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Communication

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J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.7b09947 • Publication Date (Web): 05 Dec 2017

ACS Publications

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Ni-Al Bimetallic Catalyzed Enantioselective Cycloaddition of Cyclopropyl Carboxamide with Alkyne

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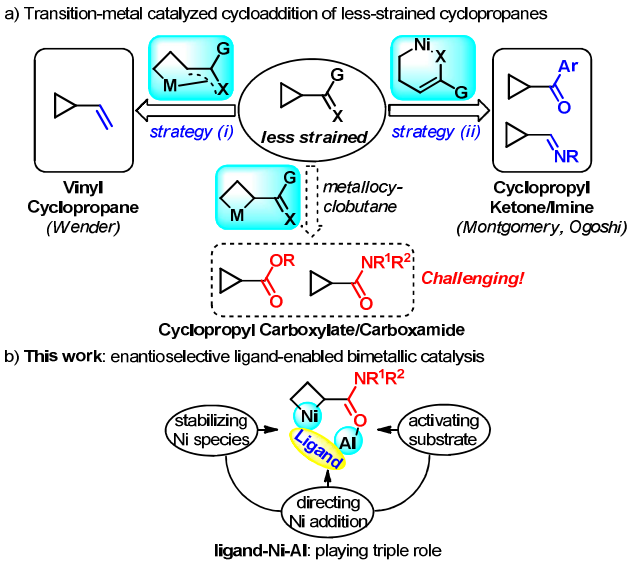
Supporting Information Placeholder

ABSTRACT: A Ni-Al bimetallic catalyzed enantioselective cycloaddition reaction of cyclopropyl carboxamides with alkynes has been developed. A series of cyclopentenyl carboxamides were obtained in up to 99% yield and 94% ee. The bifunctional-ligand-enabled bimetallic catalysis proved to be an efficient strategy for the C–C bond cleavage of unreactive cyclopropanes.

Transition-metal-catalyzed cycloaddition of cyclopropane with π-unsaturated compound has emerged as a powerful tool for the construction of cyclic structural units during the past decades.[1,2] Among various functionalized cyclopropanes used in cycloaddition reactions, cyclopropyl carboxylates, including carboxylic acids, esters and amides, are one of the most attractive classes of substrates because carboxylate groups are not only readily available, but also participate in versatile transformations in organic synthesis. However, their cycloaddition reaction still remains an elusive challenge. Different from highly-strained cyclopropanes bearing fused π-unsaturation (cyclopropene[3] and alkylidenecyclopropane[4]), less-strained cyclopropanes bearing adjacent π-unsaturation (vinylcyclopropane[5] and cyclopropanes containing polar π-bonds[6-9]) prove quite inert in the oxidative addition to transition metal. Wender and co-workers in 1995 revealed for the first time that the formation of an allyl-metal intermediate greatly facilitated the oxidative addition process (Scheme 1a, strategy (i)).[5a] Later, Montgomery group and Ogoshi group independently found that the formation of an oxa(aza)-nickelacycle intermediate also greatly improved the oxidative addition and the subsequent cycloaddition with an activated π-compound (strategy (ii)).[10–14] However, in sharp contrast, cyclopropyl carboxylates could generate neither allyl-metal nor oxa(aza)-nickelacycle intermediates, so that a high activation energy barrier has to be overcome for the formation of unstable metallocyclobutane species. Herein, we report a Ni-Al bimetallic synergism to facilitate the cycloaddition reaction of cyclopropyl carboxamide with alkyne for the first time, in which the ligand-Ni-Al combination probably played a triple role: activating cyclopropane substrate, directing nickel oxidative addition and stabilizing the in-situ formed nickellacycle (Scheme 1b). In addition, a successful enantioselective control of this reaction was also achieved by the use of taddol-derived chiral phosphine oxide ligand with up to 94% ee.

