An Insoluble Copper(II) Acetylacetonate−Chiral Bipyridine Complex that Catalyzes Asymmetric Silyl Conjugate Addition in Water

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S *Supporting Information*

ABSTRACT: Acicular purplish crystals were obtained from Cu(acac)$_2$ and a chiral bipyridine ligand. Although the crystals were not soluble, they nevertheless catalyzed asymmetric silyl conjugate addition of lipophilic substrates in water. Indeed, the reactions proceeded efficiently only in water; they did not proceed well either in organic solvents or in mixed water/organic solvents in which the catalyst/substrates were soluble. This is in pronounced contrast to conventional organic reactions wherein the catalyst/substrates tend to be in solution. Several advantages of the chiral Cu(II) catalysis in water over previously reported catalyst systems have been demonstrated. Water is expected to play a prominent role in constructing and stabilizing sterically confined transition states and accelerating subsequent protonation to achieve high yields and enantioselectivities.

Exploring chemical reactions in water is of paramount importance in multidisciplinary research, including life science. Since water is abundant, inexpensive, nonflammable, nontoxic, and an environmentally benign medium, today's increasing awareness of environmental damage has prompted the use of water as an ideal solvent alternative to organic solvents. Moreover, the use of water as solvent sometimes leads to novel modes of transformations and can produce unusual rate acceleration and unusual stereoinduction. For instance, non-immobilized chiral heterogeneous catalysts in water have elicited much interest, and such systems have been shown to have a number of impressive characteristics.[1] Composed of insoluble metal salts or zero-valent metals with chiral modifiers, these catalyst systems are generally advantageous in terms of simplicity, durability, reusability, prevention of metal contamination into products, and suitability for integration into, for example, tandem reactions. Moreover, they sometimes exhibit superior performance in water over analogous homogeneous systems even in reactions between water-insoluble substrates.[1] In spite of the unique and unpredictable nature of such catalysts, there remain only a few examples of nonimmobilized, chiral heterogeneous catalysts in water.

The physical and electronic nature of silicon differs in a number of respects from that of carbon, and this can result in increased robustness under harsh conditions, increased lipophilicity, and significantly altered polarization and pharmacokinetic properties of organosilicon compounds compared with their carbon analogues.[2] The incorporation of a silicon atom at a specific site in a substrate allows the attractive properties of the C−Si bond to be made available in chemical synthesis and in materials and medicinal chemistry.[3] Given that α-chiral silanes are deemed to be versatile stereodefined placeholders for C−C bonds[4,5] as well as C−O bonds,[6] enantioselective installation of silicon groups has developed into an very promising area of research. Among the available methods to furnish organosilicon compounds in an enantioselective fashion, conjugate addition of silyl metal reagents is currently the most reliable. The history of this reaction commenced with classic protocols involving stoichiometric amounts of silylcuprates,[7] followed by activation of silyl reagents by catalytic amounts of metals such as Hayashi's 1,4-disilylation protocol with palladium catalysts.[8] However, the limited scope of this approach stimulated the development of more efficient catalysts for asymmetric silyl transfers. Although Hartmann and Oestreich,[9] Hoveyda,[10] and Proctor[11] developed Rh(I)-phosphine, Cu(I)-N-heterocyclic carbene (NHC), and metal-free NHC catalysts for activation of Suginome's interelement silylboron reagent [dimethylphenylsilyl pinacolatoboronate PhMe$_2$SiB(pin)] toward asymmetric conjugate addition,[12] these approaches tended to have limited coverage of acceptors and required an extensive array of ligands.

Herein, we describe our efforts to highlight the use of water-insoluble chiral Cu(II) catalysts in asymmetric silyl conjugate addition of PhMe$_2$SiB(pin) to α,β-unsaturated acceptors.[13] The absolute durability and ready availability of Cu(II) underscore the value of the Cu(II)-based catalyst over an array of traditional Cu(I)-based catalysts.[14]

