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Dynamic Asymmetric Catalysis by Diphenylphosphinoferrocene (DPPF)–Nickel Complexes through Control of Axial Chirality by Chiral Diamines

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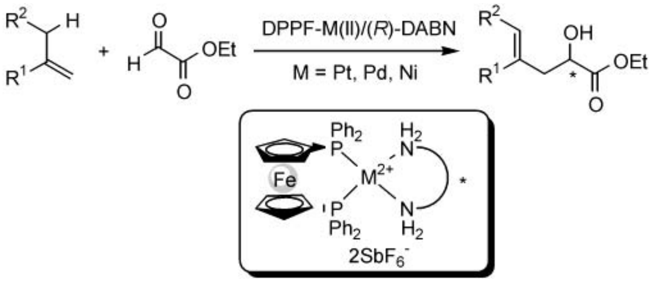
ABSTRACT



The enantio- and diastereomerically pure metal complexes of a chirally dynamic diphenylphosphinoferrocene (DPPF) ligand are obtained through coordination of enantiopure diaminobinaphthyl (DABN) to control the axial chirality of DPPF–Pt, –Pd, and –Ni complexes. The DPPF–Ni catalyst with DABN affords higher enantioselectivity and catalytic efficiency than those attained by the Pd or Pt counterparts and [Ni{(*R*)-dabn}]$(SbF_6)_2$ without DPPF ligand.

The choice of a central metal and design of a chirally stable ligand are key issues in the development of asymmetric catalysts for organic reactions to establish high enantioselectivity and catalyst efficiency.[1] Ferrocenylbisphosphine ligands,[2] such as (*R*)-*N*,*N*-dimethyl-1-[(*S*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine [(*R*)-(*S*)-BPPFA][3] have been used as chirally stable ligands with appendages of chiral centers. By contrast, chirally dynamic diphenylphosphinoferrocene (DPPF) ligands without center and planar chirality have never been used as ligands for chiral metal complexes. Herein, we report the asymmetric catalysis with DPPF ligand through control, by a chiral diamine, of dynamic axial chirality not only in the DPPF−Pd and −Pt catalysts but also in DPPF−Ni catalyst (Scheme 1),[4] the central metal of which is rarely used in asymmetric Lewis acid catalysts.[5]

First of all, a variety of chiral diols and diamines were examined to coordinate to dicationic Pd and Pt complexes with DPPF ligand (DPPF−Pd$(SbF_6)_2$, DPPF−Pt$(SbF_6)_2$) to

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(1) (a) Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H. *Comprehensive Asymmetric Catalysis*; Springer: Berlin, 1999; Vols. 1−3. (b) *Transition Metals for Organic Synthesis*; Beller, M., Bolm, C., Eds.; VCH: Weiheim, 1998. (c) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994. (d) Brunner, H.; Zettlmeier, W. *Handbook of Enantioselective Catalysis*; VCH: Weiheim, 1993. (e) *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993, 2000; Vols. I and II. (f) Kagan, H. B. *Comprehensive Organic Chemistry*; Pergamon: Oxford, 1992; Vol. 8. (g) *Asymmetric Catalysis*; Bosnich, B., Ed.; Martinus Nijhoff Publishers: Dordrecht, 1986.

(2) *Ferrocenes*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, 1995. Kagan, H. B.; Riant, O. In *Advances in Asymmetric Synthesis*, Hassner, A., Ed.; JAI Press: London, Vol. 2, pp 189−235, 1997. Richards, C. J.; Locke, A. J. *Tetrahedron: Asymmetry* **1998**, *9*, 2377. *Metallocene*; Togni, A.; Halterman, R. L., Eds.; Wiley-VCH: Weinheim, 1998.

(3) Hayashi, T.; Ohno, A.; Lu, S.; Matsumoto, Y.; Fukuyo, E.; Yanagi, K. *J. Am. Chem. Soc.* **1994**, *116*, 4421−4226 and references therein. For leading references, see: Deng, W.; You, S.; Hou, X.; Dai, L.; Yu, Y.; Xia, W.; Sun, J. *J. Am. Chem. Soc.* **2001**, *123*, 6508−6519.

