Deuterium-Labeling Studies on the Regio- and Stereoselective Intramolecular Hydrosilation of Allyl Alcohols and Allylamines Catalyzed by Platinum and Rhodium Complexes[1]

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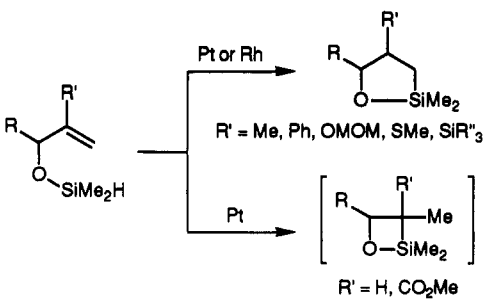
Intramolecular hydrosilation of allyl alcohols and allylamines with the deuteriodimethylsilyl group(s) on the oxygen and nitrogen atom, respectively, has been studied under the catalysis of $[Pt[\{(CH_2{=}CH)Me_2Si\}_2O]_2]$ or $[\{RhCl(CH_2{=}CH_2)_2\}_2]$. The silyl ethers examined include those of 3-hydroxy-1-alkenes (**3**) and their 2-methoxymethoxy (**1**), 2-methyl (**2**), and 1,1-dimethyl (**4**) analogues, and the silylamines are those of 3-amino-3-phenyl-1-propene (**7**) and the 2-methyl (**5** and **6**) and 1,1-dimethyl (**8** and **9**) analogues. Compound **1** forms five-membered cyclic products with Pt and Rh catalysts, which contain deuterium on C2 exclusively. In the five-membered cyclic products formed from **2**, deuterium is distributed mainly on C1 and C2 and only slightly on the 2-methyl group. Compound **3** gives a five-membered ring product with Rh catalyst, in which deuterium is found on C1 and C2. Compound **4** forms a four-membered cyclic product selectively with Pt catalyst, which contains deuterium on C1 exclusively. With Rh catalyst, **4** (nondeuterated analogue) forms six-membered cyclic product selectively via olefin isomerization. The Pt-catalyzed reactions of allylamines **5**–**9** form four-membered cyclic products exclusively: while in the products from **5** and **6** deuterium is distributed on the two exocyclic methyl groups in comparable amounts, the products from **7**–**9** contain deuterium on C1 exclusively. With Rh catalyst, **5**–**7** form five-membered cyclic products, the deuterium distributions being similar to those observed in the allyl alcohol analogues: no reaction is observed with **8** and **9**. These results are consistently analyzed mainly by the hydrometalation–reductive-elimination sequence and in terms of relative stability of the transition-metal–alkyl intermediates and the ring strain.

Introduction

We[2] and others[3] have recently demonstrated that the intramolecular hydrosilation of allyl and homoallyl alcohols and allylamines, in combination with the oxidative cleavage of the silicon–carbon bonds,[4] is useful for the regio- and stereoselective synthesis of polyols and amino alcohols. We have been, however, intrigued by the rather strange regioselectivity.

Scheme I



The regio- and stereoselectivity greatly depend on the "anchor atom", i.e., oxygen or nitrogen, the transition-metal catalyst, and the substituent on the olefin and on the silicon atom. Schemes I and II summarize several representative results on the regioselectivity observed for the basic skeletons, 3-hydroxy-1-alkenes and 3-amino-1-alkenes, studied so far in our laboratory. Allyl alcohols generally undergo endo ring closure[5] to form five-membered ring products regardless of the catalysts, platinum or rhodium, with a few exceptions which give products arising from exo ring closure[5] in the platinum-catalyzed reaction (Scheme I). Allylamines form four-membered and five-membered ring products exclusively with a platinum and a rhodium catalyst, respectively (Scheme II). Thus, the rhodium-catalyzed reactions prefer the endo

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(2) (a) Tamao, K.; Tanaka, T.; Nakajima, T.; Sumiya, R.; Arai, H.; Ito, Y. *Tetrahedron Lett.* **1986**, *27*, 3377. (b) Tamao, K.; Nakajima, T.; Sumiya, R.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1986**, *108*, 6090. (c) Tamao, K.; Yamauchi, T.; Ito, Y. *Chem. Lett.* **1987**, 171. (d) Tamao, K.; Nakagawa, Y.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 3712. (e) Tamao, K.; Maeda, K.; Tanaka, T.; Ito, Y. *Tetrahedron Lett.* **1988**, *29*, 6955. (f) Tamao, K.; Nakagawa, Y.; Ito, Y. *J. Org. Chem.* **1990**, *55*, 3438. (g) Tamao, K.; Tohma, T.; Inui, N.; Nakayama, O.; Ito, Y. *Tetrahedron Lett.* **1990**, *31*, 7333.

(3) (a) Anwar, S.; Davis, A. P. *Proc. R. Ir. Acad.* **1989**, *89B*, 71. (b) Bergens, S. H.; Noheda, P.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 2121. (c) Bergens, S.; Noheda, P.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 2128. (d) Curtis, N. R.; Holmes, A. B.; Looney, M. G. *Tetrahedron Lett.* **1992**, *33*, 671. (e) Curtis, N. R.; Holmes, A. B. *Tetrahedron Lett.* **1992**, *33*, 675.

(4) (a) Tamao, K. *J. Synth. Org. Chem., Jpn.* **1988**, *46*, 861. (b) Tamao, K.; Kakui, T.; Akita, M.; Iwahara, T.; Kanatani, R.; Yoshida, J.; Kumada, M. *Tetrahedron* **1983**, *39*, 983. (c) Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, *48*, 2120. (d) Tamao, K.; Kumada, M.; Maeda, K. *Tetrahedron Lett.* **1984**, *25*, 321. (e) Tamao, K.; Ishida, N. *J. Organomet. Chem.* **1984**, *269*, C37. (f) Fleming, I.; Sanderson, P. E. J. *Tetrahedron Lett.* **1987**, *28*, 4229. (g) Magar, S. S.; Fuchs, P. L. *Tetrahedron Lett.* **1991**, *32*, 7513.

(5) The Baldwin notation for endo and exo ring closures is used throughout the paper. Baldwin, J. *J. Chem. Soc., Chem. Commun.* **1976**, 735.

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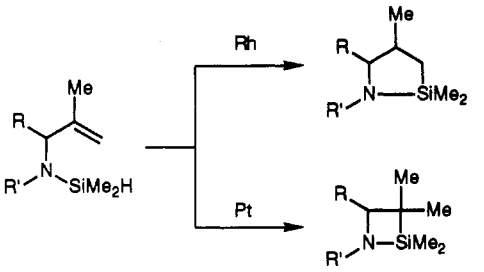
Scheme II



ring closure, while the reaction paths of platinum-catalyzed reactions depend on the structure of the substrate.

In order to get an insight into the mechanism, we have now conducted deuterium-labeling experiments by introducing a deuteriosilyl group in place of the hydridosilyl group. In this report, we will discuss the plausible mechanisms based on the deuterium distributions, mainly by the traditional Chalk–Harrod "hydrometalation" processes.[6] Possibilities for the "silylmetalation" paths[3c,7] will also be discussed. After the completion of our study, similar deuterium-labeling studies on the rhodium-catalyzed intramolecular hydrosilation of allylic alcohols by Bosnich and his co-workers appeared.[3c] They showed clearly that while "hydrometalation" processes form unproductive catalytic intermediates in which hydrogen scrambling occurs rapidly, "silylmetalation" is believed to be the turnover-limiting (and enantioselective) process in certain cases.

Possibilities for the deuterium distribution in the cyclic hydrosilation products via the hydrometalation processes are summarized in Scheme III, while those via the silylmetalation processes are visualized in Schemes IV and V; in these schemes, not all but only one possible route is shown for each product for clarity. In the mechanistic considerations which follow, it is reasonably assumed that (1) the Si–M–H bond angle in the intermediate is 90° owing to the cis oxidative addition of the Si–H bond to low-valent transition-metal complexes[8] (e.g., A → B in Scheme III), (2) the addition of the M–H or M–Si bond to the coordinated olefin proceeds in a cis fashion most favorably when these bonds become parallel to the olefin double bond (e.g., B → C in Scheme III and B → E in Scheme IV), (3) the reverse β-H elimination process is favored in a syn coplanar arrangement of the H–C–C–M moiety (e.g., B ← C in Scheme III), and (4) the silylmetalation is an irreversibly process.[9]

The following mechanistic aspects are deduced for the five- and four-membered cyclic products in light of the processes shown in Schemes III–V.

Five-Membered Cyclic Products. Hydrometalation (H–M). (1) As shown in Scheme III, if hydrosilation proceeds only through the 6-endo hydrometalation process followed by reductive elimination of the catalyst metal from intermediate C, no deuterium scrambling must be observed in the final product i, in which the deuterium atom is found on the C2 atom only. (2) As shown in Scheme III, if hydrosilation once experiences the 5-exo hydrometalation intermediate D before 6-endo hydrometalation processes, deuterium scrambling may result. Thus, the intermediate D formed from B may be in equilibrium with B′ and B″ via β-elimination from the exocyclic deuteriomethyl group. The last two undergo 6-endo hydrometalation to give intermediates C′ and C″, respectively, and subsequent reductive elimination should form ii and iii, respectively, in which the deuterium atom is found on the C1 atom. It is obvious that D is in equilibrium with B, which forms i. When $R^2 = CH_3$, β-elimination of D may occur also from this methyl group to form B‴, which gives, via C‴, the deuteriomethyl group containing product iv. It should be noted that β-H elimination from the X-bearing C3 atom in D may be restricted by the assumption 3 mentioned above.

Silylmetalation (Si–M). (3) Scheme IV summarizes silylmetalation processes for the formation of five-membered products. The common intermediate B may undergo 5-endo silylmetalation to give E, which can form i via reductive elimination. The intermediate E may also undergo β-elimination with the hydrogen atom on C1 and C3 to form F and G, respectively, which form deuterium scrambled products ii and v, respectively, via I and J. When $R^2 = CH_3$, intermediate H may be formed from E and give rise to the formation of product iv. It is the difference from the hydrometalation mechanism that the product v which contains the deuterium atom on C3 may be formed. Inspection of molecular models reveals that in the transition structures of the 5-endo silylmetalation process the M–Si bond hardly becomes parallel to the olefin but is nearly orthogonal. Thus, the 5-endo silylmetalation seems to be a less favorable, high-energy process.

Four-Membered Cyclic Products. Hydrometalation (H–M). (4) As shown in Scheme III, the four-membered cyclic product vi may be formed from the 5-exo hydrometalation intermediate D via reductive elimination. It is noted that even if D experiences B′ or B″, no deuterium scrambling is observed in the product vi. If D experiences B‴, however, stereochemical scrambling between R^2 and CH_2D groups in vi would be observed.

