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**HELICAL CHIRALITY CONTROL OF *TROPOS* SANDWICH-SHAPED  
L<sub>2</sub>M<sub>3</sub> COMPLEXES WITH C<sub>3</sub>-SYMMETRIC  
TRIS(DIPHENYLPHOSPHINOPHENYL)BENZENE LIGAND**

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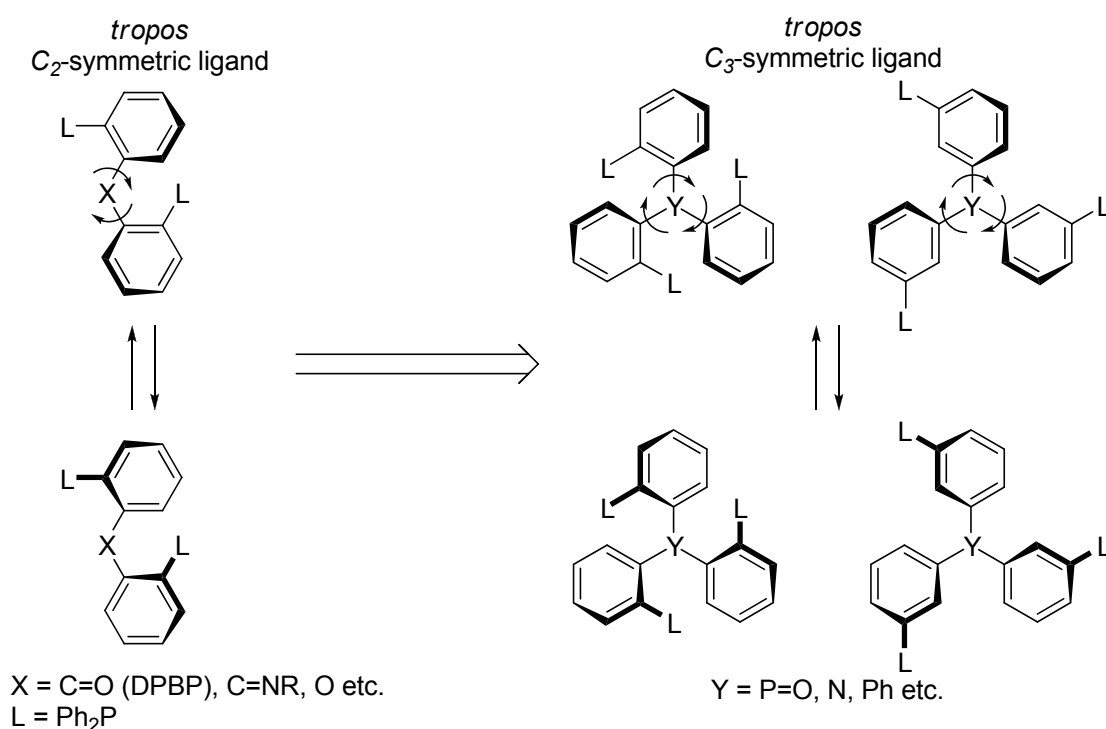
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**Abstract** – The L<sub>2</sub>M<sub>3</sub> complexes with *tropos* C<sub>3</sub>-symmetric ligands interconvert rapidly between the chiral propeller (*P*)- and (*M*)-helicity of the sandwich-shaped L<sub>2</sub>M<sub>3</sub> complexes at room temperature and are chirally controlled to adopt a single helical structure upon complexation with a chiral diamine. The L<sub>2</sub>M<sub>3</sub> complexes chirally controlled can be employed for asymmetric transfer hydrogenation.

In the honor of the celebration for the 80th birthday of Professor Emeritus, Akira Suzuki, Hokkaido University

