DOI: 10.1002/ange.200802560

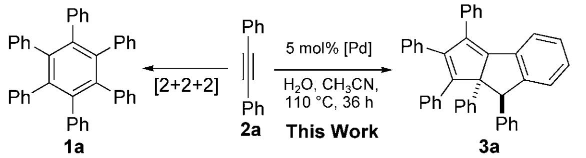
Polycycles

Synthesis, Structure, and Photophysical Properties of Highly Substituted 8,8a-Dihydrocyclopenta[*a*]indenes**

Yao-Ting Wu, Ming-Yu Kuo, Yu-Ting Chang, Chien-Chueh Shin, Tsun-Cheng Wu, Chia-Cheng Tai, Tzu-Heng Cheng, and Wei-Szu Liu*

Dedicated to Professor Armin de Meijere on the occasion of his 70th birthday

Alkynes are important building blocks and synthons for the construction of a variety of interesting and useful molecules.[1] Since the discovery of the formation of benzene from acetylene by Berthelot[2] and Reppe et al.,[3] this formal [2+2+2] cyclotrimerization has become an elegant method for the generation of benzene derivatives and polycyclic aromatic compounds, and several metal catalysts have been developed for this reaction.[4] We recently synthesized a new cycloadduct **3a**, which is formed from diphenylacetylene (**2a**) in the presence of a palladium catalyst (Scheme 1). To the best of our knowledge, this is the first example of a tricyclic [5.5.6]-fused skeleton generated by the trimerization of diarylalkynes.[5] Herein, we describe the systematic optimization of this reaction and the applicability of this method to several alkynes.



Scheme 1. Metal-catalyzed cyclotrimerizations of alkyne **2a**.

Exhaustive studies of the reaction conditions for the synthesis of cycloadduct **3a** from diphenylacetylene (**2a**) showed that the palladium catalyst, the organophosphine, water, benzoquinone (BQ), and $Cu(OAc)_2{\cdot}H_2O$ all play key roles in this reaction (Table 1). In the absence of any one of them, **3a** was only obtained in very low yield.

Table 1: Optimization of reaction conditions for the preparation of **3a**.[a]

Entry	Catalyst	Additives (equiv)	Base	Yield [%]
1	$Pd(OAc)_2$	PPh_3 (0.5)	K_2CO_3	32[b]
2	$Pd(OAc)_2$	PPh_3 (0.5)	K_2CO_3	4[c,d]
3	$Pd(OAc)_2$	PPh_3 (0.5)	K_2CO_3	0[c,e]
4	$Pd(OAc)_2$	–	K_2CO_3	3[c]
5	$Pd(OAc)_2$	PCy_3 (0.25)	K_2CO_3	32
6	$Pd(OAc)_2$	PCy_3 (0.5)	K_2CO_3	68
7	$Pd(OAc)_2$	PCy_3 (0.5)	K_2CO_3	13[c,f]
8	$Pd(OAc)_2$	PCy_3 (0.75)	K_2CO_3	67
9	$Pd(OAc)_2$	PCy_3 (0.5)	–	60
10	$Pd(OAc)_2$	PCy_3 (0.5)	Na_2CO_3	67
11	$Pd(OAc)_2$	PCy_3 (0.5)	NaOAc or NEt_3	5[c]
12	$[Pd(PPh_3)_4]$	PCy_3 (0.5)	K_2CO_3	67
13	Pd/C	PCy_3 (0.5)	K_2CO_3	23
14	$[PdCl_2(PCy_3)_2]$	PCy_3 (0.5)	K_2CO_3	56

[a] Reaction was carried out in a thick-walled sealable tube. The amounts of catalysts, oxidants, additives, and base are relative to alkyne **2a**. Pd catalyst (5 mol%), $Cu(OAc)_2{\cdot}H_2O$ (1.0 equiv), BQ (0.5 equiv), base (1.0 equiv), water, and CH_3CN were used in this reaction. [b] 1,2,3,4-Tetraphenylnaphthalene (16%) was also obtained. [c] Most of the alkyne **2a** remained. [d] In the absence of BQ. [e] In the absence of $Cu(OAc)_2{\cdot}H_2O$. [f] In the absence of water.