Silylmetalation (Si–M). (5) Four-membered cyclic products may also be formed through silylmetalation processes, as shown in Scheme V, where the 1,1-dimethyl derivative B⁗ is treated for the sake of argument. 4-Exo cyclization of B⁗ gives the four-membered cyclic intermediate L, which forms product vii, where the deuterium atom is present on the C1 atom only. The intermediate L may also undergo β-elimination and hydrometalation reactions followed by reductive elimination to form the deuterium-scrambled products viii and ix. Thus, the

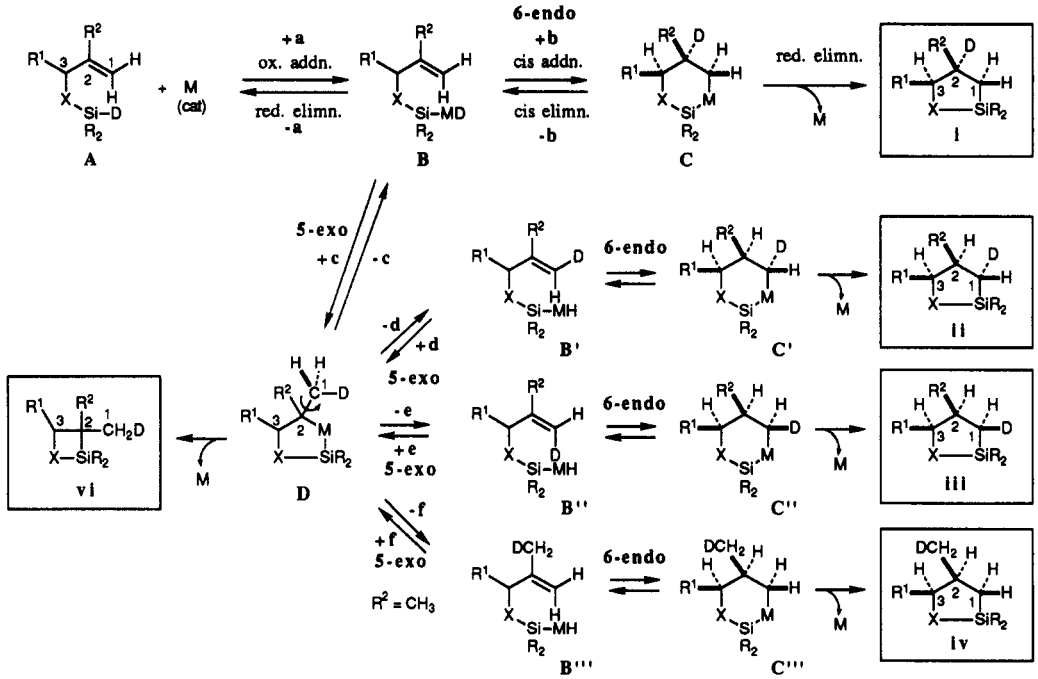
(6) (a) Harrod, J. F.; Chalk, A. J. In *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. 2, pp 673–704. (b) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *19*, 407. (c) An alternative mechanism for the platinum-catalyzed hydrosilation: Lewis, L. N. *J. Am. Chem. Soc.* **1990**, *112*, 5998.

(7) (a) Corey, J. Y. In *Advances in Silicon Chemistry*; Larson, G. L., Ed.; JAI Press: London, England, 1991; Vol. 1, pp 327–387. Fe: (b) Schroeder, M. A.; Wrighton, M. S. *J. Organomet. Chem.* **1977**, *128*, 345. Ru: (c) Ojima, I.; Fuchikami, T.; Yatabe, M. *J. Organomet. Chem.* **1984**, *260*, 335. (d) Seki, Y.; Takeshita, K.; Kawamoto, K.; Murai, S.; Sonoda, N. *J. Org. Chem.* **1986**, *51*, 3890. (e) Seki, Y.; Takeshita, K.; Kawamoto, K. *J. Organomet. Chem.* **1989**, *369*, 117. Co: (f) Takeshita, K.; Seki, Y.; Kawamoto, K.; Murai, S.; Sonoda, N. *J. Org. Chem.* **1987**, *52*, 4864. (g) Seitz, F.; Wrighton, M. S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 289. Rh: (h) Millan, A.; Towns, E.; Maitlis, E. *J. Chem. Soc., Chem. Commun.* **1981**, 673. (i) Onopchenko, A.; Sabourin, E. T.; Beach, D. L. *J. Org. Chem.* **1983**, *48*, 5101. (j) Onopchenko, A.; Sabourin, E. T.; Beach, D. L. *J. Org. Chem.* **1984**, *49*, 3389. (k) Duckett, S. B.; Perutz, R. N. *Organometallics* **1992**, *11*, 90. (l) Doyle, M. P.; Devora, G. A.; Nefedov, A. O.; High, K. G. *Organometallics* **1992**, *11*, 549. Ir: (m) Tanke, R. S.; Crabtree, R. H. *Organometallics* **1991**, *10*, 415. (n) Hostetler, M. J.; Butts, M. D.; Bergman, R. G. *Organometallics* **1993**, *12*, 65.

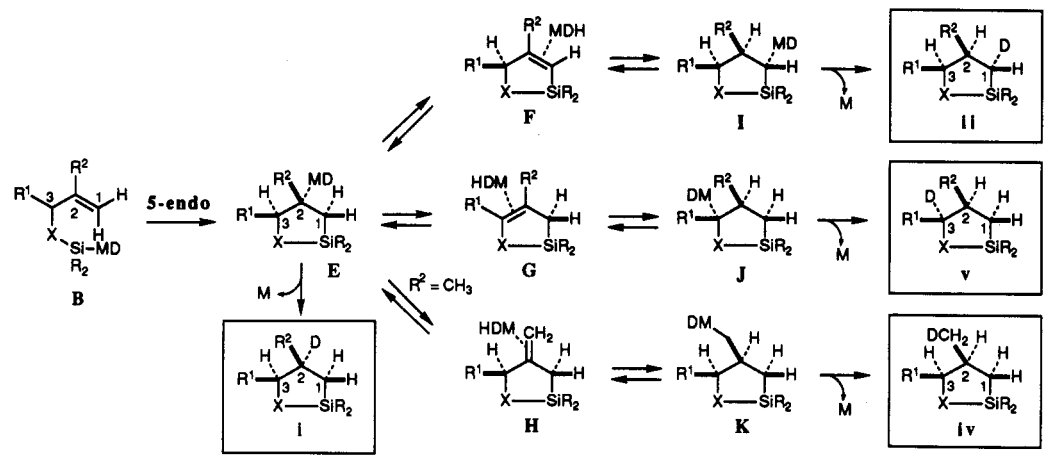
(8) (a) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, England, 1989; Chapter 24, pp 1415–1477. (b) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151. (c) Sakaki, S.; Ieki, M. *J. Am. Chem. Soc.* **1991**, *113*, 5063.

(9) For the reversibility of the silylmetalation process, see ref 7e.

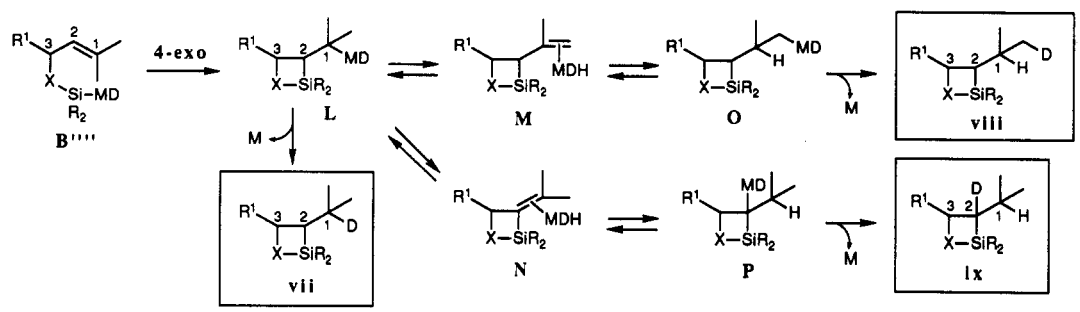
Scheme III. Hydrometalation (H–M)



Scheme IV. Silylmetalation (Si–M)



Scheme V. Silylmetalation (Si–M)



difference between the hydrometalation and silylmetalation mechanisms may reside in the formation of these deuterium-scrambled products in the latter.

The experimental results will be discussed on the basis of these analyses.

Results and Discussion

Introduction of a deuteriosilyl group into allyl alcohols was achieved by treatment with (diethylamino)dimethyldeuteriosilane, $(Et_2N)Me_2SiD$, while allylamines were deuteriosilylated by sequential treatment with *n*-butyllithium and chlorodimethyldeuteriosilane, $ClMe_2SiD$. These deuteriosilanes were readily prepared from the aminochlorosilane precursor as shown in eq 1.

Hydrosilation was carried out under the following general conditions. The platinum-catalyzed reactions were performed in hexane (about 0.5 M solution) in the presence of a solution of the platinum–divinyldisiloxane complex

$$Et_2NSiMe_2Cl \xrightarrow[Et_2O]{1/4\ LiAlD_4} Et_2NSiMe_2D \quad 70\% \qquad (1)$$

$$\xrightarrow{PhCOCl} ClSiMe_2D \quad 84\%$$

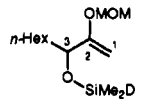
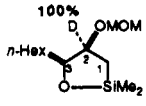
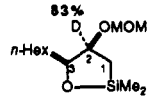
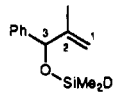
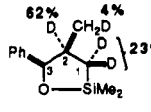
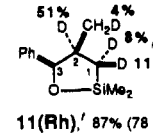
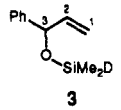
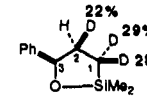
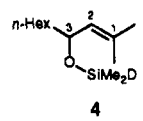
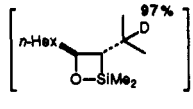
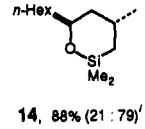
$[Pt[\{(CH_2{=}CH)Me_2Si\}_2O]_2]$[10] (0.5 mol %) as a catalyst at room temperature, while the rhodium-catalyzed reactions were conducted in 1,2-dichloroethane (about 0.5 M solution) in the presence of $[\{RhCl(CH_2{=}CH_2)_2\}_2]$ (0.5–2 mol %) at room temperature to 70 °C. Intramolecular hydrosilations usually proceeded exothermically at room temperature, except for some rhodium–catalyzed reactions of allylamines, which required heating at 70 °C. The hydrosilation product(s) were isolated by bulb-to-bulb distillation, and the D distribution was analyzed by ^1H and/or ^{13}C NMR spectroscopy after purification by preparative GLC.

The deuterium contents and the deuterium distributions in the hydrosilation products from allyl alcohols and allylamines are summarized in Tables I and II, respectively.

I. Allyl Alcohols. Intramolecular hydrosilation of **1** which contains the methoxymethoxy group on the olefinic C2 atom provides one extreme case where the five-membered cyclic product was formed exclusively without deuterium scrambling, as shown in **10(Pt)** and **10(Rh)** in Table I, cis isomers predominating in both cases. In the five-membered-ring product the deuterium is found on the C2 carbon only, suggesting that the reaction proceeds through the 6-endo hydrometalation mechanism as shown in Scheme III: neither 5-exo hydrometalation (Scheme III) nor 5-endo silylmetalation processes (Scheme IV) might occur. This is apparently due to the electronic effect in the vinyl ether moiety. Thus, as shown in Scheme VI, hydrometalation to the highly polarized double bond may proceed selectively in a 6-endo fashion to give the observed product in which the deuterium is found on the C2 carbon. While the deuterium contents and the chemical yield are quite high in the platinum case, both are rather low in the rhodium case, suggesting that some other reaction paths might be involved in the latter case; however, this point remains to be examined further.

