than those in the LDA dimer. The accessibility may stem from transannular Me–Me interactions that cause a distortion of the Li_2N_2 ring observable only in the LiTMP optimized structures (Figure 5).

The prediction that open dimers and triple ions are chemically plausible species and uniquely stabilized for LiTMP represents a notable success for MNDO. The approximate 90° twist allowed by cleaving the Li_2N_2 ring alleviates the transannular Me–Me interactions. It is also notable that the approximately equal proportions of triple ion **13** and monomer **7** observed spectroscopically are correctly predicted by MNDO. Errors resulting from the high steric effects in the dimer possibly cancel. The failure to predict the existence of cyclic dimers appears to arise more from inordinately large steric destabilization of the cyclic dimer rather than from incorrect assessments of the open dimer and triple ion stabilities. We do not know whether the high propensity of LiTMP to exist as a diverse array of monomers, open dimers, and triple ions is characteristic of hindered lithium di-*tert*-alkylamides in general or if the conformational constraints imparted by the six-membered ring play a role.

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Asymmetric Catalysis. Production of Chiral Diols by Enantioselective Catalytic Intramolecular Hydrosilation of Olefins

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Abstract: Rhodium(I) chiral diphosphine complexes efficiently and rapidly catalyze the intramolecular hydrosilation of silyl ethers derived from allylic alcohols. The efficiency and rates of intramolecular hydrosilations were determined for a variety of silyl and olefin substituents. The catalysts were found to tolerate a wide variety of silyl substituents, although terminal alkyl olefin substituents were found to retard catalysis. Terminal aryl olefin substituents were found to be hydrosilated efficiently and at reasonable rates. One of the chiral catalysts is highly enantioselective for terminal aryl olefin substituents. Almost quantitative ee's are obtained. Moreover, the ee's are only slightly sensitive to aryl and olefin substituents, suggesting that this enantioselective catalysis can provide a wide range of chiral species. Oxidative cleavage of the hydrosilation products gives chiral diols.

Enantioselective catalytic hydrosilation is a process which results in the addition of a silicon–hydrogen bond across a prochiral ketone or olefin. It is usually, but not always, mediated by low-valent transition metal complexes. The majority of enantioselective catalytic hydrosilations have been performed on ketones catalyzed by rhodium(I) chiral phosphine complexes. The advantages of using ketones are obvious. First, the hydrosilation is completely regioselective, giving the silyl ether. Second, the product is readily hydrolyzed to the chiral alcohol, and third, the turnover rate for ketones is generally rapid. There are now numerous cases where very high ee's have been obtained for the hydrosilation of ketones.[1,2] In general, the ee depends on the structures of all three catalytic partners, the ketone, the silane, and the catalyst, so that seemingly minor structural variations in any one of these elements can cause sharp changes in the ee.

On the other hand, asymmetric catalytic hydrosilation of prochiral olefins has received very little attention,[3] possibly for the following reasons. Unlike ketone substrates, the reaction rates are slow; prochiral olefins do not always undergo complete regioselective addition and are subject to double bond migration prior to hydrosilation. In addition, prochiral olefins were, until recently, difficult to cleave stereospecifically at the silicon–carbon bond to give useful organic products. Like the ketone substrates, the ee's observed for prochiral olefins are dependent on the structures of the olefin, silane, and catalyst. Unlike ketones, the ee's reported for olefins have generally been modest.

One possible method of circumventing some of the complicating features of asymmetric olefin hydrosilation is by employing substrates which can undergo intramolecular hydrosilation (eq 1).[4] The advantages of this device are the following: first, the

(1)

regioselectivity is generally ensured by the observation that 5-membered rings are formed; second, the silicon substituents can be systematically varied to maximize the rate and selectivity of the catalysis; third, the presumed formation of cyclic catalytic intermediates is likely to provide defined steric interactions which are more likely to lead to higher and more consistent ee's than

(1) Ojima, I.; Hirai, K. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, p 103. Ojima, I.; Clos, N.; Bastos, C. *Tetrahedron* **1989**, *45*, 6901. Kagan, H. B.; Peyronel, J. F.; Yamagishi, T. In *Adv. in Chemistry Series: Inorganic Compounds with Unusual Properties-II*; King, R. B., Ed.; American Chemical Society: Washington, DC, 1979; Vol. 173, p 50.

(2) Nishiyama, H.; Sakaguchi, H.; Nakamura, T.; Horihata, M.; Kondo, M.; Itoh, K. *Organometallics* **1989**, *8*, 846.

(3) Yamamoto, K.; Hayashi, T.; Zembayashi, M.; Kumada, M. *J. Organomet. Chem.* **1976**, *118*, 161. Yamamoto, K.; Hayashi, T.; Uramoto, Y.; Ito, R.; Kumada, M. *J. Organomet. Chem.* **1976**, *118*, 331. Yamamoto, K.; Kiso, Y.; Ito, R.; Tamao, K.; Kumada, M. *J. Organomet. Chem.* **1981**, *210*, 9. Hayashi, T.; Tamao, K.; Katsuro, Y.; Nakae, I.; Kumada, M. *Tetrahedron Lett.* **1980**, *21*, 1871. Tamao, K.; Tohma, T.; Inui, N.; Nakayama, O.; Ito, Y. *Tetrahedron Lett.* **1990**, *31*, 7333.

(4) Tamao, K.; Tamaka, T.; Nakajima, T.; Sumiya, R.; Arai, H.; Ito, Y. *Tetrahedron Lett.* **1986**, *27*, 337. Tamao, K.; Nakajima, T.; Sumiya, R.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1986**, *108*, 6090. Tamao, K.; Nakagawa, Y.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 3712. Tamao, K.; Yamauchi, T.; Ito, Y. *Chem. Lett.* **1987**, 171.

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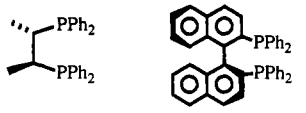
are probable for intermolecular catalysis; and, fourth, the turnover is likely to be higher.

1. Catalyst

A review of the possible catalysts[1] suggested that rhodium(I) phosphine complexes were likely to give the fastest rates and the cleanest reactions, provided certain catalyst features were present. Since, in the catalytic cycle, an intermediate is likely to form where a silicon, a hydride, and an olefin are bound to the rhodium atom, three coordination sites are required to accommodate these ligands. Because the chiral bidentate phosphines (*S*,*S*)-chiraphos **1** and (*S*)-binap **2** bind in fixed chiral conformations,[5] we have chosen these ligands for incorporation into the catalysts. The catalyst

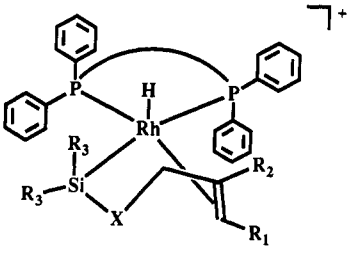


1 2

S,S-chiraphos S-binap

precursors were prepared by hydrogenation of the complexes, [Rh(diphosphine)(norbornadiene)]$^+$. For the (*S*,*S*)-chiraphos species, an aryl bridged dimer, $[Rh((S,S)\text{-chiraphos})]_2(ClO_4)_2$, can be isolated.[6,7] We were unable to isolate the analogous dimer of the (*S*)-binap ligand. The disolvento species, $[Rh((S)\text{-binap})(acetone)_2]^+$, was prepared in situ by hydrogenation of the norbornadiene complex in acetone solution. Upon dissolution in acetone, the (*S*,*S*)-chiraphos dimer splits to give the $[Rh((S,S)\text{-chiraphos})(acetone)_2]^+$ species.[7] The majority of catalytic hydrosilations were run in acetone solutions, although a few experiments with the (*S*)-binap catalyst used THF as a solvent. These complexes carry exceedingly labile solvento ligands so that catalysis is not inhibited by slow displacement of ligands.