$Pd(OAc)_2$ and $[Pd(PPh_3)_4]$ were found to be the most efficient catalysts in this reaction. PCy_3 was determined to be the best reagent for the reaction; PPh_3 led not only to the desired product, but also to 1,2,3,4-tetraphenylnaphthalene.[6] It was necessary to use half an equivalent of PCy_3 to get the optimal yield (Table 1, entries 1, 5, 6, and 8). The use of a carbonate base slightly improved the yield of the reaction, whereas triethylamine or NaOAc inhibited the formation of **3a** (Table 1, entry 11). Under the optimized conditions, the desired product **3a** was obtained in 68% yield, along with trace amounts of by-product **1a** (Table 1, entry 6). Crystals of **3a**[7] were grown from CH_2Cl_2/MeOH, and the structure was determined by X-ray diffraction analysis. The phenyl groups at positions C8 and C8a in **3a** adopt a *trans* configuration and the torsional angle between the cyclopentadienyl and benzo planes is approximately 34°. The overcrowded and nonplanar structure causes this compound to exhibit unusual photophysical properties (see below).

The reactivity of several alkynes was examined under the optimized conditions (Table 2). Alkynes **2b**–**2m** underwent the cyclotrimerization to generate **3** in moderate to excellent yields (28–85%). The lowest yield was obtained for **3g**, which

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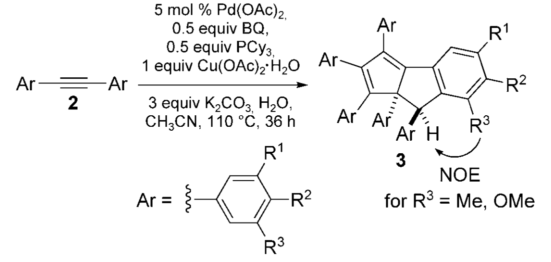
[*] Prof. Y.-T. Wu, Y.-T. Chang, C.-C. Shin, T.-C. Wu, C.-C. Tai, T.-H. Cheng
Department of Chemistry, National Cheng Kung University
No. 1 Ta-Hsueh Rd., 70101 Tainan (Taiwan)
Fax: (+886) 6274-0552
E-mail: ytwuchem@mail.ncku.edu.tw
Prof. M.-Y. Kuo, W.-S. Liu
Department of Applied Chemistry, National Chi Nan University
No. 1 University Rd., 54561 Puli, Nantou (Taiwan)

[**] Metal-Catalyzed Reactions of Alkynes. Part III. This work was supported by the Landmark Project of National Cheng Kung University and the National Science Council of Taiwan (NSC 96-2113M-006-008-MY2). We also thank Prof. S.-L. Wang and C.-Y. Chen (National Tsing Hua University, Taiwan) for the X-ray structure analyses. Part II: Y.-T. Wu, W.-C. Lin, C.-J. Liu, C.-Y. Wu, *Adv. Synth. Catal.* **2008**, *350*, 1841.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200802560.

Table 2: Preparation of tricyclic adducts **3** from alkynes **2**.

