microreactor that had previously been evacuated and filled with argon. The reaction was stirred at 60 °C under 22 atm of H_2 for 24 h. The pale yellow reaction mixture was concentrated on a rotary evaporator and the residue partitioned between 10 mL of CH_2Cl_2 and 10 mL of 10% NaOH. The aqueous layer was separated and washed with ether (2 × 10 mL). The aqueous layer was then acidified with HCl and extracted with ether (3 × 10 mL). The combined ether extracts were washed with 5 mL of H_2O, dried over $MgSO_4$, and concentrated to yield 0.90 g of crude acid. Distillation in a Kugelrohr apparatus (100 °C, 0.5 mm) afforded 0.75 g (89%) of 3,7-dimethyloct-6-enoic acid: $[\alpha]^{25}_D$ +4.48° (c 4.9323, $CHCl_3$); 44% optical purity. The acid was converted to its methyl ester by using CH_2N_2. The ester had $[\alpha]^{25}_D$ +3.23° (c 5.0191, $CHCl_3$) and was shown by Eu(dcm)$_3$-perturbed NMR to have an R/S ratio (at the C_3 methyl) of 28/11 (44% ee).

Acknowledgment. We are grateful to Professors G. Whitesides and J. D. Morrison for many helpful discussions, to Dr. U. Hengartner for preparation of **10** and **12**, to Mr. W. Conradi for supplying neral and geranial, to Dr. T. Williams and R. Pitcher for NMR analyses, and to Dr. F. Scheidl for microanalytical services.

Registry No. (*E*)-**8**, 4698-08-2; (*Z*)-**8**, 4613-38-1; (*R*)-**9**, 18951-85-4; (*S*)-**9**, 2111-53-7; (*R*)-**9** methyl ester, 20425-48-3; (*S*)-**9** methyl ester, 56994-89-9; (*Z*)-**10**, 69203-27-6; D-**11**, 66920-63-6; (*Z*)-**12**, 74298-23-0; D-**13**, 56777-76-5; (*R*)-**14**, 74345-43-0; (*S*)-**14**, 60149-04-4; geranial, 141-27-5; neral, 106-26-3; (*S*)-2-methoxy-2-phenylacetic acid, 26164-26-1; (*S*)-2-methoxy-2-phenylethanol, 66051-01-2; (*S*)-2-methoxy-2-phenylethanol tosylate, 61825-54-5; μ,μ'-dichloro-bis(1,5-cyclooctadiene)rhodium(I), 12092-47-6; geranic acid, 459-80-3.

Enantioselective Hydrogenations of a Terpenic Acrylic Acid Catalyzed by Rhodium Complexes of Chiral Diphosphines

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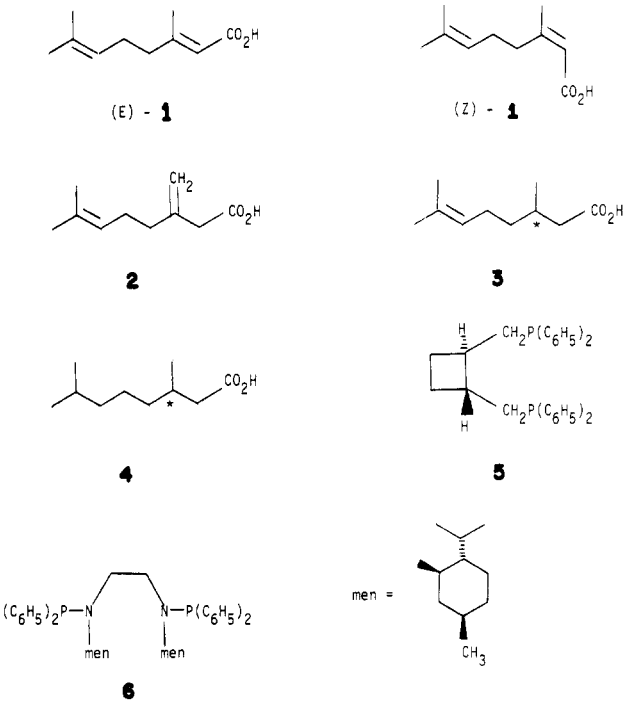
Hydrogenations of (*E*)-3,7-dimethylocta-2,6-dienoic acid ((*E*)-**1**) catalyzed by rhodium complexes of the chiral diphosphine (1*R*,2*R*)-bis[(diphenylphosphino)methyl]cyclobutane (**5**) in chloride-free methanol (23 °C, 2–3 atm of H_2) were rapid (~300 turnovers per hour) and gave (*S*)-(−)-3,7-dimethyloct-6-enoic acid ((*S*)-(−)-**3**) in ca. 40–42% ee. Under the same conditions, (*Z*)-**1** was converted to (*R*)-(+)-**3** in 45% ee. The Rh-**5**-catalyzed hydrogenation of (*E*)-**1** in chloride-free methanol was strongly promoted by triethylamine, with maximum rates of ca. 2500 turnovers per hour. The product enantiomeric excess was not changed by addition of triethylamine. A study of the amine-promoted hydrogenation of (*E*)-**1** is reported. It is concluded that the carboxylate anion of (*E*)-**1** complexes with rhodium more strongly than does the parent acid and that the resulting rhodium(I) substrate complex adds H_2 more rapidly in the deprotonated form.

