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CHIRALITY CONTROL OF *TROPOS* DIPHENYLMETHANE-DERIVED PHOSPHORAMIDITES BY CHIRAL DIENES: ITS APPLICATION TO ASYMMETRIC MICHAEL ADDITION

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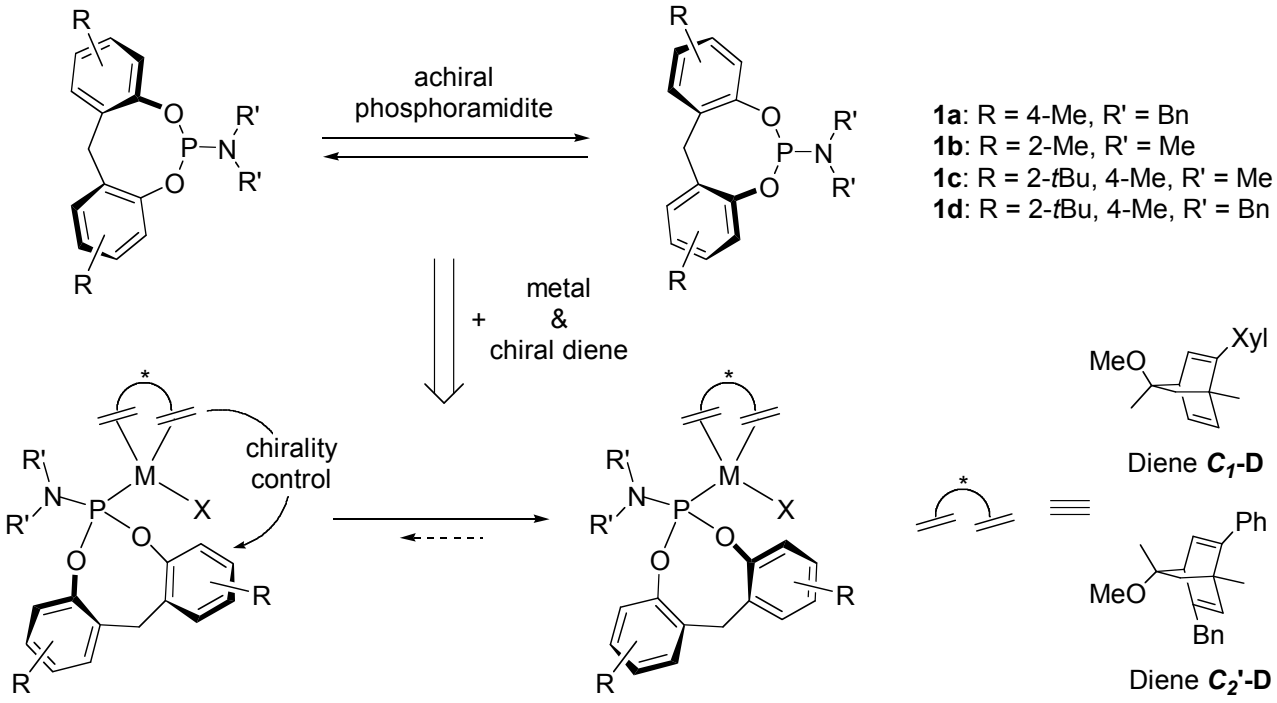
[§]In honor of Professor Emeritus Keiichiro Fukumoto on 75th birthday

Abstract – The Rh complex of *tropos* diphenylmethane-derived phosphoramidite could be chirally controlled to adopt single chiral conformation upon addition of a chiral diene. In the asymmetric Michael addition of α-cyanocarboxylates catalyzed by the Rh complexes, the chiral diene and bisphenylmethane-derived phosphoramidite functioned to attain higher enantioselectivity and catalytic activity via asymmetric activation.

INTRODUCTION

Various asymmetric catalysts with atropisomeric (*atropos* in Greek)[1] ligands have been developed to attain high enantioselectivity.[2] For example, Rh complexes with *atropos* BINOL-derived phosphoramidites were used as catalytically active and enantioselective catalysts for a variety of asymmetric reactions.[3] On the other hand, we have reported that chirally flexible (*tropos*)[1] benzophenone-derived ligands can be chirally controlled to a single chiral conformation by a chiral activator to attain higher catalytic activity and enantioselectivity via "asymmetric activation".[2f,g,4] Herein, we report that the Rh complexes with *tropos* diphenylmethane-derived phosphoramidites **1a-d** can be controlled to a single chiral conformation by a chiral diene (Scheme 1) to attain higher catalytic activity and enantioselectivity in the asymmetric Michael addition. Chiral dienes[5] could not only control the conformation of Rh complexes with *tropos* diphenylmethane-derived phosphoramidites but also increase catalytic activity and enantioselectivity of the resultant Rh-phosphoramidite complexes than that with achiral ethylene. In the asymmetric Michael addition, both chiral dienes and diphenylmethane-derived phosphoramidites in the Rh complexes could function to attain higher enantioselectivity and catalytic activity via asymmetric activation.[2f,g,6]



Scheme 1

RESULTS AND DISCUSSION

Complexation of achiral diphenylmethane-derived phosphoramidites **1a-d** and [RhCl(***C*****$_1$-D**)]$_2$ was found to give single enantiomeric RhCl(***C*****$_1$-D**)(phosphoramidite) complex. Even though excess **1a-d** was added, only RhCl(***C*****$_1$-D**) complexes with one phosphoramidite were obtained along with an excess amount of phosphoramidite remained. In ^{31}P NMR analysis of RhCl(***C*****$_1$-D**)(**1c**), one doublet peak was observed to show that RhCl(***C*****$_1$-D**)(**1c**) possessed a single conformation.

The most stable conformation of RhCl(***C*****$_1$-D**)(**1c**) was deduced by DFT calculation using RhCl(***C*****$_1$-D'**)(**1c'**) as the model (Figure 1).[7] The front view shows that the dimethylamino group of **1c'** stays away from the xylyl group of chiral diene ***C*****$_1$-D'** and the phosphoramidite (**1c'**) exists in the opposite side of chiral diene ***C*****$_1$-D'**. Different from RhCl(***C*****$_1$-D**)(**1c'**), the conformation of phosphoramidite in RhCl(***C*****$_2$'-D'**)(**1c'**) (the model of RhCl(***C*****$_2$'-D**)(**1c**) complex) is determined by the steric repulsion between the diphenylmethane group of **1c'** and the benzyl group of ***C*****$_2$'-D'**. Therefore, the conformations of phosphoramidite were different between RhCl(***C*****$_1$-D'**)(**1c'**) (upper) and RhCl(***C*****$_2$'-D'**)(**1c'**) (lower). On the other hand, the top right view shows that the phosphoramidite (**1c'**) adopts a chiral C_1-symmetric conformation because of the steric interaction between the diphenylmethane and chiral diene. ^{1}H NMR spectrum of RhCl(***C*****$_1$-D**)(**1c**) indeed showed the C_1-symmetric conformation of **1c**; 2-*tert*-Butyl-4-methylphenyl group in the phosphoramidite (**1c**) exhibited two singlets of the *tert*-butyl group and two singlets of the methyl group.