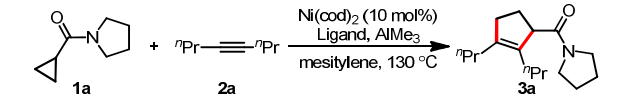
Scheme 1. Transition-Metal-Catalyzed Cycloaddition of Cyclopropane with π-unsaturated compound



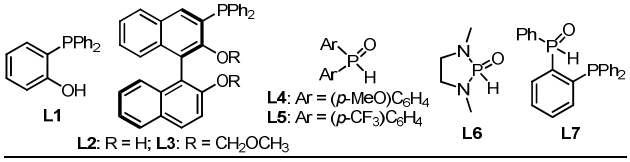
We commenced our studies by treatment of cyclopropyl carboxamide (**1a**) with oct-4-yne **2a** under 10 mol% of $Ni(cod)_2$ as the catalyst and 1.0 equivalent of $AlMe_3$ as the promoter. Initially, various arylphosphines, alkylphosphines and carbenes were employed to promote the cycloaddition reaction under similar conditions to Ogoshi's reaction,[13] while no desired product was detected under varying temperatures. Then we envisioned that a bifunctional ligand could be used to simultaneously bind nickel catalyst and Lewis acid promoter to accelerate the oxidative addition of nickel to cyclopropane. Phenolic (**L1**) and naphtholic phosphine (**L2** and **L3**), were firstly selected to be tested (entries 1–3). Gratifyingly, trace amounts of desired product (**3a**) were indeed detected by GC analysis for **L1** and **L2**, and even 8% yield was observed for O-protected ligand **L3**. Inspired by Cramer's and others' reports on unique bifunctional secondary-phosphine-oxide (SPO) ligand,[15,16] we chose various trivalent phosphorus compounds such as Ph_2POMe, Ph_2PCl and $Ph_2P(O)H$ for further optimization (entries 4–6). Results showed that Ph_2POMe was inefficient for this reaction, whereas Ph_2PCl slightly improved the

yield to 11%. Most delightedly, $Ph_2P(O)H$ was found to be an excellent ligand, affording **3a** in 44% yield.

Table 1. Ligand Effects

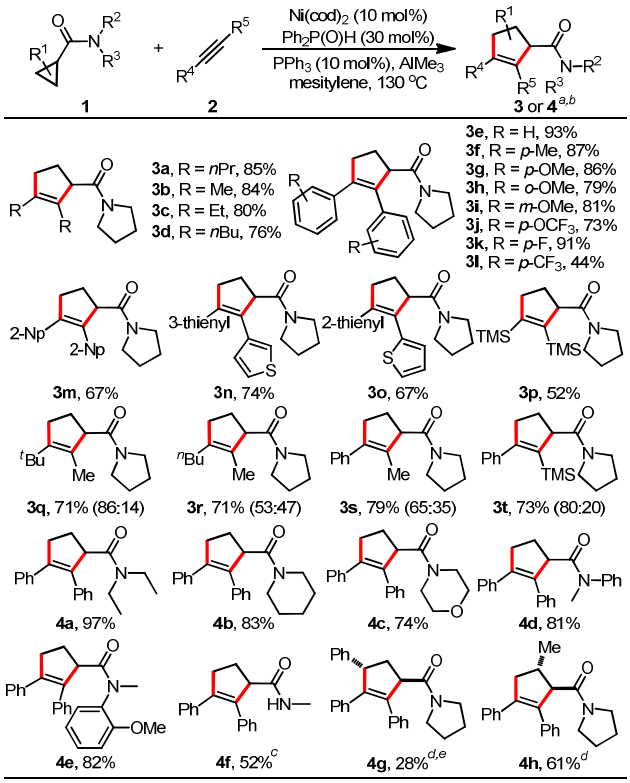


entry	ligand (mol%)	yield of **3a** (%)[a]	entry	ligand (mol%)	yield of **3a** (%)[a,b]
1	**L1**	trace	9	$Ph_2P(O)H$ (30)	86
2	**L2**	trace	10	$Ph_2P(O)Ph$ (30)	0
3	**L3**	8	11	**L4** (30)	53
4	Ph_2POMe (10)	trace	12	**L5** (30)	51
5	Ph_2PCl (10)	11	13	$Cy_2P(O)H$ (30)	13
6	$Ph_2P(O)H$ (10)	44	14	$^tBu_2P(O)H$ (30)	trace
7	$Ph_2P(O)H$ (20)	74	15	**L6** (30)	41
8	$Ph_2P(O)H$ (30)	81	16[c]	**L7** (20)	32



[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), mesitylene (2 mL), under N_2 for 24 h; GC yield using *n*-dodecane as the internal standard. [b]Ph_3P (0.02 mmol) was added. [c]Without Ph_3P.

