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Palladium-Catalyzed Trimerizations of Terminal Arylalkynes: Synthesis of 1,3-Diaryl-2-arylethynyl-1,3-butadienes[1]

Yao-Ting Wu,[a,*] Wei-Chih Lin,[a] Chia-Ju Liu,[a] and Chuan-Yi Wu[a]

[a] Department of Chemistry, National Cheng-Kung University, No.1 Ta-Hsueh Road, 70101 Tainan, Taiwan, R.O.C.
Fax: (+886)-6-274-0552; e-mail: ytwuchem@mail.ncku.edu.tw

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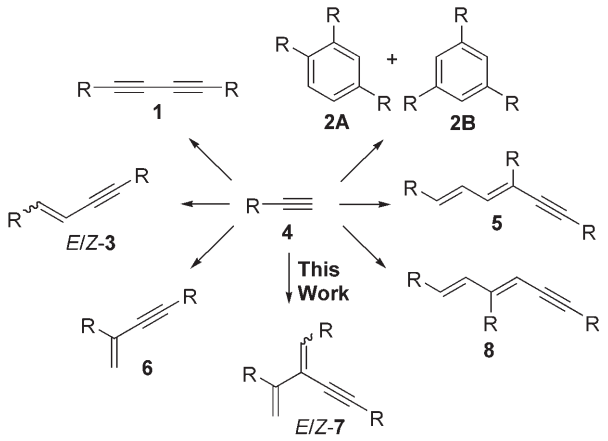
Abstract: Various 1,3-diaryl-2-arylethynyl-1,3-butadienes **7** have been prepared by the Pd-catalyzed trimerization of arylalkynes **4**. Their structures and stereochemistry have been confirmed by X-ray crystal analyses. This procedure provides high regioselectivity to generate adducts *Z*-**7** in moderate to excellent yields. The scope, limitations and regioselectivity of this reaction have been investigated. In DMSO at 180 °C, 1,3-di(1-naphthalenyl)-2-(1-naphthalenylethynyl)-1,3-butadiene (**7m**) underwent 6π-electrocyclization to form 2-(1-naphthalenyl)-3-(1-naphthalenylethynyl)-1,2-dihydrophenanthrene (**21**). Under acidic conditions, (1*Z*)-1,3-diphenyl-2-(1-phenylethynyl)-1,3-butadiene (*Z*-**7a**) was converted to 1-methyl-3-phenyl-2-(2-phenyl-1-ethionyl)-2-indene (**22**) in 75% yield.

Keywords: alkynes; cross-coupling; enynes; hydroalkynylation; palladium

Introduction

Alkynes are important building blocks and synthons for the construction of interesting and useful molecules.[2] The dual σ and π nature of terminal acetylenes allows for various reaction types, particularly for C–C bond formation. In the presence of metal catalysts, a terminal alkyne can be converted either to a σ-alkynyl, a η^2-alkynyl or a η^1-vinylidene (carbene) complex.[3] The σ-alkynyl complex is the key intermediate for the generation of new internal alkynes. For example, symmetrical 1,3-butadiynes **1** can be accessed from a terminal alkyne by an oxidative dimerization (Scheme 1).[4] This reaction can be classified as Eglinton,[5] Glaser,[6] Hay,[7] or Pd-catalyzed[8] coupling, depending on the metal complexes and catalysts utilized.[9] A η^2-alkynyl complex provides the possibility to generate a 1-metallaalkenyl species for further transformation. Based on this reaction route, trisubstituted benzenes **2A** and **2B** can be prepared from an alkyne by a formal [2+2+2] cycloaddition.[10] A η^1-vinylidene complex is able to exhibit several reaction types due to the high reactivity of the carbene carbon.[11] Applying both the σ and π nature of a terminal alkyne, 1,4-disubstituted enynes *E*-**3**[12] and *Z*-**3**,[12d,13] and 1,3-disubstituted enynes **6**[13b,14] are formed from the head-to-head and head-to-tail dimerization of alkynes, respectively.[15] Selective formation of adducts *E*/*Z*-**3** or **6** can be achieved by a suitable choice of reaction conditions and catalysts.[16] In Pd-catalyzed protocols, terminal alkynes **4** usually undergo dimerizations to form enynes **6**.[14] Nolan[12h] and Gevorgyan[12i] independently developed new catalytic systems for the regioselective generation of enynes *E*-**3**. Moreover, linear trimerization adducts, such as dienynes **5**[17] and **8**,[18] can be generated by several catalysts. Compounds **5** should be formed by *syn*-hydroalkyny-



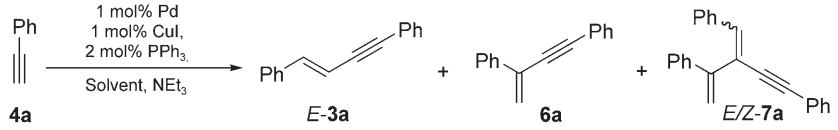
Scheme 1. Metal-catalyzed oligomerizations of terminal alkynes.

lation of the intermediate *E*-**3**. Formation of hexa-1,3-dien-5-ynes **8** may involve a vinylidene intermediate. Recently, we observed that a new trimerization adduct **7** could be synthesized directly from alkynes **4**. Herein, we have optimized the reaction conditions and studied their regioselectivity and applications in organic synthesis.