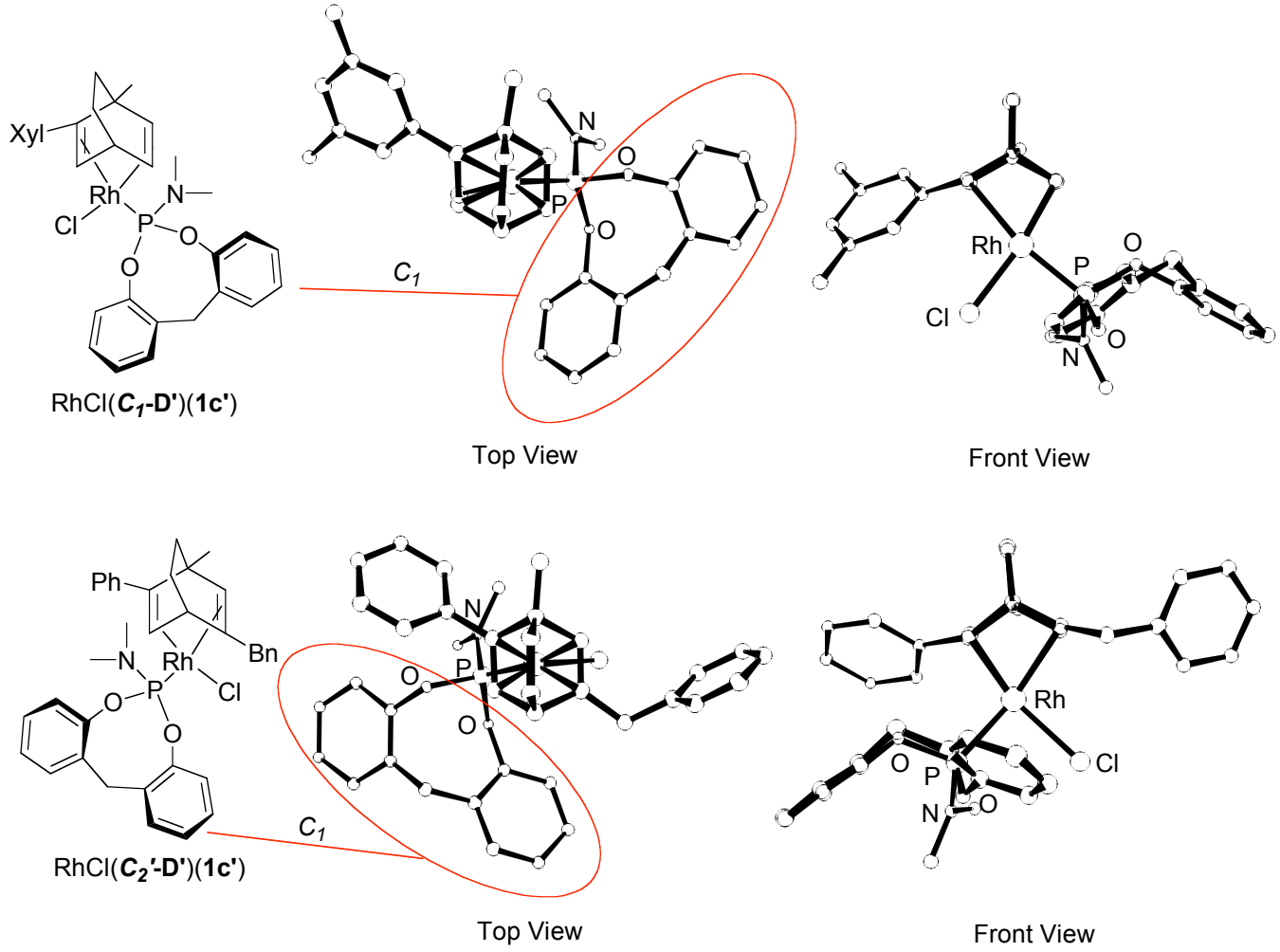
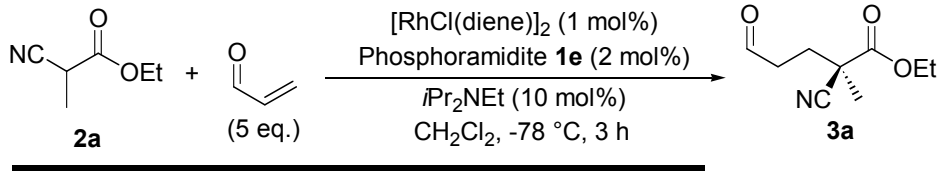


Figure 1. DFT calculation of RhCl(chiral diene)(phosphoramidite) complex

There are few reports on the complexes with only single phosphoramidite as highly enantioselective catalysts. For example, the Ir-cod complex with single chiral phosphoramidite has recently been reported to attain higher catalytic activity and enantioselectivity in the asymmetric hydrogenation.[8] On the other hand, we found that the Rh-chiral diene complexes with diphenylmethane-derived phosphoramidites attain high catalytic activity in the asymmetric Michael addition of α-cyanocarboxylate.[9] The Rh-diene complexes with single phosphoramidite catalyzed the asymmetric Michael addition without dissociation of the chiral diene part. Therefore, the diene part increases the catalytic activity and enantioselectivity. To clarify the effect of the diene part, the asymmetric Michael additions catalyzed by the Rh catalysts of the chiral phosphoramidite (**1e**) and several achiral dienes were examined (Table 1). RhCl(nbd)(**1e**) catalyzed the Michael addition even at -78 °C to afford product **3a** in 96% yield with 48% *ee* (entry 1).[10] 1,5-Cycloocatadiene (cod) and 1,5-dimethylcycloocatadiene (DM-COD) gave lower enantioselectivities (entries 4 and 5) but 1,2-dibromonorbornadiene (Br-nbd) provided higher enantioselectivity (entry 3). These results indicate that six-membered bicyclic dienes attained higher enantioselectivity than eight-membered monocyclic dienes.

