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Asymmetric hydroformylation catalyzed by an Rh(I)-(*R*,*S*)-BINAPHOS complex: substituent effects in olefins on the regioselectivity

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Abstract

Olefins bearing the larger substituents at the allylic position were hydroformylated in the higher iso/normal selectivity when Rh(I)-(*R*,*S*)-BINAPHOS was used as a catalyst. Deuterioformylation of 4,4,4-triphenyl-1-butene suggests that the higher iso/normal ratio may be attributed to the accelerated CO insertion to the *iso*-alkylrhodium **7***i*.

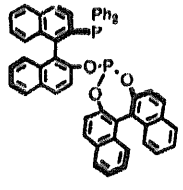
Keywords: Hydroformylation; Rhodium; Alkene; Chirality; Carbon monoxide; Carbonylation

1. Introduction

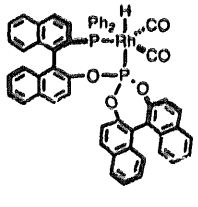
As optically pure *oxo*-aldehydes have enormous potential as building blocks in organic synthesis, asymmetric hydroformylation has been paid much attention in which chiral aldehydes can be produced in one step (for review articles, see Ref. [1]; for other recent references, see Ref. [2]). Platinum(II) and rhodium(I) complexes of chiral phosphines and phosphites have been used for this purpose, but most of them suffer from low regioselectivities, low enantiomeric excesses of the product and the presence of side reactions such as hydrogenation.

Recently, we have demonstrated that Rh(I)-(*R*,*S*)-BINAPHOS ((*R*,*S*) – BINAPHOS = (*R*)-2-diphenylphosphino-1,1′-binaphthalen-2′-yl (*S*)-1,1′-binaphthalen-2,2′-diyl phosphite) system is an excellent catalyst for asymmetric hydroformylation of styrene and its derivatives [3,4], vinyl esters [3,4], *N*-vinylphthalimide [3,4], sulfur-containing olefins [5] and some kinds of diene [6]. $RhH(CO)_2$((*R*,*S*)-BINAPHOS) has been characterized as an intermediate for this reaction [3]. In a series of studies, we have found that the iso/normal ratio of the products increases when the bulkiness of the substituents on the sulfur atom increases in aliphatic vinyl sulfides [5]. The fact is contradictory to the conventional explanation of the regioselectivities that the larger steric repulsion due to the bulkier substituents results in smaller iso/normal ratios [1,2]. Thus we became interested in the effects of the bulkiness of substituents and their positions with respect to the C=C double bond on the regioselectivities. In this report, olefins without hetero-atom functional groups are examined in order to discuss the steric factors of substrates apart from coordination effects.

A number of studies have been dedicated to clarify the reaction mechanism of hydroformylation process [7–9]. Deuterioformylation is one of the most effective methods, especially for probing reversible alkylrhodium formation [10]. Here, we also report a possible mechanism of asymmetric hydroformylation catalyzed by Rh(I)-(*R*,*S*)-BINAPHOS on the basis of deuterioformylation of 4,4,4-triphenyl-1-butene.



(*R*,*S*)-BINAPHOS



$RhH(CO)_2$((*R*,*S*)-BINAPHOS)

* Corresponding author.

[1] Deceased on October 4, 1995.

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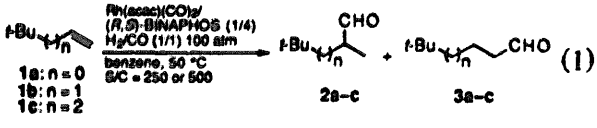
2. Results and discussion

2.1. Hydroformylation of olefins with the ^{t}Bu group at varying positions

We chose simple olefins bearing the ^{t}Bu group at vinylic, allylic, and homoallylic positions to examine the effect of bulky substituents on regioselectivities in Rh(I)-(*R*,*S*)-BINAPHOS-catalyzed hydroformylation. The results are given in Table 1.