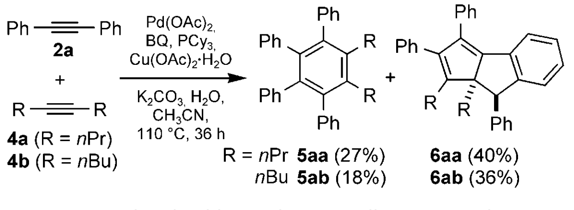


Entry	Alkyne	R^1	R^2	R^3	Product	**1**/**3**[a]	Yield [%][b]
1	**2a**	H	H	H	**3a**[c]	5:95	68
2	**2b**	H	Me	H	**3b**[c]	13:87	72
3	**2c**	H	CF$_3$	H	**3c**[c]	4:96	59
4	**2d**	H	F	H	**3d**[c]	11:89	77
5	**2e**	H	*t*Bu	H	**3e**[c]	5:95	40
6	**2f**	H	OMe	H	**3f**[c]	8:92	51
7	**2g**	H	CO$_2$Me	H	**3g**[d]	9:91	28[e]
8	**2h**	Me	H	H	**3h**[c]	6:94	78
9	**2i**	OMe	H	H	**3i**[c]	4:96	70
10	**2j**	Me	F	H	**3j**[c]	9:91	71
11	**2k**	Me	H	Me	**3k**[c]	8:92	65
12	**2l**	OMe	H	OMe	**3l**	0:100	85
13	**2m**	OMe	OMe	OMe	**3m**[d]	19:81	82

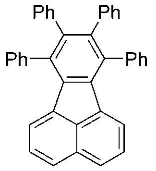
[a] The ratios were determined from the ^{1}H NMR spectra of the products, which were obtained after purification by simple chromatography. [b] The combined yields for isomers **1** and **3**. [c] Separation from **1** by crystallization from CH$_2$Cl$_2$/MeOH. [d] Separation from **1** by chromatography. [e] 30% **2g** was recovered.

was isolated together with 30% of the starting material (Table 2, entry 7). In general, by-products **1** were also produced in small amounts under these reaction conditions, but they can be removed by either careful chromatography or crystallization. The three 3,3′-disubstituted diarylethynes **2h**–**2j** furnished only one regioisomer (Table 2, entries 8–10).[8] The structures of **3h** and **3i** can be assigned on the basis of the crystal structures of **3j** and **3k**[7,9] and their 2D NMR spectra. It was also determined that sterically congested di(2-tolyl)-ethyne and heteroaryl acetylenes, such as di(2-thiophenyl)-ethyne and di(3-pyridinyl)ethyne, did not form the desired product under these conditions.[10]

The possibility of crossed cycloadditions between different alkynes was also investigated. The reaction of **2a** with dialkylalkynes **4** in our catalytic system produced cycloadducts **5** and **6** (Scheme 2).[11] Other tricyclic regioisomers of **6** were not observed in appreciable amounts. Unfortunately, a mixture of 1,8-bis(phenylethynyl)naphthalene and alkyne **2a** did not furnish the desired product, but 7,8,9,10-tetraphenylfluoranthene (**7**) was obtained in 65% yield.[12]



Scheme 2. Crossed cycloadditions between alkynes **2a** and **4**.



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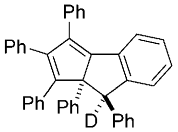
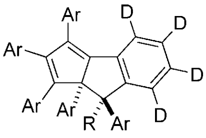


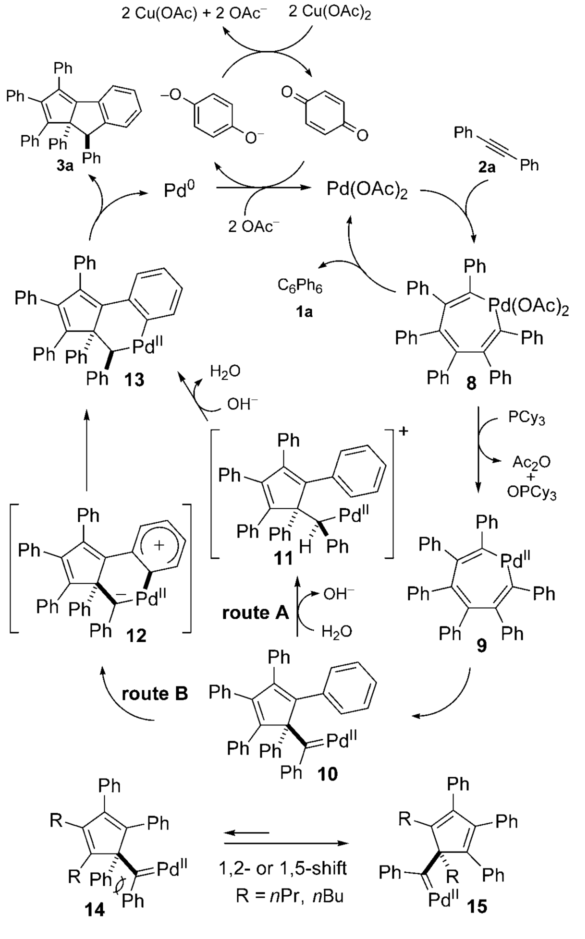
[D$_1$]-**3a**



Ar = C$_6$D$_5$
[D$_{29}$]-**3a** (R = H)
[D$_{30}$]-**3a** (R = D)