Hydrosilation of **2**, which contains the methyl group on the olefinic C2 carbon atom, also proceeded in an endo cyclization mode to form five-membered-ring product **11** exclusively in high yields with both platinum and rhodium catalysts, but extensive deuterium scrambling was observed, as shown in Table I, cis isomers being predominant in both cases. We cannot, however, completely rule out the possibility that a trace amount of unstable four-membered cyclic products were also formed, since they might have been transformed into uncharacterizable nonvolatile materials. The deuterium distribution was analyzed by ^1H, ^{13}C, and ^{13}C-DEPT NMR spectroscopy on **11** in the platinum case and by ^1H NMR spectroscopy on the acetonides **11′** of 1,3-diols obtainable by hydrogen peroxide oxidation (see the Experimental Section for details). The deuterium distributions are quite similar to each other in both the platinum and rhodium cases. Thus, in both cases, *no* deuterium is found on the oxygen-bearing C3 atom, while most of the deuterium is distributed on the methylene C1 (19–23%) and the methyl-bearing C2 atoms (51–62%) and little deuterium (4%) is found on the methyl group. In the platinum case, it has also been found that the recovered allylic alcohol (11% recovery), obtained by quenching the reaction after 11 min with 1% hydrochloric acid, has 4% deuterium on the terminal olefin carbon C1 only, as estimated by ^{13}C NMR. There seems to be no sign suggesting a mechanistic difference between platinum- and rhodium-catalyzed reactions. These results can be analyzed by the hydrometalation mechanism (Scheme III) rather than the silylmetalation mechanism (Scheme V), because the product consists mainly of i, ii, and iii, but no deuterium on C3 (product v) is found. There are two points to be noted. First, only a small amount of the DCH_2-group-containing product iv is formed. The result is consonant with that for 2-methylallyl alcohol with a rhodium complex reported by Bosnich and his coworkers.[3c] They observed, however, no deuterium on the methyl group and attributed the result to the exceedingly fast hydrometalation and β-elimination processes (±c in Scheme III). In our case, the oxygen-bearing carbon has the phenyl group additionally and thus a steric factor may also be important, as shown in Scheme VII. Thus the isomerization from B to B‴ must pass through several transition states and intermediates such as B_{tr}, D, D′, and B'''_{tr}. The interconversion between B and D may be fast, but the process from D to D′ may be unfavorable since the Ph/DCH_2 eclipsed conformer must be involved. The β-hydride elimination may thus occur from the newly formed methyl group preferentially, leaving the existing methyl group intact. Second, the low deuterium content in the recovered allyl alcohol demonstrates that reductive elimination back to A from B (step −a) (and similar steps from B′ and B″) is a rather slow step in comparison with the addition and β-elimination steps (±b, ±c, ±d, and ±e) in Scheme III. The total deuterium contents are 89% in

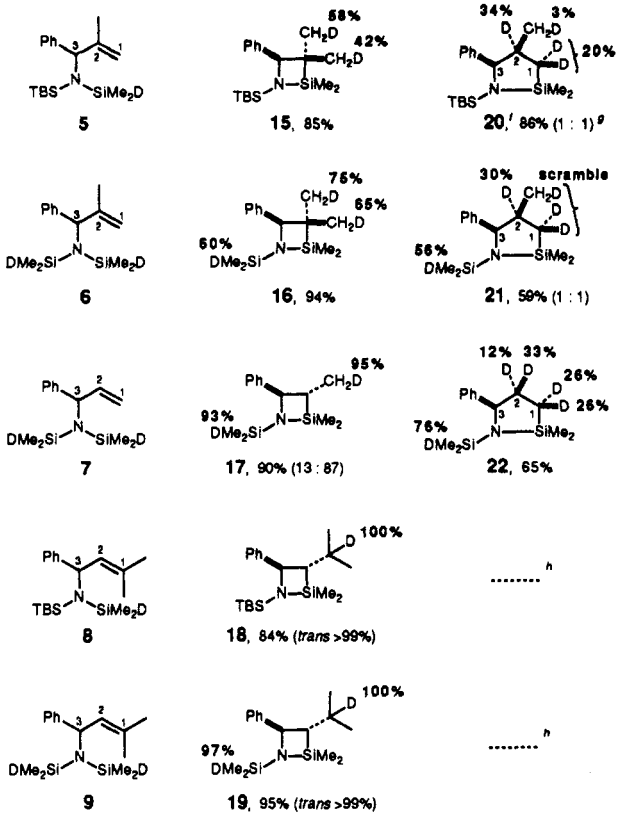
Table I. Intramolecular Hydrosilation of Allylic Alcohols

		
1	**10(Pt)**, 87% (95 : 5)	**10(Rh)**, 55% (83 : 17)
		
2	**11(Pt)**,[e] 87% (86 : 14)	**11(Rh)**,[f] 87% (78 : 22)
	..... [g]	
3		**12**, 89%
		
4	**13**[h]	**14**, 88% (21 : 79)[f]

[a] The D contents were estimated by integral intensities of the ^1H NMR spectra, unless otherwise stated. [b] Determined by GLC. The major isomer is shown. [c] $[Pt[\{(CH_2{=}CH)Me_2Si\}_2O]_2]$ (0.5 mol %), room temperature. [d] $[\{RhCl(CH_2{=}CH_2)_2\}_2]$ (0.5–2 mol %), room temperature. [e] The D contents were estimated by ^{13}C NMR. [f] The D contents were estimated by ^1H NMR of acetonides of 1,3-diols obtainable by oxidation (see text). [g] A complex mixture was formed. [h] Possible intermediate (see text for detail). [i] The D-labeling experiment was not conducted.

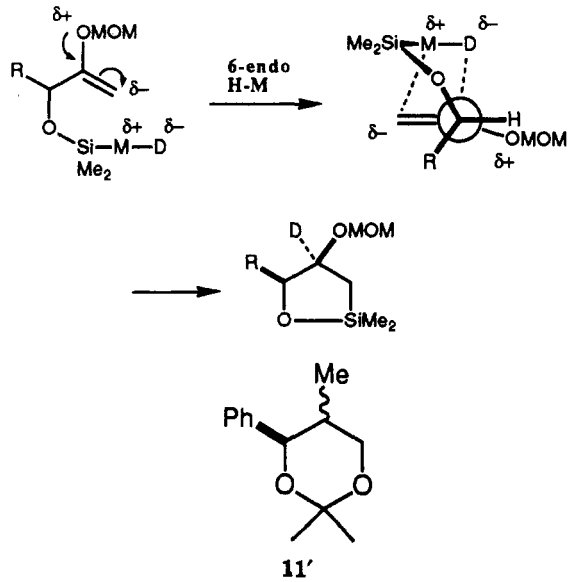
(10) (a) Chandra, G.; Lo, P. Y.; Hitchcock, P. B.; Lappert, M. F. *Organometallics* **1987**, *6*, 191. (b) Hitchcock, P. B.; Lappert, M. F.; Warhurst, N. J. W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 438.

Table II. Intramolecular Hydrosilation of Allylic Amines



[a] The D contents were estimated by integral intensities of the ^{1}H NMR spectra, unless otherwise stated. [b] Determined by GLC. The major stereoisomer is shown. [c] TBS = *t*-BuMe$_2$Si. [d] [Pt[{(CH$_2$=CH)Me$_2$Si}$_2$O]$_2$] (0.5 mol %), room temperature. [e] [{RhCl(CH$_2$=CH$_2$)$_2$}$_2$] (0.5–2 mol %), room temperature, unless otherwise stated. [f] The D contents were estimated by ^{13}C NMR. [g] At 70 °C. [h] No reaction.

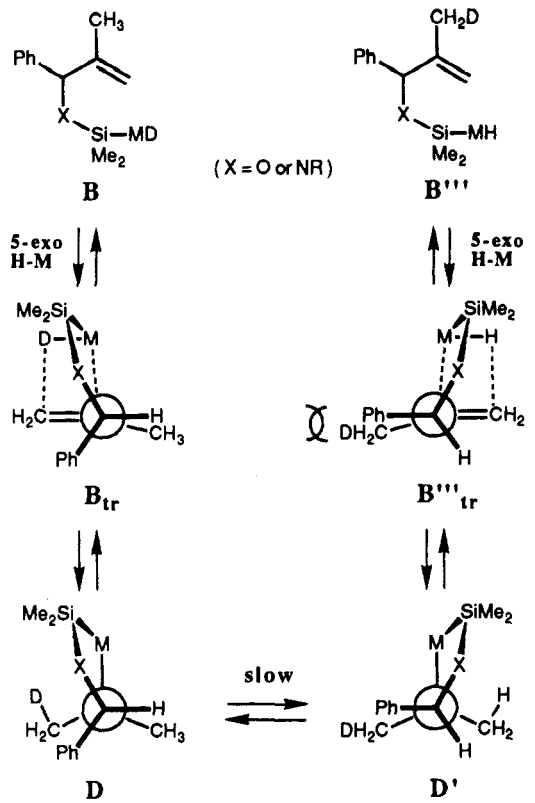
Scheme VI



the Pt case and 74% in the Rh case, indicating that 10–25% of the deuterium has been lost during the cyclization reaction owing to unknown intermolecular exchange processes.

In the case of **3**, which has no substituent on the C2 carbon, the platinum-catalyzed reaction formed only a small amount of five-membered cyclic product and a nonvolatile complex mixture of product, possibly due to the predominant formation of unstable four-membered

Scheme VII



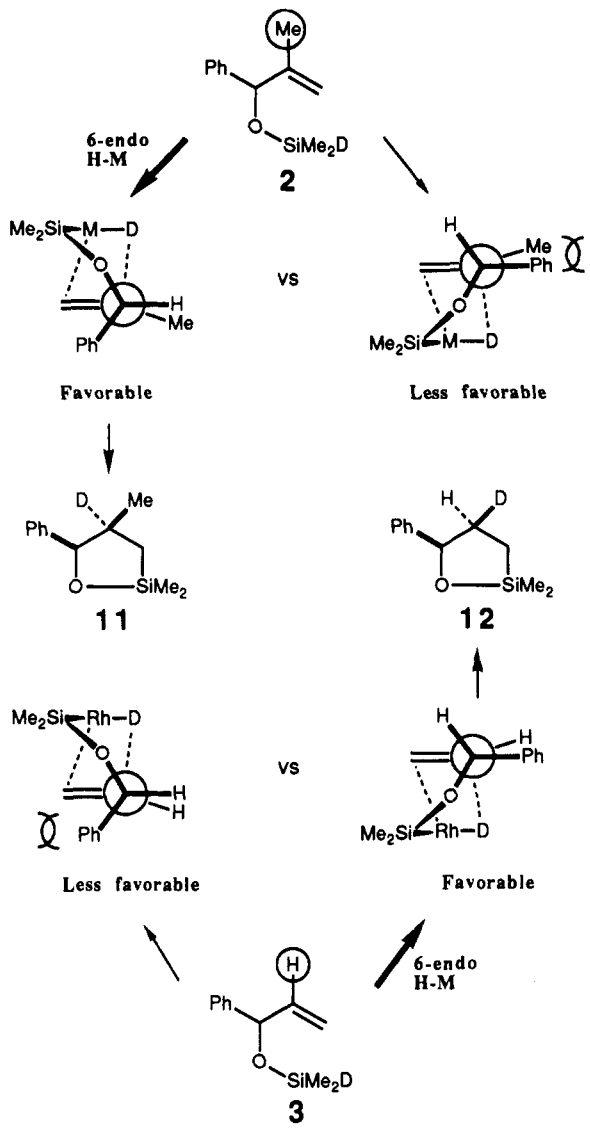
cyclic products (vide infra), while the rhodium-catalyzed reaction gave the five-membered cyclic product **12** in high yield. Here again, deuterium is distributed on C1 and C2 only, no deuterium being found on the C3 atom, as is observed in **11**, suggesting a hydrometalation mechanism similar to that shown in Scheme III.