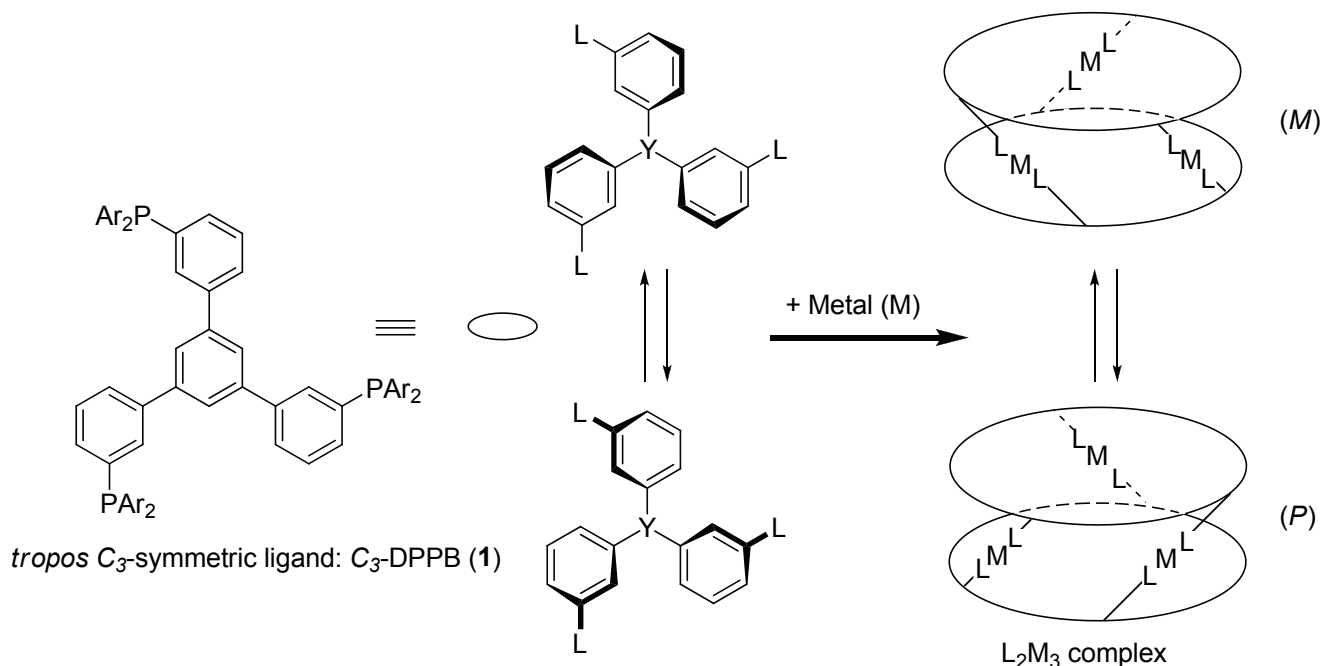
Various asymmetric catalysts with atropisomeric (*atropos* in Greek)<sup>1</sup> ligands have been developed to attain high enantioselectivity.<sup>2</sup> In contrast, we have reported that chirally flexible (*tropos*)<sup>1</sup> benzophenone-derived ligands can be controlled to a single chiral conformation by a chiral activator and to attain higher enantioselectivity.<sup>3,4</sup> For example, *tropos* benzophenone-derived ligands, 2,2'-diphenylphosphinobenzophenones (DPBP) could be chirally controlled to a single conformation with chiral diamines such as 1,2-dipenylethylenediamine (DPEN) to provide higher enantioselectivity in the Ru complex-catalyzed asymmetric hydrogenation of simple ketone substrates (up to >99%, 99% *ee*).<sup>3a,b</sup> DPBP can also be employed to give much higher enantioselectivity than the enantiopure *atropos* BINAP in the Rh complex-catalyzed asymmetric transfer hydrogenation of simple ketone substrates (up to >99%, 99% *ee*).<sup>4</sup> Furthermore, DPBP is now commercially available from Sigma-Aldrich Co. (Catalog No. 845821-92-3). Other *tropos* ligands also adopt a chiral conformation even in a solution phase and

exhibit advantageous properties over *atropos* ligands.<sup>5</sup> In modification of the benzophenone-derived diphenylphosphine ligand (DPBP), the introduction of one more diphenylphosphinophenyl part was executed to construct  $C_3$ -symmetric *tropos* ligands (Scheme 1) which could adopt a chiral propeller conformation. We report here that the  $C_3$ -symmetric *tropos* ligand can also be controlled to a single chiral conformation upon addition of a chiral diamine.



