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Cooperative Copper(I) and Primary Amine Catalyzed Room-Temperature Carbocyclization of Formyl Alkynes

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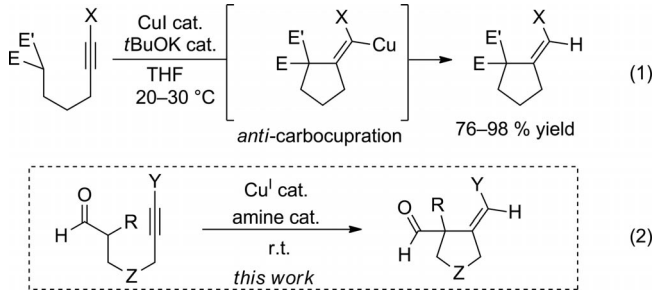
An efficient Cu^{I}/amine catalytic system is described for the carbocyclization of α-disubstituted formylalkynes at room temperature. Merging aminocatalysis to the copper(I)-catalyzed activation of alkynes led to clean carbocyclization of a wide range of functionalized substrates under mild conditions. This novel cooperative catalytic system allowed the formation of a variety of carbo- and heterocycles, including pyrrolidines, in good to excellent yields. Mechanistic aspects of this process are also discussed.

Introduction

Over the past few years, we have witnessed the tremendous expansion of carbophilic Lewis acid catalysis. Transition metals, typically palladium, platinum, and gold, while coordinating to C–C unsaturations, allow the addition of various nucleophiles onto the π system.[1] Heteroatom nucleophiles were shown to exhibit good reactivities,[2] whereas carbon nucleophiles, aside from carbon–carbon unsaturations,[3] usually required stabilized enol forms[4] or surrogates.[5] Although less explored, the akin activation of alkynes by copper(I) complexes was also proven to be effective.[1,5] In 1992, Balme et al. described for the first time the intramolecular stoichiometric carbocupration of unactivated alkynes bearing an α-sulfonylester moiety at room temperature.[6a,7] This Conia–ene type reaction,[8] based on the use of copper(I) iodide and *t*BuOK and proceeding through an *anti*-carbometalation pathway, was later extended to a catalytic version applicable to a broader range of stabilized nucleophiles [Scheme 1, Equation (1)];[6b] it was later used in tandem "Michael addition/carbocupration" reactions.[9]

Very recently, a copper(I)-catalyzed asymmetric Conia–ene reaction of alkynyl-β-keto esters was reported by Dixon and co-workers, whilst the cooperative use of a cinchona-based thiourea organocatalyst, accountable for the enantioselectivity, led to *syn*-carbocupration.[10]



Scheme 1. Intramolecular carbocupration of unactivated alkynes.

We and others recently reported the carbocyclization of α-disubstituted aldehydes onto nonactivated alkynes by merging aminocatalysis to indium[11] or gold[12] catalysis.[13] Under such cooperative "metallo–organocatalysis" conditions,[14] the metal catalyst allows the electrophilic activation of the alkyne moiety, whereas the nucleophilicity of the aldehyde is induced through the formation of an enamine. As a straight benefit of such catalytic systems, the Conia–ene-type reaction of α-disubstituted aldehydes was achieved without using stabilized enols or enol surrogates, affording directly carbocyclized quaternary carbaldehydes. One limitation of these metallo–organocatalytic systems being the rather elevated temperature (80 to 100 °C) required for such carbocyclization reactions, we decided to investigate the ability of copper(I)/amine combinations to activate triple bonds at room temperature [Scheme 1, Equation (2)]. We wish to report herein our endeavors towards the discovery of an efficient metallo–organocatalytic system based on copper(I)/amine allowing the room-temperature carbocyclization of α-disubstituted formylalkynes.

