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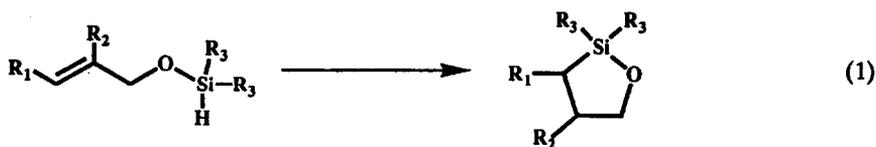
Asymmetric Catalysis. Asymmetric Catalytic Intramolecular Hydrosilation and Hydroacylation.

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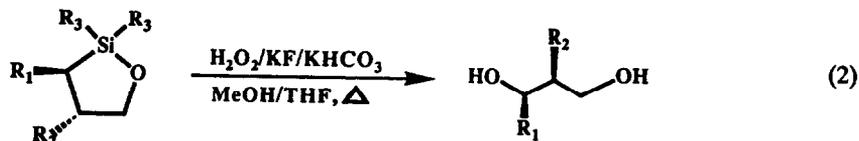
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Abstract: Catalysts of the type $[Rh(\text{chiral diphosphine})]^+$ efficiently catalyse the intramolecular hydrosilation of silyl ethers derived from allylic alcohols. The products can be converted to chiral 1,3-diols. High enantiomeric excesses (*ee*'s) are observed for substrates bearing an aryl group at the olefin terminus. These same catalysts produce chiral cyclopentanones from 4-substituted 4-pentenals. Tertiary, acyl and ester substituents give nearly quantitative *ee*'s. The mechanism of hydrosilation is inferred to involve silyl olefin insertion, whereas the key step in hydroacylation probably involves reductive elimination of the metallacyclohexanone intermediate.

That metal complexes catalyse the hydrosilation of olefins has been widely known¹ but the exploitation of the reaction in asymmetric catalysis has been impeded by a number of factors. Among these are the lack of regioselectivity as well as double bond migration during catalysis which generally leads to formation of a terminal silicon-carbon bond irrespective of the original double-bond position,² the lack of suitable mild methods for cleaving silicon carbon bonds to useful products and the generally low *ee*'s encountered.³ One possible solution to all three of these problems is to employ intramolecular hydrosilation⁴ with substrates of the type depicted in eq 1. The intramolecular cyclization ensures the



regioselectivity of the catalysis because 5-membered ring products are nearly always formed. The presence of a silicon-oxygen bond in the product allows for the stereospecific oxidative cleavage⁴ depicted in eq 2 to give chiral 1,3-diols. The intramolecular cyclization is likely to produce cyclic transition states or intermediates, which are likely to have more restricted configurations than the intermolecular



analogues, and hence higher and more consistent *ee*'s are expected for the intramolecular processes. This notion is supported by the fact that many asymmetric reactions depend on chelation for their success.⁵

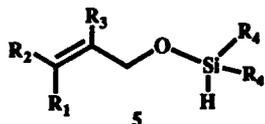
norbornadiene (NBD) complexes, $[\text{Rh}(\text{diphosphine})(\text{NBD})]^+$ by hydrogenation of the olefin (eq 4) in CH_2Cl_2 , acetone or methanol.⁷ The $[\text{Rh}((\text{S,S})\text{-chiraphos})]\text{ClO}_4$ complex can be isolated as the aryl bridged dimer, $[\text{Rh}((\text{S,S})\text{-chiraphos})]_2(\text{ClO}_4)_2$ which upon dissolution in CH_2Cl_2 and acetone dissociates to the bis-solvent monomer,⁷ $[\text{Rh}((\text{S,S})\text{-chiraphos})(\text{solvent})_2]\text{ClO}_4$. The binap dimer¹⁰ is more difficult to isolate, and it is more convenient to prepare the $[\text{Rh}((\text{S})\text{-binap})(\text{solvent})_2]\text{ClO}_4$ catalyst *in situ*.

In this paper we include a summary of previously published work on hydrosilation together with new work on hydroacylation. The reason for this is to demonstrate how two superficially similar reactions most probably operate by distinctly different mechanisms and consequently may require different considerations for the selection of substrates. Mechanistic considerations are an essential prerequisite to the rational development of effective asymmetric catalysts. Although as yet not all of the mechanistic details are known, the present comparison serves to indicate how these catalytic reactions may be developed.