In seems interesting to compare the deuterium distribution in **12** formed from **3** with that in **11** obtained from **2**. Thus, in **12** the deuterium contents on C2 are roughly 30% lower than those in **11** and those on C1 are nearly 3 times as much as those in **11**. The data might reflect the relative easiness for the formation of the 6-endo intermediate C that carries deuterium on C2 and the 5-exo intermediate D that bears deuterium on C1, as shown in Scheme III. It is noted that the carbon–transition-metal σ-bond in the 5-exo cyclization intermediate D involves a tertiary carbon when R^2 = Me as in **2** and a secondary carbon when R^2 = H as in **3**, while the 6-endo cyclization intermediate C has a primary carbon–metal bond in either case. In view of the relative stability order of transition-metal–alkyl species, i.e., primary > secondary > tertiary,[11] the 5-exo cyclization would be a much less favorable process than the 6-endo cyclization in **2**, in comparison with **3**. The observed deuterium contents on C1 and C2 in **11** and **12** are consistent with this argument.

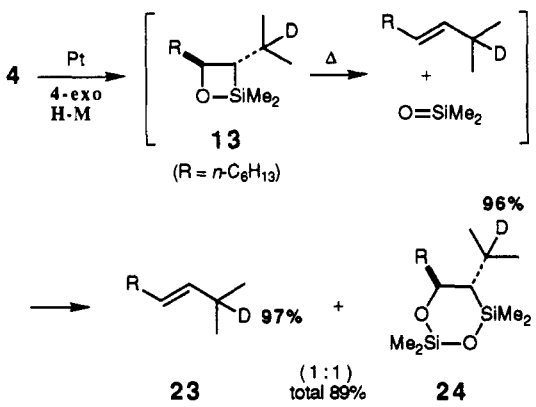
Another interesting point is that the stereoselectivity in the deuterium introduction in **12** is different from that in **11**. Thus, since the cis isomer predominates in **11**, the deuterium atom on C2 is found mainly trans to the phenyl group on C3, while in **12** the deuterium atom is introduced into the cis position to the phenyl group, no deuterium being found on the trans position. The difference may be interpreted by the conformational analysis of transition

(11) E.g.: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; *University Science Books*: Mill Valley, CA, 1987; pp 94–101.

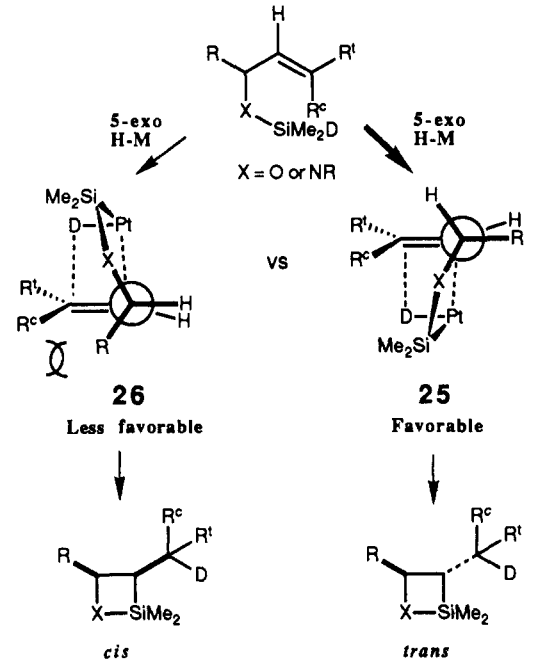
Scheme VIII



Scheme IX



Scheme X



structures for each case, as shown in Scheme VIII. Thus, the preferred conformation might be reversed in these two cases, depending on the presence or absence of the methyl group on the C2 atom.

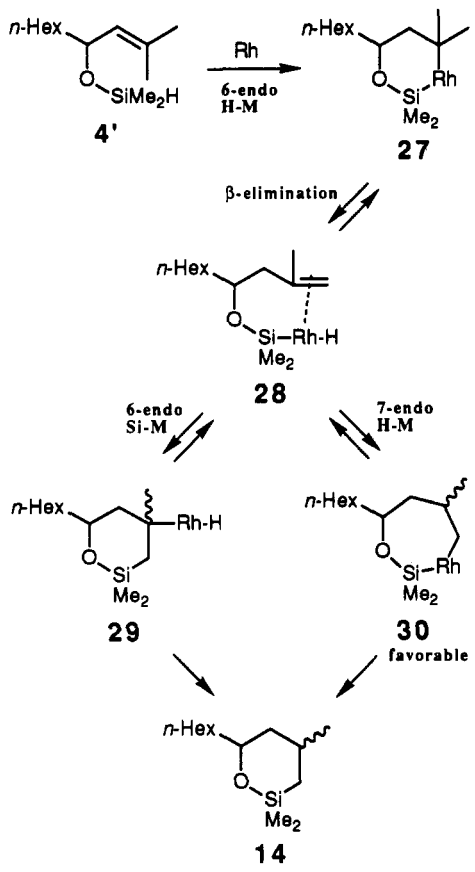
Compound **4** provides the other extreme case. Thus, with the platinum catalyst four-membered cyclic product **13** was formed as the presumed unstable product in which the deuterium was attached to the C1 carbon atom only, while with the rhodium catalyst six-membered cyclic product **14** was obtained selectively via double-bond migration. The formation of **13** was deduced by the isolation of two stable products, olefin **23** and cyclic siloxane **24**, in the ratio of 1:1 in high total yields, as shown in Scheme IX. Thus, the primary product **13** might decompose to the olefin and a reactive silanone species[12] and the latter might undergo insertion into **13** to form the observed cyclic siloxane **24**. A similar observation has been reported by Frye.[13] The deuterium atoms in **23** and **24** are found on the olefin C1 carbon exclusively. The results suggest that the hydrosilation of **4** proceeds by a 5-exo hydrometalation mechanism via an intermediate such as D in Scheme III, from which the four-membered cyclic product vi may be formed by reductive elimination. The 6-endo cyclization which leads to the formation of a tertiary carbon–metal bond should be a disfavored process. The alternative silylmetalation processes may also be ruled out by the absence of deuterium scrambled products such as viii and ix in Scheme V. The trans selectivity in **13** may be explained by analysis of the transition structures shown in Scheme X, where X = O and $R^c = R^t$ = Me. Thus, an allylic strain, R^c/H, encountered in the favorable transition structure **25** should be much smaller than the R^c/R strain present in the less favorable structure **26**, the R^c/X strain being comparable in both cases.

The exclusive formation of **14** with rhodium catalyst is also noted. Although the deuterium-labeling experiment was not performed for this reaction, it is obvious that the reaction proceeds through the hydrometalation/β-elimination sequence leading to the terminal olefin intermediate which undergoes ring closure to the observed **14**, as shown in Scheme XI. The first 6-endo hydrometalation step forms **27**, which contains the tertiary carbon–rhodium bond and hence would readily undergo β-elimination to form **28**. Two possible routes from **28** may be envisaged: while the 6-endo silylmetalation route gives another tertiary

(12) 1-Oxa-2-silacyclobutane skeletons have been known to undergo this type of thermal [2 + 2] cycloreversion. (a) Raabe, G.; Michl, J. *In The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, England, 1989; Chapter 17. (b) Brook, A. G.; Chatterton, W. J.; Sawyer, J. F.; Hughes, D. W.; Vorspohl, K. *Organometallics* **1987**, *6*, 1246.

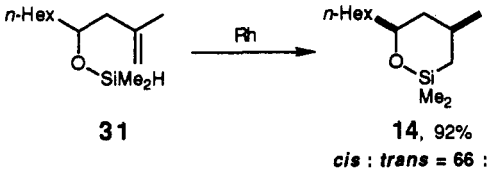
(13) Lane, T. H.; Frye, C. L. *J. Organomet. Chem.* **1979**, *172*, 213.

Scheme XI



carbon–rhodium species, **29**, the 7-endo hydrometalation process forms **30**, which contains the primary carbon–rhodium bond. The latter might thus be a more favorable process than the former.

A control experiment was carried out in connection with the structure of the terminal olefin complex **28**, as shown in eq 2. Thus, the hydrosilyl ether of homoallyl alcohol



(2)

31, a double-bond isomer of **4'**, was subjected to the standard rhodium-catalyzed hydrosilation condition to give **14** in high yield. Significantly, the cis isomer was formed preferentially in the ratio of cis:trans = 66:34 in contrast to the high trans selectivity observed with the allyl alcohol **4'**. These two cases may involve the common intermediate **28**, but the olefin face selectivities are different from each other. The result demonstrates that the olefin part in the intermediate **28** from **4'** is not free from the rhodium center, the β-elimination may thus be immediately followed by the hydrometalation step.

The above results have all been consistently explained by the hydrometalation mechanism, and there might be no evidence that suggests a possibility for the silylmetalation mechanism. There is a striking difference in the regiochemistry between the platinum- and rhodium-catalyzed intramolecular hydrosilations of allylic alcohols. However, both reactions seem to prefer 5-exo hydrometalation processes as lower-energy steps, unless strong electronic effects dominate as in **1**. Differences are present in the final product-forming reductive-elimination steps. Thus, in the platinum case tertiary carbon–metal species hardly undergo reductive elimination but secondary and primary carbon–metal species can, while in the rhodium case only the primary carbon–metal species can reach the final product, secondary and tertiary carbon–metal species undergoing β-elimination exclusively.

II. Allylamines. The results are summarized in Table II. There is a striking difference in the regiochemistry between the platinum- and rhodium-catalyzed reactions. Thus, while the platinum-catalyzed reactions form four-membered cyclic compounds exclusively in all cases examined, five-membered cyclic products are obtained with the rhodium catalyst. The platinum-catalyzed reactions will be discussed first separately.

