Asymmetric Catalysts

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Enantiodiscrimination and Enantiocontrol of Neutral and Cationic Pt^{II} Complexes Bearing the *Tropos* Biphep Ligand: Application to Asymmetric Lewis Acid Catalysis**

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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 that bear chiral and atropisomeric ligands, which require the enantioresolution and synthetic transformation of a chiral pool (atropisomeric is from the Greek *atropos*, *a* meaning not and *tropos* meaning turn).[2] However, we have already demonstrated that chirally flexible (*tropos*) 2,2′-bis(diphenylphosphanyl)biphenyl (biphep)[3] can act as a chiral ligand for Ru,[4] Rh,[5] and Pd[6] complexes through axial chirality control by chiral diamines. Therefore, the biphep complexes of Ru, Rh, and Pd can provide high levels of enantioselectivity in asymmetric hydrogenation, ene-type cyclization, and hetero-Diels–Alder reactions, respectively. Similarly, in the neutral biphep–Pt complex the chirality

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[**] Biphep is 2,2′-bis(diphenylphosphanyl)biphenyl.

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control of the biphep moiety by chiral 1,1'-binaphthalene-2,2'-diol (binol) was reported not high enough (95:5) and hence recrystallization was essential to obtain the single biphep–Pt diastereomer and enantiomer.[7a,b]

Herein, we report the complete chirality control of both neutral and cationic biphep–Pt complexes without the need for recrystallization and the application of this complex to asymmetric Lewis acid catalysis (Scheme 1). Interestingly, both enantiopure (*S*)- and (*R*)-biphep–Pt complexes can be obtained quantitatively through enantiodiscrimination by using (*R*)-2,2′-bis(trifluoromethanesulfonylamino)-1,1′-binaphthyl (dabnTf) and (*R*)-2,2′-diamino-1,1′-binapthyl (dabn) with the same absolute configuration.

The highly effective enantiodiscriminating agent dabnTf was first used for enantiomer-selective complexation[8] of the neutral racemic biphep-$PtCO_3$ complex **1** (Figure 1)[7a] with complete enantiomer discrimination. Complexation of racemic complex **1** and (*R*)-dabnTf at a specified temperature was monitored by NMR spectroscopy until product (*S*)/(*R*)-**2** was precipitated. A combination of racemic complex **1** with 1.0 equivalent of (*R*)-dabnTf in [D$_8$]toluene gave the single diastereomer (*S*,*R*)-**2** along with the remaining (*R*)-**1** and (*R*)-dabnTf (0.5 equiv), which form a hydrogen bond between the proton of the diamide and oxygen atom of the carbonate complex (*R*)-**1**. In fact, treatment of [{(*S*)-binap}$PtCO_3$] with (*R*)-dabnTf (1.0 equiv) gave the (*S*,*R*) diastereomer complex, but the combination of [{(*R*)-binap}$PtCO_3$] with (*R*)-dabnTf (1.0 equiv) did not.[8] There was no isomerization of the remaining (*R*)-**1** enantiomer, which did not form a complex with (*R*)-dabnTf even at 50 °C after 120 h (Figure 1). Therefore, these results imply that complex **1** is *atropos* below 50 °C. At higher temperatures, isomerization of complex (*R*)-**1** followed by complexation with remaining (*R*)-dabnTf was observed. These results indicate that complex **1** is *tropos* at higher (> 60 °C) temperatures.

