Azulene Synthesis

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Azulenophenanthrenes from 2,2′-Di(arylethynyl)biphenyls through C−C Bond Cleavage of a Benzene Ring**

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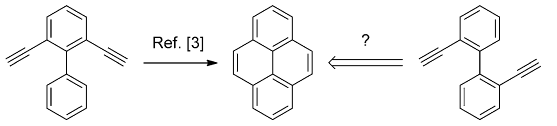
Dedicated to Professor Teruaki Mukaiyama

A diverse range of skeletal-rearrangement reactions catalyzed by π-acidic platinum and gold complexes have been developed over the last decade.[1] The π-acidic metals induce unique reorganization of organic frameworks, particularly those with alkyne moieties, to offer direct access to molecular structures that are difficult to construct by conventional synthetic methods.

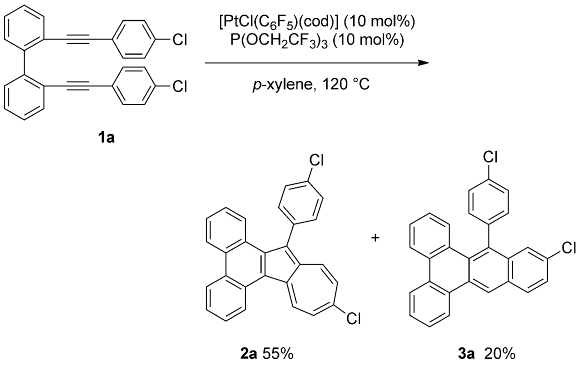
Fürstner and co-workers reported the synthesis of phenanthrenes by a platinum-catalyzed intramolecular hydroarylation reaction of 2-alkynylbiphenyls.[2] We applied their hydroarylation reaction to the synthesis of pyrenes (Scheme 1); 4,10-disubstituted pyrenes were successfully synthesized by the gold-catalyzed twofold hydroarylation reaction of 2,6-dialkynylbiphenyls.[3] A phenyl ring having two alkynyl substituents at the 2 and 6 positions forms two vinylene bridges with a pendant phenyl ring, in parallel, to construct a pyrene skeleton. We envisaged that 2,2′-dialkynylbiphenyl would be an alternative starting material for another related intramolecular twofold hydroarylation. A pyrene skeleton would result if each phenyl ring forms one vinylene bridge to the other phenyl ring.



Scheme 1. Pyrene synthesis through twofold hydroarylation of dialkynylbiphenyls.

This idea led us to examine a reaction of 2,2′-dialkynylbiphenyl, and a totally unexpected result was obtained. Herein, we report a platinum(II)-catalyzed skeletal rearrangement of 2,2′-di(arylethynyl)biphenyls that results in the construction of an azulenophenanthrene framework. The seven-membered ring of the azulene unit in the product is constructed through dearomatization of the six-membered benzene ring and subsequent electrocyclic C−C bond cleavage.

When 2,2′-bis[(4-chlorophenyl)ethynyl]biphenyl (**1a**) was heated at 120 °C in *p*-xylene for 12 h in the presence of a platinum(II) catalyst generated in situ from [PtCl(C_6F_5)(cod)] (10 mol%) and P(OCH_2CF_3)$_3$ (10 mol%), two polycyclic aromatic compounds were formed in 75% combined yield in a ratio of 73:27 [Eq. (1); cod = cycloocta-1,5-diene]. They were separated by chromatography and their ^1H NMR spectra were unlike those expected for a symmetrical pyrene, instead they were suggestive of unsymmetrical structures. The minor product was benzo[*f*]tetraphene **3a**, which could be regarded as an intramolecular dehydro-Diels–Alder product (see below).[4,5] On the other hand, the structural elucidation of the major product necessitated a single-crystal X-ray analysis, which proved it to be azuleno[1,2-*l*]phenanthrene **2a** (Figure 1).[6] Thus, one phenyl ring of **1a** had been expanded into a seven-membered ring.[7]



(1)

We propose the pathways depicted in Schemes 2 and 3 as plausible mechanistic scenarios for the formation of **2a** and **3a** from **1a**. Initially, an alkyne moiety acts as a π-base, coordinating to the π-acidic Pt^{II} center to induce 6-*exo-dig* cyclization involving the other alkyne moiety. The resulting vinylic cation **A** is then attacked intramolecularly by the 4-chlorophenyl ring at two sites. Attack at the *ipso*-carbon atom forms the spirocyclic intermediate **B**, leading to the major

