Influence of 1,4-Bis(diphenylphosphino)butane on the Hydroformylation of α,β-Unsaturated Esters Catalyzed by Zwitterionic, Cationic, and Neutral Rhodium(I) Complexes. The Asymmetric Hydroformylation of α-Methylene-γ-butyrolactone

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An investgation was made of the effect of 1,4-bis(diphenylphosphino)butane (dppb) on the regioselectivity of the hydroformylation of α,β-unsaturated esters with synthesis gas, catalyzed by rhodium(I) complexes. Excellent regioselectivity was obtained when dppb was added as a ligand for the reaction of methyl acrylate and α-methylene-γ-butyrolactone with synthesis gas. However, it inhibits the reaction when methyl methacrylate is used as the substrate. The asymmetric hydroformylation of α-methylene-γ-butyrolactone using [Rh(1,5-hd)(phen)]$^+$Cl$^-$ as the catalyst and (*R*)-BINAP as the chiral ligand (6:1 ratio of (*R*)-BINAP/Rh) gave an aldehydic lactone, containing a quaternary chiral center, in up to 37% ee.

Introduction

The hydroformylation of α,β-unsaturated esters is an attractive synthetic route for the preparation of 1,3- and 1,4-difunctional compounds, which can subsequently be converted to malonic acid derivatives and γ-butyrolactones.[1,2] Numerous neutral and cationic rhodium compounds have been investigated as catalysts,[1-9] and recently the zwitterionic rhodium compound, Rh(cod)(η^6-PhBPh$_3$) (**1**), has been shown to be an excellent precatalyst for the reaction.[10,11] The regiochemistry of the reaction strongly depends on the catalyst system and the substrates employed. For example, Prokai-Tatrai et al.[9] investigated the hydroformylation of methyl methacrylate and found that the ratio of α-formyl to β-formyl product is 94/6 in the case of $Rh_4(CO)_{12}$ as the catalyst, but it changes to 9/91 for the $Rh_4(CO)_{12}$–PBu_3–NEt_3 catalyst system. It has been known that the presence of 1,4-bis(diphenylphosphino)butane (dppb) as an added ligand in metal-catalyzed carbonylation reactions enables reactions to occur which do not otherwise proceed[12] and can alter the regiochemistry of a reaction in some cases.[13]

The catalytic asymmetric hydroformylation of olefins with chiral phosphine rhodium complexes has been investigated and several papers have been published on this subject.[14-21] Recently Sakai and co-workers obtained 97% enantiomeric excess (ee) in the asymmetric hydroformylation of 1,2-disubstituted olefins using a chiral phosphine–phosphite–Rh(I) catalyst.[14] However, little has been reported about the asymmetric hydroformylation of α,β-unsaturated esters. Specifically, Consiglio et al. obtained 37% ee in the hydroformylation of methyl methacrylate at 120 °C and 216 atm, using $PdCl_2$[(*R*,*R*)-Diop] as the catalyst.[22] There are no reports, to our knowledge, on asymmetric hydroformylation resulting in the formation of aldehydes containing a quaternary chiral center. Also, no papers have appeared on the asymmetric hydroformylation of unsaturated lactones.

We now describe, in more detail, how the use of dppb as an added ligand influences the zwitterionic Rh(I)-catalyzed hydroformylation of α,β-unsaturated esters and the effect of the bidentate phosphine ligand when cationic or neutral rhodium complexes are employed as catalysts. In addition, the asymmetric hydroformylation of α-methylene-γ-butyrolactone was examined using chiral phosphine ligands.

Results

The hydroformylation reactions of the α,β-unsaturated esters, methyl acrylate, methyl methacrylate, and α-methylene-γ-butyrolactone were carried out at 50–130 °C under 600 psi of synthesis gas (CO/H_2 = 1/1) using zwitterionic, cationic, and neutral rhodium(I) complexes as catalyst precursors, in the presence or absence of dppb. Rh(cod)(η^6-PhBPh$_3$) (**1**), [Rh(cod)(dppb)]$^+$BF$_4^-$ (**2**), and

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Table 1. Rhodium-Catalyzed Hydroformylation of Methyl Acrylate with Synthesis Gas (CO/H_2 = 1/1)[a]