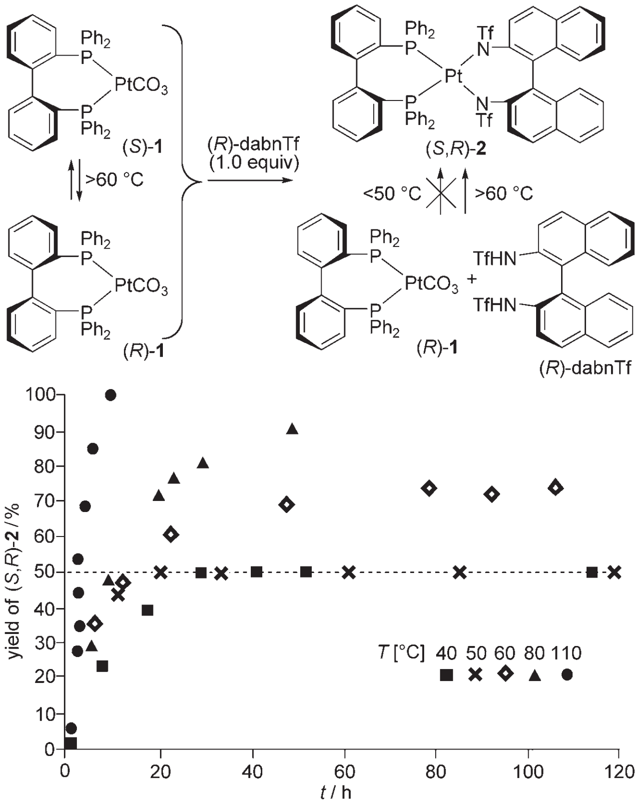
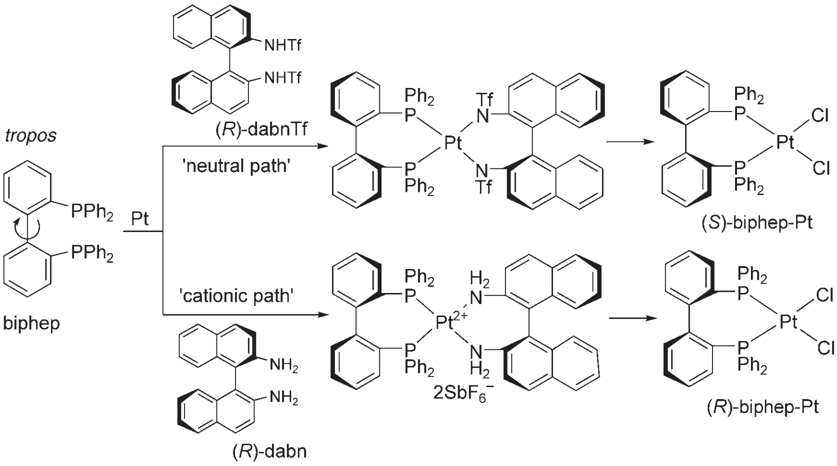


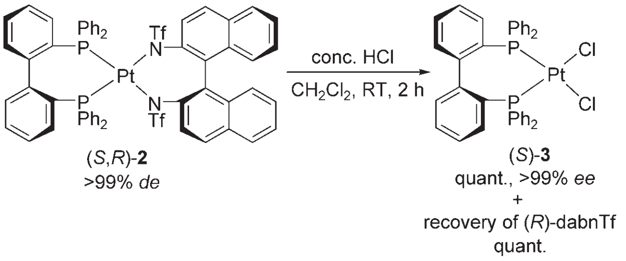
Figure 1. Temperature dependence of the isomerization of complex **1**.



Scheme 1. Complete chirality control of both neutral and cationic biphep–Pt complexes.

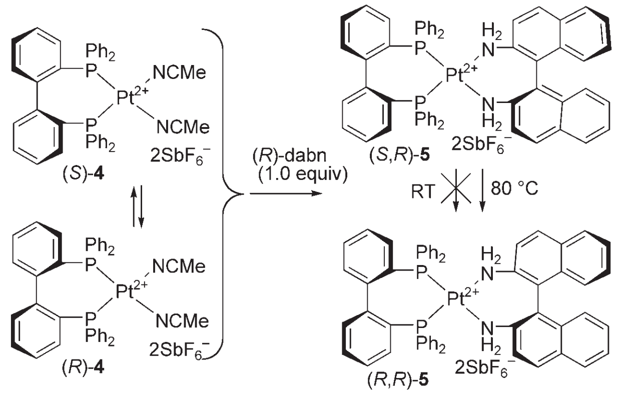
After proving the *atropos* nature of biphep–Pt species even at 50 °C, we tried to isolate the enantiopure biphep–$PtCl_2$ complex **3** without epimerization. Upon addition of concentrated HCl in dichloromethane at room temperature, complex (*S*,*R*)-**2** provided the enantiopure (*S*)-**3** (> 99% *ee*) quantitatively (Scheme 2).[7b] Pure dabnTf could also be recovered quantitatively. The enantiomeric excess (% *ee*) of (*S*)-**3** was determined by ^1H and ^{31}P NMR spectroscopies after complexation with enantiopure (*S*,*S*)-diphenylethylenediamine (dpen) and upon addition of 2.0 equivalents of $AgSbF_6$. In sharp contrast to the Pt complex, the Pd complex was protonated with concentrated HCl in dichloromethane even at 0 °C and the biphep moiety was epimerized (24% *ee*) as biphep–Pd is stereochemically less stable through decomplexation of the sterically demanding dabnTf. These results show that the Pt center coordinates to the biphep diphosphine ligand more strongly than the Pd center.

