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Asymmetric hydroformylation catalyzed by rhodium(I) complexes of novel chiral spiro ligands

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Abstract

Chiral diphosphites and phosphinite-phosphites derived from spiro[4.4]nonane-1,6-diol were synthesized. Using Rh(I)–7 complex in asymmetric hydroformylation of styrene, high regioselectivity (97%) and moderate enantioselectivity (65% *ee*) have been obtained. This catalyst system was also effective for aryl-substituted olefins. The diphosphites **8** and **9** bearing 1,1'-binaphthyl backbones were tested and the opposite configuration of the product indicates that the sense of enantioface selection is mainly dictated by the configuration of the terminal groups. Phosphinite–phosphite ligands gave low enantiomeric excesses (up to 48% *ee*) and low *b/n* ratios. These results suggest that the regio- and enantioselectivity is mainly affected by the bulky substituents on terminal groups. The crystal structure of Rh(7)(acac) are presented. The distortion in the structure is indicative of a crowded rhodium center. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Hydroformylation; Chirality; Spiro ligands; X-ray structure

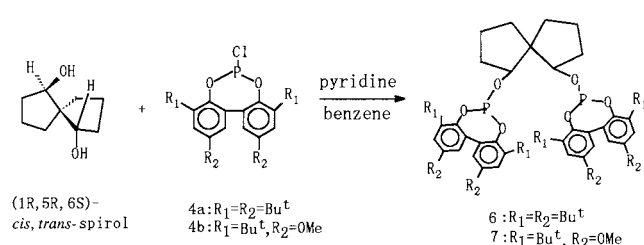
1. Introduction

Catalytic asymmetric hydroformylation of olefins is a process of great interest for the preparation of optically pure aldehydes, useful for the synthesis of many biologically active compounds [1]. Platinum–tin and rhodium catalysts modified by chiral phosphines and diphosphines have been mostly used as the catalysts [2–4]. Since van Leeuwen [5] reported high catalytic activity of bulky phosphite ligands in rhodium-catalyzed hydroformylation, there has been growing interest in the use of these ligands [6–10]. Up to now, the highest enantioselectivity in an asymmetric hydroformylation of olefins was obtained with the phosphine–phosphite ligands reported by Nozaki and coworkers [11–13].

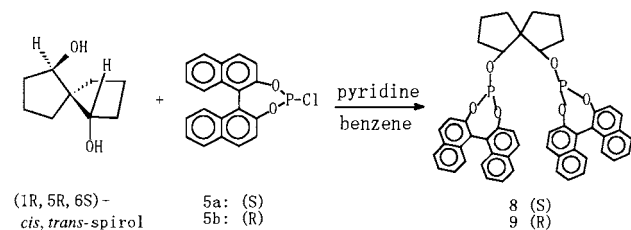
Recently, we have synthesized novel chiral diphosphite ligands derived from *cis,trans*-spiro[4.4]nonane-1,6-diol (abbreviated spiro) and used them for the Rh(I)-catalyzed asymmetric hydroformylation of styrene [14]. These diphosphite–Rh(I) catalyst systems show moderate enantioselectivities and high regioselectivities in styrene and its derivatives. We sought to extend our studies to other ligands containing spiro backbone. Diphosphites containing a chiral centre in the spiro backbone and a chiral axis in the terminal groups were prepared for their cooperativity, since chiral cooperative effects have been observed in rhodium and platinum catalyzed asymmetric hydroformylation [13,15,16]. Bisphosphinite derived from *cis,cis*-spiro was found to be an efficient chiral ligand for the catalytic asymmetric hydrogenation of enamides [17]. Here, we also wish to report the synthesis of phosphinite–phosphite ligands derived from *cis,cis*-spiro and their catalytic properties in the asymmetric hydroformylation of styrene.

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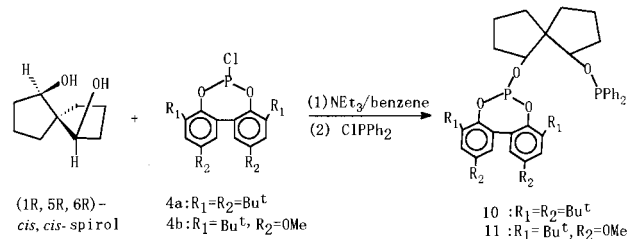
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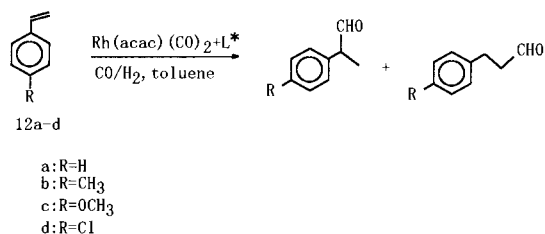
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

