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Copper Catalysis

An *exo*- and Enantioselective 1,3-Dipolar Cycloaddition of Azomethine Ylides with Alkylidene Malonates Catalyzed by a N,O-Ligand/$Cu(OAc)_2$-Derived Chiral Complex**

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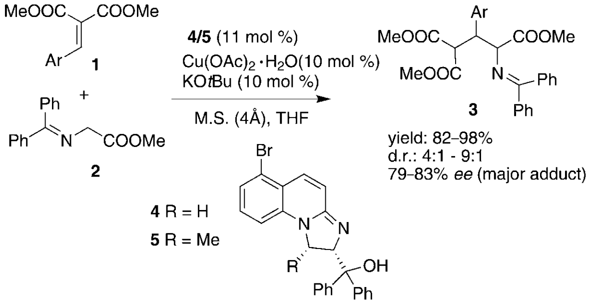
Highly functionalized pyrrolidines are of great importance with applications in the synthesis of biologically active compounds,[1] natural products,[2] and organocatalysts.[3,4] Catalytic asymmetric 1,3-dipolar cycloadditions of azomethine ylides with dipolarophiles, in principle, should provide efficient access to these versatile skeletons.[4,5] Zhang and co-workers first reported a successful example of this strategy in the reaction of azomethine ylides with dimethyl maleate catalyzed by AgOAc/FAP (FAP = bis-ferrocenyl amide phosphine).[6] Inspired by this achievement, many efforts have been made towards the development of asymmetric 1,3-dipolar cycloadditions of azomethine ylides with a variety of electron-deficient alkenes as dipolarophiles using chiral complexes of silver,[7] copper,[8] zinc,[9] nickel,[10] calcium,[11] and organocatalysts.[12] In spite of the relatively broad scope in available dipolarophiles such as maleates,[8c,13] fumarates,[8f,h] maleimides,[7d–e,8e–f,10] acrylates,[8a,i,11,14] nitroalkenes,[8g,15] α-enones,[7a,8b,16] β-phenylsulfonyl enones,[17] and vinyl sulfones,[8d,18] alkylidene malonates[19] have rarely been employed as dipolarophiles in asymmetric 1,3-dipolar cycloadditions of azomethine ylides. Recently, Wang and co-workers reported the first asymmetric enantioselective 1,3-dipolar cycloaddition of azomethine ylides with alkylidene malonates catalyzed by AgOAc/TF-BiphamPhos (TF-BiphamPhos = 4,4′,6,6′-tetrakis(trifluoromethyl)biphenyl-2,2′-diamine).[20] In catalytic systems, a variety of β-alkyl/aryl alkylidene malonates and iminoesters delivered exclusively *exo* adducts. Sterically hindered *tert*-butylalkylidene malonates were found to be the best substrates in terms of enantioselectivities, and the highest enantioselectivity was obtained when a cyclohexane carbaldehyde derived iminoester was used. The development of more versatile and atom-economical variants of 1,3-dipolar cycloadditions of azomethine ylides to alkylidene malonates with excellent enantioselectivity is still a great challenge.

We reported asymmetric catalytic 1,4-Michael addition reactions of glycine derivative **2** with alkylidene malonates **1** to afford the corresponding 1,4-*anti* adducts **3** as the major products in excellent yields and high enantioselectivities catalyzed by novel chiral N,O-**4**/**5**/$Cu(OAc)_2\cdot H_2O$ complexes,[21a] the ligands of which bear resemblance to the nucleophilic catalysts we also recently reported (Scheme 1).[21b]



Scheme 1. Asymmetric Michael addition reactions of glycine derivative **2** with alkylidene malonates **1** catalyzed by a chiral N,O-ligated copper complex.

Encouraged by this finding, we envisaged that our newly developed chiral N,O-ligated copper complexes may also be applicable to the asymmetric catalytic 1,3-dipolar cycloaddition of azomethine ylides with alkylidene malonates. Herein, we report an *exo*-selective and enantioselective 1,3-dipolar cycloaddition of azomethine ylides with alkylidene malonates catalyzed by a complex derived from N,O-**5** and $Cu(OAc)_2\cdot H_2O$ to give highly functionalized pyrrolidines in excellent yields and with good to excellent enantioselectivities (up to 99 % *ee*).

