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Regioselective Haloaromatization of 1,2-Bis(ethynyl)benzene via Halogen Acids and $PtCl_2$. Platinum-Catalyzed 6-π Electrocyclization of 1,2-Bis(1′-haloethenyl)benzene Intermediates

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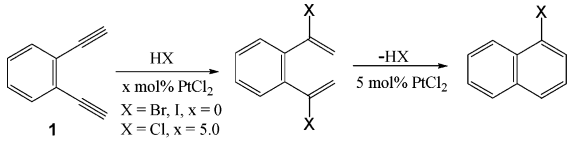

X =Cl (**2-Cl**), Br (**2-Br**), I (**2-I**) X =Cl (**3-Cl**), Br (**3-Br**), I (**3-I**)

Treatment of 1,2-bis(ethynyl)benzene (**1**) with aqueous HX (X = Br, I) in hot 3-pentanone (100−105 °C, 2 h) afforded 1,2-bis(1′-haloethenyl)benzene species **2-Br** and **2-I** in 98% and 95% yields, respectively. The hydrochlorination of endiyne **1** failed to proceed at elevated temperature but was implemented efficiently by $PtCl_2$ (5 mol %) in hot 3-pentanone (100 °C, 2 h) to give 1,2-bis(1′-chloroethenyl)benzene **2-Cl** in 80% yield. In the presence of $PtCl_2$ (5 mol %), these halides **2-Cl**, **2-Br,** and **2-I** were subsequently converted to 1-halonaphthalenes **3-Cl**, **3-Br,** and **3-I** in the mother solution via sequential 6-π electrocyclization and dehalogenation reactions. $PtCl_2$ (5 mol %) also effected direct haloaromatization of endiyne **1** with HX (X = Cl, Br, I) and gave 1-halonaphthalenes **3-Cl**, **3-Br**, and **3-I** in 64−71% yields. This investigation reports the scope and the regioselectivity of haloaromatization of various enediynes catalyzed by $PtCl_2$.

Introduction

Bergman aromatization of enediynes[1] has attracted considerable attention because of its perspective applications in materials and medicinal chemistry.[2,3] Although cyclization of unfunctionalized enediynes has been attempted with various approaches, including diradical pathways,[1b,4] electrophilic additions,[5a−c] and radical cations,[5d] these reactions only gave benzene or fulvene products of special types. In contrast, the aromatization of enediynes via nucleophilic addition (anionic Bergman cyclization) is more useful because organic functionality can be introduced onto aromatic products via suitable nucleophiles.[6,7] A widespread application of this method suffers from its limited scope: the reaction requires either anionic nucleophiles, such as sodium methoxide and thiophenoxide, or strained enediynes. The ruthenium-catalyzed cyclization of enediynes with nucleophiles that we recently reported proceeded highly regioselectively[8] and was compatible with a wide range of nucleophiles including water, alcohols, aniline, pyrrole, acetylacetone,

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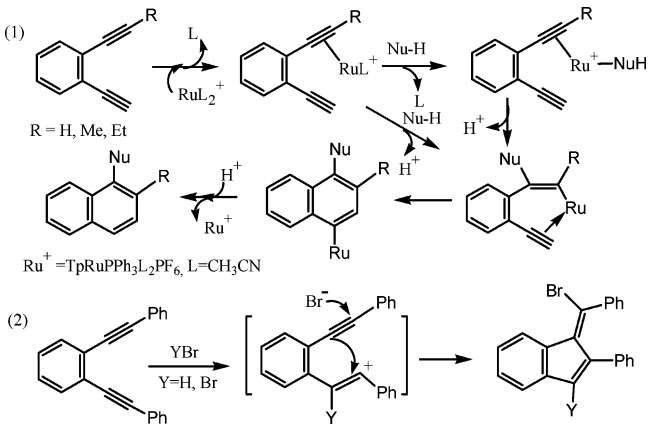
SCHEME 1



and dimethyl malonate (Scheme 1. eq 1). The mechanism of this aromatization has been elucidated to involve ruthenium-π-alkyne intermediates.[8] Unfortunately, this catalytic cyclization failed to work with hydrohalogenation (NuH = HCl, HBr, HI) to give desired 1-halonaphthalenes, which are important building blocks in many synthetic applications. In this study, we report the first realization of this catalytic process using $PtCl_2$ catalyst, and the mechanism proceeds via a distinct pathway from those shown in Scheme 1 (eq 1). Prior to this study, haloaromatization of enediyne was shown to give fulvene products via a postulated vinyl cation intermediate (Scheme 1, eq 2).[5a−5c]

