Asymmetric Catalytic Reduction with Transition Metal Complexes. II. Asymmetric Catalysis by a Supported Chiral Rhodium Complex[1]

Willy Dumont, Jean-Claude Poulin, Tuan-Phat Dang, and Henri B. Kagan*

Contribution from Laboratoire de Synthèse Asymétrique Université de Paris-Sud, Centre d'Orsay, 91405-Orsay, France.
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Abstract: An insoluble chiral polymer-supported rhodium complex closely related to the soluble Rh(I)–diop complex (diop = 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (**1**)) was prepared using a Merrifield resin. This insoluble system (suspended in benzene) catalyzes the asymmetric hydrogenation of α-ethylstyrene and methyl atropate with a much lower efficiency than in solution, and ethanol inhibits the catalysis. In contrast, both catalytic systems, soluble and insoluble, are very efficient for asymmetric hydrosilylation of ketones (acetophenone, methyl benzyl ketone, isobutyrophenone). For a given ketone, the optical yield strongly depends upon the silane used. Dihydrosilanes (diphenylsilane, phenylmethylsilane, α-naphthylphenylsilane) are always better than monohydrosilanes (triethylsilane, triethoxysilane, triphenylsilane). Optical yields up to 58% were obtained. In all cases, the insoluble catalyst can be filtered and easily reused.

One of the most recent and important advances in asymmetric synthesis is the use of a soluble chiral catalyst. Soluble catalysts can be better defined than the heterogeneous ones, and in such complexes it is often easy to vary widely the steric and electronic environment of the catalytically active site in order to optimize both the chemical and optical yields of an asymmetric synthesis.

The best results have been obtained in oligomerization of olefins with nickel catalysts[2] or in reduction with a rhodium catalyst[1,3–6] or cobalt complexes.[7] Optical yields as high as 70–90% have been observed.

However, in the use of a soluble catalyst, a problem of practical importance is encountered: the separation of the catalyst from the reaction products requires special treatment which usually destroy it. One way to solve this problem would be to fix the catalyst on a solid support in a way that retains the advantages observed in solution. Recently some authors described the introduction of phosphine groups into polystyrene. This phosphinated resin has been used as a ligand in rhodium or platinum complexes in order to catalyze the hydrogenation,[8–10] hydrosilylation,[9] and hydroformylation[11] of olefins. In all cases, the insoluble catalyst could be filtered off from the reaction mixture and reused.

For asymmetric synthesis, we were interested in preparing a chiral phosphinated polymer. To achieve this goal we could try to introduce either achiral phosphine unit into a chiral natural polymer or chiral phosphinated units into a synthetic achiral resin. The latter way was preferred and we tried to link covalently a known chiral ligand to a commercial resin.[12]

We reported recently[1] the synthesis of the diphosphine **1** (diop) which gave very good results in the homogeneous hydrogenation of α-acylaminoacrylic acids. We will now describe in detail the synthesis of an insoluble analog **7** and its use in heterogeneous asymmetric catalysis involving rhodium complexes.[13]

Synthesis of the Supported Chiral Complex 8

We started from a Merrifield resin[14] (0.7 mequiv of Cl/g, 200–400 mesh, 2% divinylbenzene) **2** which was oxidized with DMSO by the method of Frechet and Schuerch.[15] Elemental analysis or a modified Volhard titration indicated that the resin **3** was free from chlorine.

The insoluble aldehyde **3** was then treated with the (+) diol **5** obtained by ethanolysis of the corresponding acetonide **4** to give the ditosylate **6**.[16] The elemental analysis of resin **6** showed that the acetalization had taken place to an extent of 70%. Finally the reaction of resin **6** with lithium diphenylphosphide in THF solution gave the phosphinated polymer **7** which contained, from elemental analysis, 0.5 mequiv of diphosphine unit per gram (Scheme I).

