Asymmetric hydroformylation of conjugated dienes catalysed by [(*R*)-2-diphenylphosphino-1,1′-dinaphthalen-2′-yl] [(*S*)-1,1′-dinaphthalene-2,2′-diyl]phosphite–rhodium(I)

Toshihide Horiuchi, Tetsuo Ohta, Kyoto Nozaki*† and Hidemasa Takaya‡

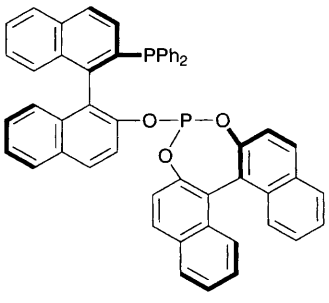
Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

Asymmetric hydroformylation of conjugated dienes such as vinylcyclohexene, (*E*)-phenyl-buta-1,3-diene and 4-methyl-penta-1,3-diene using BINAPHOS–Rh^{I} complexes as catalysts {(*R,S*)-BINAPHOS = [(*R*)-2-diphenylphosphino-1,1′-dinaphthalen-2′-yl] [(*S*)-1,1′-dinaphthalene-2,2′-diyl]-phosphite} gives optically active β,γ-unsaturated aldehydes in high regio- (81–91%) and enantio-selectivities (84–97% ee).

As optically active oxo-aldehydes are very important intermediates for the synthesis of various biologically active compounds, asymmetric hydroformylation has attracted a great deal of interest.[1] Most attention, however, has so far been focused on the hydroformylation of monoolefins such as arylethenes and vinyl carboxylates. Asymmetric hydroformylation of conjugated dienes has not been extensively studied, though the resulting optically active β,γ-unsaturated aldehydes are attractive synthetic intermediates. In most cases, hydroformylation of 1,3-dienes mediated by conventional catalysts have been carried out under relatively severe conditions to give complex mixtures containing saturated and unsaturated mono- and di-aldehydes.[2] Asymmetric hydroformylation of buta-1,3-diene and 2-methylbuta-1,3-diene catalysed by $HRh(CO)(PPh_3)_3$–(−)-DIOP afforded 2-methylbutanal and 3-methylpentanal in < 1 and 32% optical yields, respectively, and in less than 25% regioselectivities.[3] In the latter reaction, it was suggested that the optically active aldehyde was formed by the asymmetric hydrogenation of the intermediate 3-methyl-pent-3-enal.

Recently we have reported that the complexes of the chiral phosphine–phosphite (*R,S*)-BINAPHOS [(*R,S*)-**1**] or its enantiomer are highly efficient catalysts for enantioselective hydroformylation of a variety of mono-[4] and 1,2-disubstituted-olefins.[5] Here we report a highly regio- and enantio-selective monohydroformylation of 1,3-dienes catalysed by BINAPHOS–Rh^{I} complexes under mild conditions to give optically active β,γ-unsaturated aldehydes.§

The catalyst species was prepared *in situ* by mixing $Rh(acac)(CO)_2$ and 4.0 equiv. of (*R,S*-**1** in benzene. Thus, a degassed solution of vinylcyclohexene **2a** (4.0 mmol), $Rh(acac)(CO)_2$ (0.020 mmol) and (*R,S*)-**1** (0.082 mmol) in benzene (0.5 ml) prepared in a Schlenk tube was transferred into a 50 ml stainless steel autoclave and stirred at 40 °C for 96 h under hydrogen and carbon monoxide (1 : 1, 100 atm). ^{1}H NMR analysis of the reaction mixture using Ph_2CH_2 as internal standard showed that unsaturated aldehydes **3a** and **5a** were



(*R,S*)-BINAPHOS [(*R,S*)-**1**]

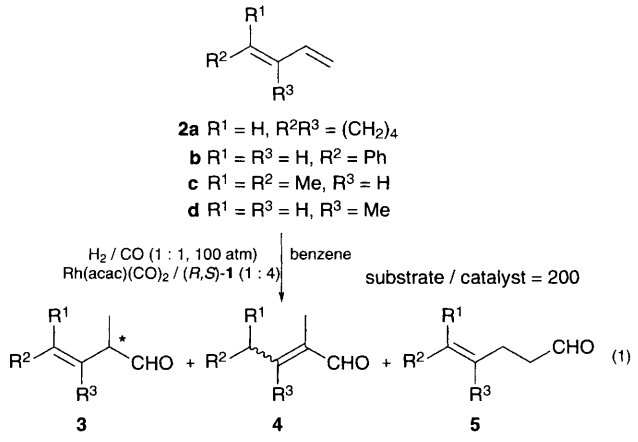


Table 1 Asymmetric hydroformylation of conjugated dienes **2** catalysed by (*R,S*)-BINAPHOS–Rh^{I} complex[a]

Run	Substrate **2**	*T*/°C	*t*/h	Conv. (%)[b]	**3** : **4** : **5**[b]	ee of **3** (%)	Config.[c]
1	**a**	60	18	85	86 : 0 : 14	96[d]	*R*
2	**a**	40	96	78	88 : 0 : 12	96[d]	*R*
3	**a**	30	108	60	88 : 0 : 12	97[d]	*R*
4	**b**	30	48	62	91 : 4[e] : 5	89[f]	—
5	**b**	30	72	90	42 : 57[e] : 1	56[f]	—
6	**c**	30	96	67	81 : 0 : 19	84[d]	*R*