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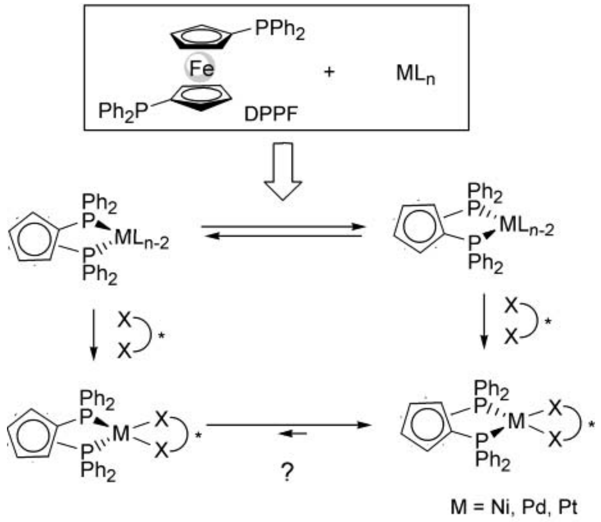
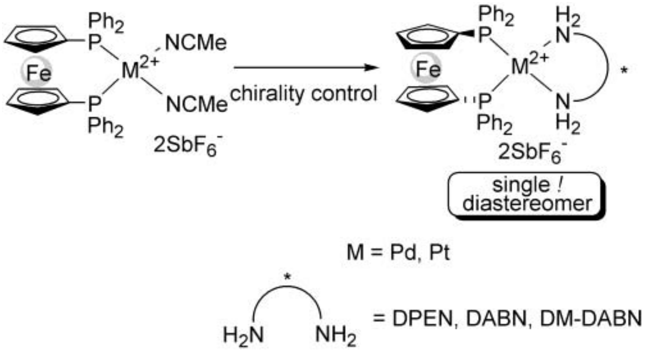
Scheme 1. Dynamic Chirality Control of DPPF Ligand



provide single diastereomeric complexes. Unfortunately, chiral diols such as binaphthols (BINOLs) and their derivatives did not coordinate to the dicationic DPPF−Pd and −Pt complexes. More coordinating diamines such as diphenylethylenediamine (DPEN), diaminobinaphthyl (DABN), and 3,3′-dimethyldiaminobinaphthyl (DM-DABN) did coordinate to control axial chirality of DPPF−Pd and −Pt complexes, giving the single diastereomers within seconds (Scheme 2),[6] e.g., ^{31}P NMR (CDCl$_3$) (*P*)-DPPF−Pd(SbF$_6$)$_2$/(*R*)-DABN, 39.1 ppm.[7] The (*P*)/(*R*)-configuration of the DPPF-M/DABN diastereomer was determined by X-ray analysis of a single crystal of [Pd{(*P*)-dppf}{(*R*)-dabn}](OTf)$_2$ complex obtained from dichloromethane−hexane (Figure 1).[8]

Scheme 2



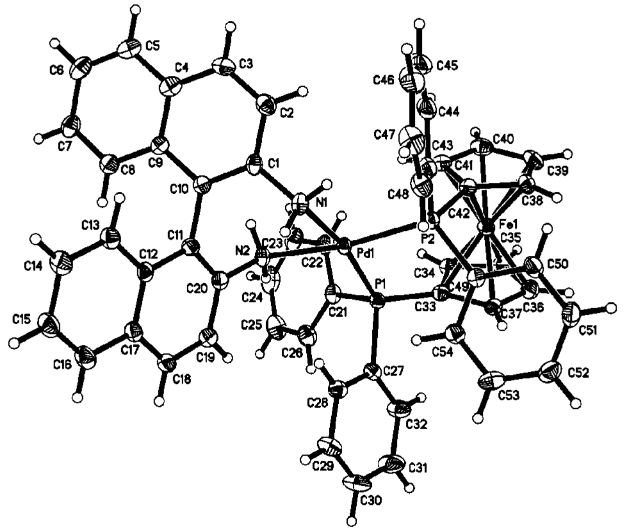


Figure 1. ORTEP drawing of [Pd{(*P*)-dppf}{(*R*)-dabn}]-(OTf)$_2$.

In sharp contrast to the biphenylphosphine (BIPHEP)−Pd and −Pt complexes, the present DPPF counterparts are chirally stable only as the complexes with chirality controllers (X-*-X) (Scheme 1). In turn, the present DPPF complexes are chirally dynamic[9] and subjected to more facile chirality control by chiral diamines than the BIPHEP complexes.

These DPPF−Pd[10] and −Pt complexes with diamine controllers were examined as asymmetric catalysts for carbon−carbon bond forming reactions such as ene reactions. A variety of diamines were examined for the asymmetric ene reaction of ethyl glyoxylate and α-methylstyrene (Table 1). The complex with DPEN hardly catalyzed the glyoxylate-

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(4) Crystal structures of DPPF-M complexes. Pt(dppf)Cl$_2$: Clemente, A.; Corain, B.; Longato, B.; Tiripicchio-Camellini, M.; Pilloni, G. *Inorg. Chim. Acta* **1986**, *115*, L9−11. Pd(dppf)Cl$_2$: Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc*. **1984**, *106*, 158−163. Ni(dppf)Cl$_2$: Casellato, U.; Ajo, D.; Valle, G.; Corain, B.; Longato, B.; Graziani, R. *J. Crystallogr. Spectrosc. Res.* **1988**, *18*, S83−S90.