It was determined that cycloadduct **3a** is not generated from a rearrangement of hexaphenylbenzene (**1a**). When **1a** was heated in the presence of our catalytic system, it remained unchanged. Moreover, when a control experiment was carried out with deuterium oxide, instead of water, [D$_1$]-**3a** was obtained in 62% yield with 70% isotopic purity.[13,14] Further study of the reaction with [D$_{10}$]diphenylacetylene ([D$_{10}$]-**2a**) in water gave a mixture of [D$_{29}$]-**3a** and [D$_{30}$]-**3a** in a ratio of approximately 75:25.[15] These results indicate that the majority of the hydrogen atoms at position C8 in **3a** come from the external water, but some of them (ca. 25%) are provided by the phenyl ring in **2a** (see Scheme 3, route B).[16]

Based on literature precedent and the above control experiments, a proposed mechanism was formulated (Scheme 3). The reaction of an active Pd^{II} species with three molecules of alkyne **2a** generates 1-palladacycloheptatriene **8**,[17,18] which can either undergo a reductive elimination to form hexaphenylbenzene (**1a**)[19] or can be reduced to Pd^{II} complex **9** by PCy$_3$.[20] Intermediate **9** subsequently rearranges



Scheme 3. Proposed mechanism for the formation of cycloadduct **3a**.

to a Schrock-type carbene complex **10**,[21] in which the carbene metal atom is electrophilic and the carbene carbon atom is nucleophilic.[22] Protonation of the carbene carbon atom with water leads to the formation of σ-complex **11**,[23] which produces complex **13** by intramolecular electrophilic palladation[24] and subsequent deprotonation (route A). Alternatively, the carbene complex **10** could cyclize to yield the zwitterionic intermediate **12** (route B). An intramolecular proton shift or reaction with water would then furnish **13**. The steric repulsion in **12** or **13** can be minimized when the two phenyl groups adopt a *trans* configuration. Reductive elimination of **13** gives the desired product **3a** and a Pd^0 species. The active Pd^{II} complex can eventually be regenerated by oxidation with $Cu(OAc)_2{\cdot}H_2O$ and BQ.[25] However, the formation of **6** should occur via key intermediates **15**, which could be generated from **14** by a 1,2- or 1,5-shift, as is observed in other cyclopentadiene derivatives.[26] This rearrangement is likely promoted by the steric repulsion between the palladium–carbene moiety and the phenyl group at C5 in **14**.

Compound **3a** is virtually nonfluorescent in dichloromethane or THF, but is highly luminescent in the solid state (or crystal). To quantify this aggregation-induced emission,[27] a solution of **3a** (ca. 10^{-5} M) in a mixture of THF and water was excited at 372 nm.[11] A dramatic change in the fluorescence intensity and relative quantum yield (Φ) could be observed as the amount of water in the solution was increased (Figure 1). The Φ value of a solution of **3a** in THF/water (10/90, W90) is about 70 times higher than in pure THF (W0). Moreover, the size of the particles plays a key role in their luminescent properties. In a mixture of THF and water (ca. 1:2), **3a** aggregates to form spherical nanoparticles with a mean diameter of approximately 10–30 nm.[11] The aggregation of these molecules can efficiently inhibit the nonradiative vibration and rotation of phenyl groups, and thus enhance the luminescence.[27b] As with other compounds that exhibit aggregation-induced emission,[27k] **3a** could potentially be used as a sensor for detecting organic solvents.