2. Results and discussion

2.1. Synthesis

Spirol has three diastereomers (Fig. 1). We have successfully synthesized *cis,cis*-spirol and *cis,trans*-spirol by stereoselectively reduction of spiro[4.4]nonane-1,6-dione with lithium *n*-butyldiisobutylaluminum hydride and BH₃·THF [18], respectively. The optically pure *cis,cis*-spirol and *cis,trans*-spirol were used as starting materials for the synthesis of our chiral ligands.

Compounds **6** and **7** have been synthesized by the reaction of (1*R*,5*R*,6*S*)-*cis,trans*-spirol **2** with the corresponding chlorophosphites **4** in benzene in the presence of pyridine [14] (Scheme 1). Compounds **8** and **9** have also been prepared by mixing the (1*R*,5*R*,6*S*)-*cis,trans*-spirol **2** with the chlorophosphites (*S*)-**5a** or (*R*)-**5b**, respectively (Scheme 2) and they contain axial as well as central chirality. This pair of diastereomers, as less electron-rich diphosphites, may cause dramatic changes in the reactivity and selectivity. However, when (1*R*,5*R*,6*R*)-*cis,cis*-spirol **1** was treated with chlorophosphites **4** at the same procedure, diphosphites cannot be obtained, and that may be attributed to the steric constraints between the bulky substituents on bi(phenol) moieties. Thus, phosphinite–phosphite ligands were synthesized in benzene in the presence of NEt₃ (Scheme 3).

2.2. Catalysis

The aldehyde derived from aryl-substituted olefins can be converted to various pharmaceuticals such as antiinflammatory agents [19,20]. The catalytic proper-

ties of compounds **6–11** containing rhodium have been evaluated in the asymmetric hydroformylation of styrene (**12a**) and its derivatives (**12b–d**) (Scheme 4). The catalyst species were prepared in situ by simply mixing Rh(acac)(CO)₂ and 1.5 equivalents of the ligands. A little excess of ligands is useful for preventing the reaction catalyzed by unmodified rhodium species [13,20]. An incubation period is necessary for the formation of Rh(L)(CO)₂ from Rh(acac)(CO)₂ and diphosphites [7,21]. In order to increase the reaction rate, the catalyst was prepared under typical conditions [40°C, 10 atm of syn gas, 10 h] before substrate was added. The results are summarized in Table 1.

A high yield of aldehyde (89%) and moderate enantioselectivity (62% *ee*) were achieved in toluene under CO/H₂=5/5 atm, at 40°C for 10 h (run 1). As a solvent, CH₂Cl₂, cyclohexene and THF gave comparable *ee* values of the product, but they resulted in a low yield of aldehyde (runs 2–4). Compounds **6–11** were also evaluated under the typical hydroformylation reaction conditions [40°C, 20 atm, 10 h]. Compound **6**, in which the bis(phenol) moiety is substituted with *tert*-butyl group at *para* position, showed relatively high catalytic activity and gave 92% yield of aldehyde (run 6). The enantioselectivity is slightly lower than that found in compound **7** (run 5 versus 6), which might be

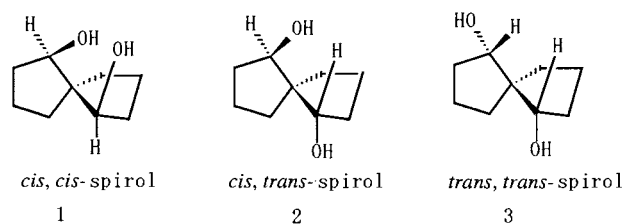


Fig. 1. Three diastereomers of spiro[4.4]nonane-1,6-diol.

due to electronic effects on the phosphorus atom. Compounds **8** and **9**, a pair of diastereomers, showed considerably lower catalytic activity and *b/n* ratios. Enantiomeric excess decreased markedly and the opposite configuration of product was obtained (runs 8 and 9). The cooperative effect between central and axial chirality was not observed in these two diphosphites. Diastereomers differing in the configuration of the terminal groups afforded the opposite prevailing enantiomer in the product and this implies that enantioselection is dictated by the terminal groups. These results show that the catalytic efficacy of diphosphite–Rh[I] complex is mainly controlled by the large bulky substituents of the terminal group and/or the increase of the electron density on the phosphorus atom. Compounds **10** and **11** derived from (1*R*,5*R*,6*R*)-*cis,cis*-spirol gave low catalytic activity and selectivity compared to compounds **6** and **7**. High yield of aldehyde was obtained when the pressure of syn gas was decreased, but this resulted in the loss of the *ee* value (run 10 versus 11). Hydroformylations of *para*-substituted styrene derivatives **12b–d** with the Rh(acac)(CO)₂–**7** catalyst system also gave aldehydes in high regioselectivities and moderate enantioselectivities (runs 15–17).