In a typical experiment, 0.5 g of the phosphinated resin **7** was stirred during 21 hr, under nitrogen or

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(11) (a) W. O. Haag and D. D. Whitehwist, Proceedings of the 5th International Congress on Catalysis, Amsterdam, 1972, North-Holland Publishing Co., Amsterdam, in press; (b) K. G. Allam, R. D. Hancock, J. McKenzig, and R. C. Pitkethy, *ibid.*, in press.
(12) The first way was used by M. Bursian and H. Pracejus [East German Patent 92,031 (1972); *Chem. Abstr.*, **78**, 72591 (1973)]. They described an asymmetric hydrogenation using a rhodium complex with a phosphinated cellulose.
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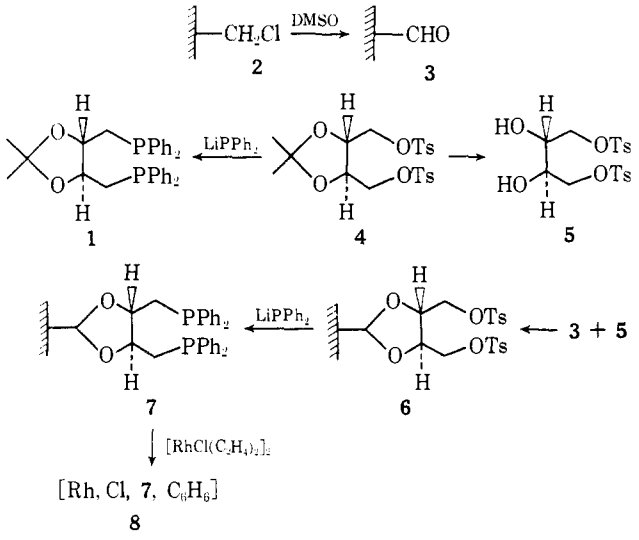
(16) In all experiments described in this paper, we used the (+)-diop **1** and the (+) diol **4** which were obtained from D(−)-tartaric acid.

Scheme I



argon, at room temperature in a solution of 23.4 mg (0.06 mmol) of $[RhCl(C_2H_4)_2]_2$ in benzene (10 ml) to give the insoluble complex **8** [Rh, 7, Cl, C_6H_6]. When this complex was filtered, the residual solution was colorless and no longer contained rhodium.

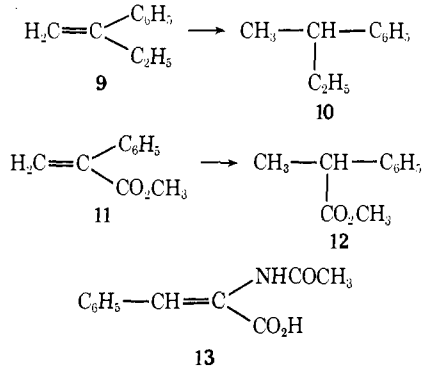
Catalysis of Asymmetric Hydrogenation of Olefinic Double Bonds by Complex 8

We first tested the catalytic activity of the insoluble complex **8** for hydrogenation of simple olefins: α-methylstyrene and 2-ethyl-1-hexene were easily and quantitatively hydrogenated at room temperature in the presence of complex **8** suspended in benzene. These reactions were followed by vpc. After completion of the reactions, the catalyst was separated by filtration in the air (without any special care) and reused in similar experiments. In a second step, we studied several asymmetric hydrogenations in the presence of **8**; 13.6 mmol of α-ethylstyrene **9** was quantitatively hydrogenated in 12 hr (maximum observed rate = 0.30 ml of H_2/min) at room temperature in the presence of 0.5 g of the insoluble catalyst (prepared as described above) suspended in benzene. After removal of the catalyst and distillation of the reaction mixture, we found for the pure (*R*)-(−)-2-phenylbutane **10** an optical purity of 1.5%.[17] The hydrogenation of α-ethylstyrene with soluble Rh–diop catalyst was achieved with both higher optical yield (15%) and higher rate of reaction (using a lower quantity of catalyst, 0.06 mmol of Rh, the maximum rate is 0.75 ml of H_2/min for the same amounts of substrate and solvent).