Table 2. Scope of Alkyne and Amide

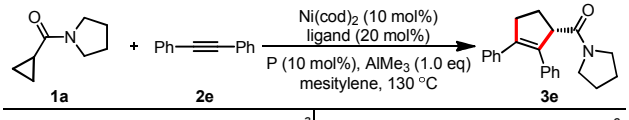


[a]Reaction conditions: **1** (0.2 mmol), **2** (0.6 mmol), $AlMe_3$ (0.2 mmol), mesitylene (2 mL), under N_2 for 24 h. [b]Isolated yield and isomer ratios in parentheses were determined by ^1H NMR. [c]The starting amide is a Weinreb amide. [d]$Ni(cod)_2$ (15 mol%) and $AlMe_3$ (0.4 mmol). [e]Isolated yield for all isomers (81:9:10 isomer ratio). Np = naphthyl.

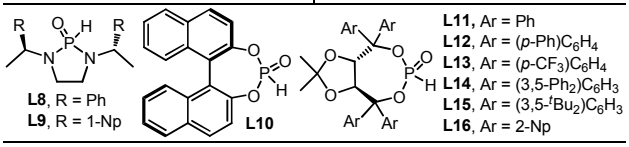
Encouraged by this result, we then examined a wide range of reaction parameters using $Ph_2P(O)H$ as the ligand (see the Supporting Information). The reaction was found to be highly dependent on loadings of the ligand. Increasing loadings of $Ph_2P(O)H$ to 20 mol% and 30 mol%, the yield of **3a** was elevated significantly to 74% and 81%, respectively (entries 7 and 8). Using additional PPh_3 (10 mol%) further enhanced the yield to 86% (entry 9). Under the combined-ligand conditions, triphenylphosphine oxide was completely inefficient (entry 10), suggesting secondary phosphine oxide structure was critical to the reaction. Other phosphine oxides did not give better results (entries 11–16).

With the above optimized reaction conditions in hand, we first explored an array of alkynes to test the generality of the reaction (Table 2). Various symmetrical alkynes bearing dialkyl (**3a**–**3d**), di(hetero)aryl (**3e**–**3o**) and bistrimethylsilyl (**3p**) were well tolerated, providing the corresponding cyclopentene in 44% to 93% yield. Various unsymmetrical alkynes (**3q**–**3t**) were also compatible with this reaction, but providing a mixture of regioisomers with varying ratios from 53:47 to 86:14. Amides bearing different substituents on N atom (**4a**–**4e**) did not have big influence on the current reaction. Notably, the Weinreb amide bearing a reactive N-O bond afforded a desmethoxy product in 52% yield (**4f**), whereas mono-substituted amide with a proton on the N atom was not tolerated in this reaction. In addition, a phenyl group in the cyclopropyl ring led to a different regioselective product (**4g**), suggesting that the substrate could play a donor-acceptor-cyclopropane role in this case. Instead, the methyl group still provided the same regioselective product (**4h**), and an epimerized isomer from the enolization of the corresponding nickelacycle was not observed.[13] But unfortunately, the current method was not applicable to cyclopropyl carboxylic ester, likely owing to its weaker interaction with $AlMe_3$.

Table 3. Asymmetric Control



entry	ligand	P	yield%(ee%)[a]	entry	ligand	P	yield%(ee%)[a]
1	**L8**	Ph_3P	70 (4)	9	**L16**	Ph_3P	91 (79)
2	**L9**	Ph_3P	72 (11)	10	**L16**	Ph_3P	78 (88)[b]
3	**L10**	Ph_3P	43 (22)	11	**L16**	Ph_3P	40 (90)[c]
4	**L11**	Ph_3P	95 (8)	12	**L16**	$(o\text{-Tol})_3P$	99 (93)[c]
5	**L12**	Ph_3P	92 (50)	13	**L16**	Cy_2PTipp	99 (79)[c]
6	**L13**	Ph_3P	77 (2)	14	**L16**	Cy_2PPh	65 (57)[c]
7	**L14**	Ph_3P	90 (47)	15	**L16**	$CyPPh_2$	37 (88)[c]
8	**L15**	Ph_3P	36 (32)	16	**L16**	Cy_3P	46 (40)[c]



