New Chiral Diphosphines, 2,3-Bis(siloxy)-1,4-bis(diphenylphosphino)butanes, and Their Cationic Rh(I) Complexes: Synthesis and Structures

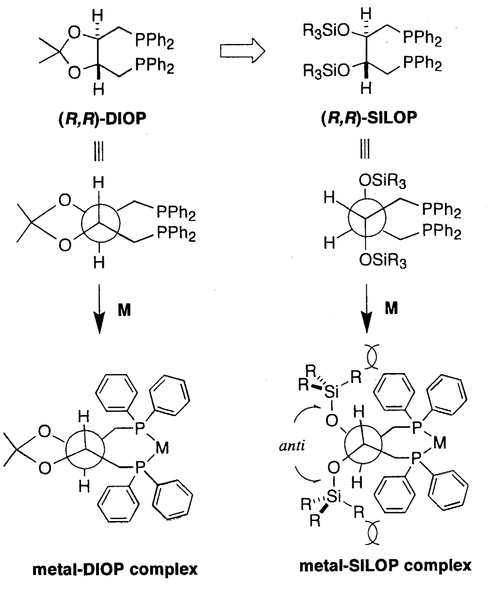
Kohei Tamao,* Kazunori Nakamura, Shigehiro Yamaguchi, Motoo Shiro,† and Seiki Saito*††
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611
†Rigaku Corporation, Akishima, Tokyo 196
††Department of Bioengineering Science, Faculty of Engineering, Okayama University, Tsushima, Okayama 700

(Received August 12, 1996)

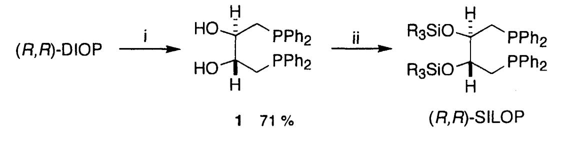
A series of 2,3-bis(siloxy)-1,4-bis(diphenylphosphino)-butanes SILOPs, possessing various siloxy groups, and their Rh(I) complexes have been prepared. The X-ray structure of a SILOP shows a staggered conformation with two siloxy groups in the anti positions. The X-ray crystal structure of a cationic Rh(I)-SILOP complex, however, shows an *anti* arrangement of not the two siloxy groups but the two silyl groups with respect to the O–O axis, which reinforces the C_2-symmetrical environment around the metal center.

Chiral phosphine ligands have played a significant role in various types of transition-metal catalyzed asymmetric synthesis and have still attracted the attention of synthetic organic chemists.[1] Especially, chiral diphosphines of C_2-symmetry are of special interest due to their high asymmetric induction abilities in many catalytic asymmetric reactions.[2] We now report the design and synthesis of new C_2-symmetrical diphosphines, 2,3-bis(siloxy)-1,4-bis(diphenylphosphino)butanes, SILOPs.

One of us has recently introduced a new concept to synthetic organic chemistry that two bulky siloxy groups on the vicinal 2,3-carbon atoms in a butane skeleton may occupy the anti positions in a staggered conformer to fix the chiral environment.[3] We thus primarily anticipated that, if this concept is applicable to SILOPs, the chiral environment could be opposed to that of DIOP[4] in which the conformation is fixed by the cyclic acetonide structure, as visualized in Scheme 1.



Scheme 1.



1 71 % (*R,R*)-SILOP

R_3Si = Me_3Si: **(*R,R*)-TM-SILOP** 78 %
t-$BuMe_2Si$: **(*R,R*)-TBDM-SILOP** 69 %
i-Pr_3Si: **(*R,R*)-TIP-SILOP** 90 %
Ph_3Si: **(*R,R*)-TP-SILOP** 58 %

Reagents and Conditions: i) *p*-TsOH (x 0.2), $EtOH/H_2O$ = 95/5, reflux, 24 h. ii) R_3SiOTf (x 3~4), Et_3N (x 5), CH_2Cl_2, room temp., 1~3 h.

Scheme 2.

A series of (*R,R*)-SILOPs have been prepared in two steps from the commercially available (*R,R*)-DIOP,[4] as shown in Scheme 2. The first step is deprotection of the acetonide using a catalytic amount of *p*-toluenesulfonic acid in ethanol, giving dihydroxy-diphosphine **1** in 71% yield.[5] Diol **1** was next silylated using various silyl triflates[6] and triethylamine to afford four SILOPs, trimethylsiloxy- (TM-), *t*-butyldimethylsiloxy- (TBDM-), triisopropylsiloxy- (TIP-), and triphenylsiloxy- (TP-) SILOPs, in 58–90% yields.[7]

The X-ray crystal structure of TBDM-SILOP is shown in Figure 1.[8] As expected, the two siloxy groups occupy the anti positions in the staggered conformer. Significantly, this is the first clear-cut structural determination of the basic concept mentioned above.