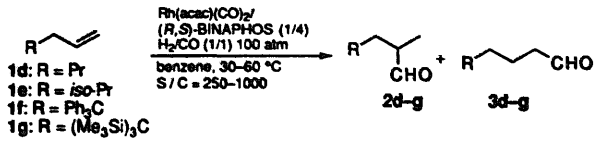


(1)

When 3,3-dimethyl-1-butene (**1a**) was treated with H_2 (50 atm) and CO (50 atm) at 50 °C in the presence of Rh(acac)$(CO)_2$-(*R*,*S*)-BINAPHOS in benzene, normal aldehyde, 4,4-dimethyl-1-pentanal (**3a**) was obtained, exclusively. In those series of substrates (**1a-c**), the highest *i*/*n* ratio, 43/57, was observed when 4,4-dimethyl-1-pentene (**1b**) was hydroformylated. 5,5-Dimethyl-1-hexene (**1c**) gave the corresponding aldehydes in *i*/*n* = 26/74 and this regioselectivity is comparable with that of normal terminal olefin, 1-hexene (**1d**) (*i*/*n* = 24/76, see Table 2). These results show a good agreement with the tendency observed in our previous study [5], where we found that vinyl sulfides with bulkier substituents at the β-position of the C=C bond were converted to the *oxo*-aldehydes in higher *i*/*n* ratios.

2.2. Hydroformylation of olefins with bulky substituents at the allylic position

We then focused our attention on the relationship between the bulkiness of substituents at the allylic position and the regioselectivities of the present hydroformylation. The results are listed in Table 2.



(2)

With all the substrates employed here, the corresponding *oxo*-aldehydes were obtained in moderate to good *ee* values. ^{i}Pr-substituted 4-methyl-1-pentene (**1e**) gave the corresponding *oxo*-aldehyde in *i*/*n* = 26/74. The value is similar to that obtained from linear olefin, 1-hexene (**1d**), and much lower compared with that from ^{t}Bu-substituted **1b**. In contrast, *oxo*-aldehyde was obtained in a much higher *i*/*n* ratio of 60/40, when 4,4,4-triphenyl-1-butene (**1f**) was used as a substrate. The *iso*-aldehyde was the major product this time. When a much bulkier substituent, the tris(trimethylsilyl)methyl group $(Me_3Si)_3C$-, was attached to the allylic position (**1g**), the *i*/*n* ratio of the product decreased to 7/93. Thus, the size of substituent that fits either ^{t}Bu or trityl group could favor the formation of *iso*-aldehydes in Rh(I)-(*R*,*S*)-BINAPHOS-catalyzed asymmetric hydroformylation.

2.3. A mechanistic study on the asymmetric hydroformylation of 4,4,4-triphenyl-1-butene (1f) by deuterioformylation

The trityl-substituted olefin **1f**, which gave the highest *ee* in the previous study, was employed as a substrate for a mechanistic study. In an autoclave a benzene solution of Rh(acac)$(CO)_2$, (*R*,*S*)-BINAPHOS and **1f** was stirred at 50 °C under D_2–CO atmosphere for 3-4 h. The results are given in Table 3. The contents of

Table 1
Asymmetric hydroformylation of olefins having the ^{t}Bu group at varying positions [a]

Run	Substrate	S/C [b]	Temperature (°C)	Time (h)	Conversion (%) [c]	*i*/*n* [c]	*ee* (%)	Configuration [d]
1	**1a**	500	50	49	71	0/100	—	—
2	**1b**	500	50	87	94	43/57	92 [e]	(−)
3	**1c**	250	50	68	90	26/74	77 [f]	(−)

