Asymmetric Organocatalysis

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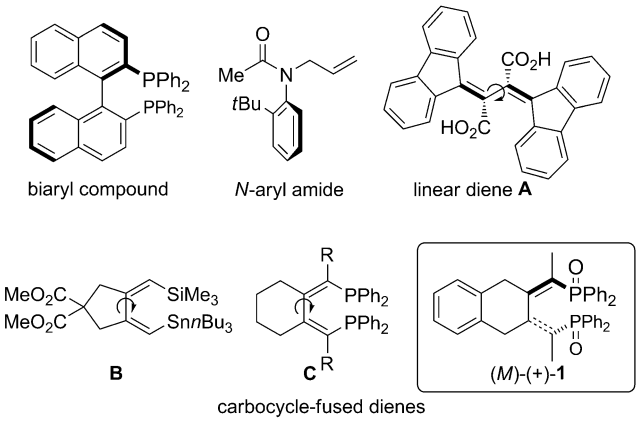
Atropisomeric Chiral Dienes in Asymmetric Catalysis: C_2-Symmetric (*Z*,*Z*)-2,3-Bis[1-(diphenylphosphinyl)ethylidene]tetralin as a Highly Active Lewis Base Organocatalyst**

Masamichi Ogasawara, Shunsuke Kotani, Hikaru Nakajima, Haruka Furusho, Mitsuru Miyasaka, Yasushi Shimoda, Wei-Yi Wu, Masaharu Sugiura, Tamotsu Takahashi,* and Makoto Nakajima**

"Atropisomeric chirality" is chirality resulting from restricted rotation about a single bond.[1] The most important atropisomeric compounds are appropriately substituted biaryl compounds,[2] which have been utilized in various asymmetric reactions as useful chiral scaffolds. Other atropisomeric systems, which are often referred as "non-biaryl atropisomers",[3] include aryl amides[4] and diaryl ethers,[5] as well as other compounds,[6] and have undergone rapid development during the last decade. Analogous atropisomerism in conjugated dienes is also feasible. The possibility of diene atropisomerism was pointed out in the 1950s;[7] however, such enantiomerically resolvable dienes are still rare.[8] The energy barrier to rotation about the C–C single bond in a conjugated diene is generally low, and thus the majority of atropisomeric dienes reported so far (e.g., **A** in Scheme 1)[7b] show rapid racemization at ambient temperature.[7,9,10] For this reason, the application of atropisomeric dienes in asymmetric reactions has scarcely been examined. Apparently, the development of diene systems in which atropisomerization is completely frozen is indispensable for the application of these molecules as chiral catalysts or reagents.

The incorporation of a fused cyclic structure at the C2–C3 bond of a 1,3-diene increases the conformational rigidity of the molecule, and bulky substituents on the "inner" sides of the 1- and 4-positions of the diene force the diene to adopt a nonplanar helical conformation. In 2000, RajanBabu and co-workers reported that the palladium-catalyzed cyclized silylstannylation of 1,6-diynes gave carbocycle-fused diene derivatives, such as **B**.[10] Detailed analysis of these helically chiral molecules revealed that the dienes were fluxional in solution. Analogous diene structures could be assembled by the zirconium-mediated reductive cyclization of diynes.[11a] Doherty, Knight, and co-workers prepared a series of bisphosphines by this method.[11] Their dienyl bisphosphines (e.g., **C**) are also fluxional as free ligands, but their helical-sense conformation can be frozen upon coordination to a transition metal.[11] Recently, Doherty and co-workers reported the preparation of a resolvable atropisomeric diene phosphine by extensive substitution of the diene skeleton.[12]



Scheme 1. Examples of atropisomeric compounds.

Herein, we report a novel C_2-symmetric conformationally rigid atropisomeric chiral diene **1**, which possesses operational Lewis basic functionality. The compound, which can be prepared in enantiomerically pure form on a multigram scale, is an extremely effective Lewis base organocatalyst[13] in the enantioselective allylation of aldehydes with allylsilanes.[14–16] Due to the high activity of **1**, the allylation reaction can be conducted at a lower temperature with a lower catalyst loading. Furthermore, **1** can be used for reactions with (β-hydrocarbylallyl)trichlorosilanes, the Lewis base catalyzed asymmetric addition of which to aldehydes is rather difficult.[15a,16c,17]

Bisphosphine **2** was prepared from 1,2-bis(2-butynyl)benzene by a simple one-pot operation based on a reported method.[11a] Subsequent oxidation of **2** with H_2O_2 afforded phosphine oxide **1** in quantitative yield (Scheme 2). In the

