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Cyclopropanation of Olefins with Diazo Compounds Catalyzed by a Dicopper-substituted Silicotungstate [γ-$H_2SiW_{10}O_{36}Cu_2(\mu$-1,1-$N_3)_2]^{4-}$

Keigo Kamata,[1,2] Toshihiro Kimura,[1] and Noritaka Mizuno*[1,2]
[1]*Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656*
[2]*Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi 332-0012*

(Received April 13, 2010; CL-100360; E-mail: tmizuno@mail.ecc.u-tokyo.ac.jp)

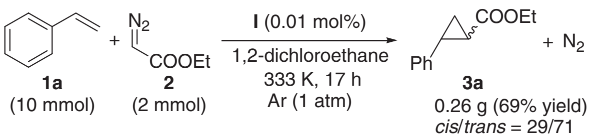
The dicopper-substituted γ-Keggin silicotungstate $(TBA)_4$-[γ-$H_2SiW_{10}O_{36}Cu^{II}_2(\mu$-1,1-$N_3)_2$] (**I**, TBA = tetra-*n*-butylammonium) could act as an efficient precatalyst for the chemoselective cylopropanation of olefins with diazo compounds. Various kinds of olefins were efficiently converted to the corresponding cyclopropane derivatives in good yields.

Cyclopropanes are important chemical compounds because they have been used as starting materials and intermediates in organic synthesis.[1] Many efficient systems have been developed for the copper-catalyzed efficient diastereo- and enantio-selective synthesis of cyclopropanes.[1,2] An electrophilic copper(I) carbene intermediate $L_nCu{=}C(R)R'$ has been proposed on the basis of mechanistic, kinetic, and computational studies.[3] Very recently, the syntheses and structures of the mono- and dinuclear copper carbene species with neutral iminophosphanamide and/or anionic β-diketiminate ligands have been reported and the reactivities of these compounds are discussed.[4] Although some dinuclear Ru- and Rh-based compounds are efficient catalysts for the cyclopropanation,[1,2,5] the cyclopropanation of olefins by dinuclear copper catalysts has scarcely been reported.[6]

The catalysis of metal-substituted POMs (polyoxometalates), which are synthesized by the introduction of substituent metal cations into the vacant site(s) of lacunary POMs, have attracted much attention because of the unique reactivity that results from the composition and structure of the catalytically active sites.[7] Recently, we have reported the cooperative activation of organic substrates such as alkynes and azides by a dicopper-substituted γ-Keggin silicotungstate with bis-μ-1,1-azido ligands $(TBA)_4$[γ-$H_2SiW_{10}O_{36}Cu^{II}_2(\mu$-1,1-$N_3)_2$] (**I**, Figure S1).[8,9] Compound **I** shows high catalytic activity for oxidative alkyne–alkyne homocoupling, 1,3-dipolar cycloaddition of organic azides to alkynes, and three-component reaction of organic halides, NaN_3, and alkynes to produce 1,4-disubstituted-1,2,3-triazole derivatives.[8] In this communication, we report that **I** acts as a precatalyst for the chemoselective cyclopropanation of various kinds of olefins with diazo compounds.

First, the cyclopropanation of styrene (**1a**) with ethyl diazoacetate (**2**) was carried out under various conditions (Table S1).[9] In the present system, diastereomeric mixture of the corresponding cyclopropane **3a** was obtained with the co-production of diethyl maleate and diethyl fumarate (**4**) by the dimerization of **2**. The cyclopropanation of **1a** with **2** in the presence of **I** efficiently proceeded in dichloromethane and 1,2-dichloroethane solvents (**I**:**1a**:**2** = 1:250:100) and the *cis*/*trans* ratios of **3a** were 44/56 and 45/55, respectively. In the absence of **2**, **4** was formed in 85% yield with ≥99% selectivity. The mono-copper-substituted silicotungstate $(TBA)_4$[α-$H_2SiW_{11}CuO_{39}$] showed low catalytic activity and selectivity to **3a**. The dilacunary silicotungstate $(TBA)_4$[γ-$SiW_{10}O_{34}(H_2O)_2$] and saturated silicotungstate $(TBA)_4$[γ-$SiW_{12}O_{40}$] were almost inactive, suggesting that the tungsten species are not involved in the present catalytic system. The chemoselectivity to **3a** could be increased by the slow addition of **2** into the reaction solution of **I** and **1a**. Upon the addition of **2** in five portions, the cyclopropanation proceeded efficiently and chemoselectively to give **3a** in 83% yield.

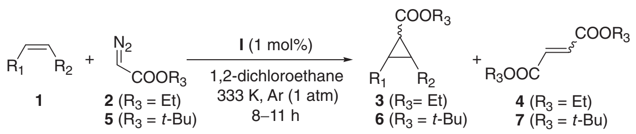
The cyclopropanation of **1a** with **2** with low catalyst loading of **I** (0.01 mol % with respect to **2**) chemoselectively proceeded and 0.26 g of analytically pure **3a** was isolated (eq 1). In this case, the turnover number (TON) reached 6926 and the value was much higher than those for $CH_3C(CH_2NPCp_3)_3Cu(OTf)_2$ (175, Cp = cyclopentyl), $[Cu(dppipa)_2]ClO_4$ (425, dppipa = $(Ph_2P)_2N(^iPr)$), $Tp^{Ms}Cu$ (485, Tp^{Ms} = hydrotris[3-(2,4,6-trimethylphenyl))pyrazolylborate], $[Rh(C_7H_{15}CO_2)_2]_2$ (168), $Fe(TDCPP)/CoCp_2$ [970, TDCPP = *meso*-tetra(2′,6′-dichlorophenyl)porphyrinato], $Rh(NCTMP)I_2$ [1860, NCTMP = *N*-confused tetrakis(mesityl)porphyrin] systems.[10,11]