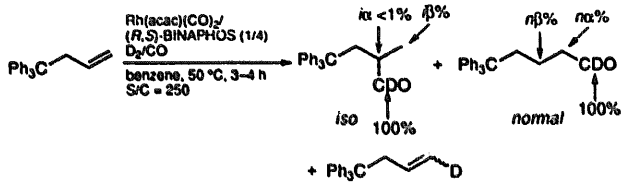
[a] Reactions were carried out in benzene (solvent/substrate = 1.4–2.4) with the substrate **1** (2.5–5.0 mmol), Rh(acac)$(CO)_2$ (0.5–1.0 × 10^{-2} mmol) and (*R*,*S*)-BINAPHOS (Ligand/[Rh] = 4.0) in a 50 ml autoclave under 1:1 mixture of H_2 and CO at initial total pressure of 100 atm. [b] Substrate/[Rh]. [c] Conversions and *i*/*n* ratios were determined by ^{1}H NMR. [d] Configurations of the iso-isomers were determined by the signs of optical rotations which are given in parentheses. [e] Determined by GLC analysis of the corresponding acid using a capillary column (Chrompack cp-Cyclodex β-236 M). [f] Determined by ^{1}H NMR analysis using Eu(hfc)$_3$ as a chiral shift agent.

Table 2
Asymmetric hydroformylation of olefins bearing bulky substituents at the allylic position [a]

Run	Substrate	S/C [b]	Temperature (°C)	Time (h)	Conversion (%) [c]	*i/n* [c]	*ee* (%)	Configuration [d]
1	**1d** [e]	1000	30	93	90	24/76	75 [f]	(*R*)-(−)
2	**1d**	1000	60	42	>99	24/76	48 [f]	(*R*)-(−)
3	**1e**	500	50	68	54	26/74	83 [g]	(−)
4	**1f**	250	50	20	>99	60/40	>99 [h]	(+)
5	**1g**	250	60	69	51	7/93	nd [i]	nd [i]

[a] The reaction was carried out under the same condition as Table 1. [b] Substrate/[Rh]. [c] Conversions and *i/n* ratios were determined by ^{1}H NMR. [d] Configurations of the iso-isomers were determined by the signs of optical rotations which are given in parentheses. [e] Reported in Ref. [3]. [f] Determined by GLC analysis of the corresponding acid using a capillary column (Chrompack cp-Cyclodex β-236 M). [g] Determined by ^{1}H NMR analysis using Eu(hfc)$_3$ as a chiral shift agent. [h] Determined by HPLC analysis of the alcohol derived from the corresponding aldehyde with DAICEL CHIRALCEL OD column. [i] Not determined.

deuterium in the products were calculated from the integration using the aldehyde deuterium as standards in ^{2}H NMR. Conversions of the products were determined by ^{1}H NMR using allylic protons as standards.

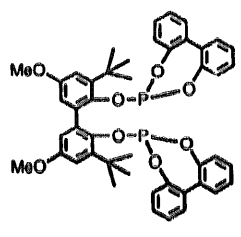


(3)

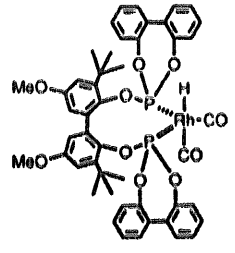
The results are summarized as follows. (1) The α-position of the *n*-aldehyde, n_α was dueterated to some extent (2-32% based on -CDO). (2) No deuterium was observed at the α-carbon of the *iso*-aldehyde. (3) The 1-position of the recovered olefin was deuterated while no deuterium was seen at the 2-position. (4) The *i/n* ratios of the products mainly depend on the CO partial pressure (runs 1 and 4 or runs 2 and 3) and are almost independent of the D_2 partial pressure (runs 1 and 3 or runs 2 and 4).

In order to interpret these results, Wilkinson's generally accepted mechanism of hydroformylation [7] should be considered (Scheme 1). Formation of *n*-aldehyde is mainly drawn. *iso*-Aldehyde also follows the same reaction path, but the olefin coordinates in the opposite regioselectivity. In this scheme, the alkylrhodium complex is first formed by olefin insertion to the rhodium hydride. Insertion of carbon monoxide gives the acylrhodium complex which goes back to the rhodium hydride by hydrogenolysis. It is suggested that all the steps except for the last hydrogenolysis are reversible.

