Alkynes

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Access to Acyclic *Z*-Enediynes by Alkyne Trimerization: Cooperative Bimetallic Catalysis Using Air as the Oxidant

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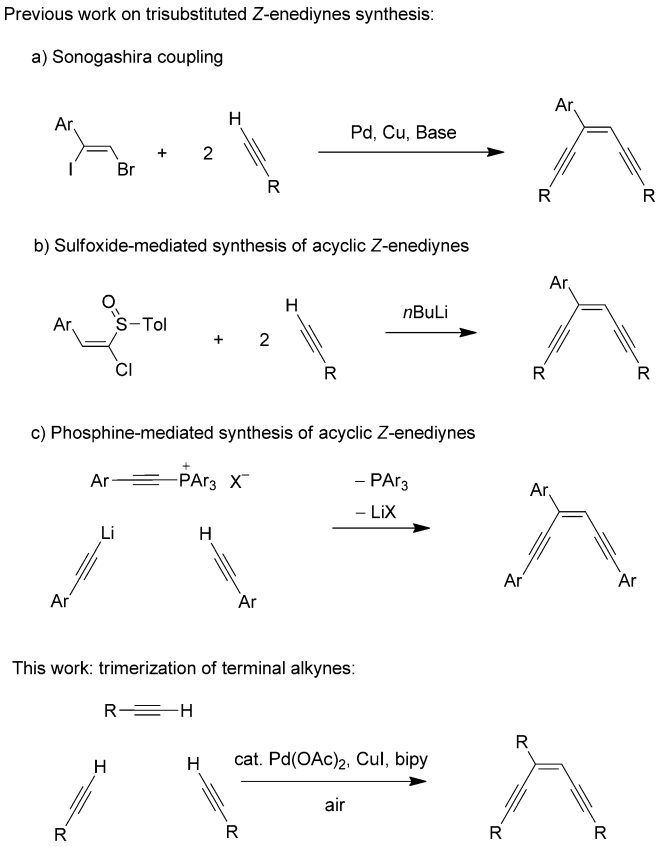
Abstract: *Presented herein is a mild, operationally simple, mix-and-go procedure for the synthesis of acyclic trisubstituted Z-enediynes, from readily available terminal alkynes, in good yields. This method stems from a serendipitous discovery, and makes use of cooperative palladium/copper bimetallic catalysis and air as an oxidant to effect an intriguing alkyne trimerization to yield the valuable Z-enediyne moiety.*

Natural *Z*-enediynes are a class of compounds with exceptional anticancer properties.[1] The presence of *cis*-arranged conjugated carbon–carbon bonds in these natural *Z*-enediynes allows for Bergman cyclization,[2] thus generating diradicals which may serve as potent warheads in cancer cell destruction. The potency of these natural *Z*-enediynes in fighting cancer cells have motivated numerous research groups to synthesize small organic molecules bearing the *Z*-enediyne framework, and to test these molecules for their efficacy in cancer cell treatment. Several of these artificial *Z*-enediynes, containing an acyclic *Z*-enediyne moiety, have proven to be excellent warheads in cancer cell destruction.[3] The development of practical methods for the synthesis of acyclic *Z*-enediynes from commercially available starting materials would thus be desirable in further advancing the field of *Z*-enediyne anticancer research.

Various methods have been used in the synthesis of acyclic *Z*-enediynes (Scheme 1).[4] Most of these methods, however, require the use of precursors which are difficult to access or pyrophoric in nature, and unavoidably generate waste in the process. The use of a Sonogashira coupling, for instance, requires the preparation and use of a geometrically pure (*Z*)-1,2-dihaloethylene.[5] More recently, *p*-tolyl sulfoxide[6] and phosphonium salts[7] have also been reported as precursors in the synthesis of acyclic *Z*-enediynes. Besides requiring several steps in the preparation of these precursors, the use of pyrophoric organometallic reagents like butyl lithium and lithium acetylides limits the application of these methods for the synthesis of acyclic *Z*-enediynes for high-throughput drug discovery. Herein, we reveal an operationally simple method for the synthesis of acyclic *Z*-enediynes by trimerization of commercially available terminal alkynes and it is effected by cooperative palladium/copper catalysis. This process utilizes air as the oxidant and generates minimal waste along the way.



Scheme 1. A comparison between known synthetic methods and this work.

