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Efficient and environment-friendly Glaser coupling of terminal alkyne catalyzed by multinuclear copper complexes under base-free condition [†]

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An efficient catalytic system with dinuclear complex $[Cu_2(ophen)_2]$ **1** and tetranuclear complex $[Cu_4(ophen)_4(tp)]$ **2** as catalyst has been developed for the Glaser coupling reaction, which adopts environment-friendly water as solvent at room temperature under air/O₂ atmosphere and avoids the utilization of any base. Satisfyingly, due to poor solubility in common solvents, tetranuclear compound **2** served as a molecular heterogeneous catalyst and could be reusable five times without loss of activity. Both catalysts could be prepared in high yield via simple hydrothermal reactions with cheap ligands, which in combination environment-friendly water media and mild catalytic reaction conditions makes the approach accords with the concept of green chemistry in synthesis of 1,3-diynes.

Introduction

Over the past decades, the concept of green chemistry in organic synthesis has attracted increasing attention around the world. Hence, the challenges of effective synthetic method are not only high-yielding but also environment-friendly.¹ All of above request chemists to find nontoxic/renewable materials, easy bulk preparation of catalysts and green/free solvent reaction conditions in a green synthetic strategy. In this work, we describe a green and effective method towards the construction of symmetrical 1,3-diynes.

1,3-Diynes have obtained widespread applications in the synthesis of material chemistry, natural products, pharmaceuticals,² such as polymers,^{2a,d} polyradical,^{2b} Ivorenolide A,^{2f} Debilisone C,^{2e,g} phosphoiodyns A^{2h} etc. In contrast to the homocoupling of various alkynyl organometallics³ (organotin,^{3a} organosilicon,^{3b} organolithium,^{3c} organoboron,^{3d} organomagnesium,^{3e} compounds), alkynyltellurides⁴ or iodoalkynes,⁵ the homocoupling of terminal alkynes is widely believed to be an economic and practical method to construct 1,3-diynes, for instance, Glaser-Hay coupling⁶ and Cadiot-Chodkiewicz coupling,⁷

Since 1869 year, Glaser firstly found the oxidative coupling of copper acetylides to access diynes, numerous metal calalytic systems like CoBr₂,⁸ palladium reagents,⁹ [Ru(dppp)₂(CH₃CN)CI][BPh₄],¹⁰ Au nanoparticles,¹¹ Au(I)/Au(III)¹² etc have been studied on this reaction. However, most of their widely applications are limited because of their higher price or unstability in air. Copper-catalyzed aerobic homocoupling of terminal alkynes remains the most popular due to copper being an abundant and inexpensive metal. Numerous modifications, like CuI/iodine,¹³ Cu¹-USY,¹⁴ CuNPs/MagSilica,¹⁵ CuAl-LDH,¹⁶ {Cu²⁺-M³⁺-Cu²⁺}¹⁷ etc have been demonstrated to exhibit good catalytic activity. In addition, looking for more green solvents such as PEG,¹⁸ ionic liquid,¹⁹ fluorous media,²⁰ ScCO₂,²¹ water²² or solvent-free²³ conditions also have been attracted much attention. In spite of the significant progress offered by these methods, there are still certain limitations because of complicated

preparation process of catalyst,¹⁷ hash reaction conditions, including excess bases (for example, Na₂CO₃, KOAc, CH₃ONa and Et₃N),^{13,15,24} or high temperature $(110^{\circ}C)^{14}$ etc. Therefore, it is still necessary to develop more simple, effective, and environmentally friendly method for the construction of symmetrical 1,3-Diynes compounds by the Glaser coupling.

In recent years, we have focused on the synthesis of metal organic complexes with novel structures and exploration of their application on catalytic organic synthesis.²⁵ Compared with other copper complexes synthesized in our group,²⁶ metal center of planar dinuclear complex Cu₂(ophen)₂ (1, Fig S2) with hydroxylated Nheterocyclic ligands complex is redox active.²⁷ Driven by our continuing interest in catalytic application of copper-based complexes, we envisioned whether the aerobic Glaser-Hay coupling reaction could occur with compound 1 as catalyst. As expected, we detected that Cu₂(ophen)₂ provided access to an effectively active species for the Glaser coupling reaction using environmentally friendly water as media and without any base. Satisfyingly, $[Cu_4(ophen)_4(tp)]$ (2, Fig S3) with a tetranuclear mixed-valence dumbbell structure which is the derivative of compound 1 also showed obviously catalytic activity under similar conditions. It is noteworthy that compound 2, which is inexpensive and easy prepared, can serve as a heterogeneous catalyst. In previous reports, the preparation process of copper-based heterogeneous catalyst were usually complicated.28

