(*R*)-2,2′-Bis(stannyl)-1,1′-binaphthyls as a New Chiral Bis-Metallic Binaphthyl Catalyst

Takashi Hoshi,* Hiroshi Shionoiri,[†] Masayoshi Katano,[†] Toshio Suzuki, Masayoshi Ando, and Hisahiro Hagiwara*,[†]
Faculty of Engineering, Niigata University, 2-nocho, Ikarashi, Niigata 950-2181
[†]*Graduate School of Science and Technology, Niigata University, 2-nocho, Ikarashi, Niigata 950-2181*

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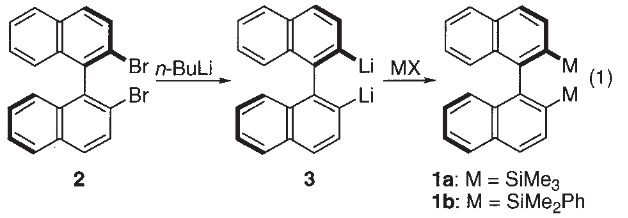
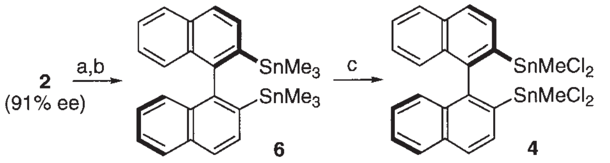
Dilithiation followed by bis-stannylation with Me_3SnCl of (*R*)-2,2′-dibromo-1,1′-binaphthyl (**2**) and the subsequent redistribution reaction of resulting (*R*)-2,2′-bis(trimethylstannyl)-1,1′-binaphthyl (**6**) with $SnCl_4$ gave the novel chiral Lewis acid catalyst (*R*)-2,2′-bis(dichloromethylstannyl)-1,1′-binaphthyl (**4**). The catalytic properties of **4** and its triflate **5** were investigated as the first chiral bis-metallic binaphthyl catalyst.

Chiral bis-metallic binaphthyl catalysts of the general type **1** have recently attracted growing attention as a new class of multifunctional chiral catalysts from several viewpoints:[1–4] (1) Corresponding chiral binaphthyl ligands such as BINAP have achieved remarkable success in asymmetric syntheses.[5] (2) Metals are directly attached to the C2 and C2′ positions of binaphthyl framework so that the substrate would be activated in the closer proximity to asymmetric environment than conventional metal-BINOL complexes. (3) The bis-metallic cavity would be a candidate for active site of bidentate chiral catalysts. However, any chiral bis-metallic binaphthyl catalysts has not been reported because general synthetic operations for optically active binaphthyls such as optical resolution of the racemic bodies or asymmetric naphthyl coupling reaction are inapplicable to synthesize reactive catalysts. For the solution of this problem, we have been exploring the possibility that dilithiation of optically active 2,2′-dibromo-1,1′-binaphthyl (**2**) followed by metal exchange of the resulting dilithio-intermediate (**3**) with metal halide (MX) would be a general protocol to an array of chiral bis-metallic binaphthyl catalysts (eq 1). We recently reported the syntheses and the structural characterizations of (*R*)-2,2′-bis(silyl)-1,1′-binaphthyls (**1a**) and (**1b**) as the first optically active bis-metallic binaphthyls.[1c] Because bis-stannyl analogue would be a much more prospective Lewis acid catalyst, we herein report the syntheses and the reactions of (*R*)-2,2′-bis(dichloromethylstannyl)-1,1′-binaphthyl (**4**) and its triflate (**5**) as the first chiral bis-metallic binaphthyl catalyst.