2.3. Crystal structure of Rh(7)(acac)

Slow crystallization from toluene of Rh(7)(acac) complex afforded pale yellow crystals which proved to be suitable for X-ray investigation. Data were collected on a crystal of Rh(7)(acac), as summarized in Table 4. Fig.

2 shows the molecular structure and the adopted numbering scheme. Table 2 lists atomic coordinates and Table 3 gives selected bond lengths and bond angles. The figure shows a square planar surrounded rhodium. The P(1)–Rh–P(2) angle of 96.69(5)° is large compared to the analogous triphenyl phosphite complex [22] (94.8(2)°) and demonstrates the steric hindrance of the diphosphite. The enlarged P–Rh–P angle of 97.5(1)° [23] and 99.87(3)° [24] have been observed for Rh(acac)P₂. The decreased P(1)–Rh–P(2) bond angle in Rh(7)(acac) is ascribed to the rigidity of spiro cycle and the eight-membered metallacycle. The metal–phosphorus bonds (P(1)–Rh = 2.1586(14) Å; P(2)–Rh = 2.168(2) Å) are similar to those found in the previously reported complexes containing phosphites [23,24]. The O(1)–Rh–O(2) angle of 89.7(2)° is somewhat larger than that in the reported literature (87.2(3)°) [23]. The distortion is also noticeable from the various P–O–C angles. A study of P–O–C angles of Cr(CO)₅L complexes (L = phosphite) [25] revealed that the average angles in this complex increased with increasing bulkiness of the phosphite with a maximum of 127.5° for P(O-*t*-Bu)₃ as ligand. In Rh(7)(acac) the P(1)–O(6)–C(26) angle of 132.7(4)° is determined, meaning that steric hindrance has led to distortions within the diphosphite. The P(1)–O(4)–C(4) angle of 128.2(4)° is larger than the angle of P(2)–O(3)–C(9) (119.0(3)°), thus indicating that the two terminal groups induce different hindrance, and O(4) atom is at *cis* position of spiro cycle and O(3) at *trans* position. A analysis of transition metal complexes of bis(diphenylphosphanyl)ethane type ligands shows the phenyl rings prefer

Table 1
Asymmetric hydroformylation of styrene and its derivatives **12** catalyzed by Rh[I] complexes^a

Run	Substrate	Ligand	Solvent	<i>P</i> (atm)	Yield (%) ^b	<i>b/n</i> ^b	<i>ee</i> % ^c
1	12a	7	Toluene	10	89	97/3	62(<i>S</i>)
2		7	CH ₂ Cl ₂	10	66	96/4	64(<i>S</i>)
3		7	Cyclohexane	10	62	97/3	60(<i>S</i>)
4		7	THF	10	63	96/4	61(<i>S</i>)
5		7	Toluene	20	85	97/3	65(<i>S</i>)
6		6	Toluene	20	92	98/2	59(<i>S</i>)
7		8	Toluene	20	74	80/20	29(<i>S</i>)
8		9	Toluene	20	34	81/19	24(<i>R</i>)
9		9	Toluene	10	61	82/18	24(<i>R</i>)
10		10	Toluene	20	45	84/16	42(<i>S</i>)
11	10	Toluene	10	81	83/17	31(<i>S</i>)	
12	10	Cyclohexane	20	67	82/18	48(<i>S</i>)	
13	10	CH ₂ Cl ₂	20	40	84/16	38(<i>S</i>)	
14	11	Toluene	20	61	85/15	26(<i>S</i>)	
15	12b	7	Toluene	20	71	96/4	63(+)
16	12c	7	Toluene	20	63	96/4	65(+)
17	12d	7	Toluene	20	85	97/3	70(+)

^a Reactions were carried out in a 40 ml autoclave under the reaction conditions [syn gas (CO/H₂ = 1/1), S/C = 500, 40°C; L/Rh = 1.5]. The complex was incubated under 10 atm of syn gas at 40°C for 10 h before substrate was added.

^b Yields and *b/n* ratios were determined by GC (β-236 M, 0.25 mm × 25 m) using *cis*-decahydronaphthalene as an internal standard.