[*] Prof. M. Ogasawara, H. Nakajima, Dr. W.-Y. Wu, Prof. T. Takahashi
Catalysis Research Center and Graduate School of Life Science
Hokkaido University
Kita-ku, Sapporo 001-0021 (Japan)
E-mail: ogasawar@cat.hokudai.ac.jp
Prof. S. Kotani
Priority Organization for Innovation and Excellence
Kumamoto University
Kumamoto 862-0973 (Japan)
H. Furusho, Y. Shimoda, Prof. M. Sugiura, Prof. M. Nakajima
Graduate School of Pharmaceutical Sciences, Kumamoto University
Kumamoto 862-0973 (Japan)
E-mail: nakajima@gpo.kumamoto-u.ac.jp

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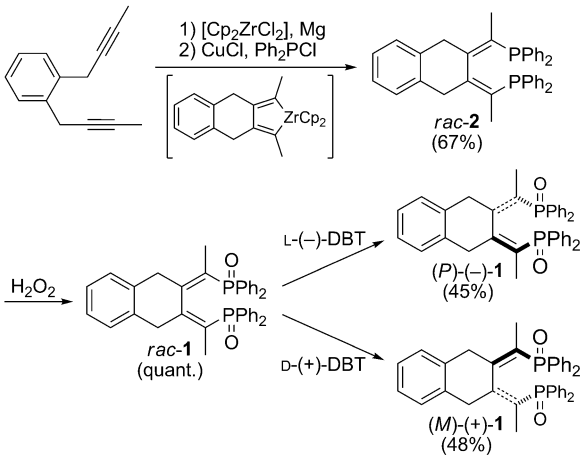


Scheme 2. Synthesis and chiral resolution of the atropisomeric chiral dienyl bisphosphine dioxide **1**.

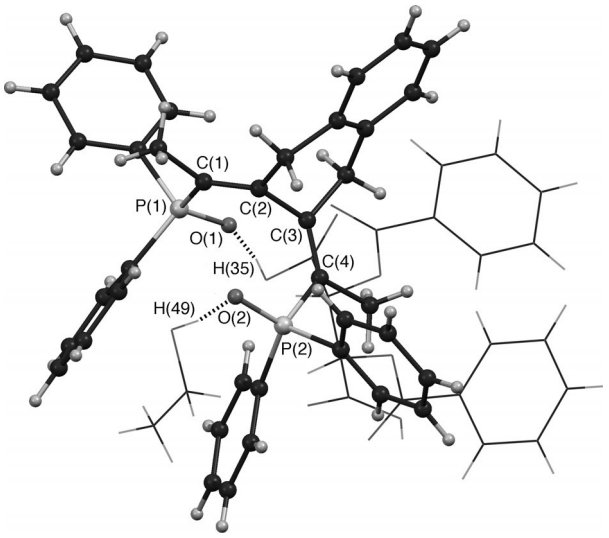


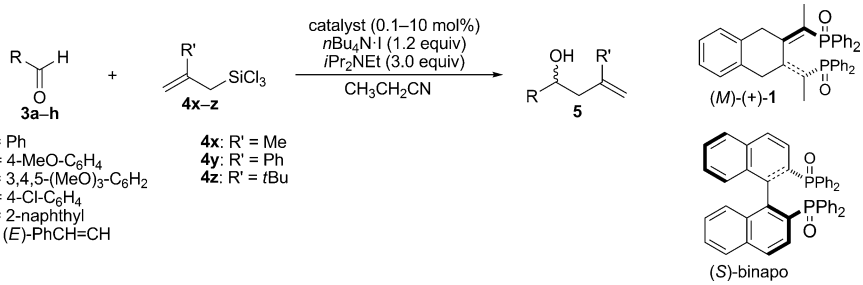
Figure 1. Ball-and-stick drawing of the single-crystal X-ray structure of [(*M*)-(+)-**1**/D-(+)-DBT]·EtOH with selected atom numbering. The (+)-DBT and EtOH moieties are shown as wireframe drawings for clarity.