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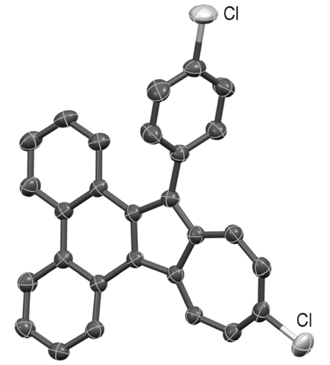
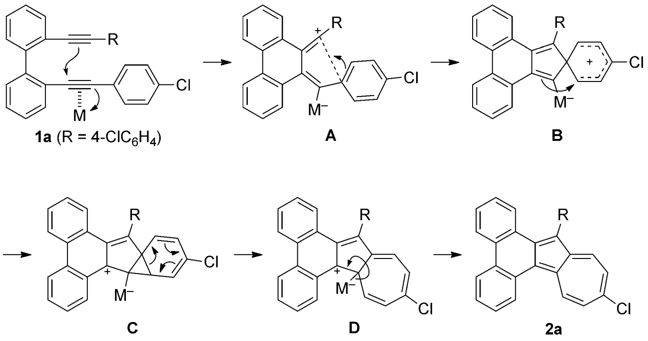
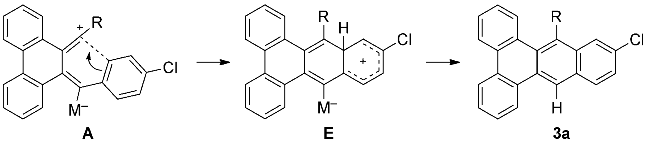


Figure 1. X-ray crystal structure of **2a** (thermal ellipsoids at 50% probability, hydrogen atoms are omitted for clarity).



Scheme 2. Mechanism for the formation of azuleno-[1,2 *L*]phenanthrene **2a** from **1a** ($M = Pt^{II}$).

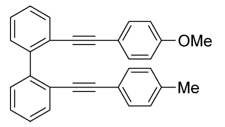


Scheme 3. Mechanism for the formation of benzo[*f*]tetraphene **3a**.

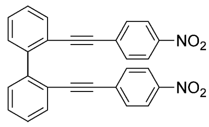
product **2a** (Scheme 2), and attack at the *ortho*-carbon atom gives intermediate **E**, leading to the minor product **3a** (Scheme 3). The spirocyclic structure of **B** consists of a platinum-substituted cyclopentadinenyl moiety and a pendant cyclohexadienyl cation moiety. The former subsequently attacks the latter to generate the cationic norcaradiene intermediate **C**, which is relatively stable because its cationic center is a tertiary one next to phenyl, vinyl, and cyclopropyl groups. The six-membered ring of the norcaradiene opens through the Cope rearrangement to afford cycloheptatriene **D**.[8,9] Finally, demetalation establishes aromaticity to give the azulene skeleton. On the other hand, the intermediate **E** simply rearomatizes with demetalation to give the dehydro-Diels–Alder adduct **3a** as the minor product.

Of note is the contrast observed in the reaction patterns of 2,6-dialkynylbiphenyl and 2,2′-dialkynylbiphenyl. Whereas the two alkynyl substituents of 2,6-dialkynylbiphenyl are located on the opposite sides of the biphenyl backbone and react independently with the backbone, the two alkynyl substituents of 2,2′-dialkynylbiphenyl are located close enough to react with each other without participation of the backbone.

Other 2,2′-di(arylethynyl)biphenyls **1b–g** were subjected to the reorganization reaction (Table 1). The phenylethynyl derivative **1b** and (4-methoxyphenyl)ethynyl derivative **1c** gave azulenophenanthrenes **2** and benzotetraphenes **3** in 75% and 84% combined yields, respectively, with the azulenophenanthrenes predominating (entries 1 and 2). It was possible to lower the catalyst loading to 1 mol% without any decrease in yield in the reaction of **1c** (entry 3). Analogous results were obtained when $P[OCH(CF_3)_2]_3$ and tricyclohexylphosphane were used instead of $P(OCH_2CF_3)_3$ as the ligand of platinum (entries 4 and 5) and when [(*t*BuXPhos)AuNTf$_2$] was used as the catalyst (entry 6). However, $PtCl_2$ alone gave an inferior result to the [PtCl(C_6F_5)(cod)]/$P(OCH_2CF_3)_3$ catalyst (entry 7). The reactions of 2- and 3-methoxyphenylethynyl derivatives (**1d** and **1e**, respectively) were also examined. Whereas in the reaction of **1d** the azulenophenanthrene **2d** was favored in preference to benzotetraphene **3d** (entry 8), the reaction of **1e** gave no azulenophenanthrene but an almost 1:1 mixture of isomeric benzotetraphenes (entry 9). In the cases of diynes **1f**, having six methoxy groups, and **1g**, having sterically demanding 1-naphthyl groups, the corresponding azulenophenanthrenes **2f** and **2g** were exclusively produced without formation of benzotetraphenes **3** (entries 10 and 11). We prepared the diyne **1h**, which was unsymmetrically disubstituted with methoxy and methyl groups and diyne **1i** substituted with two nitro groups, and they were subjected to the standard reaction conditions. The π-basicities of the two arylethynyl groups of **1h** were similar, therefore a complex mixture consisting of two isomeric azulenophenanthrenes and two isomeric benzotetraphenes resulted. The diyne **1i** failed to react and remained intact, thus supporting the involvement of cationic intermediates in the mechanism.

