Synthesis and Structure of Chiral (*R*)-2,2'-Bis-Silyl-Substituted 1,1'-Binaphthyl Derivatives

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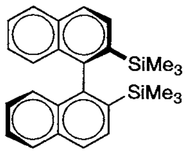
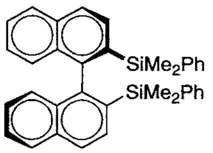
First synthesis of optically active 2,2'-bis-silyl-substituted 1,1'-binaphthyl derivatives, (*R*)-(+)-2,2'-bis(trimethylsilyl)-1,1'-binaphthyl ((*R*)-(+)-**1**) and (*R*)-(–)-2,2'-bis(dimethylphenylsilyl)-1,1'-binaphthyl ((*R*)-(–)-**2**), has been accomplished by the direct bis-silylation of chiral 2,2'-dibromo-1,1'-binaphthyl (DBBN). The molecular structure and the absolute configuration of (*R*)-(–)-**2** have been determined by means of X-ray crystallography.

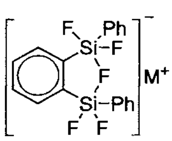
Chiral Lewis acids have been playing a major role as catalytic as well as stoichiometric reagents in the contemporary organic synthesis. The electron-deficient main group and transition metal elements such as boron, aluminum, tin, and titanium have been extensively employed as successful chiral Lewis acids. Silicon, which is also the positively charged element, would be promising the well-designed chiral Lewis acid, though utility of the organosilicon compounds as Lewis acids has been rather limited in the synthetic chemistry due to its low Lewis acidity. However, Tamao recently reported enhanced Lewis acidity of *ortho*-bis(fluorosilyl)benzene (**3**), in which bidentate Lewis acidic silicon atoms cooperatively show much stronger Lewis acidity than corresponding mono-silane.[1] They found that the synchronized mode of two silicon atoms chelate a fluoride anion to collaborate on the rigid Si---F---Si bridging structure. Since then, there has been rapidly growing interest in the bidentate and tridentate organosilicon compounds (**4**, **5**) from the structural, reactive, and mechanistic points of view.[2] Last year, Maruoka reported the synthetic application of the *ortho*-phenylene bis-allylsilane to the allylation of various aldehydes.[3] To the best of our knowledge, however, optically active multidentate organosilicon compounds have rarely been reported. We anticipated that C_2 symmetrical 1,1'-binaphthyl skeleton, which has achieved remarkable success in asymmetric synthesis, would be the most suitable for the construction of the chiral bidentate bis-silyl Lewis acid.[4] We wish herein to report the first synthesis of chiral 2,2'-bis-silyl-substituted 1,1'-binaphthyl derivatives, (*R*)-(+)-2,2'-bis(trimethylsilyl)-1,1'-binaphthyl ((*R*)-(+)-**1**) and (*R*)-(–)-2,2'-bis(dimethylphenylsilyl)-1,1'-binaphthyl ((*R*)-(–)-**2**),[5,6] by the direct bis-silylation of chiral 2,2'-dibromo-1,1'-binaphthyl (DBBN) (Scheme 1). We have also determined the molecular structure and the absolute configuration of (*R*)-(–)-**2** by means of X-ray crystallography.



(*R*)-(+)-**1**



(*R*)-(–)-**2**



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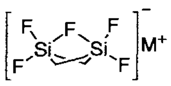

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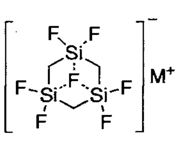

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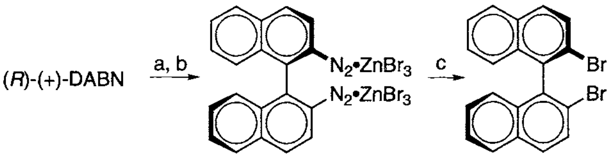
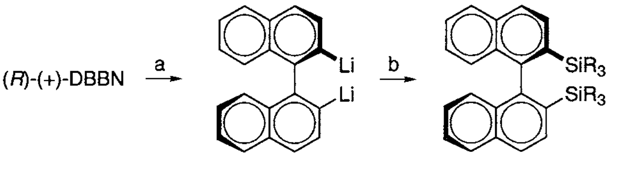
$M^+ = K^+$, 18-crown-6

