Dual chirality control of palladium(II) complexes bearing *tropos* biphenyl diamine ligands[†]

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Axial and center chirality of Pd complexes with *tropos* biphenyl secondary diamine ligands is shown to be controlled by chiral amide (R)-DABNTf, which can efficiently discriminate between two enantiomeric Pd complexes.

The development of asymmetric catalysts for organic reactions is one of the most challenging subjects in modern science and technology.¹ These catalysts are generally metal complexes bearing chiral and atropisomeric ligands such as BINAP. Through enantio-resolution and synthetic transformation, many enantiopure atropisomeric (*atropos* in Greek; a = not, tropos = turn)² ligands are synthesized and used in catalytic asymmetric reactions. By contrast, we have already reported that chirally flexible (tropos) bis(phosphanyl)biphenyl (BIPHEP) ligands,^{2,3} of which the axial chirality can be controlled by a chiral diamine as a chiral activator, effectively act like atropisomeric ligands for Ru, Rh, and Pd complexes.^{2,4,5} On the other hand, when a biphenyl diamine, instead of a biphenyl phosphine such as BIPHEP, coordinates to a metal, two centers of chirality in the diamine are generated in addition to the chiral axis (Eq. 1). In this paper, we report dual control of N-center chirality⁶ and axial chirality⁷ in Pd complexes with the tropos diamines bearing the biphenyl backbone like BIPHEP ligands (Eq. 1).



The various *tropos* diamine ligands (**1a–d**) were prepared in short steps. Treatment of 2,2'-dinitrobiphenyl with sodium borohydride over 10% palladium on carbon in MeOH/H₂O afforded 2,2'-diaminobiphenyl (DABP) in 91% yield.⁸ Upon treatment of DABP with 2.5 equiv. of aldehydes under toluene reflux, the DABP imines were obtained. The imines were reduced with sodium borohydride in toluene/MeOH to give the secondary diamines **1a–d** respectively, in good yields.⁹ Complexation of PdCl₂(CH₃CN)₂ and 1.0 equiv. of **1a–d** in dichloromethane at room temperature was successful, giving diamine Pd complexes **2a–d** in good yields (81–97%) (Eq. 2). All the ¹H NMR spectra of

the complexes **2a–d** indicated the single diastereomer [R/R,R and S/S,S or R/S,S and S/R,R (axial chirality/center chirality, respectively)]. The combination of PtCl₂(CH₃CN)₂ complex and 1.0 equiv. of diamine **1a** in dichloroethane at 80 °C resulted in the desired diamine Pt complex, which is very similar to the Pd complex **2a** in ¹H NMR.



In the case of the racemic complexes 2a and 2c, the relative configuration of the single diastereomers was determined by X-ray analyses of a single crystal obtained from dichloromethane–hexane solution (Fig. 1).‡ It was clarified that the coordination of diamine ligands provides the axial chirality of the biphenyl backbone and *N*-chirality on secondary amines by coordinating to the Pd center. The chirality of the complex 2a is described as *S/S,S* and no symmetry in the solid. On the other hand, the chirality of complex 2c is also described as *S/S,S* and *C*₂-symmetry in the solid state. Interestingly, the *N*-substituents adopt the axial orientations. In sharp contrast, it has been reported that the *N*-substituents occupy the equatorial orientations in diamine ligands bearing an ethylene



Fig. 1 ORTEP drawings of complexes 2a and 2c.

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Fig. 2 Axial orientations of the N-substituents of complex 2a.

backbone.^{6,10} It was indicated that there were $CH-\pi$ interactions between benzyl protons and the benzene ring of the biphenyl backbone. We thus propose that the axial orientations of the *N*-substituents stem from the $CH-\pi$ interactions (Fig. 2).

The racemic complex 2a in dichloromethane at room temperature did not complex with a soluble chiral source (R)-M2BINOL (M = Na, K) in THF obtained by *in situ* deprotonation of (R)-BINOL with MO'Bu.⁶ When (R)-DABNTf bearing higher acidity due to a trifluoromethanesulfonyl substituent was used instead of BINOL under similar conditions, the (R)-DABNTf complex 3a was obtained after recrystallization from dichloromethane-acetone-hexane solution in 81% yield (Eq. 3). It was confirmed by ¹H and ¹⁹F NMR analyses that this isolated complex 3a was a single diastereomer. The other diastereomers were not observed by NMR analyses of the crude mixture before recrystallization. Using the complexes 2b and 2c with a mesityl and 1-naphthyl substituent respectively, (R)-DABNTf complexes 3b and 3c were not obtained due to steric hindrance. The use of complex 2d led to the complex with (R)-K₂DABNTf, to give the single diastereomer 3d in 75% yield.