We also clarified the *atropos* nature of cationic biphep–Pt complexes at room temperature. Chiral diamine



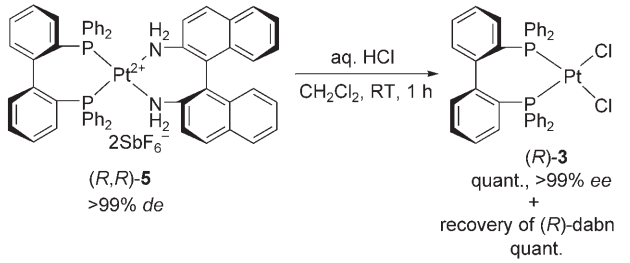
Scheme 2. Quantitative isolation of enantiopure (*S*)-**3**.

dabn was used for nonselective complexation and axial chirality control of the racemic cationic complex **4** (Scheme 3).[6b] With 1.0 equivalent of (*R*)-dabn, complexation of both enantiomers took place to afford a 1:1 ratio of a diastereomer mixture of (*R*,*R*)-**5** and (*S*,*R*)-**5** complexes. The complex **5** bearing (*R*)-dabn did not isomerize at room temperature over 3 days but did isomerize at 80 °C after 30 h to afford exclusively the favorable (*R*,*R*)-**5** (> 99 % *de*). In the Pd complex, the favorable (*R*,*R*) complex is obtained exclusively after an even shorter period.[6b]



Scheme 3. Complete chirality control of cationic biphep–Pt complex **4**.

The complex (*R*,*R*)-**5** provided enantiopure (*R*)-**3** (> 99 % *ee*) quantitatively upon addition of aqueous HCl at room temperature (Scheme 4); dabn could also be recovered quantitatively. The enantiomer excess of (*R*)-**3** was determined by addition of enantiopure dpen under the same conditions as those shown in Scheme 2. The opposite axial chirality to that controlled by its amide (*R*)-dabnTf can be controlled by (*R*)-dabn with the same absolute configuration.



Scheme 4. Quantitative isolation of the enantiopure (*R*)-**3**.

The structure of racemic complex **3** was determined by X-ray crystal structure analysis of a single crystal obtained from dichloromethane/hexane solution.[9] Indeed, the orientations of axial and equatorial phenyl groups in biphep portion were quite similar to those of biphep–Pd complexes.[6,10] In the enantiodiscrimination of the neutral (*R*,*R*)-**2** complex, there is strong steric repulsion between equatorial phenyl group of biphep and the trifluoromethanesulfonyl substituent (Tf) of chiral amide dabnTf (Figure 2 a). In contrast, there is no steric repulsion in complex (*S*,*R*)-**2**. As a result, (*R*)-dabnTf could complex only with the single enantiomer (*S*)-**1** after isomerization of the opposite enantiomer (*R*)-**1**. In the cationic (*S*,*R*)-**5** complex, there is strong repulsion between equatorial phenyl group of biphep and hydrogen atom of chiral diamine dabn. In contrast, there is no steric repulsion in the complex (*R*,*R*)-**5** (Figure 2 b).