Given that the $[Rh(diphosphine)(solvento)_2]^+$ species are essentially 2-coordinate, we can imagine that a crucial intermediate in asymmetric catalytic intramolecular hydrosilation will resemble structure **3**. The (*S*,*S*)-chiraphos and (*S*)-binap ligands provide a chiral array of phenyl groups which will discriminate between the faces of the bound prochiral cyclic substrate. Because the

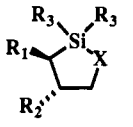


3

substrate can exist as a chelated intermediate, we expect that, with the correct combination of R substituents, strong diastereomeric discrimination will occur since the chelation provides a restricted number of orientations. Such an intermediate, or one resembling it, suggests that the rate and selectivity of catalysis may be tuned by varying R_3, the silicon substituents. Thus, our first concern in this study was to examine the rates and selectivities of substrates with various permutations of R groups.

2. Substrates

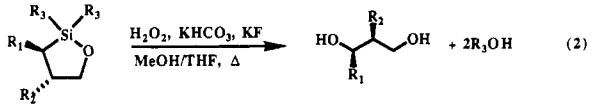
A key consideration in the choice of substrates was whether the cyclized products could be readily converted to useful organic products. The initial products of hydrosilation are of the type **4**. Recently, clean, stereochemically defined methods for cleaving silicon–carbon bonds have been developed.[8] These methods,



4

however, are restricted to silicon compounds bearing only certain substituents. Thus, restrictions were imposed on our choice of substrates.

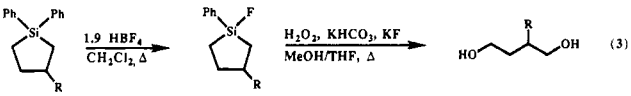
Silicon–alkyl bonds can be oxidatively cleaved under basic, neutral, or acidic conditions, provided there is at least an alkoxide[4,8] or a fluoride[9] bound to the silicon atom. We chose the basic method of cleavage because of its convenience and because it is known to proceed with retention of configuration at the cleaved carbon atom. The method is outlined in eq 2. Thus, intramo-



(2)

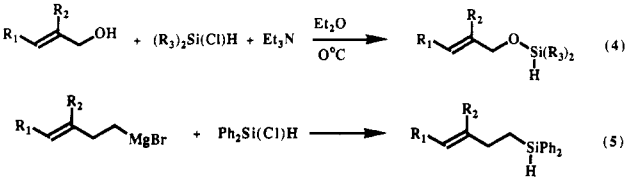
lecular asymmetric catalytic hydrosilation converts allylic alcohols to chiral 1,3-diols and, moreover, the relative stereochemistry of the R_1 and R_2 substituents is stereospecifically determined by the requirement that the silicon and hydride be added cis to the olefin.[10]

If the product does not contain an alkoxyl group bound to the silicon, then at least one phenylsilicon substituent is required. The phenyl group is first cleaved to give the fluoro compound,[9] which is now susceptible to normal cleavage[8] (eq 3). Thus, chiral 1,4-diols can be derived from hydrosilation.



(3)

The synthesis of the substrates is relatively simple. In general,[11] the allylic silyl ethers were prepared as outlined in eq 4. The $(R_3)_2Si(Cl)H$ compounds were readily obtained.[12] In a similar manner, the γ-alkenylsilanes were prepared from the homoallylic magnesium bromides (eq 5).



(4)

(5)

3. Catalysis and Analysis

Nearly all of the catalyses were carried out in acetone solvent at 25 °C using 2 mol % $[Rh(diphosphine)(acetone)_2]^+$ catalyst ($[Rh] = 2.8 \times 10^{-3}$ M). Other solvents such as methylene chloride, nitromethane, and methanol tended to give lower chemical yields and slower rates. Surprisingly, less than 1% intermolecular hydrosilation of the acetone solvent occurred, despite the observation that hydrosilation of ketones is generally much faster than for olefins. Presumably the intramolecular nature of this process makes it sufficiently fast to compete effectively with the intrinsically faster intermolecular process. The relative rates and the yields of hydrosilation were determined by following the reactions with ^1H NMR spectroscopy. The ee's were obtained by trans-

(5) (a) Fryzuk, M. D.; Bosnich, B. *J. Am. Chem. Soc.* **1977**, *99*, 6262. (b) Tani, K.; Yamagata, T.; Akutagawa, S.; Kumobayashi, H.; Taketomi, T.; Takaya, H.; Miyashita, A.; Noyori, R.; Otsuka, S. *J. Am. Chem. Soc.* **1984**, *106*, 5208.

(6) Halpern, J.; Riley, D. P.; Chan, A. S. C.; Pluth, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 8055.

(7) Fairlie, D. P.; Bosnich, B. *Organometallics* **1988**, *7*, 936 and 946.

(8) Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, *2*, 1694. Tamao, K.; Kakui, T.; Akita, M.; Iwahara, T.; Kanatani, R.; Yoshida, J.; Kumada, M. *Tetrahedron* **1983**, *39*, 983. Tamao, K. In *Organosilicon and Bioorganosilicon Chemistry*; Sakurai, H., Ed.; Ellis Horwood: Chichester, England, 1985; p 231.

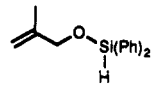
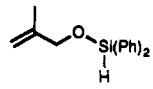
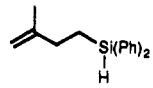
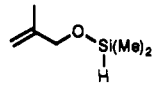
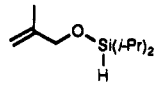
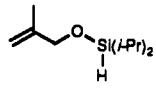
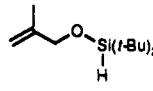
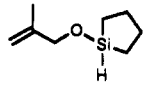
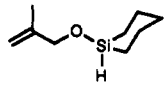
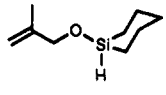
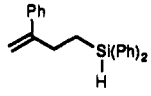
(9) Fleming, I.; Henning, R.; Plaut, H. *J. Chem. Soc., Chem. Commun.* **1984**, 29.

(10) Selin, T. G.; West, R. *J. Am. Chem. Soc.* **1962**, *84*, 1863.

