

Asymmetric Hydroformylation of Vinyl Acetate By Use of Chiral Bis(triarylphosphite)—Rhodium(I) Complexes

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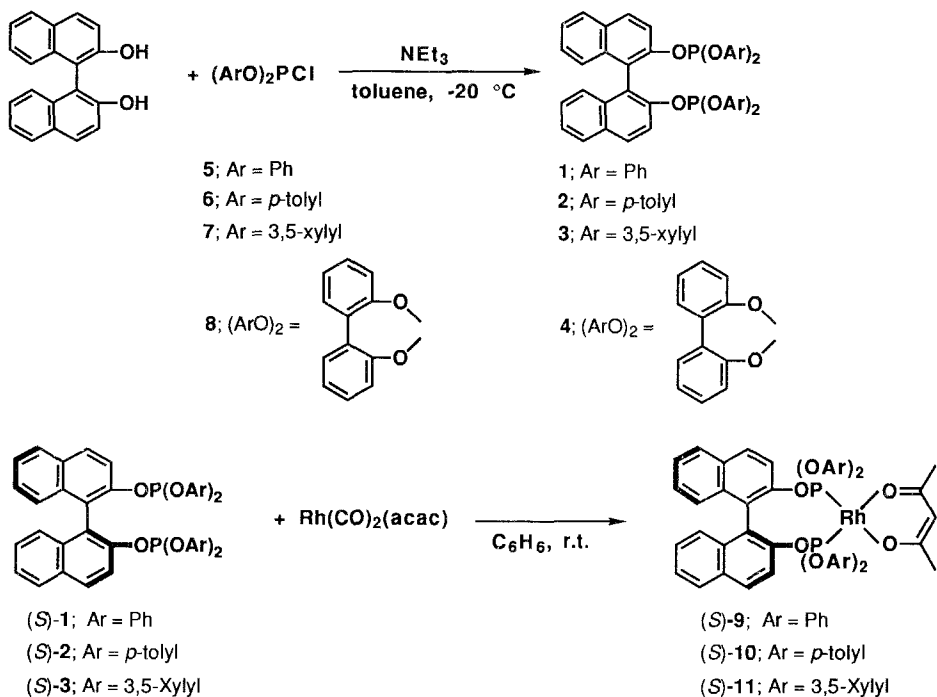
Abstract: Bis(triarylphosphite) ligands **1**—**4** were prepared in optically pure forms from (*R*)- or (*S*)-binaphthol and (*ArO*)₂PCl, and their Rh(I) complexes have been used as catalysts for hydroformylation of vinyl acetate. The corresponding branched aldehyde, 2-acetoxypropanal, was given in up to 95% regioselectivity and in 49% ee.

Asymmetric hydroformylations have attracted much attention in organic synthesis due to the high synthetic utility of optically active aldehydes.¹ A great deal of effort has been made for development of chiral catalysts efficient for both high regioselectivity (branch/normal ratio) and high stereoselectivity in carbon—carbon bond forming step. Rhodium or platinum complexes modified by optically active diphosphines have been used as catalysts, but the results have so far been unsatisfactory in many cases from a synthetic point of view.^{1—4} In spite of the high catalytic activity of Rh(I)—phosphite complexes for hydroformylation, they have rarely been employed as catalysts for asymmetric hydroformylations.⁴ We report here asymmetric hydroformylation of vinyl acetate catalyzed by chiral bis(triarylphosphite)—Rh(I) complexes.

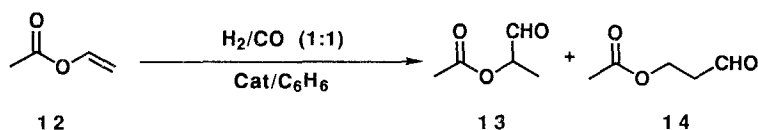
Optically pure bis(triarylphosphite) ligands **1**—**4** were readily prepared by the reaction of (*R*)- or (*S*)-binaphthol with the corresponding chlorophosphites **5**—**8** in the presence of triethylamine. Phosphites **1**—**4** are stable in air and moisture, and can be easily purified by column chromatography on silica gel. The structures of **1**—**4** were supported by their elemental analyses and spectral data.⁵ HPLC analysis of (*R*)- or (*S*)-**1**—**4** with chiral column (DAICEL CHIRALSEL OD, hexane—2-propanol (97:3)) showed that these compounds are optically pure. ³¹P NMR spectrum of ligand **4** exhibited a singlet which indicates that only one diastereomer has been obtained. Such formation of single diastereomer has been reported in the reaction of 2,2'-biphenol with PCl₃.^{6a}

Treatment of (*S*)-**1** with Rh(CO)₂(acac) in benzene resulted in a displacement of CO by (*S*)-**1**. After recrystallization of the product from a mixture of hexane and benzene (4:1) at -20 °C, pure complex (*S*)-**9** was obtained as yellow needles whose structure was characterized based on their elemental analysis and spectral data.⁷ Complex (*S*)-**9** exhibited only one ³¹P resonance at δ 128.81 (*J*_{Rh—P} = 299 Hz), almost the same chemical shift with that of the free ligand (δ 129.03). Similar reactions of (*R*)- or (*S*)-**2** or **3** with Rh(CO)₂(acac) gave (*R*)- or (*S*)-**10** and **11**, respectively.