1. Hydrosilation.

Our initial concerns with using these new catalysts for hydrosilation were the following. First, are these good catalysts for hydrosilation? Second, if so, which solvents are the most effective? Third, after suitable catalytic conditions are established, what substitution patterns on the olefin and silicon promote or impede the reaction? Fourth, for substrates which proceed in high chemical yields, which of these substitution patterns give high ee's?

We found that the proposed catalysts were indeed effective promoters of the reaction, particularly in acetone solutions.¹¹ Catalysis proceeded rapidly for many substrates at 25° C using 4 mol % catalyst. The catalytic effectiveness was critically dependent on the substituents on the generic substrate 5.



The rate of catalysis roughly parallels the bulk of the R_4 groups and when they are very bulky (such as *t*-butyl) no catalysis occurs, even when the other R groups are hydrogen atoms. When two substituents are present at the olefin terminus, R_1 and R_2 , no catalysis occurs. A single substituent at the terminal olefin position tends to retard the reaction except when it is an aryl group. The catalysis tolerates the presence of all R_3 groups, even a *t*-butyl substituent. Contrary to our expectations, the ee's are not very sensitive to the nature of the R_4 groups on the silicon atom; only the rate of catalysis is affected. Thus with the allylic substrate, $\text{R}_1 = \text{R}_2 = \text{H}$ and $\text{R}_3 = \text{CH}_3$, varying the R_4 groups causes only minor variations in the ee, which in all cases were found to be less than 50%.¹¹

We found, however, that when an aryl group is present at the terminal olefin position high ee's are obtained with the binap catalyst and that the ee's are only slightly affected by the R_3 group. Table 1 lists the results obtained for these types of substrates. We found that cyclized silicon substitution gave convenient rates and high ee's. It will be noted that the *cis* and *trans* cinnamyl derivatives give identical chemical yields, rates of catalysis and ee's. Further, the chiraphos catalyst consistently gives lower ee's than the binap analogue. Presumably this reflects the subtle conformational differences that obtain for the two chiral ligands. Given the results in Table 1 it seems reasonable to suggest that the binap catalyst will give high ee's for substrates which possess a terminal aryl group and that the R_3 substituent will

generally have a minor effect.

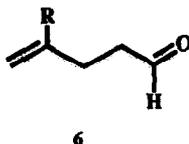
Table 1
Asymmetric Catalytic Intramolecular Hydrosilation of Aryl Olefins
 using ~2 mole % [Rh(diphosphine)]ClO₄ Catalysts in Acetone at 25°C.

Substrate	Time	Yield %	ee % (config)	Diphosphine
	5min	75	97(R)	S-binap
	6h	61	74(R)	S,S-chiraphos
	1.5h	75	96(R)	S-binap
	1.5h	75	96(R)	S-binap
	45min	90	97(R)	S-binap
	20min	75	94(R)	S-binap
	1.25h	100	90(R,R)	S-binap
	17h	75	88(?)	S-binap

Data taken from reference 11.

2. Hydroacylation.

Since hydroacylation produces chiral cyclopentanones directly it is a more attractive transformation than hydrosilation. With the present catalysts, however, it is restricted to only substrates of the type 6. The reaction proceeds poorly or not at all when terminal olefin substituents are present in the substrate. Substrates of the type 6 are efficiently transformed to the cyclopentanones even when



R is bulky, using ~ 4 mol% catalyst at 25° C. The chemical yields are greater than 98% with little or no decarbonylation of the substrate.

We have investigated this enantioselective catalysis using the chiraphos and binap catalysts with substrates of the type 6 bearing a variety of R groups. Generally modest to good ee's (40 - 80%) were observed for primary and secondary alkyl groups and for aryl groups. When, however, tertiary groups^{6c} or ester groups or acyl groups were present spectacular ee's were obtained with the binap catalyst. Tables 2 and 3 list some of the observed ee's together with other data. In all cases the chemical yields are essentially quantitative and in most cases so are the ee's for the binap catalyst. As in the case of hydrosilation the chiraphos catalyst gives lower ee's. It is clear from these results that hydroacylation is an attractive method of generating essentially enantiomerically pure 3-substituted cyclopentanones which, in turn, can be introduced into synthetic strategies.

