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HELICAL CHIRALITY CONTROL OF *TROPOS* SANDWICH-SHAPED L_2M_3 COMPLEXES WITH C_3-SYMMETRIC TRIS(DIPHENYLPHOSPHINOPHENYL)BENZENE LIGAND

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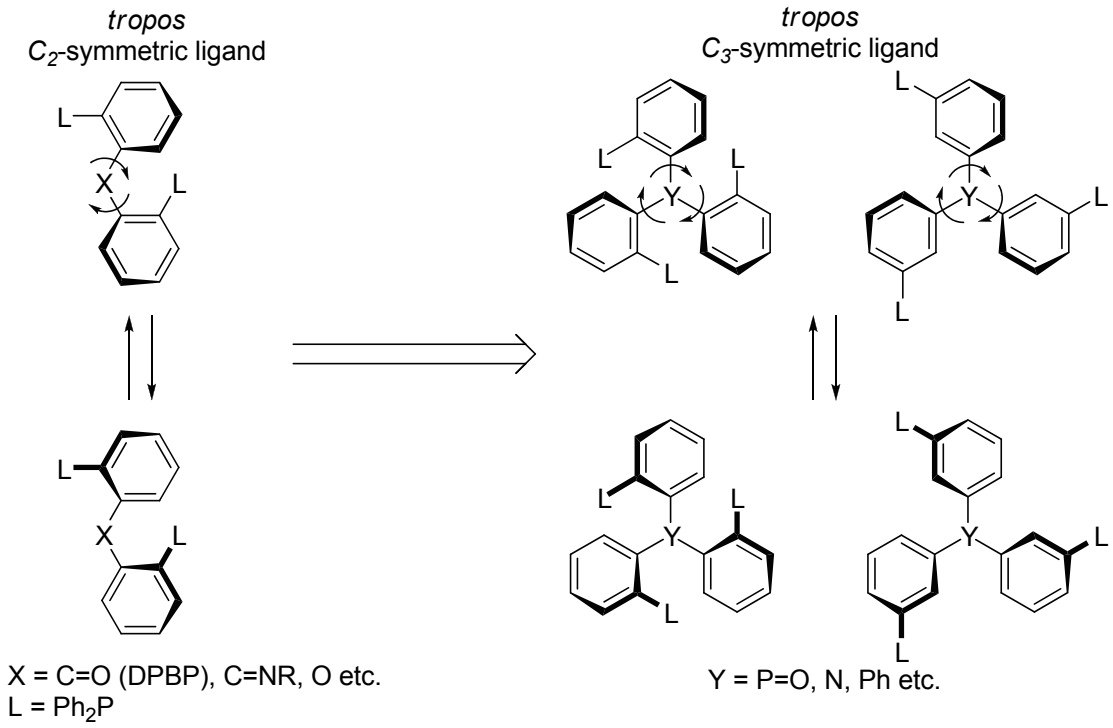
Abstract – The L_2M_3 complexes with *tropos* C_3-symmetric ligands interconvert rapidly between the chiral propeller (*P*)- and (*M*)-helicity of the sandwich-shaped L_2M_3 complexes at room temperature and are chirally controlled to adopt a single helical structure upon complexation with a chiral diamine. The L_2M_3 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