Results and Discussion

Heating a mixture of enediyne **1** (1.0 equiv) and HI (1.0−2.0 equiv) with $TpRuPPh_3(CH_3CN)_2PF_6$ (10 mol %) catalyst in hot 3-pentanone (100−105 °C, 2 h) led to polymerization and 1,2-bis(1′-iodoethenyl)benzene **2-I** in 12% yield.[8] We found that treatment of enediyne **1** with aqueous HI (2 equiv) in hot 3-pentanone alone (2 h) afforded vinyl iodide species **2-I** in 95% yield (Scheme 2, entry 1). The yield of product **2-I** remained at 91% for a prolonged period (24 h). A similar hydrobromination occurs for enediyne **1** with HBr under similar conditions (entry 2). In contrast, the hydrochlorination reaction was unattainable through heating **1** with HCl (2 equiv) alone in hot 3-pentanone (entry 3); it was achieved efficiently with $PtCl_2$ catalyst[9] (3 mol %, entry 4) in a short period (100 °C, 2 h) to give **2-Cl** in 80% yield. Heating pure 1,2-divinylbenzenes **2-Cl**, **2-Br,** and **2-I** in hot 3-pentanone (100 °C, 24 h) or 1,4-xylene (150 °C, 36 h) did not lead to 6-π-electrocyclization reaction[10] (entries 5−6), consistent with literature reports.[11] Thermal 6-π-electrocyclization of 1,2-divinylbenzenes to 1,2-dihydronaphthalenes normally proceeds at elevated temperatures (250−300 °C).[11] We were pleased to find that $PtCl_2$ (10 mol %) species effected the aromatization of 1,2-divinylbenzenes **2-Br** and **2-I** and gave 1-halonaphthalene **3-Br** and **3-I** in 46−56% yields (entries 7 and 8), whereas unreacted **2-Br** and **2-I** were recovered in 23% yields. In these two cases, species **2-Br** and **2-I** were generated in situ from endiyne **1** and HX (X = Br, I) according to the operations in entries 1 and 2, and $PtCl_2$ catalyst was subsequently added to the same solution. Naphthalenes **3-Cl**, **3-Br,** and **3-I** were produced more efficiently (64−71%) from simultaneous treatment of of diyne **1**, aqueous HX (2.0 equiv), and $PtCl_2$ catalyst (10 mol %) in hot 3-pentanone, and the reaction period is considerably shorter (entries 9−11). In the iodoaromatization of species **1**, 1,2-divinylbenzene **2-I** was confirmed to be the reaction intermediate and isolated in 26% yield in a short period (100 °C, 1 h). Notably, $PtCl_2$ catalyst (10 mol %) failed to catalyze haloaromatization of isolated and pure **2-Cl**, **2-Br,** and **2-I** alone in hot 3-pentanone even at a prolonged period (100 °C, 24 h). Based on these observations, we conclude that the $PtCl_2$ complex serves as precursors for generation of unknown active platinum species. Such an active platinum catalyst has dual roles in catalytic activities: acceleration of the hydrohalogenation of diynes to generate 1,2-bis(1′-halovinyl)benzene intermediates and the subsequent catalytic 6-π-electrocyclization of these 1,2-bis(1′-halovinyl)benzene species.

The preceding platinum-catalyzed cyclization of 1,2-bis(ethynyl)benzene **1** with HX (entries 10−12, Scheme 2) comprises consecutive hydrohalogenation and aromatization reactions. According to the same approach, Scheme 3 shows the cyclization efficiency of 1,2-bis(ethynylbenzene) (**1**) with HI-catalyzed by various metal chloride salts (10 mol %) including $RuCl_3$, $PdCl_2$, $PdCl_2(PhCN)_2$, $IrCl_3$, $RhCl_3$, and $AuCl_3$, and only $RuCl_3$ showed low activity for such a cyclization to give 2-iodonaphalene **3-I** in 24% yield in addition to the 1,2-divinylbenzene intermediate **2-I** (53%, entry 1). The remaining metal catalysts gave only hydroiodonation product **2-I** (70−78% yields) exclusively (entries 2−6).