^c Enantiomeric excesses were determined by GC analysis (β-236M, 0.25 mm × 25 m) of the corresponding acid. Optical rotations or absolute configurations are drawn in parentheses.

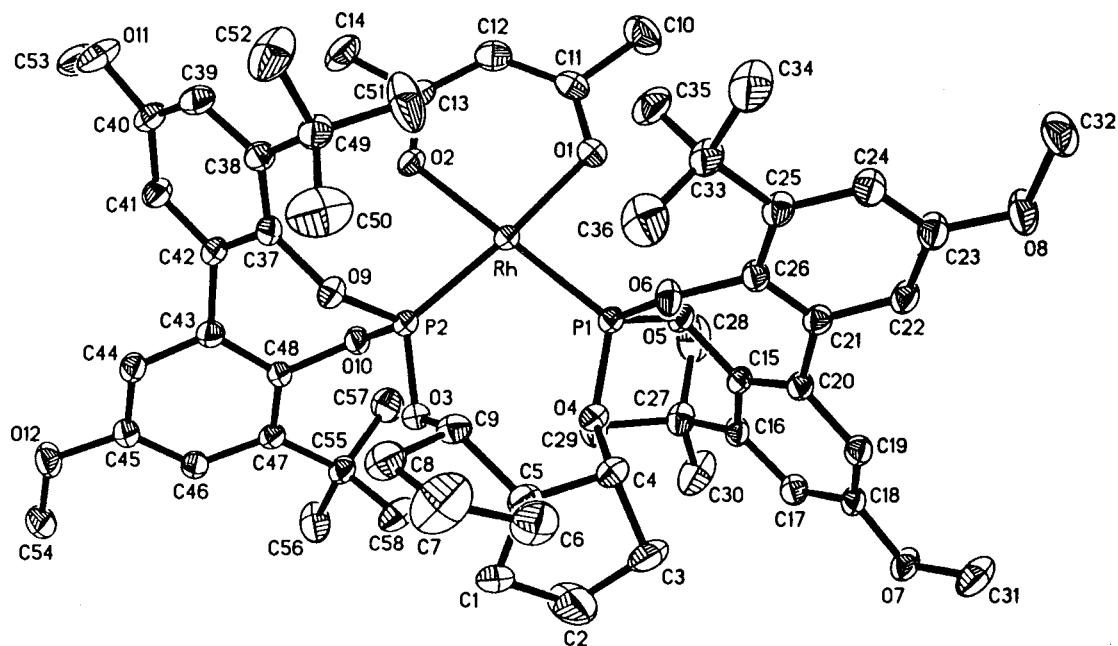


Fig. 2. The structure of Rh(7)(acac). Hydrogen atoms and the minor disorder contribution were left out for clarity.

certain orientation depending on their axial or equatorial position and the ligand chirality [26]. When the Rh(7)(acac) complex is viewed from the observer (Fig. 3), two *tert*-butyl groups are above the plane defined by P(1)–Rh–P(2) and two others under the plane. Different dihedral angles of the two bis(phenol) moieties were observed, 41.4° for C(15)–C(20)–C(21)–C(26) and 47.1° for C(37)–C(42)–C(43)–C(48). The bis(phenol) moiety at *cis* position shows higher twisting resistance. The chiral spiro cycle controls the orientations of the four phenyl rings and *tert*-butyl groups, which form a chiral array responsible for the regio- and enantioselectivity in hydroformylation. Compound **8** containing (*S*)-binaphthyl backbone showed higher catalytic activity in hydroformylation of styrene than compound **9** containing (*R*)-binaphthyl backbone and also gave the production of the same configuration of compound **7**. These results might imply that the configuration of (*S*)-binaphthyl backbone accords with the orientation of bis(phenol) moiety in Rh[I]–**7** complex.

3. Experimental

3.1. General

All reactions were carried out in oven-dried glassware using Schlenk techniques under pure nitrogen. Benzene and toluene were distilled from sodium-benzophenone, pyridine from CaH₂. PCl₃ and styrene were distilled before use and stored under pure nitrogen. 4,4',6,6'-Tetra-*tert*-butyl-2,2'-bis(phenol) and 6,6'-di-

tert-butyl-4,4'-dimethoxy-2,2'-bis(phenol) were prepared according to literature procedures [27,28]. Compounds **6** and **7** were synthesized as in the reported literature [14]. Melting points were determined on Southend SS25PH apparatus and are uncorrected. Elemental analyses were recorded on a Carlo Erba-1106 instrument. Gas chromatographic analyses were performed by SC-7 gas chromatography. ³¹P-NMR spectra were obtained on a Varian FT-80A using H₃PO₄ (85%) as an internal standard and ¹H-NMR spectra on a Bruker 300 spectrometer. Optical rotations were measured on a Perkin–Elmer 241 polarimeter. Enantiomeric excesses were measured after Jones oxidation of the aldehyde to the corresponding acids on a SC-7 gas chromatograph with a Chrompack β-236M, 0.25 × 25 m chiral capillary column. Hydroformylation reactions were carried out in a laboratory-made stainless-steel autoclave (40 ml).