Table 2
Asymmetric Catalytic Intramolecular
Hydroacylation of 4-Pentenals using ~4 mol %
[Rh(diphosphine)]ClO₄ Catalysts 25°C.^a

Substrate	S,S-chiraphos ee%(config)	S-binap ee%(config)	Product (S-binap)
	29 (R)	>99 (S)	
	41 (R)	>99 (S)	
	32 (R)	>99 (S)	
	8 (R)	>99 (S)	
	15 (R)	>99 (S)	
	22 (R)	>99 (S)	

(a) Catalysis CH₂Cl₂.

Table 3
Asymmetric Catalytic Intramolecular
Hydroacylation of 4-Pentenals using ~4 mol %
[Rh(diphosphine)]ClO₄ Catalysts at 25°C.

Substrate	S,S-chiraphos ^a ee%(config)	S-binap ee%(config)	Product (S-binap)
	13 (R)	87 (S) ^a	
	64 (R)	94 (S) ^a	
	63 (R)	94 (S) ^a	
	35 (S)	>99 (S) ^b	
	11 (R)	>99 (S) ^b	

(a) Catalysis in CH₂Cl₂, (b) Catalysis in acetone.

3. Mechanism.

The mechanism of hydrosilation had been the subject of numerous investigations^{12,13} but certain key features of the mechanism remained in dispute. Further, no systematic study of the mechanism of asymmetric hydrosilation had appeared. Without discussing the historical context of the possible mechanisms, it suffices to pose the questions in terms of a mechanistic scheme directly related to the present substrates and catalysts (Figure 1). The mechanism illustrated in Figure 1 begins with oxidative addition of the silyl hydride (A → B). The intermediate, B, can form C, which upon β -hydride elimination regenerates B. Intermediate B can also produce the metallocycle, D, by hydride olefin insertion or E, by silyl olefin insertion. According to the Chalk-Harrod mechanism, D can reductively

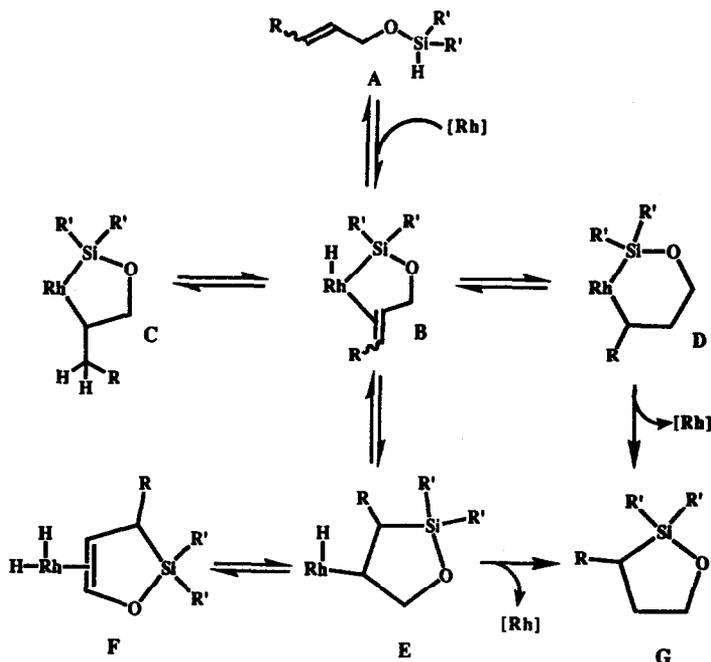


Fig. 1. Possible mechanistic paths for intramolecular hydrosilation using rhodium(I) catalysts.

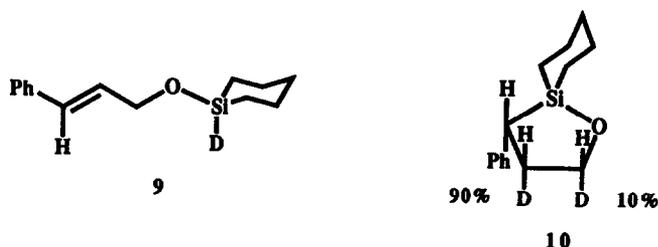
eliminate to give the product, G. Intermediate E can form F, by β -hydride elimination, or the product G, by hydride insertion into the Rh-carbon bond.

By deuterium labeling studies¹⁴ we have established the following. Both the steps, A → B and B → C are rapid and reversible. Intermediate D is probably formed but reverts to B. The intermediate E, from silyl olefin insertion, is formed and gives the product. The reversibility, B ⇌ E, was not established.