[a] Reactions were carried out in benzene (*ca.* 8 mol dm^{-3}) in a 50 ml stainless-steel autoclave under an atmosphere of H_2 and CO (1 : 1) at 100 atm. initial total pressure. [b] Conversions and **3** : **4** : **5** ratios were determined by ^{1}H NMR using Ph_2CH_2 as internal standard. [c] Determined by the signs of optical rotations of the corresponding acids where possible. [d] Determined by HPLC analyses (Daicel Chiralcel OJ for **3a** and OD for **3c**) of the anilides derived from the corresponding acids and aniline in the presence of DCC. [e] A mixture of *E*- and *Z*-isomers. [f] Determined by HPLC analyses (Daicel Chiralcel OD) of the methyl esters derived from the corresponding acids.

exclusively formed in 97% combined yield based on the consumed **2a** [eqn. (1)]. Reactions were also carried out at 30 and 60 °C. Neither products from hydrogenation or double bond migration were formed. Regio- (86–88%) and enantio-selectivities (96–97%) observed for **2a** were comparable to those of styrene[4] and were almost independent of reaction temperature (Table 1, runs 1–3). Efficient stirring of the reaction mixture was indispensable in obtaining high regio- and enantioselectivities. Otherwise, variable amounts of isomerised product **4a** were formed in addition to **3a** with considerably lower ee.

Hydroformylation of (*E*)-phenyl-buta-1,3-diene **2b** afforded **3b** in high regioselectivity and in 89% ee at 30 °C (Table 1, run 4). Introduction of a formyl group at either the C1- and C2-positions was not observed. Such a high regioselectivity has also been reported for nickel-catalysed hydrocyanation of **2b**.[6] However, prolonged reaction time or higher reaction temperatures resulted in double bond migration of the product **3b** to give a mixture of (*E*)- and (*Z*)-**4b**. Moreover, considerably lower ee was observed for **3b** (run 5). Therefore, careful control of the reaction conditions are requisite for the best yield of **3b**.

We also carried out hydroformylation of simple 1,3-dienes. When 4-methyl-penta-1,3-diene **2c** was subjected to hydroformylation, unsaturated aldehydes **3c** and **5c** were obtained (run 6). Regio- and enantio-selectivities, however, were somewhat lower than those of **2b**. From *trans*-piperylene **2d**, **3d** was formed in 84% selectivity at 30 °C, but the enantioselectivity was as low as 24%. Hydroformylation of buta-1,3-diene, the simplest 1,3-diene, afforded an *E*/*Z* mixture of pent-3-enal as exclusive products at 30 °C, which were probably formed by 1,4-addition of the intermediate rhodium hydride species to buta-1,3-diene. At 60 °C, pent-3-enal was still the predominant product, although a more complex mixture was obtained. This result forms a striking contrast to those reported by Botteghi *et al.* in which saturated monoaldehydes, pentanal and 2-methylbutanal were mainly formed at 95 °C (90 atm, H_2/CO = 1/1).[3]

In conclusion, we have found that asymmetric hydroformylation of certain conjugated dienes catalysed by BINAPHOS–Rh^I complexes gives optically active β,γ-unsaturated aldehydes in high regio- and enantio-selectivities. The present asymmetric catalysis provides a new and direct route to optically active β,γ-unsaturated aldehydes *via* asymmetric hydroformylation of 1,3-dienes.

This work has been partially supported by the Grant-in-Aid for Scientific Research on Priority Area of Reactive Organometallics No. 05236106 and the Grant-in-Aid for Developmental Scientific Research No. 06555272 from the Ministry of Education, Science, Sports and Culture, Japan. Financial support from the Mitsubishi Foundation is also gratefully acknowledged.

Footnotes

† E-mail: Nozaki@npc05.kuic.kyoto-u.ac.jp

‡ Deceased, 4th October 1995.

§ Satisfactory spectral data was obtained for all aldehyde products.

References

1 For recent reviews see: C. Botteghi, S. Paganelli, A. Schionato and M. Marchetti, *Chirality*, 1991, **3**, 355; J. K. Stille, in *Comprehensive Organic Synthesis*, ed. B. M. Trost, Pergamon Press, New York, 1991, vol. 4, ch 4.5, pp. 915–950; C. Botteghi, R. Ganzerla, M. Lenarda and G. Moretti, *J. Mol. Catal.*, 1987, **40**, 129; G. Consiglio and P. Pino, *Top. Curr. Chem.*, 1982, **105**, 77.

2 B. Fell and H. Bahrmann, *J. Mol. Catal.*, 1977, **2**, 211; H. Bahrmann and B. Fell, *J. Mol. Catal.*, 1980, **8**, 329; P. W. N. M. van Leeuwen and C. F. Roobeek, *J. Mol. Catal.*, 1985, **31**, 345.

3 C. Botteghi, M. Branca and A. Saba, *J. Organomet. Chem.*, 1980, **184**, C17.

4 N. Sakai, S. Mano, K. Nozaki and H. Takaya, *J. Am. Chem. Soc.*, 1993, **115**, 7033.

5 N. Sakai, K. Nozaki and H. Takaya, *J. Chem. Soc., Chem. Commun.*, 1994, 395.

6 E. M. Campi, P. S. Elmes, W. R. Jackson, C. G. Lavel and M. K. S. Probert, *Aust. J. Chem.*, 1987, **40**, 1053.

Received, 12th September 1995; Com. 5/06027C