Asymmetric Catalysis

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A Chiral Cagelike Copper(I) Catalyst for the Highly Enantioselective Synthesis of 1,1-Cyclopropane Diesters**

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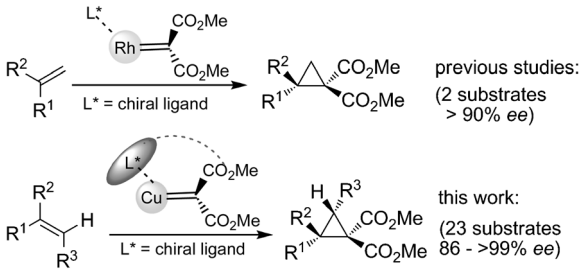
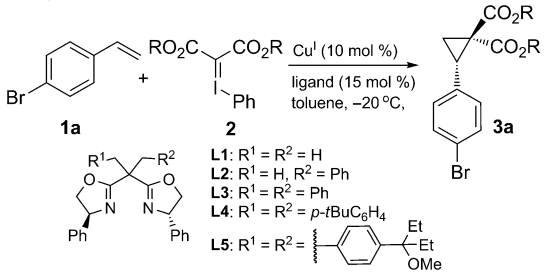
Optically active 1,1-cyclopropane dicarboxylates are widely applied in the total synthesis of natural products, as well as important chiral building blocks in organic synthesis.[1,2] Asymmetric cyclopropanation of olefins with metallocarbenes of malonate provides an easy and direct access to these compounds.[3] Although the asymmetric cyclopropanation of olefins with unsymmetric disubstituted metal carbenes,[4] such as those derived from aryl diazoacetates,[4a,b,e] α-nitrodiazoacetates,[4c,g] and α-cyanodiazoacetates,[4j,k] has proven efficient for the highly enantioselective synthesis of 1,1-disubstituted cyclopropanes, only a very few examples of the cyclopropanation of malonate-derived metallocarbenes[5] have been achieved with high enantioselectivity and diastereoselectivity.[5b,e] The main reason might be that the carbon atom of the malonate metallocarbenes is not pro-stereogenic, which causes a negative effect on the enantiocontrol.[4i,5a] Thus, the design of chiral ligands that discriminate the two prochiral faces during asymmetric cyclopropanation is regarded as quite a challenging problem.[4j] The research groups of Hayashi and Müller designed C_1-symmetric chiral diene-rhodium(I)[5e] and -rhodium(II) carboxylates[5b] respectively, which proved to be elegant catalysts for the enantioselective cyclopropanation of terminal olefins with metallocarbenes of malonate (16–96% yield, 29–90% *ee*[5e] and 56–75% yield, 65–98% *ee*[5b]). To date, the cyclopropanation of multisubstituted olefins with metallocarbenes of malonate has been rarely explored and has proved to be less enantioselective (25% *ee*).[5c] Very recently, we designed a cagelike bisoxazoline-derived Cu^I catalyst and found it can promote the asymmetric cyclopropanation reaction of malonate-derived metallocarbenes with both terminal and multisubstituted olefins with high selectivity (Scheme 1). Herein, we wish to report the preliminary results.

We employed phenyliodonium ylide **2**[6] as the carbene transfer reagent for the study it had previously been shown to be more active than diazomalonate for the formation of metallocarbenes.[7] As shown in Table 1, the in situ prepared bisoxazoline [Cu(**L1**)$(CH_3CN)_4$]PF_6[8,9] could catalyze the



Scheme 1. Asymmetric cyclopropanation between olefins and metallocarbenes of malonate.

Table 1: Optimization of the reaction conditions.[a]



Entry	Cu^I	Ligand	R	Yield [%][b]	*ee* [%][c]
1	[Cu$(CH_3CN)_4$]PF_6	**L1**	Me	97	66
2	[Cu$(CH_3CN)_4$]PF_6	**L2**	Me	98	64
3	[Cu$(CH_3CN)_4$]PF_6	**L3**	Me	72	86
4	[Cu$(CH_3CN)_4$]PF_6	**L4**	Me	95	92
5	[Cu$(CH_3CN)_4$]PF_6	**L5**	Me	80	88
6[d]	[Cu$(CH_3CN)_4$]PF_6	**L4**	Me	99	95

[a] **1a** (36.6 mg, 0.20 mmol), **2** (0.60 mmol), Cu^I (0.02 mmol), ligand (0.03 mmol), and 3 Å MS (200 mg), −20 °C, $c = 0.1$ mol L^{-1}, reaction time: 36–43 h. [b] Yield of isolated product. [c] Determined by chiral HPLC analysis (Chiralcel AD-H). [d] At −40 °C, 76 h.