(11) For a closely related procedure, see: Langer, S. H.; Cornell, S.; Wendler, I. *J. Org. Chem.* **1958**, *23*, 50.

(12) Gillian, W. F.; Liebhafskey, H. A.; Winslow, A. F. *J. Am. Chem. Soc.* **1941**, *63*, 801. Sommer, L. H.; Tyler, L. J. *J. Am. Chem. Soc.* **1954**, *76*, 1030. Corey, E. J.; Venkateswarl, V. *J. Am. Chem. Soc.* **1972**, *94*, 6190.

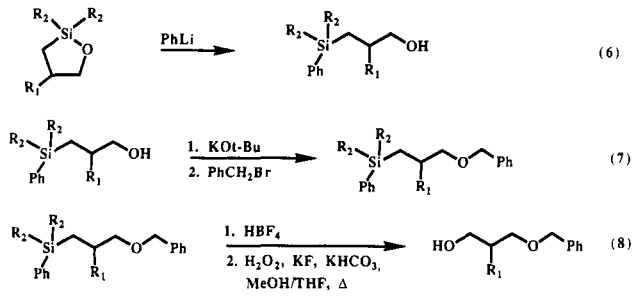
Table I. Asymmetric Catalytic Intramolecular Hydrosilation of Internally Substituted Olefins Using [Rh(diphosphine)]$^+$ as Catalysts[a]

entry	substrate	time[b]	yield, %[c]	ee,% (abs conf)	diphosphine
1		15 min	94	23 (*S*)	(*S*,*S*)-chiraphos
2		12 h	85	25 (*S*)	(*S*)-binap
3		3 h	84	60 (*R*)	(*S*,*S*)-chiraphos
4		1 min	100	0.7 (*S*)	(*S*,*S*)-chiraphos
5		6 min	96	56 (*R*)	(*S*,*S*)-chiraphos
6		2.5 h	100	20 (*R*)	(*S*)-binap
7		nc[d]			(*S*,*S*)-chiraphos
8		10 min	60	33 (*R*)	(*S*)-binap
9		8 min	82	41 (*R*)	(*S*)-binap
10		55 min	100	8 (*R*)	(*S*,*S*)-chiraphos
11		8 h	100	38 (*S*)	(*S*,*S*)-chiraphos

[a] All reactions were carried out with 2 mol % catalyst at 25 °C in acetone solutions. [b] Time required for complete consumption of the substrate. [c] Yield of cyclic product based on the amount of diol isolated from the large-scale reaction and ^{1}H NMR data of the small-scale reaction after all of the substrate was consumed. [d] nc = no cyclization; double bond migration occurred instead.

formation of the products from larger scale catalyses.

The absolute configurations of the diols were determined by comparing the sign of optical rotation with literature values of materials of known configuration. The ee's were determined by ^{1}H NMR analysis of the diastereomeric Mosher esters[13] of the diols. That the diastereomeric ^{1}H NMR signals were identified was checked by preparing the Mosher esters of the racemic diols. The ee's of hydrosilation products which, upon oxidative cleavage, would produce achiral 1,3-diols were determined by the sequence of reactions represented in eqs 6–8.[4] The benzyl ether alcohol (eq 8) was converted to its Mosher ester, and the ee's were determined as before.



(13) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.

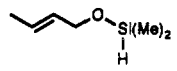
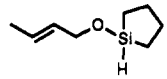
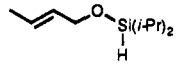
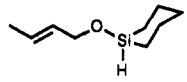
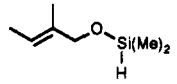
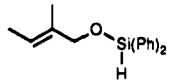
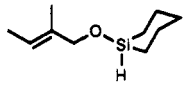
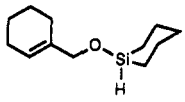
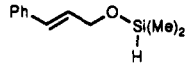
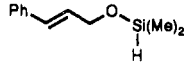
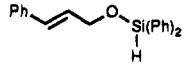
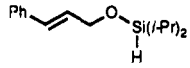
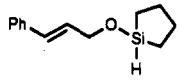
Given the fact that in some cases almost enantiomerically pure products are obtained, the manipulations to generate the diols appear to proceed without loss of configurational integrity.

4. Results

With respect to choice of substrates, we addressed three principal questions. First, which silyl substituents gave the best rates, chemical yields, and ee's? Second, which combination of allylic olefin substituents provided acceptable rates, chemical yields, and ee's? Third, which combination of olefin and silyl substituents gave consistently high rates, yields, and ee's?

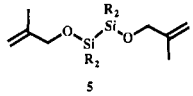
The first question is addressed by the results contained in Table I. As we shall see, having a substituent at the inner olefin position causes the least steric impediment to the rate so that the effect of the silyl substituents on the rates and yields can be ascertained. As can be seen from the entries in Table I, the (*S*,*S*)-chiraphos and (*S*)-binap catalysts tolerate a wide range of substituents, and the two catalysts behave similarly. The di-*tert*-butylsilyl-substituted substrate (Table I, entry 7) does not undergo hydrosilation with the (*S*,*S*)-chiraphos catalyst, presumably because of steric factors. This substrate undergoes double bond migration to form the vinyl silyl ether. This observation illustrates that for successful hydrosilation other possible catalytically induced processes, such as double bond migration, have to be much slower than catalytic hydrosilation. The results in Table I show that this is generally the case although there are instances where the hydrosilation yield

Table II. Asymmetric Catalytic Intramolecular Hydrosilation of Terminally Substituted Olefins Using [Rh(diphosphine)]$^+$ as Catalysts[a]

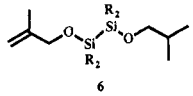
entry	substrate	time[b]	yield, %[c]	ee, % (abs conf)	diphosphine
12		10 min	70	21 (*S*)	(*S*,*S*)-chiraphos
13		5 min	100	28 (*R*)	(*S*,*S*)-chiraphos
14		nc[d]			(*S*,*S*)-chiraphos
15		7 min	15		(*S*)-binap
16		nc[d]			(*S*)-binap
17		nc[d]			(*S*,*S*)-chiraphos and (*S*)-binap
18		nc[d]			(*S*)-binap
19		nc[d]			(*S*,*S*)-chiraphos
20		18 min	76	77 (*R*)	(*S*,*S*)-chiraphos
21		nc[d]			(*S*)-binap
22		24 h	90	6.4 (*S*)	(*S*,*S*)-chiraphos
23		48 h	50	4.3 (*R*)	(*S*,*S*)-chiraphos
24		14 min	100	56 (*R*), 25 °C 83 (*R*), −50 °C	(*S*,*S*)-chiraphos

[a] All reactions were carried out with 2 mol % catalyst at 25 °C in acetone solutions. [b] Time required for complete consumption of the substrate. [c] Yield of cyclic product based on the amount of diol isolated from the large-scale reaction and ^{1}H NMR data of the small-scale reaction after all of the substrate was consumed. [d] nc = no cyclization; the substrate was converted into disilanes or unidentified compounds.

