Enantiofacial Control of Planar Chiral Arene Ru Complexes Bearing *Tropos* Biphenyl Ligands

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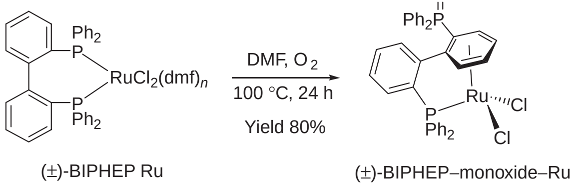
A variety of planar chiral Ru-complexes bearing *tropos* ortho-substituted biphenyl ligands were synthesized. The planar chirality control of the Ru complexes by enantiopure (*R*)-H_8–DABN selectively gave the thermodynamically stable diastereomers via association of solvents employed.

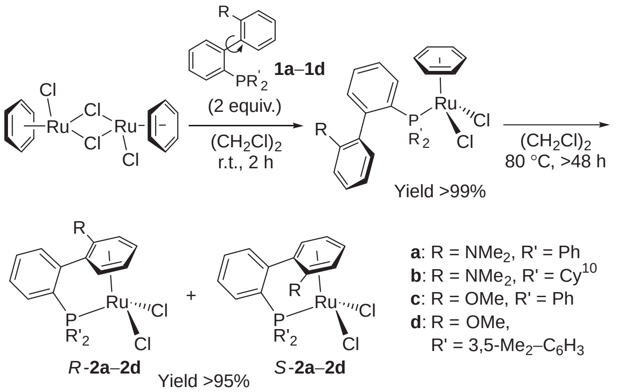
Asymmetric catalysis is the most powerful for the production of a various enantio-enriched molecules.[1] In asymmetric catalysis, atropisomeric or planar chiral metal complexes bearing particularly ferrocenyl–diphosphine ligands, for example (*R*)-*N*,*N*-dimethyl-1-[(*S*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine [(*R*)-(*S*)-BPPEA][2] with appendages of stereogenic centers, are generally used. These planar chiral metal complexes[3] have been synthesized in diastereofacial selective fashion. There has been no example of enantiofacial selective synthesis of planar chiral Ru complex without any appendage of stereogenic center. We have already succeeded in axial chirality control of Ru-complexes bearing chirally flexible (*tropos*) bis(phosphanyl)biphenyl (BIPHEP) ligands.[4] The axial chirality can be controlled by enantiopure (*R*)-2,2′-diamino-1,1′-binaphthyl ((*R*)-DABN). During the course of our study on the axial chirality control, we have found that the BIPHEP–Ru complex bearing axial chirality could be transformed to BIPHEP–monoxide–Ru complex bearing planar chirality (Scheme 1).[5] We herein report the enantiofacial control of planar chiral Ru complexes of *tropos* biphenyl ligands.[6]

Axial chiral BIPHEP–Ru complex[7] was synthesized through addition of 2 equiv. of BIPHEP to $[RuCl_2(benzene)]_2$ in DMF at room temperature under argon atmosphere and then at 100 °C within 10 min. Heating over 24 h gave BIPHEP–monoxide–Ru complex bearing planar chirality through oxidation of one phosphine portion in 80% yield, by virtue of the *tropos* nature (Scheme 1). In sharp contrast, when the *atropos* BINAP or SEGPHOS[8] counterparts were used as a ligand, their planar Ru-complexes were not obtained but the axial chiral complexes decomposed for their air sensitivity. It was thus clarified that the *tropos* biphenyl backbone is the key in obtaining the planar complexes.

A variety of planar chiral Ru complexes **2a**–**2d** bearing ortho-substituted *tropos* biphenyl ligands **1a**–**1d** were thus prepared (Scheme 2). The complexation of $[RuCl_2(benzene)]_2$ and two equimolar amounts of *tropos* biphenyl ligands **1a**–**1d** in dichloroethane at room temperature was examined to give first benzene phosphine complexes quantitatively within 2 h. Subsequently, intramolecular ligand exchange[9] was observed to give planar chiral Ru-complexes **2a**–**2d** bearing *tropos* biphenyl ligands over 48 h even at 80 °C in dichloroethane.



Scheme 1. Transfer of axial chirality to planar chirality.



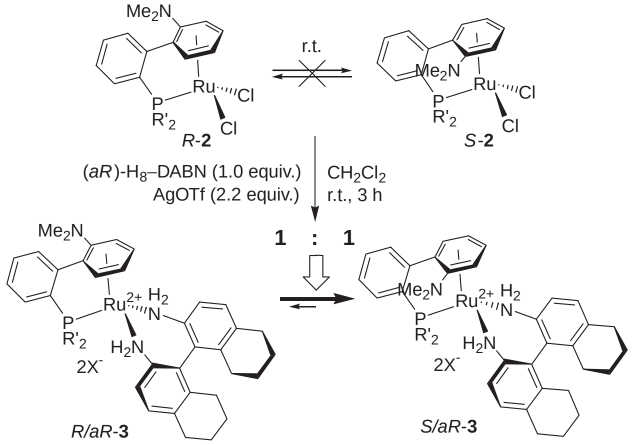
Scheme 2. Synthesis of planar arene Ru complexes.