cyclopropanation of *p*-bromostyrene with phenyliodonium ylide malonate to afford **3a** in 97% yield with 66% *ee* (entry 1). Ligand **L2**, bearing a pendant benzyl group, was able to promote the cyclopropanation in 98% yield with 64% *ee* (entry 2). Installing two pendant benzyl groups at the bridged carbon atom of the phenyl-bisoxazoline resulted in the enantioselectivity dramatically increasing (72% yield, 86% *ee*; entry 3). Further study showed that steric hindrance of the pendant group also played an important role in promoting both the enantioselectivity and reactivity. For example, the highly sterically demanding ligand **L4**, which possessed two large bulky side arms, turned out to be the optimal one (95% yield, 92% *ee*; entry 4). Increasing the steric hindrance of the pendant group further destroyed the enantioselectivity (80% yield, 88% *ee*; entry 5 versus

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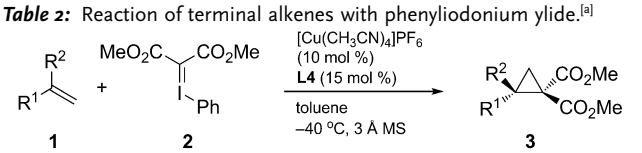
entry 4). Noticeably, the enantioselectivity could be enhanced by lowering the reaction temperature, which provided the desired product in 99% yield with 95% *ee* (entry 6).

The scope of terminal alkenes with a variety of different substituents was next examined under the optimized reaction conditions. As shown in Table 2, high yields and high to

Table 2: Reaction of terminal alkenes with phenyliodonium ylide.[a]



1 2 3

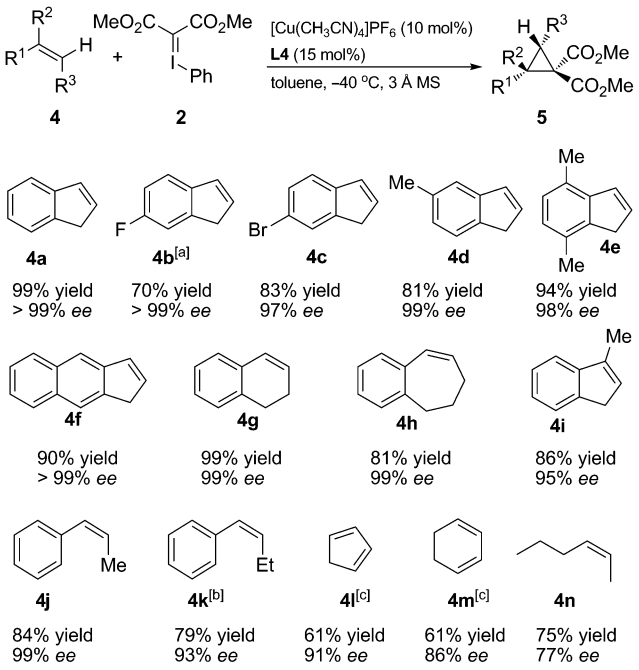
Entry	R^1, R^2	Yield [%][b]	*ee* [%][c]
1	*p*-BrC_6H_4, H (**1a**)	99 (**3a**)	95
2	Ph, H (**1b**)	85 (**3b**)	91 (*S*)[d]
3	*p*-ClC_6H_4, H (**1c**)	93 (**3c**)	95
4	*p*-$CF_3C_6H_4$, H (**1d**)	99 (**3d**)	96
5	*p*-$ClCH_2C_6H_4$, H (**1e**)	79 (**3e**)	94
6	*p*-MeC_6H_4, H (**1f**)	99 (**3f**)	92
7	*o*-MeC_6H_4, H (**1g**)	99 (**3g**)	92
8	*m*-MeC_6H_4, H (**1h**)	97 (**3h**)	93
9[e]	*p*-$MeOC_6H_4$, H (**1i**)	96 (**3i**)	87
10	*p*-PhC_6H_4, H (**1j**)	95 (**3j**)	92
11	$PhOCH_2$, H (**1k**)	21 (**3k**)	80

[a] **1** (0.40 mmol), **2** (400 mg, 1.20 mmol), Cu^I (14.9 mg, 0.04 mmol), **L4** (35.9 mg, 0.06 mmol), toluene (4.0 mL) and 3 Å MS (300 mg), −40 °C, $c = 0.1\ mol\,L^{-1}$, reaction time: 50–131 h. [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] The absolute configuration of **3b** was determined as *S* by comparing the optical rotation with the literature values.[4h,10] [e] **L6** was employed with 5 mol% of catalyst; **L6**: *i*Pr-bisoxazoline, $R^1 = R^2 = p\text{-}tBuC_6H_4$.

excellent enantioselectivities (87–96% *ee*) were obtained (entries 1–10) for both electron-withdrawing and -donating groups at the *para*, *ortho*, and *meta* positions of the phenyl ring of substrates **1a**–**1j**. Aliphatic substrate **1k** showed lower reactivity and gave the cyclopropane **3k** in 21% yield with 80% *ee* (entry 11).