Table 1. Asymmetric Michael addition of α-cyanocarboxylate

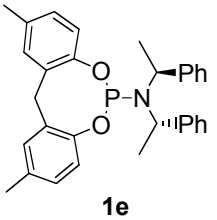


2a **3a**

Entry	Diene	Yield (%)	*Ee* (%)
1	nbd	96	48
2[a]	nbd	n.r.	-
3	Br-nbd	95	56
4	cod	96	39
5	DM-cod	95	2

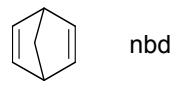
a. without *i*Pr_2NEt

Phosphoramidite:

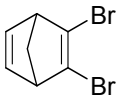


1e

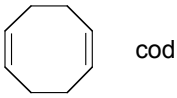
Diene:



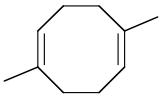
nbd



Br-nbd



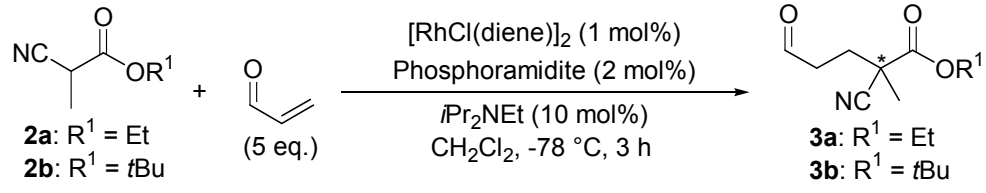
cod



DM-cod

The Rh complexes with chiral six-membered bicyclic diene ***C*$_1$-D** and ***C*$_2$'-D** were thus used as asymmetric catalysts (Table 2). Chiral dienes ***C*$_1$-D** and ***C*$_2$'-D** controlled the conformation of achiral phosphoramidite to attain higher enantioselectivity in the asymmetric Michael addition. Low catalytic activity of RhCl(ethylene)$_2$ (**1a**) (entry 3) clearly shows that both phosphoramidites and *chiral* dienes exert to give higher catalytic activity (entries 4 and 5).

Table 2. Asymmetric Michael addition with RhCl(chiral dienes)(achiral phosphoramidites)

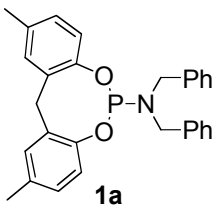


2a: R^1 = Et
2b: R^1 = *t*Bu

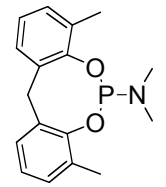
3a: R^1 = Et
3b: R^1 = *t*Bu

Entry	OR^1	Phosphoramidite	Diene	Yield (%)	*Ee* (%)
1	OEt	-	*C*$_1$-D	92	15 (*S*)
2	OEt	-	*C*$_2$'-D	90	32 (*S*)
3	OEt	1a	$(C_2H_4)_2$	70	-
4	OEt	1a	*C*$_1$-D	95	54 (*S*)
5	OEt	1a	*C*$_2$'-D	92	43 (*R*)
6	OEt	1b	*C*$_1$-D	94	38 (*S*)
7	OEt	1c	*C*$_1$-D	95	63 (*S*)
8	OEt	1c	*C*$_2$'-D	94	41 (*R*)
9	**O*t*Bu**	**1c**	***C*$_1$-D**	**95**	**86 (*S*)**
10	O*t*Bu	1d	*C*$_1$-D	81	78 (*S*)

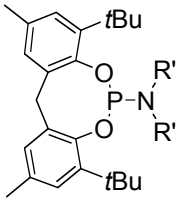
Phosphoramidite:



1a



1b



1c (R' = Me)
1d (R' = Bn)

The Rh-chiral diene (***C*$_1$-D**) complexes with the achiral phosphoramidite (**1a**) attained higher enantioselectivity than Rh-chiral diene (***C*$_2$'-D**) complexes (entries 4 *vs*. 5). The 4-methyl group of the phosphoramidite (**1a**) did not affect the enantioselectivity, but the bulky 2-*tert*-butyl group of the phosphoramidite (**1c**) attained higher enantioselectivity (entries 4 *vs*. 7). Furthermore, the asymmetric Michael addition of 2-cyanopropionic acid *tert*-butyl ester catalyzed by RhCl(***C*$_1$-D**)(**1c**) gave product **3b** in 95% yield with 86% *ee* (entry 9). However, the phosphoramidite (**1d**) bearing benzyl amine and *tert*-butyl group was too bulky to decrease the catalytic activity and enantioselectivity (entry 10).

The absolute configuration of products could be dictated by the chiral dienes (entries 4 *vs.* 5 and 7 *vs.* 8). Figure 1 shows that the conformation of phosphoramidite (**1c**) is different between RhCl(***C*$_1$-D**)(**1c**) and RhCl(***C*$_2$'-D**)(**1c**). In the case of the Rh-catalyzed Michael addition of α-cyano carboxylate, the active intermediate has been reported to be the *N*-bonded enolate complex of α-cyanocarboxylate.[9a,c] The enantioface of the *N*-bonded enolate complex is reversed (entries 4 *vs.* 5 and 7 *vs.* 8) by changing the chiral dienes from RhCl(***C*$_1$-D**)(**1c**) to RhCl(***C*$_2$'-D**)(**1c**) (Figure 2). Both the *N*-bonded enolate complexes are attacked by an electrophile from the opposite side of the phosphoramidite (**1c**); Therefore, the Rh complex with C_1-symmetric chiral diene ***C*$_1$-D** gives (*S*)-enriched products and the Rh complex with pseudo C_2-symmetric chiral diene ***C*$_2$'-D** affords (*R*)-enriched products.

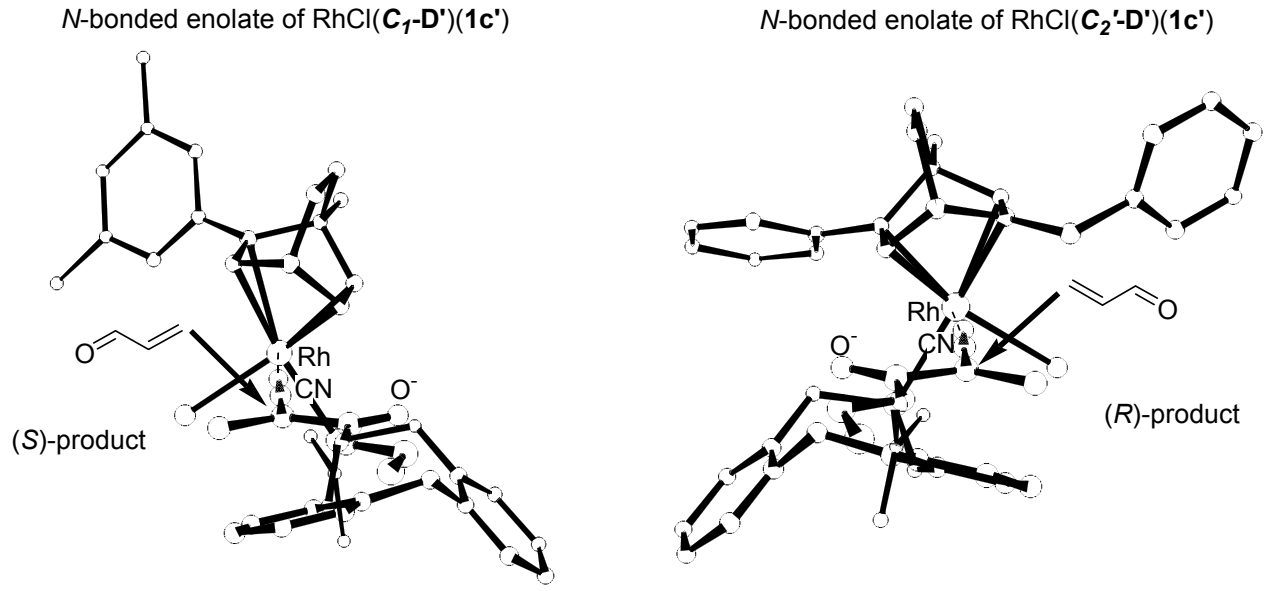


Figure 2. The conformation of cyanoester in two *N*-bonded enolate complexes

CONCLUSION

In the Rh complexes, the monodentate diphenylmethane-derived phosphoramidite can be controlled by a chiral diene to possess a single chiral conformation. The complex with the chirally controlled

phosphoramidite could be used in the asymmetric Michael additions of α-cyanocarboxylates. Both the chiral diene and achiral diphenylmethane-derived phosphoramidite cooperated to give higher yields and enantiomeric excesses.