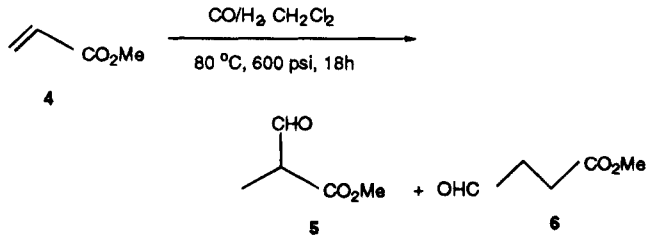
entry	[Rh]	L (L/Rh)	conv[b] (%)	yield[b] (%)	α-selectivity[c] (%)
1	**1**	–	71	51 (35)	76
2	**1**	dppb (2)	100	93 (68)	97
3	**1**	$P(OPh)_3$ (4)	96	90 (57)	98
4	**2**	–	34	25 (18)	79
5	**2**	dppb (2)	100	89 (63)	99
6	**3**	–	16	5	75
7	**3**	dppb (1)	33	25 (16)	91
8	**3**	dppb (2)	100	94 (71)	98
9	**3**	dppb (3)	100	94 (70)	99

[a] Reaction conditions: **4**, 4 mmol; Rh, 0.04 mmol; CH_2Cl_2, 10 mL; 80 °C; 600 psi; 18 h. [b] Calculated by GLC analysis using biphenyl as an internal standard. Isolated yield in parentheses. [c] Analyzed by proton NMR. Enol/**5** = 0.75/1.0 in $CDCl_3$ at rt.

$[Rh(cod)Cl]_2$ (**3**) were used as the zwitterionic, cationic, and neutral rhodium complexes, respectively.

Hydroformylation of Methyl Acrylate (4). The rhodium-catalyzed hydroformylation of **4** gave both methyl α-formylpropionate (**5**) and methyl β-formylpropionate (**6**). A small amount (<5%) of methyl propionate was formed as a byproduct. The results are summarized in Table 1. The NMR spectra of **5** shows that it is in equilibrium with its enol form [CH_2=C(CHOH)CO_2Me]. The ratio of the enol to the aldehyde in $CDCl_3$ at room temperature is 0.75/1.0.

In the absence of dppb, the catalytic activities of rhodium complexes were low to moderate, and the regioselectivity for **5** was 75–79%. The order of the catalytic activity was **1** > **2** > **3** in the absence of dppb. However, addition of dppb as a ligand significantly increased both the catalytic activity and the degree of regioselectivity. Almost the same results were observed regardless of the nature of the rhodium complex. The most dramatic example was observed when **3** was used as the catalyst. In the absence of dppb, the conversion, yield, and α-selectivity were 16, 5, and 75%, respectively. However, the conversion, yield, and α-selectivity increased to 100, 94, and 98%, respectively, when 2 equiv of dppb were present in the reaction system.



Triphenylphosphite, $P(OPh)_3$, showed excellent β-selectivity with $Rh(acac)(CO)_2$ in the hydroformylation of ethyl acrylate.[3] On the contrary, the phosphite gave excellent α-selectivity using the zwitterionic rhodium complex (entry 3, Table 1).

Hydroformylation of Methyl Methacrylate (7). The hydroformylation of **7** was carried out at 100 °C under 600 psi of synthesis gas in dichloromethane for 18 h and the results are presented in Table 2. When **1** was used as the catalyst in the absence of dppb, the reaction proceeded rapidly and the ratio of α-isomer **8** to β-isomer **9** was 20:80. A trace amount (<2%) of the hydrogenation product was formed in this case. The catalytic activity of the zwitterionic compound **1** was superior to that of the cationic (**2**) or the neutral (**3**) complex. Interestingly, the hydrogenation product was formed in 47% yield using

Table 2. Rhodium-Catalyzed Hydroformylation of Methyl Methacrylate with Synthesis Gas (CO/H_2 = 1/1)[a]

entry	[Rh]	L (L/Rh)	conv[b] (%)	yield[b] (%)	α-selectivity[c] (%)
1	**1**	–	98	96 (78)	20
2	**1**	dppb (2)	72	72 (54)	91
3	**2**	–	29	24 (22)	16
4	**2**	dppb (2)	nr[d]	–	
5[e]	**3**	–	100	53 (47)	16
6	**3**	dppb (2)	nr[d]	–	

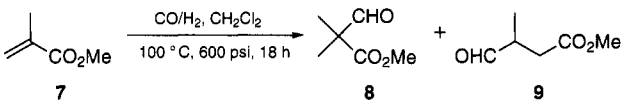
[a] Reaction conditions: **7**, 4 mmol; Rh, 0.04 mmol; CH_2Cl_2, 10 mL; 100 °C; 600 psi; 18 h. [b] Calculated by GLC analysis using biphenyl as an internal standard. Isolated yield in parentheses. [c] Analyzed by proton NMR. [d] No reaction. [e] 47% hydrogenation product was formed.