The insoluble catalyst was reused in a new experiment using the same amount of substrate and solvent to give quantitatively in 30 hr the (*R*)-(−)-2-phenylbutane **10** with an optical yield of 0.6%. The complex **8** suspended in benzene also catalyzed slowly the asymmetric hydrogenation of methyl atropate (**11**) to (*S*)-(+)-methyl hydratropate (27%) with an optical yield of 2.5%[17] (*vs.* 7% with the soluble Rh–diop catalyst[18]). In these two cases it appears that the optical yields are always much lower with the insoluble catalyst. This unfavorable effect must be due to the support but more experiments are needed before we can understand this fact.

Finally, we were unable to hydrogenate α-acetamidocinnamic acid (**13**) in the presence of **8** suspended in a benzene–ethanol solution (α-acetamidocinnamic acid is practically insoluble in pure benzene). We observed that the resin **8** contracts strongly in the presence of ethanol and we suspected that this fact was perhaps responsible for the inactivity of our catalyst. Indeed the hydrogenation of simple olefins such as α-methylstyrene or ethylhexene could not be achieved if instead of benzene we used as solvent a mixture of benzene and ethanol, presumably because of the highly hydrophobic nature of the polystyrenic support. All these experiments led us to the conclusion that the supported catalyst **8** is not a good catalyst for asymmetric hydrogenation. It catalyzes effectively the hydrogenation of olefins but with optical yields lower than those observed with the soluble Rh–diop complex. It was of interest to test the reduction of ketones by this complex and since reduction by hydrogen is not catalyzed by neutral rhodium–phosphine complexes we examined the possibility of using silanes as the reducing reagent.

Scheme II



Catalysis of the Asymmetric Hydrosilylation of Ketones

Recently several authors[19] described the hydrosilylation of ketones catalyzed by the Wilkinson complex $RhCl(PPh_3)_3$. The mechanism of this reaction seems to be closely related to that of the hydrogenation of olefins and involves an oxidative addition of the silane to the tris(triphenylphosphine)–rhodium chloride complex leading to a species $(PPh_3)_2RhH(SiR_3)Cl$. Ojima and Nihonyanagi[19b] isolated a complex of this kind in which R is an ethyl group.

With respect to the asymmetric hydrosilylation of ketones, we found only one report in the literature[20]: alkyl phenyl ketones were hydrosilylated by methyl dichlorosilane in the presence of a soluble platinum(II)–chiral phosphine complex. The best optical yield (18.6%) was obtained with *tert*-butyl phenyl ketone.

(17) Optical yields are calculated with respect to the following values for the optically pure compounds: (*R*)-2-phenylbutane, $\alpha^{23}D$ −24.3° (1 dm, neat) [D. J. Cram, *J. Amer. Chem. Soc.*, **74**, 2137 (1952)]; (*S*)-methyl hydratropate, $[\alpha]^{23}D$ +104.5° (*c* 4.35, C_2H_5OH) [A. Pracejus, *Justus Liebigs Ann. Chem.*, **634**, 9 (1960)].

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Table I. Homogeneous Catalytic Hydrosilylation of Acetophenone and Methyl Benzyl Ketone by Monohydrosilanes[a]

Ketone	Silane	Ketone/Rh ratio	Time, hr	Isolated alcohol; chemical yields,[c] %	Optical yield, %[d]
$C_6H_5COCH_3$[b]	$HSiCl_3$	200	24	0	
$C_6H_5COCH_3$	$HSi(C_2H_5)_3$	60	26	(*S*)-(−)-Phenylmethylcarbinol; 47	3.8
$C_6H_5COCH_3$	$HSi(C_6H_5)_3$	50	24	Phenylmethylcarbinol; 15	0
$C_6H_5COCH_3$	$HSi(OC_2H_5)_3$	200	24	(*S*)-(−)-Phenylmethylcarbinol; 60	10
$C_6H_5CH_2COCH_3$	$HSi(C_2H_5)_3$	60	20	(*S*)-(+)-Benzylmethylcarbinol; 50	1
$C_6H_5CH_2COCH_3$	$HSi(OC_2H_5)_3$	60	48	(*S*)-(+)-Benzylmethylcarbinol; 39	5.3
$C_6H_5COCH_3$	Polymethyl H siloxane[e]	50	24	(*S*)-(−)-Phenylmethylcarbinol; 56	3.6
$C_6H_5CH_2COCH_3$	Polymethyl H siloxane[e]	50	48	Benzylmethylcarbinol; 64	0