Planar chirality control of complexes **3a** and **3b** was next attempted to convert the less favorable diastereomer to the favorable diastereomer (Table 1). A planar chiral Ru-complex was mixed with one equimolar amount of (*R*)-H_8–DABN and an excess amount of AgOTf salt to give a 1:1 (*R*/*aR*:*S*/*aR*) mixture of diastereomers quantitatively. No change was observed in the diastereomeric ratio at room temperature. However, the isomerization of **3a** proceeded in 2-propanol/$(CH_2Cl)_2$ at 80 °C for 72 h to give the *S*/*aR*-**3a** as the major diastereomer (Entry 1). On the other hand, the complex **3b**[11] bearing PCy_2 was decomposed in 2-propanol/$(CH_2Cl)_2$ (Entry 2). The use of chlorobenzene gave the thermodynamically stable diastereomer *S*/*aR*-**3b** selectively (85:15) without decomposition (Entry 3). Complex **3b** with SbF_6^- as a counter anion was decomposed under the same conditions (Entry 4). The isomerization rate in chlorobenzene was influenced by the concentration of **3b** (See SI, Figure S1).[12] Two possible mechanisms can thus be envisaged for isomerization of **3b**. One is intermolecular migration of Ru via the chlorobenzene-complex produced by dissociation of biphenyl ligand **2b**. The other is intramolecular migration of Ru through direct assistance of other Ru-complexes.

The configuration of the diastereomer *R*/*aR*-**3b** bearing SbF_6^- was determined by X-ray analysis of a single crystal obtained in dichoromethane solution of 1:1 diastereomer mixture (Figure 1).[12]

The complexes **3c** and **3d** bearing OMe instead of NMe_2 were next examined (Table 2). The isomerization of **3c** proceeded in 2-propanol/$(CH_2Cl)_2$ at 80 °C to give the *S*/*aR*-**3c** as the major diastereomer (Entry 1). Using **3d** with sterically demand-

Table 1. Enantiofacial control of planar chiral complexes **3a** and **3b** in 2-propanol/$(CH_2Cl)_2$ or chlorobenzene



Entry	Complex	R′	X	Conditions	S/aR:R/aR
1	**3a**	Ph	OTf	IPA/$(CH_2Cl)_2$ 80 °C, 72 h	72:28
2	**3b**	Cy	OTf	IPA/$(CH_2Cl)_2$ 80 °C, 72 h	decompose
3	**3b**	Cy	OTf	PhCl 100 °C, 72 h	85:15
4	**3b**	Cy	SbF_6	PhCl 100 °C, 72 h	decompose

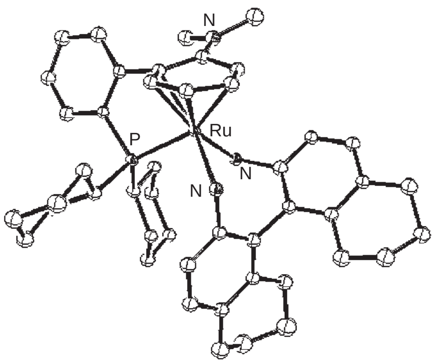
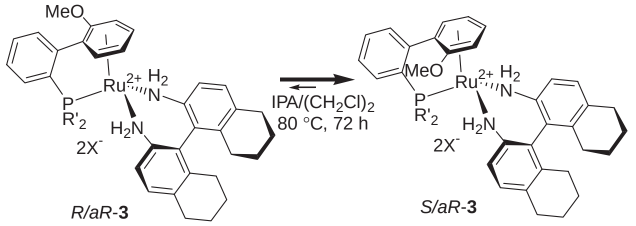


Figure 1. ORTEP drawing for the diastereomer R/aR-**3b** bearing SbF_6^-. Two counter anions (SbF_6^-) were omitted for clarity.

ing xylyl substituent, the isomerization completely proceeded to give solely S/aR-**3d** (Entry 2). The use of SbF_6^- instead of OTf^- also led to the single diastereomer (Entry 3). In chlorobenzene, in contrast, the isomerization of **3d** did not take place. Since the isomerization rate was not influenced by the concentration of the complexes (See SI, Figure S2),[12] isomerization may involve the intramolecular migration of Ru via the arene-complex;[13] 2-Propanol presumably stabilizes the arene-complex intermediate generated through dissociation of phosphine–Ru bond.

In conclusion, we have succeeded in the enantiofacial control of planar chiral Ru-complexes by virtue of *tropos* biphenyl ligands. Further mechanistic studies on the planar chirality control and applications of the enantio- and diastereopure Ru-complexes in asymmetric catalysis are in progress.

Table 2. Enantiofacial control of planar chiral complexes **3c** and **3d** in 2-propanol/$(CH_2Cl)_2$



Entry	Complex	R′	X	S/aR:R/aR
1	**3c**	Ph	OTf	84:16
2	**3d**	3,5-Me_2–C_6H_3	OTf	100:0
3	**3d**	3,5-Me_2–C_6H_3	SbF_6	100:0

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