^{1}H NMR spectrum of **2** in C_6D_6, the methylene hydrogen atoms at the 1- and 4-positions of the tetralin skeleton were detected at $\delta = 3.60$ and 3.95 ppm ($J = 16.9$ Hz) as a pair of well-resolved AB doublets. This observation indicates that the two bulky diphenylphosphanyl substituents in **2** interact with each other, which prevents the molecule from adopting a coplanar conformation. The diene-based helical chirality thus induced in **2** makes the two hydrogen atoms in each CH_2 moiety diastereotopic with each other. Indeed, **2** could be resolved into the two helical enantiomers in practically enantiomerically pure form by HPLC on a chiral stationary phase. However, to our disappointment, **2** showed slow interconversion between the two enantiomers (i.e., racemization). Although the resolved sample of **2** had an *ee* value of $> 99.5\%$ immediately after resolution, the enantiomeric purity dropped to 49.5% *ee* over 12 h when stirred as a solution in *n*-octane at 40 °C. The activation energy of the racemization at this temperature was calculated to be $\Delta G^{\ddagger}(313\ \mathrm{K}) = 25.3 \pm 0.3$ kcal mol^{-1}. On the other hand, phosphine oxide **1** displayed remarkable conformational rigidity with respect to the diene helicity. Optical resolution of racemic **1** with commercial (+)- or (−)-dibenzoyl tartaric acid (DBT) as the resolving reagent gave (+)- and (−)-**1** in isomerically pure form. The resolved sample of (+)-**1** was dissolved in xylenes and heated at 135 °C for 24 h. After this time, the HPLC analysis of (+)-**1** on a chiral stationary phase showed no signs of racemization. On the basis of an assumed detection limit of 0.2% *ee* for this HPLC analysis, we estimated the lower limit of the activation energy of the racemization of **1** at 135 °C to be $\Delta G^{\ddagger}(408\ \mathrm{K}) \geq 38.4$ kcal mol^{-1}. Both the preparation and the resolution of *rac*-**1** are simple operations that can be scaled up readily: a 20-gram scale synthesis was conducted without any difficulties.

A 1:1 complex of (+)-**1**, $[\alpha]_D^{30} = +0.17$ ($c = 1.02$ in $CHCl_3$), and D-(+)-DBT was recrystallized from ethanol to yield colorless crystals suitable for X-ray crystal-structure analysis (Figure 1).[18] The molecular complex cocrystallized with one molecule of ethanol, and hydrogen bonds were detected between O(1) and H(35) as well as between O(2) and H(49). By internal comparison with (+)-DBT, the absolute configuration of the dextrorotatory enantiomer of **1** was unambiguously defined as *M*. As shown in Figure 1, the array of the four conjugated P=O and C=C double bonds [O(1)–P(1)–C(1)–C(2)–C(3)–C(4)–P(2)–O(2)] forms a characteristic helical motif in **1**. The two phosphinyl oxygen atoms, O(1) and O(2), interact considerably with each other, which might be a major factor preventing **1** from racemization.

We next investigated the potential of the novel helically chiral phosphine oxide **1** as a chiral organocatalyst.[13] Although the Lewis base catalyzed asymmetric allylation of aldehydes has been studied extensively, most allylsilane pronucleophiles used in previous studies had an unsubstituted or γ-substituted allyl group.[14–16] Reaction with (β-hydrocarbylallyl)trichlorosilanes are relatively unexplored, and most reported examples showed unsatisfactory enantioselectivity.[15a,16c,17] The results of our allylation studies with β-substituted allylsilanes are summarized in Table 1. As a prototypical reaction, the addition of methallyltrichlorosilane (**4x**) to benzaldehyde (**3a**) was examined under our previously described reaction conditions with slight modifications.[15a] In the presence of (*M*)-**1** (1.0 mol%) in propionitrile, the reaction of **3a** with **4x** proceeded smoothly at −78 °C to give the homoallylic alcohol **5ax** in 87% yield with 87% *ee* (Table 1, entry 1). Phosphine oxide **1** showed unusually high catalytic activity, in contrast with the much lower activity of other chiral phosphine oxide catalysts used so far in enantioselective allylation reactions, in which a catalyst loading of more than 10 mol% is typically required for the completion of the reaction.[14–17] For example, under identical conditions, the reaction catalyzed by (*S*)-binapo (binap dioxide), which is one of the best catalysts described to date for this type of reaction,[15a] gave **5ax** in only 22% yield with 79% *ee* (Table 1, entry 2). We took advantage of the high catalytic activity of (*M*)-**1** to decrease the catalyst loading to as low as 0.1 mol% without appreciable loss of enantioselectivity, although the reaction took longer to reach completion (Table 1, entry 3).

Table 1: Enantioselective addition of (β-hydrocarbylallyl)trichlorosilanes to aldehydes with chiral phosphine oxide catalysts.