3.2. Synthesis of **8** and **9**

(*S*)-1,1'-Dinaphthol (305 mg, 1.2 mmol) dried under reduced pressure at 80°C for 30 min was dissolved in benzene (10 ml) and pyridine (0.4 ml). This solution was added dropwise to a cooled solution (0°C) of PCl₃ (0.2 ml) and pyridine (0.1 ml). The reaction mixture was stirred for 6 h at 60°C. The solvent and excess of PCl₃ were removed under vacuum. The last trace of PCl₃ in the residue was removed by benzene (3 ml) under reduced pressure and this procedure was repeated three times. Compound **5a** formed in situ was dissolved in benzene (10 ml) and pyridine (0.5 ml). (1*R*,5*R*,6*S*)-(cis,trans)-spiro[4.4]nonane-1,6-diol (78 mg, 0.5 mmol)

dissolved in benzene was added dropwise to the solution of compound **5a** at 0°C. The reaction mixture was stirred overnight at room temperature. The resulting pyridine salts were filtered off. Evaporation of the solvent gave a white plaster that was purified by flash column chromatography using toluene as eluent. White solid (243 mg, 62%) was obtained. $[\alpha]_D^{20} = -720.4^\circ$ (0.25, toluene); m.p. = 142–144°C; $^{31}\text{P-NMR}$ (CD_3COCD_3 , δ) 144.49, 135.92 ppm; $^1\text{H-NMR}$ (CD_3COCD_3 , δ) 8.22–7.16 (m, 24H), 4.93 (m, 1H), 4.22 (m, 1H), 2.01–1.28 (m, 12H). Anal. Calc. for $\text{C}_{49}\text{H}_{38}\text{O}_6\text{P}_2$: C, 74.99; H, 4.88. Found: C, 75.21; H, 4.97. Compound **9** was similarly prepared and a white solid (57% yield) was obtained. $[\alpha]_D^{20} = +435.1^\circ$ (0.30, toluene); m.p. = 146–149°C; $^{31}\text{P-NMR}$ (CD_3COCD_3 , δ) 148.44, 137.64 ppm; $^1\text{H-NMR}$ (CD_3COCD_3 , δ) 8.19–7.03 (m, 24H), 4.86 (m, 1H), 4.34 (m, 1H), 2.08–1.28 (m, 12H). Anal. Calc. for $\text{C}_{49}\text{H}_{38}\text{O}_4\text{P}_2$: C, 74.99; H, 4.88. Found: C, 75.42; H, 5.05.

3.3. Synthesis of **10** and **11**

(1*R*,5*R*,6*R*)-(cis,cis)-spiro[4.4]nonane-1,6-diol (110 mg, 0.7 mmol) was dissolved in benzene (10 ml) and NEt_3 (1 ml). A stock solution of **4a** in benzene (2.6 ml, 0.3 mol dm^{-3}) was added and stirred for 6 h. Then CIPPh_2 (0.15 ml) was added dropwise to this solution at 0°C. The reaction mixture was stirred overnight at room temperature and the salts formed were filtered off. Evaporation of the solvent gave a white paste that was purified by flash column chromatography using toluene as eluent. White solid (216 mg, 40%) was obtained. $[\alpha]_D^{20} = -34.0^\circ$ (0.37, toluene); m.p. = 58–59°C; $^{31}\text{P-NMR}$ (CD_3COCD_3 , δ) 145.67, 101.81 ppm; $^1\text{H-NMR}$ (CD_3COCD_3 , δ) 7.56–7.13 (m, 14H), 4.69 (m, 1H), 4.37 (m, 1H), 1.92–1.15 (m, 48H). Anal. Calc. for $\text{C}_{49}\text{H}_{64}\text{O}_4\text{P}_2$: C, 75.55; H, 8.28. Found: C, 75.08; H, 8.17. Compound **11** was similarly prepared and white