Recrystallization of **3a** from dichloromethane–methanol gave crystals suitable for X-ray diffraction. The X-ray analysis revealed that complex **3a** was the single diastereomer (R/R, R/R: diamine axial chirality/diamine center chirality/DABNTf axial chirality) (Fig. 3).[‡] The *N*-benzyl substituents in complex **3a** also occupy the axial orientations.

In the S/S,S/R-3a complex, there is strong steric repulsion between the equatorial benzyl group of the diamine and the trifluoromethanesulfonyl substituent (Tf) of the chiral amide DABNTf (Fig. 4).¹¹ In sharp contrast, there is no steric repulsion in the complex R/R,R/R-3a. As a result, (*R*)-DABNTf could complex only with the single enantiomer R/R,R-2a after isomerization of the opposite enantiomer S/S,S-2a (Fig. 3).

In summary, we have succeeded in the dual chirality (axial chirality and center chirality) control of Pd complexes bearing *tropos* secondary amines by chiral (R)-DABNTf rather than (R)-BINOL. Interestingly, it is clarified by X-ray analyses that the N-substituents of the diamine moiety adopt axial orientations in both the dichloride and DABNTf complexes.



Fig. 3 ORTEP drawing of complex 3a.



Fig. 4 Enantiomer discrimination of (R)-DABNTf.

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Notes and references

‡ Crystal data for 2a in X-ray analysis: formula C26H24Cl2N2Pd·CH2Cl2, monoclinic, space group $P2_1/n$, a = 14.333(5) Å, b = 10.700(4) Å, 1.534 g cm^{-3} , $\mu = 10.97 \text{ cm}^{-1}$, $F_{000} = 1264.0$. All measurements were made on a Rigaku Saturn CCD area detector with graphite monochromated Mo-K α ($\lambda = 0.71070$ Å) radiation at 193 K and the structure was solved by direct methods (SIR92). Of the 24204 reflections that were collected, 7849 were unique ($R_{int} = 0.054$). R = 0.094, Rw = 0.144, goodness of fit = 1.000, shift/error = 0.000. CCDC reference number 277174. Crystal data for 2c in X-ray analysis: formula C34H28Cl2N2Pd, monoclinic, space group P21/n, a = 8.376(3) Å, b = 14.977(6) Å, c = 22.767(9) Å, $\beta = 93.923(5)^{\circ}$, $V = 2849.4(19) \text{ Å}^3, Z = 4, D = 1.496 \text{ g cm}^{-3}, \mu = 8.65 \text{ cm}^{-1}, F_{000} = 1304.0.$ All measurements were made on a Rigaku Saturn CCD area detector with graphite monochromated Mo-K α ($\lambda = 0.71070$ Å) radiation at 193 K and the structure was solved by direct methods (SIR92). Of the 25322 reflections that were collected, 8328 were unique ($R_{int} = 0.042$). R = 0.070, Rw = 0.112, goodness of fit = 0.770, shift/error = 0.000. CCDC reference number 277175. Crystal data for 3a in X-ray analysis: formula $C_{25}H_{19}Cl_{1.5}F_3N_2O_3Pd_{0.5}S$, tetragonal, space group $P4_32_12$, a 12.3252(5) Å, b = 12.3252(5) Å, c = 33.675(3) Å, V = 5115.6(5) Å³, $Z = 8, D = 1.534 \text{ g cm}^{-3}, \mu = 6.76 \text{ cm}^{-1}, F_{000} = 2388$. All measurements were made on a SMART APEX diffractometer with CCD detector using Mo-K α ($\lambda = 0.71073$ Å) radiation at 90 K and the structure was solved by direct methods (SHELXL97). Of the 51634 reflections that were collected, 4678 were unique ($R_{int} = 0.0628$). R = 0.0745, Rw = 0.1860, goodness of fit = 1.179, shift/error = 0.003, the Flack parameter = 0.06(7). CCDC 277176. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b510910h

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