Herein, we wish to report a novel and mild Cu-promoted direct Csp-Csp coupling reaction through aerobic homocoupling of terminal alkynes. The protocol has the advantages of broad substrates scope, green reaction conditions, easy operation and good yields (Scheme 1).

$$2 \text{ R} \longrightarrow \begin{bmatrix} Cu_2(\text{ophen})_2 \\ H_2O, \text{TBAB,r.t.} \end{bmatrix} \text{ R} \longrightarrow R \quad (R = Aryl, Alkyl)$$

Scheme 1. Homocoupling of terminal alkynes.

Experimental section

Materials and physical measurements

 $[Cu_2(ophen)_2]$ (1) and $[Cu_4(ophen)_4(tp)]$ (2) were synthesized according to our previous methods.²⁷ Other chemicals were analytically pure from commercial sources and used without further purification. The catalyst was dried at room temperature before the catalytic reactions. The conversion of terminal alkynes was obtained by GC or ¹HNMR. Gas chromatography (GC) analyses were obtained by Agilent 7820A (FID from AGILENT 7820) equipped with a cross-linked (95%)-dimethyl-(5%)- diphenylpolysil-oxane column (HP-5, 30 m * 0.32 mm * 0.25 µm), helium, injector temperature 250°C, detector temperature 300°C, and oven temperature program 45°C (3 min)-20°C/min-280°C (2 min). ¹H and ¹³C NMR spectras were recorded with ASCend TM 600 MHz in CDCl₃ with TMS as the internal standard. Powder X-ray diffraction (XPRD) datas were collected in a Rigaku Ultima IV diffractometer.

General procedure for the Cu₂(ophen)₂ catalyzed_homocoupling for Table 2.

A solution of the corresponding terminal alkynes (1.0 mmol), Cu₂(ophen)₂ (6.5 mg, 5 mol%), TBAB (8 mg, 5 mol %) and water (1.0 mL) in 5 mL round-bottomed flask was stirred under air and the reaction was monitored by TLC. After the substrate was consumed, the reaction conversions were determined by gas chromatography (GC) analysis. The resulting mixture was poured into brine (10 mL), and extracted with dichloromethane (3 * 10 mL). The organic layer was washed with brine, dried over Mg₂SO₄, the residue was chromatographed via a short column of silica gel and evaporated under reduced pressure. The products were determined by ¹HNMR and ¹³CNMR spectroscopy.

General procedure for Table 3.

A suspension of terminal alkynes (1.0 mmol), $[Cu_4(ophen)_4(tp)]$ (7.5 mg, 5 mol%) with TBAB (8 mg) in H₂O (1 mL) was stirred at 60°C under O₂ (1 atm). After the substrate was consumed, the reaction conversions were determined by GC analysis.

Recycle Experiment

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At the end of the reaction, the catalyst was centrifuged and washed with ethanol and water (5 * 10 mL) respectively and drying in air. It was reused directly without further purification. The recovered catalyst was used in the next run, and almost consistent activity was observed for 5 consecutive cycles.

Results and discussion

The copper-catalyzed alkyne coupling reaction was initially evaluated using phenylacetylene (1a) as substrate for optimization of reaction conditions. Firstly, the reaction was carried out in DMF, with $Cu_2(ophen)_2(1)$ (5 mol%) as catalyst and KF (5 mol%) as base, under air at different temperatures. It was found that the reaction proceeded perfectly and the conversions had no significant differences at r.t. or 60°C (Table 1, entries 1-2). Fortunately, we found that the homocoupling reaction still performed well in 99.5% conversion under base-free condition (Table 1, entry 3). Decreasing the amount of catalyst resulted in decrease of conversions and extension of reaction times (Table 1, entries 4-5). A control experiment conducted in N₂ atmosphere showed that the reaction did not occur (Table 1, entry 6). When the reaction was conducted in EtOH and H₂O respectively, the high conversion was obtained although it took a long time in H₂O because of the poor solubility of substrate (Table 1, entries 7-8). Adding TBAB (5 mol%) as the phase transfer catalyst, the reaction time can be obviously shortened using water as solvent (Table 1, entry 9). Therefore, the optimal base-free system under air for this reaction involves $Cu_2(ophen)_2$ (5 mol%) and TBAB (5 mol%) in greener water at room temperature.