Table 3. Temperature Effect on the Rhodium-Catalyzed Hydroformylation of Methyl Methacrylate with Synthesis Gas (CO/H_2 = 1/1)[a]

entry	temp (%)	time (h)	conv[b] (%)	yield[b] (%)	**8**:**9**[c] (%)
1	50	18	44	43	70:30
2		24	52	50	69:31
3		48	73	69	69:31
4		66	83	76 (67)	70:30
5	60	64	86	84 (71)	53:47
6	84	18	93	90 (73)	25:75
7	100	18	98	96 (78)	20:80
8	130	18	100	94 (77)	6:94
9[d]	130	18	39	36 (18)	3:97

[a] Reaction conditions: **7**, 4 mmol; **1**, 0.04 mmol; CH_2Cl_2, 10 mL; 600 psi. [b] Calculated by GLC analysis using biphenyl as an internal standard. Isolated yield in parentheses. [c] Analyzed by proton NMR. [d] 200 psi CO/H_2.

3 as the catalyst in the absence of dppb. The addition of dppb to the zwitterionic (**1**) reaction system increased the α-selectivity remarkably to 91% (2:1 ratio of dppb:**1**) from 20%. However, in marked contrast to the hydroformylation of **4**, the conversion and yield decreased by the addition of dppb to catalyst **1**. Also note that when **2** and **3** were used in the presence of 2 mol equiv of dppb, the catalyst system was totally inactive.



The effect of temperature on the regiochemistry was investigated using the zwitterionic rhodium catalyst **1**, in the absence of dppb, and the results are summarized in Table 3. As the temperature increases, the conversion and the yield of aldehydes are increased but at the expense of α-selectivity. Thus, when the temperature was raised from 50 °C to 130 °C, the ratio of α- to β-isomer changed from 70:30 to 6:94. In the hydroformylation of ethyl acrylate catalyzed by $Rh(acac)(CO)_2$–$P(OPh)_3$, Yamashita et al. found that the β-selectivity depends on the reaction time.[3] However, we observed that the regioselectivity was constant with time at 50 °C (entries 1–4, Table 3). The β-selectivity can be increased slightly by reducing the pressure (entries 8 and 9, Table 3).

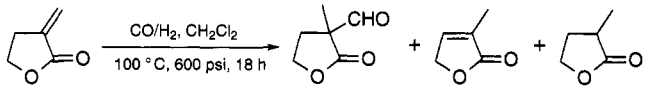
Hydroformylation of α-Methylene-γ-butyrolactone (10). In the absence of dppb, the reaction of **10** with synthesis gas did not afford any aldehyde, although the conversion was very high (>90%). Instead, the isomerized lactone **12** was the predominant product, and some hydrogenation occurred to give **13**. Therefore, it seems that CO insertion does not take place effectively in the absence of dppb. However, in the presence of dppb, the branched aldehyde **11** containing a quaternary carbon

Table 4. Rhodium-Catalyzed Hydroformylation of α-Methylene-γ-butyrolactone with Synthesis Gas (CO/H_2 = 1/1)[a]

entry	catalyst	temp/time (°C/h)	conv[b] (%)	product distribution (%)[b] 11	12	13
1	**1**	60/24	100	0	94	6
2	**1** + dppb (2)	60/24	90	92	5	3
3	**1**	100/18	100	0	89	11
4	**1** + dppb (2)	100/18	100	82 (69)	11	7
5	**1** + dppb (4)	100/18	100	80	10	10
6	**1**	130/24	100	0	61	39
7	**1** + dppb (4)	130/24	100	67 (49)	9	24
8	**2**	100/18	100	0	86	14
9	**2** + dppb (2)	100/18	100	81 (70)	13	6
10	**3**	100/18	100	0	96	4
11	**3** + dppb (2)	100/18	100	81 (67)	14	5