[a] Rh = 25–40 mmol/l; (+)-diop was used. Ratio diop/Rh = 1; 50° unless otherwise stated. Reactions were carried out under argon. Solvent: C_6H_6 (3–4 ml); silane/ketone = 2:1. [b] Reaction tried at room temperature. [c] Based on vpc. [d] Optical yields are calculated with respect to the following values for the optically pure compounds: phenylmethylcarbinol, $[\alpha]^{23}D$ −52.5° (*c* 2.27, CH_2Cl_2) [U. Nagai, T. Shishido, R. Chiba, and H. Mitsuhashi, *Tetrahedron*, **21**, 1701 (1965)]; benzylmethylcarbinol, $[\alpha]^{25}D$ −20.2° (*c* 5, ether) [J. Kenyon, H. Phillips, and V.P. Pittmann, *J. Chem. Soc.*, 1072 (1935)]. [e] Polymethyl H siloxane, $(-OSi(H)(CH_3)-)_n$.

Table II. Homogeneous Catalytic Hydrosilylation of Acetophenone and Isobutyrophenone by Dihydrosilanes[a]

Ketone	Silane	Ketone/ Rh ratio	Ketone/ silane ratio	Time, hr	Isolated alcohol; chemical yields, %	Optical yield,[b] %
1, $C_6H_5COCH_3$	$H_2Si(C_6H_5)CH_3$	60	2	24	(*S*)-(−)-Phenylmethylcarbinol; 48	13
2, $C_6H_5COCH_3$	$H_2Si(C_6H_5)_2$	50	1,5	20	(*S*)-(−)-Phenylmethylcarbinol; 93	25
3, $C_6H_5COCH_3$	$H_2Si(C_6H_5)_2$	50	2	20	(*S*)-(−)-Phenylmethylcarbinol; 100	28
4, $C_6H_5COCH_3$	$H_2Si(C_6H_5)(C_{10}H_7)$[c]	50	1	16	(*S*)-(−)-Phenylmethylcarbinol; 76	53
5, $C_6H_5COCH_3$	$H_2Si(C_6H_5)(C_{10}H_7)$[c]	50	2	20	(*S*)-(−)-Phenylmethylcarbinol; 100	58
6, $C_6H_5COCH(CH_3)_2$	$H_2Si(C_6H_5)CH_3$	50	2	23	(*S*)-(−)-Phenylisopropylcarbinol; 87	20
7, $C_6H_5COCH(CH_3)_2$	$H_2Si(C_6H_5)_2$	50	2	26	(*S*)-(−)-Phenylisopropylcarbinol; 100	35
8, $C_6H_5COCH(CH_3)_2$	$H_2Si(C_6H_5)(C_{10}H_7)$[c]	50	2	24	(*S*)-(−)-Phenylisopropylcarbinol; 70	24

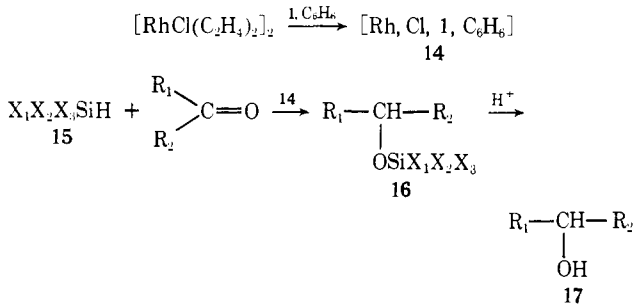
[a] Rh = 25–40 mmol/l.; (+)-diop was used. Ratio diop/Rh = 1; room temperature; solvent C_6H_6 (3–5 ml). [b] Optical yields are calculated with respect to the following values for the optically pure compounds: phenylmethylcarbinol, see Table I; phenylisopropylcarbinol, $[\alpha]^{23}D$ −48.3° (*c* 7, ether) [D. J. Cram and J. E. McCarty, *J. Amer. Chem. Soc.*, **79**, 2866 (1957)]. [c] $H_2Si(C_6H_5)(C_{10}H_7)$, phenyl-1-naphthyldihydrosilane.