Results and Discussion

Upon heating phenylacetylene (**4a**) in acetonitrile with a mixture of $PdCl_2(PPh_3)_2$, PPh_3, NEt_3 and CuI, angular dienyne **7a** can be synthesized with high regioselectivity in 94% yield (entry 16 in Table 1). To the best of our knowledge, this is the first example for the generation of a dienyne with this skeleton by the trimerization of a terminal alkyne. Systematic studies of the reaction conditions revealed that palladium catalyst, base, solvent and temperature all play key roles.[19] $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$ gave the best yield and regioselectivity relative to other Pd catalysts, such as, $PdCl_2(acac)_2$, $PdCl_2(dppf)$, $Pd(OAc)_2$ and $PdCl_2(PCy_3)_2$. In contrast to other solvents, that is, NMP, DMSO and toluene, acetonitrile and DMF achieved excellent results, but the former with its low boiling point has an advantage for the purification. In the absence of a base, the desired product cannot be furnished (entry 6 in Table 1). Of the bases used triethylamine turned out to be superior to diisopropylamine and pyridine (entries 7 and 8 in Table 1). However, low regioselectivity was observed when triethylamine was utilized as the solvent (entry 15 in Table 1). Suitable reaction temperature is 80 °C, since at 110 °C the yield was slightly decreased, and at room temperature 1,4-diphenyl-1,3-butadiyne (**1a**) was isolated as the major product. The cocatalyst CuI and the additive PPh_3 can improve the regioselectivity and yield (entries 4, 5 and 17 in Table 1), but CuI does not have any critical influences in this reaction.

Table 1. Optimization of reaction conditions for the preparation of *Z*-**7a**.[a]



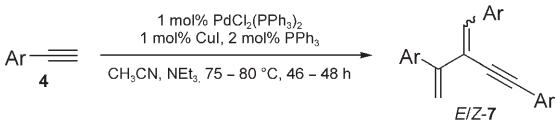
Entry	Catalyst	Solvent	Temperature [°C]	Time [h]	*E*-**3a**:**6a**:*E*-**7a**:*Z*-**7a**[b]	Yield [%][c]
1	$PdCl_2(PPh_3)_2$	DMF	80	48	1:1:1:97	87
2	$PdCl_2(PPh_3)_2$	DMF	25	168	–	–[d]
3	$PdCl_2(PPh_3)_2$	DMF	110	48	0:0:1:99	84
4	$PdCl_2(PPh_3)_2$	DMF	110	21	11:1:1:87	–[e]
5	$PdCl_2(PPh_3)_2$	DMF	110	21	33:11:1:55	–[f]
6	$PdCl_2(PPh_3)_2$	DMF	110	48	–	–[g]
7	$PdCl_2(PPh_3)_2$	DMF	110	24	35:1:1:63	–[h]
8	$PdCl_2(PPh_3)_2$	DMF	80	46	58:13:4:25	–[i]
9	$PdCl_2(acac)_2$	DMF	110	24	73:1:1:25	–
10	$PdCl_2(dppf)$	DMF	80	48	3:0:2:95	–
11	$Pd(OAc)_2$	DMF	110	24	57:1:17:25	–
12	$PdCl_2(PPh_3)_2$	DMSO	80	46	30:10:9:51	–
13	$PdCl_2(PPh_3)_2$	toluene	110	42	45:1:32:22	–
14	$PdCl_2(PPh_3)_2$	NMP	80	46	5:3:2:90	–
15	$PdCl_2(PPh_3)_2$	NEt_3	80	48	55:1:1:43	–
16	$PdCl_2(PPh_3)_2$	CH_3CN	80	48	3:0:0:97	94
17	$PdCl_2(PPh_3)_2$	CH_3CN	80	48	9:3:3:85	80[e]
18	$Pd(PPh_3)_4$	CH_3CN	80	45	1:1:1:97	87
19	$PdCl_2(PCy_3)_2$	CH_3CN	80	62	15:1:35:49	–[j]

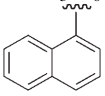
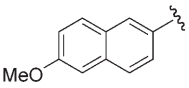
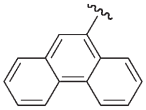
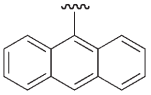
[a] 3 mmol scale. 2.5 mL of solvent and 1.5 mL of base were used in this reaction.
[b] The ratios were determined by the ^1H NMR spectra of the crude products. The conversion cannot be analyzed. Starting material **4a** could be removed during the preparation of the sample for NMR study.
[c] Isolated yield for *Z*-**7a**.
[d] 18% of 1,4-diphenylbutadiyne (**1a**) was isolated.
[e] In the absence of CuI.
[f] In the absence of PPh_3.
[g] In the absence of base.
[h] *i*-Pr_2NH was used as the base.
[i] Pyridine was used as the base.
[j] Instead of PPh_3, PCy_3 was used.