Another important reference has recently been reported by Gladfelter and coworkers [8]. They used a bisphosphite ligand bbmb (see formula drawn below). They characterized the structure of the intermediate complex, $RhH(CO)_2$(bbmb), in which both of the two phosphorus atoms occupy the equatorial positions of the coordination sites. The rapid, reversible nature of the olefin insertion was revealed by using 3,3-dimethyl-1-butene for this catalyst.



bbmb



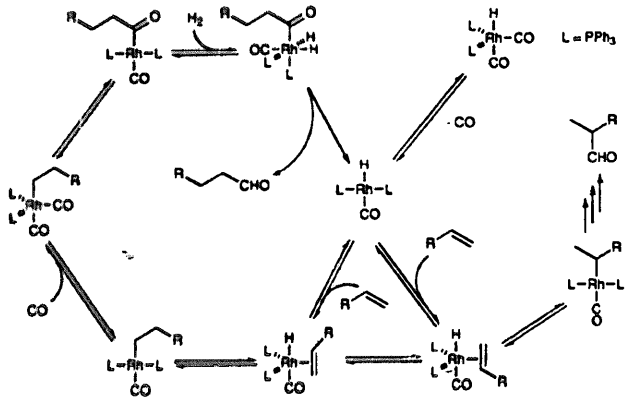
$RhH(CO)_2$(bbmb)

In contrast, our deuterioformylation of 4,4,4-triphenyl-1-butene (**1f**) indicates some unique features of

Table 3
Deuterioformylation of **1f** catalyzed by Rh(acac)(CO)$_2$-(*R,S*)-BINAPHOS [a]

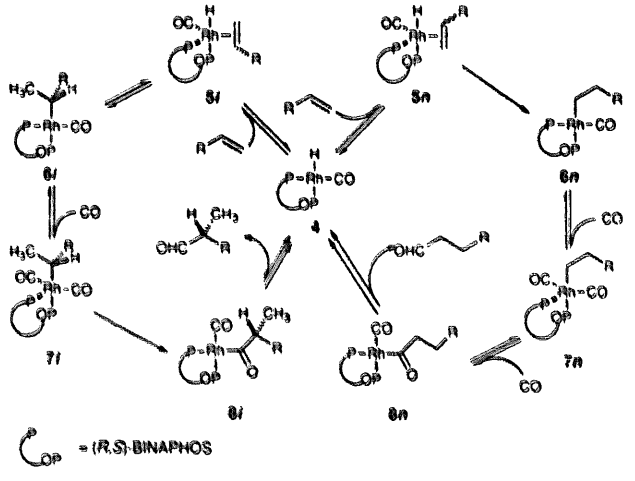
Run	P_{D_2}/P_{CO} (atm/atm)	Time (h)	Conversion (%) [b]	*i/n* [b]	i_β [c] (%D)	n_α [d] (%D)	n_β [e] (%D)	Olefin [f] (%D)
1	5/5	3	27	39/61	142	6	104	5
2	0.5/0.5	3	14	6/94	98	4	60	5
3	0.5/5	4	15	39/61	96	2	71	3
4	3.5/0.5	4	64	13/87	173	32	87	33

[a] The reaction was carried out under the same condition as Table 1. [b] Conversions and *i/n* ratios were determined by ^{1}H NMR. [c] Ratio of deuterium at the β position of the *iso*-aldehyde based on the aldehyde deuterium. [d] Ratio of deuterium at the α position of *n*-aldehyde based on the aldehyde deuterium. [e] Ratio of deuterium at the β position of *n*-aldehyde based on the aldehyde deuterium. [f] Molar ratio of deuterium at the 1 position of recovered olefin vs. molar of the recovered olefin.



Scheme 1. Wilkinson's generally accepted mechanism of hydroformylation.

