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Aldehyde–alkyne–amine (A^3) coupling catalyzed by a highly efficient dicopper complex†

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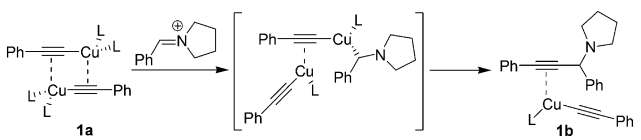
A dicopper(I) complex, $Cu^{I}_2(pip)_2$ (pip = (2-picolyliminomethyl)pyrrole anion), was utilized to catalyze A^3 coupling reactions, which led to the formation of propargylamines. Aldehydes, alkynes and amines with a variety of structures have been tested. A low catalyst loading of 0.4 mol% was sufficient to give good to excellent yields. The low catalyst loading, broad scope of substrate and easy preparation make this dicopper complex a useful catalyst for A^3 coupling.

Introduction

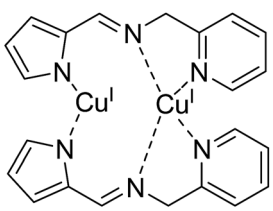
Propargylamines are versatile building blocks for the synthesis of various nitrogen-containing heterocyclic compounds,[1] and important intermediates for the preparation of complex natural products and biologically active molecules.[2] Further, some propargylamines have been clinically used or are currently tested for the treatment of Parkinson's disease[3] and Alzheimer's disease.[4] Classically, propargylamines are synthesized by the nucleophilic addition of a metal alkynylide to C=N electrophiles, which often requires stoichiometric amount of highly active organometallic reagents such as organolithium,[5] Grignard reagents,[6] and organozinc reagents,[7] and hence is less attractive due to low tolerance of functional groups, harsh reaction conditions, and operational complexity. In the past decade, transition-metal catalyzed three-component coupling of an aldehyde, an alkyne, and an amine (generally referred as A^3-coupling) has received more and more attention due to its atom economy, step efficiency, and high chemical selectivity.[8] This reaction was proposed to proceed through the addition of an *in situ* generated metal-alkynylide to an imine (or iminium ion), which is also formed *in situ* from a reaction between an aldehyde and an amine, and water was formed as the only side product.

Transition metal salts and complexes, especially those from coinage metals (Cu, Ag, and Au),[8] as well as Zn,[9] Ni,[10] Fe,[11] In,[12] Ir,[13] Co,[14] Mn,[15] Bi,[16] Hg[17] and Cd[18] have been developed as the catalysts for A^3-coupling, among which copper compounds have been studied most. Recently, Heaney and co-workers proposed that in the mechanism of copper(I)-catalyzed A^3-coupling, a dimeric copper(I) acetylide **1a** (Scheme 1) forms in the early stage of the catalytic cycle.[19] The intermediate **1a** then binds to the imine or iminium ion, which leads to the addition of the alkynylide to the imine or iminium ion, and yields the intermediate **1b** (Scheme 1). It is worth mentioning that this mechanism is similar to those of copper-catalyzed alkyne–azide cycloaddition (CuAAC),[20] Kinugasa reaction,[21] and Glaser coupling.[22] In fact, several dicopper catalysts have been shown to be highly efficient for CuAAC.[23] To our best knowledge, only one type of dicopper catalyst based on pybox ligands has been reported for A^3 coupling.[24] The pybox catalysts were used for asymmetric synthesis and a loading of 5–10% was commonly used. Based on the mechanism, the primary function of a dinuclear structure should be improving its catalytic efficiency. Therefore, exploring new dicopper catalysts is important for enhance catalytic efficiency as well as understanding the mechanism of A^3 coupling.

Previously we reported that a dinuclear copper(I) complex, $Cu^{I}_2(pip)_2$ (pip = (2-picolyliminomethyl)pyrrole anion) (Scheme 2) efficiently catalyzed the alkyne–azide cycloaddition at a low loading of 0.2 mol%.[23a] The catalyst has a stable



Scheme 1 Proposed catalytic intermediates in A^3-coupling.[19]



Scheme 2 Structure of $Cu^{I}_2(pip)_2$.

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dimeric structure in solutions and is easy to prepare. Given the similarity between the proposed mechanisms of copper catalyzed A^3 and alkyne–azide cycloaddition reactions, we hypothesized that this catalyst could also possess a high activity for A^3 reaction. Herein, we reported our study on the catalytic behaviors of this dicopper(I) compound for a series of A^3 reactions with different substrates.

