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Platinum-Catalyzed Chemoselectively Hydrative Dimerization of 2-Alkynyl-1-acetylbenzenes for One-Pot Facile Synthesis of Chrysene Derivatives

Arindam Das, Hsuan-Hung Liao, and Rai-Shung Liu*

Department of Chemistry, National Tsing-Hua University, Hsinchu, Taiwan, ROC

rsliu@mx.nthu.edu.tw

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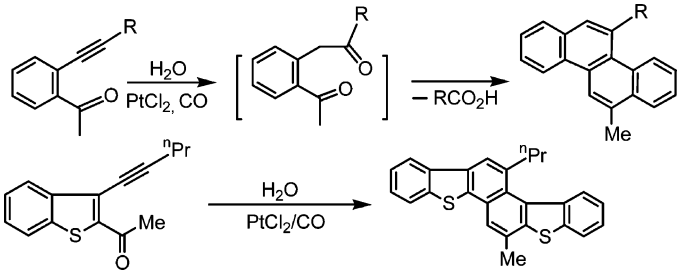
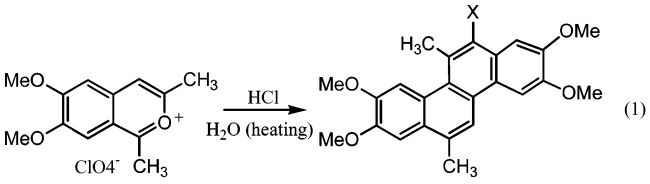


We report one-pot syntheses of chrysene compounds via $PtCl_2$-catalyzed hydrative dimerization of readily available 2-alkynyl-1-acetylbenzenes. This new tandem catalysis comprises an initial selective hydration of the alkyne, followed by chemoselective dimerization of diketone intermediates. The mechanism of this cyclization has been elucidated by ^{13}C labeling experiments as well as isolation of reaction intermediates.

Introduction

One advance in contemporary catalytic science is to achieve one-pot syntheses of complex molecules through metal-catalyzed multicomponent coupling reactions.[1,2] Such reactions are typically accompanied by tandem cyclizations to form two or three rings sequentially. This synthetic approach has found widespread applications in synthetic organic chemistry,[3,4] but less impact on material chemistry. Chrysene derivatives represent polycyclic aromatic hydrocarbons of one important class, which exhibit good hole[5] and electron transport capabilities.[6] Such compounds can also serve as blue emitters in organic electroluminescent devices because of their high fluorescence quantum efficiency.[7] Published procedures for the synthesis of chrysene derivatives[8] are based exclusively on naphthalenes bearing special functional groups,[9] which generally require a tedious synthetic procedure. Kuznetsov et al. reported[10] that treatment of benzopyrylium salt **I** with HCl gave a mixture of the chrysene products **II** (22%) and **III** (30%) as depicted in eq 1.



I X = H (**II**, 22%), X = COR (**III**, 30%) (1)

Unfortunately, the chrysene syntheses were only reported for the related species of 6,7-dimethoxybenzopyrylium **I**. The difficult preparation[11] of general benzopyrylium salts and the lack of chemoselectivity limit the extensive application of this method for chrysene synthesis. In this investigation, we report one-pot syntheses of chrysene compounds via Pt(II)-catalyzed

(1) For general reviews, see: (a) Ho, T.-L. *Tactics of Organic Synthesis*; Wiley-Interscience: New York, 1994; p 79. (b) Tietze, L. F. *Chem. Rev.* **1996**, *96*, 115. (c) Winkler, J. D. *Chem. Rev.* **1996**, *96*, 167. (d) Denmark, S. E.; Thorarensen, A. *Chem. Rev.* **1996**, *96*, 137.

(2) For selected examples, see: (a) de Meijere, A.; von Zezschwitz, P.; Brase, S. *Acc. Chem. Res.* **2005**, *38*, 413. (b) Kamijo, S.; Jin, T.; Huo, Z.; Yamamoto, Y. *J. Am. Chem. Soc.* **2003**, *125*, 7786. (c) Patel, S. J.; Jamison, T. F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1364. (d) Yoshida, H.; Fukushima, H.; Ohshita, J.; Kunai, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 3935. (e) Tamaru, Y.; Yasui, K.; Takanabe, H.; Tanaka, S.; Fugami, K. *Angew. Chem., Int. Ed.* **1992**, *31*, 645. (f) Yoshida, M.; Fujita, M.; Ishii, T.; Ihara, M. *J. Am. Chem. Soc.* **2003**, *125*, 4874. (g) Varela, J. A.; Rubin, S. G.; Gonzalez-Rodriguez, C.; Castedo, L.; Saa, C. *J. Am. Chem. Soc.* **2006**, *128*, 9262.