The concept of cooperative bimetallic catalysis[8] has been successfully employed in classical reactions such as Sonogashira coupling,[9] Wacker oxidation,[10] etc. In addition, great advances, particularly in cooperative or synergistic palladium/copper catalysis, have also been achieved in recent years.[11] In our own studies, we attempted to perform a 1,4-addition of phenylacetylene (**1a**) to cyclohexenone catalyzed by palladium acetate and copper iodide in the presence of the 2,2′-bipyridine ligand. Instead of obtaining the anticipated ynone **2**, an unexpected product, (*Z*)-1,3,6-triphenylhexa-3-en-1,5-diyne (**3a**), was isolated in 31% yield (Scheme 2). It is noteworthy that the oxidative homodimerization of phenylacetylene, catalyzed by copper and palladium, to yield the Glaser–Hay-type diyne product **4** (for structure see Table 1) is well-established in the literature.[12] In addition, palladium-

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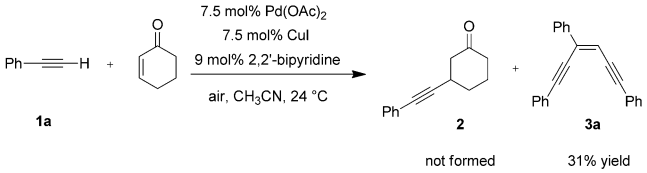


Scheme 2. The discovery of the unexpected trimerization of phenylacetylene.

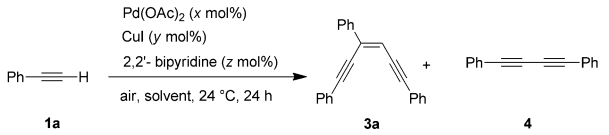
catalyzed conversion of terminal alkynes into enynes is also reported.[13] Furthermore, there have also been several reports on transition-metal-catalyzed trimerization of alkynes to form dienynes.[14] The formation of highly valuable endiynes from trimerization of alkynes, however, is not known, to the best of our knowledge. Recognizing the immense potential of this method in providing a single-step access to acyclic *Z*-enediynes by an operationally simple "mix-and-go" procedure, systematic optimization was carried out to improve the yield of **3a**.

Notably, **3a** cannot be formed when either $Pd(OAc)_2$, CuI, or 2,2′-bipyridine is absent (Table 1, entries 1–4), thus lending weight to a bimetallic catalysis pathway for its formation. Systematic screening of solvents revealed that a mixture of acetonitrile/methanol (1:1) gave an improvement in the yield to 45% (entries 5–9). With the best solvent system in hand, different oxidants were screened. The use of oxygen, inorganic oxidants like sodium nitrite, and organic oxidants like *p*-benzoquinone all led to a significant reduction in the yield of **3a** (entries 10–12). In fact, the use of these oxidants resulted in an unwanted increase in the formation of the 1,4-diphenylbutadiyne side product **4**. Air thus remained the best oxidant for this transformation. In addition, performing the reaction under the strict exclusion of air led a dramatic decrease in yield to less than 5% (entry 13), thus confirming the need for air as an oxidant for this transformation.

Further to this, the catalytic loadings of $Pd(OAc)_2$, CuI, and 2,2′-bipyridine were optimized. During the optimization, it was observed that both the increase in the loading of $Pd(OAc)_2$ (Table 1, entry 14), and the decrease in the loading of CuI (entry 15), led to a slight decrease in yield. Through decreasing the loading of $Pd(OAc)_2$ to 5 mol% and increasing the loading of CuI to 10 mol%, an improvement in yield of **3a** to 64% was obtained (entry 17). A loading of 10 mol% 2,2′-bipyridine led to an optimized yield of 70% (entry 18). The optimization process also revealed that the palladium/bipyridine complex is likely an important catalytic species for this transformation as attempts to coordinate 2,2′-bipyridine to CuI prior to the addition of $Pd(OAc)_2$ and phenylacetylene substrate resulted in much lower yield (33%).