In its absence, *Z*-**7a** can also be obtained in 80% yield.[20]

The reactivity of several alkynes has been examined in this reaction. For example, phenylacetylene (**4a**) and alkynes **4b–h** produced the corresponding dienynes **7** in good yields with *Z*-regioselectivity (Table 2). In other examples, the electronic and steric properties of the aryl substituent in alkyne **4** affected the yield and the regioselectivity. Methyl 4-ethynylbenzoate (**4i**) afforded the sole regioisomer *Z*-**7i** in very low yield and left the starting material in large amounts. Although **4i** was completely consumed at higher reaction temperature (110 °C), the yield was only slightly improved. In contrast to **4i**, electron-rich alkynes furnished the corresponding adducts **7** in moderate to excellent yields. Unlike other dienynes in Table 2, the *E*/*Z* ratio of dienynes **7j** and **7k** could not be accurately reported due to the random appearance of their values (entries 10 and 11 in Table 2). However, the products provided by 3-ethynylanisole (**4b**) and 1-ethynyl-3,5-dimethoxybenzene (**4c**) contained only traces (less than 5%) of *E*-isomers. Angular trimerization of an alkyne with a sterically congestive substituent led to the formation of a significant amount of intermediate **6** as well as the *E*-adduct. 1-Ethynylnaphthalene (**4m**), 2-ethynylnaphthalene **4n** and 9-ethynylphenanthrene (**4o**) yielded the corresponding *Z*-**7** as major products (entries 13–15 in Table 2). The two regioisomers generated from 2-ethynyltoluene (**4l**) were produced in approximately equal amounts. The more bulky alkyne **4p** exclusively underwent dimerization to give enyne **6p** (R = 9-anthracenyl) in 70% yield. In

Table 2. Preparation of various adducts **7** from alkynes **4**.



Entry	Alkyne	Ar	Product	*E*/*Z* Ratio	Yield [%][a]
1	**4a**	Ph	*Z*-**7a**	–	94 (73[b])
2	**4b**	3-OCH_3-C_6H_4	*Z*-**7b**	–	66
3	**4c**	3,5-$(OCH_3)_2$-C_6H_3	*E*/*Z*-**7c**	<5:95	62
4	**4d**	4-CH_3-C_6H_4	*Z*-**7d**	–	70
5	**4e**	3,5-$(CH_3)_2$-C_6H_3	*Z*-**7e**	–	66
6	**4f**	4-*t*-Bu-C_6H_4	*Z*-**7f**	–	80
7	**4g**	4-Ph-C_6H_4	*Z*-**7g**	–	60
8	**4h**	4-F-C_6H_4	*Z*-**7h**	–	65
9	**4i**	4-(CO_2CH_3)-C_6H_4	*Z*-**7i**	–	23
10	**4j**	4-OCH_3-C_6H_4	*E*/*Z*-**7j**	n.r.[c]	87
11	**4k**	4-$N(CH_3)_2$-C_6H_4	*E*/*Z*-**7k**	n.r.[c]	55[e]
12	**4l**	2-CH_3-C_6H_4	*E*/*Z*-**7l**	55:45	60[d]
13	**4m**		*E*/*Z*-**7m**	12:88 (57:43[e])	83 (80[e])
14	**4n**		*E*/*Z*-**7n**	<5:95	65
15	**4o**		*E*/*Z*-**7o**	6:94	63[f]
16	**4p**		*Z*-**7p**	–	0[g]

[a] 3 mmol scale. Each example was repeated at least twice. Traces of by-products **1** and **6** were also formed but neglected, if not otherwise mentioned. The ratios of regioisomers were determined according to the ^{1}H NMR spectra.
[b] 60 mmol scale.
[c] This reaction has been repeated four times. The accurate value could not be reported.
[d] Enyne **6l** was isolated in 20% yield.
[e] Instead of the combinations of $PdCl_2(PPh_3)_2$ and PPh_3, a mixture of $PdCl_2(PCy_3)_2$ and PCy_3 was used.
[f] Enyne **6o** was isolated in 13% yield.
[g] Enyne **6p** was isolated in 70% yield.