We initially tested the chiral N,O-ligand **4** in the reaction of iminoester **6a** and alkylidene malonate **7a** using 11 mol % of **4** and 10 mol % of $Cu(OAc)_2\cdot H_2O$ in the presence of 10 mol % KO*t*Bu in THF at room temperature (Table 1). The reaction proceeded smoothly to afford the corresponding *exo* adduct **8aa** exclusively and in 79 % yield with moderate enantioselectivity (Table 1, entry 1, 62 % *ee*). Screening metal salts showed $Cu(OAc)_2\cdot H_2O$ to give optimal results both in terms of yields and enantioselectivities of adduct **8aa** (Table 1, entries 2–6). Screening solvents revealed CH_2Cl_2 to be optimal of those tried in terms of both yields and enantioselectivities (Table 1, entry 11). Next, the effect of

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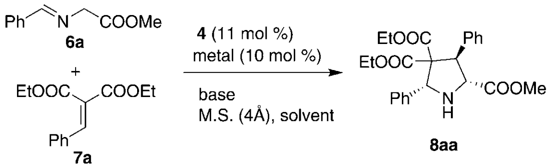
Table 1: Asymmetric 1,3-dipolar cycloaddition of azomethine ylide **6a** with alkylidene malonate **7a**.[a]



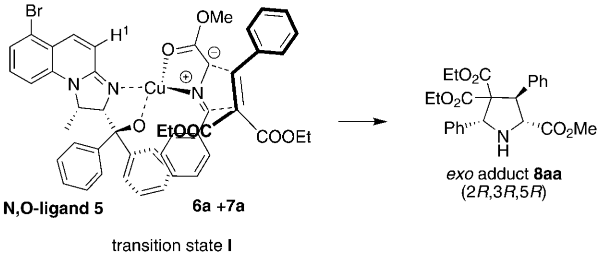
Entry	Metal	Base (%)	Solvent	Yield [%][d]	*ee* [%][e]
1	$Cu(OAc)_2$	KO*t*Bu (10)	THF	79	62
2	$Cu(OTf)_2$	KO*t*Bu (10)	THF	16	9
3	$Zn(OTf)_2$	KO*t*Bu (10)	THF	trace	–
4	$CuCl_2$	KO*t*Bu (10)	THF	48	10
5	AgOAc	KO*t*Bu (10)	THF	30	4
6	$AgSbF_6$	KO*t*Bu (10)	THF	45	14
7	$Cu(OAc)_2$	KO*t*Bu (10)	toluene	trace	–
8	$Cu(OAc)_2$	KO*t*Bu (10)	Et_2O	87	64
9	$Cu(OAc)_2$	KO*t*Bu (10)	$CHCl_3$	18	16
10	$Cu(OAc)_2$	KO*t*Bu (10)	CH_3CN	84	44
11	$Cu(OAc)_2$	KO*t*Bu (10)	CH_2Cl_2	83	67
12	$Cu(OAc)_2$	NaHMDS (10)	CH_2Cl_2	85	62
13	$Cu(OAc)_2$	Cs_2CO_3 (20)	CH_2Cl_2	48	67
14	$Cu(OAc)_2$	Et_3N (20)	CH_2Cl_2	62	74
15	$Cu(OAc)_2$	K_2CO_3 (2 equiv)	CH_2Cl_2	92	75
16[b]	$Cu(OAc)_2$	K_2CO_3 (2 equiv)	CH_2Cl_2	89	71
17	$Cu(OAc)_2$	KOAc (2 equiv)	CH_2Cl_2	trace	–
18	$Cu(OAc)_2$	Ag_2O (2 equiv)	CH_2Cl_2	60	28
19	$Cu(OAc)_2$	–	CH_2Cl_2	trace	–
20[c]	$Cu(OAc)_2$	K_2CO_3 (2 equiv)	CH_2Cl_2	93	88

[a] The reactions were carried out with 0.2 mmol of **6a** and 0.1 mmol of **7a** in 1 mL of solvent at room temperature, and $Cu(OAc)_2$ presented in above table is $Cu(OAc)_2 \cdot H_2O$. [b] Reaction proceeded in the absence of 4 Å M.S. [c] Ligand **5** was used instead of **4**. [d] Yield of isolated product. [e] Determined by HPLC analysis on a chiral phase.

different bases was probed; among the bases tested, two equivalents of K_2CO_3 was found to be optimal giving the corresponding adduct in 92 % yield and 75 % *ee* (Table 1, entry 15). There were only trace amounts of desired product formed in absence of base or when KOAc was used (Table 1, entries 17 and 19). The *ee* value of the *exo* adduct **8aa** dramatically increased to 88 % when ligand **5**, bearing two stereogenic centers on the imidazole ring, was employed.