We prepared various 1,2-bis(ethynyl)benzenes **5**−**7** to study the generality of this cyclization. The catalytic reactions were performed via treatment of species **5**−**7** with aqueous HX (2.0 equiv) and $PtCl_2$ (10 mol %) in hot 3-pentanone (100 °C, 2−10 h). As shown in Table 1, diynes **1** and **2** bearing an electron-rich benzene are very suitable for this haloaromatization, and their 1-chloro- and 1-bromonaphthalene products **8-Cl**, **8-Br**, **9-Cl**, and **9-Br** were obtained with yields as high as 81−92%. Although the iodination reaction has a shorter period (2 h, entries 3 and 6), 1-iodonaphthalenes **8-I** and **9-I** were obtained in lower yields (63−64%). This catalytic reaction is less efficient with 4,5-difluoro-1,2-bis(ethynyl)benzene **7**, and the its cyclized products **10-Cl**, **Br**, and **I** were obtained only in 32−45% yields.

(7) For the cyclization of strained enediynes with anionic nucleophiles, the enediynes actually underwent traditional Bergman or Saito−Myers diradical processes after attack of anionic nucleophiles. For examples, see: (a) Nicolaou, K. C.; Dai, W. M. *Angew. Chem., Int. Ed. Engl*. **1991**, *30*, 1387 and references therein. (b) Hirama, M.; Fujiwara, K.; Shigematsu, K.; Fukazara, Y. *J. Am. Chem. Soc*. **1989**, *111*, 4120. (c) Wender, P. A.; Hartmata, M.; Jefferey, D.; Mukai, C.; Suffert, J. *Tetrahedron Lett.* **1988**, *29*, 909. (d) Bekele, T.; Brunette, S. R.; Lipton, M. A. *J. Org. Chem*. **2003**, *68*, 8741.

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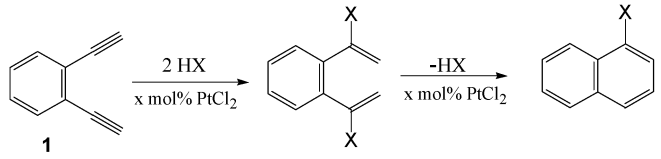
SCHEME 2[a]

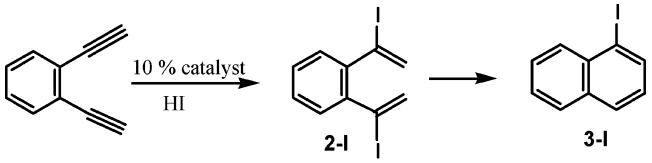


X =Cl (**2**-Cl), Br (**2**-Br), I (**2**-I) X =Cl (**3**-Cl), Br (**3**-Br), I (**3**-I)

entries	substrates	HX[a]	x mol% ($PtCl_2$)	solvents	temp (h)[b]	products (yields)[c]
1	**1**	HI	0	3-pentanone	100 ^{0}C (2 h, 24 h)	**2-I** (95%, 91%)
2	**1**	HBr	0	3-pentanone	100 ^{0}C (1.5 h)	**2-Br** (98%)
3	**1**	HCl	0	3-pentanone	100 ^{0}C (8 h)	N. R.
4	**1**	HCl	3	3-pentanone	100 ^{0}C (2 h)	**2-Cl** (80%)
5	**2Cl-2I**	—	0	3-pentanone	100 ^{0}C (24 h)	N. R.
6	**2Cl-2I**	—	0	1,4-xylene	150 ^{0}C (36 h)	N. R.
7	**2Br**[d]	—	10	3-pentanone	100 ^{0}C (12 h)	**3-Br** (56%), **2-Br** (23%)
8	**2I**[d]	—	10	3-pentanone	100 ^{0}C (16h)	**3-I** (46%), **2-I** (23%)
9	**1**	HCl	10	3-pentanone	100 ^{0}C (6 h)	**3-Cl** (65%)
10	**1**	HBr	10	3-pentanone	100 ^{0}C (4 h)	**3-Br** (71%)
11	**1**	HI	10	3-pentanone	100 ^{0}C (4 h)	**3-I** (64%)
12	**1**	HI	10	3-pentanone	100 ^{0}C (1 h)	**3-I** (48%), **2-I** (26%)
13	**2Cl-2I**[e]	—	10	3-pentanone	100 ^{0}C (2h)	N. R.