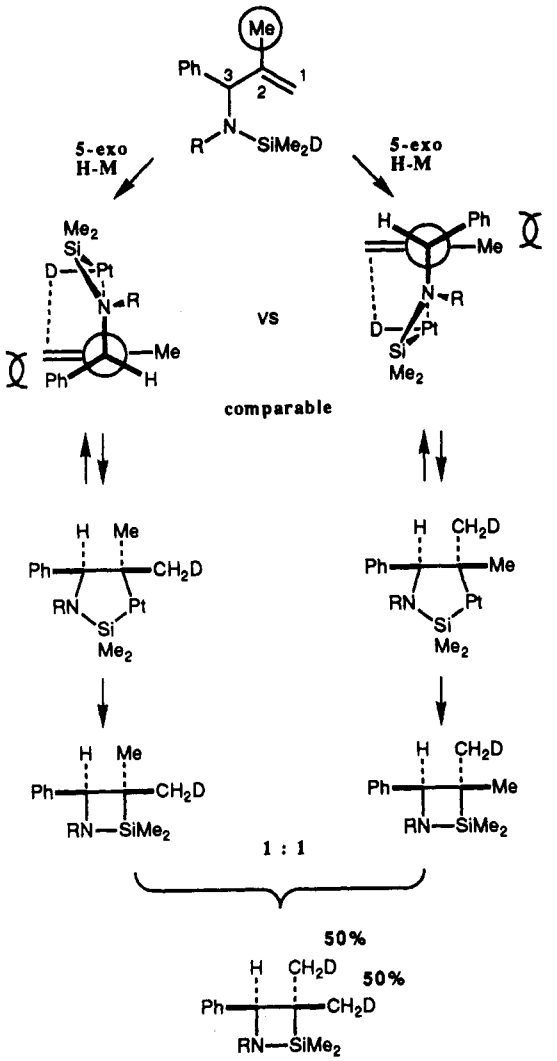
Compounds **5** and **6** have a common (2-methylallyl)-amine skeleton, but **5** contains one DMe_2Si group and one t-$BuMe_2Si$ group on nitrogen, while **6** has two DMe_2Si groups. The platinum-catalyzed reactions formed **15** and **16**, respectively, which contain a tertiary carbon–silicon bond. The following two points are noted: (1) deuterium atoms are distributed to the two methyl groups in comparable amounts, this puzzling result being discussed later; (2) in addition, **16** contains a roughly statistical distribution of deuterium atoms even to the extracyclic silyl group, no total deuterium loss being observed during the reaction. The latter result demonstrates that the two DMe_2Si groups in **6** have become undistinguishable prior to the cyclization. This is attained by fast equilibrium between A and B (±a) as well as between B and D (±c) in Scheme III, where X stands for DMe_2SiN. The fast reductive-elimination (step −a) in this case is in sharp contrast to the result observed for the allyl alcohol counterpart **2**, in which step −a seems to be rather slow, as mentioned above.

The almost statistical deuterium distribution to the two methyl groups in **15** and **16** is also different from the result with the allyl alcohol analogue **2**: little deuterium is found on the existing methyl group in the product **11** from the latter, regardless of the catalyst metals, platinum or rhodium, as discussed above (cf. Scheme VII). Two possibilities may be envisaged for the deuterium distributions in the allylamine cases. One possibility is that the transition structures are similar to those shown in Scheme VII, but the β-elimination steps from D to B (also D′ to B‴) are comparable to or slower than the ring-flipping process between D and D′. This might be possible when the cyclic intermediates D and D′ are more stable for allylamine cases (X = $NSiR_3$) than for the allyl alcohol cases (X = O). One reason for this situation might reside in the bond length difference between nitrogen and oxygen, typical Si–N bond lengths (1.73 Å) being slightly longer than Si–O bond lengths (1.64 Å);[14] the bond angles, Si–N–R and Si–O–R, are comparable (ca. 120°). It is noted here that the final four-membered cyclic product, the 1-aza-2-silacyclobutane ring, appears to be less angle-strained and hence more stable than a 1-oxa analogue, as determined by X-ray analysis.[15] Another possibility is a non-face-selective hydrosilation, as shown in Scheme XII. The two energetically comparable transition structures might

(14) (a) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, England, 1989; Chapter 3, pp 254–266. (b) Gundersen, G.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Dalton Trans.* **1985**, 191.

(15) Tamao, K.; Nakagawa, Y.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 218.

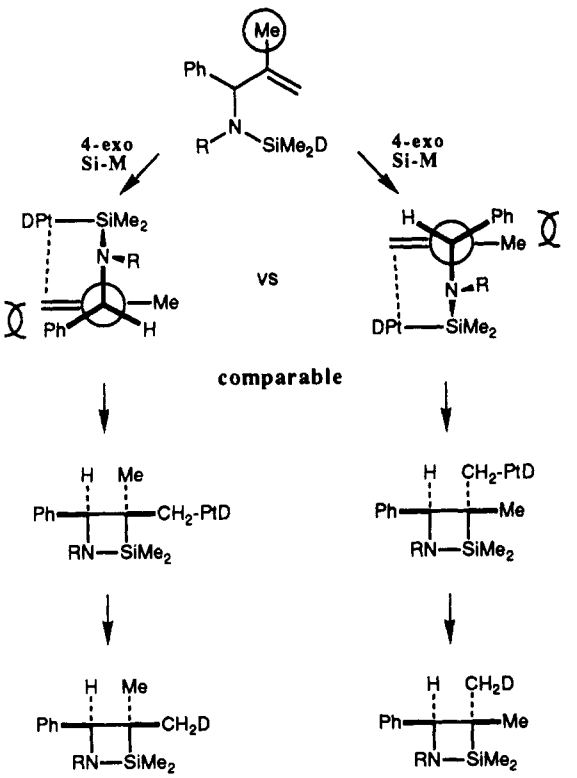
Scheme XII



thus be formed by a subtle conformational change from the face-selective conformers shown in Scheme VII due to a slightly longer Si–N bond. Products arising from these two structures should have the observed deuterium distributions. We cannot specify, however, which possibility is more plausible for the deuterium scrambling.

There are two possibilities for the final product-forming steps. As shown in Schemes III and XII, the four-membered cyclic product may be formed via reductive elimination of metal from the hydrometalation intermediates. Since the intermediates, however, contain the tertiary carbon–platinum bond, the reductive elimination would be an unfavorable process. Alternatively, a silylmetalation mechanism is visualized in Scheme XIII. Thus, 4-exo silylmetalation may form energetically comparable transition structures via non-face-selective addition to the olefin. The resulting intermediates contain the primary carbon–platinum bond and hence may undergo reductive elimination readily. Therefore, the above consideration might suggest that the platinum-catalyzed hydrosilation of **5** and **6** may proceed through nonproductive 5-exo hydrometalation processes for deuterium scrambling followed by a productive 4-exo silylmetalation process. In connection with the last process, it may be noted that insertion of olefin into the platinum–silicon bond has

Scheme XIII



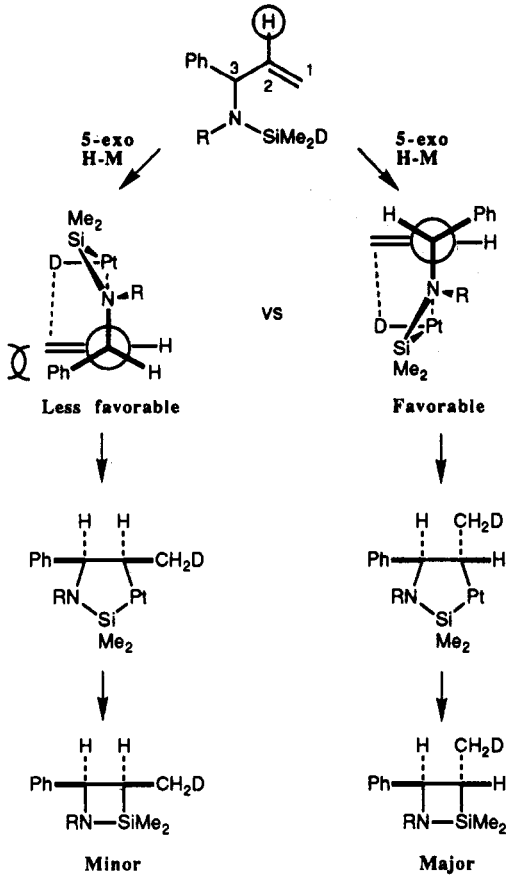
recently been reported.[16] The present study, however, has not clarified the reason why 6-endo hydrometalation processes leading to five-membered cyclic products, as observed in the rhodium case, are not involved at all in the product-forming step in these platinum cases.

Compound **7**, which has no substituent on the C2 carbon atom, formed **17**, the trans isomer being preferred. Deuterium atoms are found on the methyl group and the exocyclic silyl group only. In contrast to **16**, **17** shows little deuterium scrambling between the methyl group and the exocyclic silyl group. Thus, in scheme III (R^2 = H), there may well be rapid equilibrium between B and D, but the reductive elimination from B (step –a) must be relatively slow in comparison with the reductive elimination from D to form vi. The trans stereoselectivity may be visualized in Scheme XIV. Thus, without a substituent on C2, one transition structure should be more favorable than the other to account for the stereoselectivity. The five-membered cyclic intermediates contain the secondary carbon–platinum bond, which may be ready for the reductive elimination. Although the observed results can equally be explained by an alternative silylmetalation mechanism, the hydrometalation mechanism may be more plausible in light of the results with compounds **8** and **9**, described below.

Allylamine derivatives **8** and **9**, which contain two methyl groups on the terminal olefin carbon C1, cleanly formed **18** and **19**, respectively. Deuterium was found on the C1 atom quantitatively in both cases and also without loss of deuterium content on the exocyclic silyl group in **19** from **9**, which has two DMe_2Si groups on the nitrogen atom. These results can be explained by a sequence of 5-exo hydrometalation (giving D) and reductive elimination (leading to vi) in Scheme III, as discussed above for the

(16) (a) Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1989**, 467. (b) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *Organometallics* **1991**, *10*, 16.

Scheme XIV

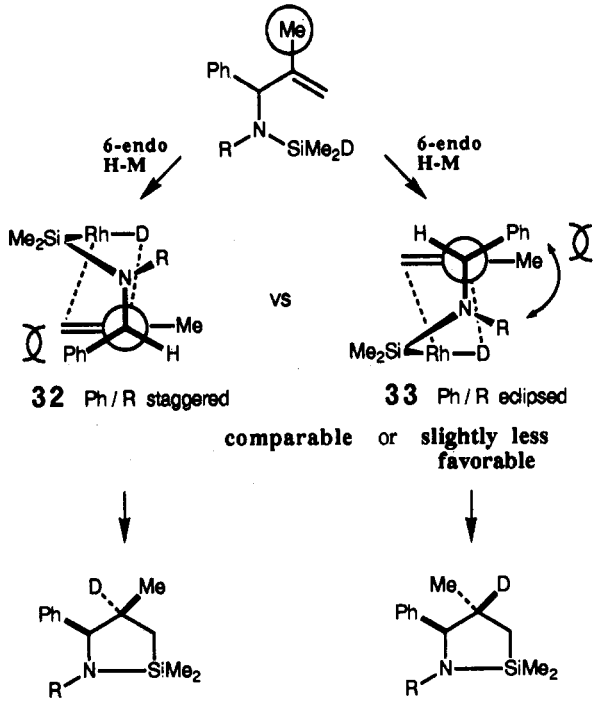


formation of **13** from allylic alcohol **4**; we will not repeat the same discussion.