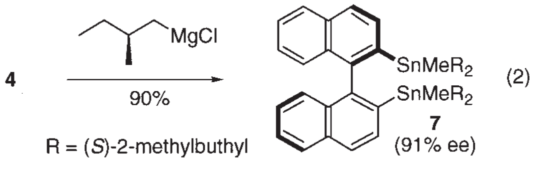


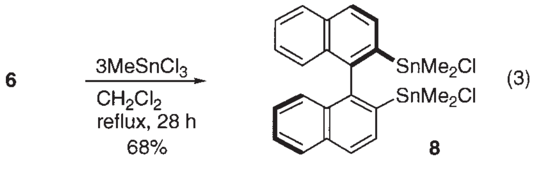
In the synthesis of **4**, $MeSnCl_3$ is the pertinent bis-stannylation reagent for our synthetic strategy illustrated in eq 1. However, the bis-stannylation using $MeSnCl_3$ is obviously impractical because the product **4** would be also the good stannylation reagent to lead further undesired reactions with remaining lithio-intermediates. Thus, we first of all synthesized (*R*)-2,2′-bis(trimethylstannyl)-1,1′-binaphthyl (**6**) using Me_3SnCl instead of $MeSnCl_3$ and subsequently transferred **6** to the desired catalyst **4** in enantiofacial manner (Scheme 1). Dilithiation of **2** (91% ee)[6] was carried out using 2.4 equiv of *n*-BuLi at $-73\,°C$ for 1 h, and then cooled to $-90\,°C$. To the resulting dilithio-intermediate **3** was slowly added 3-fold excess of Me_3SnCl. After addition, the reaction mixture was gradually warmed to $-50\,°C$ for an additional 4 h to give **6** in 51% yield. The reaction temperature controlled below $-50\,°C$ during the bis-stannylation reaction is crucial to suppress racemization of **3**.[1c,6] The requisite enantiofacial chlorination reaction of **6** was accomplished by the redistribution reaction with $SnCl_4$ and **4** was obtained in 77% yield.[7] The optical purity of **4** secured by ^1H NMR analysis of the diastereomeric ratio of 2,2′-bis(methyldi((*S*)-2-methylbutyl)stannyl)-1,1′-binaphthyl (**7**) was consistent with that of starting material **2** (eq 2).[8] The reaction of **6** with $MeSnCl_3$ also gave (*R*)-2,2′-bis(chlorodimethylstannyl)-1,1′-binaphthyl (**8**) in 68% yield with retention of the axial chirality (eq 3). The reactions of (±)-**6** with tin chlorides were reported by Kuivila and co-workers.[4] However, they used only racemic bodies so that the enantiospecificity has been unknown to date. Because chlorostannanes are versatile intermediates in syntheses of organotin compounds, the enantiofacial chlorination reactions of **6** with tin chlorides suggest that the trimethylstannyl precursor **6** is the prospective equivalent for various optically active bis-stannyl binaphthyl derivatives.



Reagents and conditions: (a) *n*-BuLi (2.4 equiv), THF, –73 °C, 1 h. (b) Me_3SnCl (3 equiv), –90 °C to –50 °C, 4 h, 51% for two steps. (c) $SnCl_4$ (6 equiv), CH_2Cl_2, rt, 25 h, 77%.

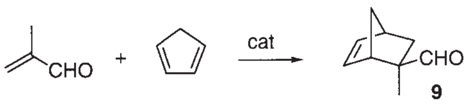
Scheme 1.





Our first investigation of the catalytic activity of the novel chiral bis-stannyl binaphthyl **4** has focused on the asymmetric

Diels-Alder reaction (eq 4).[9] In the presence of the catalyst **4** (100 mol%, 91% ee), a CH_2Cl_2 solution of methacrolein and 3-fold excess of cyclopentadiene was stirred at 20 °C for 10 h to give the Diels-Alder adducts **9** (exo/endo = 88/12) in 57% yield and 12% ee for the major exo-isomer. After the reaction, the catalyst **4** was recovered in 61% yield. However, the catalytic activity of the tin chloride **4** was so modest that the stoichiometric amounts of **4** must be employed for full conversion. We therefore turned our attention to the triflate derivative **5**, which was prepared via the metathetic reaction of **4** with 4 equiv of AgOTf (eq 5).[4] As expected, the reaction was much more accelerated only using 10 mol% of **5** at −60 °C to give **9** (exo/endo = 86/14) in 51% yield within 1 h. However, no enantioselectivity was found in the major exo-isomer.



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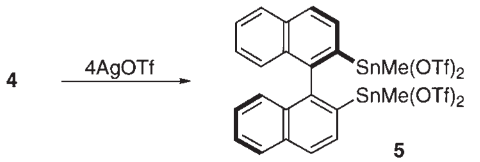
(4)

100 mol% **4**
20 °C, 10 h
57% (exo/endo = 88/12)
exo: 12% ee

10 mol% **5**
−60 °C, 1 h
51% (exo/endo = 86/14)
exo: 0% ee



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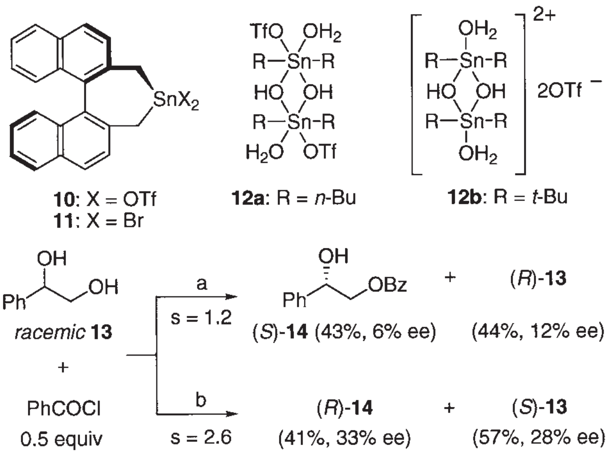
(5)