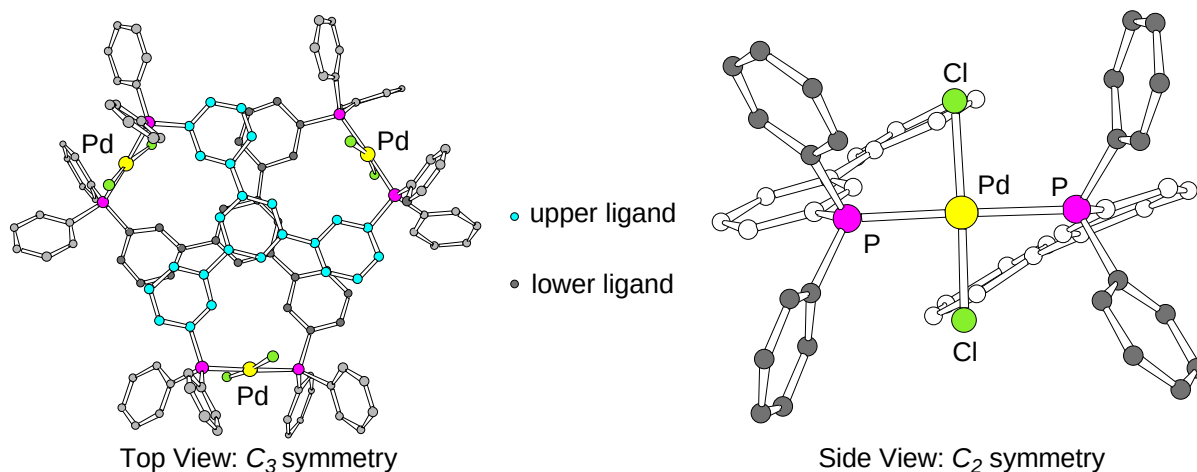
**Scheme 1**

The  $C_3$ -symmetric *tropos* ligand consists of the three coordination parts and the central core (Y). Just like the benzophenone (DPBP) ligand, the rotational barrier around the single bond between the coordinating part and the core (Y) should be low. We synthesized the more stable  $C_3$ -symmetric *tropos* ligand with the coordinating 3-(diphenylphosphino)phenyl part and the benzene core (Y = Ph) (Scheme 2). The 1,3,5-tris(3'-diphenylphosphinophenyl)benzene ( $C_3$ -(diphenylphosphino)phenylbenzene:  $C_3$ -DPPB) was synthesized from 1,3,5-tris(3'-hydroxyphenyl)benzene according to the synthetic method of BIPHEP from biphenol.<sup>5b</sup> 1,3,5-Tris(3'-hydroxyphenyl)benzene was prepared from 1,3,5-tribromobenzene and 3-methoxyphenylboronic acid by the Suzuki-Miyaura coupling.<sup>6</sup>