EXPERIMENTAL

^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were measured on Bruker AV300 (300 MHz) spectrometer. Capillary gas chromatographic analysis (GC) was conducted on Shimadzu GC-14B instrument equipped with FID detector and capillary column coated with PEG-20 M by using N_2 as a carrier gas. Peak area was calculated by Shimadzu C-R6A as an automatic integrator. CP-Chirasil-Dex CB (i.d. 0.25 mm x 25 m, CHROMPACK; GL Science) was used as chiral column. Optical rotations were measured on a JASCO DIP-370. TOF Mass spectra were measured on a JEOL JMS-T100LC. Computational calculations were executed on Sun Fire X4600 (Tokyo Institute of Technology).

All experiments were carried out under an argon atmosphere otherwise noted. Analytical thin layer chromatography (TLC) was performed on a glass plates pre-coated with silica-gel (Merck Kieselgal 60 F254, layer thickness 0.25 mm). Visualization was accomplished by UV light (254 nm), anisaldehyde, $KMnO_4$. Column chromatography was performed on KANTO Silica Gel 60N (spherical, neutral) or ICN Alumina N (neutral, Activity Super I). Dichloromethane (dehydrate) and toluene (dehydrate) were purchased from Kanto Chemical Co., Inc.

1,5-Dibromocycloocta-1,5-diene[11] and 2-cyanopropionic acid *tert*-butyl ester (**2b**)[12] were prepared by the reported method. 2,3-Dibromobicyclo[2.2.1]hepta-2,5-diene (Br-nbd),[13] (2*S*,8*R*)-2-(3,5-dimethylphenyl)-8-methoxy-1,8-dimethylbicyclo[2.2.2]octa-2,5-diene (***C*$_1$-D**),[5] (1*S*,4*S*,8*S*)-5-benzyl-2-phenyl-8-methoxy-1,8-dimethyl-bicyclo[2.2.2]octa-2,5-diene (***C*$_2$'-D**)[5] and [RhCl(***C*$_1$-D**)]$_2$[6] were also prepared by the reported method.

(2,10-Dimethyl-12*H*-5,7-dioxa-6-phosphadibenzo[*a*,*d*]cycloocten-6-yl)dibenzylamine (1a)

To a solution of 2,2'-methylenebis(4-methylphenol) (45.7 mg, 0.2 mmol) in toluene (2 mL) was added HMPT (hexamethylphosphoric triamide) (45 μL, 0.24 mmol) at rt under an argon atmosphere. After stirred for 2 h at 100 °C, toluene and excess HMPT were evaporated under reduced pressure. The residue and 1H-tetrazole (21.1 mg, 0.3 mmol) were dissolved in toluene. To the mixture was added dibenzylamine (38 μL, 0.2 mmol) at rt. After stirred for 24 h at 100 °C, the reaction mixture was quenched with H_2O three times. The organic layer was dried over K_2CO_3. After concentration under reduced pressure, the residue was purified by alumina column chromatography (hexane/CH_2Cl_2 = 10/1) to give phosphoramidite **1a** (68.9 mg, 76% yield).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.32 (s, 6H), 3.54 (d, 1H, *J* = 12.9 Hz), 4.33 (d, 4H, *J* = 10.2 Hz), 4.35 (dd,

1H, *J* = 12.6, 3.0 Hz), 6.99 (br, 4H), 7.16 (s, 2H), 7.29-7.46 (m, 10H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.78, 34.13, 47.86, 48.14, 122.51, 127.11, 128.40, 128.56, 128.63, 130.40, 133.93, 134.71, 134.74, 138.38, 148.82, 148.88.

^{31}P NMR ($CDCl_3$, 121 MHz) δ 138.18.

TOF-HRMS (ESI), Calcd for $C_{29}H_{29}NO_2P$ $[M+H]^+$: 454.1936, Found: 454.1946.

(4,8-Dimethyl-12*H*-5,7-dioxa-6-phosphadibenzo[*a*,*d*]cycloocten-6-yl)dimethylamine (1b)

To a solution of 2,2'-methylenebis(6-methylphenol) (45.7 mg, 0.2 mmol) in toluene (2 mL) was added HMPT (45 μL, 0.24 mmol) at rt under an argon atmosphere. After stirred for 2 h at 100 °C, toluene and excess HMPT were evaporated under reduced pressure. The residue was purified by alumina column chromatography (hexane/CH_2Cl_2 = 10/1) to give phosphoramidite **1b** (36.8 mg, 61% yield).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.27 (s, 6H), 2.97 (d, 6H, *J* = 10.8 Hz), 3.48 (d, 1H, *J* = 12.3 Hz), 4.46 (dd, 1H, *J* = 12.3, 3.0 Hz), 6.93 (t, 2H, *J* = 7.5 Hz), 7.04 (d, 2H, *J* = 7.5 Hz), 7.19 (d, 2H, *J* = 7.5 Hz).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.95, 16.99, 33.99, 34.53, 35.16, 35.40, 124.10, 124.12, 127.42, 127.44, 129.01, 131.10, 131.14, 135.71, 135.75, 149.34, 149.40.

^{31}P NMR ($CDCl_3$, 121 MHz) δ 138.72.

TOF-HRMS (ESI), Calcd for $C_{17}H_{21}NO_2P$ $[M+H]^+$: 302.1310, Found: 302.1298.

(4,8-Di-*tert*-butyl-2,10-dimethyl-12*H*-5,7-dioxa-6-phosphadibenzo[*a*,*d*]cycloocten-6-yl)dimethylamine (1c)

Phosphoramidite **1c** was prepared from 2,2'-methylenebis(6-*tert*-butyl-4-methylphenol) in a similar manner to phosphoramidite **1b** (90% yield).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.40 (s, 18H), 2.30 (s, 6H), 2.96 (d, 6H, *J* = 9.3 Hz), 3.33 (d, 1H, *J* = 12.3 Hz), 4.35 (dd, 1H, *J* = 12.3, 3.0 Hz), 7.02 (d, 2H, *J* = 2.1 Hz), 7.11 (d, 2H, *J* = 2.1 Hz).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.05, 30.75, 30.81, 34.73, 35.60, 35.86, 126.39, 128.56, 132.73, 136.16, 136.20, 141.61, 141.66, 148.30, 148.40.