Further studies showed that the current catalytic system exhibited excellent enantiocontrol for nonterminal olefins (Scheme 2). Various electron-poor and -rich indenes **4a**–**4f** with different substitution patterns on the aromatic ring reacted smoothly with phenyliodonium ylide malonate (**2**) to give the corresponding cyclopropanes in good to high yields with excellent enantioselectivities (70–99% yields, 97–>99% *ee*). Six- and seven-membered cyclic alkenes **4g** and **4h** readily participated in this transformation, and almost enantiopure products were obtained in high yields. Moreover, trisubstituted alkene **4i** gave rise to product **5i** with 95% *ee*. The acyclic *cis*-alkenes **4j** and **4k** were also suitable substrates for the cyclopropanations, and led to **5j** in 84% yield with 99% *ee* and **5k** in 79% yield with 93% *ee*, respectively. Cyclopentadiene (**4l**) and 1,3-cyclohexadiene (**4m**) also worked well, affording the monocyclopropanation products in moderate yield with up to 91% *ee*. In addition, aliphatic-substituted olefin **4n** afforded cyclopropane **5n** in 75% yield and 77% *ee*.

To understand the asymmetric induction of the current reaction, a single crystal of the $[Cu(CH_3CN)_4]PF_6$/**L4** complex



Scheme 2. Cyclopropanation of nonterminal alkenes. Reaction conditions: **1** (0.40 mmol), **2** (400 mg, 1.20 mmol), Cu^I (14.9 mg, 0.04 mmol), **L4** (35.9 mg, 0.06 mmol), toluene (4.0 mL), and 3 Å MS (300 mg), at −40 °C, $c = 0.1\ mol\,L^{-1}$, reaction time: 69–133 h. The yield is of the isolated product. The *ee* values were determined by HPLC analysis on a chiral stationary phase. [a] The absolute configuration of **5b** was determined as *S*,*S* by X-ray crystallographic analysis.[11] [b] At −20 °C. [c] Toluene (2.0 mL), $c = 0.2\ mol\,L^{-1}$. MS = molecular sieves.

was analyzed by X-ray crystallography (Figure 1).[11] The copper center adopts a distorted square-planar geometry, with N1 and N2 of ligand **L4** and a nitrile molecule (the sum of the bond angles of N3-Cu-N1, N3-Cu-N2, and N1-Cu-N2 is 359.99°). Both pendant phenyl groups swing towards the copper center and shield both the upper and lower faces of the

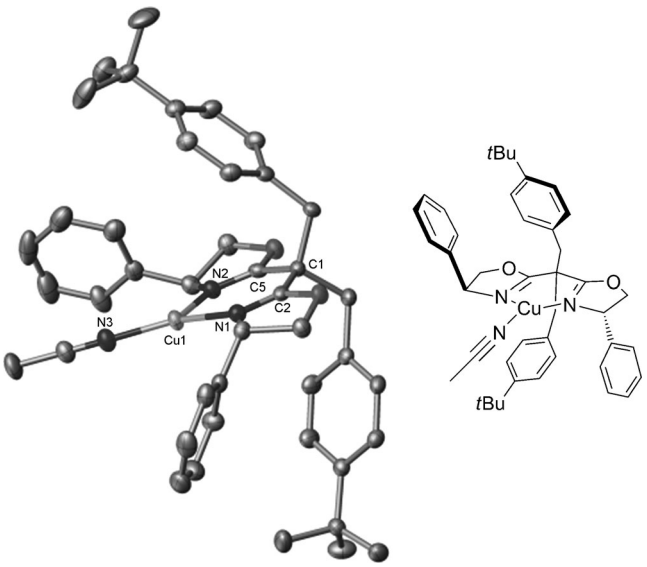


Figure 1. X-ray structure of $[Cu(\mathbf{L4})(CH_3CN)]^+$ (unless labeled, hydrogen atoms and PF_6^- are omitted for clarity).

bisoxazoline–copper(I) coordination plane (N1-Cu-N2-C5-C1-C2). As the bond angle of N3-Cu-N1 is distinctively larger than that of N3-Cu-N2 (148.38(10)° versus 118.69(10)°) and the Cu–N1 bond is shorter than that of Cu–N2 (1.945(2) Å versus 2.012(2) Å), a nonsymmetric chiral cage is formed.