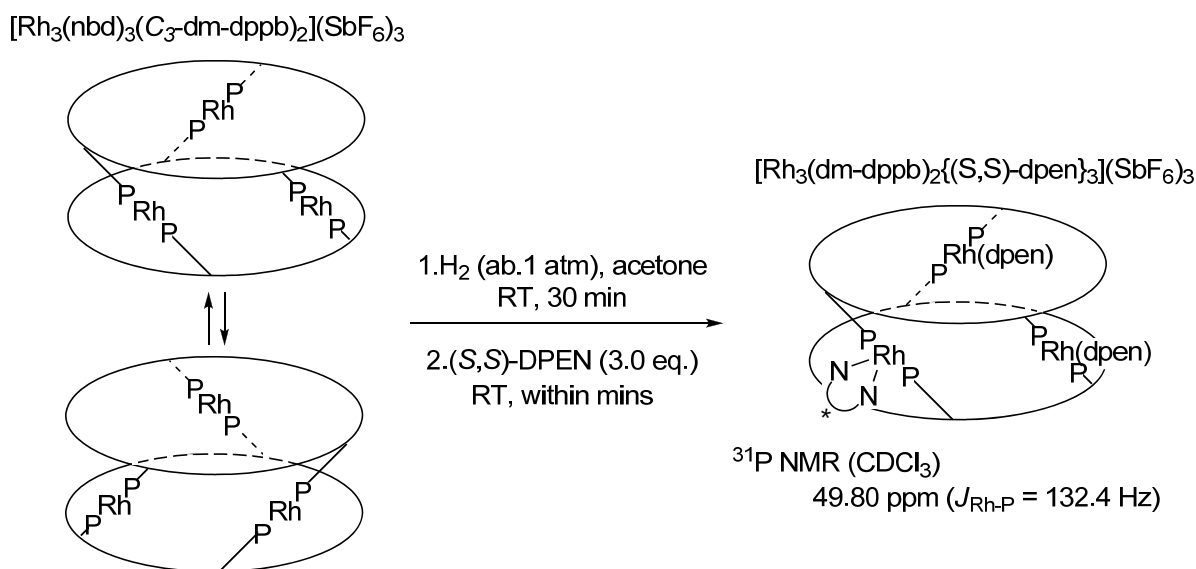
**Scheme 2**

The  $C_3$ -DPPB ligand has three freely rotational single bonds between the phenyl core and, hence, interconverts rapidly between the helical conformations ((P) and (M)). The  $C_3$ -symmetric triphosphine ligands with metal sources (M = Pd, Rh) gave the sandwich-shaped  $L_2M_3$  complexes,<sup>7,8</sup> which rapidly interconverted between (P)- and (M)-helical conformations (Scheme 2).

The X-ray structural analysis of  $Pd_3Cl_6(C_3\text{-dppb})_2$  showed that the  $L_2M_3$  complex with the  $C_3$ -symmetric ligand adopted  $D_3$ -symmetric conformation (Figure 1).<sup>9</sup> The top view of  $Pd_3Cl_6(C_3\text{-dppb})_2$  showed the  $C_3$ -helical conformation. On the other hand, the side view of  $Pd_3Cl_6(C_3\text{-dppb})_2$  showed the  $C_2$ -symmetric conformation around the Pd metal.

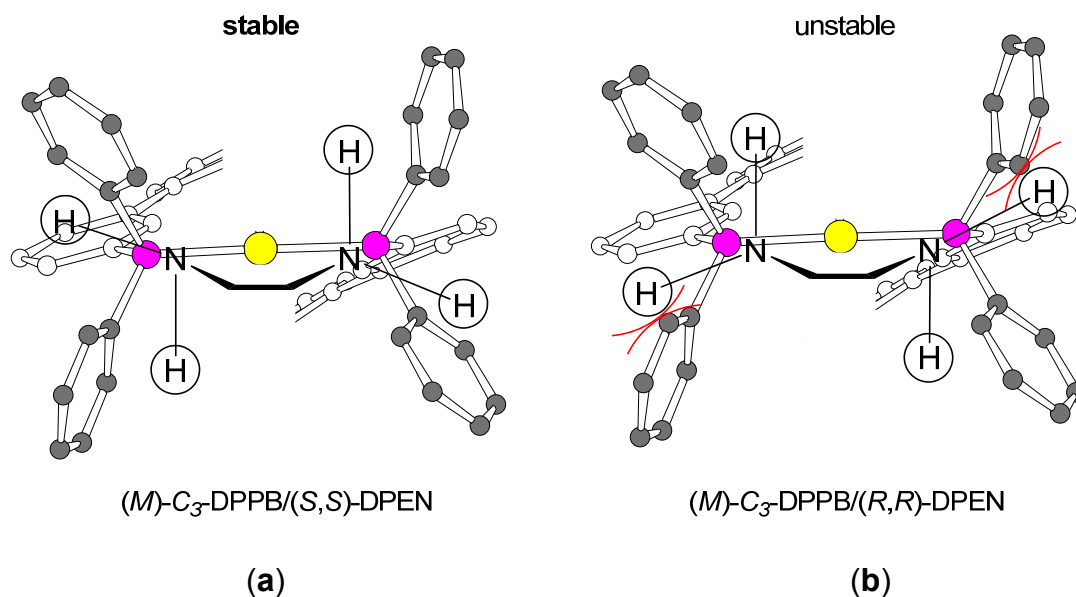
**Figure 1.** X-Ray structural analysis of  $D_3$ -symmetric  $Pd_3Cl_6(C_3\text{-dppb})_2$  complex