^{31}P NMR ($CDCl_3$, 121 MHz) δ 144.28.

TOF-HRMS (ESI), Calcd for $C_{25}H_{37}NO_2P$ $[M+H]^+$: 414.2562, Found: 414.2561.

(4,8-Di-*tert*-butyl-2,10-dimethyl-12*H*-5,7-dioxa-6-phosphadibenzo[a,d]cycloocten-6-yl)dibenzylamine (1d)

Phosphoramidite **1d** was prepared from 2,2'-methylenebis(6-*tert*-butyl-4-methylphenol) and dibenzylamine in a manner similar to phosphoramidite **1a** (88% yield).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.58 (s, 18H), 2.44 (s, 6H), 3.52 (d, 1H, *J* = 12.6 Hz), 4.53 (d, 4H, *J* = 7.2

Hz), 4.64 (dd, 1H, *J* = 12.6, 2.7 Hz), 7.19 (d, 2H, *J* = 2.1 Hz), 7.28 (d, 2H, *J* = 2.1 Hz), 7.38-7.56 (m, 10H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.18, 31.40, 31.47, 34.90, 35.11, 48.53, 48.79, 126.72, 127.19, 128.23, 128.59, 129.79, 133.18, 136.75, 136.78, 137.75, 137.82, 141.72, 141.77, 147.56, 147.64.

^{31}P NMR ($CDCl_3$, 121 MHz) δ 137.53.

TOF-HRMS (ESI), Calcd for $C_{37}H_{45}NO_2P$ $[M+H]^+$: 566.3194, Found: 566.3188.

(*S*,*S*)-*N*-(2,10-Dimethyl-12*H*-5,7-dioxa-6-phosphadibenzo[*a*,*d*]cycloocten-6-yl)bis(1-phenylethyl)-amine (1e)

To a solution of 2,2'-methylenebis(4-methylphenol) (45.7 mg, 0.2 mmol) in toluene (2 mL) was added HMPT (hexamethylphosphoric triamide) (45 μL, 0.24 mmol) at rt under an argon atmosphere. After stirred for 2 h at 100 °C, toluene and excess HMPT were evaporated under reduced pressure. The residue and 1H-tetrazole (21.1 mg, 0.3 mmol) were dissolved in toluene. To the mixture was added bis[(*S*)-1-phenylethyl]amine (45 μL, 0.2 mmol) at rt. After stirred for 24 h at 100 °C, the reaction mixture was quenched with H_2O three times. The organic layer was dried over K_2CO_3. After concentration under reduced pressure, the residue was purified by alumina column chromatography (hexane/CH_2Cl_2 = 10/1) to give phosphoramidite **1e** (38.4 mg, 40% yield).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.87 (d, 6H, *J* = 7.2 Hz), 2.32 (s, 3H), 2.33 (s, 3H), 3.48 (d, 1H, *J* = 12.9 Hz), 4.42 (dd, 1H, *J* = 12.9, 3.0 Hz), 4.94 (dq, 2H, *J* = 11.7, 7.2 Hz), 6.64 (d, 1H, *J* = 8.1 Hz), 6.93 (d, 1H, *J* = 8.1 Hz), 6.99 (s, 2H), 7.16-7.30 (m, 12H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.80, 22.08, 22.21, 34.08, 53.00, 53.16, 122.57, 122.61, 122.73, 122.78, 126.58, 127.80, 128.03, 128.07, 128.49, 130.22, 130.38, 133.75, 135.13, 143.55, 143.57, 149.45, 149.54, 149.71, 149.80.

^{31}P NMR ($CDCl_3$, 121 MHz) δ 142.20.

TOF-HRMS (ESI), Calcd for $C_{31}H_{32}NO_2PNa$ $[M+Na]^+$: 504.2068, Found: 504.2060.

$[\alpha]_D^{27}$ -66 (c 0.50 in $CHCl_3$).

[RhCl(*C*$_2$'-D)]$_2$

A mixture of (1*S*,4*S*,8*S*)-5-benzyl-2-phenyl-8-methoxy-1,8-dimethylbicyclo[2.2.2]octa-2,5-diene (chiral diene ***C*$_2$'-D**) (33.0 mg, 0.1 mmol) and [RhCl(ethylene)$_2$] (21.4 mg, 0.055 mmol) in benzene (4.0 mL) was stirred under an argon atmosphere at rt for 24 h, and then the reaction mixture was filtered through Celite. After the filtrate was evaporated under reduced pressure, the yellow residue was washed with Et_2O. Prolonged evacuation of the product at 50 °C gave [RhCl(***C*$_2$'-D**)]$_2$ (90% yield). The product was diastereomeric mixture.

^{1}H NMR (300 MHz, $CDCl_3$) *major diastereomer* δ 0.89 (d, *J* = 13.8 Hz, 1H), 1.09 (d, *J* = 13.8 Hz, 1H), 1.14 (s, 3H), 1.78 (s, 3H), 2.91 (d, *J* = 15.9 Hz, 1H), 3.00 (d, *J* = 15.9 Hz, 1H), 3.07 (s, 3H), 3.30 (s, 1H), 3.40-3.42 (m, 1H), 4.06 (d, *J* = 5.4 Hz, 1H), 7.22-7.39 (m, 6H), 7.95-8.00 (m, 4H).
^{1}H NMR (300 MHz, $CDCl_3$) *minor diastereomer* δ 0.85 (d, *J* = 14.1 Hz, 1H), 1.03 (d, *J* = 14.1 Hz, 1H), 1.14 (s, 3H), 1.63 (s, 3H), 3.05 (s, 3H), 3.21-3.30 (m, 3H), 3.36 (s, 1H), 4.12 (d, *J* = 6.3 Hz, 1H), 7.22-7.39 (m, 4H), 7.52-7.47 (m, 2H), 7.79-7.81 (m, 2H), 7.95-8.00 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) *major diastereomer* δ 21.80, 41.21, 46.22 (d, J_{Rh-C} = 10.9 Hz), 47.68, 49.56, 49.76 (d, J_{Rh-C} = 3.6 Hz), 53.13 (d, J_{Rh-C} = 2.9 Hz), 55.85 (d, J_{Rh-C} = 10.8 Hz), 70.84 (d, J_{Rh-C} = 12.1 Hz), 71.46 (d, J_{Rh-C} = 11.2 Hz), 77.24, 81.10, 126.22, 127.12, 128.15, 130.41, 130.85, 131.12, 137.66, 138.39.
^{13}C NMR (75 MHz, $CDCl_3$) *minor diastereomer* δ 21.90, 41.31, 44.90 (d, J_{Rh-C} = 11.6 Hz), 47.58, 49.46, 54.12, 55.01 (d, J_{Rh-C} = 10.1 Hz), 71.74 (d, J_{Rh-C} = 11.2 Hz), 81.03, 120.33, 127.20, 130.92, 137.72, 138.49.
Anal. Calcd for $C_{48}H_{52}Cl_2O_2Rh_2 \cdot 2H_2O$: C, 57.10; H, 5.99. Found: C, 57.10; H, 5.99. H_2O was derived from ether that washed the yellow residue (^{1}H NMR: 1.52 (s, 4H)).
$[\alpha]_D^{27}$ -76 (c 1.2 in $CHCl_3$).