[a] Reaction conditions: **10**, 2 mmol; Rh, 0.04 mmol; CH_2Cl_2, 10 mL; 600 psi. [b] Calculated by proton NMR and GLC analysis using biphenyl as an internal standard. Isolated yield in parentheses.

atom, to which was attached the formyl group, was obtained in excellent yield. Consistent with our previous results[11], the hydroformylation process is regiospecific (see Table 4). When the zwitterionic complex **1**, the cationic complex **2**, and the neutral rhodium complex **3** were used as catalysts in the absence of dppb at 100 °C under 600 psi, the isomerization product was the major one with the yield being 86–96%. When dppb was added as a ligand (2:1 ratio of dppb/Rh), the branched aldehyde **11** was formed as the main product in 81–82% yield (isolated yield of 67–70%). As the temperature is increased, the yield of the aldehyde decreases, with increased isomerization and hydrogenation.



10 **11** **12** **13**

In order to investigate the nature of the isomerization process, several experiments were carried out at 100 °C for 18 h. (1) Treatment of **10** with synthesis gas (CO/H_2 = 1/1) in the presence of a catalytic amount of **1** afforded **12** and **13** in 89 and 11% yield, respectively. (2) Only the isomerization product was formed in 39% yield (conversion = 39%) when **10** is treated with 300 psi of CO and **1**. Addition of 300 psi of hydrogen to the reaction mixture containing the CO promotes the isomerization process as well as hydrogenation. The conversion was 100% and the ratio of **12** and **13** was 96:4. In this case, it seems that the hydrogenation of **12** is minimal, since the product ratio of **12** and **13** due to unconverted **10** in the proceeding reaction is 89:11. (3) When 300 psi of hydrogen was introduced in the absence of CO, **13** was formed in 93% yield and **12** was obtained in 7% yield. However, a black precipitate was formed in the reaction. (4) No reaction occurred when **10** was treated with **1** in a nitrogen atmosphere.

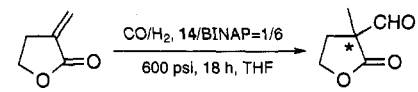
Asymmetric Hydroformylation of 10. The hydroformylation reaction was carried out using various rhodium(I) catalysts and chiral phosphorus ligands such as (*R*)-BINAP and (*S,S*)-CHIRAPHOS with BINAP affording better results than CHIRAPHOS (Table 5). From the point of view of percentage of enantiomeric excess, [Rh(1,5-hd)(phen)]$^+Cl^-$ (**14**) and the neutral rhodium complex **3** afforded the best results among the rhodium compounds used. The ratio of BINAP to **1** has an appreciable influence on the asymmetric hydroformylation of **10**. Poor ee resulted when an equimolar amount of BINAP and **1**

Table 5. Asymmetric Hydroformylation of α-Methylene-γ-butyrolactone with Synthesis Gas (CO/H_2 = 1/1)[a]

entry	catalyst[b]	solvent	temp/time (°C/h)	conv (%)	yield[c] (%)	% ee[d]
1	**1** + A (1 eq)	CH_2Cl_2	60/42	100	13 (9)[e]	2
2	**1** + A (2 eq)	CH_2Cl_2	60/42	5	5 (4)	17
3	**1** + A (2 eq)	CH_2Cl_2	100/48	73	69 (58)	18
4	**1** + B (2 eq)	CH_2Cl_2	100/66	100	10 (9)[e]	0
5	**2** + A (2 eq)	CH_2Cl_2	100/66	95	80 (68)	4
6	**2** + A (2 eq)	CH_2Cl_2	100/66	92	65 (60)	4
7	**3** + B (2 eq)	CH_2Cl_2	100/66	9	6 (5)	20
8	**14** + A (2 eq)	CH_2Cl_2	100/66	37	32 (29)	21
9	**14** + A (6 eq)	THF	80/170	15	15 (12)	37
10	**14** + A (6 eq)	THF	100/66	37	36 (33)	35
11	**14** + A (15 eq)	THF	100/144	56	56 (50)	36
12	**3** + A (6 eq)	THF	105/66	22	22 (20)	35

[a] Reaction conditions: **10**, 1 mmol; Rh, 0.01 mmol; solvent 10 mL; 600 psi. [b] A, (*R*)-BINAP; B, (*S,S*)-CHIRAPHOS. [c] GLC yield. Isolated yield in parentheses. [d] Calculated by GLC analysis using capillary chiral column (Supelco β-DEX 120, 30 m, 0.25 mm i.d., 0.25 μm df). [e] The isomerization product, **13**, was the principal product.

was used compared with twice the amount of BINAP. The % ee increases to 35 from 21%, when the ratio of BINAP to **14** was raised to 6 from 2. However, a further increase of the ratio of BINAP to **14** of 15:1 does not result in enhanced ee's. The best % ee was obtained at 80 °C using the same catalyst system.