In the preceding paper,[1] we described enantioselective hydrogenations of the terpenic acrylic acids (*E*)-**1** and (*Z*)-**1**, (see Chart I) catalyzed by rhodium complex catalysts containing chiral monophosphine ligands. This paper describes hydrogenations of the same substrates catalyzed by rhodium complexes of chiral diphosphines. We have also briefly studied enantioselective hydrogenations of **2**.

The main subject of this paper is the hydrogenation of (E)-**1** catalyzed by Rh-**5** in chloride-free methanol. In the absence of added base this hydrogenation has a modest rate (~300 turnovers per hour), and (*S*)-(−)-**3** is obtained in 40–42% ee. Addition of triethylamine in amounts less than the amount of substrate results in dramatic rate increases (~2500 turnovers per hour) without changing the enantioselectivity. The use of triethylamine in Rh-**5**-catalyzed hydrogenations of (*E*)-**1** was suggested by reports that addition of amine to some apparently similar hydrogenations resulted in increased enantioselectivities.[2] In the present case, consideration of the appropriate acid–base equilibria indicated that the added triethylamine was converted quantitatively to the ammonium salt of **1**.[3] A kinetic study described in this paper provides an explanation of the increased reactivity of the carboxylate anion compared to the parent acid **1** in the Rh-**5**-catalyzed hydrogenation.

Chart I



Results

We have studied the enantioselective hydrogenations of **1** and **2** catalyzed by soluble rhodium complexes of the chiral diphosphines **5**–**9**.[4a-e] Phosphines **5** and **6** were converted to the complexes **10**[4a] and **11**[4b] (Chart II).

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(1) Valentine, D., Jr.; Johnson, K. K.; Priester, W.; Sun, R.; Toth, K.; Saucy, G. *J. Org. Chem.*, preceding paper in this issue.

0022-3263/80/1945-3703$01.00/0

Table I. Hydrogenations of (*E*)-1 Catalyzed by Rhodium Complexes of 5-9[a]

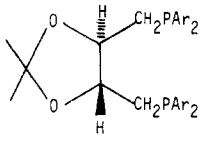
phosphine[b]	solvent	S/C[h]	[(*E*)-1][c]	base (amt)[d]	rate[e]	% conv	select,[f] %	product op,[g] %
5 (10)[b]	CH_3OH	227	1:5	A (0.9)	753	100	100	41 (*S*)
5 (10)[b]	CH_3OH	210	1:5	M (0.1)	628	100	90	39 (*S*)
5 (10)[b]	CH_3OH	210	1:5	none	300	100	60	36 (*S*)
5	CH_3OH	418	1:1	A (1.1)	419	100	100	40 (*S*)
5	CH_3OH	210	1:5	A (1.1)	628	100	100	40 (*S*)
5	CH_3OH	172	1:5	M (0.1)	3	100	100	35 (*S*)
5 (10)[b]	THF-CH_2Cl_2	422	1:5	none	158	100	80	32 (*S*)
5	toluene	210	1:5	A (1.1)	slow	80	100	6 (*S*)
6 (11)	CH_3OH	300	1:20	A (0.9)	700	100	100	30 (*R*)
7	CH_3OH	110	1:5	A (1:1)	165	100	100	35 (*S*)
7	THF	110	1:5	A (1:1)	1	29	100	1
8	CH_3OH	259	1:5	A (1:1)	119	100	100	35 (*S*)
9	CH_3OH	236	1:5	A (1:1)	472	100	100	39 (*S*)

[a] Conditions: 20-23 °C; the initial $P(H_2)$ = 3 atm, decreasing to ca. 1.5 atm at the end of the reaction. The substrate was 98% (*E*)- and 2% (*Z*)-1. [b] Systems where the catalyst was delivered as compound 10 were chloride free; in all others [Rh] = [Cl^-]. [c] Grams of substrate per milliliter of solvent. [d] Moles of base per mole of substrate. A = $N(C_2H_5)_3$; M = $NaOCH_3$. [e] Moles of H_2 absorbed per hour per mole of Rh. [f] Selectivity, from the ratio of (3/(3 + 4)) × 100. [g] Optical purities were based on the rotations, $[\alpha]^{25}_D$, of +10.29 and +7.25° (both *c* 5.0, $CHCl_3$) for (*R*)-(+)-3 and (*R*)-(+)-4, respectively. When both 3 and 4 were present, the reference value was taken as a weighted average of $[\alpha]^{25}_D$ values. [h] Molar ratio of S (substrate) to C (catalyst).