A cationic rhodium(I) complex, {Rh(cod)[(*R,R*)-tp-silop]}SbF_6 **2**, has been prepared from $[Rh(cod)_2]SbF_6$ and (*R,R*)-TP-SILOP (cod = 1,5-cyclooctadiene) by the standard method[9] and characterized by X-ray crystallography.[10] Stereoview of **2** is shown in Figure 2. Noteworthy is that upon formation of the transition metal complexes, the anti conformation is no longer retained; the skeletal conformation has become similar to that of DIOP. Obviously, this conformational

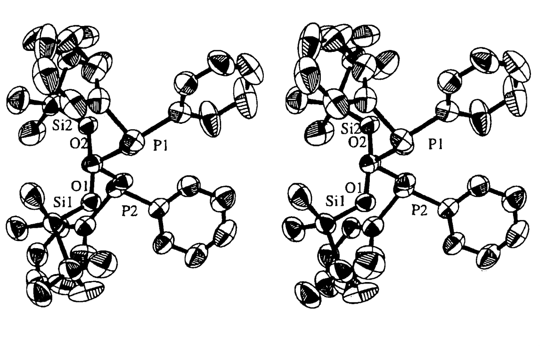


Figure 1. Stereoview of (*R,R*)-TBDM-SILOP as determined by X-ray crystallography.

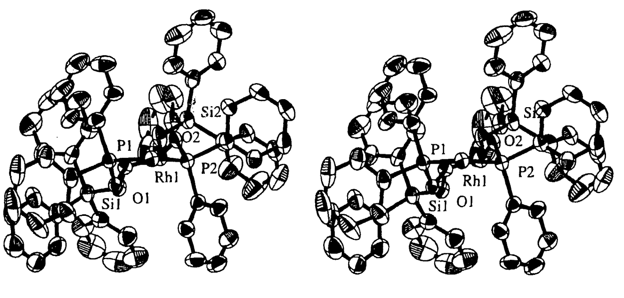
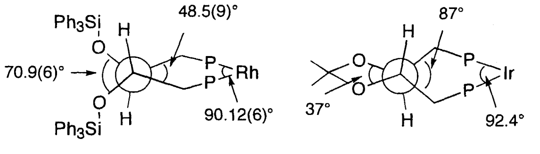


Figure 2. Stereoview of {Rh(cod)[(*R*,*R*)-tp-silop]}SbF_6 as determined by X-ray crystallography; SbF_6 and COD groups are omitted for clarity.



[Rh(cod)(tp-silop)]SbF_6
2

Ir(cod)(diop)Cl
3

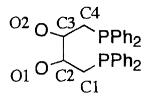


Figure 3. Schematic drawings of X-ray crystal structures of **2** and **3**.

change has occurred which avoids the severe steric congestion present in the anti-conformer of the ligand. Instead, in the complex, the two silyl groups are oriented far from each other to minimize mutual steric repulsion; the Si-O--O-Si array is close to the anti conformation. In such an anti arrangement, the R groups on the silicon atoms become close to the phenyl groups on the phosphorus atoms, to cause reinforcement of the chiral environment around the transition metal center. Thus, as seen from the structure shown in Figure 2, the "equatorial" phenyl groups[1a] on the phosphorus atoms are fixed by the phenyl groups on the silicon atoms from the backside. This concept is unique to the SILOP-complexes as visualized in Scheme 1 for comparison with the DIOP complexes.

Structural comparisons have been made between the metal-SILOP complex **2** and a metal-DIOP complex, Ir(cod)(diop)Cl **3**,[11] as shown in Figure 3, although a strict comparison could not be made because of no reported crystal structures of the cationic Rh(I)-DIOP complexes in the literature.[12] The most significant differences between **2** and **3** are the dihedral angles along with the C2-C3 bond; the angle ∠O1-C2-C3-O2 (71°) in **2** is fairly larger than that in **3** (37°), resulting in the smaller dihedral angle ∠C1-C2-C3-C4 in **2** (49°) comparing with that in **3** (87°).

To test the asymmetric induction abilities of SILOPs as ligands, we have preliminary examined the Rh(I)-complex catalyzed asymmetric hydrogenation of methyl acetamidoacrylate.[13] The reactions were carried out in the presence of a catalytic amount of the Rh(I)/(*R*,*R*)-SILOP complexes prepared in situ from $[Rh(cod)_2]BF_4$ and SILOPs,[14] to give the following results: TM-SILOP, 23%ee (*R*); TBDM-SILOP, 50%ee (*R*); TIP-SILOP, 57%ee (*R*); TP-SILOP, 69%ee (*R*); cf. (*R*,*R*)-DIOP, 60%ee (*R*);[15] the absolute configurations of the products are given in parentheses. These results clearly indicate that the bulkier the silyl groups on SILOPs, the higher the %ee's. Only the last two afforded asymmetric inductions comparable to or somewhat higher than that with DIOP. This tendency is consistent with the previously mentioned concept. It should be noted that the direction of the asymmetric induction by the (*R*,*R*)-SILOPs is same as that with (*R*,*R*)-DIOP.