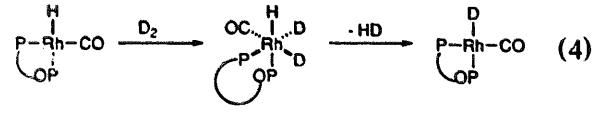
the present system. In our previous study, we have characterized the structure of $RhH(CO)_2\{(R,S)$-BINAPHOS$\}$ in which hydride and phosphite are placed at the apical sites [3]. Accordingly, a plausible mechanism described in Scheme 2 has been derived from the following four reasons (the structures of **4**-**8** are drawn tentatively; their cis/trans or apical/equatorial isomers are also possible). (1) The formation of *n*-α-deuterioaldehyde suggests that the existence of the β-hydride (β-deuteride) elimination from the *iso*-alkylrhodium complex **6*i*** to the rhodium-olefin complex **5*i*** which may be followed by the olefin insertion to produce the *n*-alkylrhodium complex **6*n***. That is, the olefin insertion step to give the *iso*-alkylrhodium complex **6*i*** is reversible. (2) However, no *iso*-α-deuterioaldehyde was obtained. That means, the insertion of olefin to form *n*-alkylrhodium complex **6*n*** is irreversible and the β-hydride elimination reaction is not undergone in this case. Therefore, it is probable that the rate determining step of the *n*-aldehyde formation should be the irreversible insertion of olefin into the Rh-H bond (**5*n*** → **6*n***). (3) The presence of the recovered 1-deuterioolefin and the absence of the 2-deuterioolefin



Scheme 2. A proposed mechanism for hydroformylation of **1f** catalyzed by Rh(I)-(*R,S*)-BINAPHOS.

also support the considerations of (1) and (2). (4) The formation of *iso*-aldehyde was favored under the higher CO pressure. This suggests that the CO insertion to an *iso*-alkylrhodium complex (**7*i*** → **8*i***) has a significant effect on the reaction rate.

It is noteworthy that the content of deuterium at i_β-, n_α-, and n_β-positions increased as the partial pressure of D_2 increased. This can be explained by Eq. (4). The hydride on rhodium can be replaced by deuteride by oxidative addition of D_2 and reductive elimination of H-D. Thus, in both of the iso- and normal-isomers, the sum of the contents of deuterium at the α- and β-positions of the products, i.e. $i\beta$ and $n\alpha + n\beta$ respectively, becomes significantly larger than aldehyde deuterium under the high pressure of D_2 (runs 1 and 4 in Table 3).



(4)

It is widely known that the mechanism of the hydroformylation reaction is greatly affected not only by the nature of catalyst but also by substrate olefins [7–9]. Nevertheless, if we assume the above mechanistic observation shown with **1f** could be applicable to other substrates **1a-e**, we might consider that the *iso*-acylrhodium formation step (**7*i*** → **8*i***) would be accelerated when the bulkier substituent is introduced at the allylic position of olefins. Some steric repulsion between the allylic substituent and the ligand may be regarded as the reason for this acceleration. As a result, the bulkier substituents at the allylic position might cause the higher *i*/*n* ratios. The higher *i*/*n* ratio observed in our previous study with the bulkier vinyl sulfide could be explained in a similar manner [5]. In contrast, the tris(trimethylsilyl)methyl group contributed to give the *n*-aldehyde predominantly from **1g**. The extremely strong blocking effect of this substituent might keep the substrate away from the formation of the *iso*-alkylrhodium intermediate (**6*i***).

In conclusion, we have examined asymmetric hydroformylation of olefins with various sizes of substituent at different positions. The absence of any coordinating hetero-atoms has enabled us to discuss the steric effect on the regio- and enantioselectivities. The fact that the bulkier substituents at the allylic position cause higher *i*/*n* ratios of the resulting aldehyde may be explained by the acceleration of the carbonyl insertion to the *iso*-alkylrhodium complex.