All these results led us to the conclusion that our catalytic systems, both the soluble and the insoluble ones, would be interesting to test in the asymmetric hydrosilylation of ketones.

Homogeneous Asymmetric Hydrosilylation of Ketones

The procedure is illustrated Scheme III. To the

Scheme III



solution of complex Rh–diop **14** (prepared *in situ* by reacting diop **1** with $[RhCl(C_2H_4)_2]_2$ according to ref 1), we added under argon the silane **15** and then a prochiral ketone. The siloxane **16** was not isolated but hydrolyzed by aqueous HCl in acetone to give a carbinol **17**.

In the first set of experiments (Table I), the homogeneous catalyzed reactions between several monohydrosilanes (X_1, X_2, $X_3 \neq H$) and acetophenone or methylbenzyl ketone were studied.

With each silane, the optical yield is always better for acetophenone than for methyl benzyl ketone. The best optical yield (10%) was obtained for the reaction between acetophenone and triethoxysilane.

In all cases, we had to heat the reaction mixture (50°) in order to obtain a reasonable rate of hydrosilylation. This fact led us to study the reaction between acetophenone and dihydrosilane (X_1 = H, X_2 and $X_3 \neq$ H) with the hope that this type of silane would be more reactive.

This is, in fact, what we observed. At room temperature, hydrosilylation proceeded easily to give, after hydrolysis, the carbinol in high chemical yield (75–100% except in one case) (results summarized in Table II).

The optical yields were also higher than with monohydrosilanes. The best result (58%) was obtained when phenylnaphthyldihydrosilane was reacted with acetophenone. A slight influence of the silane/ketone ratio on the optical yield (Table II, cases 2–3 and 4–5) was noticed.

The reaction of isobutyrophenone with diphenylsilane and phenylmethylsilane gave higher optical yields than in the case of acetophenone. But with phenylnaphthylsilane the reverse effect was observed: the optical yield was lowered to 24% (*vs.* 58% in hydrosilylation of acetophenone). These last results clearly demonstrate the need for a match of ketone and dihydrosilane in order to obtain the best optical yield.

Heterogeneous Asymmetric Hydrosilylation of Ketones

For the study of the behavior of the insoluble chiral catalyst, the reactions between acetophenone or isobutyrophenone and several dihydrosilanes were investigated. To a suspension in C_6H_6 of the insoluble catalyst **8** prepared as described earlier was added the dihydrosilane followed by the ketone. The mixture

Table III. Asymmetric Heterogeneous Catalytic Hydrosilylation of Acetophenone and Isobutyrophenone by Dihydrosilane[a]