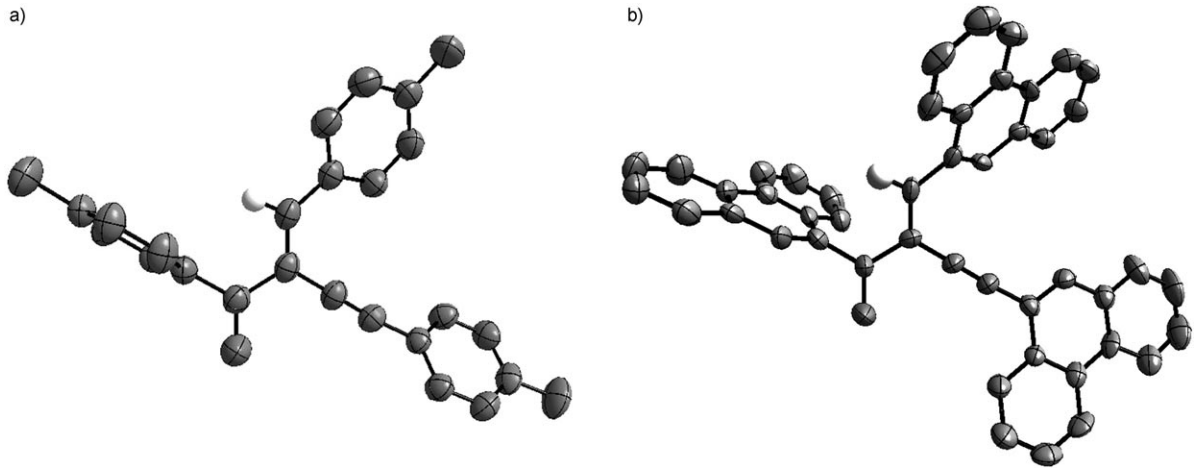


Figure 1. The molecular structures of *Z*-**7d** (*left*) and *Z*-**7o** (*right*) showing 50% probability ellipsoids (Diamond version 3.0). Hydrogen atoms except for 3-H have been omitted for clarity.[21]

addition, the ratio of *E*/*Z*-**7m** can also be influenced by the catalytic combinations of $Pd(PCy_3)_2Cl_2$ and PCy_3 (entry 13 in Table 2). The skeleton, but not the *E*/*Z* stereochemistry, of dienynes **7** could be assigned by 2D-NMR spectra. Fortunately, *Z*-**7d** and Z-**7o** were crystallized from $CHCl_3$/MeOH and their structures were confirmed by the X-ray analyses (Figure 1).[21]

Unlike arylethynes, 1-hexyne (**4q**),[22] trimethylsilylethyne, 3,3-dimethyl-1-butyne and 1-ethynyl-1-cyclohexene did not afford the corresponding adducts **7**. This information led us to study the reaction between enynes **9** and alkynes **4**[23] because dienynes **7** should be formed from enynes **6** by hydroalkynylation. It turned out that hydroalkynylation of enynes **9** did not give satisfactory results, but the scope, limitations and regioselectivity of this reaction can be elucidated (Table 3). Addition of an alkyne to aryl-substituted enynes **9a–d** yielded dienynes **10**, whereas 2-*n*-hexyldeca-1-en-3-yne (**9e**) and 1,3-di(9-anthracenyl)but-3-en-1-yne [**9f** (≡**6p**)] did not participate in this reaction. The lack of reactivity of **9f** possibly arises from the sterically congestive substituent. Triaryldienynes **10** were afforded in lower yields in comparison to the direct formation of trimerization adducts **7** (entries 4–6 and 8 in Table 3). The instability of 1,3-diphenyl-3-buten-1-yne [**9c** (≡ **6a**)] leads to lower yields.[24] In our trimerization protocol **4a** *in situ* generates enyne **6a**, which can immediately undergo hydroalkynylation with an excess of alkyne **4a** to furnish the stable coupling adduct *Z*-**7a** in high yield.[25] Therefore, the yields for the formation of dienynes **10** mainly depend on the reactivity and stability of enynes **9**.