Further applications of SILOPs in catalytic asymmetric reactions are currently under study in our laboratory. For one of them, we have already found that SILOPs are effective in the asymmetric synthesis of spirosilanes via catalytic intramolecular hydrosilation. The details will be reported elsewhere.[16]

This work was supported by a Grant-in-Aid for Scientific Research (No. 05234105) from the Ministry of Education, Science, and Culture of Japan. We thank Prof. H. B. Kagan for helpful comments.

References and Notes

1 a) R. Noyori, "*Asymmetric Catalysis in Organic Synthesis*," Wiley, New York (1994). b) "*Catalytic Asymmetric Synthesis*," ed by I. Ojima, VCH Publishers, Inc., New York (1993).
2 H. B. Kagan and M. Sasaki, in "*The Chemistry of Organo-Phosphorus Compounds*." ed by F. R. Hartley, J. Wiley, New York (1990), p. 51.
3 S. Saito, Y. Hirohara, O. Narahara, and T. Moriwake, *J. Am. Chem. Soc.*, **111**, 4533 (1989).
4 H. B. Kagan and T. -P. Dang, *J. Am. Chem. Soc.*, **94**, 6429 (1972). They also reported the "open (*R*,*R*)-DIOP" with OMe groups instead of the ketal.
5 A. Börner, J. Ward, K. Kortus, and H. B. Kagan, *Tetrahedron: Asymmetry*, **4**, 2219 (1993).
6 E. J. Corey, H. Cho, C. Rücker, and D. H. Hua, *Tetrahedron Lett.*, **22**, 3455 (1981).
7 Selected data for (*R*,*R*)-SILOPs. TM-SILOP: $[\alpha]_D^{24} = -10.2$ (*c* 1.25, $CHCl_3$). mp 44-46 °C (dec). TBDM-SILOP: $[\alpha]_D^{24} = -13.4$ (*c* 1.46, $CHCl_3$). mp 95-97 °C (dec). TIP-SILOP: $[\alpha]_D^{26} = +63.8$ (*c* 1.57, $CHCl_3$). mp 73-75 °C (dec). TP-SILOP: $[\alpha]_D^{24} = +10.1$ (*c* 1.04, $CHCl_3$). mp 118-119 °C (dec).
8 Crystal data of (*R*,*R*)-TBDM-SILOP (instrument; Rigaku AFC7R): monoclinic space group $P2_12_12_1$ (#19); a = 15.304(2) Å, b = 19.545(2) Å, c = 14.219(2) Å, V = 4252.9(6) $Å^3$, Z = 4, D_c = 1.073 g cm^{-3}, μ (Mo Kα) = 16.88 cm^{-1}, temperature 20 °C, R = 0.051, R_w = 0.082, and S = 1.36; number of unique reflections = 3558.
9 R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, **93**, 2397 (1971).
10 Crystal data of **2** (instrument; Rigaku AFC5R): monoclinic space group $P2_1/c$ (#4); a = 11.704(3) Å, b = 19.185(4) Å, c = 15.019(3) Å, β = 93.88(2)°, V = 3364(1) $Å^3$, Z = 2, D_c = 1.404 g cm^{-3}, μ (Mo Kα) = 7.89 cm^{-1}, temperature 25 °C, R = 0.034, R_w = 0.047, and S = 1.16; number of unique reflections = 6112.
11 S. Brunie, J. Mazan, N. Langlois, and H. B. Kagan. *J. Organomet. Chem.*, **114**, 225 (1976).
12 As a related metal-DIOP complex, the crystal structure of $HRh(diop)_2$ has been reported: R. G. Ball, B. R. James, D. Mahajan, and J. Trotter, *Inorg. Chem.*, **20**, 254 (1981).
13 K. E. Koenig, in "*Asymmetric Synthesis*," ed by J. D. Morrison, Academic Press, New York (1985), Vol. 5, Chap. 3.
14 Asymmetric hydrogenation was carried out under the following conditions: $[Rh(cod)_2]BF_4$ (1 mol%), SILOP (1.2 mol%), H_2 (1 atm), CH_2Cl_2, 15 °C, 24-32 h. The enantiomeric excess of the product was determined by HPLC using SUMICHIRAL OA-3000 (hexane/1,2-dichloroethane/EtOH = 100/20/1).
15 Benzene was used as a solvent: D. Sinou and H. B. Kagan, *J. Organomet. Chem.*, **114**, 325 (1976).
16 K. Tamao, K. Nakamura, H. Ishii, S. Yamaguchi, and M. Shiro, submitted for publication.