For the preparation of chiral DBBN, it is not suitable to apply the conventional Sandmeyer reaction of optically active 2,2'-diamino-1,1'-binaphthyl (DABN) which may result in considerable racemization of the product.[7] Murdoch reported the preparation of chiral DBBN from the corresponding 2,2'-bis(diazonium tribromomercurate)-1,1'-binaphthyl followed by the thermal decomposition of the dry salt in the presence of excess KBr. However, mercury is a highly toxic metal and the reaction temperature must be rigorously controlled to suppress the racemization of binaphthyl skeleton.[8] Mildness and simplicity of operation without toxic wastes should provide new entry to versatile utilities of chiral DBBN. In order to improve such drawbacks, we investigated alternative procedures and then found that chiral DBBN was able to be furnished in comparable yield by the thermal decomposition of the chiral 2,2'-bis(diazonium tribromozincate)-1,1'-binaphthyl, which was prepared by the diazotization of chiral DABN followed by addition of $ZnBr_2$/KBr, with excess of KBr in refluxing cyclohexane solution (Scheme 1). The filtration of zinc salt followed by evaporation of cyclohexane provided optically active DBBN having the specific rotation $[\alpha]_D^{20}$ = +31.2° (*c* 1.00, pyridine) in 67% yield. Optical purity of DBBN was estimated at 95% ee on the basis of lit. value.[8] This procedure is superior in viewpoint of safety because disuse of toxic mercury salt. The facile control of the reaction temperature restricted under boiling point of cyclohexane is also advantageous to avoiding the racemization of DBBN.



Scheme 1. Reagents and conditions: (a) $NaNO_2$, H_2SO_4, 0 °C. (b) 4 equiv $ZnBr_2$/KBr. (c) 10 equiv KBr, *c*-C_6H_{12}, reflux, 2h, 67% yield (95% ee) (3 steps).

Synthesis of (*R*)-(+)-**1** and (*R*)-(–)-**2** was investigated by the direct bis-silylation of chiral DBBN as shown in Scheme 2. Dilithiation of optically active (*R*)-(+)-DBBN (95% ee) was carried out at –60 °C using 2.2 equiv of *n*-BuLi for 30 min. After the solution was cooled to –90 °C, 4-fold excess of Me_3SiCl was added over 10 min and stirring was continued for 4 h at –60 °C. After purification by MPLC followed by enantio-enrichment of (*R*)-(+)-**1** through the repeated removal of minor (*S*)-(–)-**1** as racemic powder from hexane until constant specific rotation, optically active (*R*)-(+)-**1** was isolated as viscous oil in 15% yield



(*R*)-(+)-**1** : $SiR_3 = SiMe_3$
(*R*)-(–)-**2** : $SiR_3 = SiMe_2Ph$

Scheme 2. Reagents and conditions: (a) 2.2 equiv *n*-BuLi, THF, –60 °C, 30 min. (b) 4 equiv Me_3SiCl or $PhMe_2SiF$, –90 °C to –60 °C, 4h.

having the specific rotation $[\alpha]_D^{20} = +43.7°$ (*c* 0.87, cyclohexane). However, the exact determination of $[\alpha]_D^{20}$ value was uncertain at present because recrystallization purification was ineffective for the oily (*R*)-(+)-**1** in spite of crystalline racemic **1** (mp 109-112 °C). Fortunately, optically pure (*R*)-(–)-**2** was able to be obtained as colorless crystals (mp 129-130 °C). According to the similar synthetic procedure for (*R*)-(+)-**1**, the bis-silylation reaction using $PhMe_2SiCl$ proceeded only above –44 °C; threshold for the preservation of chirality of 2,2'-dilithio-1,1'-binaphthyl dianion.[8] Actually, chirality of bis-silylation product **2** was completely lost. There is no doubt that the steric bulk of $PhMe_2SiCl$ blocked the substitution reaction at low temperature. Thus, we employed the less sterically hindered $PhMe_2SiF$ for the bis-silylation reaction, which smoothly proceeded at –60 °C and dark red dilithio-dianion completely faded within 1 h to give optically active (*R*)-(–)-**2** in 54% yield after the purification by MPLC. Further purification by repeated recrystallizations from hexane until constant $[\alpha]_D^{20}$ value gave optically pure (*R*)-(–)-**2** as colorless crystals in 29% yield having the specific rotation $[\alpha]_D^{20} = -46.7°$ (*c* 1.12, cyclohexane).