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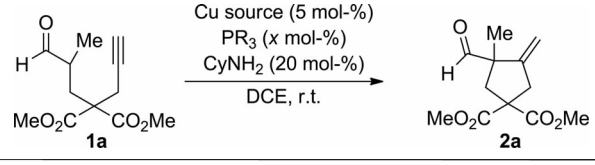
Results and Discussion

At the outset of our investigations, the carbocyclization of model substrate **1a** was realized at room temperature in 1,2-dichloroethane (DCE) in the presence of cyclohexylamine (20 mol-%) and different copper(I) sources (5 mol-%) with or without a phosphane additive (Table 1). Cyclohexylamine was selected as the organocatalyst for this study considering our recent results demonstrating that primary amines are more efficient than secondary amines for the generation of enamines from α-disubstituted aldehydes.[11b] Preliminary experiments using copper(I) iodide led, under these reaction conditions, to very sluggish reactivity, as only a few percent of desired product **2a** was detected after 16 h, whereas only half conversion was observed after 2 weeks (Table 1, Entries 1 & 2). The addition of triphenylphosphane (15 mol-%) to generate the in situ soluble $(PPh_3)_3CuI$ catalyst[9d] did not improve the carbocyclization reaction (Table 1, Entry 3). We next examined the use of cationic copper(I) complexes such as tetrakis acetonitrile copper(I) tetrafluoroborate employed by Fehr et al. for the cycloisomerization reactions of 5-enyn-3-ols.[15] Under these reaction conditions we observed an improvement in reactivity, although the **1a**/**2a** ratio only reached 88:12 after 16 h and 66:34 after 64 h (Table 1, Entries 4 & 5). Addition of an equivalent amount of triphenylphosphane to this copper source led to a significantly better conversion after 64 h, whereas twice the amount of triphenylphosphane strongly decreased the reactivity of the catalytic system (Table 1, Entries 6 & 7). The influence of the counterion was also surveyed by using perchlorate or trifluoromethanesulfonate complexes, but no significant enhancement was observed (Table 1, Entries 8 & 9). Switching from triphenylphosphane to electron-rich tricyclohexylphosphane did not meaningfully change the catalytic behavior (Table 1, Entry 10), whereas the use of electron-poor tris(*p*-trifluoromethylphenyl)phosphane merely ameliorated the conversion (Table 1, Entry 11). Important progress arose with the copper(I) trifluoromethanesulfonate benzene complex. Indeed, complete conversion of **1a** was obtained in 16 h, and cyclopentane **2a** was isolated in a promising 65% yield (Table 1, Entry 12). Addition of an equimolar amount or more of triphenylphosphane to this complex resulted in a dramatic drop in reactivity (Table 1, Entries 13 & 14).

Table 1. Optimization of the copper-based metallo–organocatalytic systems.



Entry	Copper source	PR_3 (mol-%)	Time [h]	SM/P[a]
1	CuI	–	16	>95:5
2	CuI	–	2 w	50:50
3	CuI	PPh_3 (15)	16	>95:5
4	$[Cu(CH_3CN)_4]BF_4$	–	16	88:12
5	$[Cu(CH_3CN)_4]BF_4$	–	64	66:34
6	$[Cu(CH_3CN)_4]BF_4$	PPh_3 (5)	64	30:70
7	$[Cu(CH_3CN)_4]BF_4$	PPh_3 (10)	64	85:15
8	$[Cu(CH_3CN)_4]ClO_4$	PPh_3 (5)	64	30:70
9	$[Cu(CH_3CN)_4]OTf$	PPh_3 (5)	64	70:30
10	$[Cu(CH_3CN)_4]BF_4$	PCy_3 (5)	48	50:50
11	$[Cu(CH_3CN)_4]BF_4$	$P(p\text{-}CF_3C_6H_4)_3$ (5)	48	35:65
12	Cu(OTf)·1/2benzene	–	16	<5:95[b]
13	Cu(OTf)·1/2benzene	PPh_3 (5)	16	>95:5
14	Cu(OTf)·1/2benzene	PPh_3 (15)	16	87:13
15	$Cu(OTf)_2$	PPh_3 (5)	16	76:24
16	$Cu(OTf)_2$	PPh_3 (20)	22	<5:95[c]
17	$Cu(OTf)_2$	–	24	<5:95 [d]
18	$CuBr_2$	PPh_3 (20)	16	90:10
19	$Cu(OAc)_2$	PPh_3 (20)	16	85:15
20	$CuSO_4 \cdot 5H_2O$	PPh_3 (20)	16	>95:5
21	$Cu(OTf)_2$	PPh_3 (20)	22	>95:5[e]