[a] 2.1 equiv of HX (X = Cl, 37 wt %; Br, 48 wt %; I, 52 wt %). [b] 3-Pentanone, [substrate] = 0.45 M. [c] Yields shown are after separation from a silica column. [d] **2-Cl,Br,I** were generated in situ from **1** and HX according to entries 1, 2, and 4. [e] Pure **2-Cl,Br,I** were used after purification.,

SCHEME 3[a]

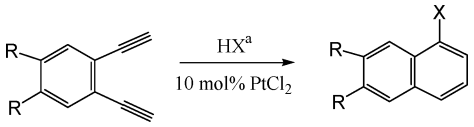


entries	catalysts[a]	solvents	products (yields)[b]
1	$RuCl_3$	3-pentanone	**2-I** (53%), **3-I** (24%)
2	$PdCl_2$	3-pentanone	**2-I** (78%)
3	$PdCl_2(PhCN)_2$	3-pentanone	**2-I** (70%)
4	$IrCl_3$	3-pentanone	**2-I** (72%)
5	$RhCl_3$	3-pentanone	**2-I** (75%)
6	$AuCl_3$	3-pentanone	**2-I** (70%)

[a] 10 mol % catalyst, [substrate] = 0.25 M, 3-pentanone, 100 °C, 24 h. [b] Yields are given after separation from a silica column.

We extended this haloaromatization to various 1,2-bis(ethynyl)benzenes **11**−**14** bearing two unequivalent terminal alkynes. The regioselectivity of the reaction is varied as noted in Table 1. For 4-methyl-1,2-bis(ethynyl)benzene **11**, only the bromo derivative **15-Br** showed mild regioselectivity (**A/B** = 76/24). The structure of **15-Br(A)** was confirmed by ^{1}H-NOE spectra.[12] In contrast, the $PtCl_2$ (10 mol %)-catalyzed aromatization of 4-methoxy-1,2-bis(ethynyl)benzene **12** with HX (X = Cl, Br, I) produced only one regioisomer and gave cyclized products **16-Cl(A)**, **16-Br(A)**, and **16-I(A)** in 65−83% yields. In such a cyclization, the halide adds selectively to the C(1′)-ethynyl carbon para to the oxygen atom. The structure assignment of **16-Br(A)** and **16-I(A)** is made on the basis

TABLE 1. Hydrohalogenation of 1,2-Bis(ethynyl)benzenes

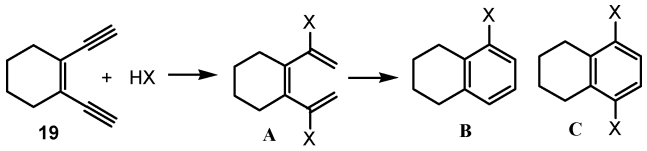


entries	substrates	HX	time (h)	products (yields, %)
1	R,R = −OCH_2O− (**5**)	HCl	6	**8-Cl** (86)
2	**5**	HBr	4	**8-Br** (81)
3	**5**	HI	2	**8-I** (63)
4	R = OMe (**6**)	HCl	6	**9-Cl** (92)
5	**6**	HBr	4	**9-Br** (88)
6	**6**	HI	2	**9-I** (64)
7	R = F (**7**)	HCl	10	**10-Cl** (45)
8	**7**	HBr	8	**10-Br** (48)
9	**7**	HI	4	**10-I** (32)

[a] 2.1 equiv of HX (X = Cl, 37 wt %; Br, 48 wt %; I, 52 wt %). [b] 3-pentanone, [substrate] = 0.45 M. [c] Yields shown are after separation from a silica column.