The chirality control of the  $L_2M_3$  complexes ( $L = C_3$ -DPPB (**1**: Ar = phenyl) and  $C_3$ -DM-DPPB (**1**: Ar = 3,5-xylyl),  $M = Pd$  and  $Rh$ ) was examined upon addition of (*S,S*)-DPEN. The  $L_2M_3$  complex with  $Rh$  ( $[Rh_3(nbd)_3(C_3\text{-dm-dppb})_2](SbF_6)_3$ )<sup>10</sup> was instantaneously controlled in a single chiral conformation upon complexation with (*S,S*)-DPEN (Scheme 3); The  $Rh$ - $C_3$ -DM-DPPB complex with (*S,S*)-DPEN could form two diastereomers, ((*P*)/(*S,S*) and (*M*)/(*S,S*)) but the  $Rh_3(C_3\text{-dm-dppb})_2[(S,S)\text{-dpen}]_3$  complex was instantly controlled in a single diastereomer.<sup>11</sup> The  $^{31}P$  NMR spectrum of the  $Rh$  complex only showed the doublet peak for the single diastereomer:  $^{31}P$  NMR ( $CDCl_3$ , 162 MHz)  $\delta$  49.80 (d,  $J_{Rh-P} = 132.4$  Hz). The  $Rh_3(C_3\text{-dppb})_2$  complex with (*S,S*)-DPEN was also controlled to a single chiral conformation:  $^{31}P$  NMR ( $CDCl_3$ , 162 MHz)  $\delta$  50.31 ppm (d,  $J_{Rh-P} = 133.6$  Hz). Unfortunately,  $Pd_3Cl_6(C_3\text{-dm-dppb})_2$  were not coordinated with DPEN.



**Scheme 3**

The helicity of diphenylphosphine complexes is thus controlled by chiral diamines where the steric interaction is operative between the equatorial amine protons of the chiral diamines and the phenyl groups on the phosphine ligands;<sup>3-5,12</sup> In Figure 2, the  $C_3$ -DPPB metal complex is exemplified in the (*M*)-conformation. With the equatorial amine protons of (*R,R*)-DPEN (Figure 2b), the phenylphosphine groups in the (*M*)-conformation exhibit the repulsive interaction. Therefore, the  $C_3$ -DM-DPPB- $Rh$  complexes with (*S,S*)-DPEN are deduced to adopt the (*M*)-conformation as shown in Figure 2a.



The Rh complexes with the C<sub>3</sub>-symmetric ligands thus chirally controlled to the single (*M*)-conformation can be used as asymmetric catalysts in the asymmetric transfer hydrogenation.<sup>13,14</sup> Under the reaction conditions, the Rh complex with C<sub>3</sub>-DPPB and (*S,S*)-DPEN was not so stable. To stabilize the C<sub>3</sub>-DPPB complex, the bulky C<sub>3</sub>-DM-DPPB ligand was employed for the transfer hydrogenation of aromatic ketone (Table 1). The C<sub>3</sub>-DM-DPPB-Rh complex with (*S,S*)-DPEN gave the hydrogenation product with 82% *ee* (entry 1). The enantioselectivity thus obtained is higher than that obtained with the *enantiopure* (*R*)-BINAP<sup>4</sup> (entry 3). The C<sub>3</sub>-DM-DPPB-Rh complex was also chirally controlled to a single helical conformation with (*S*)-diaminobinaphthyl (DABN) instead of DPEN but did not provide the hydrogenation product because of the deactivating nature of DABN<sup>12b</sup> (entry 2). The C<sub>3</sub>-DM-DPPB-Rh complex with DPEN thus gave the transfer hydrogenation product with 82% *ee*. The enantioselectivity with the *tropos* C<sub>3</sub>-DM-DPPB-Rh complex is higher than that obtained with the *atropos* and *enantiopure* BINAP counterpart.

**Table 1**

| Entry          | Triphosphine                                         | Diamine             | Yield (%) | <i>Ee</i> (%) |
|----------------|------------------------------------------------------|---------------------|-----------|---------------|
| 1              | DM-DPPB                                              | ( <i>S,S</i> )-DPEN | 77        | 82            |
| 2              | DM-DPPB                                              | ( <i>S</i> )-DABN   | 0         | -             |
| 3 <sup>a</sup> | [Rh{(R)-binap}{( <i>S,S</i> )-dpen}]SbF <sub>6</sub> |                     | 98        | 72            |

a. reaction temp. : 60 °C

DM-DPPB: Ar = 3,5-xylyl

We have thus reported the chirality control of *tropos*  $C_3$ -symmetric triphosphine ligands. The  $C_3$ -symmetric DPPB ligand gave the corresponding *tropos*  $L_2M_3$  complexes of which the helicity can be controlled by chiral diamines such as DPEN to the single helical structure. The *tropos*  $L_2M_3$  complexes thus chirally controlled can be used in the asymmetric transfer hydrogenation of a ketone substrate to attain higher enantioselectivity than the *atropos* and enantiopure BINAP counterpart.