Table 1. Optimization of reaction conditions^a

	2	Cu ₂ (ophen	<u>)</u> 2	} -=-=		
Entry	Cat(mol %)	base	Temp (°C)	Sol.	Time (h)	Conv. (%) ^b
1	5	5	r.t.	DMF-1	10	99.6
2	5	5	60	DMF-1	8	99
3	5	-	r.t.	DMF-1	10	99.5
4	1	-	r.t.	DMF-1	20	56
5	3	-	r.t.	DMF-1	20	94
6 ^c	5	-	r.t.	DMF-1	20	-
7	5	-	r.t.	EtOH-1	12	99
8	5	-	<i>r.t.</i>	H ₂ O-1	20	99
9 ^d	5	-	r.t.	H ₂ O-1	10	99

Reaction conditions: phenylacetylene (1 mmol; 55 µL), catalyst (5 mol%; 6.5 mg), solvent (1 mL), air; ^b determined by GC; ^c Nitrogen atmosphere; TBAB (5 mol%, 8 mg).

Encouraged by the efficiency and environmental friendliness of the reaction protocol described above, we investigated the substrate scope under optimized conditions. The terminal alkynes bearing electron-deficient and electron-rich aryl groups proceeded homocoupling reactions smoothly and gave the corresponding 1,3diyne derivatives 2a-j in good to excellent yields (Table 2). It seemed that the electronic and steric effects of substituents on benzene ring had no obvious effect on the Csp-Csp homocoupling reaction (Table 2, entries 1-10). The heteroaromatic alkynes 1k-1l were also compatible substrates and gave the target products 2k-2l in 98% and 99% yields respectively (Table 2, entries 11-12). Interestingly, we successfully expanded the scope of substrates to aliphatic alkynes and the yields of the obtained products being 97-99% (Table 2, entries 13-15). It was worth noting that the reaction condition of aliphatic alkynes didn't need to be strengthened and the reaction rate was faster than aromatic alkynes under same condition. For instance, the homocoupling of aliphatic alkynes 1m-o can be completed in only 5h (Table 2, entries 13-15).

Table 2. homocoupling of various terminal alkynes a

2 R		Cu ₂ ophen ₂ (5 mol%	6) ► RR (R=	Arvl. Alkvl)
2 11 =		H ₂ O (1mL);TBAB (5		
Entry		Substrates	Products	Yield%^b
1	1a	2a 2a		95
2	1b	2b		94
3	1c	2c		96
4	1d	,o-√ 2d		96
5	1e	2e		93

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^{*a*} Reaction conditions: alkynes (1 mmol), Cu₂(ophen)₂ (5 mol%, 6.5 mg), TBAB (5 mol%), H₂O (1 mL), r.t., 10 h; **1m-1o**:5h; ^{*b*} Isolated yield.

Our group found that $[Cu_4(ophen)_4(tp)]$ (2) can be obtained from dinuclear 1 in the presence of terephthalic acid as ligands under hydrothermal conditions.²⁷ Mixed-valence copper(I,II) complex 2, which consists of a pair of $[Cu_2(ophen)_2]^+$ fragment bridged by a dicarboxylate ligand, has a neutral tetranuclear dumbbell structure. It is generally known that the change of ligand has subtle influence on properties of metal complexes. To see this point, we explored the catalytic activity of compound 2 to the homocoupling of terminal alkynes. It was found that the conversion of phenylacetylene obviously rose when the temperature was increased from r.t. to 60°C as well as under oxygen atmosphere. The result indicated that the catalytic activity of complex 2 for homocoupling of alkynes was lower than compound 1 because of the change of metal complex structure based change of ligand (Table 3, entries 1-3). However, satisfyingly, catalyst 2 could be served as a heterogeneous catalyst² and still keep high activity after recycled five times (Table 3, entries 4-5). Comparison of the powder XRD patterns of the fresh and five times reused compound 2 were performed (Fig. S4), which showed similar powder XRD patterns and clearly demonstrated the practical recyclability of catalyst 2 and its remarkable stability.