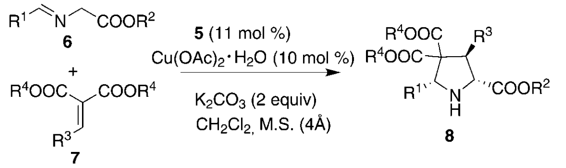
The above optimization led to 11 mol % of N,O-ligand **5**/ 10 mol % of $Cu(OAc)_2 \cdot H_2O/K_2CO_3$ (2.0 equiv)/CH_2Cl_2/4 Å molecular sieve (M.S.)/room temperature as the optimal reaction conditions for this 1,3-dipolar cycloaddition. The generality and substrate scope were then probed. The effect of variation in the ester moiety of alkylidene malonates showed that the smallest group (methyl) gave a relatively high enantioselectivity (Table 2, entry 3, 92 % *ee*), which is not consistent with previously published results, probably because of the asymmetric environment derived from novel chiral N,O-ligands.[20] Therefore, the methyl ester of alkylidene malonates was chosen for further exploration of substrates. As shown in Table 2, a wide array of alkylidene malonates **7a–f**, derived from various aromatic aldehydes, reacted smoothly with iminoesters **6a–h** to afford the corresponding highly substituted pyrrolidines **8** in excellent yields (80–99 %) and enantioselectivities (91–95 % *ee*) with exclusive *exo*-selectivity. When alkylidene malonates **7g–i** derived from aliphatic aldehydes were employed, *exo*/*endo* mixtures were obtained (Table 2, entries 17–19, d.r. 85:15, 92:8, and 92:8, respectively). Interestingly, the bulkier *i*Bu and *t*Bu groups gave enantiomeric excesses of up to 97 %, but the yield was compromised for the latter (Table 2, entries 18 and 19). Notably, the diastereoselectivity for **7g,h** was dramatically increased to exclusively *exo*-selective by replacing the methyl group of the iminoester (**6a**) with a *t*Bu group (**6b**), maintaining the same level of enantioselectivity (Table 2, entries 20 and 21, 95 % and 96 % *ee*, respectively). Moreover, when the conjugated alkylidene malonate **7j** was used for this cycloaddition reaction, the enantiomeric excesses of both *exo*- and *endo* adducts **8bj** were greater than 99 %. Although moderate diastereoselectivity (Table 2, entry 22, *exo*/*endo* = 82:18) was observed, the two diastereoisomers could be separated chromatographically, demonstrating the great benefit of this one-step process in the synthesis of both diastereoisomers of these pyrrolidines with excellent enantiomeric purities. Moreover, the double-bond-containing adduct **8bj** provides a potential site for further functionalization in the chemical transformation of **8**. The enantiomeric excesses of this 1,3-dipolar cycloaddition represent, on average, an over 10 % *ee* enhancement over those previously reported.[20]

The relative and absolute configurations of the corresponding adducts were assigned as *exo*-(2*R*,3*R*,5*R*) by comparison with literature data for **8aa** (see the Supporting Information). The exclusively *exo* selectivities and excellent enantioselectivities observed in this novel 1,3-dipolar cycloaddition can be rationalized from the proposed transition state **I** shown in Scheme 2. That 1,3-dipolar cycloaddition favors an *exo* product is potentially due to possible steric repulsion between the H^1 atom of ligand **5** and the phenyl group of alkylidene malonates, which would disfavor an *endo* mode. When the phenyl group was replaced by an alkyl group, *exo*/*endo* mixtures were formed as a result of reduction of the aforementioned steric repulsion. Two phenyl groups adjacent to the hydroxy group might block the dipolarophile's approach from the "bottom" face and form *exo*-(2*R*,3*R*,5*R*)-**8aa** through approach from the "top" face.



Scheme 2. Proposed transition state leading to the major product *exo*-**8aa**.