(3) For selected reviews, see: (a) Overman, L. E.; Abelman, M. M.; Kucera, D. J.; Tran, V. D.; Ricca, D. J. *Pure Appl. Chem.* **1992**, *64*, 1813. (b) Grigg, R. *J. Heterocycl. Chem.* **1994**, *31*, 631. (c) de Meijere, A.; Meyer, P. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2379. (d) Nie, Y.; Niah, W.; Jaenicke, S.; Chuah, G. K. *J. Catal.* **2007**, *248*, 1. (e) Ray, D.; Ray, J. K. *Org. Lett.* **2007**, *9*, 191. (f) Quinn, K. J.; Isaacs, A. K.; Arvary, R. A. *Org. Lett.* **2004**, *6*, 4143.

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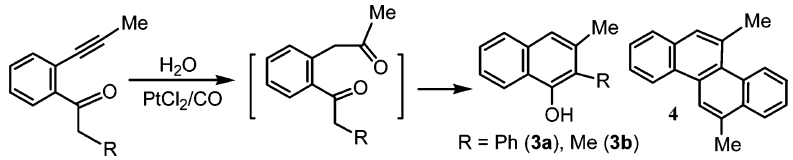
SCHEME 1 [a]



substrates	condition[a]	products[b]	substrates	condition[a]	products[b]
(1) **1a**	100 ^{0}C (5 h)	**3a** (82%)	(4) **1c**	100 ^{0}C (1 h)	**1c**(23%), **2c** (48%) **4** (13%)
(2) **1b**	100 ^{0}C (5 h)	**3b** (85%)	(5) **2c**	100 ^{0}C (10 h)	**4** (81%, 38%[c])
(3) **1c**	100 ^{0}C (12 h)	**4** (78%)	(6) **1c**	100 ^{0}C (12 h)	**2c** (65%[d])

[a] Conditions: 10 mol% of $PtCl_2$, 1,4-dioxane, H_2O (6 equiv), [substrate] = 0.80−1.0 M. [b]Yields of products are given after separation using a silica column. [c]The reaction was run in dry 1,4-dioxane as solvent. [d]This reaction was run in wet 1,2-dioxane in the presence of 2,6-lutidine (20 mol %).

hydrative dimerization of readily available 2-alkynyl-1-acetylbenzenes. This reaction sequence comprises an initial alkyne hydration, followed by a chemoselective dimerization of the resulting diketone intermediates.

Results and Discussions

We reported[12] the synthesis of 2-naphthanols **3a** via $PtCl_2$/CO-catalyzed hydrative cyclization of 1-carbonyl-2-(prop-1-yn-1-yl)benzene **1a**; the intermediate was proposed to derive from diketone species **2a** through selective alkyne hydration[13] as depicted in Scheme 1 (entry 1). When this cyclization was extended to two alkyl ketone analogues **1b** and **1c** (R = Me, Et), herein, we found that the corresponding cyclization of species **1c** proceeded distinctly from that of species **1a** and **1b**, giving chrysene **4** in 78% yield; the molecular structure of compound **4** is unambiguously determined by an X-ray diffraction study.[14] Entries 4 and 5 affirm the intermediacy of diketone species **2c** because it was isolable from the reaction at a short reaction time and was subsequently convertible to chrysene **4** efficiently by $PtCl_2$/CO[15] in wet 1,4-dioxane. Water is crucial for the efficient transformation of diketone species **2c** into product **4** (entry 5); the corresponding yield decreased to 38% in dry 1,4-dioxane. In the presence of 2,6-lutidine (20 mol %), treatment of species **1a** with $PtCl_2$ gave only diketone **2c** in 65% yield (entry 6). The value of this chrysene synthesis is manifested by readily available starting material **1a**, prepared from commercially available 2-bromoacetophenone via a single coupling reaction (Supporting Information).