The experiments which encapsulate some of the features necessary to infer these conclusions involve the use of the substrates 7 and 8 with the binap catalyst. Following the catalysis of 8 with the binap catalyst by ¹H and ²H NMR reveals that during catalysis the deuterium and silicon hydrogen



atoms switch positions simultaneously with the formation of the trans isomer **9**. The product has the deuterium distribution illustrated in **10**. The absence of deuterium in the benzylic position of **10** infers



that cis \rightarrow trans isomerism occurs before catalytic cyclization, namely, all of the catalysis proceeds via the trans isomer, **9**. This explains why the cis and trans isomers give the same ee (Table 1). The presence of 10% deuterium on the carbon α to the oxygen atom and cis to the phenyl group in **10** implies the operation of the silyl olefin insertion step B \rightarrow E \rightarrow F (Figure 1). These conclusions are summarized by the mechanistic outline shown in Figure 2.

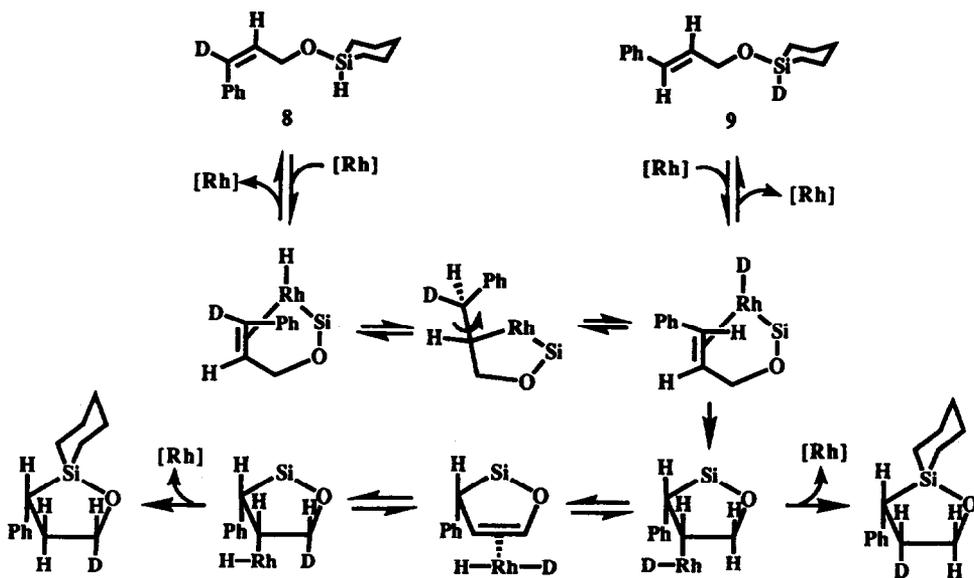


Fig. 2. The proposed mechanism of intramolecular hydrosilation of **8**, a process which first involves isomerization to **9** which then forms the products by silyl olefin insertion.

These deuterium scrambling experiments provide a persuasive case for the silyl olefin insertion mechanism which has been resisted because of the absence of chemically defined examples. Recent work derived from various sources,¹⁵ however, suggests that it is the preferred mechanism for hydrosilation of olefins and ketones.

The hydroacylation mechanism appears to be different. From previous work,^{6,7b} it appears that at least the steps depicted in Figure 3 require consideration. This work also indicates that the catalytically unproductive steps $L \rightarrow M \rightarrow N$ are rapid and reversible so that deuterium at the acyl group