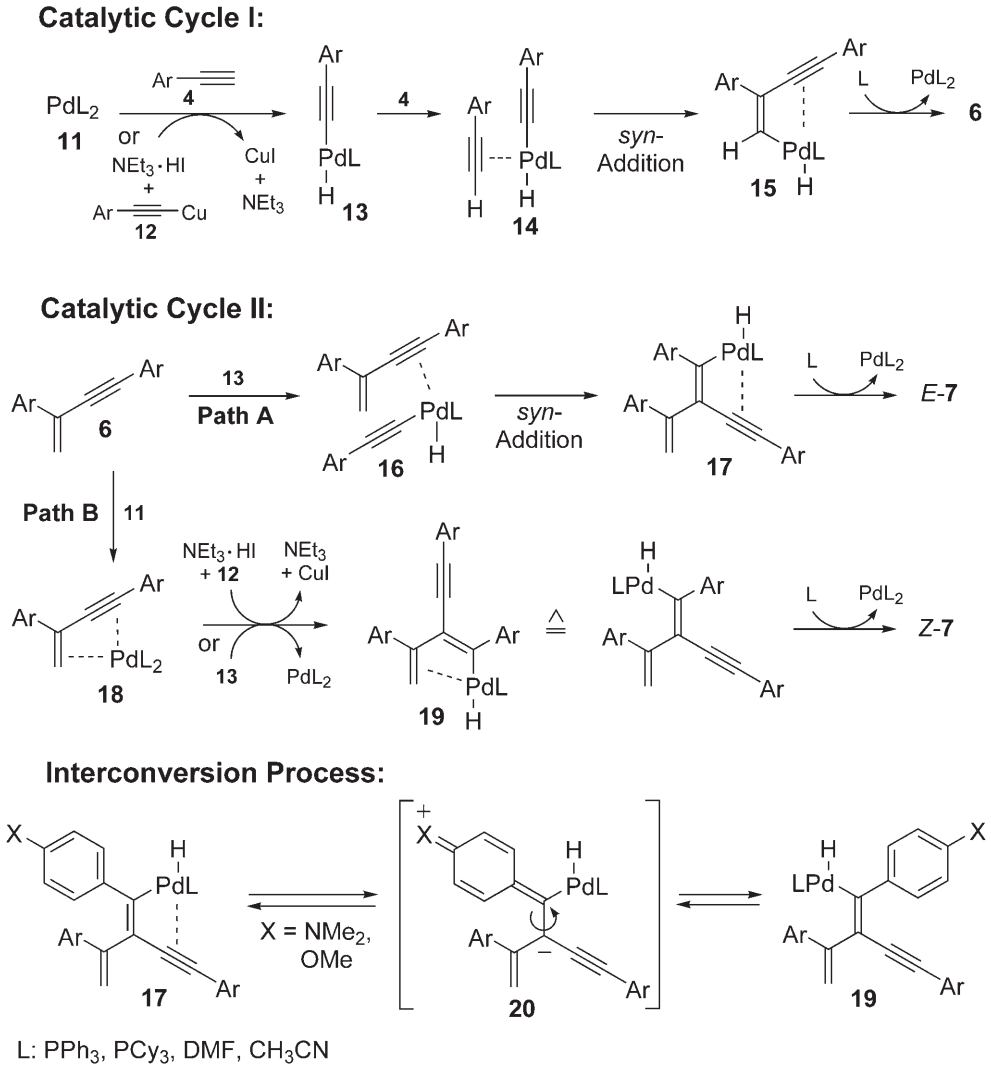
Table 3. Palladium-catalyzed coupling reaction of an enyne **9** with an alkyne **4**.[a]

Entry	Enyne	R^1	R^2	Alkyne	R^3	Product	**9**:**10**[b]	*E*/*Z*-**10**[b]	Yield [%]
1	**9a**	Me	Ph	**4a**	Ph	**10aa**	43:57	44:56	44
2	**9a**	Me	Ph	**4q**	*n*-Bu	**10aq**	12:88	67:33	75
3	**9b**	Ph	*n*-Bu	**4a**	Ph	**10ba**	21:79	38:62	32
4	**9c** (≡**6a**)	Ph	Ph	**4a**	Ph	**10ca** (≡**7a**)	0:100	0:100	40
5	**9c**	Ph	Ph	**4b**	3-OCH_3-C_6H_4	**10cb**	0:100	2:98	44
6	**9c**	Ph	Ph	**4j**	4-OCH_3-C_6H_4	**10cj**	0:100	41:59	46
7	**9c**	Ph	Ph	**4q**	*n*-Bu	**10cq**	0:100	76:24	34
8	**9d** (≡**6j**)	4-OCH_3-C_6H_4	4-OCH_3-C_6H_4	**4a**	Ph	**10da**	0:100	17:83	33
9	**9e** (≡**6r**)	*n*-Hex	*n*-Hex	**4a**	Ph	**10ea**	83:17	29:71	traces
10	**9f** (≡**6p**)	9-anthracenyl	9-anthracenyl	**4a**	Ph	**10fa**	100:0	–	0

[a] Starting materials enyne **9** and alkyne **4** (ratio 1:1.2) were utilized in this reaction.
[b] The ratios were determined by the ^1H NMR spectra of the crude products.

It has also been observed that alkynes **4** and enynes **9** affected the stereochemistry of dienynes **10**. Phenylacetylene (**4a**) and 1-hexyne (**4q**) provided different regioselectivities for the formation of dienynes **10**, and the former alkyne gave the *Z*-regioisomer as the major adduct. Reaction of enyne **9c** with either phenylacetylene (**4a**) or 3-ethynylanisole (**4b**) yielded the corresponding adducts **10** with almost *Z*-regioselectivity, but the same conditions using 4-ethynylanisole (**4j**) afforded *E*/*Z*-**10cj** with a ratio of 41:59 (entries 4–6 in Table 3). In contrast to enyne **9c**, electron-rich enyne **9d** (≡**6j**) formed a mixture of *E*/*Z* adducts (entries 4 and 8 in Table 3). According to results of these studies, the random stereochemistry for the formation of **7j** and **7k** can be elucidated (entries 10 and 11 in Table 2).