Table 1 shows the activity screening of common π-acids for hydrative dimerization of 2-prop-1-yn-1-yl-1-acetylbenzene **1c**. In the absence of CO, $PtCl_2$ alone gave a diminished yield (58%, entry 2) of chrysene **4** because of the decreased catalyst electrophilicity compared to $PtCl_2$/CO catalyst, whereas AgOTf, HOTf, HCl, and $Zn(OTf)_2$ were less efficient for the production of chrysene **4** with 15−42% yields (entries 3−6). Gold catalysts,

(4) For selected examples, see: (a) Trost, B. M.; Shi, Y. *J. Am. Chem. Soc.* **1991**, *113*, 701. (b) Overman, L. E.; Ricca, D. J.; Tran, V. D. *J. Am. Chem. Soc.* **1993**, *115*, 2042. (c) Trost, B. M.; Shen, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 2313. (d) Trost, B. M.; Calkins, T. L.; Bochet, C. G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2632. (e) Vorogushin, A. V.; Wulff, W. D.; Hansen, H.-J. *J. Am. Chem. Soc.* **2002**, *124*, 6512.

(5) Masakazu, F. Eur. Patent Application EP 1 561 794 A1.

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(8) For chrysene synthesis, see refs 9 and: (a) Clar, E. *Polycyclic Hydrocarbons*; Academic Press: New York, 1964. (b) Wood, C. S.; Mallory, F. B. *J. Org. Chem.* **1964**, *29*, 3373. (c) Lee-Ruff, E.; Hopkinson, A. C.; Dao, L. H. *Can. J. Chem.* **1981**, *59*, 1675. (d) Gore, P. H.; Kamonah, F. S. *Synthesis* **1978**, 773. (e) Davies, W; Wilmshurst, J. R. *J. Chem. Soc.* **1961**, 4079. (f) Corbett, T. G.; Porter, Q. N. *Aust. J. Chem.* **1965**, *18*, 1781. (g) Levy, L. A.; Sashikumar, V. P. *J. Org. Chem.* **1985**, *50*, 1760.

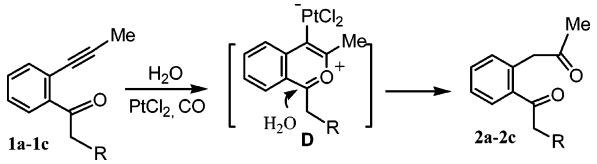
(9) For chrysene synthesis using functionalized naphthalenes, see: (a) Fonken, G. F. *Chem. Ind.* (*London*) **1962**, 1327. (b) LeHoullier, C. S.; Gribble, G. W. *J. Org. Chem.* **1983**, *48*, 1682. (c) Blackburn, E. V.; Loader, C. E.; Timmons, C. J. *J. Chem. Soc.* **1970**, 163. (d) Leznof, C. C.; Hayward, R. J. *Can. J. Chem.* **1972**, *50*, 528. (e) Leznof, C. C.; Hayward, R. J. *Can. J. Chem.* **1970**, *48*, 1842. (f) Carruthers, W.; Evans, N.; Pooranamoorthy, R. *J. Chem. Soc.* **1973**, 144. (g) Casagrande, M.; Gennari, G.; Cauzzo, G. *Gazz. Chim. Ital.* **1974**, *104*, 1251. (h) Masetti, F.; Bartocci, G.; Galiazzo, G. *Gazz. Chim. Ital.* **1975**, *105*, 419. (i) Nagel, D. L.; Kupper, R.; Antonson, K.; Wallcave, L. *J. Org. Chem.* **1977**, *42*, 3626. (j) Harvey, R. G. *Tetrahedron Lett.* **1988**, *29*, 3885. (k) Lyle, T. A.; Daub, G. H. *J. Org. Chem.* **1979**, *44*, 4933.

(10) Discussion of the formation mechanism of acylchrysene III will be provided in Supporting Information; for related Kuznetsov's papers, see: (a) Korobka, Kuznetsov, E. V. *Khim. Geterotsikl. Soedin.* **1982**, 1184. (b) Korobka, I. V.; Voloshina, A. I.; Kuznetsov, E. V. *Khim. Geterotsikl. Soedin.* **1984**, 1472. (c) Korobka, I. V.; Revinskii, Yu. V.; Kuznetsov, E. V. *Khim. Geterotsikl. Soedin.* **1985**, 910.

(11) For synthesis of benzopyrylium salt, see the review paper: Kuznetsov, E. V.; Shcherbakova, I. V.; Balaban, A. T. *Adv. Heterocycl. Chem.* **1990**, *50*, 157−254.

(12) Chang, H.-K.; Datta, S.; Das, A.; Odedra, A.; Liu, R.-S. *Angew. Chem., Int. Ed.* **2007**, *46*, 4744.

