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ARTICLE TYPE

Cyclotrimerization of terminal alkynes catalyzed by the system of NiCl₂/Zn and (benzimidazolyl)-6-(1-(arylimino)ethyl)pyridines

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Chanjuan Xi,*^{*a,b*} Zelin Sun^{*a*} and Yongbing Liu^{*a*}

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An effectively regioselective cyclotrimerization of terminal alkynes is achieved by direct utilization of NiCl₂·6H₂O, Zn, and 2-(benzimidazolyl)-6-(1-(arylimino)ethyl)pyridine in one-step under ambient temperature.

- ¹⁰ Since the first transition-metal-catalyzed trimerization of alkynes to benzene derivatives was demonstrated by Reppe in 1948,¹ the [2+2+2] cycloaddition of alkynes has been extensively studied.² Although this approach has become one of the most powerful methods to assemble benzene derivatives; however, critical
 ¹⁵ problems remained with chemo- and regio- selectivity, because of commonly forming mixture of products, and retarding the synthetic utility. Fortunately the cyclotrimerization was achieved by (partially) intramolecular reactions^{3,4} and it has been elegantly used in the total synthesis of both natural and artificial
 ²⁰ compounds. On the other hand, more elaborate catalytic systems have been described by employing palladium,⁵ rhodium,⁶ iridium,⁷ ruthenium,⁸ cobalt,⁹ and other transition metals¹⁰ with various ligands. Nonetheless, the selectivity of catalytic intermolecular reaction has remained unclear.
- ²⁵ Nickel is an ideal core for the active species, given its lower cost and increased reactivity toward readily available reagents; for example nickel-catalyzed bond-forming reactions of carboncarbon^{11,12} and carbon-heteroatom¹³ were achieved by Ni(0) catalyst supported by 1,5-cyclooctadiene(COD), phosphines,
- ³⁰ phosphites, and N-heterocyclic carbenes.^{11a-c} However, the Ni(0) reagents would be difficult to handle and manipulate because of their high air sensitivity and thermal instability. By contrast, Ni(II) reagents are readily available and conveniently handled, as pre-catalysts and thus are of more practical use. In most cases, the
- ³⁵ Ni(II)-associated with ancillary ligands such as phosphines, Nheterocyclic carbenes, and amines or imines were evaluated as pre-catalyst,^{11d-e} which was prepared in advanced by the reaction of nickel salts and ligands. Recently, the nickel(II)-ligated by 2-(benzimidazolyl)-6-(1-(arylimino)ethyl)pyridines were proven to
- ⁴⁰ be efficient pre-catalysts in ethylene oligomerization and polymerization,¹⁴ illustrating effective carbon-carbon bond formation by nickel species. To consider the application of these nickel complexes as pre-catalysts in trimerization of alkynes, the nickel-ligated by 2-(benzimidazolyl)-6-(1-
- ⁴⁵ (arylimino)ethyl)pyridines¹⁵ is initially explored. We found that the effective cyclotrimerization of terminal alkynes was achieved by direct utilization of NiCl₂·6H₂O, Zn, and 2-(benzimidazolyl)-6-(1-(arylimino)ethyl)pyridine in one-step (Scheme 1). Herein we

would like to report this reaction in detail.