Substrate, solvent, and catalyst preparations, setup of hydrogenations, and analyses of hydrogenation products were carried out generally as described in the preceeding paper.[1]

We studied first the hydrogenations of (*E*)-1 in methanol (23 °C, 2-3 atm of H_2) catalyzed by soluble rhodium complexes of 5-9, prepared in situ by the reaction of Rh(diolefin)$(Cl)_2$[5] with the phosphine, followed by hydrogenation to remove the diolefin. In such systems, without some added base, the homogeneous catalysts rapidly decomposed, giving rhodium-containing precipitates which were active catalysts for the hydrogenation of (*E*)-1 to racemic 4. When either sodium methoxide or triethylamine was added, the system remained homogeneous. In an initial series of experiments, the amount of base was typically 0.5 equiv compared to the amount of substrate, the optimum amount for hydrogenations of (*E*)-1 catalyzed by rhodium complexes of chiral monophosphines as described in the previous paper.[1] Very slow hydrogenations of 1 (<10 turnovers per hour) were observed. Much faster rates were obtained when a slight excess of triethylamine compared to the amount of substrate was added. In this case, rates of ca. 300 turnovers per hour were obtained. The effect of triethylamine in excess of the amount required to deprotonate 1 was ascribed to its ability to remove chloride from the rhodium coordination sphere. This led us to try the cationic catalyst precursor 10 to obtain a chloride-free reaction medium. Again, fast rates (~200 turnovers per hour) were obtained. The hydrogenations

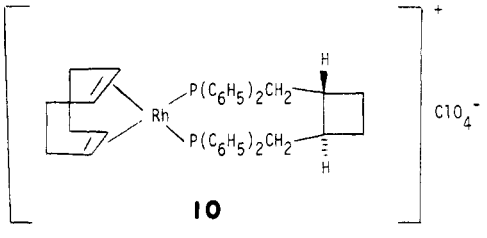
Chart II



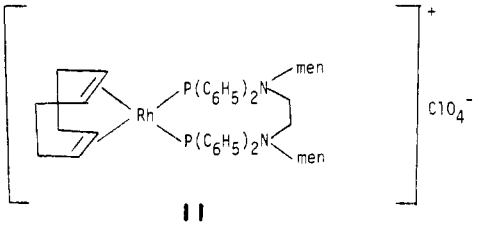
7 Ar = C_6H_5 -

8 Ar = 3-$CH_3OC_6H_4$ -

9



10



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in chloride-free methanol were also found to be strongly promoted by added triethylamine (rate ~750 turnovers per hour). In the chloride-free hydrogenation systems, the concentration of amine, [A], had to be lower than the concentration of (*E*)-1 added (denoted here and below by $[S]_0$). In one experiment where [A] = 1.1$[S]_0$ and no chloride was present, very rapid catalyst decomposition occurred. Our preliminary hydrogenation experiments are summarized in Table I.

In hydrogenations of (*E*)-1 catalyzed by soluble rhodium complexes of 5-9 the selectivity to form 3 was high. Formation of the doubly hydrogenated product was observed in methanol solutions only when the system was chloride free and no triethylamine was added. Under these conditions, addition of dihydrogen to the unconjugated

(2) Previous examples of the use of triethylamine as a promoter for rhodium complex catalyzed enantioselective hydrogenations include the following: (a) Dang, T.-P.; Kagan, H. B. *J. Chem. Soc., Chem. Commun.* **1971**, 481; (b) Suess, R.; Stoll; A. P. *Helv. Chim. Acta* **1974**, *57*, 2487-91; (c) Knowles, W. S.; Sabacky, M. J.; Vineyard, B. D.; Weinkauff, D. J. *J. Am. Chem. Soc.* **1975**, *97*, 2567-69; (d) Achiwa, K. *Ibid.* **1976**, *98*, 8265-6; (e) Ojima, I.; Kogure, T.; Yoda, N. *Chem. Lett.* **1979**, 495-8; (f) Achiwa, K. *Tetrahedron Lett.* **1978**, 4683-6; (g) *Ibid.* **1978**, 1475-8; (h) Achiwa, K. *Chem. Lett.* **1978**, 561-5; (i) Christophel, W. C.; Vineyard, B. D. *J. Am. Chem. Soc.* **1979**, *101*, 4406-8.