No.[b]	Ketone	Silane	Ketone/Rh[c]	Time, hr	Isolated alcohol; chemical yield, %	Optical yield,[d] %	Optical yield, % with the soluble Rh-(+)-diop catalyst[f]
1	$C_6H_5COCH_3$	$H_2Si(C_6H_5)CH_3$	25	42	(*S*)-(−)-Phenylmethylcarbinol; 71	12	13
1′	$C_6H_5COCH_3$	$H_2Si(C_6H_5)CH_3$	25	26	(*S*)-(−)-Phenylmethylcarbinol; 33	8	
2	$C_6H_5COCH_3$	$H_2Si(C_6H_5)_2$	35	24	(*S*)-(−)-Phenylmethylcarbinol; 82	29	28
2′	$C_6H_5COCH_3$	$H_2Si(C_6H_5)_2$	35	18	(*S*)-(−)-Phenylmethylcarbinol; 52	22.5	
3	$C_6H_5COCH_3$	$H_2Si(C_6H_5)(C_{10}H_7)$[e]	33	45	(*S*)-(−)-Phenylmethylcarbinol; 100	58.5	58
3′	$C_6H_5COCH_3$	$H_2Si(C_6H_5)(C_{10}H_7)$[e]	20	24	(*S*)-(−)-Phenylmethylcarbinol; 95	55	58
3″	$C_6H_5COCH_3$	$H_2Si(C_6H_5)(C_{10}H_7)$[e]	25	30	(*S*)-(−)-Phenylmethylcarbinol; 84.5	52	
4	$C_6H_5COCH(CH_3)_2$	$H_2Si(C_6H_5)CH_3$	25	48	(*S*)-(−)-Phenylisopropylcarbinol; 55	6.5	20
5	$C_6H_5COCH(CH_3)_2$	$H_2Si(C_6H_5)_2$	25	48	(*S*)-(−)-Phenylisopropylcarbinol; 100	28	35

[a] 0.12 mequiv of catalytic units fixed on the resin **8** which was prepared from resin **7** containing 0.5 mequiv of diphosphine unit per gram; silane/ketone = 2; solvent, C_6H_6; room temperature. [b] In each series (1–1′), (2–2′), (3–3′–3″), the insoluble complex was just prepared for the first experiment of the series and then reused for other experiment(s) of the series. [c] Ratio between the number of mmoles of ketones and the total number of catalytic units (0.12). [d] References for the optically pure alcohols are indicated in Table II. [e] $H_2Si(C_6H_5)(C_{10}H_7)$, 1-naphthylphenyldihydrosilane. [f] Results corresponding to experiments where silane/ketone = 2.

was stirred at room temperature under argon. After a time ranging from 16 to 45 hr, the catalyst was filtered off in the air (without any special care). The siloxane was then hydrolyzed to give the alcohol which was finally distilled (as described in Scheme III in the case of the soluble Rh–diop catalyst).

The results of the experiments are given in Table III. In this table, we also note the corresponding optical yields observed with the soluble Rh–diop catalyst.

In hydrosilylating acetophenone with fresh catalyst (Table III, 1–3) we always obtained optical yields very similar to those observed with the homogeneous Rh–diop catalyst. This was no longer true with isobutyrophenone, especially when we used phenylmethyldihydrosilane (6.5% optical purity *vs.* 20% with the soluble catalyst). As the monomeric chiral groups linked to the resin **8** are expected to have the same steric effect as diop **1**, the observed difference in optical yield can be ascribed to the specific role of the support. In Table III, we have also indicated the results obtained by reusing the catalyst. We used intentionally the most simple procedure: after the first reaction, the catalyst was filtered off in the air without any special care, then quickly transferred into a flask and washed with argon. Three sets of experiments were carried out ((1–1′); (2–2′); (3–3′–3″)). In all cases, the optical yields were only slightly lowered. This slight decrease must be attributed to a very slow oxidation of the catalyst by atmospheric oxygen which perhaps leads partially to another catalytic species. Indeed if the catalyst remained in the air for 2 hr, the optical yield of the second hydrosilylation was much lower (for instance, 15 *vs.* 28% in the hydrosilylation of isobutyrophenone with diphenylsilane). However, as we verified, the insoluble catalyst was much more stable toward oxidation than the soluble Rh–diop catalyst. We feel that the phenyl groups of the polymer may have a favorable effect in the protection of the catalytic complex by occupying some vacant sites around the central rhodium ion. Finally, we looked at the influence of the ratio (ρ) between the total number of diphosphine units on the resin and the number of milliequivalents of rhodium (Table IV).