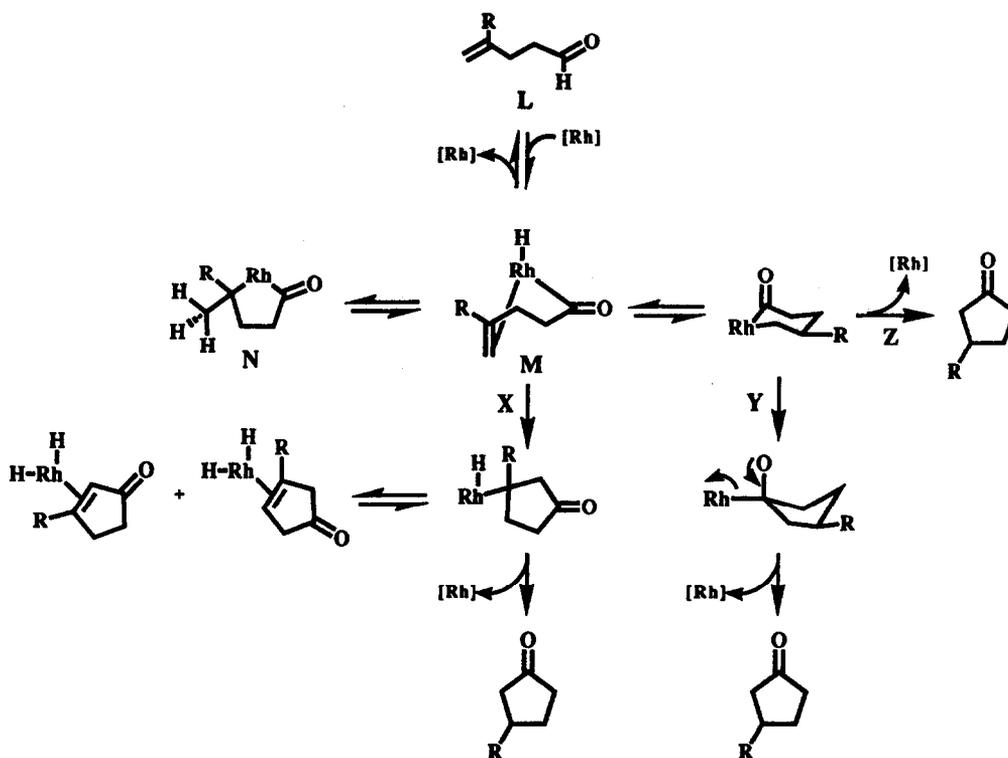
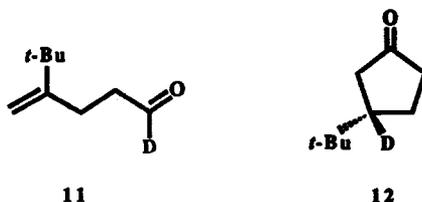


Fig. 3. The possible mechanistic paths involving hydroacylation of L to the product.

is scrambled with the two hydrogen atoms at the terminus of the double bond. It was not established, however, how productive steps occur. These could occur by the three paths, X, Y or Z (Figure 3). Path X involves acyl olefin insertion and were it to obtain we might expect the kind of deuterium distribution found for hydrosilation when an appropriately labeled substrate is used. Path Y involves attack at the acyl carbon atom followed by reductive elimination as shown. The third path, Z, is the conventional carbon-carbon coupling mechanism.

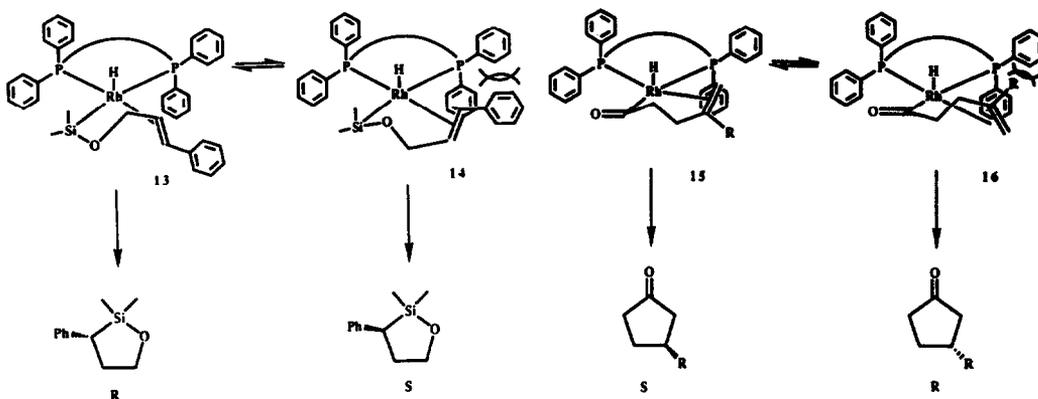
In an attempt to distinguish some of these alternatives the substrate 11 was used with the binap catalyst. Surprisingly, the only deuterated species detected was 12. This result suggests that the species N (Figure 3) is not formed, presumably because the steric bulk of the *t*-butyl group hinders the formation



of the Rh-carbon bond in the metallocycle N. Further, the steric effects may suppress acyl olefin insertion were it a viable mechanism. The absence of deuterium in other than the tertiary position of the product is consistent with this supposition. It seems probable, therefore, that either the paths Y or Z operate. We are disposed to prefer path Y for a number of circumstantial reasons, principally because path Y has been established in model compounds.¹⁶ It thus appears that although hydrosilation and hydroacylation superficially seem to be similar processes their mechanisms are different.