3a: R = Ph
3b: R = 4-MeO-C_6H_4
3c: R = 3,4,5-$(MeO)_3$-C_6H_2
3d: R = 4-Cl-C_6H_4
3e: R = 2-naphthyl
3f: R = (*E*)-PhCH=CH

4x: R' = Me
4y: R' = Ph
4z: R' = *t*Bu

Entry	3	4	Catalyst	Catalyst loading [mol%]	*T* [°C][a]	*t* [h]	Yield [%][b]	*ee* [%][c]
1	**3a**	**4x**	(*M*)-**1**	1.0	−78	3	87 (**5ax**)	87 (*S*)
2	**3a**	**4x**	(*S*)-binapo	1.0	−78	3	22 (**5ax**)	79 (*R*)
3	**3a**	**4x**	(*M*)-**1**	0.1	−78	24	87 (**5ax**)	86 (*S*)
4	**3a**	**4x**	(*M*)-**1**	1.0	−90	9	88 (**5ax**)	90 (*S*)
5	**3a**	**4y**	(*M*)-**1**	1.0	−78	24	70 (**5ay**)	85 (*S*)
6	**3a**	**4y**	(*S*)-binapo	1.0	−78	24	22 (**5ay**)	85 (*R*)
7	**3a**	**4z**	(*M*)-**1**	10	−78	48	89 (**5az**)	92 (*S*)
8	**3a**	**4z**	(*S*)-binapo	10	−78	48	< 5 (**5az**)	–[d]
9	**3b**	**4z**	(*M*)-**1**	10	−78	48	92 (**5bz**)	93
10	**3c**	**4z**	(*M*)-**1**	10	−78	48	90 (**5cz**)	93
11	**3d**	**4z**	(*M*)-**1**	10	−78	48	55 (**5dz**)	90
12	**3e**	**4z**	(*M*)-**1**	10	−78	48	77 (**5ez**)	93
13	**3f**	**4z**	(*M*)-**1**	10	−78	48	91 (**5fz**)	83
14[e]	**3d**	**4x**	(*M*)-**1**	1.0	−78	24	85 (**5dx**)	90 (*S*)
15[e]	**3e**	**4x**	(*M*)-**1**	1.0	−78	24	87 (**5ex**)	89

[a] Bath temperature. [b] Yield of the isolated product after silica-gel chromatography. [c] The *ee* value was determined by HPLC analysis on a chiral stationary phase (see the Supporting Information for details). [d] The *ee* value was not determined. [e] The reaction was carried out without $nBu_4N{\cdot}I$.

The high catalytic activity of (*M*)-**1** enabled us to conduct the reaction at −90 °C, at which temperature the enantioselectivity could be further improved to 90 % *ee* (Table 1, entry 4).

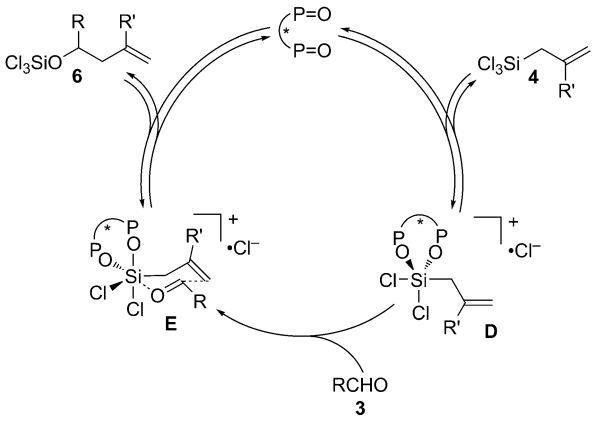
The enantioselectivity and reactivity of the asymmetric allylation reaction are both greatly influenced by the R′ substituent in the allylsilane reagent. The reactions of **4y** (R′ = Ph) were somewhat slower. Although both **1** and binapo gave the β-phenylallylated product **5ay** in 85 % *ee*, **5ay** was formed in higher yield with **1** than with binapo (Table 1, entries 5 and 6). The introduction of a *tert*-butyl substituent in **4z** improved the enantioselectivity of the reaction, and **5az** was obtained with 92 % *ee* and in 89 % yield with (*M*)-**1** (Table 1, entry 7). The allylsilane **4z** was much less reactive than **4x** and **4y**, probably because of its steric bulkiness, and a catalyst loading of 10 mol % and a longer reaction time were required for a reasonable yield of **5az**. The binapo catalyst was completely ineffective in the reaction with **4z**: a trace amount of **5az** was formed under otherwise identical conditions (Table 1, entry 8).

