HETEROCYCLES, Vol. 76, No. 2, 2008, pp. 1525 - 1535. © The Japan Institute of Heterocyclic Chemistry
Received, 9th May, 2008, Accepted, 22nd July, 2008, Published online, 28th July, 2008. COM-08-S(N)116

BENZOPHENONE-DERIVED CATALYST WITH SELF-ADAPTATION: HIGHLY ENANTIOSELECTIVE HYDROGENATION IRRESPECTIVE OF KETONE SUBSTRATES[§]

Kazuki Wakabayashi, Kohsuke Aikawa, and Koichi Mikami*

Department of Applied Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan. E-mail: mikami.k.ab@m.titech.ac.jp

[§]Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract – The Ru complex with the *tropos* benzophenone-derived diphosphine ligand could be chirally controlled to a single chiral conformation instantaneously with a chiral diamine to attain high enantioselectivity in the asymmetric hydrogenation irrespective of ketone substrates. In the asymmetric hydrogenation of not only 1-acetonaphthone but also 9-acetylanthracene, the *tropos* Ru complex fits well with the substrate change to give high catalytic activity and enantioselectivity upon addition of silver salts such as AgOTf.

INTRODUCTION

BINAP (2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) is one of the most prominent atropisomeric (*atropos* in Greek)[1] ligand that has been developed by Noyori for various asymmetric catalyses;[2] The Ru complexes bearing BINAP and DPEN (1,2-diphenylethylenediamine) derivatives have been reported to attain high enantioselectivity in the asymmetric hydrogenation of simple ketone substrates.[3,4] On the other hand, we have already reported a chirally flexible (*tropos*)[1] benzophenone-derived ligands; 2,2'-Diphenylphosphinobenzophenones, namely DPBP, could be chirally controlled to a single conformation with chiral diamines such as DABN (2,2'-diaminobinaphathyl) and DPEN to provide higher enantioselectivity in the asymmetric hydrogenation of simple ketone substrates (up to >99%, 99% *ee*) than BINAP.[5]

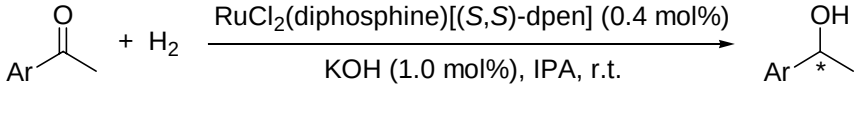
We report here a full paper that the *tropos* benzophenone DPBP-Ru/DPEN complex treated with a silver salt exhibits high catalytic activity and enantioselectivity in the asymmetric hydrogenation of both 1-acetonaphthone and 9-acetylanthracene; In *atropos* BINAP-$RuCl_2$/DPEN complex, the absolute configuration of BINAP has to be changed in order to afford high enantioselectivities depending on the

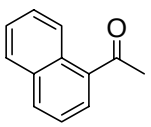
ketone substrates.[6,7] In sharp contrast, *tropos* benzophenone complexes[5,8] can be chirally controlled by external factors, such as the metal, counter anion, chiral activator[8] and substrate etc. Therefore, the *tropos* DPBP-Ru/DPEN catalyst has a great advantage to adopt a proper chiral conformation to fit well with the steric and/or electronic effects of the substrate (ketone), ligand (DPBP) and chiral activator (DPEN). The optimization of chiral catalyst conformations to adapt to the stereoelectronic effects of substrates and so forth can thus be called "self-adaptation" of catalysts.[9] Self-adaptable *tropos* catalysts are advantageous over *atropos* ligands and catalysts, which cannot adapt or tune as the word *atropos* means.

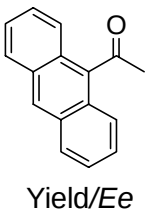
RESULTS AND DISCUSSION

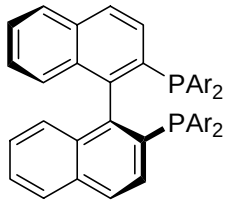
(*S*)-BINAP-$RuCl_2$/(*S*,*S*)-DPEN has been developed by Noyori to attain high catalytic activity and enantioselectivity in the asymmetric hydrogenation of aromatic (or α,β-unsaturated) ketones such as 1-acetonaphthone (>99%, 97% *ee*).[4a] Compared with the result of 1-acetonaphthone with (*S*)-BINAP-$RuCl_2$/(*S*,*S*)-DPEN, however, the asymmetric hydrogenation of 9-acetylanthracene required the change in the absolute configuration of BINAP from *S* to *R*.[6,7] The asymmetric hydrogenation of 9-acetylanthracene with (*R*)-tolBINAP-$RuCl_2$/(*S*,*S*)-DPEN gave the product in high enantioselectivity (99%, 81% *ee*), while (*S*)-tolBINAP-$RuCl_2$/(*S*,*S*)-DPEN provided lower enantioselectivity (91%, 41% *ee*).[7] In sharp contrast, *tropos* benzophenone DPBP-$RuCl_2$/(*S*,*S*)-DPEN, upon treatment with 1 equiv of AgOTf, can provide high enantioselectivity in the asymmetric hydrogenation irrespective of ketone substrates: 1-acetonaphthone (>99%, 96% *ee*) and 9-acetylanthracene (95%, 91% *ee*).