## REFERENCES AND NOTES

1. The word *atropos* consists of “a” meaning “not” and “*tropos*” meaning “turn” in Greek. Therefore, the chirally rigid or flexible nature of a ligand can be called *atropos* or *tropos*, respectively. K. Mikami, K. Aikawa, Y. Yusa, J. J. Jodry, and M. Yamanaka, [Synlett, 2002, 1561](#). Also see: W. Kuhn, 'Stereochemie', ed. by K. Freudenberg, Franz Deuticke, Leipzig, 1933, pp. 803-824.
2. a) 'Catalytic Asymmetric Synthesis' Vol. I and II, ed. by I. Ojima, VCH, New York, 1993, 2000; b) H. Brunner and W. Zettlmeier, 'Handbook of Enantioselective Catalysis', VCH, Weinheim, 1993; c) R. Noyori, 'Asymmetric Catalysis in Organic Synthesis', Wiley, New York, 1994; d) 'Transition Metals for Organic Synthesis', ed. by M. Beller and C. Bolm, VCH: Weinheim, 1998; e) 'Comprehensive Asymmetric Catalysis', Vol. 1-3, ed. by E. N. Jacobsen, A. Pfaltz, and H. Yamamoto, Springer, Berlin, 1999; f) 'New Frontiers in Asymmetric catalysis', ed. by K. Mikami and M. Lantens, Wiley, New York, 2007.
3. a) K. Mikami, K. Wakabayashi, and K. Aikawa, [Org. Lett., 2006, 8, 1517](#); b) K. Wakabayashi, K. Aikawa, and K. Mikami, [Heterocycles, 2008, 76, 1525](#); c) Q. Jing, C. A. Sandoval, Z. Wang, K. Ding, [Eur. J. Org. Chem. 2006, 3606](#); d) K. Wakabayashi, K. Aikawa, and K. Mikami, [J. Am. Chem. Soc., 2008, 130, 5012](#); e) Chirality control of benzophenone-type phosphoramidite ligands by a chiral diene: K. Wakabayashi, K. Aikawa, and K. Mikami, [Heterocycles, 2009, 77, 927](#).
4. K. Mikami, K. Wakabayashi, Y. Yusa, and K. Aikawa, [Chem. Commun., 2006, 2365](#).
5. BIPHEPs-Ru complexes: a) K. Mikami, T. Korenaga, M. Terada, T. Ohkuma, T. Pham, and R. Noyori [Angew. Chem. Int. Ed., 1999, 38, 495](#). BIPHEPs-Pd complexes; b) K. Mikami, K. Aikawa, Y. Yusa, and M. Hatano, [Org. Lett., 2002, 4, 91](#); c) K. Mikami, K. Aikawa, and Y. Yusa, Y. [Org. Lett., 2002, 4, 95](#); BIPHEPs-Rh complexes: d) K. Mikami, S. Kataoka, Y. Yusa, and K. Aikawa, [Org. Lett., 2004, 6, 3699](#); BIPHEPs-Pt complexes: e) J. J. Becker, P. S. White, and M. R. Gagné, [J. Am. Chem. Soc., 2001, 123, 9478](#); f) K. Mikami, H. Kakuno, and K. Aikawa, [Angew. Chem. Int. Ed., 2005, 44, 7257](#).
6. N. Miyaura and A. Suzuki, [Chem. Rev., 1995, 95, 2457](#).
7. A disk-shaped  $C_3$ -symmetric ligand has been reported to self-assemble to the sandwich-shaped  $L_2M_3$