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for Rh(7)(acac)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}	Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Rh	6420(1)	17994(1)	6595(1)	32(1)	C(23)	7742(5)	13743(4)	8112(3)	52(2)
P(1)	6621(1)	17343(1)	7639(1)	33(1)	C(24)	8334(5)	14032(4)	7462(3)	54(2)
P(2)	7049(1)	19201(1)	6778(1)	33(1)	C(25)	8271(5)	14945(4)	7275(3)	45(1)
O(1)	5747(3)	16921(3)	6324(2)	44(1)	C(26)	7577(4)	15578(4)	7763(3)	38(1)
O(2)	6193(3)	18617(3)	5600(2)	45(1)	C(27)	3853(5)	17813(4)	9125(3)	48(2)
O(3)	7528(3)	19393(2)	7487(2)	39(1)	C(28)	3324(6)	17376(6)	8575(5)	79(2)
O(4)	6831(3)	17918(2)	8300(2)	39(1)	C(29)	4266(6)	18642(4)	8743(4)	67(2)
O(5)	5631(3)	16892(2)	8041(2)	37(1)	C(30)	3030(6)	18131(6)	9803(4)	86(3)
O(6)	7552(3)	16489(2)	7583(2)	43(1)	C(31)	5980(6)	15221(5)	11249(4)	72(2)
O(7)	5321(4)	15961(3)	11019(2)	51(1)	C(32)	8260(6)	12148(4)	7816(4)	71(2)
O(8)	7720(4)	12862(3)	8327(3)	74(2)	C(33)	8921(5)	15231(4)	6545(3)	52(2)
O(9)	7996(3)	19475(2)	6153(2)	38(1)	C(34)	9621(7)	14413(5)	6137(4)	91(3)
O(10)	6149(3)	20052(2)	6796(2)	36(1)	C(35)	8203(6)	15626(5)	6010(3)	68(2)
O(11)	7470(4)	20755(3)	3356(2)	67(1)	C(36)	9605(6)	15899(6)	6698(5)	80(2)
O(12)	6445(4)	23684(3)	6395(2)	59(1)	C(37)	7903(4)	19813(4)	5434(3)	37(1)
C(1)	7896(6)	19299(5)	8999(3)	60(2)	C(38)	8487(5)	19357(4)	4803(3)	40(1)
C(2)	7193(9)	18911(7)	9613(5)	115(4)	C(39)	8325(5)	19726(4)	4121(3)	50(2)
C(3)	7316(8)	17944(6)	9513(4)	81(3)	C(40)	7612(5)	20501(4)	4063(3)	48(2)
C(4)	7715(5)	17775(4)	8666(3)	50(2)	C(41)	7108(5)	20984(4)	4702(3)	43(1)
C(5)	83370(5)	18517(4)	8441(3)	47(2)	C(42)	7268(4)	20653(4)	5396(3)	36(1)
C(6)	9517(6)	18194(6)	8457(5)	75(2)	C(43)	6795(4)	21263(4)	6057(3)	36(1)
C(7)	10094(7)	18739(9)	7887(6)	117(4)	C(44)	6853(5)	22182(4)	5983(3)	41(1)
C(8)	9405(5)	19275(5)	7468(4)	62(2)	C(45)	6318(5)	22796(4)	6524(3)	44(1)
C(9)	8445(5)	18809(4)	7620(3)	44(1)	C(46)	5708(5)	22503(4)	7136(3)	43(1)
C(10)	5000(6)	15998(5)	5630(5)	71(2)	C(47)	5633(4)	21584(4)	7253(3)	37(1)
C(11)	5452(5)	16843(4)	5706(4)	46(1)	C(48)	6231(4)	20977(3)	6719(3)	33(1)
C(12)	5485(5)	17454(4)	5118(3)	51(2)	C(49)	9281(5)	18483(4)	4818(3)	51(2)
C(13)	5833(5)	18292(4)	5093(3)	45(1)	C(50)	9990(8)	18585(7)	5381(5)	110(4)
C(14)	5784(6)	1887(5)	4417(4)	68(2)	C(51)	8726(7)	17680(5)	4984(6)	103(4)
C(15)	5553(4)	16637(4)	8793(3)	35(1)	C(52)	10034(7)	18295(6)	4064(4)	91(3)
C(16)	4727(5)	17100(4)	9333(3)	40(1)	C(53)	6547(7)	21315(6)	3287(4)	73(2)
C(17)	4698(5)	16825(5)	10070(3)	44(1)	C(54)	5866(6)	24345(4)	6926(4)	59(2)
C(18)	5434(5)	16139(4)	10267(3)	40(1)	C(55)	4878(5)	21296(4)	7938(3)	44(1)
C(19)	6207(5)	15695(4)	9732(3)	42(1)	C(56)	4183(7)	22114(5)	8354(4)	76(2)
C(20)	6253(4)	15927(4)	8980(3)	36(1)	C(57)	4137(5)	20720(5)	7674(4)	60(2)
C(21)	6990(4)	15315(4)	8425(3)	37(1)	C(58)	5457(6)	20751(5)	8473(3)	67(2)
C(22)	7092(5)	14385(4)	8585(3)	46(2)					