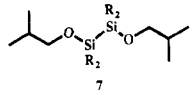
is low because of catalytic side reactions. We have determined by ^{1}H NMR spectroscopy that the major catalytic side reactions produce three disilyl species of the types **5**, **6**, and **7**. The ^{1}H



5



6



7

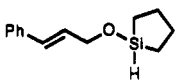
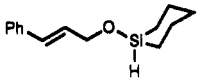
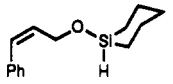
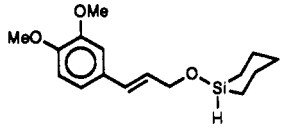
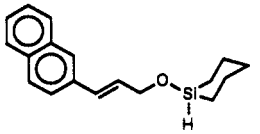
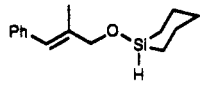
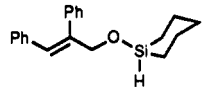
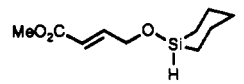
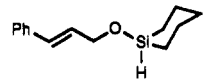
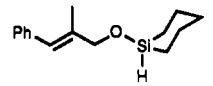
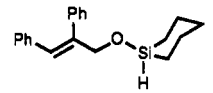
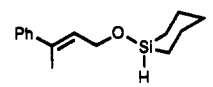
NMR spectrum of **5** resembles that of the substrate. The disilyl ethers form with production of H_2, which was detected by ^{1}H NMR at the initial stages of reaction. This H_2 engages the catalyst to hydrogenate the olefins to give **6** and **7**. The mechanism for the disilyl formation is a matter of speculation, but it is a common side product.

The ee's listed for the substrates in Table I are generally modest and suggest that a more extensive permutation of silyl substituents is unlikely to give high ee's for substrates with inner olefin groups. We note one curious feature illustrated in the ee's shown in entries 1 and 3 where the replacement of a methylene group by an oxygen atom results in a substantial reversal of the sense of the induction.

Taking into account the factors affecting rates and yields illustrated in Table I, we next addressed the tolerance of the catalysts to terminal olefin substituents. Some of these results are collected in Table II. Taken as a whole, these results indicate that terminal olefin substituents can have a strong impeding effect on the hydrosilation process. Moreover, when terminal olefin substituents are present, the efficacy of catalysis is dependent more strongly on the silyl substituent and on the phosphine than in the cases recorded in Table I. Thus, entries 12–14 illustrate the effect of the silyl substituents and entries 20 and 21 reveal the effect of the phosphine on the catalysis. It is also apparent that terminal aryl olefin substituents are less inhibiting than terminal alkyl groups. The tiglic (entries 16–18) and cyclohexenyl (entry 19) alcohols do not undergo hydrosilation under the present conditions. The substrates undergo silicon–silicon bond formation or are decomposed. The results obtained for the cinnamyl alcohol substrates suggest that with the proper catalyst and silyl substituents high ee's and acceptable chemical yields might be obtained. This expectation is borne out by the results tabulated in Table III.

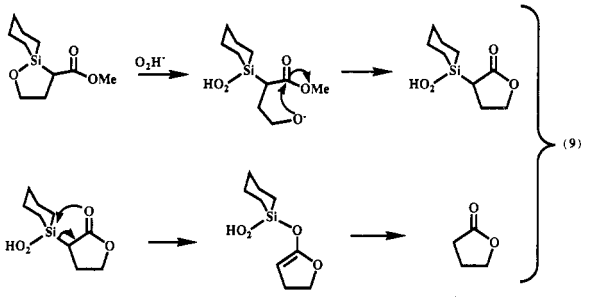
We chose the silacyclohexyl substituent because a high-yield preparation of the substrate silacyclohexyl chloro hydride was developed although it is probable that similar high ee's could be obtained for the silacyclopentyl analogue. We note the following. When the (*S*)-binap catalyst is used, the *cis*- and *trans*-cinnamyl substrates undergo hydrosilation with the same rate, chemical

Table III. Asymmetric Catalytic Intramolecular Hydrosilation of Aryl Olefins Using [Rh(diphosphine)]$^+$ as Catalysts[a]

entry	substrate	time[b]	yield, %[c]	ee, % (abs conf)	diphosphine
25		5 min	75	97 (*R*)	(*S*)-binap
26		15. h	75	96 (*R*)	(*S*)-binap
27		1.5 h	75	96 (*R*)	(*S*)-binap
28		45 min	90	97 (*R*)[d]	(*S*)-binap
29		20 min	75	94 (*R*)[d]	(*S*)-binap
30		1.25 h	100	90 (*R*,*R*)	(*S*)-binap
31		17 h	75	88 (?)	(*S*)-binap
32		18 h	90	78 (?)	(*S*)-binap
33		6 h	61	74 (*R*)	(*S*,*S*)-chiraphos
34		1 h	100	0	(*S*,*S*)-chiraphos
35		15 h	90	55 (?)	(*S*,*S*)-chiraphos
36		nc[e]			(*S*)-binap and (*S*,*S*)-chiraphos

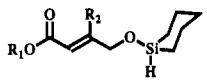
[a] All reactions were carried out with 2 mol % catalyst at 25 °C in acetone solutions. [b] Time required for complete consumption of the substrate. [c] Yield of cyclic product based on the amount of diol isolated from the large-scale reaction and ^{1}H NMR data of the small-scale reaction after all of the substrate was consumed. [d] Determined by comparing the ^{1}H NMR spectrum of the di-Mosher's ester to that from entry 26. [e] nc = no cyclization; the substrate was converted into unidentified products.

yield, and ee. This suggests that the two isomers proceed via a common catalytic intermediate. We demonstrate this fact in the mechanistic paper to follow. Terminal olefin aryl substituents (entries 25–29) all give nearly quantitative optical yields. Further, the presence of substituents at the inner olefin position does not alter the ee to any great extent (entries 30 and 31). Hydrosilation proceeds by cis addition of the silicon and hydride to the double bond (entry 30). Although we have not established the absolute configuration of the product of entry 31, we believe the prevailing enantiomer has the same absolute configuration as the one obtained in entry 30. We have established that the product of entry 31 results from cis addition. It is curious, however, that the (*S*,*S*)-chiraphos and (*S*)-binap catalysts give quite different ee's. In particular, the substrate in entry 34 gives 0% ee with (*S*,*S*)-chiraphos, but a 90% ee is observed for (*S*)-binap. This perhaps illustrates how subtle effects can have a profound influence on the ee. Entry 36 refers to a terminally disubstituted olefin substrate which does not undergo hydrosilation, presumably because of steric hindrance. Finally, the substrate in entry 32 is included to suggest that a new class of substrates may give high ee's by variation of the ester functionality. There are, however, difficulties

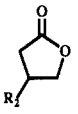


with the oxidative cleavage of the product of this substrate. The product is the achiral γ-butyrolactone, which we believe is produced by the sequence of steps illustrated in eq 9 under the cleavage conditions given in eq 2. A similar sequence has been proposed before for related reactions.[14] Although the cleavage

reaction eliminates the chirality at the α-position of the hydrosilation product, it may be possible to produce β-substituted products **9** from substrates of type **8**. We are investigating this possibility.