Table 1. Asymmetric hydrogenation of both 1-acetonaphthone and 9-acetylanthracene



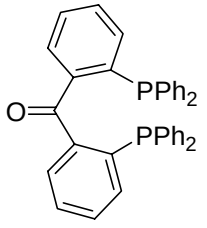






Ar=Ph: (*S*)-BINAP
Ar=4-MePh: (*S*)-tolBINAP

Diphosphine	Yield/*Ee*	Yield/*Ee*
(*S*)-BINAP	>99%/97% *ee* (*R*)[a]	91%/41% *ee* (*R*)[b,c]
(*R*)-BINAP	>99%/14% *ee* (*S*)[b]	99%/81% *ee* (*R*)[b,c]
DPBP + AgOTf (1.0 eq.)	**>99%/96% *ee* (*R*)[d]**	**95%/91% *ee* (*R*)**



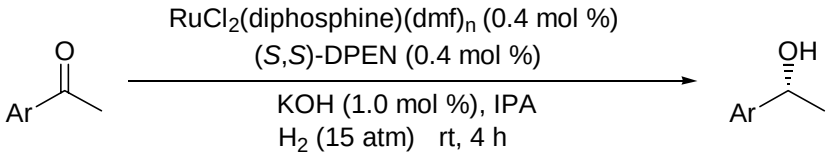
DPBP

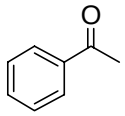
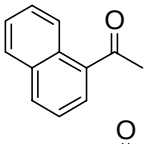
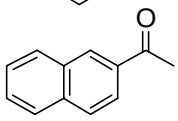
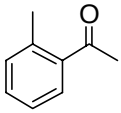
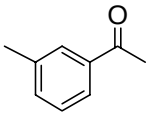
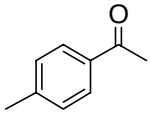
[a]Ref 4a. [b]Ref 6,7.
[c]Reaction temperature was 80 °C. tolBINAP was used instead of BINAP.
[d]Ref 5a,b. The use of $RuCl_2$(dpbp)[(*S*,*S*)-dpen] without the addition of AgOTf gave 99% *ee* in >99% yield.

Described below is a full detail that the DPBP-Ru/DPEN complex treated with a silver salt exhibits high catalytic activity and enantioselectivity in the asymmetric hydrogenation of both 1-acetonaphthone and 9-acetylanthracene. In sharp contrast, we have found that the addition of 1 equiv of silver salts to BINAPs-$RuCl_2$/(*S*,*S*)-DPEN complexes led to decomposition of the resultant cationic complexes.

Tropos benzophenone DPBP-$RuCl_2$/(*S*,*S*)-DPEN could be instantaneously controlled to a single chiral conformation to attain high catalytic activity and enantioselectivity in hydrogenation of aromatic ketones (Table 2), 1-acetonaphthone in particular (>99%, 99% *ee*: entries 3 *vs.* 4).[5a,b] Therefore, DPBP-$RuCl_2$/(*S*,*S*)-DPEN was also examined in the asymmetric hydrogenation of 9-acetylanthracene, for which the BINAP-$RuCl_2$/(*S*,*S*)-DPEN system has to be changed in the absolute configuration of BINAP.

Table 2. Hydrogenation of aromatic ketones with benzophenone DPBP-$RuCl_2$/(*S*,*S*)-DPEN

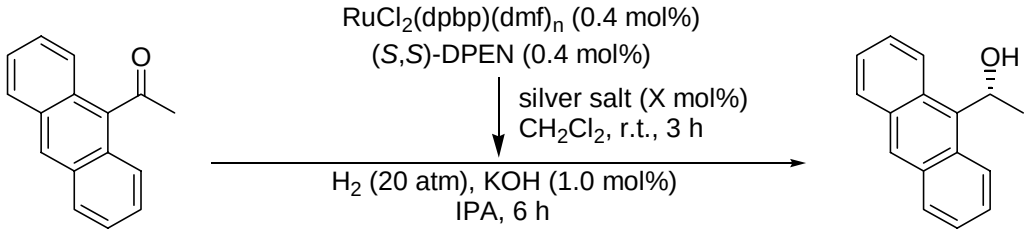


Entry	Substrate	Diphosphine	Conv (%)	Ee (%)
1		**DPBP**	**>99**	**90**
2		(*S*)-BINAP	>99	86
3		**DPBP**	**>99**	**99**
4[a]		(*S*)-BINAP	>99	97
5		**DPBP**	**99**	**87**
6		(*S*)-BINAP	99	79
7		**DPBP**	**>99**	**98**
8[b]		(*S*)-BINAP	**-**	95
9[a]		(*S*)-tol-BINAP	>99	94
10		**DPBP**	**>99**	**92**
11		(*S*)-BINAP	>99	89
12		**DPBP**	**>99**	**91**
13		(*S*)-BINAP	>99	87

a. Ref 4a.
b. Ref 4e.