Table 3
Selected bond distances (Å) and bond angles (°) of Rh(7)(acac)

Bond distances			
Rh–P(1)	2.1586(14)	Rh–O(1)	2.074(4)
Rh–P(2)	2.168(2)	Rh–O(2)	2.069(4)
P(1)–O(4)	1.589(4)	P(2)–O(3)	1.598(4)
P(1)–O(5)	1.627(4)	P(2)–O(9)	1.636(4)
P(1)–O(6)	1.617(4)	P(2)–O(10)	1.593(4)
O(3)–C(9)	1.438(7)	O(4)–C(4)	1.446(7)
Bond angles			
P(1)–Rh–P(2)	96.69(5)	P(2)–Rh–O(1)	173.48(11)
P(1)–Rh–O(1)	89.56(11)	P(2)–Rh–O(2)	83.97(11)
P(1)–Rh–O(2)	178.70(13)	O(1)–Rh–O(2)	89.7(2)
Rh–P(1)–O(4)	119.8(2)	Rh–P(2)–O(3)	125.7(2)
Rh–P(1)–O(5)	113.4(2)	Rh–P(2)–O(9)	118.7(2)
Rh–P(1)–O(6)	115.4(2)	Rh–P(2)–O(10)	107.7(2)
O(4)–P(1)–O(5)	102.3(2)	O(3)–P(2)–O(9)	95.9(2)
O(4)–P(1)–O(6)	101.6(2)	O(3)–P(2)–O(10)	102.1(2)
O(5)–P(1)–O(6)	102.0(2)	O(9)–P(2)–O(10)	103.8(2)
P(1)–O(4)–C(4)	128.2(4)	P(2)–O(3)–C(9)	119.0(3)
P(1)–O(5)–C(15)	119.1(3)	P(2)–O(9)–C(37)	125.2(3)
P(1)–O(6)–C(26)	132.7(4)	P(2)–O(10)–C(48)	128.5(3)
Rh–O(1)–C(11)	124.4(4)	Rh–O(2)–C(13)	126.3(4)

solid (48% yield) was obtained. $[\alpha]_D^{20} = -41.3^\circ$ (0.52, toluene); m.p. = 65–66°C; $^{31}\text{P-NMR}$ (CD_3COCD_3 , δ) 145.86, 102.59 ppm; $^1\text{H-NMR}$ (CD_3COCD_3 , δ) 7.58–7.43 (m, 10H), 6.97–6.74 (m, 4H), 4.78 (m, 1H), 4.44 (m, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 2.07–1.32 (m, 30H). Anal. Calc. for $\text{C}_{43}\text{H}_{52}\text{O}_6\text{P}_2$: C, 71.06; H, 7.21. Found: C, 71.51; H, 7.33.