Scheme 1. NiCl₂· 6H₂O as precatalyst for cyclotrimerization of alkynes

To optimize the reaction conditions, phenylacetylene 1a was explored for cyclotrimerization. Firstly, NiCl₂·6H₂O/Zn/ZnI₂ was used to trimerize phenylacetylene 1a with observing low yield 55 (Table 1, entry 1). With the presence of 2-(benzimidazolyl)-6-(1-(arylimino)ethyl)-pyridine L1 and L2 (entries 2-3), the cyclotrimerization of phenylacetylene 1a was effectively achieved with excellent yields along with high regioselectivity. The ligand L3 having bulky substituent showed a moderate 60 activity and high regioselectivity to mainly form 1,2,4triphenylbenzene (entry 4). Meanwhile 2,2'-bipyridine L4 (entry 5), 2-iminopyridine L5 (entry 6), 2-imidazolylpyridine L6 (entry 7), [(benzimidazol-2-yl)pyridin-2-yl]ethanone L7 (entry 8) also gave moderate yields with lower regioselectivity, respectively. 65 Therefore, the ligand L2 was further explored in different solvents (entries 3 and 9-12), indicating the suitable solvent as acetonitrile (entry 3). Other zinc salts such as ZnCl₂ and ZnBr₂ were utilized in these reactions (entries 13-14), whilst the use of ZnI₂ afforded the best result (entry 3). Presumably, ZnI₂ initiates ⁷⁰ the catalytic system by ligand exchange.¹⁶ Use of NiI₂ instead of NiCl₂ afforded the product in 90% yield (entry 15). Interestingly, it was noteworthy that the cyclotrimerization was carried out in low yield with 1,3,5-triphenylbenzene as major product without addition of any zinc salt (entry 16). When complex C2 (Fig. 1) 75 prepared by the reaction of NiCl₂·6H₂O and L2^{14c} was used as

pre-catalyst and the products formed in 93% (entry 17). In addition, use of Ni(COD)₂ instead of NiCl₂ and Zn dust afforded the product in 34% yield (entry 18).

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Ph—=== 1a		NiCl ₂ ·6H ₂ O (5 mol %) ligand (6 mol %) Zn (10 mol %) ZnX ₂ (10 mol %) Solvent, rt		Ph Ph Ph 2a	Ph Ph Ph 3a	
Entry	Ligand	Solvent	Time (h)	Additive	Yield (%) ^b 2a+3a	2a:3a ^c
1	-	CH₃CN	24	ZnI_2	trace	-
2	L1	CH ₃ CN	1	Znl ₂	93	92:8
3	L2	CH ₃ CN	1	Znl ₂	94	95:5
4 ^d	L3	CH ₃ CN	1	Znl ₂	85	97:3
5	L4	CH ₃ CN	1	Znl ₂	65	80:20
6	L5	CH ₃ CN	1	Znl ₂	74	84:16
7	L6	CH ₃ CN	1	Znl ₂	83	81:19
8	L7	CH ₃ CN	1	Znl ₂	85	83:17
9	L2	THF	1	ZnI_2	20	79:21
10	L2	DMF	1	Znl_2	9	88:12
11	L2	Toluene	6	Znl ₂	0	-
12	L2	CH ₂ Cl ₂	6	Znl ₂	0	-
13	L2	CH ₃ CN	1	ZnBr ₂	76	91:9
14	L2	CH ₃ CN	1	ZnCl ₂	68	92:8
15 ^e	L2	CH ₃ CN	1	Znl ₂	90	93:7
16	L2	CH ₃ CN	3	-	33	8:92
17 ^f	C2	CH₃CN	1	Znl ₂	93	95:5
18 ^g	L2	CH ₃ CN	3	Znl ₂	34	91:9

^aReaction conditions: phenylacetylene 1a (110 mL, 1 mmol), NiCl₂·6H₂O (12 mg, 0.05 mmol), ligand (0.6 mmol), zinc powder (6.5 mg, 0.10 mmol),
⁵ZnX₂ (0.10 mmol), solvent (2.0 mL). ^bIsolated yield. ^cThe isomeric ratio was determined via careful integration of ¹H NMR spectra. ^aTrace amount of 1,4-diphenylbuta-1,3-diene was detected by GC-MS. ^cReaction conditions: phenylacetylene 1a (110 mL, 1 mmol), NiI₂ (16 mg, 0.05 mmol), L2 (22 mg, 0.6 mmol), zinc powder (6.5 mg, 0.10 mmol), ZnI₂ ¹⁰ (32 mg, 0.10 mmol), Solvent (2.0 mL). ^fReaction conditions: phenylacetylene 1a (110 mL, 1 mmol), C2 (24 mg, 0.05 mmol), zinc powder (6.5 mg, 0.10 mmol), ZnI₂ (32 mg, 0.10 mmol), ZnI₂ (32 mg, 0.10 mmol), Ni(COD)₂ (14 mg, 0.05 mmol), L2 (22 mg, 0.6 mmol), ZnI₂ (32 mg, 0.10 mmol), Ni(COD)₂ (14 mg, 0.05 mmol), L2 (22 mg, 0.6 mmol), ZnI₂ (32 mg, 0.10 mmol), Solvent (2.0 mL).



