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A novel, C_2-symmetric, chiral bis-cyclosulfinamide-olefin tridentate ligand in Rh-catalyzed asymmetric 1,4-additions

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ABSTRACT

A C_2-symmetric, chiral bis-cyclosulfinamide-olefin ligand composed of two 1-oxo-2,3-dihydro-1,2-benzisothiazole moieties with rigid skeletons and a conformationally flexible butenylene chain is disclosed for the first time. HRMS and ^{1}H NMR analyses verify that the in situ-generated complex of the ligand and $[Rh(C_2H_4)_2Cl]_2$ possesses a rhodium (I) center coordinated to the tridentate ligand via two sulfinyl moieties and a CdbndC bond. The chiral ligand provided extremely high enantioselectivity (up to >99% ee) in the Rh-catalyzed asymmetric 1,4-additions of arylboronic acids to cyclohexenone and cyclopentenone. The tridentate ligand gave much higher enantioselectivity than the analogous chiral bidentate ligands.

Olefins have a long history as ligands, including in the very first transition metal alkene complex, Zeise's salt [1], and in 2004, chiral di-olefin ligands were pioneered by Hayashi [2] and Carreira [3] and used as a highly efficient chiral ligands in asymmetric catalysis. Since then, great progress has been made with chiral olefin ligands containing heteroatoms [4], especially in rhodium-catalyzed asymmetric reactions. Among these ligands, sulfur-containing olefin ligands, mainly including chiral sulfoxide-olefin ligands [5] and chiral sulfinamide-olefin ligands [6], demonstrate high asymmetric inductions due to the strong and thus efficient coordination between the soft acid, rhodium (I), and soft bases, the olefin and sulfur of the chiral sulfoxides and sulfinamides. To date, most of the reported sulfinyl-olefin chiral ligands are C_1-symmetric bidentate ligands (Fig. 1) [4].

A number of C_2-symmetric chiral ligands, such as DIPAMP, BINAP, DuPhos, and dialkyl tartrates, are privileged ligands and have been shown to provide high enantioselectivity, and they even have been applied in the industrial production of chiral chemicals. It has been well established that C_2 symmetry actually improves the enantioselectivity of a complex by reducing the number of transition states with unique geometries [7]. To date, only two papers have reported C_2-symmetric sulfinamide and olefin ligands. One class is Chen's C_2-symmetric chiral sulfur-containing diamides with a sulfinyl group and two allyl or cinnamyl groups (Fig. 1) [8], and these compounds are regarded as sulfinamide-olefin bidentate chiral ligands with a redundant olefin moiety. The other class is Prasad's C_2-symmetric bis-sulfinamides, which includes two kinds of ligands (Fig. 1) [9]. One of their kinds of ligands has two sulfinyl groups and two allyl groups, which act as chiral ligands in rhodium-catalyzed 1,4-additions (Fig. 1). The other kind has two sulfinyl groups and a cyclohexene moiety, which are not suitable for that reaction (Fig. 1) [9].

Although no efficient bis-sulfinamide-olefin tridentate chiral ligands have been reported, a small number of chiral tridentate ligands that are highly efficient in asymmetric catalysis have been reported [10]. For example, pyridine-2,6-bis(oxazolines) (abbreviated Pybox) [10a], chiral tridentate ligands, show unique versatility for a number of catalytic asymmetric reactions and can bind a wide range of metals. Recently, additional chiral tridentate ligands have been reported for Rh-catalyzed reactions, such as chiral diene-phosphine tridentate ligands [10c] and tris-sulfoxide ligands [10d].

Recently, we developed cyclic sulfinamide-olefin and N-aryl sulfinamide-olefin chiral ligands that are highly efficient in rhodium-catalyzed 1,4-additions (Fig. 1) [11]. In view of the readily available highly enantiopure cyclic sulfinamides in our laboratory [12] and based on our previous studies on asymmetric catalysis [11,13], we envisioned that a novel C_2-symmetric dicyclosulfinamide-olefin (systematic name: 1,4-di(1-oxo-2,3-dihydro-1,2-benzisothiazolyl)