8



9

5. Discussion

This paper describes the first systematic attempt to achieve high ee's for asymmetric catalytic hydrosilation of olefins. The effects of the silyl and olefin substituents have been addressed, and the interplay between these two factors has been accentuated by devising an intramolecular process. From the present results it seems probable that substrates with terminal aryl olefin substituents will give high ee's with the present catalysts. Further, with appropriate ester functionalities terminal olefin esters are likely to give high ee's. The precise origins of the enantioselection are not clearly defined by these experiments. Such a determination awaits a detailed mechanistic analysis of the catalytic reaction. This is provided in the following paper.

As a method of producing chiral diols, catalytic hydrosilation requires refinement of the oxidative cleavage reactions. Although the present methods are reasonably efficient, they are, nonetheless, cumbersome. Were simple methods found for transforming the hydrosilation products to functionalized organic precursors, the present catalytic method would be an attractive route to a variety of functionalized organic building blocks.

6. Experimental Section

Instrumentation. ^{1}H NMR spectra were measured on General Electric (GE) GN 500, GN 300, and QE 300 Fourier transform spectrometers operated at 500.1, 300.1, and 300.2 MHz, respectively. ^{31}P NMR spectra were measured on a GE GN 300 Fourier transform spectrometer operating at 121.7 MHz. ^{1}H NMR chemical shifts were measured relative to a TMS external reference. ^{31}P NMR chemical shifts were measured relative to an 85% H_3PO_4 external reference. The optical rotations were measured on a Perkin-Elmer 141 Polarimeter. Elemental analyses were carried out by Huffman Laboratories.

Reagents. The solvents, Et_2O ($LiAlH_4$), *n*-hexane (CaH_2), pentane (3-Å molecular sieves), methylene chloride (CaH_2), THF (K, Ph_2CO), methanol ($(MeO)_2Mg$), acetone and acetone-d_6 (3-Å molecular sieves), and chloroform (3-Å molecular sieves) were distilled from drying agents under nitrogen or argon, except absolute and 95% ethanol and ethyl acetate, which were used as supplied.

The argon and nitrogen gases were purified by passing them through a bed of Drierite drying agent. The hydrogen gas was passed through an Oxiclear oxygen and water scrubber.

Unless stated otherwise, all reagents were used as supplied by the Aldrich Chemical Co., Inc. The following reagents were obtained from Aldrich and distilled under either an inert atmosphere (nitrogen or argon gas) or vacuum (0.1 mm), depending on the boiling point: 2-methyl-2-propen-1-ol, *trans*-2-methyl-3-phenyl-2-propen-1-ol, 3-methyl-3-buten-1-ol, *trans*-3-phenyl-2-propen-1-ol, pyridine (from CaH_2), triethylamine (from CaH_2), methanesulfonyl chloride, benzyl bromide, and norbornadiene. *trans*-3-Buten-1-ol was supplied as a mixture containing 6% of the corresponding cis isomer from Fluka Chemie AG and was distilled from 3-Å molecular sieves before use. Phenylpropargyl alcohol was used as supplied by Lancaster Synthesis Ltd. The potassium fluoride (anhydrous), 30% solution of hydrogen peroxide in water, and magnesium sulfate were used as supplied from the Baker Chemical Co. (*S*)-Binap was generously supplied by Professor H. Takaya.

trans-2-Methyl-2-buten-1-ol,[15] *trans*-3-carbomethoxy-2-propen-1-ol,[16] 1-bromo-3-phenyl-3-butene,[17] chlorodiphenylsilane,[18] *rac*-1-phenyl-1,3-propanediol,[19] [Rh((*S*)-binap)(NBD)]ClO_4,[5b] [Rh((*S,S*)-chiraphos)(NBD)]ClO_4, and $[Rh(dppe)]_2(ClO_4)_2$[6,7] were prepared as described previously.

***trans*-3-(3,4-Dimethoxyphenyl)-2-propen-1-ol.** This compound was prepared by methylation of ethyl 4-hydroxy-3-methoxycinnamate with methyl iodide and potassium carbonate in acetone solution.[20] The resulting ester was then reduced ($AlCl_3$ + $LiAlH_4$)[15] to the desired alcohol with >99% purity. The ^{1}H NMR spectrum of the silacyclohexyl ether is shown in Table IV given in the supplementary material.

***trans*-2,3-Diphenyl-2-propen-1-ol.** This compound was prepared in >99% purity by esterification of *trans*-2,3-diphenylpropenoate with methanol using sulfuric acid as catalyst followed by reduction ($AlCl_3$ + $LiAlH_4$)[15] of the resulting ester to the alcohol. The ^{1}H NMR spectrum of the silacyclohexyl ether is shown in Table IV.

1-(Hydroxymethyl)cyclohexene. This compound was prepared in >99% purity by reduction ($AlCl_3$ + $LiAlH_4$)[15] of 1-carbomethoxycyclohexene. The ^{1}H NMR spectrum of the silacyclohexyl ether is shown in Table IV.

***trans*-3-(2-Naphthyl)-2-propen-1-ol.** This compound was prepared in >99% purity using the procedure for *trans*-3-(1-naphthyl)-2-propen-1-ol,[21] except that 2-naphthaldehyde was used instead of 1-naphthaldehyde. The ^{1}H NMR spectrum of the silacyclohexyl ether is shown in Table IV.

***trans*-3-Methyl-3-phenyl-2-propen-1-ol.** This compound was prepared in >99% purity by reduction ($LiAlH_4$ + $AlCl_3$)[15] of ethyl *trans*-3-methyl-3-phenylpropenoate. The ^{1}H NMR spectrum of the silacyclohexyl ether is shown in Table IV.

***cis*-3-Phenyl-2-propen-1-ol.** This compound was obtained as a mixture with *trans*-3-phenyl-2-propen-1-ol (11.4%) and 3-phenylpropan-1-ol (12.6%) using a literature procedure.[22] These proportions were maintained when the alcohol was converted into the silacyclohexyl ether. The ^{1}H NMR spectrum of the silacyclohexyl ether is shown in Table IV.

1-Bromo-3-methyl-3-butene. This compound was prepared by conversion of 3-methyl-3-buten-1-ol to the methanesulfonate by treatment with methanesulfonyl chloride and triethylamine in methylene chloride solution.[23] The methanesulfonate was then treated with lithium bromide in acetone solution.[17] The ^{1}H NMR spectrum of the corresponding diphenylsilane is shown in Table IV.

***rac*-2-Methyl-1,4-butanediol.** This compound was prepared by reduction ($LiAlH_4$) of methylsuccinic acid. The ^{1}H NMR spectrum of the di-Mosher's ester is shown in Table IV.

***rac*-2-Phenyl-1,4-butanediol.** This compound was prepared by reduction ($LiAlH_4$) of phenylsuccinic acid. The ^{1}H NMR spectrum of the di-Mosher's ester is shown in Table IV.