4. Origins of Enantioselection.

As in all asymmetric catalysis the origins of the chiral discrimination are difficult to establish. There are, however, a number of factors which appear to be important in controlling the enantioselection. The major interaction of the substrate is with the phenyl groups of the chiral phosphine.¹⁷ These phenyl groups are arranged in quasi-axial and quasi-equatorial dispositions, but the axial phenyl groups of binap are more axially defined compared to those of chiraphos. These binap axial phenyl groups are more inclined to the chelate ring and the equatorial phenyl groups are further away from the chelate ring than in chiraphos. These conformational differences may provide a reason for the greater enantioselectivity observed with the binap catalysts. We assume that for both hydrosilation and hydroacylation that enantioselection is governed by olefin face selection in the hydrido intermediates as depicted in 13 versus 14 for hydrosilation and in 15 versus 16 for hydroacylation using S-binap. Molecular models suggest that the disastereomer 14 is less stable than 13 and that 16 is less stable than 15 because of the depicted interactions between the substrate substituents and the equatorially disposed



phenyl groups. Of course these models are very primitive and are useful only in suggesting what interactions may be important.

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EXPERIMENTAL SECTION.

Since reactions using the catalyst precursor $[\text{Rh}((\text{S})\text{-binap})(\text{NBD})]\text{ClO}_4$ generally gave higher *ee*'s, the experimental details will focus on reactions involving this compound. The reactions involving $[\text{Rh}((\text{S,S})\text{-chiraphos})]_2(\text{ClO}_4)_2$ ¹¹ were performed analogously except the chiraphos dimer can be dissolved and used directly without the H_2 reduction step required to activate $[\text{Rh}((\text{S})\text{-binap})(\text{NBD})]\text{ClO}_4$.

Preparation of $[\text{Rh}((\text{S})\text{-binap})(\text{NBD})]\text{ClO}_4$. $[\text{Rh}(\text{NBD})_2]\text{ClO}_4$ ¹⁸ (0.22g, 0.58 mmol) and (S)-binap (0.36g, 0.58 mmol) were dissolved in dry, deoxygenated CH_2Cl_2 (15 mL) under argon. The dark red solution was stirred at room temperature for 1 h, filtered through Celite[®], and the Celite[®] was washed with CH_2Cl_2 (3 x 1 mL). Dry, deoxygenated THF (18 mL) was added to the solution over 3 min followed by dry, deoxygenated hexane (8 mL) added over 5 min causing crystallization to begin. More hexane (15 mL) was added in small portions over 4 h to complete the precipitation of dark red crystalline plates or microcrystals. The crystals were filtered from solution under argon, washed with THF (3 x 5 mL) and hexane (2 x 5 mL), and dried under an argon flow and under vacuum. **[CAUTION: Use care when handling potentially explosive perchlorate salts.]** Yield of $[\text{Rh}((\text{S})\text{-binap})(\text{NBD})]\text{ClO}_4$: 0.47g (88%) as dark red crystalline plates.

Preparation of $[\text{Rh}((\text{S,S})\text{-chiraphos})]_2(\text{ClO}_4)_2$. $[\text{Rh}((\text{S,S})\text{-chiraphos})(\text{NBD})]\text{ClO}_4$ was prepared by the method described above. It was converted to the dimer in 80% yield by H_2 reduction of the norbornadiene in methanol.¹¹

Typical Large Scale Catalytic Hydrosilation Reaction. $[\text{Rh}((\text{S})\text{-binap})(\text{NBD})]\text{ClO}_4$ (0.0158g, 1.72×10^{-5} mol) was dissolved in dry, deoxygenated acetone (13 mL) under argon. Hydrogen gas was bubbled through the solution for 3 min causing a color change from yellow-orange to red-orange. The solution was stirred for 15 min, and then argon was bubbled through the solution for 5 min to purge all hydrogen gas. Then 1-[(*cis*-3-phenyl-2-propenyl)oxy]-silacyclohexane¹¹ (0.400g, 1.72 mmol) was added by syringe, and the solution was stirred for 3.5 h. In general, the large scale reactions were allowed to react 2 h longer than the times determined for completion of the small scale reactions. The acetone was removed on a rotary evaporator and the residue was dissolved in a 2:1 mixture of pentane and CH_2Cl_2 and then passed through a Florisil[®] plug (~5 g) to remove the catalyst from the solution. The solvents were removed on a rotary evaporator, yielding 4-phenyl-1-oxa-5-silaspiro[4.5]decane, 0.30 g (75%) as a light yellow oil.