The effect of silver salt[10] on $RuCl_2$(dpbp)[(*S*,*S*)-dpen] was examined in the highly enantioselective hydrogenation of 9-acetylanthracene (Table 3), because $RuCl_2$(dpbp)[(*S*,*S*)-dpen] itself provides only low catalytic activity and enantioselectivity without silver salt (entry 1). The kinds of silver salts did not affect the catalytic activity and enantioselectivity, but the addition of a silver salt remarkably increased the catalytic activity (entries 1 *vs.* 2-5). In contrast to the hydrogenation of 9-acetylanthracene with (*R*)-tolBINAP-$RuCl_2$/(*S*,*S*)-DPEN at 80 °C, the hydrogenation with the DPBP-$RuCl_2$/DPEN complex and AgOTf proceeded even at room temperature and attained higher enantioselectivity (entries 7 *vs.* 8).

Table 3. Asymmetric hydrogenation of 9-acetylanthracene with DPBP-Ru/DPEN and silver salts



Entry	Silver salt	X (mol%)	Temp. (°C)	Yield (%)	*Ee* (%)
1[a]	-	-	60	3	40
2	$AgSbF_6$	0.4	60	92	86
3	$AgPF_6$	0.4	60	99	85
4	$AgBF_4$	0.4	60	98	87
5	AgOTf	0.4	60	99	86
6	AgOTf	1.0	60	91	85
7[a]	**AgOTf**	**0.4**	**r.t.**	**95**	**91**
8[b]	$RuCl_2${(*R*)-tolbinap}{(*S*,*S*)-dpen}		80	99	81

a. Reaction time was 24 h.

b. Ref 3a and 7.

The X-ray structural analysis of [RuCl(OTf)(dpbp){(*S*,*S*)-dpen}]$_2$AgOTf proves the enantiopure structure of the chirally controlled DPBP-Ru/DPEN complex with AgOTf (Figure 1).[5,11] Based on the X-ray structural analysis, the addition of silver salt to the $RuCl_2$(dpbp)[(*S*,*S*)-dpen] complex led to the coordination of the carbonyl group of DPBP to the Ru metal. It is estimated that the coordination of carbonyl group by the addition of silver salts changes the conformation of the ruthenium-hydride complex with DPBP and (*S*,*S*)-DPEN, which would be the active species of the asymmetric hydrogenation.

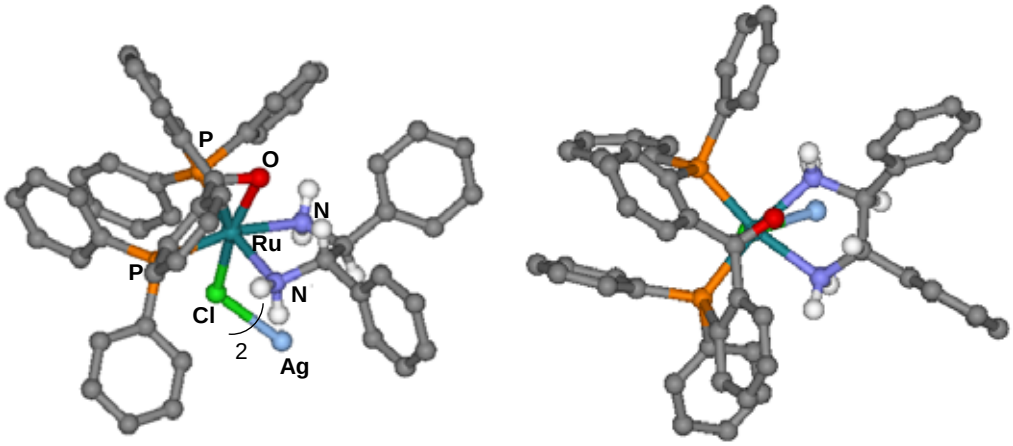


Figure 1. X-Ray structural analysis of [RuCl(OTf)(dpbp){(*S*,*S*)-dpen}]$_2$AgOTf. Three anions (OTf^-) were omitted for clarity.

It has been reported by Noyori that *trans*-RuH(η^1-BH_4)(binap)(dpen) was synthesized from BINAP-$RuCl_2$/DPEN and $NaBH_4$.[12] The RuHX(dpbp)[(*S*,*S*)-dpen] (X = η^1-BH_4 or TfO) complexes could also be synthesized (Figure 2). Hydride peaks in ^{1}H NMR spectra were different between RuH(η^1-BH_4)(dpbp)[(*S*,*S*)-dpen] and [RuH(dpbp){(*S*,*S*)-dpen}](OTf). In ^{1}H NMR analysis, the hydride peak of RuH(η^1-BH_4)(dpbp)[(*S*,*S*)-dpen] obtained with the combination of $NaBH_4$ and $RuCl_2$(dpbp)[(*S*,*S*)-dpen] was observed as one triplet (-13.9 ppm, $J_{H\text{-}P}$ = 24.0 Hz) to indicate the production of *trans*-RuH(η^1-BH_4)(dpbp)[(*S*,*S*)-dpen] (Figure 2a). Compared with the *trans*-RuH(η^1-BH_4)(dpbp)[(*S*,*S*)-dpen], the hydride peak of [Ru<u>H</u>(dpbp){(*S*,*S*)-dpen}](OTf) shifts downfield (-2.8 ppm, $J_{H\text{-}P}$ = 34.3, 34.0 Hz) and splits into two doublets (Figure 2b). The two doublets of [Ru<u>H</u>(dpbp){(*S*,*S*)-dpen}](OTf) implies that the carbonyl group of DPBP would adapt the *trans* position of hydride and that the octahedral conformation would be distort as shown in the X-ray analysis of the chloride precursor (Figure 1).