We first prepared chiral Cu(II) complexes with fixed coordination geometry from Cu(II) salts and chiral 2,2′-bipyridine **L1**.[15] After examining several conditions, it was found that acicular purplish crystals were obtained from Cu(acac)$_2$ and **L1**. The crystals were fully characterized by spectrometric methods (see the Supporting Information (SI)) and were used in the reaction of chalcone **1a** with PhMe$_2$SiB-(pin) **2** in water, providing the desired product with high selectivity (Table S1, entry 1). The heterogeneity of the Cu(II) complex was confirmed by inductively coupled plasma (ICP) analysis (see SI). The use of insoluble Cu(OH)$_2$ also afforded good results (entry 2). In contrast, use of a possible conformational mixture of complexes that was prepared *in situ* in water led to a reduction in both the yield and selectivity (entries 3 and 4). The use of highly soluble Cu(II) salts also resulted in poor results (entries 5−7), whereas Cu(II) halides gave moderate enantioselectivities (entries 8 and 9). Although all components involved in the reaction under the conditions

detailed in entry 1 are immiscible with water, the reaction did not proceed at all without any solvent even in the presence of 1 equiv of water (entry 10). The reaction in anhydrous solvents did not furnish any product including a β-silyl boron enolate (entry 11). The reaction run in diethyl ether in the presence of an equimolar amount of methanol, which worked well in boron conjugate addition,[14] provided reduced yield and enantioselectivity (entry 12). The reaction run in alcohol alone also afforded poor results (entries 13 and 14). Finally, it was established that the desired catalysis could be exerted only in water.

The scope of the reaction was surveyed under the optimized reaction conditions (Table 1). Chalcone derivatives bearing

Table 1. Scope of the Reaction with α,β-Unsaturated Carbonyl Compounds

Entry	R^1	R^2		Yield (%)[a]	Ee (%)[b]
1	Ph	Ph	1a	92 (90)[c]	93 (93)[c]
2	4-MeOC$_6$H$_4$	Ph	1b	88	94
3	Ph	4-MeC$_6$H$_4$	1c	91	98
4	Ph	4-ClC$_6$H$_4$	1d	87	92
5	Ph	2-ClC$_6$H$_4$	1e	89	90
6	Ph	3-NO$_2$C$_6$H$_4$	1f	87	96
7	4-FC$_6$H$_4$	4-ClC$_6$H$_4$	1g	88	90
8	4-FC$_6$H$_4$	4-MeC$_6$H$_4$	1h	91	87
9	Me	Ph	1i	85	88
10	Me	4-MeOC$_6$H$_4$	1j	88	87
11	Ph	Me	1k	91	84
12	Ph	^{t}Bu	1l	83	88
13		-(CH$_2$)$_2$-	1m	91	87
14		-(CH$_2$)$_3$-	1n	85	86
15	Ph $\overset{O}{\underset{}{}}$ Me Ph		1o	87	89
16[d]	MeO	Ph	1p	87	88
17[d]	EtO	Ph	1q	81	90
18[d]	EtO	4-MeC$_6$H$_4$	1r	84	85
19[e]		-OCH$_2$-	1s	85	91
20[e]		-O(CH$_2$)$_2$-	1t	91	93
21			1u	80	87
22[f]	Me	CH=CHPh	1v	90	92
23[f]	Ph	CH=CHPh	1w	95	96

[a]Isolated yield. [b]Determined by HPLC analysis. [c]Gram-scale synthesis to give the product (1.13 g). [d]Performed for 48 h. [e]At 10 mol % catalyst loading. [f]Triton X-100 (25 mg) was added.

either electron-donating or -withdrawing groups at any position of the benzene ring reacted smoothly with **2** to afford the desired products in high yields with high enantioselectivities (**1a–h**). The catalyst was suitable for use in a gram-scale reaction without any loss of enantioselectivity. Not only acyclic aliphatic α,β-unsaturated ketones (**1i–l**), but also cyclic ketones (**1m** and **1n**) were also applicable without significant erosion of enantioselectivity. The silyl group could be transferred to a crowded position to generate a quaternary carbon center bearing a C–Si bond (**3o**). Similarly, acyclic α,β-unsaturated esters (**1p–r**) and

lactones (**1s** and **1t**) reacted with **2** in a highly enantiomeric manner. Of the two possible isomers, the 1,4-addition products were obtained exclusively in high yields and with high enantioselectivities when acyclic α,β,γ,δ-unsaturated dienones **3v** and **3w** were applied as substrates. The produced allylsilanes can be employed in Hosomi−Sakurai reactions[16] and other transformations such as 1,4-phenyl migration from the silyl group to a carbocation at the δ-position upon treatment with HBF$_4$[17] and intramolecular allylation.[2b] It was therefore apparent that a wide range reactions could be catalyzed by the Cu(II)-based catalyst with multifarious substrates.