In an effort to further optimize the reaction, other palladium salts and copper salts were screened. $Pd(OAc)_2$ proved to be essential for this catalytic system to work (Table 2, entries 1–5), while replacing CuI with other substitutes led to dismal results (entries 6 and 7). Similarly, the use of other analogues of 2,2′-bipyridine (entries 8–10) and other common bis(phosphine) ligands (entries 11–13) did not

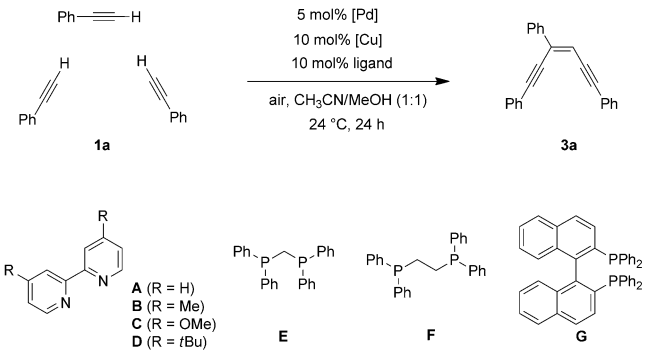
Table 1: Optimization of **3a** formation by bimetallic catalysis.[a]



Entry	*x*	*y*	*z*	Oxidant	Solvent	Yield [%][b]
1	7.5	7.5	9	air	CH_3CN	31
2	0	7.5	9	air	CH_3CN	< 2
3	7.5	0	9	air	CH_3CN	< 2
4	7.5	7.5	0	air	CH_3CN	< 2
5	7.5	7.5	9	air	MeOH	34
6	7.5	7.5	9	air	THF	15
7	7.5	7.5	9	air	toluene	< 5
8	7.5	7.5	9	air	DMSO	13
9	7.5	7.5	9	air	CH_3CN/MeOH[c]	45
10	7.5	7.5	9	O_2	CH_3CN/MeOH[c]	39
11	7.5	7.5	9	$NaNO_2$	CH_3CN/MeOH[c]	21
12	7.5	7.5	9	*p*-quinone	CH_3CN/MeOH[c]	< 2
13	7.5	7.5	9	none	CH_3CN/MeOH[c]	< 5
14	10	7.5	9	air	CH_3CN/MeOH[c]	42
15	7.5	5	9	air	CH_3CN/MeOH[c]	42
16	5	5	5	air	CH_3CN/MeOH[c]	45
17	5	10	5	air	CH_3CN/MeOH[c]	64
18	5	10	10	air	CH_3CN/MeOH[c]	70

[a] Unless otherwise stated, reaction was performed by stirring the catalysts and ligand in the solvent in a capped vial for 30 min followed by the addition of **1a** (1 mmol). [b] Determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [c] Used in a 1:1 ratio. DMSO = dimethylsulfoxide, THF = tetrahydrofuran.

Table 2: Catalyst optimization for the formation of **3a** by bimetallic catalysis.[a]