(5) (a) Kanemasa, S.; Oderanotoshi, Y.; Sakaguchi, S.; Yamamoto, H.; Tanaka, J.; Wada, E.; Curran, D. P. *J. Am. Chem. Soc.* **1998**, *120*, 3074−3088. (b) Iwasa, S.; Tsushima, S.; Shimada, T.; Nishiyama, H. *Tetrahedron Lett.* **2001**, *42*, 6715−6717.

(6) We denote the dppf chirality in terms of descriptors of chirality sense of a helix: (*P*) plus, clockwise; (*M*) minus, counterclockwise.

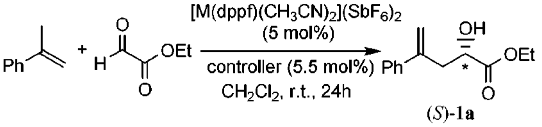
(7) (*P*)-DPPF-Pd(SbF$_6$)$_2$/(*R*)-DABN: ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz) δ 4.21 (br, 4H), 4.52 (br s, 2H), 4.58 (br s, 2H), 4.66 (br s, 2H), 4.85 (br s, 2H), 6.73 (d, J = 9.0 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 7.30 (t, J = 8.1 Hz, 2H), 7.39−7.44 (m, 4H), 7.54−7.67 (m, 8H), 7.76−7.81 (m, 4H), 7.85−7.94 (m, 6H), 8.05 (d, J = 8.1 Hz, 2H), 8.11 (d, J = 9.0 Hz, 2H).

(8) The single-crystal growth was carried out in a hexane/dichloromethane mixed solvent at room temperature. X-ray crystallographic analysis was performed with a Bruker SMART 1000 diffractometer (graphite monochromator, Mo Kα radiation, λ = 0.71073 Å). Crystal data for [Pd{(*P*)-dppf}{(*R*)-dabn}](OTf)$_2$•2CH$_2$Cl$_2$: C$_{58}$H$_{48}$Cl$_4$FeN$_2$O$_6$P$_2$PdS, dark red, crystal dimension 0.51 × 0.36 × 0.25 mm^3, orthorhombic, space group $P2_1$, a = 14.0774(6) Å, b = 13.2027(5) Å, c = 15.4943(7) Å, V = 2879.6(2) Å^3, Z = 2, ρ_{calcd} = 1.630 gcm^{-3}, μ(Mo Kα) = 0.95 cm^{-1}, T = 100 K. 15753 reflections were independent and unique, and 767 with $I > 2\sigma(I)$ ($2\,\theta_{\max}$ = 31.5°) were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. R = 0.0444, w$R2$ = 0.1218. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication N lo. CCDC-173071. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (Fax: (+44) 1223-336-033. E-mail deposit@ccdc.cam.ac.uk) Selective bond lengths [Å], bond angles [deg] and torsion angles [deg]: Pd1−P1 2.3036(9), Pd1−P2 2.2904(9), Pd1−N1 2.169(3), Pd1−N2 2.152(3); P1−Pd1−P2 94.87(3), N1−Pd1−N2 83.53(11): C1−C10−C11−C20 65.92, P1−C33−C42−P2 34.86.

(9) For spectroscopic characteristics of DPPF−Pt(CH$_2$SiMe$_2$R)$_2$ complexes, see: Kelly, R. D.; Young, G. B. *Polyhedron* **1989**, *8*, 433−435. Ankianiec, B. C.; Young, G. B. *Polyhedron* **1991**, *12*, 1411−1421.

(10) [Pd(dppf)(PhCN)$_2$](BF$_4$)$_2$: Oi, S.; Kashiwagi, E.; Terada, E.; Ohuchi, K.; Inoue, Y. *Tetrahedron Lett.* **1996**, *37*, 6351−6354.

Table 1. Effect of Chirality Controller in Glyoxylate-Ene Reaction



(*S*)-**1a**

entry[a]	controller	M	yield (%)[b]	ee (%)[c]
1	DPEN	Pd	trace	-
2	DABN	Pd	92	27
3	DABN	Pt	96	7
4	DM-DABN	Pd	80	44
5	H_8-DABN	Pd	64	24

[a] General reaction conditions: 0.010 mmol of catalyst and 0.011 mmol of controller, 0.24 mmol of ethylglyoxylate, 0.20 mmol of α-methylstyrene in CH_2Cl_2 (1.0 ml). [b] Isolated yield. [c] Determined by HPLC analysis using Daicel CHIRALPAK AS (*n*-hexane/*i*-PrOH 75:25).