Table 2: Asymmetric 1,3-dipolar cycloaddition of azomethine ylides **6** with alkylidene malonates **7** using **5**/Cu(OAc)$_2$·H$_2$O.[a]



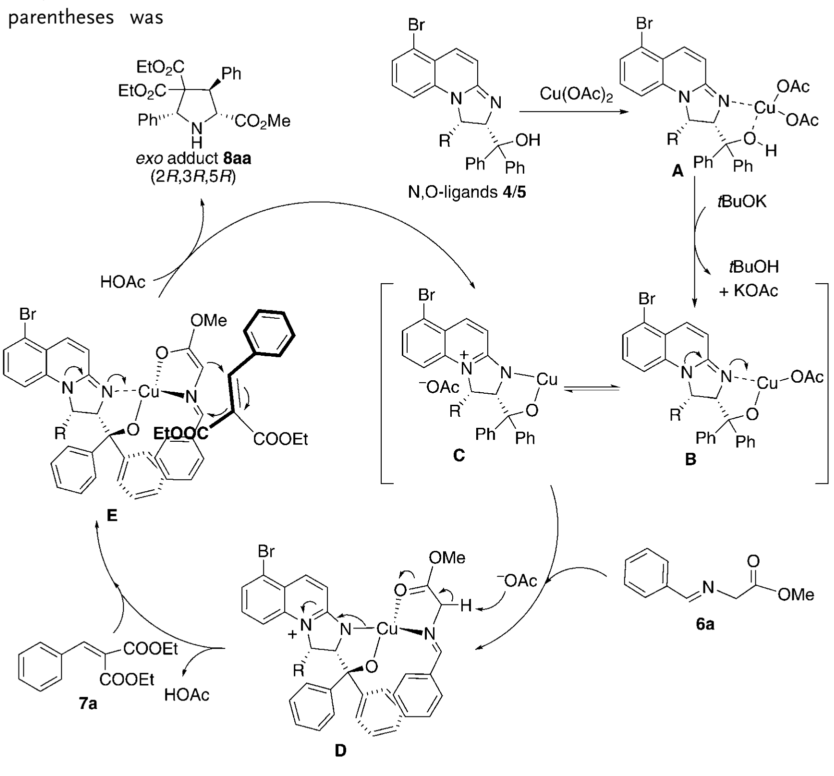
Entry	R^1/R^2	R^3/R^4	Yield [%]	*ee* [%][f]
1	Ph/Me (**6a**)	Ph/Et (**7a**)	93	88
2	Ph/Me (**6a**)	Ph/*i*Pr (**7b**)	87	88
3	Ph/Me (**6a**)	Ph/Me (**7c**)	85	92
4	Ph/*t*Bu (**6b**)	Ph/Me (**7c**)	95	95
5	*p*-ClPh/Me (**6c**)	Ph/Me (**7c**)	81	95(99)
6	*p*-ClPh/*t*Bu (**6d**)	Ph/Me (**7c**)	83	94
7	Ph/Me (**6a**)	*p*-OMeC$_6$H$_4$/Me (**7d**)	92	95
8	Ph/Me (**6a**)	2-furyl/Me (**7e**)	89	94
9	Ph/*t*Bu (**6b**)	2-furyl/Me (**7e**)	97	93
10	*p*-ClPh/Me (**6c**)	2-furyl/Me (**7e**)	99	94
11	*p*-ClPh/*t*Bu (**6d**)	2-furyl/Me (**7e**)	98	92
12	*p*-ClPh/Me (**6c**)	*p*-BrC$_6$H$_4$/Me (**7f**)	80	93(>99)
13	*m*-ClPh/Me (**6e**)	Ph/Me (**7c**)	89	91
14	*p*-MePh/Me (**6f**)	Ph/Me (**7c**)	83	94
15	*m*-MePh/Me (**6g**)	Ph/Me (**7c**)	87	92
16	*p*-OMePh/Me (**6h**)	Ph/Me (**7c**)	87	94
17	Ph/Me (**6a**)	Et/Me (**7g**)	82[b]	96
18	Ph/Me (**6a**)	*i*Bu/Me (**7h**)	85[c]	97
19	Ph/Me (**6a**)	*t*Bu/Me (**7i**)	28[d]	97
20	Ph/*t*Bu (**6b**)	*i*Bu/Me (**7h**)	81	95
21	Ph/*t*Bu (**6b**)	Et/Me (**7g**)	92	96
22	Ph/*t*Bu (**6b**)	C(Me)=CHEt/Me [(*Z*)-**7j**)	84[e]	>99