The results provided in Table 3 can be explained in that enynes **6** are the key intermediates for the synthesis of dienynes **7**. Based on this information and literature processes, a putative mechanism for the generation of **7** can be formulated as shown in Scheme 2. Initially, σ-complex **13** is formed,[26] and subsequently coordinates and inserts alkyne to afford σ-complex **15** by "*syn*-palladaalkynylation" (catalytic cycle **I**).[27] Coupling adduct **6** is released after reductive elimination of complex **15**. However, enyne **6** has a higher affinity than alkyne **4** for complexes **11** and **13**, and makes catalytic cycle **II** more efficient. Reaction of enyne **6** with **13** forms η^2-complex **16**, which yields *E*-**7** by *syn*-palladaalkynylation and subsequent reductive elimination (**Path A**). Alternatively, Pd-complexed enyne **18** offers the possibility to produce *Z*-**7** by *anti*-hydroalkynylation (**Path B**). An alkynyl moiety in **12** or **13** and proton are concertedly or stepwisely transferred to **18** to give complex **19**. Dienyne *Z*-**7** is accessed after reductive elimination. In general, **Path B** is the main reaction route in this protocol and dienynes *Z*-**7** are obtained as the predominant products. A bulky phosphine ligand L, such as PCy_3, or an alkyne with a sterically congestive substituent, espe-



Scheme 2. Proposed mechanism for the formation of a dienyne **7**.

cially 2-ethynyltoluene (**4l**), perhaps makes complex **18** less favorable and enhances the formation of *E*-**7**. Moreover, the random appearance of the *E*/*Z* ratio of dienynes **7j** and **7k** perhaps arises from the interconversion process between complexes **17** and **19** *via* a stable species **20** (entries 10 and 11 in Table 2 and Scheme 2).

Thermal rearrangement of dienynes **7** does not follow the same reaction type that 1,3-hexadien-5-yne does.[28] When a mixture of *E*/*Z*-**7m** (ratio 57:43) was heated in DMSO at 180 °C for 12 h, 2-(1-naphthalenyl)-3-(1-naphthalenylethynyl)-1,2-dihydrophenanthrene (**21**; Figure 2) was generated in *ca.* 40% yield

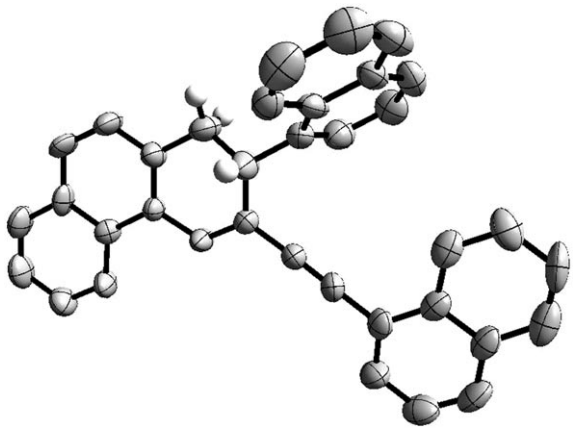
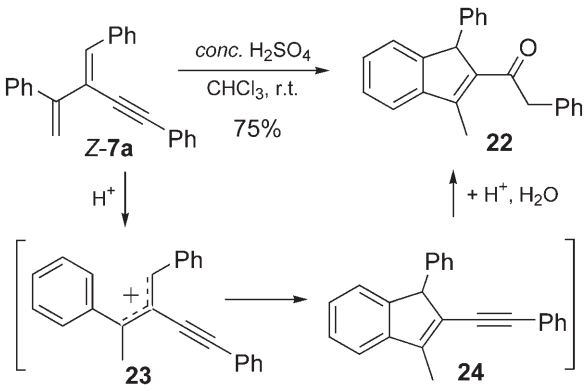


Figure 2. The molecular structure of **21** showing 50% probability ellipsoids (Diamond version 3.0). Hydrogen atoms except for 1- and 2-H have been omitted for clarity.[29]

(based on *E*-**7m**) and 91% of *Z*-**7m** was recovered. The structure of **21** has been analyzed by X-ray diffraction.[29] Compound **21** should be formed from *E*-**7m** by 6π-electrocyclization and subsequent 1,5-hydrogen shift.[30] Preparation of an indene derivative **22** is another synthetic application of dienynes **7** (Scheme 3). Under acidic conditions, *Z*-**7a** converts to



Scheme 3. Synthesis of indene **22** from dienyne *Z*-**7a** in acidic conditions.

allylic intermediate **23** and subsequently, the intramolecular cyclization makes compound **24** accessible. Further hydrolysis of the alkynyl moiety in **24** generates **22** with a more stable conjugated enone form.

Conclusions

We provide a new and simple procedure for generating trimerization adducts **7** from terminal arylalkynes **4** in one pot. This protocol indicates that enynes **6** are much more reactive than alkynes **4** towards hydroalkynylation to yield dienynes *Z*-**7**. The scope, limitations and regioselectivity for the formation of 2-ethynyl-1,3-butadiene **7** and **10** have been elucidated. Elaboration of this methodology and investigation of other catalytic applications in the construction of complex aromatic molecules and polymers are in progress.