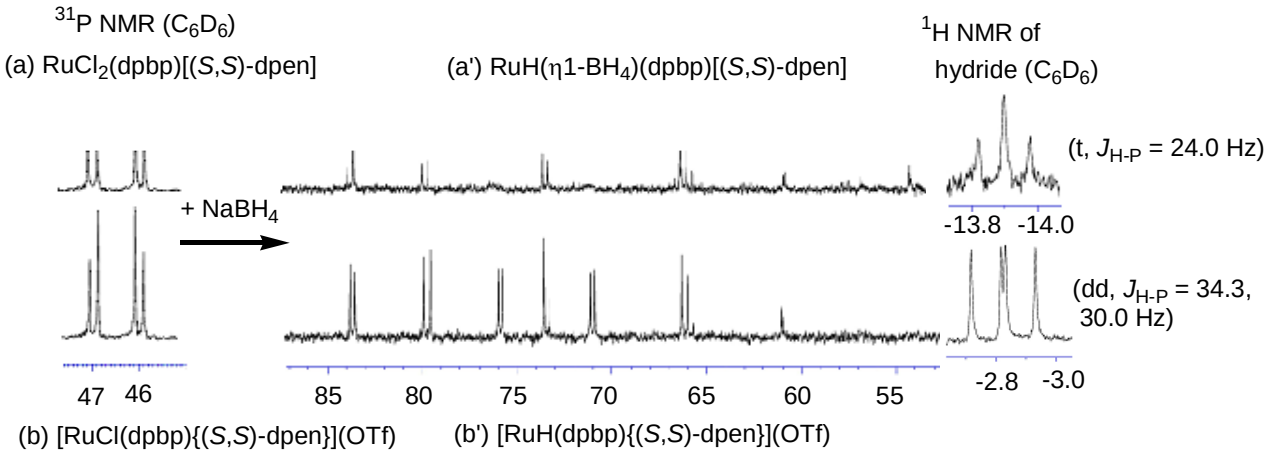
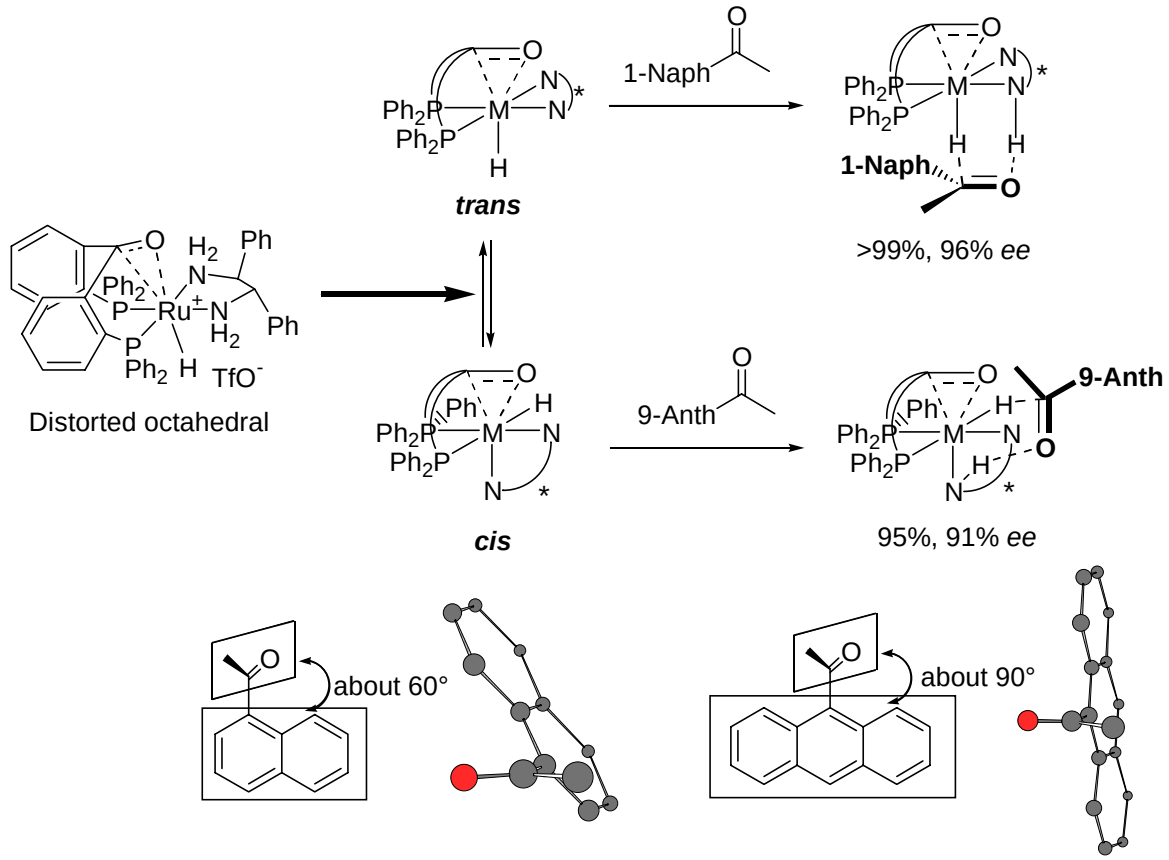