Aldehydes **3** were screened as substrates for this reaction with pronucleophile **4z** and catalyst (*M*)-**1** (Table 1, entries 9–13). Aromatic aldehydes **3b** and **3c** bearing electron-donating groups afforded the corresponding alcohols **5bz** and **5cz** with 93 % *ee* in good yields (Table 1, entries 9 and 10). On the other hand, **3d**, which contains an electron-withdrawing *p*-chloro substituent, was less reactive and gave the addition product **5dz** in 55 % yield, but the enantioselectivity was still excellent (Table 1, entry 11). The reaction with 2-naphthaldehyde (**3e**) afforded **5ez** with 93 % *ee* (Table 1, entry 12). The present reaction could be applied to an aliphatic conjugated enal: the reaction of **4z** with cinnamaldehyde (**3f**) proceeded smoothly to provide **5fz** with 83 % *ee* (Table 1, entry 13). The excellent performance of (*M*)-**1** was further demonstrated in reactions of **4x** with **3d** and **3e** in the presence of 1 mol % of the catalyst at −78 °C to give **5dx** and **5ex** with 90 and 89 % *ee*, respectively (Table 1, entries 14 and 15).

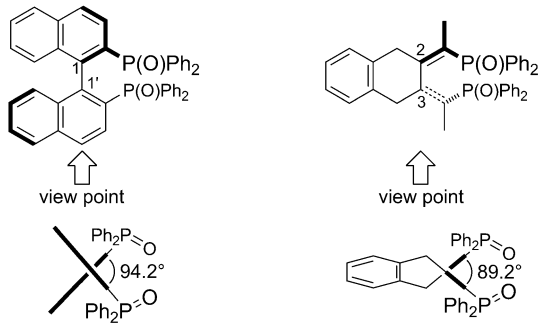
Phosphine oxide **1** is robust under the reaction conditions described in Table 1 and could be recovered readily from the reaction mixture by standard silica-gel column chromatography. HPLC analysis of recovered (*M*)-**1** on a chiral stationary phase showed no racemization with respect to the atropisomeric chirality.

The key intermediate in the allylation reaction, a cationic five-coordinate silicon species **D**, is generated by the coordination of the phosphine oxide to the allylsilane **4** (Scheme 3).[13,15a] Intermediate **D** is Lewis acidic and captures aldehyde **3** to form a six-coordinate intermediate **E**, in which the stereoselective formation of a C–C bond takes place. Subsequent decomplexation of **E** releases the silyl homoallyl ether **6** and the phosphine oxide catalyst for further turnover.

The high catalytic activity of **1** may be attributed to the distorted structure in **D** upon the coordination of **1**. The X-ray crystal structures of **1** and binapo are described schematically in Scheme 4. Whereas the naphthyl–naphthyl dihedral angle



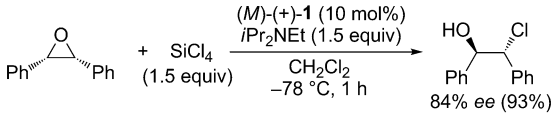
Scheme 3. Catalytic cycle of the phosphine oxide catalyzed allylation of aldehydes.



Scheme 4. Comparison of the structures of (*R*)-binapo and (*M*)-**1**.

in binapo is 94.2°, the dihedral angle between the two P–C=C planes in **1** is much smaller at 89.2°. The smaller dihedral angle in **1** leads to a narrower O–Si–O angle in **D** coordinated with **1**. This distortion around the silicon atom may enhance the Lewis acidity and nucleophilicity of **D**. The increased Lewis acidity of skewed four-coordinate silicon compounds has been well documented as "strain-release Lewis acidity",[19] and an analogous explanation may account for the reactivity of the five-coordinate silicon species. Alternatively, the high catalytic activity of **1** could be explained in terms of a wider pocket provided by the smaller O–Si–O angle at the silicon center in **D**; this wider pocket would accommodate the incoming aldehyde more readily.

The potential usefulness of **1** as a chiral organocatalyst was further examined in the enantioselective ring opening of a *meso* epoxide.[20] As shown in Scheme 5, *cis*-stilbene oxide



Scheme 5. Enantioselective ring opening of a *meso* epoxide under the catalysis of the chiral phosphine oxide (*M*)-(+)-**1**.

reacted with silicon tetrachloride in the presence of (*M*)-**1** (10 mol%) to give the corresponding 1,2-chlorohydrin in 93% yield with 84% *ee*. Additional applications of **1** are now under investigation by our research group and will be reported in due course.

In summary, we have found that C_2-symmetric (*Z*,*Z*)-2,3-bis[1-(diphenylphosphinyl)ethylidene]tetralin (**1**) is atropisomeric and conformationally static. After optical resolution into the two atropisomeric enantiomers, the optically pure compound was applied as a chiral Lewis base organocatalyst and showed excellent enantioselectivity as well as unusually high catalytic activity in reactions of various aldehydes with β-substituted allyltrichlorosilanes.

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