10 **11**

It is noteworthy that the branched aldehyde is the only product formed (i.e. hydrogenation or isomerization is inhibited) when the BINAP to rhodium ratio is greater than 6. The effect of temperature on the % ee was small and almost the same results were observed when the reaction was performed at 60–100 °C.

Discussion

The rhodium(I) complex–dppb system is very effective for the selective α-formylation of α,β-unsaturated esters such as methyl acrylate, methyl methacrylate, and α-methylene-γ-butyrolactone. The results can be summarized as follows:

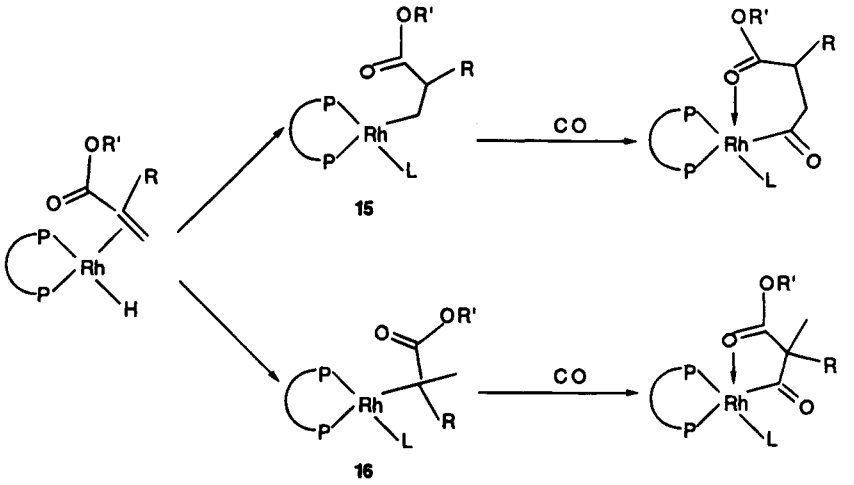
(1) The presence of dppb as an added ligand enhances the α-selectivity, affording the α-formyl product almost regiospecifically.

(2) When methyl methacrylate and α-methylene-γ-butyrolactone are used as substrates, dppb promotes the hydroformylation process. However, in the case of methyl methacrylate, dppb inhibits the reaction.

(3) When methyl methacrylate is hydroformylated in the presence of **1** and dppb, the β-selectivity increases with increasing temperature.

It is interesting to consider why the α-formyl product is obtained regioselectively in the presence of dppb. Regardless of the nature of the rhodium complex, almost the same results were realized in the presence of dppb. Alper and Zhou[23] observed the same trend in the hydroformylation of allyl acetate catalyzed by cationic and zwitterionic rhodium complexes. They postulated that the rhodium catalyst precursor may be converted to an active species such as [Rh(cod)(dppb)]$^+X^-$, which carries out the regioselective hydroformylation, with the cod

Scheme 1



ligand likely replaced by CO, hydride, and olefin ligands in subsequent steps.[23] The rhodium-catalyzed hydroformylation mechanism proposed by Wilkinson suggests that the four-coordinated rhodium hydride species is a key intermediate and that the rate-determining step involves cis oxidative addition of dihydrogen to the four-coordinated acyl rhodium complex.[2] The rhodium hydride species can be formed from the rhodium diene complex in the presence of dihydrogen.[24] As shown in Scheme 1, both linear and branched alkyl rhodium species, **15** and **16**, can be generated. Successive CO insertion into the resulting Rh–C bond produces the corresponding Rh–acyl complexes. It was reported that if a thermodynamically stable six-membered ring is formed in the hydroformylation of vinyl acetate, by the coordination of carbonyl group to the four-coordinate rhodium complex to form a five-coordinate complex, the cis oxidative addition of dihydrogen is suppressed owing to the saturation of a vacant coordination site.[4] In the case of the linear Rh–acyl species, a six-membered ring is possible by the coordination of a carbonyl group to Rh. The cis oxidative addition of dihydrogen to the linear Rh–acyl complex may be suppressed since the carbonyl group blocks a vacant site. The formation of the more stable five-membered ring chelate from **16**, compared with that from **15**, may be responsible for the control of the regiochemistry of the reaction.