Chlorodiisopropylsilane. This entire procedure was carried out under an atmosphere of dry argon. A mixture of oven-dried Mg shavings (9.70 g, 339 mmol), dry Et_2O (20 mL), a crystal of iodine, and several drops of 2-bromopropane was refluxed for 30 s, causing the brown color of the iodine to fade. A solution of 2-bromopropane (32.64 g total (including the several drops already reacted with the Mg), 265 mmol) in Et_2O (25 mL) was then added to the magnesium mixture dropwise at a rate that allowed the heat liberated by the reaction to maintain a gentle reflux of the Et_2O (1.5 h). The mixture was refluxed for 1 h after the addition was complete and then was transferred with a double-ended needle into a pressure-equalized addition funnel (30 mL of Et_2O was used for the transfer) connected to a flask charged with trichlorosilane (17.97 g, 133 mmol) and Et_2O (150 mL) and fitted with an efficient condenser to prevent the trichlorosilane from escaping. The flask was cooled with a −15 °C dry ice–EtOH bath, and the Grignard solution was added dropwise over 2 h while maintaining the bath temperature. A large quantity of a granular, white solid formed during the addition. The mixture was stirred for 15 min at −15 °C after the addition was complete. The cooling bath was then removed, and the mixture was allowed to warm to room temperature. The mixture was then stirred for 18 h, refluxed for 3 h, and filtered through a filter-paper plug (3 × 30 mL portions of Et_2O used for filtration). The Et_2O solvent was then distilled from the filtrate under atmospheric pressure leaving a colorless oil with a white precipitate. The residue was treated with hexane (40 mL), causing more precipitate to form, and then was filtered through a Schlenk tube containing a fine glass sinter (30 mL of hexane was used for the filtration). The hexane was distilled from the filtrate, and the remaining oil was distilled under atmospheric pressure to yield pure (by ^{1}H NMR) chlorodiisopropylsilane (8.92 g, 45% yield, bp 143 °C (760 mm)). The

(14) Colvin, E. In *Silicon in Organic Synthesis*; Butterworths: London, 1981; p 34.
(15) Gastaminza, A. E.; Ferracutti, N. N.; Rodinques, N. M. *J. Org. Chem.* **1984**, *49*, 3859.
(16) Tufariello, J. J.; Tette, J. *J. Org. Chem.* **1975**, *40*, 3866.
(17) Maercker, A.; Weber, K. *L. Ann. Chim.* **1972**, *756*, 20.
(18) Corey, J. Y.; West, R. *J. Am. Chem. Soc.* **1963**, *85*, 2430.
(19) Han, B.-H.; Boudjouk, P. *J. Org. Chem.* **1982**, *47*, 5030. Schaal, C. *Bull. Soc. Chim. Fr.* **1973**, 3083.
(20) Vyas, G. N.; Shah, N. M. *Org. Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 836.
(21) Stokker, G. E.; Hoffman, W. F.; Alberts, A. W.; Cragoe, E. J., Jr.; Deanna, A. A.; Gilfillan, J. L.; Huff, J. W.; Novello, F. C.; Prugh, J. D.; Smith, R. L.; Willard, A. K. *J. Med. Chem.* **1985**, *28*, 347.
(22) Sato, F.; Ishikawa, H.; Watanabe, H.; Miyake, T.; Sato, M. *J. Chem. Soc., Chem. Commun.* **1981**, 718.
(23) Payne, N. C.; Stephan, D. W. *J. Organomet. Chem.* **1981**, *221*, 203.

^{1}H NMR spectrum is shown in Table IV.

Preparation of 1-Chlorosilacyclopentane and 1-Chlorosilacyclohexane. These complexes were prepared using the same procedure as for chlorodiisopropylsilane except that the solutions of the di-Grignard reagents (formed from 1,4-dibromobutane and 1,5-dibromopentane for 1-chlorosilacyclopentane and 1-chlorosilacyclohexane, respectively) were quite viscous and had to be heated to ~40 °C to allow transfer through a double-ended needle into the pressure-equalized addition funnel. 1-Chlorosilacyclopentane: 34% yield, bp 117–120 °C (760 mm). 1-Chlorosilacyclohexane: 43% yield, bp 150–151 °C (760 mm). Both products were pure by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra are shown in Table IV.

Preparation of the Allylic Silyl Ethers. This entire procedure was carried out under an atmosphere of dried argon. A solution of the allylic alcohol (30 mmol) and triethylamine (3.26 g, 32 mmol) in Et_2O (30 mL) was added dropwise over 20 min to a rapidly stirred solution of the chlorodialkylsilane (32 mmol) in Et_2O (100 mL) that was cooled to 0 °C with an ice bath. Large quantities of a fluffy white precipitate (Et_3NHCl) formed. The mixture was stirred at 0 °C for 20 min after the addition was complete, the cooling bath was removed, and stirring was continued for 18 h further at room temperature. The solution was then filtered through a Celite plug, the solvent was removed, and the residue was distilled to yield the product. The products were obtained in >99% purity by ^{1}H NMR after distillation. The chemical yields ranged from 30 to 70%. The ^{1}H NMR spectra are listed in Table IV. Interestingly, the silacyclohexyl ether of 3-(2-naphthyl)-2-propen-1-ol (Table III, entry 29), obtained by distillation (bp 178–180 °C (0.1 mm)), contained 20% of the intramolecular hydrosilation product. The high temperatures required to distill this substrate likely were enough to induce the thermal (uncatalyzed) hydrosilation. This was removed by flash chromatography with *n*-hexane eluent on silanized silica gel (Silica Gel 60, particle size 0.063–0.200 nm (70–230 mesh as TMS), Merck).

Preparation of γ-Alkenyldiphenylsilanes. A mixture of dried Mg shavings (1.85 g, 76 mmol), dry Et_2O (8 mL), and a crystal of iodine was treated with one drop of 1,2-dibromoethane under argon, causing the brown color to rapidly fade, and gas evolution ensued. Stirring was continued until gas evolution ceased. A solution of 1-bromo-3-phenyl-3-butene (8.08 g, 38 mmol) in Et_2O (7 mL) was added dropwise over 2 h to the activated Mg while the reaction temperature was maintained at 25 °C. Stirring was continued at 25 °C for 40 min after the addition was complete. The Grignard solution was then removed from the excess Mg with a syringe and was added dropwise over 1.5 h to a solution of chlorodiphenylsilane (4.17 g, 19 mmol) in Et_2O (15 mL) at room temperature. Stirring was continued at 25 °C for 45 min after the addition was complete. The reaction was then carefully hydrolyzed by the addition of a saturated ammonium chloride solution (20 mL) with vigorous stirring over 10 min, resulting in a two-layered mixture with a white solid. The organic phase was separated from the aqueous phase, and the aqueous phase was extracted with 2 × 20 mL portions of Et_2O. The combined Et_2O extracts were washed with 2 × 40 mL portions of H_2O and 2 × 40 mL portions of brine and were dried (Na_2SO_4). The solvent was removed with a rotary evaporator, and the remaining oil was passed through a plug of neutral alumina (25 g) using hexane as eluent. The solvent was removed using a rotary evaporator, yielding 5.90 g of a clear, colorless oil. The material was distilled under a 0.1 mmHg vacuum. A large quantity of a low-boiling forerun (bp 38 °C (0.1 mm)) was collected in a dry ice–ethanol cooled trap before the product distilled over. The ^{1}H NMR spectrum of the low-boiling forerun is consistent with the formulation $CH_2C(Ph)(CH_2)_4C(Ph)CH_2$, the 1-bromo-3-phenyl-3-butene coupling product. The product (1.5 g, 25% yield, bp 178–182 °C (0.1 mm)) was isolated with 2% of an unidentified impurity and was used without further purification. The ^{1}H NMR spectrum is shown in Table IV.