Figure 2. ^{1}H and ^{31}P NMR spectra of DPBP-Ru complexes reacted with $NaBH_4$

In the transition state of asymmetric hydrogenation, it is estimated that the distorted *trans* conformation of [RuH(dpbp){(*S*,*S*)-dpen}](OTf) transforms to the *cis* conformation depending on the stereoelectronic effect of ketone substrates (Scheme 1). The transformation affects the catalytic activity and enantioselectivity of the Ru complex to adapt well to the substrate change. The dihedral angle of 9-acetylanthracene between carbonyl group and anthryl group was calculated to be ~90° because of the steric repulsion, in contrast to ~60° of 1-acetonaphthone.[7] In the hydrogenation with *trans*-$RuCl_2$(dpbp)[(*S*,*S*)-dpen], the huge anthryl group prevents the approach to the *trans*-Ru complex (*cf.* Table 3, entry 1). The conformational change of the benzophenone Ru complex from *trans* to *cis* would lead to the high catalytic activity and enantioselectivity in the asymmetric hydrogenation of both 1-acetonaphthone (*via* the *trans*-conformation) and 9-acetylanthracene (*via* the *cis*-conformation).



Scheme 1. Transition state models for asymmetric hydrogenation of 1-acetonaphthone and 9-acetylanthracene, respectively.

CONCLUSION

The cationic benzophenone DPBP-Ru/DPEN complexes prepared with silver salts have thus attained high catalytic activity and enantioselectivity irrespective of ketone substrates, *via* the interconversion between *cis*- and *trans*-conformations. The high enantioselectivities attained by DPBP-Ru/DPEN complex

exemplifies the advantage of the instantaneous chirality control of the *tropos* catalyst with self-adaptation.

EXPERIMENTAL

^{1}H NMR and ^{13}C NMR spectra were measured on Varian Gemini 300 (300 MHz), Varian Inova-400 (400 MHz) and Bruker AV300 (300 MHz) spectrometers, ^{19}F NMR and ^{31}P NMR spectra were measured on Varian Inova-400 (400 MHz) and Bruker AV300 (300 MHz) spectrometers. 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-Cyclodextrin-β-2,3,6-M-19 (i.d. 0.25 mm x 25 m, CHROMPACK; GL Science) was used as chiral column. High performance liquid chromatographic (HPLC) was conducted on JASCO PU-980, LG-980-02, DG-980-50, and CO-966 instrument equipped with model UV-975 spectrometers as an ultra violet light. Peak areas were calculated by JASCO-BORWIN (Windows NT) as an automatic integrator. DAICEL Chemical-AS was used as chiral column. Optical rotations were measured on a JASCO DIP-370. Elemental analyses were measured on a LECO CHNS-932 (Center for Advanced Materials Analysis in Tokyo Institute of Technology). X-Ray crystal analyses were measured on Bruker APEXII and Bruker SMART CCD area detector (MoKα radiation, graphite monochrometer, λ = 0.71073 Å) (Nippon Bruker AXS K.K.). The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods based on F^2 with all measured unique reflections. All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were input at calculated positions and refined with a riding model.

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). Dichloromethane (dehydrated), DMF (dehydrated), and 2-propanol (dehydrated) were purchased from Kanto Chemical Co., Inc.

$RuCl_2(dpbp)(dmf)_n$

To a mixture of 2,2'-bis(diphenylphosphino)benzophenone (DPBP) (55.0 mg, 0.1 mmol) and $[RuCl_2(C_6H_6)]_2$ (25.0 mg, 0.05 mmol) was added DMF (2 mL) at rt under an argon atmosphere in a Schlenk tube. After stirred for 20 min at 100 ºC, the reaction mixture was concentrated under reduced pressure to give $RuCl_2(dpbp)(dmf)_n$. $RuCl_2(dpbp)(dmf)_n$ is air sensitive.

^{31}P NMR ($CDCl_3$, 162 MHz) δ 31.55, 32.01, 46.64, 49.56, 59.33, 59.47, 60.21.