It seems that the inhibition effect of dppb in the hydroformylation of methyl methacrylate is partly due to the steric hindrance between two methyl groups and the bulky diphosphine ligand, dppb, of the branched Rh–acyl compound. However, the electronic effect may also be important.[5]

Regarding the temperature effect on the regioselectivity in the hydroformylation of **7**, it was previously proposed that the extent of the skeletal isomerization of the Rh-branched alkyl complex to the Rh-linear alkyl species is an important factor in determining the product distribution.[5] The linear alkyl–Rh species is preferably formed initially since the α-carbon has a δ^- charge which can stabilize the cationic rhodium center. Consequently the activation energy of **15**, R = Me, will be lower than that of **16**, R = Me. Assuming that the product distribution is only dependent on the reaction rate at the same

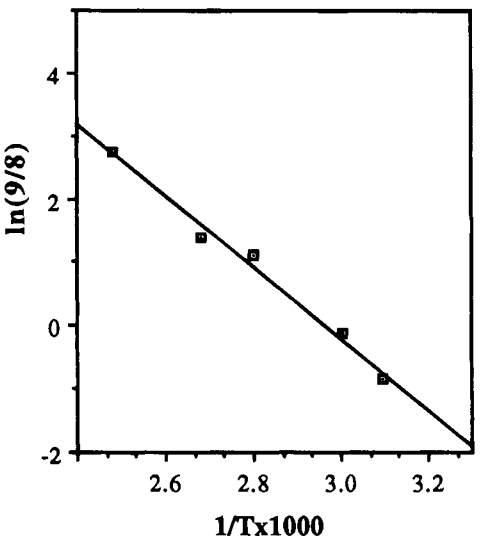


Figure 1. Effect of temperature on the regioselectivity of the hydroformylation of **7** with synthesis gas. Reaction conditions: **1**, 0.04 mmol; **7**, 4 mmol; CH_2Cl_2 10 mmol; 600 psi (CO/H_2= 1/1).

conditions, the activation energy difference can be calculated. As depicted in Figure 1, the plot of ln(**9**/**8**) vs $1/T$ shows a good linear relationship. From the slope, the apparent activation energy difference between the formation of **9** and **8** was found to be 11.3 kcal/mol in the case of catalyst **1**. In the presence of dppb, a skeletal isomerization is likely to be inhibited by the stabilization of the α-metalated species by a strongly coordinated phosphine ligand.

It has been reported that olefin isomerization takes place during the hydroformylation reaction.[2] The thermodynamically more stable internal olefin is formed in the hydroformylation of **10**. It is conceivable that this isomerization reaction takes place via an η^3-allyl–Rh intermediate, although the mechanism via a σ-alkyl intermediate cannot be ruled out. η^3-Allyl–Rh compounds have been prepared[25] and proposed as intermediates in the hydroformylation of butadiene.[26] A possible mechanism is presented in Scheme 2. In this mechanism the C–H bond at the activated allylic position of **10**

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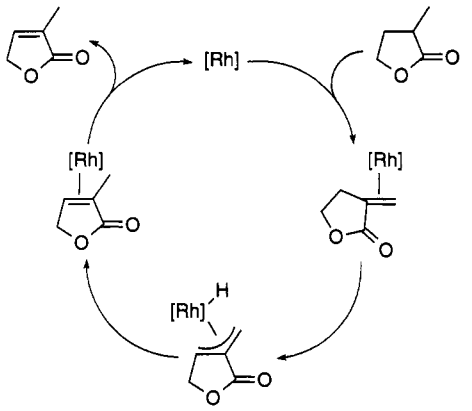
Scheme 2



undergoes oxidative addition to the Rh metal. Since two vacant sites are required,[27] the isomerization process is retarded by the presence of dppb, while **12** was formed as the major product and aldehyde was not detected in the absence of dppb. It is known that CO insertion rarely occurs into the Rh–C bond of an η^3-allyl–Rh compound.[26]

Conclusion

Excellent α-selectivity occurs when dppb is added as a ligand in the hydroformylation of α,β-unsaturated esters catalyzed by rhodium(I) complexes. When methyl acrylate and α-methylene-γ-butyrolactone are used as substrates, dppb significantly promotes the hydroformylation. However, dppb inhibits the reaction when methyl methacrylate is used as the substrate. In the absence of dppb, the hydroformylation of methyl methacrylate catalyzed by **1** shows increasing β-selectivity with increasing temperature.