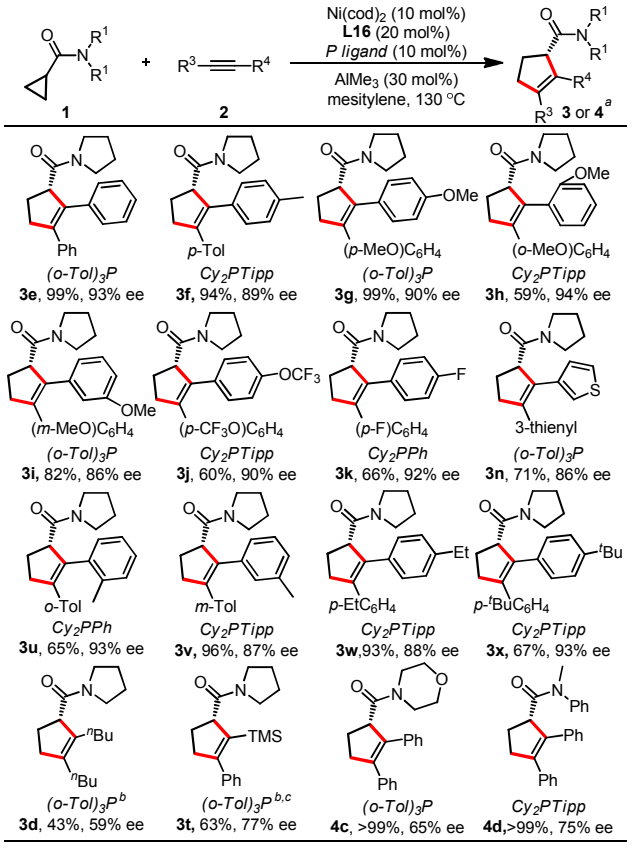
[a]Reaction conditions: **1a** (0.1 mmol), **2e** (0.3 mmol), mesitylene (1.0 mL), under N_2 for 24 h; isolated yield and ee in parentheses determined by chiral HPLC. [b]$AlMe_3$ (0.06 mmol). [c]$AlMe_3$ (0.03 mmol). Tipp = (2,4,6-triisopropyl)phenyl.

Next, we proceeded to investigate the asymmetric version. A series of ligands derived from commonly-used chiral diamine- and dihydroxyl-backbones were synthesized and examined in the cycloaddition reaction of **1a** and **2e** (Table 3). Results showed that taddol-derived chiral ligands gave better asymmetric controls (entries 1–9), especially 2-naphthyl-derived ligand **L16** provided 91% yield and 79% ee (enantiomeric excess) (entry 9). Decreas-

ing the loadings of $AlMe_3$ gave a better ee, while the yield dropped significantly (entries 10 and 11). However, the use of different additional phosphine ligand could achieve a good balance between the yield and the ee (entries 12–16), which was presumably attributed to an assisted coordination of the phosphine to the nickel center. For cyclopropane **1a**, the best P ligand is $(o\text{-Tol})_3P$, providing the product **3e** in 99% yield and 93% ee (entry 12). The absolute configuration of major enantiomer of the product was determined by a single crystal X-ray diffraction (see the Supporting Information).

After obtaining the optimal conditions, we first explored various diarylalkynes **2** in the cycloaddition reaction with cyclopropanes **1** (Table 4). In the presence of different additional tertiary phosphine ligands, diarylalkynes bearing various substituted groups on the phenyl ring such as Me (**3f**, **3u**, **3v**), Et (**3w**), *t*Bu (**3x**), MeO (**3g-i**), CF_3O (**3j**) and F (**3k**) were well compatible with the current reaction, providing 60–99% yield and 86–94% ee. In addition, di(3-thienyl)alkyne (**3n**) also led to a good enantioselective control (86% ee). However, the current method was not suitable for dialkylalkynes (**3d**) and unsymmetrical alkynes (**3t**), often leading to low yields and low ees. Notably, when the pyrrolidinyl of the amide was replaced by other amine groups (**4c** and **4d**), the ee of product declined significantly, albeit an excellent yield, suggesting that the stereroselective control was highly sensitive to steric hindrance of both amides and alkynes.