3. Experimental details

3.1. General

Nuclear magnetic resonance (^1H (270 MHz) and ^{13}C (67.8 MHz) NMR) spectra were recorded on a Jeol

JNM-EX270 spectrometer with chemical shifts reported in δ values relative to residual protonated solvent (^{1}H internal) and $CDCl_3$ (^{13}C internal) references respectively. ^{2}H NMR spectra were obtained on a Jeol JNM-EX270 spectrometer operating at 41.3 MHz with $CDCl_3$ as an internal standard. Optical rotations were measured on a Jasco DIP-360.

Gas chromatographic (GLC) analyses were conducted on a Shimadzu GC-15A equipped with a flame ionization detector. HPLC analyses were performed on a Toyo Soda CCPM equipped with a UV-8000 detector. All manipulations involving air- and moisture-sensitive organometallic compounds were carried out with the standard Schlenk-tube technique under an argon atomosphere purified by passing it through a BASF-Catalyst R3-11 column at 80°C. Deuteriochloroform was distilled over P_2O_5 and vacuum-transferred into an NMR tube prior to use. Diethyl ether, benzene and THF were distilled from sodium–benzophenone ketyl under an argon atomosphere. Dichloromethane was distilled over P_2O_5 under an argon atomosphere. $Rh(CO)_2(acac)$ was purchased from Aldrich Chemical Company, Inc. and used without further purification. 3,3-Dimethyl-1-butene, 4,4-dimethyl-1-pentene, 1-hexene and 4-methyl-1-pentene were purchased from Tokyo Kasei Kogyo Co., Ltd. and were degassed after distillation.

3.2. Synthesis of 5,5-dimethyl-1-hexene (1c)

A solution of 3,3-dimethyl-1-butene (15.0 ml, 116 mmol), $Rh(acac)(CO)_2$ (60.0 mg, 0.233 mmol) and $P(OPh)_3$ (0.611 ml, 2.33 mmol) in benzene (6 ml) was prepared in an 80 ml Schlenk tube. The mixture was degassed three times by freeze-thaw cycles and transferred into a 50 ml autoclave. Then the solution was stirred at 60°C under H_2/CO (1/1) pressure of 100-50 atm until the decrease in the pressure ceased. The aldehyde obtained was distilled and converted to 5,5-dimethyl-1-hexene (**1c**) by the Wittig reaction as reported (15.5% yield) [11].

3.3. Synthesis of 4,4,4-triphenyl-1-butene (1f)

To triphenylmethyl bromide (10.0 g, 30.9 mmol) in CH_2Cl_2 (100 ml) was added $TiCl_4$ (3.38 ml, 30.8 mmol) at room temperature. The brown solution obtained was stirred for another 15 min and then allyltrimethylsilane (4.91 ml, 30.9 mmol) in CH_2Cl_2 (60 ml) was added dropwise from a dropping funnel. The solution was stirred for 42 h. The reaction mixture was poured into ice-water, and the organic layer was separated. The aqueous layer was washed twice with CH_2Cl_2 (2 × 100 ml) and the combined organic layers were dried over magnesium sulfate and the solvent was removed. This crude product was purified by recrystallization from hexane to obtain **1f** as colorless crystals (78.6% yield). **1f**: m.p. ca. 130°C (sublimation). ^{1}H NMR ($CDCl_3$) δ 7.3-7.2 (m, 15H, aromatic protons), 5.6-5.7 (m, 1H, C*H*=CH_2), 4.9-5.1 (m, 2H, CH=CH_2, 3.47 (d with fine splitting, 2H, J = 6.6 Hz, Ph_3CCH_2). ^{13}C NMR ($CDCl_3$) δ 147.26, 135.94, 129.38, 127.73, 125.93, 117.23, 56.246, 45.52. Anal. Found C, 92.68; H, 7.24. $C_{22}H_{20}$. Calc.: C, 92.91; H, 7.09%.