$RuCl_2(dpbp)[(S,S)$-dpen]

To a mixture of $RuCl_2(dpbp)(dmf)_n$ (8.7 mg, 0.01 mmol) and (*S*,*S*)-DPEN (2.1 mg, 0.01 mmol) was added CH_2Cl_2 (1 mL) at rt under an argon atmosphere in a Schlenk tube. After stirred for 10 min, the reaction mixture was concentrated under reduced pressure to give $RuCl_2$(dpbp)[(*S*,*S*)-dpen] quantitatively.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.94-3.15 (m, 4H), 4.45-4.64 (m, 2H), 6.91-7.33 (m, 32H), 7.42-7.54 (m, 2H), 7.68-7.80 (m, 2H), 8.03-8.11 (m, 2H); 5.23 (s, 2H, CH_2Cl_2), 2.97 (s, 3H, DMF), 3.02 (s, 3H, DMF), 8.00 (s, 1H, DMF).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 63.37, 64.39, 126.74, 126.86, 128.33, 128.45, 128.86, 129.00, 129.10, 129.19, 129.26, 129.41, 129.57, 129.60, 129.77, 130.13, 130.19, 130.22, 130.27, 130.30, 130.35, 130.51, 130.55, 130.72, 131.00, 131.04, 131.13, 131.17, 131.36, 132.24, 132.35, 132.47, 132.59, 132.71, 132.77, 132.89, 133.14, 133.77, 134.23, 134.47, 134.89, 135.22, 137.29, 137.52, 149.89 (dd, $J_{C\text{-}P}$ = 24.8, 18.8 Hz, *C*=O); 53.2 (CH_2Cl_2), 30.91 (DMF), 35.85 (DMF), 162.24 (DMF).

^{31}P NMR ($CDCl_3$, 162 MHz) δ 46.38 (d, *J* = 23.6 Hz, 1P), 47.23 (d, *J* = 23.6 Hz, 1P).

$[\alpha]_D^{27}$ -88 (c 0.15 in $CHCl_3$).

Anal. Calcd for $C_{51}H_{44}Cl_2N_2OP_2Ru\cdot CH_2Cl_2\cdot$DMF: C, 60.45; H, 4.89; N, 3.84%. Found: C, 60.08; H, 5.23; N, 3.75%. Dichloromethane was derived from solvent and DMF was derived from $RuCl_2(dpbp)(dmf)_n$. The sample was evacuated at 100 ºC for 12 h.

[RuCl(dpbp){(*S*,*S*)-dpen}]]OTf

To a mixture of $RuCl_2(dpbp)(dmf)_n$ (8.7 mg, 0.01 mmol) and (*S*,*S*)-DPEN (2.1 mg, 0.01 mmol) was added CH_2Cl_2 (1 mL) at rt under an argon atmosphere in a Schlenk tube. After stirred for 15 min, AgOTf (2.6 mg, 0.01 mmol) was added to the reaction mixture. After stirred for 3 h, the reaction mixture was filtered through Celite® to remove AgCl. The filtrate was concentrated under reduced pressure to give [RuCl(dpbp){(*S*,*S*)-dpen}]OTf.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.97-3.16 (m, 4H), 4.42-4.59 (m, 2H), 6.89-7.29 (m, 32H), 7.39-7.52 (m, 2H), 7.64-7.78 (m, 2H), 8.04-8.11 (m, 2H); 5.24 (s, 2H, CH_2Cl_2).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 63.30, 64.43, 126.71, 126.79, 128.28, 128.45, 128.75, 128.81, 128.94, 129.11, 129.21, 129.51, 129.58, 129.70, 129.78, 130.06, 130.14, 130.27, 130.49, 130.85, 130.97, 131.09, 132.24, 132.35, 132.45, 132.56, 132.68, 132.79, 132.91, 133.10, 133.70, 133.75, 134.14, 134.44, 134.80, 135.66, 137.33, 137.35, 137.50, 137.52, 149.98 (dd, $J_{C\text{-}P}$ = 24.8, 12.0 Hz, *C*=O); 53.2 (CH_2Cl_2).

^{19}F NMR ($CDCl_3$, 376 MHz) δ -78.45.

^{31}P NMR ($CDCl_3$, 162 MHz) δ 46.51 (d, *J* = 22.9 Hz, 1P), 47.03 (d, *J* = 22.9 Hz, 1P).

$[\alpha]_D^{27}$ -68 (c 0.20 in $CHCl_3$).

Anal. Calcd for $C_{52}H_{44}ClF_3N_2O_4P_2RuS\cdot CH_2Cl_2$: C, 56.17; H, 4.09; N, 2.47; S, 2.83%. Found: C, 56.67; H, 4.54; N, 2.42; S, 2.68%. Dichloromethane was derived from solvent. The sample was evacuated at 100 ºC

for 12 h.

[RuCl(OTf)(dpbp){(*S*,*S*)-dpen}]$_2$AgOTf[5b]

To a mixture of $RuCl_2$(dpbp)$(dmf)_n$ (8.7 mg, 0.01 mmol) and (*S*,*S*)-DPEN (2.1 mg, 0.01 mmol) was added CH_2Cl_2 (1 mL) at rt under an argon atmosphere in a Schlenk tube. After stirred for 15 min, AgOTf (5.2 mg, 0.02 mmol) was added to the reaction mixture. After stirred for 3 h, the reaction mixture was filtered through Celite® to remove AgCl. The filtrate was concentrated under reduced pressure to give [RuCl(OTf)(dpbp){(*S*,*S*)-dpen}]$_2$AgOTf.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.86-2.94 (m, 2H), 3.29-3.45 (m, 2H), 4.50-4.63 (m, 2H), 6.91-7.51 (m, 34H), 7.65-7.77 (m, 2H), 7.99-8.07 (m, 2H).