(3) In water the equilibrium constant for salt formation is high: i.e., $RCO_2H + N(C_2H_5)_3 \rightleftharpoons RCO_2^- + HN(C_2H_5)_3^+$ ($K_{eq} \geq 10^6$). We presume that in methanol also for the above reaction $K_{eq} \gg 1$.

(4) (a) Aviron-Violet, P.; Coueuille, Y.; Varagnat, J. *J. Mol. Catal.* **1979**, *5*, 41-50. See also: Aviron-Violet, P. U.S. Patent 3 949 000, 1976. *Chem. Abstr.* **1975**, *82*, 171186. (b) Fiorini, M.; Marcati, F.; Giongo, G. M. *J. Mol. Catal.* **1978**, *4*, 125-34. (c) Kagan, H. B.; Dang, T.-P. *J. Am. Chem. Soc.* **1972**, *94*, 6429-33. (d) Hengartner, U.; Valentine, D. Jr.; Johnson, K. K.; Larscheid, M. E.; Pigott, F.; Scheidl, F.; Scott, J. W.; Sun, R. C.; Townsend, J. M.; Williams, T. H. *J. Org. Chem.* **1979**, *44*, 3741. (e) Achiwa, K. *J. Am. Chem. Soc.* **1976**, *98*, 8265-6.

(5) Chatt, J.; Venanzi, L. *J. Chem. Soc.* **1957**, 4735-41.

Table II. Rates of Hydrogenations of (*E*)-1 Catalyzed by Rh-5 in Chloride-Free Methanol without Added Base

[substr], M	10^3[catal], M	$P(H_2)$, atm[a]	10^3 rate, mol h^{-1}	select[b,c] %	$[\alpha]^{25}_D$ (*c* 5, $CHCl_3$) of product, deg
0.15	1.38	2.72	1.79	84	−3.90
0.30	1.38	2.72	2.75	79	−3.98
0.30	0.69	2.72	1.41		
0.60	1.38	1.72	3.30	84	−4.08
0.90	1.38	2.72	2.87	100	−4.14

[a] Initial H_2 pressure, allowed to decrease ca. 10%. [b] Selectivity, from the ratio of (3/(3 + 4)) × 100. [c] There was 100% conversion in all cases.

Table III. Rates of Hydrogenations of (*E*)-1 Catalyzed by Rh-5 in Chloride-Free Methanol with Added Triethylamine[a]

[substr],[b] M	[amine], M	10^3[catal], M	$P(H_2)$, atm	obsd rate, mol h^{-1}	predicted rate, mol h^{-1}	$[\alpha]^{25}_D$ of product, deg
0.075	0.065	1.38	2.72	0.036	0.039	−4.30
0.15	0.09	1.38	2.72	0.037	0.039	−4.33
0.30	0.045	1.38	2.72	0.020	0.019	−4.28
0.30	0.09	1.38	2.72	0.028	0.027	−4.33
0.30	0.18	1.38	2.72	0.034	0.034	−4.20
0.30	0.27	1.38	2.72	0.037	0.037	−4.40
0.45	0.09	1.38	2.72	0.020	0.02	−4.46
0.45	0.27	1.38	2.72	0.022	0.027	
0.45	0.36	1.38	2.72	0.024	0.027	
0.45	0.42	1.38	2.72	0.022	0.028	
0.60	0.014	1.38	2.72	0.015	0.07	−4.12
0.60	0.03	1.38	2.72	0.014	0.010	−4.30
0.60	0.18	1.38	2.72	0.019	0.016	−4.30
0.60	0.27	1.38	2.72	0.016	0.021	−4.16
0.60	0.36	1.38	2.72	0.016	0.021	−4.30
0.60	0.53	1.38	2.72	0.020	0.022	−3.97
0.60	0.53	5.52	2.72	0.076		−4.50
0.60	0.53	2.76	2.72	0.039		−4.29
0.60	0.53	0.69	2.72	0.013		−4.23
0.90	0.27	1.38	2.72	0.011	0.013	−4.30

[a] Catalyst delivered as 10. Conditions: 20–23 °C; $P(H_2)$ was the initial pressure and decreased ca. 10% during rate measurements. [b] There was 100% conversion in all cases. The selectivity [ratio of (3/(3 + 4)) × 100] was also 100% in every case.

olefinic moiety was at least 50 times slower than its addition to the conjugated olefin. Essentially pure **3** was isolated when hydrogenation was terminated promptly after 1 equiv of H_2 had been absorbed. The enantioselectivities observed for hydrogenations of (*E*)-1 were modest (≤42% ee).[6] In hydrogenations of (*E*)-1 catalyzed by Rh-5 in methanol, (*S*)-(−)-**3** was obtained in 40–42% ee under all conditions studied.