(12) The ^{1}H-NOE map of compounds **15-Br(A)**, **16-Br(A)**, **16-I(A)**, **18-Cl(A)**, **18-Br(A)**, and **18-I(B)** is provided in the Supporting Information.

SCHEME 4[a]



entries	HXa	$PtCl_2$	time[a]	products (yields)[b]
1	HCl	—	8 h	**20-Cl** (**B**) 54%
2	HBr	—	8 h	**20-Br** (**B**) 51%
3	HI	—	1 h	**20-I** (**B**) 46%, **20-I** (**A**) 33%
4	HI	—	8 h	**20-I** (**B**) 75%
5	HCl	5 mol%	3 h	**20-Cl** (**B**) 52%
6	HBr	5 mol%	2 h	**20-Br** (**B**) 48%
7	HI	5 mol%	1 h	**20-I** (**B**) 3%, **20-I** (**C**) 73%

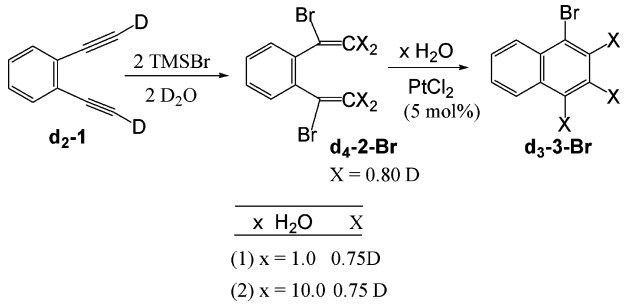
[a] 2.1 equiv of HX (X = Cl, 37 wt %; Br, 48 wt %; I, 52 wt %). [b] 3-Pentanone (100 °C), [substrate] = 0.45 M. [c] Yields shown are after separation from a silica column.

of its proton NOE effect.[12] A high regioselectivity is also maintained for the cyclization of 2,3-bis(ethynyl)benzo-[*b*]furan **13** and its thiophene analogue **14**, but the structures of their resulting products **17-Cl**, **Br**, **I** and **18-Cl**, **Br**, **I** (74−85% yields) depend on the type of halogen substituents: the chloro- and bromo groups of **17-Cl(A)**, **17-Br(A)**, **18-Cl(A)**, and **18-Br(A)** are located at the C(1)-carbon, whereas the iodo groups of **17-I(B)** and **18-I(B)** are placed at the C(4)-carbon. The ^{1}H NMR patterns of **17-I(B)** and **18-I(B)** were very distinct from those of **17-Cl(A)**, **17-Br(A)**, **18-Cl(A)**, and **18-Br(A)**. Structural assignment of these dibenzofuran and dibenzothiophene products is made on the basis of the proton NOE effect of the representative derivatives **18-Cl(A)**, **18-Br(A)**, and **18-I(B)**.[13]

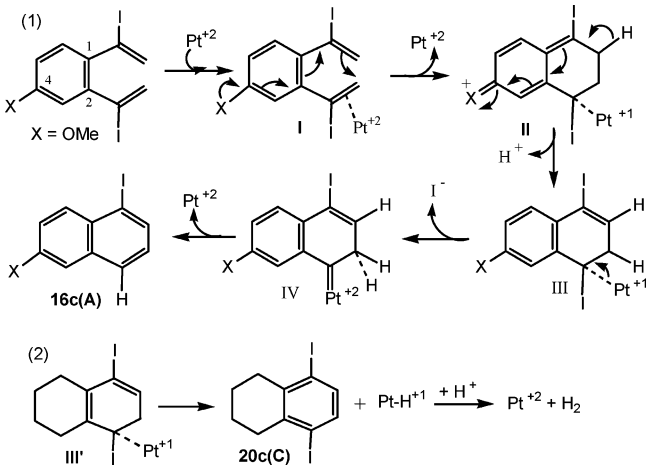
Scheme 4 shows the haloaromatization of acyclic enediyne **19** in the presence or absence of $PtCl_2$ catalyst (entries 1−4). In contrast with preceding 1,2-bis(ethynyl)-benzenes, haloaromatization of this enediyne proceeded smoothly in hot 3-pentanone in the absence of $PtCl_2$ catalyst, and the 1,2-divinyl species **20-I(A)** was evidently the reaction intermediate because it was isolated in 33% yield at a short reaction period (1 h, entry 3). The 6-π electrocyclization of intermediates **20-Cl**, **-Br**, and **-I(A)** avoids the dearomatization process, and it can proceed with 100 °C. In the presence of $PtCl_2$ (5 mol %), the same cyclized products **20-Cl(B)** and **20-Br(B)** were obtained after brief duration of reaction (2−3 h, entries 5 and 6). Notably, we obtained 1,4-diiodobenzene **20-I(C)** (73%) exclusively from the platinum-catalyzed cyclization of enediyne **19** with HI, whereas the expected iodobenzene **20-I(B)** was obtained in only 3% yield.