The catalyst system was suitable for use with other electron-deficient α,β-unsaturated compounds (Table 2). α,β-Unsatu-

### Table 2. Scope of the Reaction with Electron-Deficient Alkenes

entry	EWG	R		yield (%)[a]	ee (%)[b]
1	CN	Ph	1x	78	94
2	CN	4-MeOC$_6$H$_4$	1y	80	82
3	CN	4-FC$_6$H$_4$	1z	70	90
4	CN	2-Furyl	1aa	83	87
5	CN	Me	1bb	90	90
6[c]	NO$_2$	Ph	1cc	61	82
7	NO$_2$	4-MeC$_6$H$_4$	1dd	63	78
8	NO$_2$	4-FC$_6$H$_4$	1ee	58	81
9	NO$_2$	3-Furyl	1ff	67	87

[a]Isolated yield. [b]Determined by HPLC analysis. [c]Performed for 48 h with **2** (1.5 equiv).

rated nitriles (**1x−bb**) could be used under the optimal reaction conditions, and the reaction was not inhibited by other functional groups that were capable of coordinating to the Cu(II) core (**1aa**). It was found that the catalyst was also reactive toward a nonconjugated α,β-unsaturated nitrile (**1bb**). The first successful examples involving the application of β-nitrostyrenes (**1cc−ff**) in asymmetric silyl conjugate addition are notable because this provides a synthetic route to useful β-aminosilanes and the corresponding β-silyl diazonium intermediates,[18] which are not available even through analogous boron conjugate addition.

When cyclic α,β,γ,δ-unsaturated dienones were employed as acceptors, δ-silylated products were obtained exclusively, as expected (Scheme 1). In boron conjugate addition, the use of heterogeneous Cu(OH)$_2$-based catalysts tends to lead to the 1,6-addition pathway being followed.[1b,d] To gain insights into the mechanism of the 1,6-addition pathway, the progress of the reaction was investigated in detail (Table S2). At the beginning of the reaction, kinetically protonated δ-silylated product **4hh**, bearing a β,γ-alkene moiety, was obtained exclusively with almost

Scheme 1. Silyl Conjugate Addition to Cyclic Dienones
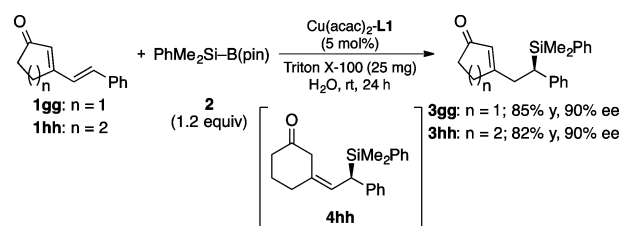
complete Z-preference. After stirring for 3 h, the reaction furnished γ-protonated isomer **3hh** predominantly. Eventually, no **4hh** remained, and a significant amount of **3hh** was obtained after 24 h. Hoveyda et al. reported that by using their NHC-Cu(I) catalyst system, **4hh** was obtained that contained 15−20% **3hh** as a result of adventitious isomerization.[10b,d] The Cu(II)-based system ultimately reached thermodynamic convergence with the formation of **3hh**. Considering that an analogous δ-borylated enolate intermediate underwent protonation at the γ-position directly,[1b,d] the preferential protonation of a δ-silylated enolate intermediate at the α-position may be interpreted as a result of a hyperconjugative interaction. It is reasonable to suppose that the reaction environment at the interface between the heterogeneous Cu(II) catalyst and water is responsible for the propagation of a stepwise process that includes protonation and subsequent isomerization.

Given that a CuBr$_2$-based complex was shown by crystallographic analysis to have a square pyramidal structure,[19] it was assumed that, in Cu(acac)$_2$-**L1** crystals, Cu(II) is coordinated by **L1** in a tridentate fashion through N,N,O-type coordination. UV−vis absorption spectroscopy indicated that the conformation of an isolated Cu(acac)$_2$-**L1** crystal in aqueous tetrahydrofuran (THF) was close to that of the X-ray crystal structure.[20] The absorption is characterized by a strong major absorption at 980 nm that may be assigned to the transition of d_{xz} or $d_{yz} \rightarrow d_{z^2}$, suggesting a trigonal bipyramidal geometry (see SI).[1c,21] The catalyst behavior in the solution state was then investigated using aqueous THF solutions (Figure 1). A sharp increase in
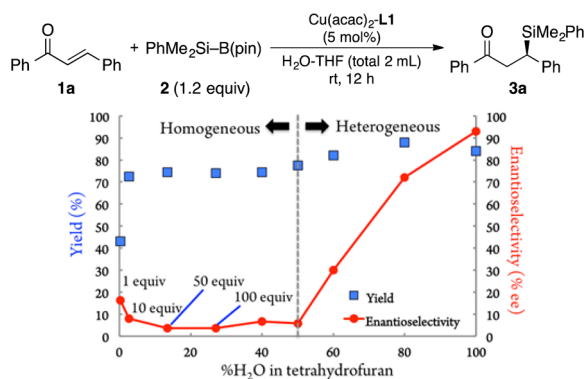