In summary, we have developed a new and versatile synthetic method for the preparation of highly substituted 8,8a-dihydrocyclopenta[*a*]indenes **3** in one pot by the cyclotrimerization of diarylalkynes. Compound **3a** displays an aggregation-induced emission with a strong blue fluorescence. Further studies of the photophysical and electroluminescence properties of functionalized derivatives of **3** are currently underway, as these molecules may potentially find use as organic light-emitting diodes (OLEDs).[28]

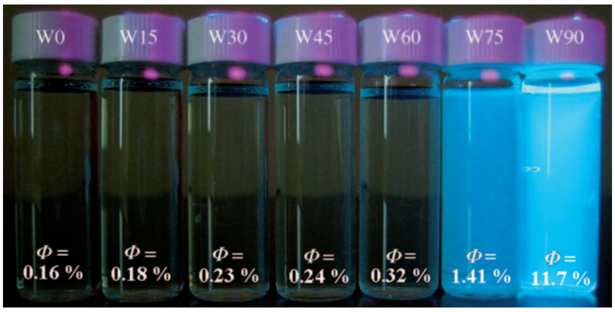


Figure 1. Aggregation-induced emission of **3a** (ca. 10^{-5} M) in a THF/water mixture under illumination with UV light (365 nm). Quantum yields of **3a** were investigated at an excitation wavelength of 372 nm, and quinine sulfate was used as the standard ($\Phi = 0.546$).[11]

Experimental Section

Preparation of **3a**: A mixture of alkyne **2a** (200 mg, 1.12 mmol), PCy_3 (157 mg, 0.56 mmol), $Cu(OAc)_2{\cdot}H_2O$ (224 mg, 1.12 mmol), benzoquinone (61.0 mg, 0.56 mmol), $Pd(OAc)_2$ (12.5 mg, 55.6 μmol), K_2CO_3 (155 mg, 1.12 mmol), H_2O (1 mL), and acetonitrile (3.5 mL) in a thick-walled pyrex tube was purged with nitrogen for 5 min. The sealed tube was kept in an oil bath at 110 °C for 36 h. After cooling the mixture to room temperature and filtration over celite, the solvent of the filtrate was removed under reduced pressure. The residue was subjected to chromatography on silica gel with hexane/CH_2Cl_2 (12:1) as the eluent to afford a mixture of **1a** and **3a** as a yellow solid (136 mg, 68 %, **1a**/**3a** = ca. 5:95). By-product **1a** could be removed by either crystallization from CH_2Cl_2/MeOH or precipitation from diethyl ether. A suitable crystal of **3a** (m.p. 194–195 °C) for X-ray diffraction analysis was grown from CH_2Cl_2/MeOH. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 5.15$ (s, 1 H), 6.66 (d, $^3J = 6.6$ Hz, 2 H), 6.81 (d, $^3J = 5.8$ Hz, 2 H), 6.86–6.90 (m, 3 H), 7.05–7.15 (m, 12 H), 7.21–7.26 (m, 7 H), 7.41 (d, $^3J = 7.0$ Hz, 2 H), 7.50 ppm (d, $^3J = 5.8$ Hz, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT): $\delta = 57.0$, 78.3, 122.2, 125.6, 126.2, 126.4, 126.5 × 2, 126.82, 126.83, 127.1 × 2, 127.3, 127.4, 127.6 × 2, 127.7, 128.0 × 4, 128.1 × 2, 128.2 × 2, 129.6 × 2, 129.7 × 2, 129.9 × 2, 135.2, 135.4, 135.7, 136.3, 140.3, 141.6, 142.4, 147.8, 148.7, 153.7, 157.5 ppm (one CH carbon atom cannot be observed because of signal overlap); EIMS (70 eV), *m/z* (%): 534 (100) [M^+]; HRMS (EI) calcd for $C_{42}H_{30}$: 534.2347; found: 534.2343. Elemental analysis calcd (%) for $C_{42}H_{30}$ (534.7): C 94.34, H 5.66; found: C 94.19, H 5.66.