Figure 1. Tested ligands and complex

On the basis of the observations, the system using NiCl₂·6H₂O/Zn/ZnI₂/2-(benzimidazolyl)-6-(1-(arylimino)ethyl)-²⁰ pyridine (entry 3) is further explored with various terminal alkynes in acetonitrile at room temperature under nitrogen atmosphere. In all cases, the 1,2,4-trisubstituted benzene derivatives **2** were found as the major products in good to excellent yields (entries 1-3, and 6-11). Aryl group could be ²⁵ incorporated with either electron-donating (entries 2-4) or

electron-withdrawing groups (entries 6-9). It is worth mentioning that the 4-ethynyl-N.N-dimethylaniline 1d transformed into only one isomer as 1,3,5-substituted product in 72% yield (entry 4). This may be attributed to the nitrogen of the amine coordination 30 with ZnI_2 to cut the role of ZnI_2 . When 2-ethynyl-N,Ndimethylaniline 1e was employed in the reaction, the cyclotrimerization proceeded in low yield (entry 5), presumably due to the steric effect of the substituent in the ortho-position of 1e. In principle, 1,2,4-trisubstituted products were mainly 35 obtained and illustrated with 4-ethynylbiphenyl 1j (entry 10), and 3-ethynylthiophene 1k (entry 11). Regarding to alkyl-substituted alkynes, the cyclotrimerization achieved in moderate yields with lower regioselectivity (entries 12-14). Cyclotrimerization of ethynyltrimethylsilane 10 afforded product in low yield with 40 producing 1,3,5-trisubstituted compound (entry 15), being attributed to bulky TMS group. Concerning internal alkynes, the reaction of 3-hexyne 1q or 1,2-diphenylethyne 1r were not proceeded (entries 17-18); however, dimethyl but-2-ynedioate 1s was effectively transformed into a fully substituted benzene 45 derivative (entry 19).

Table 2. NiCl₂ $6H_2O/Zn/ZnI_2/L2$ catalyzed cyclotrimerization of terminal alkynes^{*a*}

	$ \begin{array}{cccc} R^{1} & NiCl_{2}\cdot6F \\ L2 () \\ $	I ₂ O (5 6 mo 10 mo (10 m (10 m	5 mol ' l %) ol %) iol %) N	$ \begin{array}{c} \text{\%} \\ \text{R}^2 \\ \text{R}^2 \\ \text{R}^2 \\ \text{F} \\ \text{2} \end{array} $	R^1 R^2 +	$ \begin{array}{c} R^{1} \\ R^{2} \\ R^{1} \\ R^{2} \\ R^{2} \\ 3 \end{array} $					
Entry	R ¹	R ²		Temp. (°C)	Time (h)	Yield (%) ^b 2+3	Ration ^c 2:3				
1	Ph	Н	1a	rt	1	94	95:5				
2	4-MeC ₆ H ₄	Н	1b	rt	1	93	93:7				
3	$4-\text{MeOC}_6\text{H}_4$	Н	1c	rt	1	88	95:5				
4	4-Me ₂ NC ₆ H ₄	Н	1d	rt	4	72	0:100				
5	$2-Me_2NC_6H_4$	Н	1e	50	6	trace	-				
6	$4\text{-}\text{MeO}_2\text{CC}_6\text{H}_4$	Н	1f	rt	1	94	92:8				
7	4-AcC ₆ H ₄	Н	1g	rt	1	95	90:10				
8	4-CIC ₆ H ₅	н	1h	rt	1	95	88:12				
9	4-BrC ₆ H ₅	н	1i	50	4	68	78:22				
10	4-biphenyl	н	1j	rt	4	88	91:9				
11	3-thioyl	н	1k	rt	4	84	96:4				
12	<i>ⁿ</i> Bu	н	11	50	12	32	39:61				
13	Ph(CH ₂) ₂	н	1m	50	12	42	43:57				
14	CI(CH ₂) ₃	н	1n	50	12	14	42:58				
15	TMS	н	10	rt	4	25	0:100				
16	CO ₂ Et	н	1p	50	12	46	91:9				
17	Et	Et	1q	100	4	0	-				
18	Ph	Ph	1r	100	12	0	-				
19 ^d	CO ₂ Me	CO ₂	Me 1	s 100	12	95	-				