We performed deuterium-labeling experiments to characterize the reaction mechanism. As shown in Scheme 5, the bis(1-bromovinyl)benzene species $\mathbf{d_4}$**-2-Br** was first generated by treatment of diyne $\mathbf{d_2}$**-1** with Me_3SiBr and D_2O (2.0 equiv), and the deuterium content of species $\mathbf{d_4}$**-2** is estimated to be 0.80 D. In acidic medium, the proton exchange between 3-pentanone and water at 100 °C may account for such an incomplete deuterium content (X = 0.80 D) of species $\mathbf{d_4}$**-2**. This species was subsequently converted to 1-bromonaphthalene $\mathbf{d_3}$**-3-Br** with $PtCl_2$ (5 mol %) and H_2O in various proportions. The resulting 1-bromonaphthalene $\mathbf{d_3}$**-3-Br** contains a 0.75 deuterium content equally at the C_2−C_4-carbons (X = 0.75 D); such a deuterium distribution remained unchanged with increasing proportion of external H_2O present in hot 3-pentanone.

SCHEME 5

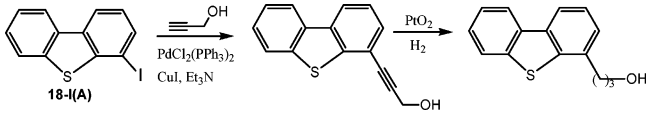


SCHEME 6



Scheme 6 shows a plausible mechanism to account for the platinum-catalyzed 6-π-electrocyclization of 1,2-bis-(1-iodovinyl)benzene, which is the key step in the haloaromatization of 1,2-bis(ethynyl)benzenes. This proposed mechanism rationalize the regioselective halogenation of 1,2-bis(ethynyl)benzene **12** bearing a methoxy group. $PtCl_2$ serves as a precursor for generation of unknown active platinum species. We propose that this active Pt^{2+} species coordinates with the C(2)-vinyl group as the methoxy activates the C(1) olefin group[14] to facilitate an intramolecular cyclization. This mechanism resembles that of the Pd(II)-catalyzed Cope rearrangement of acyclic 1,5-diene.[15] This cyclization is expected to give species **II** bearing a platinum cyclohexyl moiety, and a subsequent loss of proton leads to formation of aromatic species **III**. To account for the deuterium-labeling experiment, we propose a loss of iodide anion of intermediate **III** to

(13) The alcohol derivative of species **18-I(A)** was prepared according to the synthetic scheme shown below. The ^{1}H-NOE map of this alcohol is provided in the Supporting Information.



(14) (a) Bastian, G.; Royer, R.; Cavier, R. *Eur. J. Med. Chem.* **1983**, *18*, 365. (b) Kaluza, F.; Perold, G. *Chem. Ber.* **1955**, *88*, 597.

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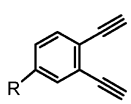
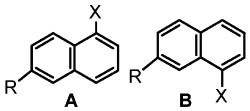
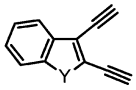
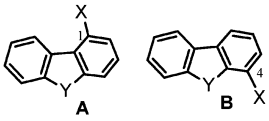
TABLE 2. Regioselectivity in the Hydrohalogenation of 4-Substituted 1,2-Bis(ethynyl)benzenes