- complex with appropriate metal ion  $\text{Ag}^+$ : a) H.-J. Kim, D. Moon, M. S. Lah, and J.-I. Hong, [Angew. Chem. Int. Ed.](#), 2002, **41**, 3174; b) S. Hiraoka, K. Harano, T. Tanaka, M. Shiro, and M. Shionoya, [Angew. Chem. Int. Ed.](#), 2003, **42**, 5182; c) S. Hiraoka, T. Tanaka, M. Shiro, and M. Shionoya, [J. Am. Chem. Soc.](#), 2004, **126**, 1214.
8. NMR data of  $\text{Pd}_3\text{Cl}_6(\text{C}_3\text{-dppb})_2$ :  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  6.93 (t, 6H,  $J = 7.8$  Hz), 7.37-7.86 (m, 72H), 8.08 (s, 6H), 9.64 (t, 6H,  $J = 7.5$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  24.79 (s).
9. Crystal data of  $\text{Pd}_3\text{Cl}_6(\text{C}_3\text{-dppb})_2$ : Empirical formula  $\text{C}_{124}\text{H}_{94}\text{Cl}_{18}\text{P}_6\text{Pd}_3$ , triclinic, space group  $P-1$ ,  $a = 14.649(19)$  Å,  $b = 15.602(19)$  Å,  $c = 30.36(4)$  Å,  $\alpha = 103.33(11)^\circ$ ,  $\beta = 93.08(12)^\circ$ ,  $\gamma = 103.33(11)^\circ$ ,  $V = 6528(14)$  Å<sup>3</sup>,  $Z = 2$ , and  $D = 1.387$  Mg/m<sup>3</sup>. The final cycle of full-matrix least-square on  $F^2$  was based on 27699 reflections and 1189 variable parameters and converged to  $R1 = 0.0939$  for 16511 observed reflections and  $wR2 = 0.2984$  for all reflections. Goodness of Fit = 1.099, Shift/Error = 0.001.
10. NMR data of  $[\text{Rh}_3(\text{C}_3\text{-dm-dppb})_2(\text{nbd})_3](\text{SbF}_6)_3$ :  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.26 (br, 72H), 2.36 (br, 6H), 4.13 (d, 6H,  $J = 19.5$  Hz), 4.48-4.72 (m, 12H), 6.78-7.81 (m, 66H);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  29.39 (d,  $J_{\text{Rh-P}} = 155.5$  Hz).
11. NMR data of  $[\text{Rh}_3(\text{C}_3\text{-dm-dppb})_2\{(\text{S,S})\text{-dppe}\}_3](\text{SbF}_6)_3$ :  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.32 (br, 72H), 4.18 (d, 6H,  $J = 7.8$  Hz), 4.86 (d, 6H,  $J = 7.8$  Hz), 4.99 (s, 6H), 6.92-7.67 (m, 96H);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  49.80 (d,  $J_{\text{Rh-P}} = 132.4$  Hz).
12. a) T. Korenaga, K. Aikawa, M. Terada, S. Kawauchi, and K. Mikami, [Adv. Synth. Catal.](#), 2001, **343**, 284; b) M. Yamanaka and K. Mikami, [Organometallics](#), 2002, **21**, 5847.
13. The Rh complex with chiral diamines have been reported as asymmetric catalysts for the transfer hydrogenation: a) K. Mashima, T. Abe, and K. Tani, [Chem. Lett.](#), 1998, 1199; b) K. Murata and T. Ikariya, *J. Org. Chem.*, 1999, **64**, 4447; c) J. X. Gao, H. Zhang, X. D. Yi, P. P. Xu, C. L. Tang, H. L. Wan, and T. Ikariya, [Chirality](#), 2000, **12**, 383; d) X. Wu, D. Vinci, T. Ikariya, and J. Xiao, [Chem. Commun.](#), 2005, 4447.
14. a) S. Gladiali, L. Pinna, G. Delogu, S. De Martin, G. Zassinovich, and G. Mestroni, [Tetrahedron: Asymmetry](#), 1990, **1**, 635; b) P. Gamez, F. Fache, P. Mangeney, and M. Lemaire, [Tetrahedron Lett.](#), 1993, **34**, 6897; c) P. Gamez, B. Dunjic, F. Fache, and M. Lemaire, [J. Chem. Soc., Chem. Commun.](#), 1994, 1417; d) P. Gamez, F. Fache, and M. Lemaire, [Tetrahedron: Asymmetry](#), 1995, **6**, 705.