Complexes **9**—**11** were used as catalysts for hydroformylation of vinyl acetate (**12**) under various



conditions to give preferentially 2-acetoxypropanal (**13**) accompanied by the linear product (**14**). Some representative results are summarized in Table 1. Use of pure samples of (*S*)-**9** and (*R*)-**11** purified by recrystallization resulted in low enantioselectivity (runs 1 and 2), while addition of 0.1 equiv. of excess ligand (*S*)-**1** to (*S*)-**9** improved the enantioselectivity to a large extent at the expense of catalytic activity (run 3). Further addition of the ligand hardly affected on the selectivity and catalytic activity (runs 4 and 5). Since complex $\text{Rh}(\text{CO})_2(\text{acac})$ catalyzes the above hydroformylation much faster than any of phosphite complexes **9**–**11** (run 7), the observed low enantioselectivity in the absence of excess ligands indicates that some phosphite free Rh(I) species formed by a dissociation of the chiral ligands worked as catalysts under such conditions. It has also been reported that the hydroformylation of vinyl acetate using Rh complexes of DIOP or its derivatives requires 3–6 equivs. of ligands to obtain moderate enantioselectivity (80 °C, 6% *ee* for 3 equivs. and 51% *ee* for 6 equivs.).² It is noteworthy that only a slight excess of phosphite ligand **1** could suppress the dissociation effectively to give good results. 3,5-Dimethyl substitution on the phenyl ring of the ligands resulted in slight decrease, if any, of the enantioselectivity (runs 1 and 2, 5 and 13). The lower reaction temperature gave higher enantioselectivity, though the reaction proceeded more slowly (runs 9–12). Interestingly, the reaction catalyzed by the Rh(I) complex of (*R*)-**4** gave the product with opposite absolute configuration compared to those with (*R*)-**1**–**3**, though enantioselectivity was rather poor (run 14).



Complex $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ could also be used in combination with **1**–**3**, to give results similar to those obtained with $\text{Rh}(\text{CO})_2(\text{acac})$ (runs 15–17). Benzene is the solvent of choice. Use of coordinating solvent such as THF resulted in decrease of both enantioselectivity and conversion (run 17). When the reaction was carried out by use of a mixture of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and excess (*R*)-BINAP (BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) (3 equivs. to Rh), the reaction proceeded much slowly (run 18). The same sense of enantioface selection has been observed for reactions by use of (*R*)-BINAP and **1**–**3** with *R* configuration. The above findings suggest that chiral bis(phosphite)—Rh(I) complexes are promising catalysts for asymmetric hydroformylations.

Table 1. Hydroformylation of Vinyl Acetate Catalyzed by Chiral Diphosphite—Rh(I) Complexes.^a

run	Rh ^b	Ligand	L/Rh	Temp, °C	Time, h	S/C ^c	% Conv. ^d	13/14 ^d	% ee ^e	Config ^f
1	A	(<i>S</i>)- 1	1.0 ^g	30	48	400	80	94/6	12	<i>R</i>
2	A	(<i>R</i>)- 3	1.0 ^g	30	40	400	75	94/6	2	<i>S</i>
3	A	(<i>S</i>)- 1	1.1	30	40	400	29	94/6	45	<i>R</i>
4	A	(<i>S</i>)- 1	1.2	30	40	400	33	94/6	46	<i>R</i>
5	A	(<i>S</i>)- 1	2.5	30	40	500	22	92/8	45	<i>R</i>
6	A	(<i>S</i>)- 1	2.5	20	40	300	11	94/6	49	<i>R</i>
7	A	None	—	30	17	1000	82	94/6	—	—
8	A	(<i>S</i>)- 2	1.1	30	40	200	38	94/6	42	<i>R</i>
9	A	(<i>S</i>)- 2	1.5	30	40	200	32	94/6	46	<i>R</i>
10	A	(<i>S</i>)- 2	1.5	40	40	200	82	93/7	45	<i>R</i>
11	A	(<i>S</i>)- 2	1.5	50	40	200	97	92/8	41	<i>R</i>
12	A	(<i>S</i>)- 2	1.5	80	3	2000	83	91/9	31	<i>R</i>
13	A	(<i>S</i>)- 3	2.5	30	40	300	12	91/9	45	<i>R</i>
14	A	(<i>R</i>)- 4	2.5	60	40	400	12	94/6	14	<i>R</i>
15	B	(<i>S</i>)- 1	2.5	20	40	100	25	94/6	49	<i>R</i>
16 ^h	B	(<i>S</i>)- 1	2.5	60	40	800	91	94/6	(41)	<i>R</i>
17 ^{h,i}	B	(<i>S</i>)- 1	2.5	60	40	800	81	93/7	(34)	<i>R</i>
18 ^h	B	(<i>R</i>)-BINAP	3.0	80	40	800	6	9/1	(47)	<i>S</i>