Organotin catalysts have been gradually employed in the acylation reaction of alcohols in viewpoints of high reactivity and selectivity. Otera and Matsumura quite recently reported the effective asymmetric acylations of meso and racemic diols catalyzed by the optically active organotin triflate **10** and the bromide derivative **11**.[10,11] While achiral catalysts, Otera also demonstrated that the dimeric organotin triflates **12**, the hydrolysis products of $R_2Sn(OTf)_2$, have much higher catalytic activity due to the increased Lewis acidity than the monomeric analogues.[12] Thus, we investigated the catalytic properties of the tin chloride **4** and its triflate **5** in the asymmetric acylation of racemic 1-phenyl-1,2-ethanediol (**13**) with 0.5 equiv of benzoyl chloride in the presence of Na_2CO_3 and H_2O according to Matsumura's condition (Scheme 2). Both catalysts **4** and **5** (2.5 mol%, 91% ee) showed high yields and regioselectivities. However, the distinct difference was found in enantioselectivities. When the tin chloride **4** catalyzed the acylation reaction, the acylation product (1*S*)-**14** was obtained in 43% yield and 6% ee with a selectivity factor of 1.2.[13] In contrast, the tin triflate **5** functioned as the reverse enantiofacial catalyst to give (1*R*)-**14** in 41% yield and 33% ee with a selectivity factor of 2.6. Though the precise structure of the hygroscopic tin triflate catalyst **5** is not yet clear, we have assumed that two stannyl groups were intramolecularly hydrolyzed into the binuclear complex similar to **12**. In fact, the catalytic activity of **5** drastically decreased in the absence of H_2O and **14** was obtained only in 10% yield.

In conclusion, we have described the syntheses and the catalytic reactions of (*R*)-2,2′-bis(dichloromethylstannyl)-1,1′-binaphthyl (**4**) and its triflate **5**. Though selectivities are still moderate, **4** and **5** functioned as the first chiral bis-metallic binaphthyl catalysts. Our present study also demonstrated that the trimethylstannyl precursor **6** is the prospective equivalent for various optically active bis-stannyl binaphthyl derivatives. The development of more efficient chiral bis-stannyl binaphthyl catalysts is underway in our laboratory.



Reagents and conditions: (a) 2.5 mol% **4**, Na_2CO_3 (1.5 equiv), H_2O (5.5 equiv), THF, 0 °C, 7 h. (b) 2.5 mol% **5**, Na_2CO_3 (1.5 equiv), H_2O (5.5 equiv), THF, 0 °C, 7 h.

Scheme 2.

References and Notes

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7 Representative procedure of the preparation of **4**: To a solution of **6** (2.5 g, 4.3 mmol) in CH_2Cl_2 (35 mL) was slowly added $SnCl_4$ (3.0 mL, 26 mmol) at −70 °C. After addition, the reaction mixture was gradually warmed to room temperature and starred for an additional 25 h. After evaporation of the solvent and subsequently removing other volatiles in vacuo, the residue was subjected to flash chromatography (silica gel, CH_2Cl_2) and recrystallized from CH_2Cl_2 to give **4** (2.2 g, 3.3 mmol) in 77% yield as colorless crystals: mp = 235–238 °C; $[\alpha]^{20}_{D}$ −9.20 (*c* 1.01, $CHCl_3$); ^1H NMR ($CDCl_3$, 200 MHz) δ 0.06 (s, 6H), 7.29 (d, $J = 8.4$ Hz, 2H), 7.45 (ddd, $J = 8.4$, 6.7, 1.4 Hz, 2H), 7.64 (ddd, $J = 8.4$, 6.7, 1.1 Hz, 2H), 8.03 (d, $J = 8.5$ Hz, 2H), 8.13 (d, $J = 8.4$ Hz, 2H), 8.21 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 5.6, 126.6, 128.4, 128.6, 128.8, 129.5, 130.6, 132.7, 134.8, 142.9, 144.1. Anal. Calcd for $C_{22}H_{18}Sn_2Cl_4$: C, 39.94; H, 2.74. Found: C, 40.10; H, 2.88.

8 ^1H NMR ($CDCl_3$, 500 MHz) δ −0.40 (s, 6H, SnMe of major isomer), −0.39 (s, 6H, SnMe of minor isomer).

9 The reactions were carried out using methacrolein (1 equiv, 0.2 M) and cyclopentadiene (3 equiv).

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