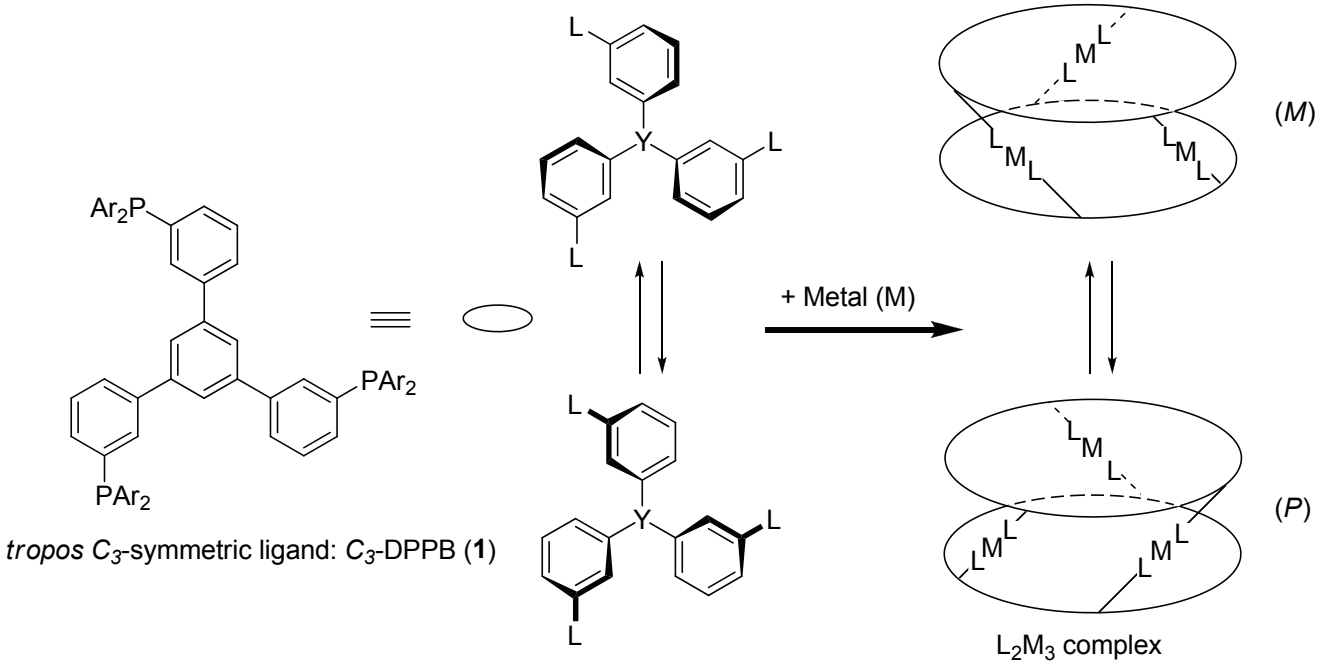
Various asymmetric catalysts with atropisomeric (*atropos* in Greek)[1] ligands have been developed to attain high enantioselectivity.[2] In contrast, we have reported that chirally flexible (*tropos*)[1] benzophenone-derived ligands can be controlled to a single chiral conformation by a chiral activator and to attain higher enantioselectivity.[3,4] 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*).[3a,b] 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*).[4] 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.[5] 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.[5b] 1,3,5-Tris(3'-hydroxyphenyl)benzene was prepared from 1,3,5-tribromobenzene and 3-methoxyphenylboronic acid by the Suzuki-Miyaura coupling.[6]



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,[7,8] which rapidly interconverted between (*P*)- and (*M*)-helical conformations (Scheme 2).

The X-ray structural analysis of $Pd_3C1_6(C_3\text{-dppb})_2$ showed that the L_2M_3 complex with the C_3-symmetric ligand adopted D_3-symmetric conformation (Figure 1).[9] The top view of $Pd_3C1_6(C_3\text{-dppb})_2$ showed the C_3-helical conformation. On the other hand, the side view of $Pd_3C1_6(C_3\text{-dppb})_2$ showed the C_2-symmetric conformation around the Pd metal.