3.4. Synthesis of 4,4,4-tris(trimethylsilyl)-1-butene (1g)

Tris(trimethylsilyl)methane was prepared [12] and lithiated [13] by the literature procedures. To $(TMS)_3CLi$ (ca. 37 mmol) in THF (100 ml) was added allyl bromide (3.6 ml, 42 mmol) drop by drop at 0°C. The stirring was continued for 3 h. To the reaction mixture were added water (100 ml) and hexane (100 ml) and the organic layer was separated. The solvent was removed in vacuo to obtain a crude product contaminated with $(TMS)_3CH$. Pure **1g** was obtained by sublimation of the crude product at 70°C in vacuo (ca. 50% yield). **1g**: m.p. 67.7-68.2°C. ^{1}H NMR ($CDCl_3$) δ 5.9-6.1 (m, 1H, C*H*=CH_2), 4.9-5.1 (m, 2H, CH=CH_2), 2.50 (d with fine splitting, 2H, J = 6.6 Hz, CH_2CH=CH_2), 0.14 (s, 27H, 3 × $(CH_3)_3Si$). ^{13}C NMR ($CDCl_3$) δ 140.25, 115.67, 35.06, 3.04, 2.66. HRMS (CI); Calc. for $C_{13}H_{32}Si_3$: 272.1811; found (M^+): 272.1808.

3.5. General procedure for asymmetric hydroformylation

A solution of 3,3-dimethyl-1-butene (**1a**) (421 mg, 5.00 mmol), (*R*,*S*)-BINAPHOS (30.8 mg, 4.00×10^{-2} mmol) (the preparation of the ligand is reported in Ref. [3]), and $Rh(acac)(CO)_2$ (2.6 mg, 1.0×10^{-2} mmol) in benzene (1.0 ml) was prepared in a 20 ml Schlenk tube. The mixture was degassed three times by freeze-thaw cycles and transferred into a 50 ml autoclave. Then the solution was stirred at 50°C for 49 h under H_2/CO (1/1) pressure of 100 atm. The conversion of **1a** (71%) and the ratio of 2,3,3-trimethylbutanal (**2a**)/4,4-dimethylpentanal (**3a**) (0/100) were determined by ^{1}H NMR analysis. Olefins **1b-1g** were hydroformylated in a similar procedure. Most of the product aldehydes were obtained as a mixture of iso- and normal-isomers. The products, 4,4-dimethylpentanal (**3a**) (926-36-3) [14], 2,4,4-trimethylpentanal (**2b**) (17414-46-9), and 2,4-dimethylpentanal (**2e**) (27944-79-2) are reported compounds. Also, 2-methylhexanal (**2d**) is shown in our literature [3].

3.6. 2-Methyl-4,4,4-triphenylbutanal (2f)

Obtained as a mixture with the normal-compound **3f**. (+)-**2f**: ^{1}H NMR ($CDCl_3$) δ 8.87 (d, 1H, J = 2.6 Hz, C*H*O), 7.4-7.2 (m, 15H, aromatic protons), 3.19 (dd, 1H, J = 7.3 Hz, 14.5 Hz, CH(*H*)CHCHO), 2.68 (dd, 1H, J = 3.0 Hz, 14.5 Hz, CH(*H*)CHCHO), 2.5-2.4 (m,

1H, C*H*CHO), 0.94 (d, 3H, $J = 7.1$ Hz, CH_3). ^{13}C NMR ($CDCl_3$) δ 202.41, 146.56, 128.90, 127.96, 126.09, 56.48, 43.47, 41.21, 16.52.

3.7. Deuterioformylation of 4,4,4-triphenyl-1-butene (1e)

The experimental procedure was similar to that of hydroformylation of 4,4,4-triphenyl-1-butene (1e). A 50 ml autoclave was used for the deuterioformylation under D_2 (5 atm) and CO (5 atm) while a 100 ml pressure bottle was used when D_2/CO pressure was 3.5/0.5 and 0.5/5 (atm/atm). The deuterioformylation under D_2/CO (1/1, 1 atm total) was carried out in an 80 ml Schlenk tube. The conversion and the *i*/*n* ratios of products were determined by ^{2}H NMR ($CHCl_3$ with trace amount of $CDCl_3$ as an internal standard, 60 s relaxation delay) using the integration of aldehyde deuterium peaks.