substrates	HX[a]	time[b]	products (yields)[c]
			 A B
(1) R = Me (**11**)	HCl	11 h	82% (**15-Cl, A/B**=66/34)
(2) **11**	HBr	8 h	82% (**15-Br**, **A/B**=76/24)
(3) **11**	HI	2 h	65% (**15-I, A/B**=50/50)
(4) R = OMe (**12**)	HCl	6 h	83% (**16-Cl, A**)
(5) **12**	HBr	4 h	82% (**16-Br**, **A**)
(6) **12**	HI	2 h	65% (**16-I, A**)
			 A B
(7) Y = O (**13**)	HCl	9 h	78% (**17-Cl, A**)
(8) **13**	HBr	3 h	80% (**17-Br**, **A**)
(9) **13**	HI	1 h	74% (**17-I, B**)
(10) Y = S (**14**)	HCl	12 h	77% (**18-Cl, A**)
(11) **14**	HBr	3 h	85% (**18-Br**, **A**)
(12) **14**	HI	1 h	80% (**18-I, B**)

[a] 2.1 equiv of HX (X = Cl, 37 wt %; Br, 48 wt %; I, 52 wt %). [b] PtCl2 (10 mol %), 3-pentanone, 100 °C, [substrate] = 0.40 M. [c] Yields shown are after separation from a silica column.

form platinum carbene intermediate **IV**, which ultimately gives the observed 1-iodonaphthalene product **16-I(A)** (Table 2, entry 6) through a 1,2-hydrogen shift.[16] To account for the doubly iodinated product **20-I(C)** given from enediyne **19**, we propose that the corresponding intermediate **III′** undergoes β-hydrogen elimination to give the desired product and $(Pt-H)^{+1}$ species, which finally regenerates Pt^{2+} and H_2 in the presence of proton. The halide-dependent regioselectivity for dibenzofurans **17-Cl(A)**, **Br(A)**, and **17-I(B)** and dibenzothiophene **18-Cl(A)**, **Br(A)**, and **18-I(B)** is somewhat surprising, particularly for the formation of **17-I(B)** and **18-I(B)** in which the iodo group was located at the C_4-carbon. Species **17-I(B)** and **18-I(B)** represent two exceptions to the proposed mechanism in Scheme 6, and their formation mechanism was unclear at this stage.

In summary, we have reported platinum-catalyzed hydrohalogenation of 1,2-bis(ethynyl)benzenes that gives 1-halonaphthalene products efficiently. This cyclization proceeds via platinum-catalyzed 6-π electrocyclization of 1,2-bis(1′-haloethenyl)benzene intermediates, and such a mechanism is distinct from that for our previous ruthenium-catalyzed aromatization of enediynes with nucleophiles.[8] $PtCl_2$ serves as a precursor for generation of unknown active platinum species. On the basis of deuterium-labeling experiments, we propose a mechanism for the platinum-catalyzed 6-π electrocyclization of 1,2-bis(1′-haloethenyl)benzene intermediates.

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Experimental Section

General Procedures. Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere in oven-dried glassware using standard syringe, cannula, and septa apparatus. Benzene, diethyl ether, tetrahydrofuran, and hexane were dried with sodium benzophenone and distilled before use. The diyne substrates **1**, **5**−**7**, and **11**−**14** were prepared according to the procedures described in the literature.[8]

Standard Procedure for Preparation of 1,2-Bis(1′-bromoethenyl)benzene (2-Br). To a 3-pentanone solution (1.0 mL) of 1,2-bis(1′-ethenyl)benzene **1** (100 mg, 0.79 mmol) was added aqueous HBr (48 wt %, 0.19 mL), and the mixture was heated at 100 °C for 1.5 h. The solution was concentrated, extracted with ether, and washed with water. The ether extract was dried over $MgSO_4$, and eluted through a silica column to give product **2-Br** as a yellow oil (223 mg, 0.78 mmol, 98%).

Synthesis of 1,2-Bis(1′-chloroethenyl)benzene (2-Cl). To a 3-pentanone solution (1.0 mL) of 1,2-bis(1′-ethenyl)-benzene (100 mg, 0.79 mmol) (**1**) were added aqueous HCl (37 wt %, 0.14 mL) and $PtCl_2$ (10.5 mg, 0.04 mmol), and the mixture was heated at 100 °C for 2 h. The solution was concentrated, extracted with diethyl ether, and washed with water. The ether extract was dried over $MgSO_4$ and eluted through a silica column to give 1,2-bis(1′-chloroethenyl)-benzene (126 mg, 0.63 mmol, 80%) (**2-Cl**) as a yellow oil.