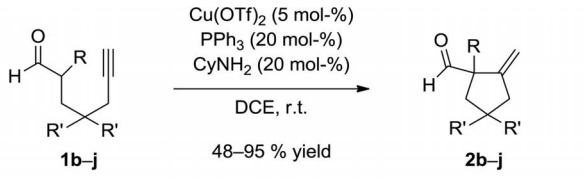
[a] Determined by ^1H NMR spectroscopic analysis of the crude reaction mixture. [b] 65% isolated yield. [c] 86% isolated yield. [d] 60% isolated yield. [e] Without cyclohexylamine.

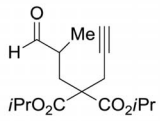
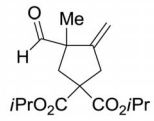
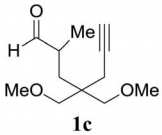
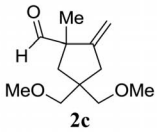
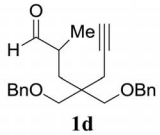
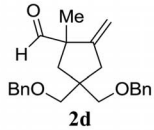
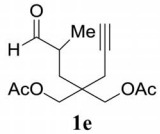
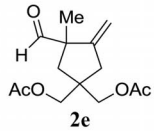
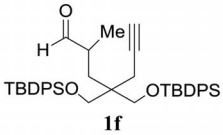
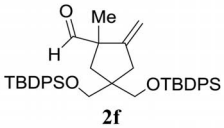
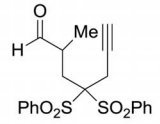
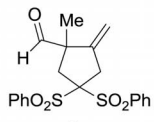
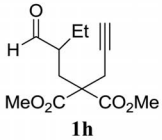
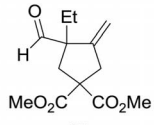
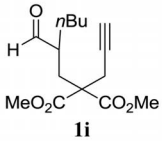
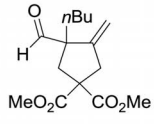
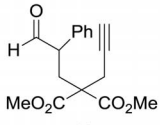
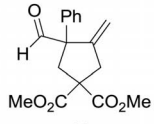
At this point, we decided to broaden our investigation while in situ generating copper(I) complexes from phosphane-mediated reduction of copper(II) sources.[16] Starting from 5 mol-% copper(II) trifluoromethanesulfonate and an equimolar amount of triphenylphosphane, the reactivity was still low (Table 1, Entry 15). However, with 4 equiv. of phosphane the presumably in situ generated $Cu^I(PPh_3)_3OTf$[13b] promoted complete conversion in 22 h at room temperature and yielded **2a** in 86% (Table 1, Entry 16). Interestingly, the use of $Cu(OTf)_2$ without triphenylphosphane also resulted in complete consumption of **1a**; however, **2a** was only isolated in 60% yield (Table 1, Entry 17).[17]

Other copper(II) precatalysts such as $CuBr_2$, $Cu(OAc)_2$, and $CuSO_4$ were tested in the presence of triphenylphosphane but none displayed a better catalytic behavior than $Cu(OTf)_2$, thus emphasizing the determining influence of the counterion (Table 1, Entries 18–20). A control experiment without cyclohexylamine led to the recovery of starting material **1a** (Table 1, Entry 21).