We measured rates for the Rh-5-catalyzed hydrogenation of (*E*)-1 at 23 °C and 1–3 atm of H_2 in chloride-free methanol. These rate measurements were carried out in sealed vessels, and rates were obtained from observations of the H_2 pressure drop as the reaction progressed. Our rate data are summarized in Tables I–III and in Figure 1. These rates are not highly precise (typical limits of ±5% of the rate) and depend somewhat on reagent and substrate histories. Our purpose in obtaining them was to define conditions for very fast hydrogenations of 1. Nevertheless, it was evident that the rate behavior of Rh-5-catalyzed (*E*)-1 hydrogenations was both striking and significant. These features are most easily seen in Figure 1 and are summarized as follows. (1) In the absence of added amine, rates for Rh-5-catalyzed (*E*)-1 hydrogenation depend on $[Rh_{tot}]$ and $P(H_2)$. As substrate concentration increases, rates pass through a shallow maximum at $[S_0] \approx 0.5$ M and then begin to decrease as the substrate concentration increases. (2) Hydrogenation rates are much faster when amine is added, but the magnitude of the effect depends on the total substrate concentration. Dramatic rate enhancements, strongly dependent on the concentration of added amine, were observed at a substrate concentration of 0.3 M. As the substrate concentration

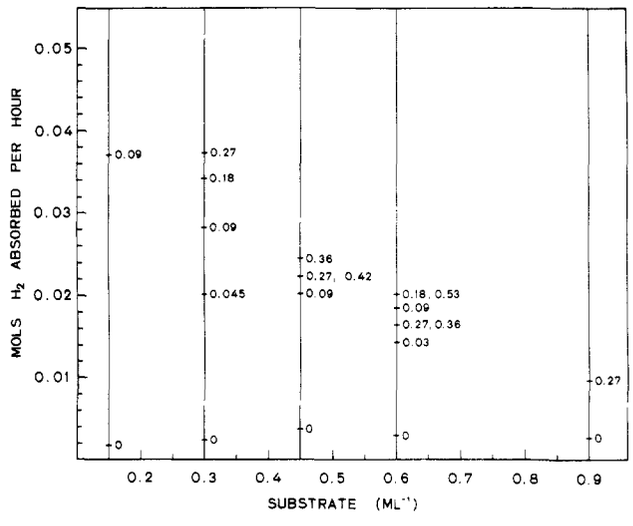

Figure 1. Rates of the hydrogenations of (*E*)-1 (0.15–0.90 mol L^{-1}) catalyzed by Rh-5 (1.38×10^{-3} mol L^{-1}) at 2.72 atm of H_2 and 23 °C in chloride-free methanol as a function of added triethylamine. The experimental data are indicated by a dash without precision limits (ca. ±5%), and the numbers next to the rate data indicate the concentration (mol L^{-1}) of triethylamine added.

(6) The enantiomeric excesses (ee) quoted in this paper were estimated from optical purities. The basis was $[\alpha]^{25}_D$ +10.19° (*c* 5, $CHCl_3$) for (*R*)-(+)-**3**.[7]

(7) Valentine, D., Jr.; Chan, K. K.; Scott, C. G.; Johnson, K. K.; Toth, K.; Saucy, G. *J. Org. Chem.* **1976**, *41*, 62–65.

Table IV. Asymmetric Hydrogenations of (Z)-1 and 2 in Methanol

substr (isomeric purity)	phosphine	S/C[a]	solvent	[substr][b]	base (amt)[c]	T, °C	rate[d]	% conv	select,[e] %	product ee,[f] %
2 (95)	5	429	CH_3OH	1:5	M (0.1)	23	1	100	100	36 (R)
2 (95)	7	47	CH_3OH	1:5	M (0.5)	23	1.5	100	100	40 (R)*
2 (95)	7	229	CH_3OH	1:5	M (0.1)	23	7	100	100	37 (R)
2 (93)	7	229	CH_3OH	1:5	A (1.1)	20	25	100	100	49 (R)
2 (93)	7	229	THF	1:5	A (1.1)	20	7	95	100	16 (R)
2 (93)	8	185	CH_3OH	1:5	M (0.1)	23	4	100	97	53 (R)
2 (93)	8	259	CH_3OH	1:5	A (1.1)	20	16	100	100	55 (R)
2 (93)	9	241	CH_3OH	1:5	M (0.1)	20	2.5	100	100	14 (R)
2 (93)	9	241	CH_3OH	1:5	A (1.1)	20	12	100	100	19 (R)
(Z)-1 (94)	5	222	CH_3OH	0.6		23	164	100	?	27 (R)[g]
(Z)-1 (94)	5	222	CH_3OH	0.6	A (0.9)	23	600	100	100	45 (R)
(Z)-1 (94)	7	222	CH_3OH	0.6	A (0.9)	23	732	100	100	43 (R)
(Z)-1 (94)	9	243	CH_3OH	0.6	A (0.9)	23	320	100	100	41 (R)