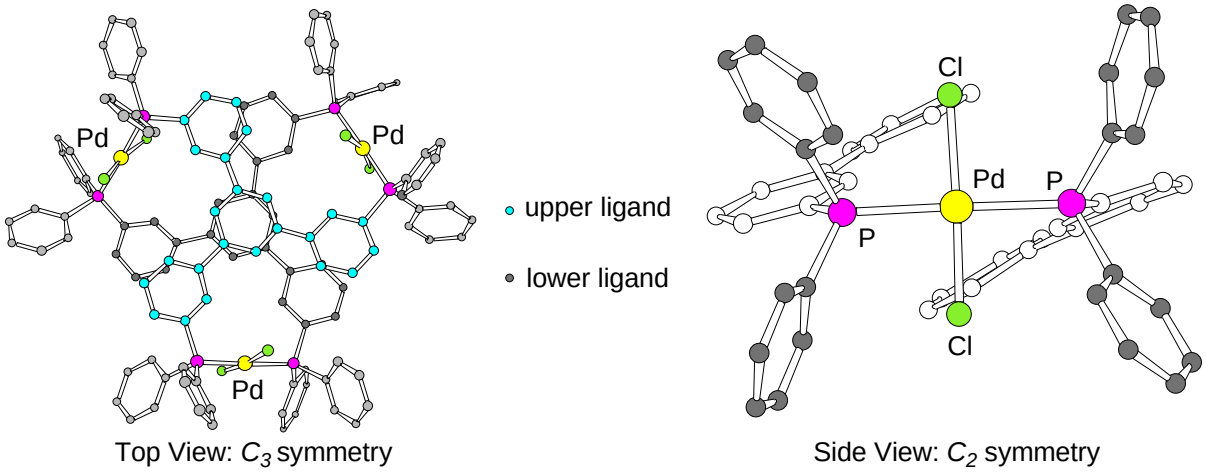
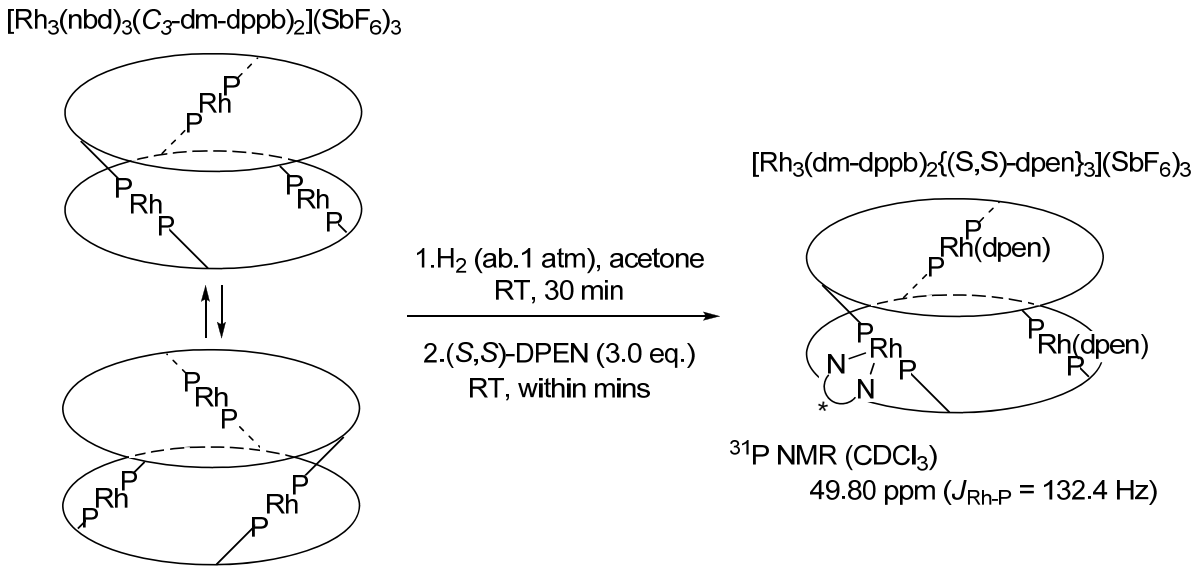


Figure 1. X-Ray structural analysis of D_3-symmetric $Pd_3Cl_6(C_3\text{-dppb})_2$ complex

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 ($[Rh_3(nbd)_3(C_3\text{-dm-dppb})_2](SbF_6)_3$)[10] 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*)-dpen]$_3$ complex was instantly controlled in a single diastereomer.[11] The ^{31}P NMR spectrum of the Rh complex only showed the doublet peak for the single diastereomer: ^{31}P NMR ($CDC1_3$, 162 MHz) δ 49.80 (d, $J_{Rh\text{-}P}$ = 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 ($CDC1_3$, 162 MHz) δ 50.31 ppm (d, $J_{Rh\text{-}P}$ = 133.6 Hz)). Unfortunately, $Pd_3C1_6(C_3\text{-dm-dppb})_2$ 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;[3-5,12] 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.