^{19}F NMR ($CDCl_3$, 376 MHz) δ -78.12.

^{31}P NMR ($CDCl_3$, 162 MHz) δ 46.51 (d, *J* = 22.9 Hz, 1P), 47.03 (d, *J* = 22.9 Hz, 1P).

X-Ray analysis: A single crystal used for X-ray analysis was prepared from CH_2Cl_2, $CHCl_3$, and toluene solution of [RuCl(OTf)(dpbp){(*S*,*S*)-dpen}]$_2$AgOTf stored at rt.

Hydrogenation of 1-acetonaphthone with $RuCl_2$(dpbp)[(*S*,*S*)-dpen][5b]

To a mixture of $RuCl_2$(dpbp)$(dmf)_n$ (10.4 mg, 0.012 mmol) and (*S*,*S*)-DPEN (2.5 mg, 0.012 mmol) was added CH_2Cl_2 (1 mL) at rt under an argon atmosphere. After stirred for 10 min, the reaction mixture was concentrated under reduced pressure. To the residue were added 2-propanol (3.3 mL) and 1-acetonaphthone (0.46 mL, 3.0 mmol), and 100-mL autoclave was charged with this reaction mixture under a stream of argon. After addition of KOH/2-propanol (0.5 M, 60 μL, 0.03 mmol), hydrogen was introduced at a pressure of 15 atm. The solution was vigorously stirred for 4 h at rt. After concentration under reduced pressure, the residue was filtered through a short column of silica gel chromatography (hexane/EtOAc = 3/1) to give (*R*)-1-(1'-naphthyl)ethanol (>99%, 99% *ee*).

GC (column, CP-Cyclodextrin-β-2,3,6-M-19, i.d. 0.25 mm x 25 m, Chrompack; carrier gas, N_2 (75 kPa); column temp, 160 ºC; injection and detection temp, 190 ºC; split rate, 100:1), t_R = 37.6 min (*S*)/38.9 min (*R*), t_R = 25.9 min (ketone substrate).

Hydrogenation of 9-acetylanthracene with [RuCl(dpbp){(*S*,*S*)-dpen}]]OTf

To a mixture of [RuCl(dpbp){(*S*,*S*)-dpen}]]OTf (12.6 mg, 0.012 mmol) and 9-acetylanthracene (660.8 mg, 3.0 mmol) were added 2-propanol (3.3 mL) and toluene (1.5 mL) under an argon atmosphere in a Schlenk tube. 100-mL autoclave was charged with this reaction mixture under a stream of argon. After addition of KOH/2-propanol (0.5 M, 60 μL, 0.03 mmol), hydrogen was introduced at a pressure of 20 atm. The solution was vigorously stirred for 24 h at rt. After concentration under reduced pressure, the residue was

filtered through a short column of silica gel chromatography (hexane/EtOAc = 3/1) to give (*R*)-1-(9'-anthryl)ethanol (95%, 91% *ee*).

HPLC (column, CHIRALPAK AS, hexane/2-propanol = 98 : 2, flow rate, 1.0 mL/min, detection UV = 254 nm), t_R = 19.0 min (*S*)/24.3 min (*R*).

NMR analyses of RuHX(dpbp)(dpen) complexes (X = BH_4 or TfO)[12]

To a solution of [RuCl(dpbp){(*S*,*S*)-dpen}]]OTf (10.5 mg, 0.01 mmol) in degassed EtOH (1 mL) and benzene (1 mL) was added $NaBH_4$ (9.5 mg, 0.25 mmol) at rt under an argon atmosphere in a Schlenk tube. After stirred for 5 min at 60 °C, the reaction mixture was cooled down to rt and stirred for 30 min. After concentration under reduced pressure, the residue was dissolved in degassed benzene. The solution filtered through Celite® under an argon atmosphere to remove white solid. The filtrate was evaporated under reduced pressure and dissolved in C_6D_6.