(3-Methyl-3-butenyl)diphenylsilane was synthesized in >99% purity (by ^{1}H NMR spectroscopy) using the same procedure (38% yield, bp 110–110.5 °C (0.1 mm)).

Preparation of [Rh((*S*,*S*)-chiraphos)]$_2$(ClO$_4$)$_2$. The entire procedure was carried out under rigorously anaerobic conditions. A reaction vessel containing [Rh((*S*,*S*)-chiraphos)NBD]ClO$_4$ (0.51 g, 0.71 mmol) was evacuated (~0.01 mm) for 1 min and then filled with argon three times. The compound was then suspended in MeOH (10 mL, distilled from $(MeO)_2Mg$), and the mixture was stirred at room temperature for 10 min, cooled to 0 °C with an ice–water bath, and placed in the dark. Hydrogen gas was bubbled through the red-orange suspension. After the mixture was stirred for 15 min at 0 °C, the cooling bath was removed, and the reaction was allowed to warm to room temperature. After hydrogen gas was bubbled at room temperature for 40 min, the solid had turned over to orange microcrystals; the solution was light-amber. Hydrogen gas was bubbled through the solution for an additional 30 min in the dark to ensure complete hydrogenation of the starting material. The excess hydrogen gas was removed, and the solution volume was decreased to ~8 mL by placing the solution under vacuum. The mixture was then placed under an atmosphere of argon, cooled to −40 °C with a dry ice–ethanol bath, and stirred at this temperature for 10 min. The solution was quickly filtered through a Schlenk tube containing a fine glass sinter. The orange microcrystals were washed with 2 × 0.5 mL portions of −78 °C MeOH and 3 × 1.5 mL portions of Et_2O and dried under vacuum to yield 0.363 g (82%) of [Rh((*S*,*S*)-chiraphos)]$_2$(ClO$_4$)$_2$. The compound was handled as a solid in air for several hours without appreciable oxidation, but was stored under argon at −15 °C. Anal. Calcd for $C_{56}H_{56}Cl_2O_8P_4Rh_2$: C, 53.48; H, 4.45; Cl, 5.64; P, 9.85. Found: C, 52.91; H, 4.48; Cl, 5.36; P, 9.45. The ^{1}H and ^{31}P NMR spectra are given in Table IV.

General Procedure for Small-Scale Catalytic Reactions. Typically, [Rh((*S*,*S*)-chiraphos)]$_2$(ClO$_4$)$_2$ (1.05 mg, 8.32 × 10^{-4} mmol dimer) was dissolved in dry acetone-d_6 (0.6 mL) under argon. The substrate (8.32 × 10^{-2} mmol, 50 equiv per Rh) was then added via syringe. The reactions were monitored by ^{1}H NMR spectroscopy. The results are summarized in Tables I–III. [Rh((*S*)-binap)NBD]ClO$_4$ was hydrogenated prior to the introduction of substrate as follows. The NBD compound (1.53 mg, 1.66 × 10^{-3} mmol) was dissolved in 0.6 mL of dry acetone-d_6 under argon. Hydrogen gas was bubbled through the mixture for 2 min, causing a rapid color change from orange-yellow to red-orange. The solutions were then purged for 4 min with argon. The substrate (8.32 × 10^{-2} mmol, 50 equiv per Rh) was then added via syringe.

General Procedure for Large-Scale Catalytic Reactions. The reactions were set up exactly as for the small-scale reactions except that everything was scaled up by a factor of 22 and nondeuterated, dry acetone was used as solvent. The reactions were in general kept for 2 h longer than the time required for completion of the small-scale counterparts. The solvent was then removed using a rotary evaporator, and the residue was dissolved in a 2:1 mixture of pentane and methylene chloride and then passed through a Florisil plug (~5 g) to remove the catalyst from the solution. The solvents were removed using a rotary evaporator, yielding in all cases a clear, pale-yellow oil. The next stages of the procedure depend on the nature of the product and will be described separately.

Oxidative Cleavage of Hydrosilation Products from Terminally Substituted Allylic Silyl Ethers. A mixture of the silacyclopentyl ether (1.83 mmol), potassium fluoride (0.43 g, 7.32 mmol), potassium hydrogen carbonate (0.73 g, 7.32 mmol), and hydrogen peroxide (3.74 g of a 30% solution in water, 32.94 mmol) in methanol (17 mL) and THF (17 mL) was refluxed for 18 h, forming a colorless solution with a white solid. The solution was reduced to ~3 mL using a rotary evaporator, treated with 15 mL of H_2O, and saturated with NaCl. The aqueous phase was extracted with 5 × 20 mL portions of Et_2O, and the combined organic layers were washed with a 5% sodium bisulfite solution in brine (30 mL), 2 × 30 mL portions of a saturated sodium bicarbonate solution in brine, and brine (30 mL) and then dried ($MgSO_4$). The solution was filtered and the solvent was removed, yielding in most cases a mixture of alcohols corresponding to the alkyl groups originally attached to the silicon center of the silacyclopentyl ether. The yields were high and corresponded to the amount of silacyclopentyl ether generated by the hydrosilation reaction. These mixtures were directly converted into the corresponding Mosher's esters to determine the ee. For cases that produced water-soluble diols from the oxidative cleavage reaction, the diol was isolated by combining the aqueous layers and continuously extracting with Et_2O. The ^{1}H NMR spectra of the diols are shown in Table IV. When necessary, the diols were purified by chromatography using ethyl acetate–methylene chloride mixtures (the ratio depended on the diol) as eluent on silica gel to measure the optical rotation.[24]

Oxidative Cleavage of Hydrosilation Products of Internally Substituted Allylic Ethers. (a) Ring Opening with Phenyllithium. Phenyllithium (1.40 mL of a 2 M solution in cyclohexane–Et_2O (70:30), 2.81 mmol) was added dropwise over 10 min to a solution of the silacyclopentyl ether (1.83 mmol) in dry Et_2O (80 mL) under argon. The mixture was stirred for 1 h at room temperature and then was carefully hydrolyzed by the addition of a saturated aqueous solution of ammonium chloride (40 mL). The organic phase was separated, and the aqueous phase was extracted with 2 × 40 mL portions of Et_2O. The combined organic extracts were washed with brine (40 mL) and then dried ($MgSO_4$). Removal of the solvent led to nearly quantitative yields of the corresponding phenylsilyl alcohols. The compounds were used without further purification. The

(24) Literature values for the standard optical rotations were obtained from the following: 1-phenyl-1,3-propanediol, Shiba, T. Personal communication; 2-methyl-1,4-butanediol, Meyers, A. I.; Michelich, E. D. *J. Org. Chem.* **1975**, *40*, 1186; 2-phenyl-1,4-butanediol, Hiyama, T.; Kobayashi, K.; Fujita, M. *Tetrahedron Lett.* **1984**, *25*, 4959; 2-methyl-3-phenyl-1,3-propanediol, Masamune, S.; Sato, T.; Kim, B.-M.; Wollman, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 8279.