With this new catalytic system in hand, we next confronted it with a broad range of α-disubstituted carbon-tethered formyl alkynes starting with α-methyl-substituted substrates (Table 2). The replacement of the *gem*-dimethyl malonate moiety by the more sterically hindered *gem*-diisopropyl malonate did not affect the carbocyclization reaction (Table 2, Entry 1). Notably, this novel metallo–organocatalytic system demonstrated good functional group tolerance, considering the efficient room-temperature carbocyclization reactions of diethers **1c** and **1d**, diacetate **1e**, and disilyl ether **1f** (Table 2, Entries 2–5). Interestingly, the mildness of this copper-based catalytic system allowed the formation of cyclopentane **2g** in 92% yield (Table 2, Entry 6), whereas some problems of retro-Michael side reactivity were previously observed, leading to 4,4-bis(phenylsulfonyl)-1-butyne starting from *gem*-disulfone **1g**.[11b] The influence of the group in the α position relative to the aldehyde moiety was then examined. When the more encumbered α-ethyl-substituted substrate **1h** was submitted to the cyclization reaction, a decrease in reactivity occurred and 64 h was required to reach full conversion. Corresponding

Table 2. Carbocyclization reactions of carbon-tethered substrates **1b–j**.

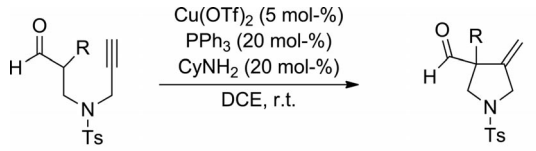


Entry	Substrate	Product	*t* [h]	Yield[a] [%]
1	 **1b**	 **2b**	16	82
2	 **1c**	 **2c**	16	92
3	 **1d**	 **2d**	16	95
4	 **1e**	 **2e**	19	93
5	 **1f**	 **2f**	22	94
6	 **1g**	 **2g**	17	92
7	 **1h**	 **2h**	64	67
8	 **1i**	 **2i**	64	48[b]
9[c]	 **1j**	 **2j**	28	90

[a] Isolated yield. [b] Incomplete conversion was observed: SM/P = 20:80. [c] Reaction performed at 50 °C.

cyclopentane **2h** was isolated in 67% yield (Table 2, Entry 7). A similar trend was encountered when the cyclizations of the sterically hindered α-butyl- and α-phenyl-substituted substrates were performed. Indeed, **1i** and **1j** poorly reacted under the same reaction conditions with 80 and 65% conversion, respectively, after 64 h at room temperature. Cyclopentane **2i** was obtained in 48% isolated yield (Table 2, Entry 8). When increasing the temperature to 50 °C, substituted substrate **1j** was efficiently cyclized to cyclopentane **2j** in 90% yield (Table 2, Entry 9), whereas such modification did not improve the cyclization of **2i**. Thus, while considering carbon-tethered substrates, the group in the α position relative to the aldehyde moiety displayed an important influence on the efficiency of the carbocyclization reaction.

Taking into account the mildness of this copper-based metallo–organocatalytic system, we finally investigated cyclization reactions leading to pyrrolidine heterocycles. Indeed, in comparison to *gem*-disulfone **1g**, the corresponding precursors usually evolved according to a retro-Michael rearrangement in the presence of our previously described $CyNH_2/InCl_3$ catalytic system.[11b] To this end, *N*-tosyl-protected α-disubstituted nitrogen tethered substrates **3a** and **3b** were prepared according to a straightforward four-step synthesis[18] and submitted to the cyclization reaction (Scheme 2).