Experimental Section

General Remarks

^{1}H and ^{13}C NMR: Bruker 300 (300 and 75.5 MHz). Multiplicities were determined by the DEPT (distortionless enhancement by polarization transfer) sequence. The symbol "+" is presented for CH or CH_3, and "−" for CH_2. MS: Bruker Daltonics Apex II30. X-ray crystal structure determination: The data were collected on a Stoe-Siemens-AED diffractometer. Melting points were determined with a Büchi melting point apparatus B545 and are uncorrected. Elemental analysis: Laboratory for elemental analyses at National Cheng Kung University. 1-Ethynyl-3,5-dimethoxybenzene (**4c**),[31] 1-ethynyl-3,5-dimethylbenzene (**4e**),[32] methyl 4-ethynylbenzoate (**4i**),[33] 9-ethynylanthracene (**4p**),[34] 1-phenyl-3-methylbut-3-en-1-yne (**9a**),[35] 2-phenyloct-1-en-3-yne (**9b**),[36] 1,3-diphenylbut-3-en-1-yne (**9c**),[14d] and 1,3-di(4-anisyl)but-3-en-1-yne (**9d**)[14d] were prepared according to or similar to published procedures. Other compounds, which are not mentioned in the experimental section, are commercially available.

General Procedure for the Preparation of Dienynes 7 (GP1)

To a solution of the respective terminal alkyne **4** (3.00 mmol) in a solvent mixture of NEt_3 (1.5 mL) and CH_3CN (2.5 mL) in a screw-capped Pyrex bottle $PdCl_2(PPh_3)_2$ (21.0 mg, 30.0 μmol), CuI (5.71 mg, 30.0 μmol) and PPh_3 (15.7 mg, 60.0 μmol) were added at ambient temperature. The reaction mixture was purged with nitrogen for 5 min. The sealed bottle was heated at 80 °C for *ca.* 48 h. After cooling to room temperature, the solvent was removed under reduced pressure, and the residue subjected to chromatography on silica gel (or alumina). Elution with hexane/CH_2Cl_2 afforded the coupling product **7**. ***Note:*** *Although compounds Z-***7** *are stable below 180 °C under an* N_2

atmosphere, they easily decompose on contact with air at room temperature.

General Procedure for the Preparation of Dienynes 10 (GP2)

To a solution of the respective terminal alkyne **4** (2.40 mmol) and enyne **9** (2.00 mmol) in a solvent mixture of NEt_3 (1.5 mL) and CH_3CN (2.5 mL) in a screw-capped Pyrex bottle $PdCl_2(PPh_3)_2$ (14.0 mg, 20.0 μmol), CuI (3.8 mg, 20.0 μmol) and PPh_3 (10.5 mg, 40 μmol) are added at ambient temperature. The reaction mixture is purged with nitrogen for 5 min. The sealed bottle is heated at 80 °C for 24 h. After cooling to room temperature, the solvent is removed under reduced pressure, and the residue is subjected to chromatography on silica gel (or alumina). Elution with hexane/CH_2Cl_2 affords the coupling product **10**. ***Note:*** *Compounds **10** easily decompose on contact with air at room temperature.*

Synthesis of 2-(1-Naphthalenyl)-3-(1-naphthalenylethynyl)-1,2-dihydrophenanthrene (21)

A mixture of *E*/*Z*-**7m** (119 mg; *E*:*Z* = 57:43) in DMSO (2.5 mL) was heated at 180 °C for 12 h. After cooling to room temperature, the solution was diluted with CH_2Cl_2 (50 mL), washed with H_2O (3 × 10 mL) and dried over $MgSO_4$. After removal of the solvent from the filtrate, the residue was subjected to SiO_2, eluting with hexane/CH_2Cl_2 (from 10:1 to 4:1) to afford 64 mg (40%, based on *E*-**7m**) of **21** and 43 mg (91%) of *Z*-**7m**.

Synthesis of 1-Methyl-3-phenyl-2-(2-phenyl-1-ethionyl)-2-indene (22)

To a solution of *Z*-**7a** (202 mg) in $CHCl_3$ (10 mL) at room temperature was dropwise added concentrated H_2SO_4 (1 mL) and stirred at the same temperature for 3.5 h. This reaction mixture was diluted with $CHCl_3$ (50 mL), washed with H_2O (3 × 10 mL) and dried over $MgSO_4$. After removal of the solvent of the filtrate, the residue was subjected to SiO_2, eluting with hexane/CH_2Cl_2 (from 5:1 to 1:1) to afford 162 mg (75%) of **22**.