[a] Molar ratio of substrate to catalyst. [b] For hydrogenations of 2, the substrate concentration is expressed as grams of 2 per milliliter of solvent. For the other cases the concentration is a molar concentration. [c] Moles of base per mole of substrate. A = triethylamine; M = sodium methoxide. [d] Moles of H_2 absorbed per hour per mole of catalyst. [e] Selectively, from the ratio of $(3/(3 + 4)) \times 100$. [f] Values marked with an asterisk are ee determined by using the method described previously.[14] Other values are optical purities. [g] Some methyl ester was present on workup. The optical purity quoted is based on acid 3 only and may be low.

was progressively increased to 0.45, 0.60, and 0.90 M, the absolute magnitude of the rates, the ratio of rates obtained with amine vs. those without amine, and the variation of rate with amine concentration at a fixed total substrate concentration all decreased as total substrate concentration increased.

Conditions defined for fast hydrogenations of (E)-1 were used to hydrogenate (Z)-1 and also the β-methylene acid 2. Our data are given in Table IV. Hydrogenations of (Z)-1 to (R)-(+)-3 were slower but about equally enantioselective (≃45% ee) compared to hydrogenations of (E)-1. Hydrogenations of 2 gave (R)-(+)-3 in ≤55% ee, but the rates were very slow.

Discussion

Our optimization studies were based initially on the assumption that the mechanism of Rh-5-catalyzed (E)-1 hydrogenation was similar to that described by Halpern et al. for olefin hydrogenations catalyzed by Rh ($Ph_2PCH_2CH_2PPh$), i.e.,[8] eq 1, where S represents the

$$RhP_2^+ \xrightarrow[K_S]{S} RhP_2S^+ \xrightarrow[\text{rate limiting}]{H_2,\ k_S} (RhP_2H_2S)^+ \rightarrow RhP_2 + SH_2 \quad (1)$$

olefinic substrate and SH_2 the hydrogenation product. Reaction 1 has been written to represent the halide-free catalyst system. Corresponding intermediates, RhP_2Cl, RhP_2ClS, and RhP_2ClH_2S, can be written for the halide-containing systems. The first question then is why are the halide-containing systems so slow? A plausible explanation is that the substrate (E)-1 is actually a bidentate ligand. If this is so, RhP_2S^+ is four coordinate, but RhP_2SCl is five coordinate d^8 and would not be expected to add H_2 readily. The concept that (E)-1 is a bidentate ligand for rhodium can be used conveniently to explain other features of our data.

As written, reaction 1 predicts that the rate of hydrogenation should increase with substrate concentration, eventually leveling off as all of the total rhodium is used to form RhP_2S^+. In fact, the rate begins to decline above concentrations of ca. 0.6 M substrate. This is consistent with reaction of RhP_2S^+ with more substrate to give

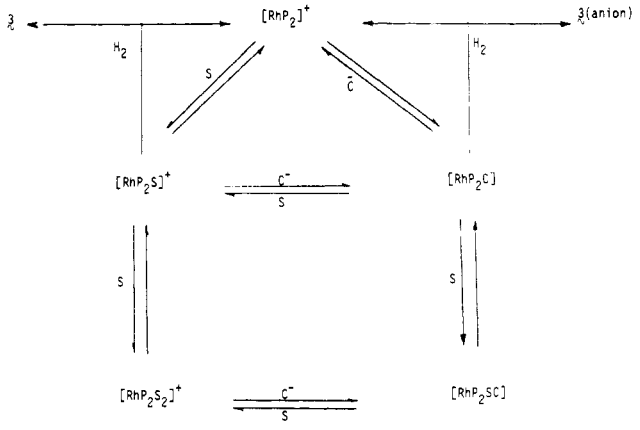

Figure 2. Possible mechanism for (E)-1 hydrogenation catalyzed by Rh-5 in chloride-free methanol: S denotes (E)-1, and C^- denotes carboxylate derived from (E)-1. The species $[RhP_2]^+$ is the product of hydrogenation of 10. Other species are defined in the text.