Results and discussion

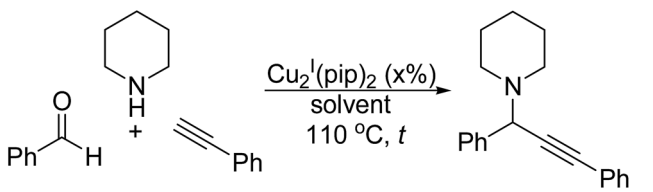
A model reaction with benzaldehyde, phenylacetylene and piperidine was studied first to evaluate the catalytic activity of $Cu^I_2(pip)_2$ and to optimize the reaction condition. The reaction was performed in refluxing toluene for 12 hours in the presence of 1 mol% of $Cu^I_2(pip)_2$. The coupling reaction proceeded well and the expected propargylamine was isolated with nearly quantitative yield (Table 1, entry 1). Other solvents were also tested for the reaction (entries 2–7). The bath temperature was set to 110 °C, and thus the reaction was either at this temperature or the boiling points of the solvents. Non-polar solvents toluene and dioxane gave much better yields than the polar solvents including DMF, DMSO, EtOH and MeCN. The moderate yield obtained by using THF (entry 3) may also be due to the its low boiling point.

The loading of the catalyst was optimized by conducting the reaction with 1–0.2 mol% of loading using toluene as the solvent (entry 1, 8–11). The results revealed that $Cu^I_2(pip)_2$ is highly active for A^3-coupling. When the catalyst loading was reduced to 0.4 mol%, the reaction still gave 98% yield (entry 10). Even a loading as low as 0.2 mol% gave 90% yield (entry 11). It is worth mentioning that homogenous A^3 reaction often requires 5–10 mol% of catalyst loading.[8] Further studies showed that the reaction time can be decreased without affect the yields. As shown in entry 12 and 13 in Table 1, 98% yield was obtained after 2 h and there was no significant difference between 2 h and 4 h reactions. The low catalyst loading and short reaction time clearly proves the high activity of $Cu^I_2(pip)_2$.

The catalytic activity of $Cu^I_2(pip)_2$ was compared to another dicopper(I) compound $(CuOAc)_2$, which has also been reported to be a high-efficiency catalyst for CuAAC reaction.[23c] However, even when 2 mol% of $(CuOAc)_2$ was used, which was 5 times more than that of $Cu^I_2(pip)_2$, the corresponding A^3-coupling only gave 67% yield (entry 14).

The structural effects of the aldehyde reactants were studied using the optimized reaction condition. Aromatic and aliphatic aldehydes with a variety of structures were examined using piperidine and phenylacetylene as the other reactants, and the results are summarized in Table 2. All the aromatic aldehydes tested showed high reactivity. Electron-withdrawing or electron-donating substituents at *ortho*-, *meta*-, or *para*-position showed almost no effects, and excellent yields were obtained from the corresponding aldehydes (entries 1–9). Sterically hindered aromatic aldehydes including 2,6-dichlorobenzaldehyde and 2,6-dimethoxybenzaldehyde also reacted well, and gave the corresponding products with yields of 88% and 98%

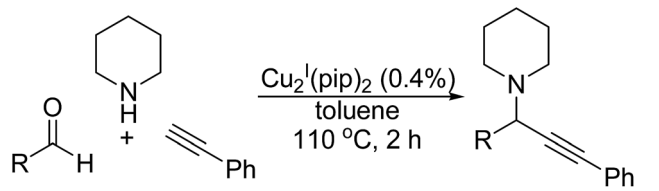
Table 1 Optimization of reaction conditions of A^3 coupling[a]



Entry	Solvent	Cat. (%)	t (h)	Yield[b] (%)
1	Toluene	1	12	99
2	MeCN	1	12	61
3	THF	1	12	71
4	Dioxane	1	12	80
5	EtOH	1	12	37
6	DMF	1	12	32
7	DMSO	1	12	25
8	Toluene	0.8	12	99
9	Toluene	0.6	12	99
10	Toluene	0.4	12	98
11	Toluene	0.2	12	90
12	Toluene	0.4	4	97
13	Toluene	0.4	2	98
14[c]	Toluene	2	2	67

[a] Reaction conditions: benzaldehyde (1.0 mmol), piperidine (1.0 mmol), phenylacetylene (1.2 mmol), catalyst, solvent (3 mL). [b] Isolated yield. [c] $(CuOAc)_2$ was used as the catalyst.

Table 2 Reaction yields of different aldehydes under optimized reaction conditions[a]



Entry	R	Yield[b] (%)
1	C_6H_5	98
2	4-FC_6H_4	97
3	3-FC_6H_4	98
4	2-FC_6H_4	98
5	4-$MeOC_6H_4$	96
6	3-$MeOC_6H_4$	97
7	2-$MeOC_6H_4$	97
8	1-Naphthyl	95
9	2-Naphthyl	97
10	2,6-$Cl_2C_6H_3$	88
11	2,6-$(MeO)_2C_6H_3$	98
12	C_4H_9	99
13	Me_2CHCH_2	99
14	C_7H_{15}	97
15	*c*-Pentyl	91
16	*c*-Hexyl	94
17	2-Furyl	89
18	2-Thiophenyl	81