Table 3. Optimization of reaction conditions with compound 2 as catalyst ^a

? _</th <th><u>}-=</u></th> <th colspan="4">[Cu₄(ophen)₄tp] (5 mol%) H₂O, TBAB</th>	<u>}-=</u>	[Cu ₄ (ophen) ₄ tp] (5 mol%) H ₂ O, TBAB			
	Entry	Cat (mol %)	Temp (°C)	Conv. (%) ^b	
	1	5	r.t.	70	
	2	5	60	80	
	3 ^c	5	60	98	
	4 ^{<i>c</i>}	5 (run 3rd)	60	94	
	5 ^{<i>c</i>}	5 (run 5th)	60	90	

^{*a*} Reaction conditions: phenylacetylene (1 mmol), Cu₄(ophen)₄(tp) (5 mol%, 7.5 mg), TBAB (5 mol%), H₂O (1 mL), air; ^{*b*} determined by GC; ^{*c*} oxygen atmosphere (1 atm).

Similarly, we then focused on our attention to substrate generality using the optimized reaction conditions (**Table 3**, entry 3). The substrates with typical electronic effect of substitute group were investigated. Both aromatic alkynes and aliphatic alkynes gave

desired 1,3-diynes in excellent conversions under the condition of heterogeneous catalysis (**Scheme 2**). Broad tolerance for various substrates proves that complex **2** is also an efficient catalyst for the Glaser coupling reaction.

2 R	ohen) ₄ tp] (5 mol%	⁶⁾ → R-==
H ₂ O,TBA	\B(5 mol%),60°C	,0 ₂
R = 4-MeO-C ₆ H ₄ ;	90 %;	R = 4-Br-C ₆ H ₄ ; 90 %;
$R = C_6H_5;$	98 %;	R = 3-CI-C ₆ H ₄ ; 91 %;
R = tert-butyl;	99 %;	R = 2-thienyl; 93 %;
R = 4-Me-C ₆ H ₄ ;	92 %;	R = 2-pyridyl; 91%.

Scheme 2. [Cu₄(ophen)₄tp] catalyzed homocoupling of terminal alkynes.

With strong interest in the synthesis of unsymmetric 1,3-diyne type compounds^[30] and to expand the application of this methodology, we also examined the cross-coupling reaction of two different terminal alkynes under the above conditions. Medium yields of unsymmetric 1,3-diynes were observed when using two different terminal alkynes as the substrates, while the corresponding homocoupling products were obtained unavoidably (**Table 4**).

Table 4. cross-coupling reaction of two different terminal alkynes a

R ¹ -	$R^1 \longrightarrow + \equiv -R^2$		Cu ₂ ophen ₂ (5 mol%) H ₂ O (1mL);TBAB (5 mol%)		$R^{1} - \frac{4}{4} - R^{1}$ $R^{1} - \frac{3}{5} - R^{2}$ $R^{2} - \frac{3}{5} - R^{2}$	
	Entry R ¹ =		R ² = Yie		ld% ^b for3 (4/5)	
-	1	Ph	4-MeO-C ₆ H ₄	3a	53 (36/20)	
	2	Ph	2-Pyridine	3b	51 (28/26)	
	3	4-F-C ₆ H ₄	4-MeO-C ₆ H ₄	3c	50 (12/48)	

On the basis of related reports and our early work,^{28, 31} the possible dimetallic mechanism of the oxidative homocoupling reaction is proposed as shown in **Scheme 3**. In the initial step, the molecular oxygen is activated by Cu(I) of catalyst **1** in the presence of water, meanwhile, Cu(II) intermediate **A** is formed along with shrink of the Cu-Cu distance.^{27, 31a} Tansmetallation of the terminal alkynes with copper(II) complex **A** to give a dimetallic intermediate **B**, while release of byproduct H₂O through attack of the hydroxyl ligand to the hydrogen of alkyne. Finally, the desired diyne product is formed by reduction from **B** and elimination from **C**, with concomitant regeneration of catalyst.



Scheme 3. A plausible mechanism of the homocoupling reaction.

Conclusions

A facile, effective, economical and environmental-friendly method for the multinuclear copper complexes catalyzed Glaser coupling of terminal alkynes to synthesize 1,3-diynes has been successfully developed. The new catalytic system has excellent functional group tolerance and good conversion under base-free condition. Remarkably, the multinuclear copper complexes exhibit excellent performance in neat water under an atmospheric pressure of air/O₂. Cheapness, easy bulk preparation of catalysts, mild reaction conditions and heterogeneous catalysis make the approach match well with the concept of green chemistry and be attractive in industrial preparation of symmetric 1,3-diynes.

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Notes and references

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