Catalytic Transformation of 1,2-Bis(1′-ethenyl)benzene (1) to 1-Iodonaphthalene (3-I). To a 3-pentanone solution (1.0 mL) of 1,2-bis(1′-ethenyl)benzene (100 mg, 0.79 mmol) (**1**) were added aqueous HI (52 wt %, 0.41 mL) and $PtCl_2$ (21 mg, 0.079 mmol), and the mixture was heated at 100 °C for 4 h. The solution was concentrated, extracted with diethyl ether, and washed with water. The ether extract was dried over $MgSO_4$ and eluted through a silica column to give 1-iodonaphthalene **3-I** (129 mg, 0.50 mmol).

Spectral Data for 1,2-Bis(1′-chloroethenyl)benzene (2-Cl). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.44 (s, 2H), 5.55 (s, 2H), 7.31−7.33 (m, 2H), 7.39−7.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 122.0, 127.4, 128.6, 129.6, 138.5. HRMS: calcd for $C_{10}H_8Cl_2$ 198.0003, found 198.0001.

Spectral Data for 1,2-Bis(1′-bromoethenyl)benzene (2-Br). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.90∼5.93 (m, 4H), 7.31−7.33 (m, 2H), 7.39−7.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 122.0, 127.4, 128.6, 129.6, 138.5. HRMS: calcd for $C_{10}H_8Br_2$ 285.8993, found 285.8995.

Spectral Data for 1,2-Bis(1′-iodoethenyl)benzene (2-I). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.22 (dd, J = 4.4, 1.2 Hz, 4H), 7.23−7.25 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 102.4, 128.2, 129.5, 131.3, 140.8. HRMS: calcd for $C_{10}H_8I_2$ 381.8715, found 381.8718.

Spectral Data for 1-Chloronaphthalene (3-Cl). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 (t, J = 7.6 Hz, 1H), 7.48−7.60 (m, 3H), 7.75 (d, J = 8.2 Hz, 1H), 7.85 (d, J = 8.2 Hz, 1H), 8.26 (d, J = 8.2 Hz, 1H) ^{13}C NMR (150 MHz, $CDCl_3$): δ 124.4, 125.7, 126.1, 126.6, 127.0, 127.1, 128.2, 130.8, 131.9, 134.5. HRMS: calcd for $C_{10}H_7Cl$ 162.0236, found 162.0235.

Spectral Data for 1-Bromonaphthalene (3-Br). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (t, J = 8.0 Hz, 1H), 7.52 (t, J = 8.0, 1H), 7.58 (t, J = 8.0 Hz, 1H), 7.76−7.83 (m, 3 H), 8.23 (d, J = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 122.8, 126.1, 126.6, 127.0, 127.3, 127.9, 128.2, 129.8, 131.9, 134.6. HRMS: calcd for $C_{10}H_7Br$ 205.9731, found 205.9731.

Spectral Data for 1-Iodonaphthalene (3-I). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.17 (t, J = 7.8 Hz, 1H), 7.50 (t, J = 7.8 Hz, 1H), 7.57 (t, J = 7.8 Hz, 1H), 7.76 (d, J = 8.2 Hz, 1H),

7.82 (d, J = 8.2 Hz, 1H), 8.07∼8.09 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 99.5, 126.6,126.8, 127.6, 128.5, 128.9, 132.0, 134.0, 134.2, 137.3. HRMS: calcd for $C_{10}H_7I$ 253.9592, found 253.9595.

Acknowledgment. We thank the National Science Council, Taiwan, for supporting this work.

Supporting Information Available: NMR spectra and spectral data of compounds **1**, **2-(Cl−I)** , **3(Cl−I)**, **5**−**7**, **8(Cl−I)**, **9(Cl−I)**, **10(Cl−I)**, **11**−**14**, **15(Cl−I)**, **16(Cl−I)**, **17(Cl−I)**, **18(Cl−I)**, **19**, and **20-I**. This material is available free of charge via the Internet at http://pubs.acs.org.

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