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[20] Although it is well reported that copper(I) acetylides are important reagents or intermediates for preparations of alkynyl derivatives, σ-alkynyl Pd complexes generated from terminal arylalkynes and Pd(0) catalysts can also exhibit a similar function. There are several examples for copper-free alkyne homocouplings (ref.[8]), copper-free synthesis of enynes **6** (refs.[14d,e]) and the copper-free Sonogarshira reactions, see: a) H. Kawanami, K. Matsushima, M. Sato, Y. Ikushima, *Angew. Chem.* **2007**, *119*, 5221; *Angew. Chem. Int. Ed.* **2007**, *46*, 5129; b) P.-H. Li, L. Wang, *Adv. Synth. Catal.* **2006**, *348*, 681; c) C. Yi, R. Hua, *J. Org. Chem.* **2006**, *71*, 2535; d) Y. Liang, Y.-X. Xie, J.-H. Li, *J. Org. Chem.* **2006**, *71*, 379; e) J.-H. Li, Y. Liang, Y.-X. Xie, *J. Org. Chem.* **2005**, *70*, 4393; f) J.-H. Li, X.-D. Zhang, Y.-X. Xie, *Eur. J. Org. Chem.* **2005**, 4256; g) B. Liang, M. Dai, J. Chen, Z. Yang, *J. Org. Chem.* **2005**, *70*, 391; h) J. Cheng, Y. Sun, F. Wang, M. Guo, J.-H. Xu, Y. Pan, Z. Zhang, *J. Org. Chem.* **2004**, *69*, 5428; i) S. Urgaonkar, J. G. Verkade, *J. Org. Chem.* **2004**, *69*, 5752; j) A. Soheili, J. Albaneze-Walker, J. A. Murry, P. G. Dormer, D. L. Hughes, *Org. Lett.* **2003**, *5*, 4191; k) Y. Ma, C. Song, W. Jiang, Q. Wu, Y. Wang, X. Liu, M. B. Andrus, *Org. Lett.* **2003**, *5*, 3317; l) D. Méry, K. Heuzé, D. Astruc, *Chem. Commun.* **2003**, 1934; m) K. Heuzé, D. Méry, D. Gauss, D. Astruc, *Chem. Commun.* **2003**, 2274.

[21] Compound *Z*-**7d**: $C_{27}H_{24}$, monoclinic crystals of space group *C2/c*, unit cell dimensions: $a=18.673(3)$, $b=6.1099(9)$, $c=36.375(6)$ Å, $\alpha=90$, $\beta=100.215(3)$, $\gamma=90°$, $V=4084.2(10)$ Å^3, $Z=8$, Crystal size: $0.30\times0.23\times0.10$ mm^3. Compound *Z*-**7o**: $C_{48}H_{30}$, triclinic crystals of space group P_1, unit cell dimensions: $a=9.0868(18)$, $b=13.068(2)$, $c=15.152(3)$ Å, $\alpha=65.804(8)$, $\beta=80.282(8)$, $\gamma=85.118(8)°$, $V=1617.4(5)$ Å^3, $Z=2$, Crystal size: $0.10\times0.10\times0.04$ mm^3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. CCDC 672448 (*Z*-**7d**) and 671872 (*Z*-**7o**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif or on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44–1223–336033; E-mail: deposit@ccdc.cam.ac.uk].

[22] Small amounts of compounds *E*/*Z*-**7q** (R = *n*-Bu) could be prepared in accordance with our procedure. The ^{1}H NMR spectra of these two regioisomers are very similar to those of their analogues, (3*E*/3*Z*)-2-butyl-3-(1-hexynyl)deca-1,3-diene, see: M. Kim, R. L. Miller, D. Lee, *J. Am. Chem. Soc.* **2005**, *127*, 12818.

[23] In these control experiments, only the reaction products of type **10** were isolated and characterized. Self-dimerization and -trimerization adducts of alkynes **4** and traces of other regioisomers were also formed but neglected.

[24] When enyne **9c** was heated at 80 °C for 1 d in our catalytic system, a complex mixture was generated and only *ca.* 30% of the starting material was recovered.

[25] Product *Z*-**7a** is a stable species. It can be heated in 1,2-dichlorobenzene at 180 °C in an N_2 atmosphere for 1 d without obvious decomposition. Attempts at the preparation of a tetramer from the reaction of *Z*-**7a** and **4a** with our protocol were also not successful.

[26] Complex **13** can be directly formed from $PdCl_2(PPh_3)_2$ and **4**, or by the transmetallation from the corresponding copper(I) acetylide.

[27] The term "*syn*-palladaalkynylation" is based on the literature, see: ref.[14d]
[28] Dienynes *Z*-**7** can be formulated to have a skeleton of 1,3-hexadien-5-yne. It has been reported that 1,3-hexadien-5-yne can generate benzene *via* isobenzenediyne, see: H. Hopf, H. Berger, G. Zimmermann, U. Nüchter, P. G. Jones, I. Dix, *Angew. Chem.* **1997**, *109*, 1236; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1187.
[29] Compound **21** (CCDC 671873): $C_{36}H_{24}$, monoclinic crystals of space group $P2_1/n$, unit cell dimensions: $a=9.4820(17)$, $b=14.912(2)$, $c=17.501(2)$ Å, $\alpha=90$, $\beta=99.524(8)$, $\gamma=90°$, $V=2440.5(6)$ Å^3, $Z=4$, Crystal size: $0.12\times0.09\times0.05$ mm^3.
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