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

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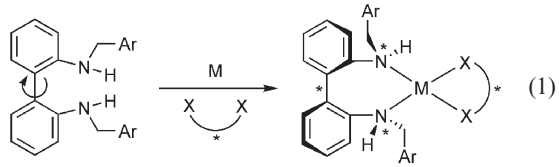
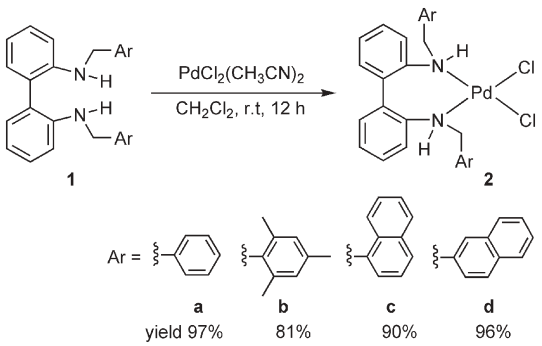
Axial and center chirality of Pd complexes with *tropos* biphenyl secondary diamine ligands is shown to be controlled by chiral amide (*R*)-DABNTf, which can efficiently discriminate between two enantiomeric Pd complexes.

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 enantio-pure 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 chirality[6] and axial chirality[7] in Pd complexes with the *tropos* diamines bearing the biphenyl backbone like BIPHEP ligands (Eq. 1).



(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/H_2O 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 the diamines **1a–d** with $PdCl_2$(cod) failed. However, complexation of $PdCl_2(CH_3CN)_2$ 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 ^{1}H 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 $PtCl_2(CH_3CN)_2$ 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 ^{1}H NMR.



(2)

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

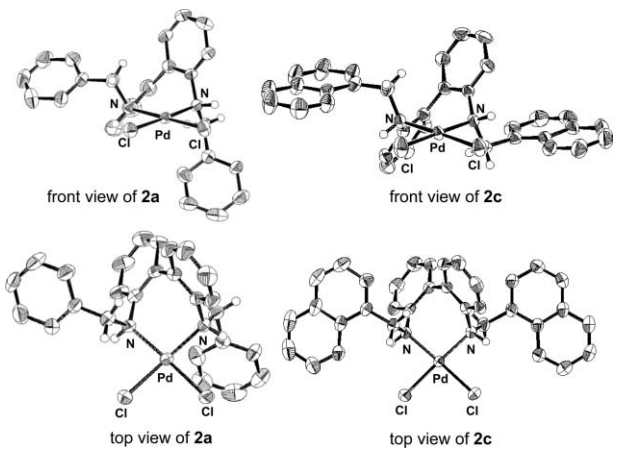


Fig. 1 ORTEP drawings of complexes **2a** and **2c**.

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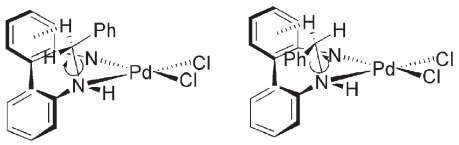
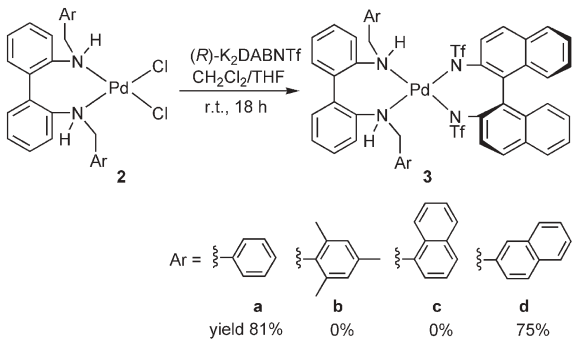


Fig. 2 Axial orientations of the *N*-substituents of complex **2a**.

backbone.[6,10] It was indicated that there were C*H*–π 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 C*H*–π interactions (Fig. 2).

The racemic complex **2a** in dichloromethane at room temperature did not complex with a soluble chiral source (*R*)-M_2BINOL (M = Na, K) in THF obtained by *in situ* deprotonation of (*R*)-BINOL with MO^{t}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 ^{1}H and ^{19}F 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*)-K_2DABNTf, to give the single diastereomer **3d** in 75% yield.



(3)

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.

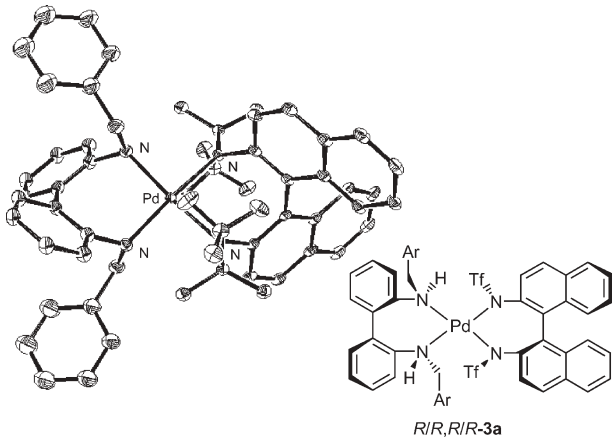


Fig. 3 ORTEP drawing of complex **3a**.

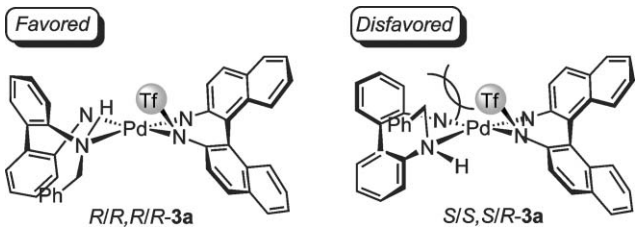


Fig. 4 Enantiomer discrimination of (*R*)-DABNTf.

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Notes and references

‡ *Crystal data for* ***2a*** *in X-ray analysis*: formula $C_{26}H_{24}Cl_2N_2Pd{\cdot}CH_2Cl_2$, monoclinic, space group $P2_1/n$, a = 14.333(5) Å, b = 10.700(4) Å, c = 17.692(6) Å, β = 91.002(5)°, V = 2712.8(16) Å^3, Z = 4, D = 1.534 g cm^{-3}, μ = 10.97 cm^{-1}, F_{000} = 1264.0. All measurements were made on a Rigaku Saturn CCD area detector with graphite monochromated Mo-Kα (λ = 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 $C_{34}H_{28}Cl_2N_2Pd$, monoclinic, space group $P2_1/n$, a = 8.376(3) Å, b = 14.977(6) Å, c = 22.767(9) Å, β = 93.923(5)°, V = 2849.4(19) Å^3, Z = 4, D = 1.496 g cm^{-3}, μ = 8.65 cm^{-1}, F_{000} = 1304.0. All measurements were made on a Rigaku Saturn CCD area detector with graphite monochromated Mo-Kα (λ = 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) Å^3, Z = 8, D = 1.534 g cm^{-3}, μ = 6.76 cm^{-1}, F_{000} = 2388. All measurements were made on a SMART APEX diffractometer with CCD detector using Mo-Kα (λ = 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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