[RhCl(Br-nbd)]$_2$

$[RhCl(Br\text{-}nbd)]_2$ was prepared from 2,3-dibromobicyclo[2.2.1]hepta-2,5-diene (Br-nbd) and $[RhCl(ethylene)_2]$ in a similar to manner as [RhCl(***C*$_2$'-D**)]$_2$ (40% yield).
^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.20-1.27 (m, 4H), 1.58 (br, 2H), 1.76 (d, 2H, *J* = 9.6 Hz), 4.32 (br, 2H), 4.57 (br, 2H).

1,5-Dimethylcycloocta-1,5-diene (DM-cod)

To a suspension of 1,5-dibromocycloocta-1,5-diene (280 mg, 1.05 mmol) and $NiCl_2$(dppp) (23 mg, 0.04 mmol) in dry Et_2O (20 mL) was added methyl Grignard reagent (1.59 mmol, 3.0 M in Et_2O) under an argon atmosphere at 0 °C. The reaction mixture was stirred for 30 min at 0 °C, for 1 h at rt and for 2 h at reflux. H_2O (20 mL) was added and the reaction mixture was extracted with Et_2O. Combined organic layer was dried over $MgSO_4$ and solvent was removed under reduced pressure. Crude product was purified by flash chromatography over silica-gel eluted with pentane to give the product (yield 90%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (d, *J* = 6.9 Hz, 12 H), 2.29-2.38 (m, 10 H), 5.32 (t, *J* = 6.0 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 26.3, 33.3, 122.5, 135.8.

[RhCl(dm-cod)]$_2$

$[RhCl(dm\text{-}cod)]_2$ was prepared from 1,5-dimethylcycloocta-1,5-diene (DM-cod) and $[RhCl(ethylene)_2]$

in a similar to manner as [RhCl(***C*$_2$'-D**)]$_2$ (30% yield). The product was diastereomeric mixture.

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.50 (s, 6H, dia. minor), 1.65-1.85 (m, 8H), 1.72 (s, 6H, dia. major), 2.05-2.23 (m, 4H), 2.47-2.64 (m, 4H), 3.79 (d, 2H, *J* = 7.2 Hz, dia. minor), 3.99 (d, 2H, *J* = 6.9 Hz, dia. major).

RhCl(*C*$_1$-D)(1c)

To a mixture of (4,8-di-*tert*-butyl-2,10-dimethyl-12*H*-5,7-dioxa-6-phosphadibenzo[*a*,*d*]cycloocten-6-yl)dimethylamine (**1c**) (8.3 mg, 0.02 mmol) and [RhCl(***C*$_1$-D**)]$_2$ (8.0 mg, 0.01 mmol) was added CH_2Cl_2 (1 mL) at rt under an argon atmosphere. After stirred for 1 h, the reaction mixture was concentrated under reduced pressure to give RhCl(***C*$_1$-D**)(**1c**) complex (16.1 mg, 98% yield).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.90 (s, 1H), 0.94 (s, 1H), 1.15 (s, 3H), 1.31 (s, 9H), 1.34 (s, 9H), 1.39 (s, 3H), 2.26 (s, 6H), 2.29 (s, 3H), 2.31 (s, 3H), 2.72 (br, 1H), 3.22 (d, 6H, *J* = 9.0 Hz), 3.27 (s, 3H), 3.57 (br, 1H), 3.90 (d, 1H, *J* = 15.6 Hz), 4.18 (t, 1H, *J* = 6.0 Hz), 5.00 (t, 1H, *J* = 4.8 Hz), 6.83 (s, 1H), 6.98 (br, 2H), 7.01 (br, 2H), 7.07 (br, 2H).

^{31}P NMR ($CDCl_3$, 121 MHz) δ 119.5 (d, $J_{P\text{-}Rh}$ = 268.6 Hz).

$[\alpha]_D^{27}$ -65 (c 0.20 in $CHCl_3$).

m/z (ESI): Calcd for Rh(***C*$_1$-D**)(**1c**) $[M\text{-}Cl]^+$: 784.3, 785.3, 786.3. Found: 784.3, 785.3, 786.3.

RhCl(nbd)(1e)

To a mixture of (*S*,*S*)-*N*-(2,10-Dimethyl-12*H*-5,7-dioxa-6-phosphadibenzo[*a*,*d*]cycloocten-6-yl)bis(1-phenylethyl)amine (**1e**) (9.6 mg, 0.02 mmol) and [RhCl(nbd)]$_2$ (4.6 mg, 0.01 mmol) was added CH_2Cl_2 (1 mL) at rt under an argon atmosphere. After stirred for 1 h, the reaction mixture was concentrated under reduced pressure to give RhCl(nbd)(**1e**) complex (11.8 mg, 98% yield).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.22 (s, 2H), 1.73 (d, 6H, *J* = 7.2 Hz), 2.31 (s, 3H), 2.32 (s, 3H), 2.86 (br, 1H), 3.23 (br, 1H), 3.46 (br, 2H), 3.79 (d, 1H, *J* = 13.8 Hz), 4.58 (d, 1H, *J* = 13.8 Hz), 5.13 (br, 1H), 5.22 (br, 1H), 5.34 (dq, 2H, *J* = 14.1, 7.2 Hz), 6.81 (d, 1H, *J* = 8.1 Hz), 6.90 (d, 1H, *J* = 8.1 Hz), 7.01 (dd, 1H, *J* = 8.1, 2.1 Hz), 7.08 (d, 1H, *J* = 2.1 Hz), 7.10 (d, 1H, *J* = 2.1 Hz), 7.21 (d, 1H, *J* = 8.1 Hz), 7.30-7.40 (m, 6H), 7.51 (d, 4H, *J* = 7.5 Hz).

^{31}P NMR ($CDCl_3$, 121 MHz) δ 125.0 (d, $J_{P\text{-}Rh}$ = 266.0 Hz).

$[\alpha]_D^{27}$ -2.4 (c 0.25 in $CHCl_3$).

m/z (ESI): Calcd for Rh(nbd)(**1e**) $[M\text{-}Cl]^+$: 676.2, 677.2, 678.2, 679.2, 680.2. Found: 676.2, 677.2, 678.2, 679.2, 680.2.