$RhP_2S_2^+$ in which one olefin is monodentate and the other is bidentate. Such a complex would be coordinatively saturated d^8 and would not be expected to add H_2 readily (eq 2).

$$RhP_2S^+ \xrightarrow[-S]{S} RhP_2S_2^+ \xrightarrow{H_2} \text{no reaction} \quad (2)$$

The promotional effects of amines can be rationalized in terms of deprotonations of the intermediates RhP_2S^+ and $RhP_2S_2^+$, giving rise to a hydrogenation pathway analogous to (1) but with neutral intermediates, i.e., eq 3,

$$RhP^+_2 + C^- \underset{K_C}{\rightleftharpoons} RhP_2C \xrightarrow[k_C]{H_2} RhP^+_2 + CH_2^- \quad (3)$$

$$RhP_2C \underset{S}{\rightleftharpoons} RhP_2CS$$

where C^- is the carboxylate anion of 1 and CH_2^- is the carboxylate anion of 3. It is reasonable to expect both that $K_C > K_S$ (carboxylate a better ligand than free acid) and that $K_C > K_S$ (addition of H_2 to neutral RhP_2C is faster than addition to positively charged RhP_2^+). Hence, the reaction pathway 3 ought to be much faster than reaction 1. The very large rate increases observed suggest that when amine is present, the deprotonated substrate pathway (eq 3) dominates the system. Coordination of S or

(8) Halpern, J.; Chan, A. S. C.; Riley, D. P.; Pluth, J. J. *Adv. Chem. Ser.* **1979**, *No. 173*, 16–25.
(9) Halpern, J. *Trans Am. Crystallogr. Assoc.* **1978**, *14*, 59–69.

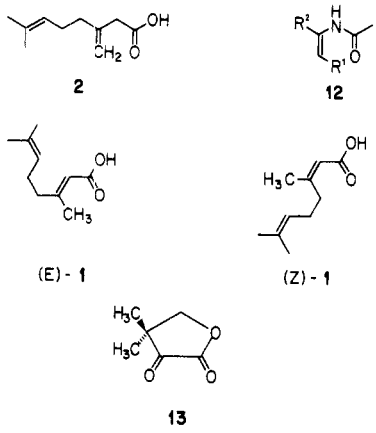

Figure 3. Schematic representations of possible coordinate geometries for olefin and ketone substrates for Rh-catalyzed asymmetric hydrogenations.

C^- to RhP_2C to give RhP_2SC and $RhP_2C_2^-$, respectively, would then explain the reduced rates which are observed at higher substrate concentrations.

Figure 2 outlines the proposed mechanism. Attempts to interpret our data quantitatively in terms of this mechanism were not successful. This was in part due to our somewhat imprecise data but also, we believe, to solvent effects on equilibria between charged and uncharged species. The empirical rate equation (eq 4) was

$$\frac{-dH_2}{dt} = (0.012[S_0] + 0.89[N(C_2H_5)_3])/(1 + 0.34[S_0] + 2.75[S_0]^2 + (63.3[S_0] - 2.1)[N(C_2H_5)_3] + 3.34[N(C_2H_5)_3]^2) \quad (4)$$

developed on the basis of a kinetic analysis of our data in terms of the mechanism in Figure 2. This equation gave the predicted rates which are listed in column six of Table III. It corresponds to the case where $k_C K_C \approx 100 K_S k_S$ and where addition of S to RhP_2S^+ or RhP_2C is about 10 times more favorable than addition of S or C^- to RhP_2^+. Inspection of Table III shows that eq 4 is qualitatively compatible with experiment but that quantitative agreement is not good. No better equation was found.

Detailed analysis of the stereochemistries of hydrogenations of **1** and **2** is inappropriate because the modest enantioselectivities indicate that $\Delta\Delta G^{\ddagger} < 1$ kcal/mol. Nevertheless, the equal enantioselectivities observed in hydrogenations of (*E*)-**1** and (*Z*)-**1** suggest that the catalyst selects a preferred orientation of the C=C—C=O (or perhaps the C=C—C(O)OH) chromophore with little regard for the geometric arrangement of methyl vs. alkyl substituents at C_3. This point is illustrated in Figure 3, where to obtain (*S*)-**3** from (*E*)-**1** and (*R*)-**3** from (*Z*)-**1** with the structures as drawn, H_2 must be added from *below* the plane of the page, i.e., to the *re–si* face of C_2=C_3 in (*E*)-**1** and the *si–si* face of C_2=C_3 in (*Z*)-**1**. In contrast to this behavior, addition of H_2 from *above* the plane of the page to the *si* face of **2**, the *si* face (of C_2) in **12**,[10] and the *si* face of **13**[11] all would give the observed enantiomers of the products. Coordination of (*E*)-**1** and (*Z*)-**1** to Rh-**5** is therefore opposite to that of either of the "models" **12** and **13**. It is interesting that in hydrogenations catalyzed by the Rh (neomenthyldiphenylphosphine) catalyst described in the preceding paper it was also found that (*E*)-**1** and (*Z*)-**1** were converted to opposite enantiomers of **3** but in the same enantiomeric excess.[1] It is also interesting that the ee of **3** obtained in Rh-**5**-catalyzed hydrogenations of (*E*)-**1** and (*Z*)-**1** does not depend on the amine concentration. Either the stereoselectivities for coordination of (*E*)-**1** and its carboxylate anion are similar or the deprotonated pathway is important even in the absence of amine.