^{*a*}Reaction conditions: alkyne (1 mmol), NiCl₂·6H₂O (11.9 mg, 0.05 mmol), 50 L2 (22 mg, 0.06 mmol), zinc powder (6.5 mg, 0.10 mmol), ZnI₂ (32 mg, 0.10 mmol) and CH₃CN (2.0 mL) were used; ^{*b*}Isolated yield; ^{*c*}The isomeric ratio was determined via careful integration of ¹H NMR-spectra. ^{*d*}The reaction did not proceed at room temperature.

Although the confirmation of the reaction mechanism must ⁵⁵ await further study, we postulate the reaction path as illustrated in Scheme 2, which based on reported metal-catalyzed reactions.^{2a} Firstly, NiCl₂ may react with ZnI₂ to afford LNiI₂ in the presence of benzimidazolyl-6-(1-(arylimino)ethyl)pyridine, which can be reduced by Zn powder to give possible intermediates 4.¹⁷ The complex 4 can quickly react with two equivalents of alkyne to give metallacyclopentadienes 5. In some cases of the reaction, a trace amount of 1,4-diphenylbuta-1,3-diene was detected. That s result confirmed that di(α -aryl)-ferrocyclopentadiene 5 would be favoured over than (α -aryl)-(β -aryl) ones. The intermediate 5 can

further be cyclized to **6** and/or **7** through an insertion or [4+2]cycloaddition pathway, respectively. Reductive elimination reaction of **6** and/or **7** yields benzene derivative **2** and regenerates ¹⁰ the low valent complex **4**.



Scheme 2. Possible Reaction Pathway

In conclusion, the cyclotrimerization of terminal alkynes can be efficiently catalyzed by direct utilization of ¹⁵ NiCl₂·6H₂O/Zn/Znl₂/2-(benzimidazolyl)-6-(1-(arylimino)ethyl)pyridine system in one-step in acetonitrile to afford trisubstitutedbenzene derivatives, the regio-selectivity to either 1,2,4trisubstituted or 1,3,5-trisubstituted benzene derivatives were

relied on the substituents of terminal alkynes and zinc salt. ²⁰ Further investigations of mechanism, additives, and applications are still in progress.

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25 Notes and references

^a Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084, China; E-mail: cjxi@tsinghua.edu.cn

- ^b State Key Laboratory of Elemento-Organic Chemistry, Nankai 30 University, Tianjin 300071, China
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Graphic Abstract

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Cyclotrimerization of terminal alkynes catalyzed by the system of NiCl₂/Zn and (benzimidazolyl)-6-(1-(arylimino)ethyl)pyridines

Chanjuan Xi,*^{*a,b*} Zelin Sun^{*a*} and Yongbing Liu^{*a*}

^aKey Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology (Ministry

of Education), Department of Chemistry, Tsinghua University, Beijing 100084,

China;

^bState Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China

E-mail: cjxi@tsinghua.edu.cn



The regioselective cyclotrimerization of terminal alkynes was effectively catalyzed by the system of $NiCl_2/Zn/ZnI_2$ and (benzimidazolyl)-6-(1-(arylimino)ethyl)pyridines in one-step.