Typical procedure for Rh-catalyzed Michael addition of α-cyanocarboxylate

To a mixture of [RhCl(***C*$_1$-D**)]$_2$ (0.8 mg, 0.001 mmol) and (4,8-di-*tert*-butyl-2,10-dimethyl-12H-5,7-dioxa-6-phosphadibenzo[*a*,*d*]cycloocten-6-yl)dimethylamine **1c** (0.8 mg, 0.002 mmol) was added CH_2Cl_2 (2.0 mL) under an argon atmosphere. After stirred for 30 min at rt, to the solution was added 2-cyanoproionic acid *tert*-butyl ester (**2b**) (15.5 mg, 0.1 mmol). After cooled down to -78 °C, to the reaction mixture were added acrolein (35 μL, 0.5 mmol) and *i*Pr$_2$NEt (1.7 μL, 0.01 mmol). After stirred for 3 h at -78 °C, the reaction mixture was evaporated under reduced pressure. The residue was purified by silica-gel chromatography (hexane/EtOAc = 3/2) to give 2-cyano-2-methyl-5-oxopentanoate acid *tert*-butyl ester (**3b**) (20.0 mg, 95% yield).

2-Cyano-2-methyl-5-oxopentanoate acid ethyl ester (3a)[9c]

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.28 (t, *J* = 7.2 Hz, 3H), 1.57 (s, 3H), 2.05 (ddd, *J* = 14.4, 10.2, 5.7 Hz, 1H), 2.22 (ddd, *J* = 14.4, 9.9, 6.0 Hz, 1H), 2.59 (ddd, *J* = 18.6, 10.2, 6.0 Hz, 1H), 2.69 (ddd, *J* = 18.6, 9.9, 5.7 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 9.73 (s, 1H).

^{13}C NMR ($CDCl_3$, 121 MHz) δ 13.98, 23.51, 30.02, 39.76, 43.03, 63.09, 119.37, 186.71, 199.12.

$[\alpha]_D^{27}$ +1.3 (c 1.0 in $CHCl_3$) for a sample that is 48% *ee* (*R*).

GC (column, CP-Chirasil-Dex CB, i.d. 0.25 mm x 25 m, Chrompack; carrier gas, N_2 (75 kPa); column temp, 110 ºC; injection and detection temp, 140 ºC; split rate, 100:1), t_R = 21.2 min (*S*)/23.9 min (*R*).

2-Cyano-2-methyl-5-oxopentanoate acid *tert*-butyl ester (3b)[9c]

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.52 (s, 9H), 1.60 (s, 3H), 2.10 (ddd, *J* = 14.4, 10.2, 5.4 Hz, 1H), 2.23 (ddd, 1H, *J* = 14.4, 10.5, 5.1 Hz), 2.64 (dddd, 1H, *J* = 18.3, 10.2, 5.4, 0.9 Hz), 2.77 (dddd, 1H, *J* = 18.3, 10.5, 5.1, 0.9 Hz), 9.82 (s, 1H).

^{13}C NMR ($CDCl_3$, 121 MHz) δ 23.51, 27.75, 29.96, 39.84, 43.77, 84.37, 119.68, 167.67, 199.26.

$[\alpha]_D^{27}$ -2.4 (c 0.90 in $CHCl_3$) for a sample that is 86% *ee* (*S*).

GC (column, CP-Chirasil-Dex CB, i.d. 0.25 mm x 25 m, Chrompack; carrier gas, N_2 (75 kPa); column temp, 115 ºC; injection and detection temp, 150 ºC; split rate, 100:1), t_R = 15.7 min (*S*)/17.1 min (*R*).

Computational Methods

All the calculations were performed with GAUSSIAN 03 program package. All the structures were optimized at B3LYP/631SDD (SDD for Rh, 6-31G(d) for others) level. The optimized geometries were verified as an equilibrium structures having no imaginary frequency.

RhCl(*C*$_1$-D')(1c')

Charge = 0, Multiplicity = 1

SCF Done: E(B3LYP/631SDD) = -2358.51183292 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	-0.467484	0.226444	0.110569
2	17	0	-0.702947	0.531228	2.480094
3	6	0	4.557692	-0.412179	-1.076132
4	6	0	4.122801	1.031689	-1.232357
5	6	0	3.773662	1.851019	0.006375
6	6	0	-2.109814	1.691030	-0.696621
7	6	0	-0.707117	-0.282779	-1.954487
8	6	0	-0.118831	0.992254	-1.823432
9	6	0	-2.734195	0.477405	-0.883954
10	1	0	-0.146096	-1.142827	-2.309328
11	6	0	-3.961428	0.066959	-0.141006
12	1	0	-2.439387	2.394898	0.061788
13	1	0	0.915855	1.194238	-2.083294
14	6	0	4.144550	3.205293	0.030181
15	6	0	3.792825	4.053581	1.078392
16	6	0	-1.152354	2.107251	-1.812082
17	6	0	-2.229070	-0.262740	-2.148249
18	6	0	-2.771180	-1.678397	-2.346544
19	1	0	-0.708602	3.086599	-1.618667
20	6	0	3.045237	3.556698	2.147435
21	6	0	2.669677	2.215972	2.159519
22	6	0	3.035147	1.378719	1.103320
23	8	0	2.720335	0.030237	1.248440
24	6	0	-2.520967	0.660258	-3.384060
25	6	0	-1.940388	2.081054	-3.159528
26	1	0	-2.738587	2.831346	-3.121410
27	6	0	3.608372	-1.442480	-1.000839
28	6	0	3.982770	-2.785535	-0.982910
29	6	0	5.336979	-3.122034	-1.017171
30	6	0	6.302475	-2.115277	-1.067150
31	6	0	5.908820	-0.776155	-1.104000
32	8	0	2.258187	-1.107355	-0.974848
33	15	0	1.495836	-0.767158	0.485250
34	7	0	1.510175	-2.165221	1.398598
35	6	0	2.616456	-2.606153	2.247700
36	6	0	0.269801	-2.912391	1.595245
37	1	0	-0.055143	-2.852447	2.642199
38	1	0	-0.525996	-2.495542	0.973170
39	1	0	0.416190	-3.967358	1.324994
40	1	0	3.516212	-2.028530	2.043904

41	1	0	2.353841	-2.483673	3.307935
42	1	0	2.829022	-3.666985	2.060658
43	1	0	-1.268155	2.365955	-3.976981
44	1	0	-2.071225	0.189534	-4.266663
45	1	0	-3.601649	0.701637	-3.563534
46	6	0	-3.980913	-0.092744	1.247775
47	6	0	-5.168889	-0.418869	1.921242
48	6	0	-6.342013	-0.576125	1.182630
49	6	0	-6.358662	-0.410564	-0.210606
50	6	0	-5.164598	-0.093898	-0.857905
51	1	0	7.358408	-2.370202	-1.092534
52	1	0	4.102193	5.094425	1.059063
53	1	0	3.255059	1.046275	-1.905865
54	1	0	4.919069	1.567531	-1.760212
55	1	0	4.723954	3.597663	-0.802715
56	1	0	2.756386	4.204826	2.969819
57	1	0	2.077698	1.795588	2.965196
58	1	0	3.210555	-3.547110	-0.942597
59	1	0	5.633559	-4.167243	-1.005102
60	1	0	6.661874	0.006052	-1.167487
61	1	0	-3.061890	0.032230	1.811584
62	6	0	-5.159091	-0.593006	3.422978
63	1	0	-7.266948	-0.829161	1.698560
64	6	0	-7.647592	-0.567346	-0.985684
65	1	0	-5.176998	0.059484	-1.933582
66	1	0	-4.491457	-1.409451	3.724156
67	1	0	-4.797120	0.312451	3.924534
68	1	0	-6.159882	-0.816366	3.806933
69	1	0	-8.075707	-1.568714	-0.851202
70	1	0	-8.405849	0.152203	-0.651973
71	1	0	-7.492123	-0.413164	-2.058417
72	1	0	-2.601939	-2.291367	-1.454610
73	1	0	-2.253844	-2.153847	-3.188538
74	1	0	-3.842333	-1.691995	-2.563111