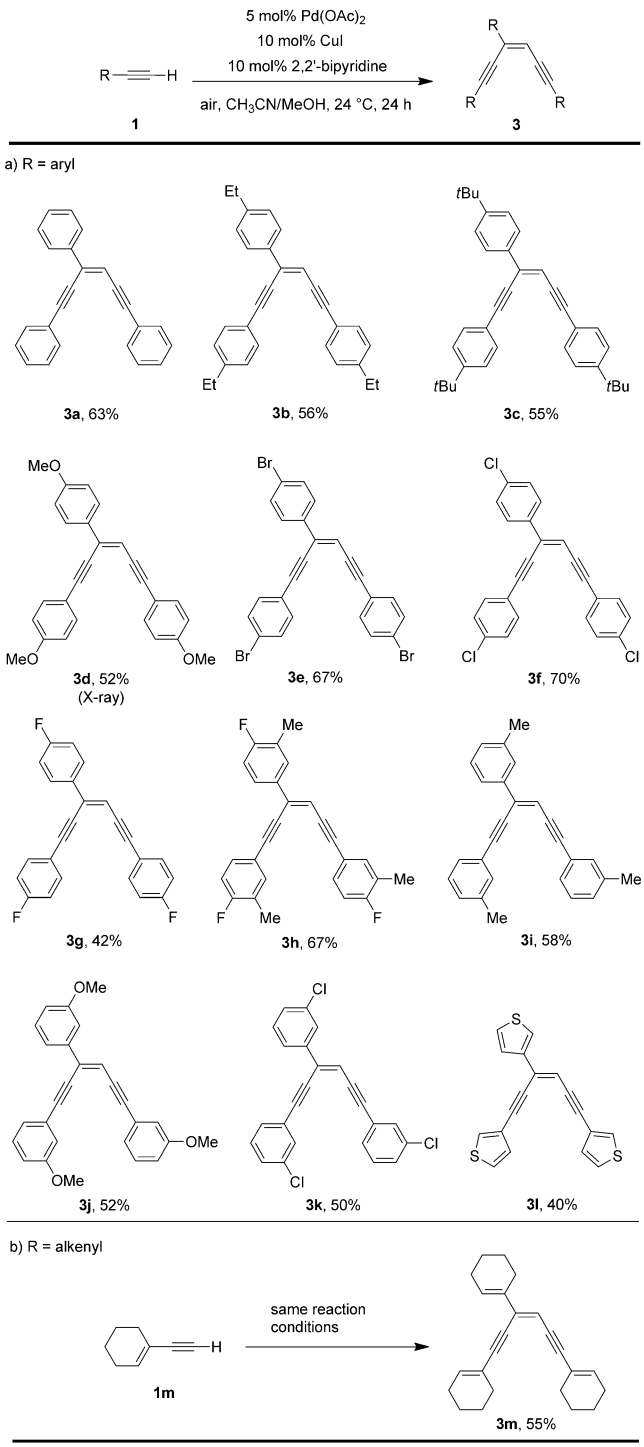


Entry	Pd salt	Cu salt	Ligand	Yield [%][b]
1	$Pd(OAc)_2$	CuI	**A**	70
2	$PdCl_2$	CuI	**A**	< 2
3	$PdCl_2(CH_3CN)_2$	CuI	**A**	< 2
4	$[Pd_2(dba)_3]$	CuI	**A**	< 2
5	$[Pd(PPh_3)_4]$	CuI	**A**	< 5
6	$Pd(OAc)_2$	CuCl	**A**	38
7	$Pd(OAc)_2$	Cu_2O	**A**	< 2
8	$Pd(OAc)_2$	CuI	**B**	48
9	$Pd(OAc)_2$	CuI	**C**	45
10	$Pd(OAc)_2$	CuI	**D**	42
11	$Pd(OAc)_2$	CuI	**E**	< 2
12	$Pd(OAc)_2$	CuI	**F**	< 2
13	$Pd(OAc)_2$	CuI	**G**	< 2

[a,b] See Table 1. dba = dibenzylideneacetone.

improve the yield of **3a** either. The original set of reaction conditions in entry 1 remained optimal.

With the optimized reaction conditions in hand, the scope of the transformation was investigated. As shown in Scheme 3, substrates containing electron-donating groups in the *para*- and *meta*-positions on the aryl ring were well tolerated, thus giving rise to reasonable yields of 52 to 58% (**3b–d, 3i,j**). Electron-withdrawing groups were similarly well tolerated. In particular, *para*-bromophenylacetylene and *para*-chlorophenylacetylene substrates led to good yields of **3e** (67%) and **3f** (70%), respectively. Strongly electron-withdrawing groups like fluorine, however, resulted in lower yield (42% for **3g**), although the presence of an additional electron-donating group at the *meta*-position increased the yield to 67% (**3h**). A *meta*-substituted electron-withdrawing group is similarly well tolerated (**3k**), and *ortho*-substituted groups, however, only led to the Glaser–Hay-type side product. Besides phenylacetylene derivatives, the transformation also worked well for heterocycles like 3-ethynylthiophene to deliver **3l** in reasonable yield. Gratifyingly, enynes such as 1-ethynylcyclohexene could also undergo similar reaction to yield the endiyne **3m**. Attempts to expand the scope of this transformation to aliphatic alkynes, however, were unsuccessful. In these cases, again the homodimerization of alkynes took place predominantly to deliver the diyne side product.



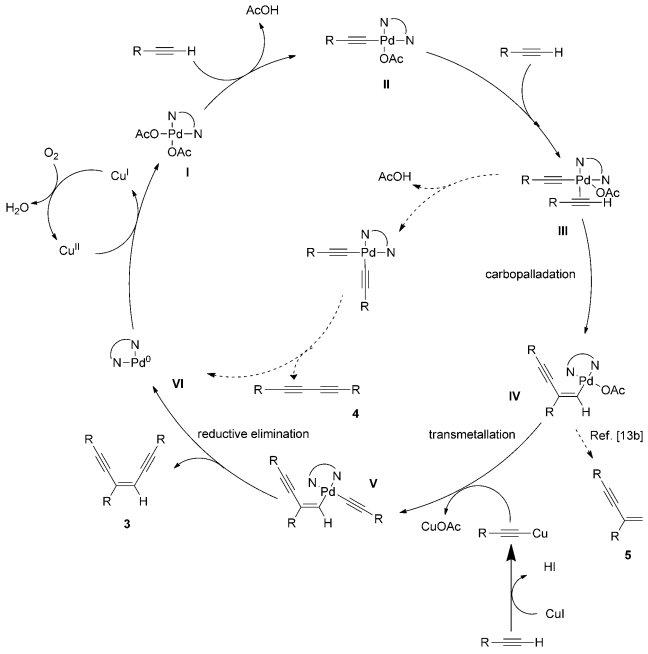
Scheme 3. Scope with respect to the *Z*-endiynes from alkyne trimerization.