Table 4. Enantioselective Cycloaddition Reaction

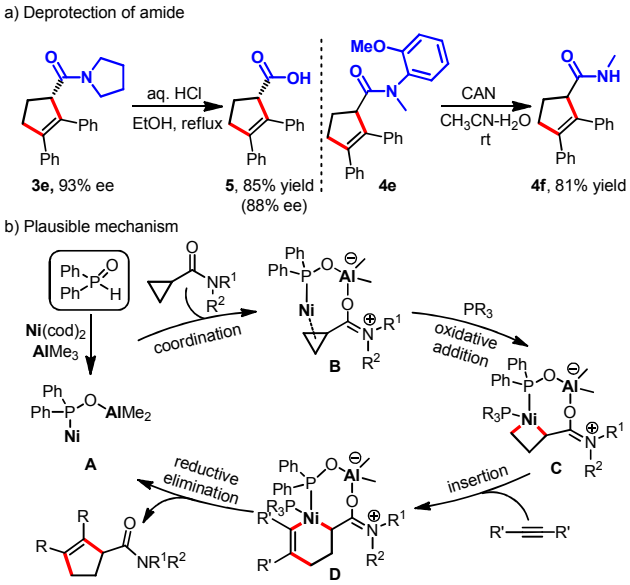


[a]Reaction conditions: **1** (0.1 mmol), **2** (0.3 mmol), P ligand (0.01 mmol), mesitylene (1.0 mL), under N_2 for 24 h; isolated yield. [b]$AlMe_3$ (0.1 mmol). [c]86:14 dr and ee of major isomer.

To demonstrate the applicability of the amide group, further transformation of products was conducted (Scheme 2a). When subjected to acidic conditions, cyclopentene (**3e**) was easily transformed into the corresponding acid (**5**), a versatile synthetic intermediate, in 85% yield but with partial racemization. Cyclopentene (**4e**) was treated by oxidation conditions to deliver a dearylated amide (**4f**) in 81% yield.

In order to understand the role of ligand and two metals in the current cycloaddition reaction, some additional experiments were conducted. Firstly, control experiments showed that the absence of any of the three components, $Ni(cod)_2$, $Ph_2P(O)H$ and $AlMe_3$, shut down this reaction, implying that each of them is essential to this reaction. In comparison with cyclopropyl carboxamide, cyclopropyl ketone under our conditions mainly led to a significant amount of byproduct that came from the addition of $AlMe_3$ to the carbonyl. We also tried to prepare a ligand-Ni-Al complex according to Cramer's method,[15] but failed. NMR experiments suggested that the interaction of $Ph_2P(O)H$, $AlMe_3$ and nickel could generate a bimetallic complex (**A**) depicted in Scheme 2 (see the supporting information).[17] However, a solid evidence on this intermediate is still missing and needs further studies in the future. Based on these results and Ogoshi's mechanism,[13] we proposed a catalytic cycle as follows (Scheme 2b): ligand-metal-binding intermediate (**A**) coordinated with the substrate to form intermediate (**B**). A subsequent PR_3-assisted oxidative addition of nickel with C–C bond of cyclopropane provided 4-membered nickelacycle (**C**), which inserted into alkyne to afford 6-membered nickelacycle (**D**). A final reductive elimination afforded the desired cyclopentenyl carboxamide and regenerated the catalytic species.

Scheme 2. Transformation and Plausible Mechanism



In summary, we have developed the first example of nickel-catalyzed enantioselective cycloaddition reaction of unreactive cyclopropyl carboxamide with alkyne. A series of synthetically-useful cyclopentenyl carboxamides are obtained in up to 99% yield and 94% ee. The cooperation of ligand with Ni and Al may provide new insights into the C–C bond activation of unreactive substrates.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI. Experimental procedures, characterization data, and spectra of new compounds (PDF)

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Author Contributions

† Q.-S.L. and D.-Y.W. contributed equally to this work.

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

We thank the National Natural Science Foundation of China (21402096, 21421062 and 21672107) for financial support.

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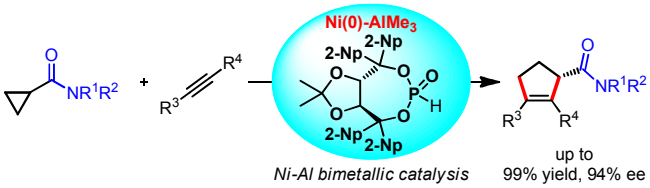
Ni(0)-AlMe3
2-Np
2-Np
2-Np
2-Np
O
O
O
O
P
H
NR1R2
R3
R4
Ni-Al bimetallic catalysis
up to
99% yield, 94% ee