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. a) K. Mikami, K. Aikawa, Y. Yusa, J. J. Jodry, and M. Yamanaka, *Synlett*, 2002, 1561. b) W. Kuhn, *Stereochemie*, ed. by K. Freudenberg; Franz Deuticke: Leipzig, Germany, 1933; pp. 803-824.
2. R. Noyori and H. Takaya, *Acc. Chem. Res.*, 1990, **23**, 345.
3. Review: a) T. Ohkuma, M. Kitamura, and R. Noyori, *Catalytic Asymmetric Synthesis*; ed. by I. Ojima; VCH: New York, 2000. b) R. Noyori and T. Ohkuma, *Angew. Chem. Int. Ed.*, 2001, **40**, 40. c) T. Ohkuma, M. Kitamura, and R. Noyori, *New Frontiers in Asymmetric Catalysis*; ed. by K. Mikami and M. Lautens; Wiley: New York, 2007.
4. a) T. Ohkuma, H. Ooka, T. Ikariya, and R. Noyori, *J. Am. Chem. Soc.*, 1995, **117**, 2675. b) T. Ohkuma, H. Ooka, M. Yamakawa, T. Ikariya, and R. Noyori, *J. Am. Chem. Soc.*, 1995, **117**, 10417. c) T. Ohkuma, H. Ikehira, T. Ikariya, and R. Noyori *Synlett*, 1996, 467. d) A. Fujii, S. Hashiguti, H. Ooka, N. Uematsu, T. Ikariya, and R. Noyori, *J. Am. Chem. Soc.*, 1996, **118**, 2521. e) T. Ohkuma, M. Koizumi, H. Doucet, T. Pham, M. Kozawa, K. Murata, E. Katayama, T. Yokozawa, T. Ikariya, and R. Noyori, *J. Am. Chem. Soc.*, 1998, **120**, 13529.
5. DPBP-Ru complex: a) K. Wakabayashi, Bachelor Presentation, March 3, 2003. b) K. Mikami, K. Wakabayashi, and K. Aikawa, 84th Annual Meeting of Chem. Soc. Jpn., March 28, 2004, 3B8-31. c) WO2005/016943 (Priority Date: 2003, Aug. 13: 2003-293145). d) Our preliminary communication: K. Mikami, K. Wakabayashi, and K. Aikawa, *Org. Lett.*, 2006, **8**, 1517. e) Q. Jing, C. A. Sandoval, Z. Wang, and K. Ding, *Eur. J. Org. Chem.*, 2006, 3606. DPBP-Rh complex: f) K. Mikami, K.

Wakabayashi, Y. Yusa, and K. Aikawa, *Chem. Commun.*, 2006, 2365. See also our BIPHEPs-Ru complexes: g) K. Mikami, T. Korenaga, M. Terada, T. Ohkuma, T. Pham, and R. Noyori, *Angew. Chem. Int. Ed.*, 1999, **38**, 495.

6. T. Ohkuma, H. Doucet, T. Pham, K. Mikami, T. Korenaga, M. Terada, and R. Noyori *J. Am. Chem. Soc.*, 1998, **120**, 1086.
7. T. Korenaga, *Ph.D. Thesis*, Tokyo Institute of Technology, 2000.
8. a) Review on 'Asymmetric Activation', K. Mikami, M. Terada, T. Korenaga, Y. Matsumoto, M. Ueki, R. Angelaud, *Angew. Chem. Int. Ed.*, 2000, **39**, 3532. BIPHEP-Pd complexes. b) K. Mikami, K. Aikawa, Y. Yusa, and M. Hatano, *Org. Lett.*, 2002, **4**, 91. c) K. Mikami, K. Aikawa, and Y. Yusa, *Org. Lett.*, 2002, **4**, 95. BIPHEP-Rh complex. d) K. Mikami, S. Kataoka, Y. Yusa, and K. Aikawa, *Org. Lett.*, 2004, **6**, 3699. BIPHEP-Pt complex. e) J. J. Becker, P. S. White, and M. R. Gagné, *J. Am. Chem. Soc.*, 2001, **123**, 9478. f) K. Mikami, H. Kakuno, and K. Aikawa, *Angew. Chem. Int. Ed.*, 2005, **44**, 7257.
9. a) R. Zalubovskis, A. Bouet, E. Fjellander, S. Constant, D. Linder, A. Fischer, J. Lacour, T. Privalov, and C. Moberg, *J. Am. Chem. Soc.*, 2008, **130**, 1845. b) K. Wakabayashi, K. Aikawa, S. Kawauchi, and K. Mikami, *J. Am. Chem. Soc.*, 2008, **130**, 5012.
10. [RuH(η^2-H_2){(*R*)-binap}{(*R*,*R*)-dpen}](BF_4) prepared, however, by the addition of HBF_4 rather than the addition of $AgBF_4$: R. J. Hamilton, C. G. Leong, G. Bigam, M. Miskolzie, and S. H. Bergens, *J. Am. Chem. Soc.*, 2005, **127**, 4152.
11. Crystal data of [RuCl(OTf)(dpbp){(*S*,*S*)-dpen}]$_2$AgOTf: formula $C_{107}H_{90.50}AgCl_{9.50}F_{7.50}N_4O_{9.50}P_4Ru_2S_{2.50}$, Orthorhombic, space group P2(1)2(1)2, a = 20.9715(16) Å, b = 39.437(3) Å, c = 13.8177(10) Å, $\alpha = \beta = \gamma = 90°$, V = 11428.0(15) Å^3, *Z* = 4, and *D* = 1.498 Mg/m^3. The final cycle of full-matrix least-squares on F^2 was based on 26825 observed reflections and 1448 variable parameters and converged to *R* = 0.0754 and *Rw* = 0.2099. Goodness of Fit = 1.145, Shift/Error = 0.04(3). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-257768. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).
12. T. Ohkuma, M. Koizumi, K. Muñiz, G. Hilt, C. Kabuto, and R. Noyori, *J. Am. Chem. Soc.*, 2002, **124**, 6508.