^a All reactions were carried out in benzene under 100 atm of H₂ and CO (1:1 mixture) unless otherwise stated. ^b Catalyst precursors: A, $\text{Rh}(\text{CO})_2(\text{acac})$; B, $[\text{Rh}(\text{CO})_2\text{Cl}]_2$. ^c Substrate/catalyst ratio. ^d Determined by GC (25% DOP on Uniprot HP, 100 °C, He 1 kg cm⁻², FID detector). ^e Determined by GLC with a chiral column (CHIRADEX B—PH, 55 °C) or by ¹H NMR (270 MHz) by the aid of chiral shift reagent Eu(hfc)₃ (values are given in parentheses). ^f Configurations were determined by the comparison of optical rotation values of the products with the literature data.² ^g The isolated complexes, (*S*)-**9** (run 1) and (*R*)-**11** (run 2) were used as catalysts. ^h Reactions were carried out under 70 atm (H₂ and CO, 1:1). ⁱ The reaction was carried out in THF.

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References and Notes

1. J. D. Morison, *Asymmetric Synthesis*, Vol. 5, p125—146, Academic Press, Orlando, 1985, and references cited therein.
2. A mixture of DIPHOL and Rh(cod)(acac) was used as catalyst in hydroformylation of vinyl acetate and 51% *ee* was obtained, which, to our knowledge, has been the highest value of enantioselectivity in all Rh-catalyzed hydroformylations including any other substrates. C. F. Hobbs and W. S. Knowles, *J. Org. Chem.*, **1981**, *46*, 4422.
3. The use of Pt catalysts in asymmetric hydroformylation has not been encouraging because of lower reaction rates and the tendency for the substrates to undergo competitive hydrogenation. Recently, Pt catalysts modified by chiral diphosphines and SnCl₂ have been used in asymmetric hydroformylations. a) Hydroformylation of styrene catalyzed by Pt complex of a DIOP derivative and SnCl₂ gives 2-phenylpropanal in up to 86% *ee*; G. Consiglio, S. C. A. Nefkens, and A. Borer, *Organometallics*, **1991**, *10*, 2046. b) Styrene was converted to 2-phenylpropanal diethylacetal with the catalyst system BPPM—PtCl₂/SnCl₂ in the presence of triethyl orthoformate in higher than 96% *ee*; J. K. Stille, H. Su, P. Brechot, G. Parrinello, and L. S. Hegedus, *Organometallics*, **1991**, *10*, 1183.
4. Recently, bis(phosphite) ligands derived from chiral diols have been reported and their Rh(I) complexes were used for hydroformylation of styrene, but no asymmetric induction was observed; D. J. Wink, T. J. Kwok, and A. Yee, *Inorg. Chem.*, **1990**, *29*, 5006.
5. All new diphosphites **1—4** gave correct elemental analyses. (±)-**1**: 64% isolation yield, white solid, mp 70—72 °C. Optically pure (*S*)-**1** is white paste, [α]_D²³ = -19.3 (*c* 1.80, CHCl₃). (±)-**2**: 62% isolation yield, white solid, mp 74.5—75.5 °C. Optically pure (*S*)-**2** is white paste, [α]_D²³ = -31.0 (*c* 1.17, CHCl₃). (*S*)-**3**: 64% isolation yield, white paste, [α]_D²³ = +20.4 (*c* 2.87, CHCl₃). (*R*)-**4**: 66% isolation yield, white solid, mp 93-95 °C, [α]_D²³ = +43.4 (*c* 1.09, CHCl₃). ³¹P NMR spectra (CDCl₃) of phosphites **1—4**: **1**, δ 129.03; **2**, δ 128.18; **3**, δ 128.18; **4**, δ 144.65.
6. Recently, bis(triarylphosphite) ligands derived from PCl₃ and biphenol^{6a} or binaphthol^{6b} were reported. A nickel complex of the phosphite was used as catalyst for asymmetric hydrocyanations.^{6b} a) M. J. Baker, K. N. Harrison, A. G. Orpen, P. G. Pringle, and G. Shaw, *J. Chem. Soc., Chem. Commun.*, **1991**, 803. b) M. J. Baker and P. G. Pringle, *J. Chem. Soc., Chem. Commun.*, **1991**, 1292.
7. (*S*)-**9**, mp 98—100 °C (dec). Calcd for C₄₉H₃₉P₂O₈Rh: C, 64.02; H, 4.27. Found: C, 63.92; H, 4.54. ¹H NMR (CDCl₃, 270 MHz) δ 1.34 (s, 2CH₃CO), 4.97 (s, CH₃COCH), and 6.11 (m, 4H), 6.55 (m, 4H), 6.64 (m, 2H), 6.95 (m, 2H), 7.07 (m, 8H), 7.25 (m, 4H), 7.37 (m, 2H), 7.54 (m, 2H), 7.80 (m, 4H) (aromatic protons). ³¹P NMR (CDCl₃) δ 128.81 (d, *J*_{Rh—P} = 299 Hz).