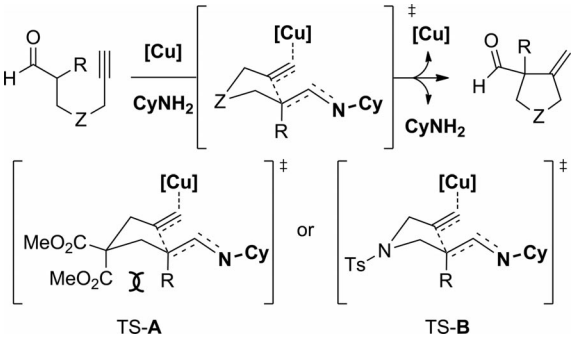


Scheme 2. Carbocyclization reactions leading to pyrrolidines.

Gratifyingly, both α-methyl- and α-butyl-substituted substrates **3a** and **3b** led to smooth and clean carbocyclization reactions, and the corresponding pyrrolidines were isolated in 86 and 91% yield, respectively. Notably, a significant increase in the rate of the reaction was observed for the synthesis of these heterocycle precursors compared to the analogous carbon-tethered substrates.

Considering that both cyclohexylamine and copper(I) are compulsory for the reaction to take place, the metallo–organocatalytic process would involve the amine catalyst as accountable for the formation of a nucleophilic enamine, whereas the copper complex would enhance the electrophilicity of the alkynyl residue (Scheme 3). Both activations would then trigger the cyclization process, and the catalysts would be regenerated by hydrolysis and protodemetalation. Some reactivity discrepancies of carbon-tethered substrates were observed compared to nitrogen-tethered substrates. Indeed, whereas malonate-linked formylalkynes reacted more sluggishly when the steric hindrance in the α position of the aldehyde moiety was higher, comparable *N*-tosyl-linked substrates were very good substrates for this transformation. In this context, the rate-determining step of this reaction would be the cyclization step in which a chair-like transition state might be at stake (Scheme 3). The low reactivity

of the α-hindered carbon-tethered substrates could be rationalized on the basis of 1,3-diaxial steric strains (Scheme 3, TS-**A**). Nitrogen-tethered substrates, in which the nitrogen atom displays a trigonal or slightly pyramidal geometry,[19] would be free from these deleterious strains (Scheme 3, TS-**B**) and thus would reach more easily the adequate conformation necessary for cyclization.



Scheme 3. Mechanism rationale.

Conclusions

In summary, we have developed a new metallo–organocatalytic system based on the synergistic use of catalytic quantities of cyclohexylamine and an in situ generated copper(I) complex, allowing efficient room-temperature carbocyclization reactions of α-disubstituted aldehydes onto unactivated alkynes. We demonstrated that this combination promotes the cyclization of a broad range of substrates leading to a variety of carbo- and heterocycles in high yields and a good functional group tolerance. The set of the experimental results tends to support a chair-like transition state for the cyclization process. Further investigations concerning an enantioselective version of this reaction are currently underway and will be reported in due course.

Experimental Section

General Procedure for the Carbocyclization Reaction: In a sealed vial under an argon atmosphere was successively introduced triphenylphosphane (0.08 mmol, 0.2 equiv.), copper(II) trifluoromethanesulfonate (0.02 mmol, 0.05 equiv.), and DCE (0.4 mL). The resulting mixture was stirred for 20 min at room temperature before the freshly purified formylalkyne (0.4 mmol, 1 equiv.) in a 0.2 M solution of amine in DCE (0.4 mL, 0.08 mmol, 0.2 equiv.) was added. After introduction of an additional amount DCE (0.2 mL), the reaction mixture was stirred at room temperature until GC or TLC analysis indicated complete conversion. The reaction mixture was then treated with an aqueous solution of AcOH (1:1, 1 mL) and then vigorously stirred for 15 min at room temperature before extraction of the aqueous layer with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered, and concentrated under reduced pressure, and the resulting crude material was purified by silica gel flash chromatography to afford the desired carbocyclized aldehyde.

Supporting Information (see footnote on the first page of this article): Experimental procedures, analytical descriptions, and copies of the ^1H and ^{13}C NMR spectra of new compounds.

Acknowledgments

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