We observed that the best optical yield was obtained when the ratio ρ was almost equal to 2. However, at the present time, we have no satisfactory explanation for the slight variation of the optical yield in this set of experiments. It is important to note that the insoluble complex **8** remains very active even when the ratio ρ is equal to or greater than 2. This is not true for the soluble Rh–diop system which, for a ratio diop/Rh greater than 2, is readily transformed into the inactive complex $(Rh\text{–}diop)_2^+ Cl^-$.[1]

Table IV. Heterogeneous Catalytic Asymmetric Hydrosilylation of Acetophenone by Diphenyldihydrosilane[a]

ρ[b]	Chemical yield of (*S*)-(−)-phenylmethylcarbinol, %	Optical yield, %
1, 1.04	80	20.5
2, 2.08	82	29
3, 4.16	86	23

[a] Solvent, C_6H_6; time, 24 hr; room temperature; diphenyldihydrosilane/ketone = 2; argon atmosphere; ketone/Rh = 25. [b] Ratio $\rho = n$ diphosphine units/Rh. A constant number (0.12) of mequiv of Rh was used; the quantities of diphosphine units were varied by using respectively 0.25, 0.5 g, and 1 g of a resin containing 0.5 mequiv of diphosphine/g.

This contrast indicates that, in the insoluble complex **8**, the active sites are rather far apart from each other (at least in our case) and that the polymeric chain is sufficiently rigid to prevent the coordination of two diphosphine units with the same rhodium ion.

Conclusion

Our experiments demonstrate for the first time that it is possible to use a chiral rhodium complex covalently bound to a synthetic insoluble support as an asymmetric catalyst.

The absolute configuration and the optical yield in an asymmetric synthesis are sensitive probes for comparing two catalytic systems and gaining some mechanistic information. From our results it is apparent that hydrogenation is much more sensitive than hydrosilylation to the change from homogeneous to heterogeneous conditions. The fact that in the hydrosilylation of acetophenone we could reproduce one asymmetric hydrosilylation with exactly the same optical

yield as in solution demonstrates that in this case the steric requirements at the catalytic sites are quite similar in both cases. However, optical yields are in general lower under heterogeneous conditions especially for the reduction of olefins, showing an effect of the support on the nature of which we are presently working.

Experimental Section

General. Optical rotations were measured in a thermostated 1-dm cell with a Perkin-Elmer 141 polarimeter. Nmr spectra were recorded on a Jeolco 60-MHz spectrometer using TMS as internal reference. Vpc was carried out on a Carlo Erba fractovap GI chromatograph.

Chemicals and Solvents. Merrifield Fluka polymer (200–400 mesh, 2% divinylbenzene, 0.7 mequiv of Cl/g) was used. α-Acetamidocinnamic acid and diphenylsilane were purchased from Fluka and used as received. α-Methylstyrene and 2-ethyl-1-hexene were purified by passing through a basic alumina column followed by distillation. These olefins were stored under argon. Acetophenone, isobutyrophenone, and methyl benzyl ketone were twice distilled before use and stored under argon. α-Ethylstyrene,[21] triethoxysilane,[22] phenylmethylsilane, $[RhCl(C_2H_4)_2]_2$,[23] and (+)-diop (**1**) were prepared according to the procedures described in the literature ((+)-diop is now available from Strem Co.).

Benzene was purified by passing through a basic alumina column followed by distillation over sodium hydride. Absolute ethanol was distilled over sodium diethyl phthalate. These solvents were stored under argon.

Synthesis of the Supported Rhodium Catalyst. Aldehydic Polymer 3.[15] The chloromethylated resin **2** (10 g) was heated at 155° for 6 hr in DMSO (120 ml) in the presence of 7.6 g of $NaHCO_3$. After filtration, the resin **3** was washed with dioxane, benzene, and methanol and dried (4 hr, 110° under vacuum). *Anal.* Calcd for a resin containing 0.7 mequiv of CHO/g: C, 91.21; H, 7.65. Found: C, 91.41; H, 7.78. The resin **3** contained no chlorine.