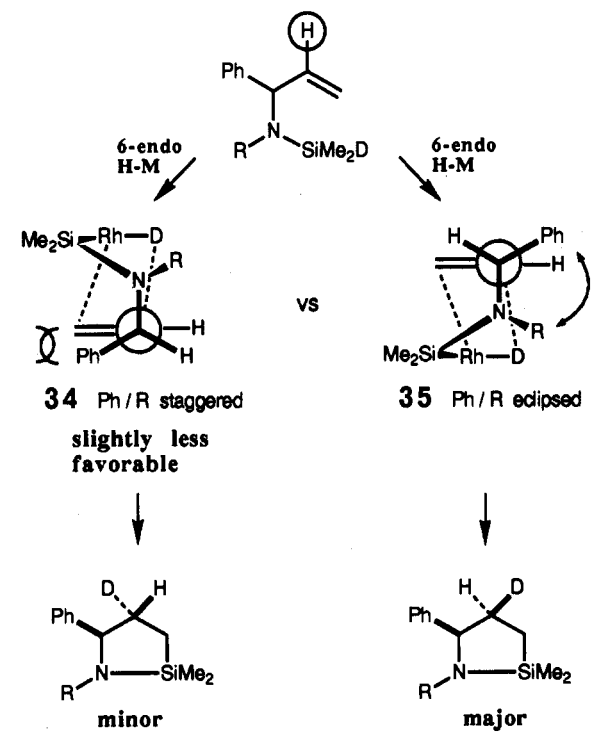
We now turn to the rhodium-catalyzed reactions. The rhodium-catalyzed intramolecular hydrosilations of allylamines proceeded relatively slowly at room temperature or at 70 °C, in comparison with those of allyl alcohols. Five-membered cyclic products **20–22** were obtained from **5–7**, respectively, as observed with the corresponding allylic alcohols discussed above, but no reaction was observed with the trisubstituted olefin derivatives **8** and **9** under the same conditions. The deuterium distributions in **20** and **21** are similar to those observed in the oxygen analogue **11** in Table I. Thus, most characteristically, only a small amount of deuterium is found on the methyl group in *cis*-**20**, as estimated by ^{13}C NMR spectroscopy. The mechanisms for the deuterium scrambling may be essentially the same as those discussed for **11** and be explained by the 5-exo hydrometalation steps shown in Schemes III and VII.

The stereoselectivity, however, has been lost in **20** and **21** in contrast to **11**. Possible transition structures in the product-forming step are shown in Scheme XV. It is noted that the conformations are different from those for the alcohol analogue shown in Scheme VIII and the differences may be attributable to the slightly longer bonds involving nitrogen, as discussed above for the platinum-catalyzed reactions of **5** and **6** (cf., Schemes XII–XIV). The two conformers **32** and **33** might be similar to each other with respect to the "allylic strain", but in **33** the Ph group on silicon and the R group on the planar nitrogen atom[14] become eclipsed, while in **32** these are staggered. Thus, totally **33** may be slightly less favorable. Actually, a nearly 1:1 mixture of cis and trans isomers has been formed. Although the deuterium contents in **21** have not been

Scheme XV



Scheme XVI



determined exactly, the substantial decrease of the deuterium contents on the exocyclic silyl group clearly demonstrates that the reductive elimination step (–a) in Scheme III must be rather fast.

Deuterium distribution in **22** obtained from **7**, which has no methyl group on the olefin C2 atom, is also similar to that observed in the oxygen analogue **12** in Table I, except that deuterium is incorporated at both sites on the C2 atom in the former, indicative of lower face-selective hydrosilation as observed in **20** and **21**. The low face selectivity may be explained by inspection of the possible transition structures **34** and **35** shown in Scheme XVI. While **34** suffers from an allylic strain, there is a Ph/R-

eclipsed strain in 35, and therefore the former may be slightly less favorable.

No reaction with 8 and 9 suggests that a 6-endo hydrometalation process would be unfavorable in the rhodium-catalyzed hydrosilation of allylamines, especially when it leads to the formation of the tertiary carbon–rhodium bond, in contrast to that of allyl alcohol analogue 4, in which the process occurs readily to eventually form 14, as discussed above.

In summary, of all the data obtained in this study, formation of 15 from 5 (and 16 from 6) with the platinum catalyst seems to be abnormal: the tertiary carbon–silicon bond is formed in the four-membered cyclic product without difficulty, and also deuterium is distributed to the two exocyclic methyl groups in comparable amounts. For this case, we have suggested a possibility of a silylmetalation mechanism in the product-forming step. Other data have been explained consistently by hydrometalation mechanisms (Scheme III). The present analyses, however, do not necessarily rule out the possibility for the silylmetalation mechanism in some cases. For example, in the formation of 11 from 2, we have ruled out the silylmetalation processes only on the basis of the absence of deuterium on the C3 carbon atom (v in Scheme V). However, there is the possibility that the β-elimination process from E to G in Scheme IV is a high-energy, less favorable process, since G is the least stable complex of the tetrasubstituted olefin. Much remains to be studied for a full understanding of the mechanism.

Experimental Section

General Remarks. ^{1}H NMR spectra were measured in $CDCl_3$ of C_6D_6 with a JEOL JNM-GX-400 (400 MHz), Varian VXR-200 (200 MHz), or Varian VXR-500 (500 MHz) spectrometer, and the chemical shifts were referenced to internal TMS or $CHCl_3$ (7.25 ppm) or C_6D_5H (7.20 ppm). ^{13}C NMR spectra were measured with a JEOL JNM-GX-400 (100 MHz), Varian VXR-200 (50 MHz), or Varian VXR-500 (126 MHz) spectrometer. Infrared spectra were obtained with a Hitachi 270-20 spectrometer. Analytical and preparative GLC measurements were performed on a Shimadzu GC-4B and/or a Gasukuro Kogyo GC-380 gas chromatograph, equipped with a 3-m column packed with 30% silicone DC550 on Celite 545. Thin-layer chromatography (TLC) was performed on plates coated with a 0.25-mm layer of silica gel 60F-254 (Merck). Column chromatography was performed by using Kieselgel 60 (70–230 mesh) (Merck). Preparative medium-pressure liquid chromatography was performed with a silica gel prepacked CIG (Kusano) column. Elemental analyses were performed at the Microanalysis Center of Kyoto University. Ether, pentane, and hexane were distilled from sodium under nitrogen. Dichloroethane was dried over calcium hydride under nitrogen. Lithium aluminum deuteride was purchased from Aldrich and *n*-BuLi from Nacalai Tesque. Chloro(diethylamino)-dimethylsilane,[17] allylic alcohols,[2d] and amines[2f,15] were prepared as reported previously. The platinum catalyst $[Pt\{(CH_2{=}CHSiMe_2)_2O\}_2]$ (0.25 M xylene solution)[10] and the rhodium complex $[RhCl(CH_2{=}CH_2)_2]_2$[18] were prepared by published procedures.

Preparation of Deuterio(diethylamino)dimethylsilane. To a suspension of lithium aluminum deuteride (1.07 g, 25.5 mmol) and dry ether (90 mL) was added with stirring chloro-(diethylamino)dimethylsilane (15.6 g, 95.9 mmol) at room temperature under nitrogen. An exothermic reaction occurred. After several hours pentane (ca. 100 mL) was added to cause separation of a gray heavy inorganic layer. The supernatant organic layer was taken out by a syringe and concentrated. The residue was distilled to give 8.91 g (70% yield) of deuterio(diethylamino)-dimethylsilane: bp 106–112 °C.

Preparation of Chlorodeuteriodimethylsilane. Freshly distilled benzoyl chloride (16.9 g, 120 mmol) was added to deuterio(diethylamino)dimethylsilane (13.3 g, 100 mmol) at 0 °C under nitrogen. The mixture was stirred at room temperature for several hours and then distilled to give 8.07 g (84% yield) of chlorodeuteriodimethylsilane boiling at 33–35 °C.

Preparation of Silyl Ethers. The silyl ethers were prepared by the reaction of the corresponding alcohols with deuterio-(diethylamino)dimethylsilane and characterized by spectral comparison with nondeuterated counterparts reported previously. A typical procedure is given for the preparation of 2 as follows. Deuterio(diethylamino)dimethylsilane (1.78 mL, 10.03 mmol) was added to 2-methyl-1-phenyl-2-propen-1-ol (1.24 g, 8.36 mmol) at room temperature under nitrogen. After the mixture stood at room temperature for 2 h, the volatile materials diethylamine and excess aminosilane were removed in vacuo. Bulb-to-bulb distillation of the residue afforded the silyl ether I (1.62 g, 94% yield) boiling over the range of 55–65 °C/1.0 mmHg (bath temperature). The product was almost pure but was further purified by preparative GLC before use. No ^{1}H atom was detected on the silyl group by ^{1}H NMR spectroscopy.

Preparation of Silylamines. The silyl amines were prepared from the corresponding amines by a sequence of metalation and silylation with an appropriate chlorosilane in essentially the same manner as reported previously[2f,15] and characterized by spectral comparison with the nondeuterated counterparts. A typical procedure is shown for the preparation of 9 as follows. To a solution of 1-amino-3-methyl-1-phenyl-2-butene (831 mg, 5.15 mmol) in ether (50 mL) was slowly added *n*-BuLi (1.58 M in hexane; 3.9 mL, 6.2 mmol) at −78 °C under nitrogen. The mixture was warmed gradually to −40 °C over 0.5 h, stirred at −40 °C for 0.5 h, and cooled down again to −78 °C. To the mixture was slowly added chlorodeuteriodimethylsilane (0.69 mL, 6.2 mmol). The mixture was warmed to room temperature over 0.5 h and stirred for 0.5 h. GLC analysis showed completion of monosilylation. After it was cooled to −78 °C, the reaction mixture was treated with *n*-BuLi (1.58 M in hexane; 3.3 mL, 5.2 mmol), stirred for 1.5 h, and then treated with chlorodeuteriodimethylsilane (0.58 mL, 5.2 mmol). The mixture was warmed to room temperature over 0.5 h and stirred for 0.5 h. GLC analysis showed completion of disilylation. The reaction mixture was diluted with hexane and filtered. The filtrate was concentrated and the remaining oil was diluted with hexane and filtered again. The filtrate was concentrated, and bulb-to-bulb distillation of the remaining oil gave 9 (1.31 g, 91% yield) boiling over the range of 110–130 °C/0.5-1.0 mmHg (bath temperature). The product was almost pure but was further purified by preparative GLC before use. No ^{1}H atom was detected on the silicon atom by ^{1}H NMR spectroscopy.

The spectral and analytical data of the nondeuterated analogue of the new compound 5 are as follows. ^{1}H NMR (200 MHz, C_6D_6): δ −0.22 (d, 3H, J = 3.6 Hz), 0.17 (d, 3H, J = 3.6 Hz), 0.28 (s, 3H), 0.36 (s, 3H), 1.09 (s, 9H), 1.61 (s, 3H), 4.72–4.85 (m, 2H), 5.17–5.23 (m, 1H), 5.40–5.46 (m, 1H), 7.04–7.20 (m, 3H), 7.36–7.44 (m, 2H). ^{13}C NMR (50 MHz, C_6D_6): δ −3.20, −1.48, 0.96, 2.45, 20.62, 21.93, 27.62, 66.37, 114.38, 130.61, 141.73, 147.84. Anal. Calcd for $C_{18}H_{33}NSi_2$: C, 67.64; H, 10.41; H, 4.38. Found: C, 67.74; H, 10.60; H, 4.41.