The aldehydic lactone, **11**, was obtained in up to 37% ee in the asymmetric hydroformylation of **10** with 600 psi of synthesis gas at 80 °C in THF using [Rh(cod)(phen)]$^+$Cl$^-$–BINAP (L*/Rh = 6) as the catalyst system. This result is quite promising, given the difficulty, often encountered, of achieving high enantiomeric excess in systems where the chiral center is a quaternary carbon.

Experimental Section

General. Dichloromethane and THF were dried and distilled under nitrogen before use. The zwitterionic rhodium complex **1**[28] and [Rh(1,5-hd)(phen)]$^+$Cl$^-$ (**14**)[29] were prepared according to literature methods. The other rhodium complexes, substrates and ligands [COD = 1,5-cyclooctadiene; 1,5-hd = 1,5-hexadiene; BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl; CHIRAPHOS = 2,3-bis(diphenylphosphino)butane; DIOP = 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane] were purchased from Aldrich Chemical Co., and were used as received. Proton and carbon NMR spectra were recorded on a Varian Gemini 200 spectrometer using $CDCl_3$ as the solvent. A 45 mL stainless steel autoclave (Parr Instruments) was used as a batch reactor.

Hydroformylation of Methyl Acrylate (4). A mixture of the ester (344 mg, 4.0 mmol), **1** (21.3 mg, 0.040 mmol),[28] and dppb (34.0 mg, 0.080 mmol) in CH_2Cl_2 (10 mL) was charged into the reactor. The gas phase in the reactor was flushed with carbon monoxide three times and pressurized to 300 psi, and then hydrogen was introduced up to the total pressure of 600 psi (Table 1, entry 2). The reactor was then placed in an oil bath at 80 °C and reacted for 18 h. The reactor was then cooled to room temperature, the reaction mixture was filtered through neutral alumina, and the solvent was removed by rotary evaporation. Quantitative analysis was carried out by a GLC (Varian 3400) equipped with a 1.5% OV-17 and 1.95% OV-210 packed column, with biphenyl as an internal standard. The ratio of **5**/**6** was determined by NMR spectroscopy. Pure **5** was isolated by silica gel column chromatography using 7:3 hexane/ethyl acetate as the eluant. Methyl 2-formylpropionate (**5**) obtained in 68% yield (316 mg) was characterized by comparison of ^{1}H NMR and mass spectral results with data for an authentic sample.[5] The same procedure was used for the reactions catalyzed by **2** or **3** instead of **1** (i.e. 0.040 mmol in each case).

Hydroformylation of Methyl Methacrylate (7). A mixture of the ester (403 mg, 4.0 mmol), **1** (21.3 mg, 0.040 mmol),[28] and dppb (33.9 mg, 0.080 mmol) in CH_2Cl_2 (10 mL) was reacted at 100 °C for 18 h at 600 psi of 1:1 CO/H_2 (Table 2, entry 2). Work-up as described for methyl acrylate afforded 280 mg (54% yield) of pure methyl 2-methyl-2-formylpropionate (**8**), identified by comparison of spectral data with an authentic sample.[5,11]

Asymmetric Hydroformylation of α-Methylene-γ-butyrolactone (10). A mixture of **10** (98 mg, 1.00 mmol), **14** (4.0 mg, 0.010 mmol), and (*R*)-BINAP (37.6 mg, 0.060 mmol) in THF (10 mL) was heated for 66 h at 100 °C and 600 psi of 1:1 CO/H_2 (Table 5, entry 10). After the reaction, the solvent was removed by rotary evaporation and the product **11** (40.0 mg, 33%) was isolated by distillation and identified by comparison with an authentic sample.[11] The enantiomeric excess was calculated using a GLC (Varian 3400) equipped with FID and capillary chiral column (Supelco β-DEX 120, 30 m, 0.25 mm i.d., 0.25 μm df) at isothermal conditions.

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