Acknowledgements

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References

[1] (a) S. Gladiali, J.C. Bayón and C. Claver, *Tetrahedron: Asymmetry, 6* (1995) 1453. (b) F. Agbossou, J.-F. Carpentier and A. Mortreux, *Chem. Rev., 95* (1995) 2485. (c) C. Botteghi, S. Paganelli, A. Schionato and M. Marchetti, *Chirality, 3* (1991) 355. (d) G. Consiglio and P. Pino, *Top. Curr. Chem., 105* (1982) 77.

[2] (a) T.V. RajanBabu and T.A. Ayers, *Tetrahedron Lett., 35* (1994) 4295. (b) C.G. Arena, F. Nicolò, D. Drommi, G. Bruno and F. Faraone, *J. Chem. Soc. Chem. Commun.*, (1994) 2251. (c) G.J.H. Buisman, P.C.J. Kamer and P.W.N.M. van Leeuwen, *Tetrahedron: Asymmetry, 4* (1993) 1625. (d) I. Tóth, I. Guo and B.E. Hanson, *Organometallics, 12* (1993) 848. (e) S. Gladiali and L. Pinna, *Tetrahedron: Asymmetry, 2* (1991) 623. (f) G. Consiglio, S.C.A. Nefkens and A. Borer, *Organometallics, 10* (1991) 2046. (g) G. Consiglio and S.C.A. Nefkens, *Tetrahedron: Asymmetry, 1* (1990) 417. (h) J.K. Stille, H. Su, P. Brechot, G. Parrinello and L.S. Hegedus, *Organometallics, 10* (1991) 1183.

[3] N. Sakai, S. Mano, K. Nozaki and H. Takaya, *J. Am. Chem. Soc., 115* (1993) 7033.

[4] (a) N. Sakai, K. Nozaki and H. Takaya, *J. Chem. Soc. Chem. Commun.*, (1994) 395. (b) T. Higashizima, N. Sakai, K. Nozaki and H. Takaya, *Tetrahedron Lett., 35* (1994) 2023.

[5] T. Nanno, N. Sakai, K. Nozaki and H. Takaya, *Tetrahedron: Asymmetry, 6* (1995) 2583.

[6] T. Horiuchi, T. Ohta, K. Nozaki and H. Takaya, *Chem. Commun.*, (1996) 155.

[7] (a) D. Evans, J.A. Osborn and G. Wilkinson, *J. Chem. Soc. A*, (1968) 3133. (b) G. Yagupsky, C.K. Brown and G. Wilkinson, *J. Chem. Soc. A*, (1970) 1392. (c) C.K. Brown and G. Wilkinson, *J. Chem. Soc. A*, (1970) 2753.

[8] B. Moasser, W.L. Gladfelter and D.C. Roe, *Organometallics, 14* (1995) 3832.

[9] A. van Rooy, E.N. Orij, P.C.J. Kamer and P.W.N.M. van Leeuwen, *Organometallics, 14* (1995) 34.

[10] (a) R. Lazzaroni, R. Settambolo, A. Raffaelli, S. Pucci and G. Vitulli, *J. Organomet. Chem., 339* (1988) 357. (b) R. Lazzaroni, A. Raffaelli, R. Settambolo, S. Bertozzi and G. Vitulli, *J. Mol. Catal., 50* (1989) 1.

[11] R. Greenwald, M. Chaykovsky and E.J. Corey, *J. Org. Chem., 28* (1963) 1128.

[12] R.L. Merker and M.J. Scott, *J. Am. Chem. Soc., 85* (1963) 2243.

[13] Z.H. Aiube and C. Eaborn, *J. Organomet. Chem., 269* (1984) 217.

[14] R. Takeuchi and N. Sato, *J. Orgamomet. Chem., 393* (1990) 1.