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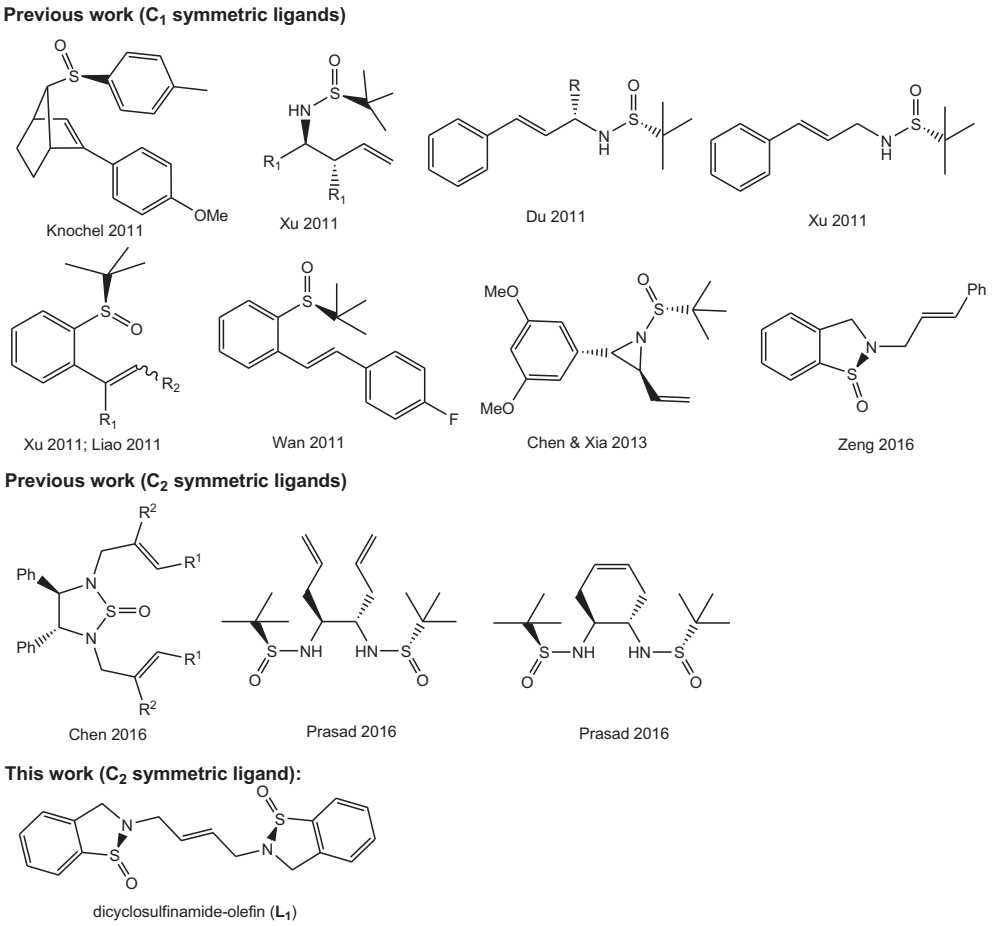


Fig. 1. Selected examples of previously reported C_1- and C_2-symmetric sulfinyl ligands and our designed C_2-symmetric dicyclosulfinamide-olefin tridentate ligand.

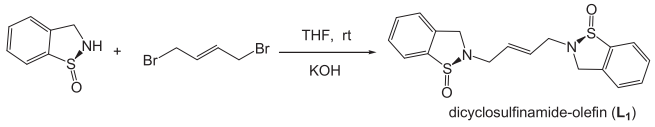
but-2-ene) (abbreviated DICSO) tridentate chiral ligand (Fig. 1) could be synthesized via nucleophile substitution of our readily accessible enantiopure cyclic sulfinamides, namely, 1-oxo-2,3-dihydro-1,2-benzisothiazole and 1,4-dibromo-2-butene, in a facile manner, and these ligands may provide excellent chiral induction. We thought that C_2-symmetric chiral ligand DICSO, with one more sulfinyl group to coordinate the with rhodium (I) center to form a more stable catalytic complex, would provide superior chiral induction [7]. Therefore, we began the project described herein.

Initially, the C_2-symmetric chiral ligand (S,S)-DICSO (systematic name: (S,S)-1,4-di(1-oxo-2,3-dihydro-1,2-benzisothiazolyl)but-2-ene) was synthesized from (S)-1-oxo-2,3-dihydro-1,2-benzisothiazole and 1,4-dibromo-2-butene (Scheme 1).

With the DICSO ligand in hand, the Rh-catalyzed 1,4-addition of phenylboronic acid to 2-cyclohexen-1-one was evaluated. Surprisingly, an extremely high enantioselectivity (99%ee) was obtained when using a 1:1 M ratio of ligand:rhodium (Table 1).

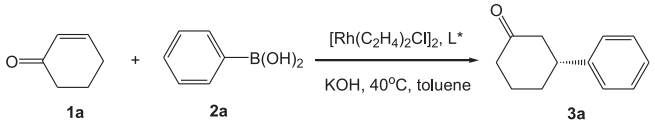
To determine if the chiral DICSO ligand acts as a tridentate ligand in the rhodium catalytic system, two structurally similar bidentate ligands were synthesized (Scheme 2). One was a chiral bidentate bis-sulfinamide ligand with a 1,4-butylene linker (systematic name: (S,S)-1,4-di(1-oxo-2,3-dihydro-1,2-benzisothiazolyl)butane) that has no olefin moiety (Scheme 2). Chiral bidentate bis-sulfinamide ligands were previously reported as organocatalysts or promoters [14], and they have never been reported as ligands for rhodium in asymmetric catalysis. The other bidentate cyclic sulfinamide-olefin ligand has a structure very similar to the DICSO tridentate ligand (systematic name: (S)-1-(1-oxo-2,3-dihydro-1,2-benzisothiazolyl)-4-(1-oxoisoindolin-2-yl)but-2-ene); however, one of the chiral cyclic sulfinamide moieties was replaced by a non-chiral isoindolin-1-one fragment (Scheme 2).

Both of the structurally related bidentate chiral ligands, L_2 and L_3, afforded much lower enantioselectivities (61%ee and 77%ee for L_2 and L_3, respectively) than DICSO (L_1) in the Rh-catalyzed



Scheme 1. Synthesis of C_2-symmetric dicyclosulfinamide-olefin chiral tridentate ligand DICSO.

Table 1
Screening of bi- and tridentate chiral ligands.



Entry	Ligand	Yield (%)	ee (%)
1	**L_1**	48	99
2	**L_2**	35	61
3	**L_3**	40	77

Reaction conditions: 2-cyclohexen-1-one (0.4 mmol), phenylboronic acid (0.8 mmol), $[Rh(C_2H_4)_2Cl]_2$ (0.01 mmol), chiral sulfinamide ligand (0.02 mmol), KOH (0.2 mmol), toluene, 4 h, argon, 40 °C. Isolated yield. The ee values of the products were determined by chiral HPLC on a Chiralcel OJ-H column.