Received: June 2, 2008
Revised: September 22, 2008
Published online: November 14, 2008

Keywords: aggregation · alkynes · cyclotrimerizations · fluorescence · palladium

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[7] **3a**: $C_{84}H_{62}$, monoclinic, space group $P2_1/c$, $a = 15.7618(17)$, $b = 16.6604(19)$, $c = 22.911(3)$ Å, $\alpha = \gamma = 90$, $\beta = 99.747(2)°$, $V = 5929.5(11)$ Å^3. **3j**·CH_3OH: $C_{49}H_{40}F_6O$, monoclinic, space group $P2_1/n$, $a = 18.2763(5)$, $b = 11.1214(4)$, $c = 21.3674(7)$ Å, $\alpha = \gamma = 90$, $\beta = 113.2580(10)°$, $V = 3990.2(2)$ Å^3. **3k**: $C_{54}H_{54}$, monoclinic, space group $C2/c$, $a = 22.8764(15)$, $b = 17.7788(11)$, $c = 22.9868(14)$ Å, $\alpha = \gamma = 90$, $\beta = 112.624(4)°$, $V = 8629.7(9)$ Å^3. CCDC 685514 (**3a**), 688340 (**3j**), and 685513 (**3k**) 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.

[8] A regioisomer of **3h** was also obtained in trace amounts. The ratio between **3h** and this regioisomer is approximately 95:5.

[9] According to the X-ray structure of **3k**, the distance between the hydrogen atom at position C8 and the hydrogen atom of the methyl group at position C7 is about 2.5–2.7 Å. NOE correlations between these two were observed.

[10] Di(2-naphthalyl)acetylene and bis(9,9-di-*n*-propyl-2-fluoryl)-acetylene can also generate corresponding cycloadducts **3**. Elucidation of their structures is in progress.

[11] See the Supporting Information.

[12] 7,8,9,10-Tetraphenylfluoranthene (**7**) can be efficiently synthesized from the same starting materials in the presence of the Wilkinson catalyst: Y.-T. Wu, T. Hayama, K. K. Baldridge, A. Linden, J. S. Siegel, *J. Am. Chem. Soc.* **2006**, *128*, 6870.

[13] A kinetic isotope effect was not observed in this reaction. The reaction of **2a** in a mixture of water and deuterium oxide (40:60) gave $[D_1]$-**3a** with an isotope purity of about 40%.

[14] Compound $[D_1]$-**3a** is not generated from **3a** by H/D exchange: Compound **3a** remained unchanged when heated with deuterium oxide in the presence of our catalytic system.

[15] In independent experiments, **3a** (10.055 mg; 18.81 μmol) and a mixture of $[D_{29}]$-**3a** and $[D_{30}]$-**3a** (15.093 mg; ca. 26.77 μmol) were dissolved in $CDCl_3$ (1.0 mL; tetramethylsilane was used as the internal standard) for ^1H NMR studies. The ratio of $[D_{29}]$-**3a** and $[D_{30}]$-**3a** can be obtained from the ^1H NMR spectra.

[16] It also explains that in the absence of water, **3a** was obtained in only 13% yield (Table 1, entry 7).

[17] Several Pd^{II} catalysts have been found to produce hexasubstituted benzenes **1** by [2+2+2] cyclotrimerzation of internal alkynes **2**. Palladacycloheptatrienes **8** should be the key intermediate in this reaction: a) Y.-S. Fu, S. J. Yu, *Angew. Chem.* **2001**, *113*, 451; *Angew. Chem. Int. Ed.* **2001**, *40*, 437; b) A. K. Jhingan, W. F. Maier, *J. Org. Chem.* **1987**, *52*, 1161;c) K. Ogura, T. Aizawa, K. Uchiyama, H. Iida, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 953; it has been shown that a Pd^{II}, not a Pd^0, species is the reactive form for the [2+2+2] cycloaddition: d) T. Yokota, Y. Sakurai, S. Sakaguchi, Y. Ishii, *Tetrahedron Lett.* **1997**, *38*, 3923.

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