Intramolecular Hydrosilation. Product analyses were carried out on the hydrosilation products obtained from the nondeuterated analogues, some of which have already been reported previously.[2b,d,f,15]

Intramolecular Hydrosilation of an Allylic Alcohol Catalyzed by a Pt Complex. Typical Procedure. To a mixture of silyl ether 2 (216 mg, 1.04 mmol) and hexane (2.0 mL) was added a solution of $[Pt\{(CH_2{=}CHSiMe_2)_2O\}_2]$ (0.25 M xylene solution; 21 μL, 5.2 × 10^{-3} mmol) at room temperature under nitrogen. After 2 h, disappearance of the olefin was confirmed by ^{1}H NMR spectroscopy. Bulb-to-bulb distillation (bath

(17) Tamao, K.; Nakajo, E.; Ito, Y. *Tetrahedron* **1988**, *44*, 3997.
(18) Cramer, R. *Inorg. Synth.* **1974**, *15*, 14.

temperature 90–105 °C/0.6 mmHg) of the reaction mixture gave the intramolecular hydrosilation product **11** (187 mg, 87% yield). The stereoisomers were separated by GLC.

Intramolecular Hydrosilation of a Nondeuterated Analogue of 4. Pt-Catalyzed Reaction. The hydrosilation was carried out in essentially the same manner as above in the presence of 1 mol % of the platinum catalyst. After completion of the hydrosilation, direct analysis of the reaction mixture by ^{1}H and ^{13}C NMR spectroscopy showed spectra consistent with the formation of the four-membered ring compound **13** (nondeuterated) as follows. ^{1}H NMR (200 MHz, C_6D_6): δ 0.42 (s, 3H), 0.48 (s, 3H), 0.80–2.10 (m, 21H), 4.07 (broad t, 1H, J = 8.9 Hz). ^{13}C NMR (50 MHz, C_6D_6): δ 1.26, 5.13, 14.35, 22.53, 22.63, 23.12, 27.13, 27.72, 29.89, 32.42, 39.96, 44.39, 75.55. The ^{13}C NMR spectra showed 13 peaks. If the product were a dimer of **13**, two diastereomers could exist and the peak number would be 26. Thus, the product was considered to be monomeric. Bulb-to-bulb distillation (bath temperature 110–140 °C/0.8 mmHg) of the reaction mixture gave a 1:1 mixture of **23** and **24** (total 71–89% yield). Each product was isolated by preparative GLC. **23** (nondeuterated): ^{1}H NMR (200 MHz, C_6D_6) δ 0.87 (t, 3H, J = 6.8 Hz), 0.95 (d, 6H, J = 6.7 Hz), 1.14–1.42 (m, 8H), 1.88–2.02 (m, 2H), 2.12–2.34 (m, 1H), 5.30–5.40 (m, 2H); ^{13}C NMR (50 MHz, C_6D_6) δ 14.10, 22.65, 22.72, 28.82, 29.65, 31.00, 31.76, 32.56, 127.25, 137.49; IR (neat, cm^{-1}) 2968, 2936, 2864, 1470, 970. Anal. Calcd for $C_{11}H_{22}$: C, 85.63; H, 14.37. Found: C, 85.75; H, 14.58. **24** (nondeuterated): ^{1}H NMR (200 MHz, C_6D_6) δ 0.26 (s, 3H), 0.28 (s, 3H), 0.31 (s, 3H), 0.33 (s, 3H), 0.89–1.00 (m, 6H), 1.03 (d, 3H, J = 7.1 Hz), 1.10 (dd, 1H, J = 4.0 Hz, J = 7.8 Hz), 1.22–1.82 (m, 10H), 1.83–2.05 (m, 1H), 4.18–4.30 (m, 1H); ^{13}C NMR (50 MHz, C_6D_6) δ −0.50, 1.04, 1.99, 4.25, 14.33, 21.16, 22.92, 23.10, 26.05, 27.80, 29.73, 32.39, 38.23, 42.63, 73.65; IR (neat, cm^{-1}) 2968, 2940, 2864, 1468, 1258, 1050, 986. Anal. Calcd for $C_{15}H_{34}O_2Si_2$: C, 59.94; H, 10.73. Found: C, 59.72; H, 10.98.

Intramolecular Hydrosilation of Allylic Alcohols Catalyzed by a Rh Complex. Typical Procedure. To a mixture of silyl ether **3** (183 mg, 0.95 mmol) and dichloroethane (1.8 mL) was added $[RhCl(CH_2{=}CH_2)_2]_2$ (1.8 mg, 4.7 × 10^{-3} mmol) at room temperature under nitrogen. After 8.5 h, disappearance of the olefin was confirmed by ^{1}H NMR spectroscopy. Bulb-to-bulb distillation (bath temperature 90–120 °C/0.6 mmHg) of the reaction mixture afforded the hydrosilation product **12** (163 mg, 89% yield): ^{1}H NMR (nondeuterated; 200 MHz, C_6D_6) δ 0.21 (s, 6H), 0.50–0.84 (m, 2H), 1.50–1.74 (m, 1H cis to Ph, 0.7% NOE enhancement upon irradiation at δ 4.86), 2.07–2.26 (m, 1H trans to Ph, 2.6% NOE enhancement upon irradiation at δ 4.86), 4.86 (dd, J = 4.9 Hz, J = 9.3 Hz, 1H), 7.10–7.35 (m, 3H), 7.40–7.52 (m, 2H); ^{13}C NMR (50 MHz, C_6D_6) δ 33.30, 45.29, 68.67, 113.11, 158.93, 160.49, 161.86, 179.07. Anal. Calcd for $C_{11}H_{16}OSi$: C, 68.69; H, 8.38. Found: C, 68.95; H, 8.60.

For the isolation of **10**, the rhodium catalyst was removed before distillation as follows, because the product decomposed substantially during distillation in the presence of the catalyst. After the hydrosilation, the solvent was removed under reduced pressure. The residue was stirred with activated charcoal (200 mg for 1 mmol of **1**) in hexane (2 mL) overnight and filtered. The filtrate was distilled bulb-to-bulb under reduced pressure to give **10**.

Intramolecular Hydrosilation of a Nondeuterated Analogue of 4. Rh-Catalyzed Reaction. The reaction was carried out in a manner similar to that above to form **14** as an isomeric mixture in the ratio cis:trans = 21:79. The stereochemistry of **14** was tentatively assigned by the ^{13}C NMR chemical shifts of the methyl groups on silicon, in light of the empirical rule for six-membered cyclic acetonides of 1,3-diols: larger chemical shift differences are assignable to the cis isomers.[19] Spectral and analytical data for **14** are as follows. cis: ^{1}H NMR (200 MHz, C_6D_6) δ 0.16–0.32 (m, 7H, including two singlets at 0.18, 0.22), 0.54–0.65 (m, 1H), 0.88–1.05 (m, 6H), 1.22–1.80 (m, 12H), 3.62–3.78 (m, 1H); ^{13}C NMR (50 MHz, C_6D_6) δ −2.19, −0.06, 14.33, 22.79, 23.06, 25.92, 27.44, 29.78, 29.84, 32.33, 39.35, 44.71, 74.01; IR (neat, cm^{-1}) 2932, 2864, 1458, 1252, 1144, 1040, 920, 846, 798. trans: ^{1}H NMR (200 MHz, C_6D_6) δ 0.21 (s, 3H), 0.25 (s, 3H), 0.36 (dd, 1H, J = 9.2 Hz, J = 14.4 Hz), 0.73 (dd, 1H, J = 4.8 Hz, J = 14.2 Hz), 0.94 (broad t, J = 6.6 Hz), 1.04 (d, 3H, J = 6.6 Hz), 1.20–1.85 (m, 12H), 1.90–2.20 (m, 1H), 4.01–4.16 (m, 1H); ^{13}C NMR (50 MHz, C_6D_6) δ 1.33, 1.52, 14.33, 21.91, 23.06, 25.03, 25.09, 26.56, 29.77, 32.39, 37.92, 41.86, 71.33; IR (neat, cm^{-1}) 2936, 2868, 1458, 1252, 1156, 1048, 1004, 916, 842, 794. Anal. Calcd for $C_{13}H_{28}OSi$ (cis, trans mixture): C, 68.35; H, 12.35. Found: C, 68.54; H, 12.61.

Intramolecular Hydrosilation of 31 Catalyzed by a Rh Complex. A mixture of **31** (221 mg, 0.97 mmol), $[RhCl(CH_2{=}CH_2)_2]_2$ (3.8 mg, 9.7 × 10^{-3} mmol) and dichloroethane (2.0 mL) was kept at room temperature under nitrogen for 4 days. Bulb-to-bulb distillation (bath temperature 85–100 °C/0.6 mmHg) of the reaction mixture afforded the hydrosilation product **14** (203 mg, 92% yield). The ^{1}H and ^{13}C NMR spectra showed the cis:trans ratio to be 66:34.

Intramolecular Hydrosilation of Allylamine Catalyzed by a Pt Complex. Typical Procedure. To a mixture of silylamine **6** (259 mg, 0.97 mmol) and hexane (1.9 mL) was added $[Pt\{(CH_2{=}CHSiMe_2)_2O\}_2]$ (0.25 M xylene solution, 19 μL, 4.9 × 10^{-3} mmol, 0.5 mol %) at room temperature under nitrogen. After 45 min, disappearance of the olefin was confirmed by ^{1}H NMR spectroscopy. Bulb-to-bulb distillation (bath temperature 95–115 °C/0.3 mmHg) of the reaction mixture gave the four-membered-ring product **16** (244 mg, 94% yield).

The TBS-bearing substrates **5** and **8** were less reactive and required somewhat larger amounts of catalyst (4.0 mol % for **5**, 1.1 mol % for **8**) to ensure the hydrosilation.

Spectral and analytical data for **15** (nondeuterated analogue) are as follows: ^{1}H NMR (200 MHz, C_6D_6) δ −0.07 (s, 3H), −0.03 (s, 3H), 0.37 (s, 3H), 0.38 (s, 3H), 0.62 (s, 3H), 0.99 (s, 9H), 1.34 (s, 3H), 4.57 (s, 1H), 7.18–7.31 (m, 5H); ^{13}C NMR (50 MHz, C_6D_6) δ −3.67, −2.71, 1.06, 1.86, 18.93, 20.95, 26.68, 27.30, 30.80, 75.09, 126.79, 127.40, 127.88, 144.86; IR (neat, cm^{-1}) 2964, 2864, 1464, 1254, 1064, 976, 858, 832. Anal. Calcd for $C_{18}H_{33}NSi_2$: C, 67.64; H, 10.41; N, 4.38. Found: C, 67.81; H, 10.59; N, 4.26.