Figure 1. Homogeneous versus heterogeneous catalysis.

enantioselection correlated with a decrease in solubility of the catalyst, whereas the yields of **3a** were maintained. When the amount of water was equal to or less than the amount of THF, the catalyst solution became transparent. Given that leaching of Cu was not detected in the absence of THF, the catalyst should be entirely heterogeneous in water. It is therefore asserted that a water-insoluble heterogeneous Cu(II) catalyst coupled with a large excess of water is required for highly stereoselective execution of asymmetric silyl conjugate addition.

The postulated catalytic cycle commences with sp^3-hybridization of the boron atom in **2** caused by association with the uncoordinated OH group of **L1** (Scheme S1). The chiral Cu(II) complex would react with sterically more congested **2** to deliver a chiral silylcopper(II) complex. The latter may involve a nonbonding π−π interaction between the slightly distorted bipyridine and the phenyl group on silicon. It was surmised that the selective transformation of the silicon group might be rationalized by the energetically favored formation of a B−O

bond. The electron-withdrawing nature of the Ph ring on the silicon atom would also facilitate polarization across the Si−B bond and subsequent cleavage. The putative silylcopper(II) species would undergo nucleophilic silyl transfer to α,β-unsaturated acceptors. Unlike the well-documented, isolable silylcopper(I) species,[22] only a few Cu(II)−carbon or silicon structures are known.[23] Although multidisciplinary research is required to comprehend the electronic nature of such species, the d^9 configuration of the copper may lead to p-character of the bond[24] with silicon, which is anticipated to play a crucial role in stereoinduction. The "soft" nature of Cu(I) has been shown to lead to high activity for couplings with sp^2 carbon centers, as represented by conjugate additions through d−π interactions; however, this entails the use of anhydrous solvents and an inert atmosphere. In contrast, Cu(II) tends to coordinate to the lone pair of electrons on the carbonyl oxygen rather than to the π-electrons of a double bond because of an intrinsic instability of the d^9−π interaction caused by its unpaired electron. This leads to a new mechanism involving an alternative sense of enantioselection via an O-enolate intermediate. The corresponding Cu(II) enolate would readily release the β-silylated carbonyl compounds. Aqueous environments would tend to stabilize the geometry of the chiral silylcopper(II) intermediate and lead to instantaneous protonation of the O-enolate intermediate to deliver the corresponding β-silylated product.

Catalyst reusability was evaluated in the reaction of cyclopentenone **1m** with **2**. After the first run, the reaction tube was centrifuged at 3000 rpm to separate the reaction mixture into aqueous, organic, and solid phases (Figure 2). No product,

Figure 2. Separated phases after centrifugation of the reaction mixture.

copper, or chiral ligand was detected in the aqueous phase, whereas the product **3m** and a trace amount of the chiral ligand were found in the organic phase (see SI). The product **3m** was isolated in 85% yield with 87% ee. The collected solid was then used in a second run, resulting in a comparable result with little erosion of the selectivity (80% yield, 82% ee).

In summary, we have isolated crystals of a chiral heterogeneous Cu(II) catalyst prepared from Cu(acac)$_2$ and **L1**, which, although not soluble in water, nevertheless catalyzes asymmetric silyl conjugate addition of lipophilic substrates in this medium. The catalytic asymmetric reactions proceed in high yields and with high enantioselectivities only in water. The reactions either did not proceed at all or gave low yields with low enantioselectivities in many organic solvents and even in mixed water/organic solvents in which the catalyst and substrates dissolved completely. This result is in striking contrast to many conventional organic reactions in which solubility is required. As a synthetic methodology, chiral Cu(II) catalysis in water has several advantages over previously reported catalyst systems, such as wide substrate scope and high enantioselectivity. The approach is also in line with the concepts of green sustainable chemistry because it leads to a reduction in the amount of organic solvents used and is amenable to catalyst recovery and recycling. The antagonistic combination of water-insoluble chiral heterogeneous catalyst coupled with the use of water as a solvent may

open new avenues in organic chemistry that are not available through the use of conventional homogeneous catalyst systems. Water may play a prominent role in building sterically confined transition states and accelerating subsequent protonation to achieve high yields and high enantioselectivities.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b11418.

> Experimental details and characterization of the products (PDF)

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Notes
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