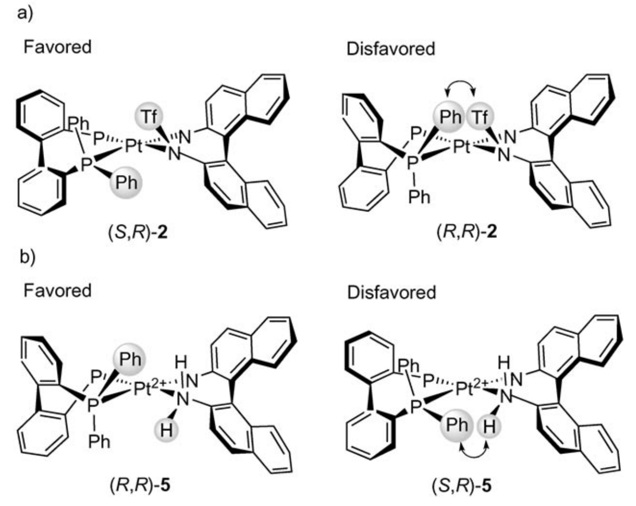
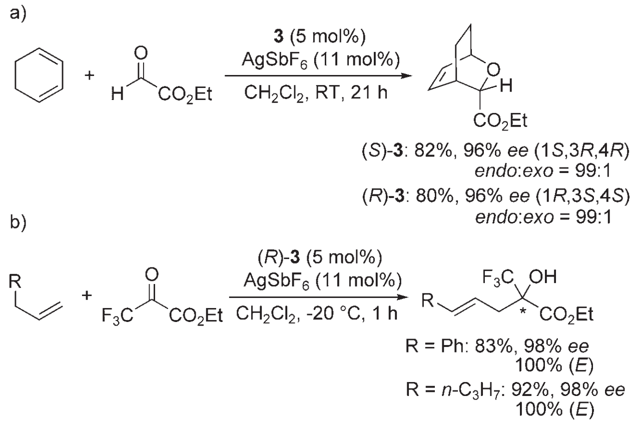


Figure 2. Enantiomer discrimination of (*R*)-dabnTf and (*R*)-dabn.

The enantiopure complex **3** thus obtained can be employed as an *atropos* asymmetric catalyst (Scheme 5).[5–7]



Scheme 5. Enantiopure **3** as an *atropos* asymmetric Lewis acid catalyst.

Indeed, the hetero-Diels–Alder reaction of 1,3-cyclohexadiene with glyoxylate[11] was catalyzed by enantiopure (*S*)-**3** (5 mol %) and $AgSbF_6$ (11 mol %) as a highly efficient Lewis acid catalyst. The hetero-Diels–Alder product was obtained with high enantioselectivity (96 % *ee*, *endo*:*exo* = 99:1) even at room temperature (Scheme 5 a). Use of enantiopure (*R*)-**3** gave the hetero-Diels–Alder product with opposite absolute configuration in equally high selectivity. The complex (*S*)-**3** was obtained with (*R*)-dabnTf, and (*R*)-**3** was obtained with (*R*)-dabn. It was confirmed by addition of enantiopure dpen that racemization of the biphep moiety did not occur during the course of reaction. Additionally, enantiopure dicationic complex **3** gave high chemical yields and high levels of enantio- and *E*-selectivity in carbonyl-ene reactions with trifluoropyruvate and with less reactive monosubstituted olefins (Scheme 5b).[12]

In summary, we have proven that the racemic Pt complexes even with *tropos* biphep ligands can be resolved as the *atropos* complex even at 50 °C but converted at higher temperatures into either enantiopure complex just by exchanging (*R*)-dabn and (*R*)-dabnTf with identical absolute configuration. In carbon–carbon bond-forming reactions, the enantiopure biphep–Pt complexes thus obtained can be used as the *atropos* catalysts to give high enantioselectivity.

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[9] Crystal data for **3**: formula $C_{36}H_{28}Cl_2P_2Pt{\cdot}CH_2Cl_2$, monoclinic, space group $P2_1/n$, $a = 10.406(4)$, $b = 17.887(6)$, $c = 18.695(7)$ Å, $\beta = 94.096(5)^\circ$, $V = 3470.8(21)$ Å^3, $Z = 4$, $D = 1.672\ \mathrm{g\,cm^{-3}}$, and $\mu = 44.52\ \mathrm{cm^{-1}}$. All measurements were made on a Rigaku Saturn CCD area detector with graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å) at 193 K and the structure was solved by direct methods (SIR92). Of the 32323 reflections that were collected, 9997 were unique ($R_{int} = 0.082$). $R = 0.080$, $Rw = 0.171$, goodness of fit = 0.993, and shift/error = 0.008. CCDC 277173 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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