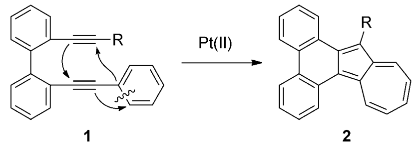


1h



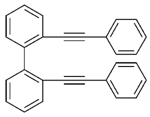
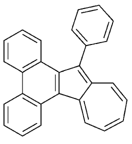
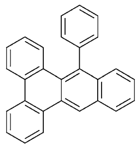
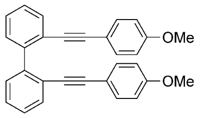
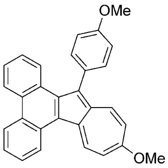
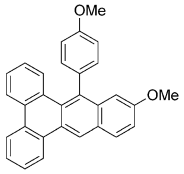
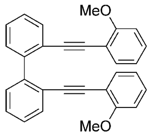
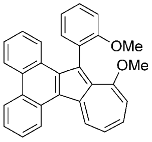
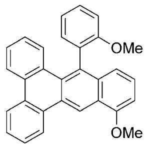
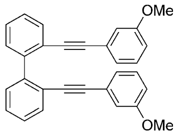
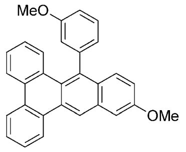
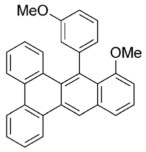
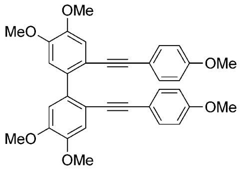
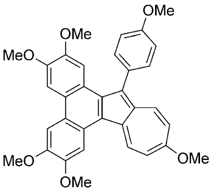
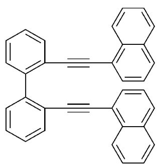
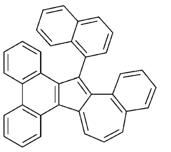
1i

In summary, a new skeletal rearrangement reaction of 2,2′-di(arylethynyl)biphenyls is reported. An azulene skeleton was formed by structural reorganization between the ethyne and arylethyne moieties. Its formal depiction is presented in Equation (2). The σ bond between the *ipso*-carbon and the *ortho*-carbon atoms of the phenyl ring is cleaved and σ-bond between the *ortho*-carbon atom and the adjacent sp-hybridized carbon atom is reformed. As a result,



(2)

Table 1: Platinum-catalyzed reaction of 2,2′-di(arylethynyl)biphenyls **1**.[a]

Entry	1	Conditions	2 (Yield [%])[b]	3 (Yield [%])[b]
				
1	**1b**	10 mol% $[PtCl(C_6F_5)(cod)]$ 10 mol% $P(OCH_2CF_3)_3$	**2b** (45)	**3b** (30)
				
2	**1c**	10 mol% $[PtCl(C_6F_5)(cod)]$ 10 mol% $P(OCH_2CF_3)_3$	**2c** (71)	**3c** (13)
3	**1c**	1 mol% $[PtCl(C_6F_5)(cod)]$ 1 mol% $P(OCH_2CF_3)_3$	**2c** (80)	**3c** (10)
4	**1c**	10 mol% $[PtCl(C_6F_5)(cod)]$ 10 mol% $P(OCH(CF_3)_2)_3$	**2c** (67)	**3c** (trace)
5	**1c**	10 mol% $[PtCl(C_6F_5)(cod)]$ 10 mol% P(*c*-Hex)$_3$	**2c** (70)	**3c** (10)
6	**1c**	20 mol% [(*t*BuXPhos)AuNTf$_2$]	**2c** (61)	**3c** (trace)
7	**1c**	10 mol% $PtCl_2$	**2c** (34)	–
				
8	**1d**	10 mol% $[PtCl(C_6F_5)(cod)]$ 10 mol% $P(OCH(CF_3)_2)_3$	**2d** (62)	**3d** (14)
				 + 
9	**1e**	10 mol% $[PtCl(C_6F_5)(cod)]$ 10 mol% $P(OCH(CF_3)_2)_3$		**3e** + **3′e** (76; ca. 1:1)
				
10	**1f**	10 mol% $[PtCl(C_6F_5)(cod)]$ 10 mol% $P(OCH_2CF_3)_3$	**2f** (62)	
				
11	**1g**	10 mol% $[PtCl(C_6F_5)(cod)]$ 10 mol% $P(OCH_2CF_3)_3$	**2g** (78)	

[a] The reaction was performed in *p*-xylene at 120 °C for 12 h. [b] Yield of the isolated product. *t*BuXPhos = 2-di-*tert*-butylphosphino-2′,4′,6′-triisopropylbiphenyl.

the six-membered ring is expanded into a seven-membered ring.

During the present process, a highly stable C–C bond of the six-membered aromatic ring is cleaved with expansion into a seven-membered ring.[9] Transition-metal-catalyzed reactions involving cleavage of C–C bonds have attracted considerable attention during the last decade.[10] Generally, a particular driving force, such as release of small-ring strain or aromatization, is required because the thermodynamically stable σ bond is to be finally transformed into a more stable form. The present reaction involving cleavage of a phenyl ring adds an exotic example to the repertoire of metal-catalyzed cleavage of C–C bonds.

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