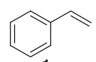
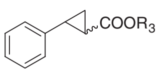
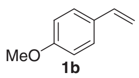
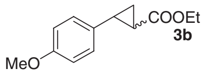
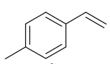
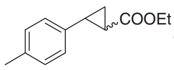
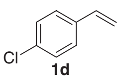
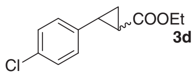
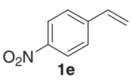
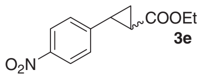
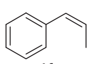
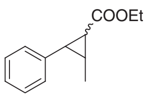
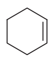
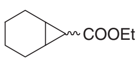
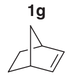
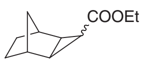
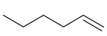


(1)

The scope of the present catalytic cyclopropanation with diazo compounds (**2** and *tert*-butyl diazoacetate (**5**)) was investigated with regard to a range of structurally diverse olefins (**I**:**1**:**2** or **5** = 1:1000:100, Table 1). Various kinds of olefins could efficiently and chemoselectively be converted to the corresponding cyclopropanes in high yields. The cyclopropanation of styrenes **1a**–**1e**, which contain electron-donating as well as electron-withdrawing *p*-substituents, proceeded selectively to afford the corresponding cyclopropanes **3a**–**3e** in good yields (Entries 1–7). The reaction of **1a** with **2** proceeded at ambient temperature under the stoichiometric conditions (**I**:**1a**:**2** = 1:100:100) (Entry 2). The reaction rates were dependent on the electronic effects of the substituents on the aromatic rings of styrenes. The Hammett plots ($\log(k_X/k_H)$ versus σ^+) for the competitive cyclopropanation of **1a** and *p*-substituted styrenes **1b**–**1e** are shown in Figure S2.[9] The negative ρ^+ value (−0.19) indicates the electrophilic active copper carbene species and partial positive charge on the styrene in the transition state.[12] The reaction of internal *cis*-β-methylstyrene **1f** proceeded stereospecifically to form the corresponding cyclopropane **3f** (Entry 8). Not only aryl olefins **1a**–**1f** but also alkyl olefins **1g**–**1i** were efficiently converted to the corresponding cyclopropanes (Entries 9–12). The cyclopropanation of cyclohexene **1g** and

Table 1. Cyclopropanation of various olefins with diazo compounds[a]



Entry	Olefin	Diazo compound	Yield /%	Product (selectivity/%)	
1	 **1a**	**2**	90	 **3a**	(92) *cis*/*trans* = 41/59
2[b]		**2**	70	**3a**	(79) *cis*/*trans* = 36/64
3		**5**	82	**6a**	(92) *cis*/*trans* = 30/70
4	 **1b**	**2**	87	 **3b**	(94) *cis*/*trans* = 42/58
5	 **1c**	**2**	90	 **3c**	(93) *cis*/*trans* = 40/60
6	 **1d**	**2**	95	 **3d**	(92) *cis*/*trans* = 39/61
7	 **1e**	**2**	84	 **3e**	(91) *cis*/*trans* = 40/60
8	 **1f**	**2**	77	 **3f**	(79) *syn*/*anti* = 42/58
9	 **1g**	**2**	89	 **3g**	(79) *endo*/*exo* = 16/84
10	 **1h**	**2**	86	 **3h**	(88) *syn*/*anti* = 16/84
11	 **1i**	**2**	72	 **3i**	(77) *cis*/*trans* = 41/59
12		**5**	67	**6i**	(79) *cis*/*trans* = 34/66

[a]Reaction conditions: **I** (1 mol % with respect to **2** or **5**), **1** (10 mmol), **2** or **5** (1 mmol), 1,2-dichloroethane (3–4.5 mL), 333 K, Ar (1 atm), reaction time (8–11 h). Detailed conditions are shown in Table S2. Yield (%) = (**3** or **6** (mol) + 2 × **4** or **7** (mol))/**2** or **5** used (mol) × 100. Selectivity to **3** or **6** (%) = **3** or **6** (mol)/(**3** or **6** (mol) + 2 × **4** or **7** (mol)) × 100. [b]**I** (1 mol % with respect to **1a** and **2**), **1a** (1 mmol), **2** (1 mmol), 1,2-dichloroethane (6 mL), 293 K, 14 h.

norbornene **1h** proceeded highly diastereoselectively and the formation of *exo*-**3g** and *anti*-**3h** was favored (Entries 9 and 10). The *anti*-**3h**/*syn*-**3h** ratio (86/14) was much higher than or comparable to those of Cu-, Rh-, and Pt-based catalytic systems,[13] suggesting the steric effect of the divacant γ-Keggin anion ligand. The reaction of the nonactivated terminal olefin **1i** also proceeded selectively to form the corresponding cyclopropane **3i** (Entry 11). The reaction also proceeded efficiently when **5** was used as the carbene source instead of **2**. The diastereoselectivities for the reaction of **1a** and **1i** were slightly increased and the *trans*/*cis* ratios were 30/70 (**6a**) and 34/66 (**6i**), respectively.

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