[a] The reactions were carried out with 0.2 mmol of **6** and 0.1 mmol of **7** in 1 mL of CH$_2$Cl$_2$ at room temperature. [b] *exo*/*endo* ratio 85:15, by HPLC, *ee* value was determined for the major product. [c] *exo*/*endo* ratio 92:8 by HPLC, *ee* value was determined for the major product. [d] *exo*/*endo* ratio 92:8 by ^{1}H NMR, *ee* value was determined for the major product. [e] *exo*/*endo* ratio 82:18, by HPLC, *ee* value was determined for both diastereoisomers of **8bj**. [f] Data in parentheses was determined after simple recrystallization.

It should be noted that a key feature for this chiral complex is the proposed equilibrium between intermediates **B** and **C** through electron transfer from the quinoline N atom to Cu (Scheme 3). Thus, coordination of iminoester **6a** to the partly exposed copper atom of intermediate **C** may be possible. Through this coordination, transition state **D** could be formed and then undergo a subsequent cycloaddition step with alkylidene malonates in the presence of in situ formed KOAc. This assumption was experimentally supported by the fact that only trace amounts of the desired product were obtained in the reaction of **6a** and **7a** in the absence of base (Table 1, entry 17), which implies that complex **A** is not the active form. Furthermore, the fact that the cycloaddition was inactive when KOAc was used as base (Table 1, entry 19) suggests that KOAc is not basic enough to remove the proton of iminoester **6a** and that the OAc anion derived from the complexation of copper complex **B** or **C** to iminoester **6a** may act as base for deprotonation to form transition state **D**. Therefore, intermediates **B** or **C** can behave as a bifunctional catalytic system similar to bifunctional AgOAc systems.[22]

To obtain direct evidence to support the proposed catalytic cycle, various attempts were made to grow crystals for X-ray crystal structure determination of N,O-ligand/Cu complexes. We obtained a crystal of protonated ligand **4** (see the Supporting Information), suitable for determining the X-ray crystal structure, from an equimolar mixture of ligand **4** and Cu(OTf)$_2$ in CH$_2$Cl$_2$. Notably, treatment of protonated ligand **4** with *t*BuOK regenerated ligand **4**. This reversible protonation process of **4** is similar to the equilibrium that exists between intermediates **B** and **C**, which provides ancillary support for our proposed catalytic cycle (**C**→**D**→**E**→**C**).

In conclusion, highly efficient catalytic enantioselective 1,3-dipolar cycloadditions of azomethine ylides **6** with various alkylidene malonates **7** were developed. The new N,O-**5**/Cu(OAc)$_2$-derived chiral complex was demonstrated as an excellent catalyst for inducing asymmetry in the synthesis of highly functionalized pyrrolidines *exo*-**8** as major products (*exo* adducts for most of substrates) in excellent yields (80–99%) and enantioselectivities (91–99% *ee*). We believe that the structural novelty of N,O-**5**, its potential behavior as bifunctional catalyst upon coordination with Cu(OAc)$_2$ and its excellent potential to induce asymmetry in both Michael additions and 1,3-dipolar cycloadditions will be of interest not only for the field of asymmetric catalysis,



Scheme 3. The proposed catalytic cycle for the 1,3-dipolar cycloaddition.

but also for organic and medicinal chemistry in general. Further investigations are ongoing in our laboratory.

Experimental Section

General procedure for an asymmetric 1,3-dipolar cycloaddition of azomethine ylides with alkylidene malonates catalyzed by a N,O-ligand/Cu(OAc)$_2$ complex: Under N_2 atmosphere, ligand **5**(4.9 mg, 0.011 mmol), K_2CO_3 (27.6 mg, 0.2 mmol), Cu(OAc)$_2$·H_2O (2.0 mg, 0.01 mmol), and activated 4 Å M.S. were dissolved in 1 mL dichloromethane, and stirred at room temperature for about 1 h. Then, iminoesters **6** (0.2 mmol) and alkylidene malonates **7** (0.1 mmol) were added sequentially. Once starting material was consumed (monitored by TLC), the residue was purified by column chromatography to give the corresponding cycloaddition products.

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