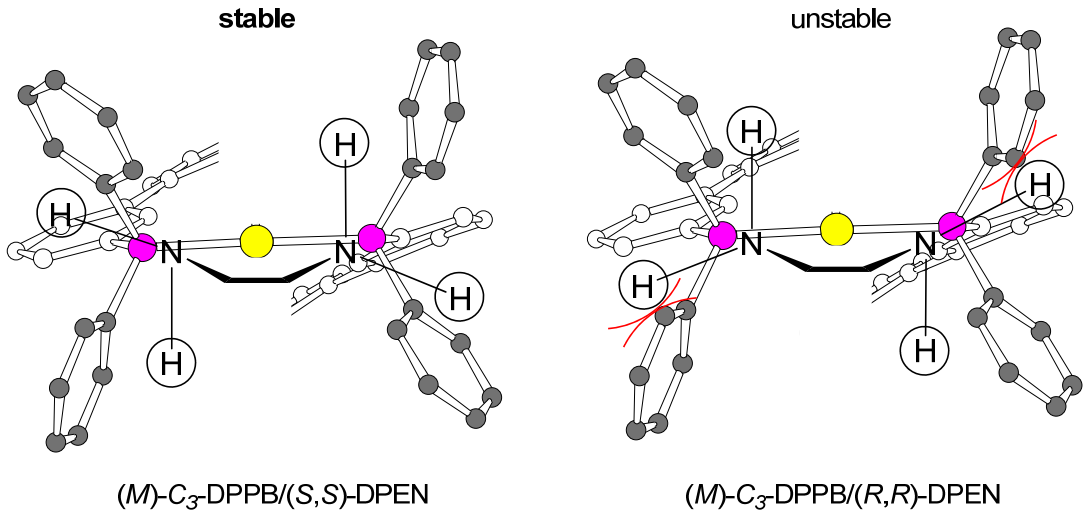
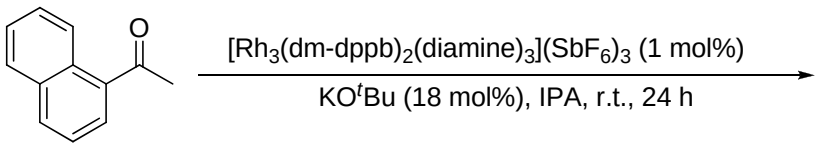


Figure 2 (**a**) (**b**)

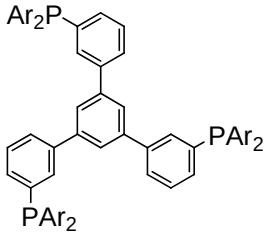
The Rh complexes with the C_3-symmetric ligands thus chirally controlled to the single (*M*)-conformation can be used as asymmetric catalysts in the asymmetric transfer hydrogenation.[13,14] Under the reaction conditions, the Rh complex with C_3-DPPB and (*S*,*S*)-DPEN was not so stable. To stabilize the C_3-DPPB complex, the bulky C_3-DM-DPPB ligand was employed for the transfer hydrogenation of aromatic ketone (Table 1). The C_3-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[4] (entry 3). The C_3-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[12b] (entry 2). The C_3-DM-DPPB-Rh complex with DPEN thus gave the transfer hydrogenation product with 82% *ee*. The enantioselectivity with the *tropos* C_3-DM-DPPB-Rh complex is higher than that obtained with the *atropos* and *enantiopure* BINAP counterpart.

Table 1



Entry	Triphosphine	Diamine	Yield (%)	*Ee* (%)
1	DM-DPPB	(*S*,*S*)-DPEN	77	82
2	DM-DPPB	(*S*)-DABN	0	-
3[a]	[Rh{(*R*)-binap}{(*S*,*S*)-dpen}]SbF_6		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.

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8. NMR data of $Pd_3Cl_6(C_3$-dppb$)_2$: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 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}P NMR ($CDCl_3$, 162 MHz) δ 24.79 (s).
9. Crystal data of $Pd_3Cl_6(C_3$-dppb$)_2$: Empirical formula $C_{124}H_{94}Cl_{18}P_6Pd_3$, triclinic, space group *P*-1, a = 14.649(19) Å, b = 15.602(19) Å, c = 30.36(4) Å, α= 103.33(11)°, β= 93.08(12)°, γ = 103.33(11)°, V = 6528(14) Å^3, Z = 2, and D = 1.387 Mg/m^3. 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 $[Rh_3(C_3$-dm-dppb$)_2(nbd)_3](SbF_6)_3$: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 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}P NMR ($CDCl_3$, 162 MHz) δ 29.39 (d, $J_{Rh\text{-}P}$ = 155.5 Hz).
11. NMR data of $[Rh_3(C_3$-dm-dppb$)_2\{(S,S)$-dpen$\}_3](SbF_6)_3$: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 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}P NMR ($CDCl_3$, 162 MHz) δ 49.80 (d, $J_{Rh\text{-}P}$ = 132.4 Hz).
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