^{1}H NMR spectra are shown in Table IV.

(b) Preparation of Benzyl Ethers. A solution of the phenylsilyl alcohol (1.83 mmol) in dry THF (10 mL) was added dropwise over 3 min to a solution of potassium *tert*-butoxide (0.24 g, 2.20 mmol) in dry THF (40 mL) under argon. The solution was then cooled to 0 °C with an ice–water bath, and benzyl bromide (1.55 g, 9.2 mmol) was added dropwise over 2 min, causing the mixture to become cloudy. The mixture was stirred for 1 h at 0 °C, after which time the mixture was allowed to warm to room temperature. The solution was stirred at room temperature for 18 h and then was hydrolyzed by the addition of a saturated solution of aqueous ammonium chloride (35 mL). The clear yellow organic phase was separated from the aqueous phase, and the aqueous phase was extracted with 3 × 80 mL portions of Et_2O. The combined organic phases were washed with 4 × 80 mL portions of water, 2 × 40 mL portions of 3 N HCl, 80 mL of water, 2 × 80 mL portions of a saturated solution of aqueous sodium carbonate, and 80 mL of brine and dried ($MgSO_4$), and the solvent was removed with a rotary evaporator, yielding a yellow oil. The excess benzyl bromide was removed by placing the oil under vacuum (0.1 mm) while heating the reaction vessel with a 70 °C oil bath for 1 h. Purification by flash chromatography on silica gel using a 7:1 mixture of *n*-hexane–methylene chloride afforded the pure (by ^{1}H NMR spectroscopy) ether in ~50% yield based on the starting amount of alcohol. The ^{1}H NMR spectra are shown in Table IV.

(c) Protolytic Cleavage of the Silicon–Phenyl Bonds of the Benzyl Ethers. A solution of HBF_4OEt_2 (0.35 g of an 85% by weight solution in Et_2O, 1.83 mmol) was added to a solution of the benzyl ether (0.92 mmol) in dry chloroform (10 mL) that was cooled to 0 °C by an ice–water bath. The mixture was stirred for 1 h at 0 °C, and then the solvent and other volatiles were removed by placing the system under vacuum (0.1 mmHg) for 30 min at 0 °C, warming the reaction mixture to room temperature, and then pumping on it for an additional 5 min. The remaining dark-brown oil was oxidatively cleaved as described for the hydrosilation products from terminally substituted allylic ethers, except that 5 equiv of potassium hydrogen carbonate were used instead of 4. The overall yields ranged from 60 to 70% of essentially pure (by ^{1}H NMR) 2-methyl-1,3-propanediol benzyl ether. The ^{1}H NMR spectrum is shown in Table IV.

Oxidative Cleavage of 1,1-Diphenylsilacyclopentanes. A solution of the 1,1-diphenylsilacyclopentane (1.83 mmol), dry methylene chloride (10 mL), and HBF_4 (0.81 g of an 85% by weight solution in Et_2O, 3.48 mmol) was refluxed under argon for 18 h. All of the volatiles were then removed under vacuum (0.1 mm, 25 °C, 30 min). The remaining dark-brown oil was then oxidatively cleaved as described for the hydrosilation products from terminally substituted allylic ethers, except that 5 equiv of potassium hydrogen carbonate were used instead of 4. The product obtained was a ~1:1 mixture of 2-methyl-1,4-butanediol and phenol. The yield of the desired diol was 45%. More diol could be obtained by continuously extracting the combined aqueous phases with Et_2O for 18 h. The combined yield of the diol was 85%. The phenol could be removed from the diol with a significant loss in yield by extracting an Et_2O solution of the diol and phenol with a 1 N sodium hydroxide in brine. The ^{1}H NMR spectrum of the di-Mosher's ester is shown in Table IV.

Preparation of Mosher's Esters. The Mosher's esters were prepared using literature procedures.[13]

Product Identification. The identities of most of the organic products were determined using the usual principles of NMR spectroscopy. Furthermore, the oxidative cleavage reaction verifies most of the assignments by acting as a degradative synthesis, converting the intramolecular hydrosilation products into known alcohols.

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Supplementary Material Available: Listing of the ^{1}H NMR data for 76 of the substrates, products, and derivatives (Table IV) (11 pages). Ordering information is given on any current masthead page.

Asymmetric Catalysis. Mechanism of Asymmetric Catalytic Intramolecular Hydrosilation

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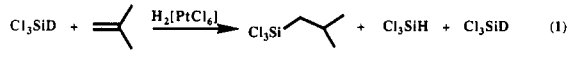
Abstract: The mechanism of asymmetric catalytic intramolecular hydrosilation using [Rh(diphosphine)]$^+$ catalysts has been investigated by the use of specifically labeled deuterated substrates. It is concluded that oxidative addition of the silicon hydride bonds to the catalysts is rapid and reversible for most systems. Both 5-membered and 6-membered metallacycles are inferred to form rapidly and reversibly. These species are unproductive catalytic intermediates. It was inferred that β-hydride elimination is very rapid and is faster than chelate ring conformational interconversion. Hydrosilation proceeds by silyl olefin insertion. The turnover-limiting and enantioselective steps are believed to be the silyl olefin insertion. It is concluded that the major diastereomeric intermediate, the silyl metal olefin hydride, produces the major enantiomer of the product.

Speier's discovery that the homogeneous catalytic hydrosilation of olefins could be effected by the catalyst precursor $H_2[PtCl_6]$[1] led to numerous associated developments. These included homogeneous hydrosilation of acetylenes, ketones, imines, and diazines and the use of numerous other metal complexes as catalysts.[2] Although over 4000 papers have appeared on the subject, certain key features of the mechanism of hydrosilation remain in dispute. Further, no systematic mechanistic study of asymmetric catalytic hydrosilation has appeared. This paper attempts to address the central aspects of the mechanism of asymmetric catalysis for the systems described in the previous paper in this issue.[3]

The generally accepted mechanism for olefin hydrosilation is depicted in Figure 1, the essential features of which were first postulated by Chalk and Harrod.[4] This mechanism accounts for a number of observations associated with hydrosilation, notably the distribution of deuterium atoms during catalysis. Thus, the catalyzed reaction shown in eq 1 leads to almost statistical scrambling of the deuterium over all of the possible sites of the carbon atoms of the product and on the silicon.[5] This result



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