(+)-1,4-Ditosylthreitol 5. Ten grams of 1,4-ditosyl-2,3-*O*-isopropylidene-D-threitol (**4**) ($[\alpha]^{22}D$ +12.3° (*c* 4.4, $CHCl_3$) (prepared as described[24]) was refluxed (24 hr) in 50 ml of ethanol in the presence of *p*-toluenesulfonic acid (50 mg). The solvent was removed by evaporation to dryness and the product crystallized from chloroform; 9 g (≃100%) of **5** was obtained, $[\alpha]^{20}D$ +4.6° (*c* 2, acetone).

Acetalic Resin 6. Resin **3** (9.6 g) suspended in benzene (100 ml) was reacted with 8 g of (+)-1,4-ditosylthreitol **5** in the presence of *p*-toluenesulfonic acid (100 mg). The benzene solution was refluxed during 24 hr and the water produced was extracted continuously. The resin **6** was then filtered, washed, and dried as usual. *Anal.* Calcd for a completely acetalyzed resin: C, 82.42; H, 7.03. Found: C, 85.20; H, 7.21. From these data, we calculated that the acetalization has taken place to a 70% extent.

Phosphinated Resin 7. $P(C_6H_5)_2Li$ was prepared according to the literature.[25] A solution of 7.6 g of triphenylphosphine in 100 ml of THF was reacted with 2.8 g of lithium. The residual lithium was then filtered off and the phenyllithium produced was selectively destroyed by adding slowly a solution of 2.78 g of *tert*-butyl chloride in 10 ml of THF; 10.2 g of resin **6** was then quickly added and allowed to react with $P(C_6H_5)Li$ during 20 hr at 20°. All these manipulations were carried out under nitrogen. Finally the resin **7** was filtered, washed, and dried as usual. *Anal.* Calcd for a resin containing 0.5 mequiv of diphosphine units per gram: C, 88.30; H, 7.32; P, 2.71. Found: C, 86.92; H, 7.33; P, 2.82.

Insoluble Catalyst 8. Unless otherwise stated in Tables III and IV, the catalyst was prepared as follows: 0.5 g of resin **7** was stirred at room temperature during 20 hr (under N_2) in a solution of 11.7 mg (0.03 mmol) of $[RhCl(C_2H_4)_2]_2$ in 10 ml of benzene.

Hydrogenations. A conventional apparatus for hydrogenation under atmospheric pressure was used. The hydrogenation flask was stoppered with a serum cap allowing addition by injection with syringes. The insoluble catalyst was directly prepared in the hydrogenation flask. After 20 hr at 20° under nitrogen, hydrogen was admitted into the flask and the unsaturated substrate was introduced. After a suitable time, the catalyst was filtered off and the solution worked up.

Hydrogenation of α-Ethylstyrene. α-Ethylstyrene (15 mmol) was quantitatively reduced in 20 hr. The resulting solution was distilled to give 2-phenylbutane (opt. yield, 1.5%). The catalyst was reused in a new and similar reduction (opt. yield, 0.6%).

Hydrogenation of Methyl Atropate. Methyl atropate (6 mmol) was reacted with H_2 during 45 hr. The resulting solution was evaporated and analyzed by nmr spectroscopy, 27% methyl hydratropate (opt. yield, 2.4%).

Hydrosilylations. The hydrosilylations were carried out under nitrogen or argon in a flask stoppered with a serum cap allowing addition by injection with syringes. To the catalytic solution (prepared as described in (1)) or suspension (prepared as described above), we added first the ketone and then the silane. After a suitable time, the reaction mixture (after filtration in the case of the insoluble catalyst) was treated as follows: evaporation of benzene under vacuum, dissolution of the residue in 20 ml of acetone containing 4 ml of an aqueous HCl solution (10%). After 2 hr at 20°, the organic products were extracted with ether and the resulting organic phase was dried over $MgSO_4$. After elimination of ether, the residue was distilled to give generally a mixture of the starting ketone and the corresponding carbinol. The yield of carbinol was determined by vpc (Carbowax 20M, 3 m, 17 ml of N_2/mm, 190°).

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