The possibility of obtaining a cross-trimerization product was also carefully investigated by varying the electronic and/or steric properties of the substrates. Reaction of electron-poor *para*-bromophenylacetylene with the electron-rich *para*-methoxyphenylacetylene under standard reaction conditions led to a complex mixture of products containing homodimers, heterodimers, homotrimers, and heterotrimers. Likewise, we were unable to isolate any crosstrimerization products when phenylacetylene was reacted with internal alkynes or aliphatic alkynes. The identification of a suitable catalytic system for such challenging transformations will be the focus of our future studies.

The structure and geometry of the endiyne product **3d** was unambiguously assigned by single-crystal X-ray analysis.[16] The structures of the other products were assigned by analogy based on the similarity of the peak pattern in the NMR spectra.

Based on important precedents from the group of Trost[15] and our experimental evidence, we propose the catalytic cycle in Scheme 4 as a working hypothesis. The optimization studies indicated that the palladium/bipyridine complex is formed and is responsible for the reactivity. The proposed catalytic cycle therefore begins with the formation of the complex **I**. Direct deprotonation of a coordinated terminal alkyne by acetate forms the 16-electron complex **II**. The introduction of another molecule of alkyne results in an 18-electron complex **III** which undergoes a carbopalladation step, in which the palladium was placed at the less substituted carbon atom to regenerate the more stable 16-electron complex **IV**. This carbopalladation step is also the stereodetermining step for this transformation. Following this, transmetallation of **IV** with copper(I) acetylide generated from CuI and the substrate leads to the formation of the intermediate **V**. Reductive elimination of **V** then generates the desired product **3** and a palladium(0) species **VI**. In another cooperative catalytic cycle, copper(I) gets oxidized by oxygen in air to generate a copper(II) species which oxidizes the palladium(0) species **VI** to regenerate **I**.

There are two complications in this proposed catalytic cycle. Firstly, the complex **III** could undergo further deprotonation of the coordinated terminal alkyne to form the



Scheme 4. The proposed mechanism.

dialkynylpalladium complex, the reductive elimination of which would generate the side product **4**. This route is indeed the major side reaction pathway in our studies. Secondly, **IV** could engage another terminal alkyne, thus leading to the enyne **5** by reductive elimination of a Pd^{IV} species as reported by the Trost group.[13b] In a related palladium/copper-catalyzed trimerization of alkynes to form dienynes, reported by the group of Wu,[14a] a palladium-phosphine complex was used and a Pd^0/Pd^{II} catalytic cycle was proposed instead. In that system, **5** was also formed as a key intermediate. Compared to these precedents, the use of a bipyridine ligand in our studies might discourage this pathway as the use of electron-rich phosphine ligands was shown to be the key for formation of **5** by reductive elimination.

In summary, we have revealed an operationally simple, one-step mix-and-go procedure for the synthesis of acyclic *Z*-enediynes from commercially available terminal alkynes in good yields. This procedure makes use of readily available precursors and catalysts, and air as an oxidant. Besides adding to the expanding list of transformation currently possible with cooperative bimetallic catalysis, the operational simplicity of this procedure makes this an attractive methodology for the synthesis of acyclic *Z*-enediynes for high-throughput anticancer drug discovery.

Experimental Section

To a vial was added $Pd(OAc)_2$ (0.0165 mmol, 3.7 mg), 2,2′-bipyridine (0.033 mmol, 5.2 mg), and CuI (0.033 mmol, 6.3 mg) in air. 1.25 mL of acetonitrile and 1.25 mL of methanol were added to the vial and capped. The mixture was stirred at room temperature for 30 min before the acetylene **1** (1.0 mmol) was added. The resulting mixture was stirred at room temperature for a further 24 h before being filtered through a short plug of silica and purified by flash column chromatography using hexanes and ethyl acetate to afford **3** in pure form.

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[16] CCDC 1507759 (**3d**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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