RhCl(C_2'-D')(1c')

Charge = 0, Multiplicity = 1

SCF Done: E(B3LYP/631SDD) = -2550.24063124 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	45	0	-0.671154	0.187146	0.448590
2	17	0	-1.412963	-1.216696	2.237715
3	6	0	4.029316	-1.205753	-1.180490
4	6	0	2.874107	-1.787459	-1.971342
5	6	0	2.031666	-2.887960	-1.337967
6	6	0	-0.397908	0.897711	-1.536092
7	6	0	-2.705829	1.119696	-0.095541
8	6	0	-2.570678	0.053841	-0.954952
9	6	0	-0.543374	2.021413	-0.683072
10	1	0	-3.403149	1.109902	0.737014
11	6	0	0.551077	3.018216	-0.488349
12	1	0	0.552126	0.682065	-2.015772
13	6	0	-3.367285	-1.244088	-0.917662
14	6	0	1.647593	-3.980902	-2.130611
15	6	0	0.814360	-4.989746	-1.649714
16	6	0	-1.694153	0.395771	-2.158961
17	6	0	-2.040426	2.424963	-0.540608
18	6	0	-2.345668	3.568049	0.426767
19	1	0	-1.529842	-0.476467	-2.797700
20	6	0	0.337384	-4.923905	-0.339584
21	6	0	0.706451	-3.855902	0.474837
22	6	0	1.545457	-2.855020	-0.020590
23	8	0	1.954328	-1.888692	0.889926
24	6	0	-2.558364	2.766087	-1.981394
25	6	0	-2.362987	1.565948	-2.941797
26	1	0	-1.723377	1.835801	-3.790416
27	6	0	3.828296	-0.123320	-0.310760
28	6	0	4.893317	0.510266	0.329262
29	6	0	6.192150	0.040410	0.130898
30	6	0	6.415765	-1.055385	-0.704925
31	6	0	5.340874	-1.661854	-1.357129
32	8	0	2.538982	0.360649	-0.127091
33	15	0	1.468567	-0.308301	0.974052
34	7	0	2.038488	0.026035	2.507138
35	6	0	3.183695	-0.637924	3.128661
36	6	0	1.277188	0.878174	3.415796
37	1	0	2.207267	-0.960786	-2.249110
38	1	0	3.272278	-2.182515	-2.912307
39	1	0	2.016480	-4.033929	-3.152634
40	1	0	0.542696	-5.821137	-2.294243
41	1	0	-0.316048	-5.698915	0.050846
42	1	0	0.347716	-3.765635	1.494301
43	1	0	-3.321094	1.231760	-3.357260
44	1	0	-3.617541	3.039951	-1.910390

45	1	0	-2.020662	3.651807	-2.340312
46	6	0	0.834794	3.592433	0.762699
47	6	0	1.851824	4.534913	0.907883
48	6	0	2.609354	4.930531	-0.197235
49	6	0	2.337510	4.375348	-1.448052
50	6	0	1.318842	3.432365	-1.590287
51	1	0	4.688562	1.362651	0.969137
52	1	0	7.024961	0.531346	0.626947
53	1	0	7.424407	-1.426939	-0.862421
54	1	0	5.519543	-2.498896	-2.028330
55	1	0	3.698680	-1.276845	2.413130
56	1	0	2.846862	-1.259719	3.970001
57	1	0	3.893425	0.108713	3.509408
58	1	0	0.983608	0.311618	4.309063
59	1	0	0.363367	1.226747	2.932129
60	1	0	1.876909	1.745838	3.725038
61	1	0	0.265084	3.281990	1.631989
62	1	0	2.917262	4.676057	-2.316939
63	1	0	3.402039	5.665238	-0.083843
64	1	0	2.055002	4.959110	1.887933
65	1	0	1.111285	3.011768	-2.570248
66	1	0	-3.463903	-1.595516	-1.953501
67	6	0	-4.748559	-1.133852	-0.296817
68	1	0	-2.778443	-2.003439	-0.390075
69	6	0	-5.859043	-0.829850	-1.096699
70	6	0	-7.133594	-0.714019	-0.539896
71	6	0	-7.316179	-0.902058	0.831995
72	1	0	-2.052899	3.318301	1.451767
73	1	0	-3.423779	3.768530	0.430092
74	1	0	-1.831255	4.489831	0.138466
75	6	0	-6.217238	-1.207660	1.637137
76	6	0	-4.942304	-1.324822	1.078276
77	1	0	-5.725664	-0.690986	-2.168167
78	1	0	-7.983307	-0.482952	-1.177511
79	1	0	-8.307976	-0.815183	1.268181
80	1	0	-6.350016	-1.360404	2.705216
81	1	0	-4.087258	-1.557842	1.707305

REFERENCES AND NOTES

1. The word *atropos* consists of "*a*" meaning "not" and "*tropos*" meaning "turn" in Greek. Therefore, the chirally rigid or flexible nature of a ligand can be called *atropos* or *tropos*, respectively. K.

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6. Asymmetric catalysts are generally prepared from chiral ligands and central metals. The asymmetric catalysts thus prepared can be evolved into more activated catalysts with higher catalytic activity and enantioselectivity by chiral activators (“Asymmetric Activation”, See ref. 2f,g). However, the additional ligation does not necessarily lead to higher catalytic activity. We have thus proposed the term “asymmetric synergy (effect)” leading to the higher enantioselectivity without increase in the catalytic activity (even with decrease). For the asymmetric synergy (effect),

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7. All the calculations were performed with GAUSSIAN 03 program package. All the structures were optimized at B3LYP/631SDD (SDD for Rh, 6-31G(d) for others) level. The optimized geometries were verified as equilibrium structures having no imaginary frequency.
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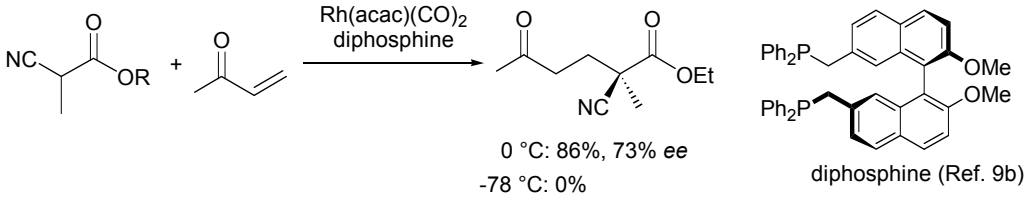

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