Because optically pure single crystals of (*R*)-(–)-**2** in hand, we for the first time characterized the molecular structure and the absolute configuration of the chiral 2,2'-bis-silyl-substituted 1,1'-binaphthyl derivative by means of X-ray crystallography (Figure 1).[9] There was an only one enantiomer (*R*)-(–)-**2** in the unit cell. The space group $P2_12_12$ (#18) also suggests that the unit cell has chirality. The absolute configuration was determined to be (*R*) on the basis of the Flack parameter 0.12(3), which is consistent with the absolute configuration of starting material (*R*)-(+)-DBBN. The dihedral angle of naphthyl planes and the intramolecular distance between two Lewis acidic silicon atoms are the most important factors in the control of the stereochemistry in asymmetric synthesis. The silyl-substituted naphthyl groups are oriented almost perpendicular to each other; the dihedral angles of C(2)-C(1)-C(1')-C(2') is 94(1)°. The intramolecular Si-Si distance (4.88 Å) suggests that the bidentate cavity is satisfactorily wide to accommodate the Lewis bases. The conformational flexibility through rotation about binaphthyl C(1)-C(1') pivot should be expected to optimize the size of the cavity for individual guest molecules in the same manner as BINAP.

In conclusion, we first synthesized the chiral 2,2'-bis-silyl-substituted 1,1'-binaphthyl derivatives (*R*)-(+)-**1** and (*R*)-(–)-**2**. The molecular structure and the absolute configuration of (*R*)-(–)-**2** were also determined by means of X-ray crystallography. Though trialkylsilyl groups have not enough Lewis acidity for the reactions promoted by Lewis acid catalysts, our present work has opened up the possibility in preparing a large variety of chiral bidentate Lewis acids directly substituted by 1,1'-binaphthyl skeleton. Further work for the activation of silyl groups is now on progress.

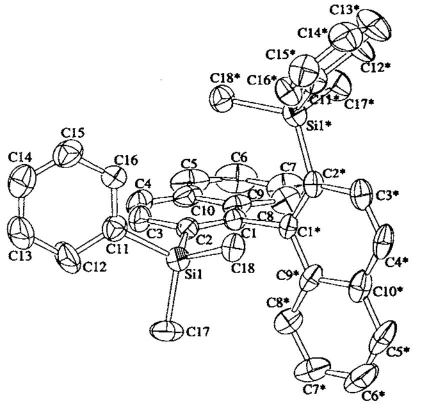


Figure 1. ORTEP drawing of (*R*)-(–)-**2** (30% probability).

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References and Notes

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5 (*R*)-(+)-**1**: viscous oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ –0.32 (s, 18H), 7.10 (d, J = 7.7 Hz, 2H), 7.18 (ddd, J = 8.0 Hz, 6.4 Hz, and 1.6 Hz, 2H), 7.14 (ddd, J = 8.0 Hz, 6.4 Hz, and 1.6 Hz, 2H), 7.73 (d, J = 7.7 Hz, 2H), 7.86 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 8.4 Hz, 2H); ^{13}C NMR (50.0 MHz, $CDCl_3$) δ 0.00, 125.64, 126.11, 126.64, 127.28, 127.58, 130.54, 133.36, 133.63, 137.93, 145.08; ^{29}Si NMR (59.6 MHz, $CDCl_3$) δ –8.08; Ms, m/z (%) 398 (M^+, 14), 295 (60), 73 (100); HRMS Found: 398.1905. Calcd for $C_{26}H_{30}Si_2$: 398.1886.

6 (*R*)-(–)-**2**: mp = 129-130 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ –0.31 (s, 6H), 0.07 (s, 6H), 7.0-7.05 (m, 4H), 7.15–7.3 (m, 10H), 7.35-7.4 (m, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ –1.73, –0.95, 125.68, 126.36, 126.71, 127.45, 127.50, 128.60, 131.50, 133.47, 133.58, 133.99, 136.00, 139.16, 145.74; ^{29}Si NMR (59.6 MHz, $CDCl_3$) δ –3.73; Ms, m/z (%) 522 (M^+, 13), 357 (17), 295 (18), 135 (100); HRMS Found: 522.2234. Calcd for $C_{36}H_{34}Si_2$: 522.2199.

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9 Crystal data for (*R*)-(–)-**2** (23 °C): colorless crystals; formula $Si_2C_{36}H_{34}$, fw = 522.8; monoclinic, space group $P2_12_12$ (#18), a = 9.024(3) Å, b = 18.788(2) Å, c = 8.931(3) Å; V = 1514.2(4) Å^3, Z = 2, D_{calc} = 1.147 g/cm^3, μ(CuKα) = 1.215 mm^{-1}. A total of reflection 1716, 746 ($I > 3.00\sigma(I)$) were used in refinement: R = 0.044, R_w = 0.033. The reflection intensities were collected on a Rigaku AFC7S diffractometer with a rotating anode (50 kV, 30 mA) using graphite monochromated CuKα (λ = 1.54178 Å).