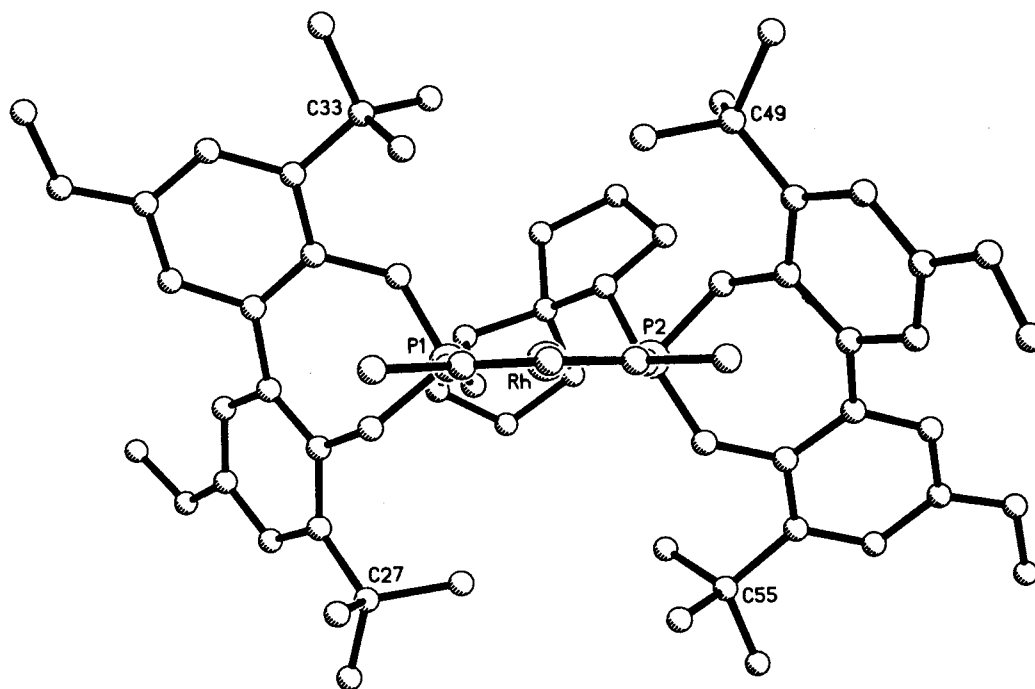


Fig. 3. Molecular structure of Rh(7)(acac) emphasizing the distribution of *tert*-butyl groups.

3.4. Synthesis of Rh(7)(acac)

In a 20 ml Schlenk tube were dissolved compound 7 (36 mg, 0.0388 mmol) and $\text{Rh}(\text{CO})_2(\text{acac})$ (10 mg, 0.0387 mmol) in toluene (2.5 ml). The solution was stirred at 40°C for 10 h and then stored at room temperature. Pale yellow crystals were obtained from the solution. $^{31}\text{P-NMR}$ (CDCl_3 , δ) 135.8 ($J_{\text{Rh-P}} = 316$ Hz, $J_{\text{P-P}} = 106$ Hz), 142.5 ($J_{\text{Rh-P}} = 307$ Hz). $^1\text{H-NMR}$ (CDCl_3 , δ) 6.98–6.63 (m, 8H), 5.17 (s, 1H), 4.83 (m, 1H), 4.55 (m, 1H), 3.83 (s, 3H), 3.81 (s, 6H), 3.78 (s, 3H), 2.08–1.05 (m, 54).

3.5. General procedure for the asymmetric hydroformylation

The autoclave filled with $\text{Rh}(\text{acac})(\text{CO})_2$ (0.0085 mmol) and diphosphite (0.025 mmol) was purged three times with syn gas ($\text{CO}/\text{H}_2 = 1/1$), then toluene (1.5 ml) was added and pressurized to 10 atm of syn gas. The reaction mixture was stirred for 10 h at 40°C to form the active catalyst. Styrene or its derivatives (4.25 mmol) and toluene (1 ml) were placed in the autoclave and the syn gas was introduced until the desired pressure was reached. After the desired reaction time, the autoclave was cooled to room temperature and depressurized. *cis*-Decahydronaphthalene as an internal standard was added. The mixture was filtered on silica gel and the filtrate was analysed by GC for the yield and regioselectivity. A sample of the filtration was oxidized to acid by Jones oxidation and analysed by GC for determination of the enantiomeric excess.

Table 4
Crystallographic data for Rh(7)(acac)

Formula	C ₅₈ H ₇₇ O ₁₂ P ₂ Rh- C _{4.75} H _{5.75} N _{0.25} O _{0.25}
<i>M_n</i>	1201.40
Color	Pale yellow
Space group	<i>P</i> 1
Crystal system	Triclinic
<i>a</i> (Å)	13.360(2)
<i>b</i> (Å)	14.926(3)
<i>c</i> (Å)	18.248(3)
α (°)	88.56(1)
β (°)	79.18(1)
γ (°)	80.44(1)
<i>V</i> (Å ³)	3524.5(11)
<i>D</i> _{calc.} (g cm ⁻³)	1.133
<i>Z</i>	2
<i>F</i> (000)	1270
μ (mm ⁻¹)	0.340
Crystal size (mm)	0.50 × 0.36 × 0.16
Temperature (K)	293(2)
Wavelength (Å)	0.71073
θ range (°)	1.57–25.00
Scan type	ω
No. of data collected	13 967
No. of unique data	12 392
<i>hkl</i> range	0:15, –17:17, –21:21
<i>R</i> _{merge}	0.0257
Observability criterion <i>n</i> , <i>I</i> > <i>nσ</i> (<i>I</i>)	2
No. of data in refinement	8516
No. of refined parameters	748
Goodness-of-fit on <i>F</i> ²	0.974
Final <i>R</i>	0.0591
<i>w_R</i>	0.1775

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