 25.0 mmol), and 300 mL of diethyl ether were treated as described for the synthesis of bis(1-indenyl)dichlorosilane, affording 5.60 g, 52.2%, of the title compound as white crystals, mp 173.5–174.0 °C. Anal. Calcd for $C_{26}H_{18}Cl_2Si$ (429.42): C, 72.72; H, 4.22; Cl, 16.51. Found: C, 72.84; H, 4.46; Cl, 16.60.

^{1}H NMR (C_6D_6): δ 7.43 (t, ^3J = 6.84 Hz, 8H), 7.13 (t, ^3J = 7.14 Hz, 4H), 6.95 (t, ^3J = 7.57 Hz, 4H), 3.94 (s, 2H, H-9). ^{13}C NMR ($CDCl_3$): δ 141.04, 139.55 (C-10, C-11, C-12, C-13), 126.66, 126.15, 124.94, 119.92 (C1–4, C5–8), 42.68 (C-9).

Acknowledgment. This work was supported by the Materials Research Laboratories of the National Science Foundation at the University of Massachusetts, Amherst.

OM930594X

---

[19] Tucker, S. U.; Whalley, M. *J. Chem. Soc.* **1949**, 50.