According to previous studies by the research groups of Doyle and Charette, malonate-derived metallocarbenes can adopt three different conformations (out-out, in-out, and in-in).[12] The in-out arrangement was regarded as the reactive conformation because one of the ester groups prefers to adopt an out-of plane conformation that could stabilize the partial positive charge formed on the β carbon atom of the alkene.[9c] On the basis of these results, and by combining the molecular structure of $[Cu(CH_3CN)/\mathbf{L4}]^+$ with the model developed by Pfaltz and co-workers,[13] a stereocontrol model has been developed to explain the stereochemistry of the reaction. As shown in Figure 2, two competing transition-state structures

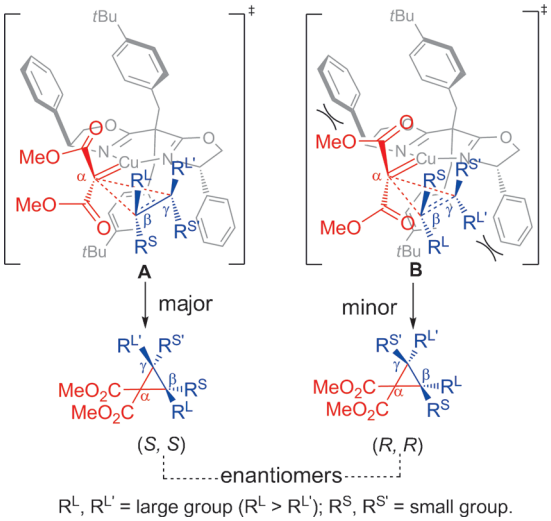


Figure 2. A possible stereochemical model for the Cu^I/**L4**-catalyzed cyclopropanation of multisubstituted olefins.

A and **B** were proposed, in which **A** more favorably gives the major *S*,*S*-configured cyclopropane than does **B**, because of the steric repulsion existing in **B** between the -OMe group of the out-of plane ester and the phenyl group of the chiral skeleton of the bisoxazoline, as well as the steric hindrance between the olefin with the chiral ligand. Thus, the *S* or *S*,*S* isomer[12] would be obtained as the major product, which is completely consistent with the experimental results observed.

In summary, we have developed a facile cagelike chiral catalyst for the catalytic enantioselective cyclopropanation of multisubstituted olefins with phenyliodonium ylide malonate. Remarkably, this newly designed and cheap bisoxazoline–copper(I) complex resulted in the cyclopropanation of a range of substrates such as terminal, disubstituted, and trisubstituted olefins, giving the desired products in excellent yield (up to 99%) with enantioselectivity (up to >99% *ee*). This protocol provides an efficient method for the synthesis of chiral 1,1-cyclopropane diesters. The single-crystal structure of the $[Cu(CH_3CN)_4]PF_6$/**L4** complex led to a proposed stereochemical model. The readily accessible starting material, cheap catalyst, high diastero- and enantioselectivities make the present reaction potentially useful in organic synthesis. Further application of this method in useful transformations is underway.

Experimental Section

Typical procedure for the asymmetric cyclopropanation (**3a** as an example): A mixture of $[Cu(CH_3CN)_4]PF_6$ (14.9 mg, 0.04 mmol) and the ligand (**L4**, 35.9 mg, 0.06 mmol) in toluene (4 mL) with activated 3 Å MS (300 mg) was stirred at room temperature for 2 h under nitrogen. Alkene **1a** (53 μL, 0.4 mmol) was then added and the resulting mixture cooled to −40°C. After stirring the mixture for 10 min, the phenyliodonium ylide (400 mg, 1.20 mmol) was added in one portion. After the reaction was complete (monitored by TLC), the suspension was filtered through a glass funnel with a thin layer (20 mm) of silica gel (100–200 mesh) and eluted with CH_2Cl_2 (ca. 150 mL). The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography to afford **3a** (124.7 mg), as a colorless oil [R_f = 0.6 (1:6 (v/v), EtOAc/petroleum ether] in 99% yield with 95% *ee* (Chiralcel AD-H, *i*PrOH/hexanes = 2:98, 0.70 mL min^{-1}, λ = 254 nm: t_S(major) = 12.8 min, t_R(minor) = 14.4 min); $[\alpha]_D^{20} = -109.2°$ (c = 1.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CHCl_3$): δ = 7.40 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 3.79 (s, 3H), 3.41 (s, 3H), 3.17 (t, J = 8.55 Hz, 1H), 2.15 (dd, J = 8.1, 5.7 Hz, 1H), 1.75 ppm (dd, J = 9.3, 5.4 Hz, 1H).

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[10] For details, see the Supporting Information.

[11] CCDC 894923 ($[Cu(CH_3CN)_4]PF_6$/**L4**) and 894922 (**5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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