Experimental Section

Substrate **1** was prepared as previously described.[1] Methanol and other solvents were purified by hydrogenation over Raney nickel. Catalysts were prepared by known methods.[4] Both the ligands and their complexes had satisfactory microanalyses. The complex $[Rh(1,5\text{-c-Oct})(Cl)]_2$ (1,5-c-Oct = 1,5-cyclooctadiene) was prepared by following the method of Chatt and Venanzi.[5] Triethylamine was purified by distillation from CaH_2.

Hydrogenations were generally carried out by using the apparatus and procedures described in the preceding paper. Kinetic runs were made at 23 ± 1 °C with (in most cases) an initial H_2 pressure of 2.72 atm. The hydrogenation vessels were sealed, and the rate of H_2 uptake was determined from the drop in pressure over the vessel. No blank was taken since the solution was initially saturated with argon. No correction was made for the effect of decreasing H_2 pressure on the rate. The hydrogen pressure decreases were usually less than 0.25 atm. Reproducibility of individual rates on the same reagents and substrates was about ±5%. Different samples of acid, solvents, etc. gave rates differing by as much as 25–30% in the base-free hydrogenations.

3-Methylene-7-methyloct-6-enoic Acid (2). An ~2:1 *E*/*Z* isomer mixture of 3,7-dimethylocta-2,6-dienoic acid was deconjugated by the method of Bedoukian and Wolinsky.[13] The product consisted of 24 parts of methyl 3-methylene-7-methyloct-6-enoate, three parts of methyl 3,7-dimethylocta-2,6-dienoate, and one part of methyl 3,7-dimethylocta-3,7-dienoate. An 11.0-g sample of this mixture was stirred 24 h under argon at 23 °C in 275 mL of 9:1 H_2O/CH_3OH (1 M NaOH). The reaction mixture was extracted with ether and then acidified (pH 2) by dropwise addition of 30% H_2SO_4. The ether extracts of the acidified mixture were combined, dried over $MgSO_4$, and concentrated. Distillation gave 8.8 g of crude 3-methylene-7-methyloct-6-enoic acid. Redistillation in a Kugelrohr apparatus gave 7.5 g (74% yield) of colorless oil [bp 95 °C (0.15 mm)] consisting of 94 parts of 3-methylene-7-methyloct-6-enoic acid, five parts of 3,7-dimethylocta-2,6-dienoic acid, and one part of 3,7-dimethylocta-3,7-dienoic acid: IR ($CHCl_3$) 1710 (CO_2H), 1650 (C=C), 908 (H_2C=C) cm^{-1}; NMR ($CDCl_3$) δ 1.26, 1.59 (2 s, 6, $(CH_3)_2C$=), 2.12, 2.14 (2 s, 4, $(CH_2)_2C$=CH_2), 4.95 (m, 2, H_2C=).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.19; H, 9.77.

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Registry No. (*E*)-**1**, 4698-08-2; (*Z*)-**1**, 4613-38-1; **2**, 55050-39-0; (*R*)-**3**, 18951-85-4; (*S*)-**3**, 2111-53-7; (*R*)-**4**, 32531-52-5; (*S*)-**4**, 55509-77-8; methyl 3-methylene-7-methyloct-6-enoate, 55298-92-5; methyl 3,7-dimethylocta-2,6-dienoate, 2349-14-6; methyl 3,7-dimethylocta-3,7-dienoate, 74298-37-6; 3,7-dimethyl-3,7-dienoic acid, 74298-38-7.

(10) Valentine, D., Jr.; Scott, J. W. *Synthesis* **1978**, 329–53.
(11) The Rh-**5**-catalyzed hydrogenation of **13**[12] gave (*R*)-(−)-pantolactone (i.e., the corresponding α-hydroxy lactone) in ca. 50% ee. Townsend, J., unpublished results.
(12) Compare: Achiwa, K.; Kogure, T.; Ojima, I. *Chem Lett.* **1977**, 4431–2.
(13) Bedoukian, R. H.; Wolinsky, G. *J. Org. Chem.* **1975**, *40*, 2154–8.
(14) Valentine, D., Jr.; Chan, K. K.; Scott, C. G.; Johnson, K. K.; Toth, K.; Saucy, G. *J. Org. Chem.* **1976**, *41*, 62–66.