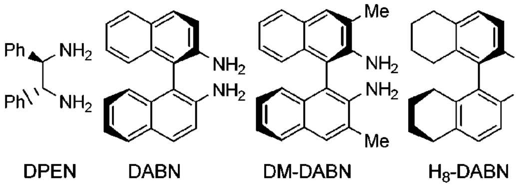
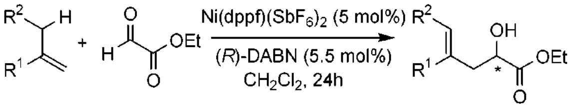
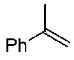
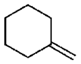


Table 2. Asymmetric Glyoxylate-Ene Reaction Using Ni Complexes



entry	alkene	temp (°C)	yield (%)[a]	ee (%)
1		r.t.	84	90 (*S*)
2[b]		r.t.	87	75 〃
3[c]		r.t.	52	76 〃
4		r.t.	91	92[d] 〃
5		0	14	91 〃
6[e]		60	96	87 〃
7[f]		r.t.	43	45 (*R*)

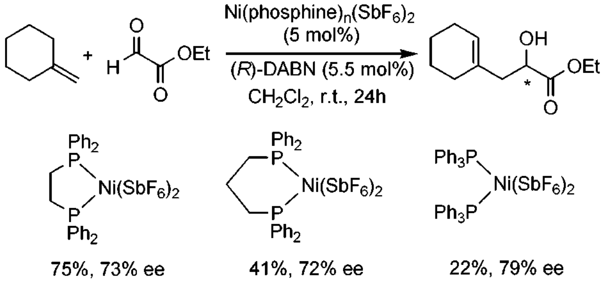
[a] Isolated yield. [b] $Ni(SbF_6)_2$ was used instead of $Ni(dppf)(SbF_6)_2$. [c] $Ni(dppf)(ClO_4)_2$ was used instead of $Ni(dppf)(SbF_6)_2$. [d] Determined by chiral GC analysis using CP-Cyclodextrin-B-2,3,6-M-19 colume. [e] Reaction time was 4 hours. [f] (*R*)-DM-DABN was used instead of (*R*)-DABN.

ene reaction (entry 1). By using DABN, the catalytic activities of Pd and Pt complexes were increased to give virtually quantitative yields (entries 1 vs 2 and 3). DM-DABN provided an increased level of enantioselectivity but lower chemical yield (entry 4). H_8-DABN gave low selectivity and yield (entry 5). Though in low enantioselectivities, the present examples represent a rarely precedented example of the DPPF ligand for asymmetric catalysts even in the well-studied Pd and Pt complexes.

To attain higher enantioselectivity, the more Lewis acidic Ni with higher coordination number was examined as the central metal. Significantly, DPPF−Ni complexes were found to exhibit higher levels of enantioselectivity in the glyoxylate-ene reaction (Table 2).[11] These Ni complexes gave virtually quantitative yields and high levels of enantioselectivity at room temperature (entries 1 and 4). The catalyst without DPPF ligand gave lower enantioselectivity (entry 2). At 0 °C, a decrease in chemical yield was observed down to 14% yield (entry 5). However, even at higher reaction temperature (60 °C), an equally high level of enantioselectivity was obtained along with the quantitative yield (entry 6). Significantly, the choice of the counteranion is critical to obtain high enantioselectivity and chemical yield; the perchlorate counterpart gave chemical yield and enantioselctivity lower than those obtained with the hexafluoroantimonate complex (entries 1 vs 3). DM-DABN as a controller gave lower chemical yield and enantioselectivity, presumably because of the steric shielding effect by the 3,3′-dimethyl groups (entries 4 vs 7).

Thus, the Ni complexes prepared with chirally dynamic DPPF ligand can be used as highly enantioselective catalysts for the carbon−carbon bond forming reaction. Indeed, the efficacy of DPPF ligand is highlighted by the higher enantioselectivity and catalytic activity compared to those obtained with diphenylphosphinoethane (DPPE) and diphenylphosphinopropane (DPPP) ligands (Scheme 3).

Scheme 3. Effects of Phosphine Ligands on Ni Complexes



In summary, we have reported that asymmetric catalysis can be established even by the use of chirally dynamic ferrocenyl DPPF ligands through facile control of axial chirality. Furthermore, those Ni complexes of the DPPF ligand associated with the DABN controller afford high levels of enantioselectivity and chemical yield for in situ asymmetric catalysis of the carbon−carbon bond forming reaction.

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(11) **Typical Experimental Procedure (Table 2).** To a solution of $NiCl_2$(dppf) (0.02 mmol, 5 mol % of alkene) and $AgSbF_6$ (0.04 mmol) in CH_2Cl_2 (2 mL) was added (*R*)-DABN (0.022 mmol) at room temperature under argon atmosphere. After the mixture was stirred at room temperature for 1 h, ethyl glyoxylate (0.5 mmol) and alkene (0.4 mmol) were added and stirred for 24 h. The reaction mixture was directly loaded onto a silica gel column and eluted with hexane/AcOEt (3:1) to give the ene product as an colorless oil.