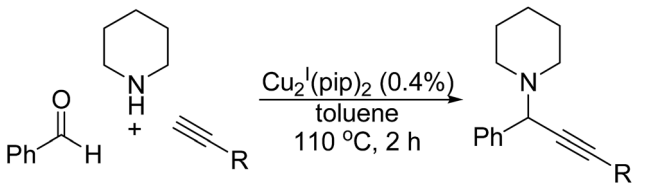
[a] Reaction conditions: aldehyde (1.0 mmol), piperidine (1.0 mmol) and phenylacetylene (1.2 mmol) in toluene (3 mL). [b] Isolated yield.

respectively (entry 10 and 11). Aliphatic aldehydes including pentanal, isopentanal, octanal, cyclopentanecarboxaldehyde and cyclohexanecarboxaldehyde, were also excellent substrates for this catalytic reaction. Yields above 90% were obtained for all the tested aliphatic aldehydes after the reactions proceeded 2 hours (entries 12–16). Heteroaromatic aldehydes including 2-furaldehyde and 2-thenaldehyde were also examined and afforded the corresponding products with yields of 89% and 81% respectively (entries 17 and 18).

The structural effects of alkynes were studied using benzaldehyde and piperidine as the other reactants, and the results are summarized in Table 3. Aromatic acetylenes, regardless of electron-withdrawing or electron-donating groups on the phenyl ring, reacted well and gave excellent yields (entries 1–6). Hept-1-yne, an aliphatic alkyne, also underwent the reaction well and afforded the corresponding product nearly quantitatively (entry 7). However, propargylic alcohol and 1-phenylprop-2-yn-1-ol gave complex mixtures (entries 8 and 9), which were difficult to separate by column chromatography. A possible reason is that the hydroxyl group on the alpha carbon of the alkynes may participate in the formation of the catalytic intermediates and cause side reactions. A heteroaromatic alkyne, 2-ethynylthiophene, were also examined, and a yield of 85% was obtained (entry 10).

Amines with different structures were also tested using the optimized reaction condition (Table 4). Secondary amines, including morpholine, pyrrolidine and Bn_2NH gave the expected products with satisfied yields (entries 1–3). However, no product was detected after the reaction when aniline was used (entry 4). This result shows that the catalytic system cannot be applied to aromatic primary amine.[25]

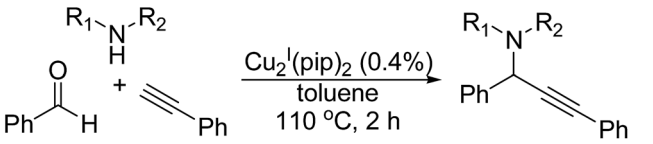
Table 3 Reaction yields of different alkynes under optimized reaction conditions[a]



Entry	R	Yield[b] (%)
1	4-$MeOC_6H_4$	97
2	3,4-$(MeO)_2C_6H_3$	95
3	4-MeC_6H_4	97
4	3-MeC_6H_4	98
5	4-FC_6H_4	93
6	4-BrC_6H_4	98
7	C_5H_{11}	99
8	CH_2OH	[c]
9	$CH(OH)C_6H_5$	[c]
10	2-Thiophenyl	85

[a] Reaction conditions: benzaldehyde (1.0 mmol), piperidine (1.0 mmol) and alkyne (1.2 mmol) in toluene (3 mL). [b] Isolated yield. [c] Complex mixture not isolated.

Table 4 Effect of different amines on A^3 coupling under optimization reaction conditions[a]



Entry	R_1R_2NH	Yield[b] (%)
1	Morpholine	96
2	Pyrrolidine	87
3	Bn_2NH	97
4	$PhNH_2$	nd

[a] Reaction conditions: benzaldehyde (1.0 mmol), amine (1.0 mmol) and phenylacetylene (1.2 mmol) in toluene (3 mL). [b] Isolated yield.

Conclusion

In conclusion, we have demonstrated that a dicopper(I) complex $Cu^I_2(pip)_2$ is highly efficient for catalyzing the A^3 coupling reaction, which produces propargylamines. Aromatic and aliphatic aldehydes, alkynes and secondary amines with various structures reacted well at a catalyst loading of 0.4 mol%, and gave good to excellent yields. The broad substrate scopes, mild reaction condition and low catalyst loadings make $Cu^I_2(pip)_2$ a useful catalyst for the A^3 reaction.

Experimental section

General procedure for A^3-coupling

To a solution of $Cu^I_2(pip)_2$ (2.0 mg, 0.4% mmol) in toluene (3 mL) was added alkyne (1.2 mmol), aldehyde (1.0 mmol) and amine (1.0 mmol) under nitrogen atmosphere. The reaction mixture was heated at 110 °C for 2 h, cooled, and then subjected to column chromatography on silica gel (300–400 mesh) eluting with petroleum ether–ethyl acetate to give the desired propargylamine.

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