Intramolecular Hydrosilation of Allylamine Catalyzed by a Rh Complex. Typical Procedure. A mixture of silylamine **5** (159 mg, 0.50 mmol), dichloroethane (1.0 mL), and $[RhCl(CH_2{=}CH_2)_2]_2$ (3.9 mg, 9.9 × 10^{-3} mmol) was stirred at 70 °C under nitrogen for 1 day. Disappearance of olefin was confirmed by ^{1}H NMR spectroscopy. Bulb-to-bulb distillation (bath temperature 180–195 °C/0.9 mmHg) of the reaction mixture afforded the five-membered-ring compound **20** (137 mg, 86% yield). The diastereomers were separated by preparative GLC.

Spectral and analytical data for the nondeuterated analogues of **20–22** are shown as follows.

cis-**20**: ^{1}H NMR (200 MHz, C_6D_6 δ −0.18 (s, 3H), 0.22 (s, 3H), 0.28–0.43 (m, 4H, including a singlet at 0.40), 0.46 (s, 3H), 0.90 (dd, 1H, J = 7.3 Hz, J = 14.5 Hz), 1.01 (s, 9H), 1.20 (d, 3H, J = 7.1 Hz), 2.17–2.35 (m, 1H), 4.42 (broad d, 1H, J = 1.4 Hz), 7.06–7.32 (m, 5H); ^{13}C NMR (50 MHz, C_6D_6) δ −2.83, −2.74, 3.42, 5.04, 17.83, 20.25, 23.39, 27.94, 43.22, 72.13, 126.44, 126.81, 148.66 (one carbon is hidden in signals of C_6D_6); IR (neat) cm^{-1}) 2968, 2864, 1258, 1016, 980, 932, 852, 830, 800. *trans*-**20**: ^{1}H NMR (200 MHz, C_6D_6) δ −0.24 (s, 3H), 0.17 (s, 3H), 0.30 (s, 3H), 0.48–0.65 (m, 5H, including a singlet at 0.51), 0.77 (d, 3H, J = 6.6 Hz), 0.99 (s, 9H), 2.21–2.48 (m, 1H), 4.49 (d, 1H, J = 6.6 Hz), 7.08–7.32 (m, 5H); ^{13}C NMR (50 MHz, C_6D_6) δ −2.96, −2.85, 2.40, 3.39, 18.47, 19.86, 20.83, 28.00, 39.06, 69.26, 126.72, 127.74, 128.36, 144.59; IR (neat, cm^{-1}) 2968, 2864, 1456, 1040, 1026, 980, 932, 852, 830. Anal. Calcd for $C_{18}H_{33}NSi_2$ (cis, trans mixture): C, 67.64; H, 10.41; N, 4.38. Found: C, 67.42; H, 10.46; N, 4.22.

21 (cis, trans mixture): ^{1}H NMR (200 MHz, C_6D_6) δ −0.07 (d, 3H of an isomer, J = 3.3 Hz), 0.01 (d, 3H of an isomer, J = 3.3 Hz), 0.09 (d, 3H of an isomer, J = 3.2 Hz), 0.12 (d, 3H of an isomer, J = 3.2 Hz), 0.26 (s, 3H of an isomer), 0.34 (s, 3H of an

(19) (a) Rychnovsky, S. D.; Skalitzky, D. *Tetrahedron Lett.* **1990**, *31*, 945. (b) Evans, D. A.; Rieger, D. L.; Gage, J. R. *Tetrahedron Lett.* **1990**, *31*, 7099.

isomer), 0.35 (s, 3H of an isomer), 0.47 (s, 3H of an isomer), 0.75 (d, 3H of an isomer, J = 6.7 Hz), 0.99 (d, 3H of an isomer, J = 6.7 Hz), 1.98–2.20 (m, 1H of an isomer), 2.20–2.45 (m, 1H of an isomer), 3.84 (d, 1H of an isomer, J = 6.6 Hz), 4.28 (d, 1H of an isomer, J = 6.8 Hz), 4.64 (septet, 1H of an isomer, J = 3.3 Hz), 4.75 (septet, 1H of an isomer, J = 3.2 Hz), 7.06–7.40 (m, 5H of two isomers) (the methylene protons $SiCH_2$ appear as multiplets in the range 0.3–0.9 ppm and cannot be assigned exactly); ^{13}C NMR (50 MHz, C_6D_6) δ −1.41, −1.07, −0.57, −0.08, 0.96, 1.62, 2.07, 18.84, 20.55, 20.88, 21.30, 38.78, 42.93, 68.87, 71.86, 126.86, 127.08, 144.37, 146.37. Anal. Calcd for $C_{14}H_{28}NSi_2$: C, 63.81; H, 9.56; N, 5.32. Found: C, 63.81; H, 9.83; N, 5.36.

22: ^1H NMR (200 MHz, C_6D_6) δ 0.03 (d, 3H, J = 3.3 Hz), 0.12 (d, 3H, J = 3.3 Hz), 0.24 (s, 3H), 0.39 (s, 3H), 0.48–0.81 (m, 2H), 1.85–2.02 (m, 1H), 2.03–2.19 (m, 1H), 4.43 (dd, 1H, J = 3.7 Hz, J = 6.4 Hz), 4.74 (septet, 1H, J = 3.3 Hz), 7.06–7.40 (m, 5H); ^{13}C NMR (50 MHz, C_6D_6) δ −1.16, −0.38, 1.19, 1.26, 10.35, 35.89, 64.33, 126.71, 127.02, 128.22, 147.33; IR (neat, cm^{-1}) 2964, 2116, 1254, 1056, 1010, 986, 906. Anal. Calcd for $C_{13}H_{28}NSi_2$: C, 62.58; H, 9.29; N, 5.61. Found: C, 62.69; H, 9.56; N, 5.53.

Analysis of the Deuterium Distribution. All deuterated products were purified by preparative GLC before analysis. While the cis and trans isomers of **10(Pt)**, **10(Rh)**, **11(Pt)**, **11(Rh)**, **17**, and **20** were separated readily, those of **21** appeared as a single peak on GLC and could not be separated. The D distribution of **10(Pt)**, **10(Rh)**, **11(Rh)**, **12**, **15**, **16**, **17**, **18**, **19**, **21**, **22**, **23**, and **24** was analyzed by 400-MHz ^1H NMR. Thus, the D distribution was evaluated by comparison of the integral intensity of the particular proton with the intensity of the appropriate, non-deuterated phenyl group, methyl groups on silicon, methoxy group, and/or methyl group in the *n*-hexyl group. The D distribution of **11(Pt)**, **20**, and the recovered allyl alcohol from **2** was analyzed by ^{13}C NMR spectroscopy under the following conditions: 126 MHz, solvent C_6D_6, acquisition time 0.5 s, delay time 20 s, and pulse width 5.8 μs. As a typical example, the ^{13}C NMR signals of four particular carbon atoms in **11(Pt)** are reproduced in Figure 1. The signals have been assigned in view of the upfield shift by deuterium, about 0.4 ppm for α and less than 0.2 ppm for β,[20] and by the ^{13}C DEPT spectrum: the signs +, −, and 0 assigned to each signal in Figure 1 denote the signal behavior in the DEPT spectrum to be positive, negative, and suppressed, respectively.

Quenching of Intramolecular Hydrosilation of 2 for Recovery of Allyl Alcohol. To a mixture of **2** (232 mg, 1.12 mmol) and hexane (2.2 mL) was added $Pt\{(CH_2{=}CHSiMe_2)_2O\}_2$ (0.25 M xylene solution, 22 μL, 5.6 × 10^{-3} mmol) at room temperature under nitrogen. After 11 min, 1% HCl (5 mL) was added to the mixture, followed by dilution with ether and stirring. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was washed with water and brine, dried over magnesium sulfate, and concentrated. The remaining oil was purified by column chromatography and preparative MPLC to give 2-methyl-1-phenyl-2-propen-1-ol (16 mg, 10% recovery). The deuterium content was examined by ^{13}C NMR, which showed the presence of 4% deuterium on the terminal olefin carbon atom only.

(20) Kalinowski, H.-O.; Berger, S.; Braun, S. *Carbon-13 NMR Spectroscopy*; Wiley: Chichester, England, 1988; p 168.

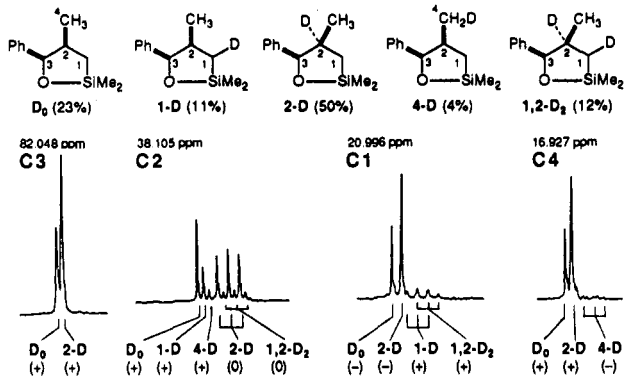


Figure 1. ^{13}C NMR signals of four carbon atoms in **11(Pt)**. Nondeuterated (D_0), monodeuterated (1-D, 2-D, 4-D), and dideuterated (1,2-D_2) structures are shown, together with the contents (%) of each component estimated from the spectra. The signs +, −, and 0, accompanying each assignment, denote the signal behavior in the ^{13}C DEPT spectrum to be positive, negative, and suppressed, respectively.

Hydrogen Peroxide Oxidation of 11. The D content of **11(Rh)** was estimated by a ^1H NMR spectrum of the acetonide **11′** of 1,3-diol obtainable by oxidation. The Rh-catalyzed intramolecular hydrosilation of **2** was carried out in the usual manner. After removal of the solvent, the mixture was stirred with activated charcoal (200 mg) in hexane overnight and filtered for removal of the catalyst. The filtrate was stirred with potassium fluoride (2 equiv), potassium hydrogen carbonate (1 equiv), and 30% hydrogen peroxide (3.6 equiv) in a 1:1 mixture of methanol and THF (2 mL for 1 mmol of **2**) at room temperature for 6 h. The usual workup followed by column chromatography on silica gel gave 2-methyl-1-phenyl-1,3-propanediol in 62% yield. The diol was converted into the acetonide by the reaction with an excess amount of 2,2-dimethoxypropane and a catalytic amount of D-10-camphorsulfonic acid. The acetonide **11′** was purified by preparative GLC. Spectral data for **11′** (nondeuterated analogue) are as follows. **11′** (cis:trans ≈ 85:15): ^1H NMR (200 MHz, C_6D_6) δ 0.37 (d, 3H of trans, J = 6.7 Hz), 0.92 (d, 3H of cis, J = 6.8 Hz), 1.30–1.42 (m including a singlet of cis (3H) at 1.36, a singlet of trans (3H) at 1.41, and a multiplet of cis (1H)), 1.63 (s, 3H of cis and 3H of trans), 1.78–2.02 (m, 1H of trans), 2.41–3.54 (m including a double doublet at 3.51, J = 1.6 Hz, J = 11.4 Hz, 1H of cis and 1H of trans), 3.71 (dd, 1H of trans, J = 5.0 Hz, J = 11.6 Hz), 3.94 (dd, 1H of cis, J = 2.7 Hz, J = 11.4 Hz), 4.31 (d, 1H of trans, J = 10.3 Hz), 4.96 (d, 1H of cis, J = 2.8 Hz), 7.10–7.43 (m, 5H of cis and 5H of trans).

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