Oxidative Cleavage of Hydrosilation Products from Terminally Substituted Allylic Silyl Ethers. A mixture of the crude 4-phenyl-1-oxa-5-silaspiro[4.5]decane (0.28 g, 1.2 mmol), potassium fluoride (0.50 g, 8.6 mmol), potassium hydrogen carbonate (0.86 g, 8.6 mmol), and hydrogen peroxide (3.5 mL of a 30% solution in water, 31.0 mmol) in methanol (17 mL) and THF (17mL) was refluxed for 18 h, forming a colorless solution with a white solid. The mixture was reduced to ~3 mL on a rotary evaporator, treated with H_2O (15 mL), saturated with NaCl, and extracted with Et_2O (5 x 25 mL). The combined organic layers were washed with a 5% sodium bisulfite solution in brine (30 mL), a saturated sodium bicarbonate solution in brine (2 x 30 mL), and brine (30 mL). The solution was dried (MgSO_4), filtered and reduced

to a colorless oil, 1-phenyl-1,3-propanediol, 0.13g (70%).

Determination of Hydrosilation Enantiomeric Excesses. The crude diols were converted to the Mosher esters using literature methods.¹⁹ The ee's were calculated from the integration of the diastereomer signals in the ¹H NMR spectra. In the case of the Mosher ester of 1-phenyl-1,3-propanediol the resonance for the benzylic proton appeared, centered at 5.92 ppm and 5.85 ppm for the major (R) and minor (S) enantiomers, respectively.

Typical Large Scale Catalytic Hydroacylation Reaction. [Rh((S)-binap)(NBD)]ClO₄ (0.0172 g, 1.87 x 10⁻⁵ mol) was dissolved in dry, deoxygenated CH₂Cl₂ (3.0 mL) under argon and activated by hydrogen gas as above. Then 4-acetyl-4-pentenal (0.0594 g, 4.69 x 10⁻⁴ mmol) was added by syringe, and the solution was stirred for 4.5 h. In general, the large scale reactions were allowed to react twice the times determined for completion of the small scale reactions. The solvent was removed on a rotary evaporator, and the residue was dissolved in a 1:1 mixture of pentane and CH₂Cl₂ and then passed through a Florisil® plug (~1 g) to remove the catalyst from the solution. The solvents were removed on a rotary evaporator, yielding 3-acetylcyclopentanone, 0.0540 g (90%) as a light yellow oil.

Determination of Hydroacylation Enantiomeric Excesses. The crude cyclopentanones were converted to the diastereomeric hydrazone derivatives using (S)-(-)-1-amino-2-methoxymethylpyrrolidine by the method of Enders.²⁰ The reactions were carried out at room temperature using 1.1 equivalents of the pyrrolidine for all cyclopentanones except the 3-acyl cyclopentanones, which were reacted with 2.5 equivalents of the pyrrolidine. The hydrazone may be either syn or anti with respect to the 3-substituent which when paired to two possible enantiomers at the 3-position gives four possible diastereomers. The syn and anti isomers are formed in approximately equal amounts. The 3-acyl substituted cyclopentanones present the possibility of forming bis-hydrazones, but 3-(2,2-dimethyl propionyl)cyclopentanone and 3-benzoylcyclopentanone formed exclusively mono-hydrazones at the cyclopentanone carbonyl. 3-Acetylcyclopentanone showed little or no discrimination between the two carbonyl groups, forming the bis-hydrazone which gives rise to two sets of eight imine carbon signals in the ¹³C NMR spectra. The ee's were calculated from the integrations of the diastereomeric imine carbon signals in the ¹³C NMR spectra. When the peaks were sufficiently separated all four signals (or sixteen in the case of 3-acetylcyclopentanone) were used to calculate the ee, summing the appropriate sets. The signal to noise ratio in the imine region was greater than 100:1. Absolute configuration assignments were made by comparing the sign of the optical rotation to known cyclopentanones where possible. In other cases, assignments were made on the basis of similar behavior of the imine carbon signals. The signals for the S enantiomer always appeared upfield from those of the R enantiomer.

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