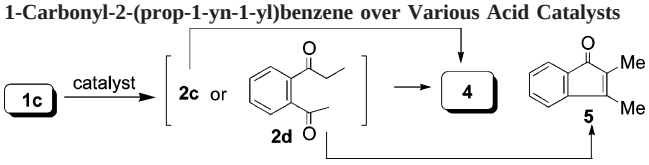
(13) In our preceding paper,[12] the selective hydration of 1-carbonyl-2-(prop-1-yn-1-yl)benzenes **1a**−**1c** to diketone species **2a**−**2c** proceeded via formation of intermediate **D**.



(14) The crystallographic data for compounds **4** and **11** were provided in Supporting Information.

(15) In the presence of CO, $PtCl_2$ was thought to form $PtCl_2(CO)_n$ which showed better electrophilicity for alkyne; see: (a) Fürstner, A.; Davies, P. W.; Gress, T. *J. Am. Chem. Soc.* **2005**, *127*, 8244. (b) Fürstner, A.; Davies, P. W. *J. Am. Chem. Soc.* **2005**, *127*, 15024. (c) Fürstner, A.; Aissa, C. *J. Am. Chem. Soc.* **2006**, *128*, 6306. (d) Taduri, B. P.; Ran, Y.-F.; Huang, C.-W.; Liu, R.-S. *Org. Lett.* **2006**, *8*, 883. (e) Lo, C.-Y.; Lin, C.-C.; Cheng, H.-M.; Liu, R.-S. *Org. Lett.* **2006**, *8*, 3153.

TABLE 1. Catalytic Dimerization of 1-Carbonyl-2-(prop-1-yn-1-yl)benzene over Various Acid Catalysts



entry	substrate[a]	catalyst	time (h)	products (yields)[b,c]
1	**1c**	10 mol % of $PtCl_2$/CO	12	**4** (78%)
2	**1c**	10 mol % of $PtCl_2$	12	**4** (58%)
3	**1c**	10 mol % of Ag(OTf)	15	**4** (42%)
4	**1c**	10 mol % of HOTf	8	**4** (32%), **5** (49%)
5	**1c**	10 mol % of HCl	12	**4** (15%), **5** (65%)
6	**1c**	10 mol % of $Zn(OTf)_2$	15	**4** (26%)
7	**1c**	5 mol % of PPh_3AuCl 5 mol % of AgOTf	13	**4** (3%), **5** (46%)
8	**1c**	5 mol % of AuCl	13	**4** (8%), **5** (51%)
9	**1c**	5 mol % of $AuCl_3$	13	**4** (2%), **5** (62%)
10	**2c**	5 mol % of AuCl	14	**4** (39%)
11	**2c**	5 mol % of $AuCl_3$	14	**4** (34%)
12	**2c**	10 mol % of $Zn(OTf)_2$	12	**4** (36%)
13	**2c**	10 mol % of HOTf	14	**4** (43%)

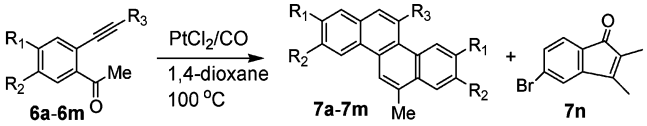
[a] At 100 °C, 1,4-dioxane, H_2O (6 equiv), [substrate] = 0.80−1.0 M. [b] Yields of products are given after separation using a silica column. [c] Starting substrates were completely consumed for entries 1−11.

including AuCl, $AuCl_3$, and PPh_3AuOTf, gave preferably the undesired 2,3-dimethylindenone **5**, via aldol condensation of another diketone intermediate **2d** (entries 7−9). We screened also the catalyst activity on the hydrative dimerization of the diketone species **2c** in wet 1,4-dioxane because it is the crucial step for this chrysene synthesis. The results in entries 10−13 reveal nevertheless that AuCl, $AuCl_3$, AgOTf, and HOTf were inefficient for this chrysene synthesis with the yields of desired chrysene **4** less than 43%.

Because of its synthetic and mechanistic interest, we further examined the generality of this catalytic reaction over various 2-alkynyl-1-acetylbenzenes **6a**−**6m**, which were easily prepared by Stille or Sonogashira coupling[16] of the corresponding 2-acetyl-1-bromobenzenes (Table 2). This chrysene synthesis provides desired products **7a**−**7m** with various functionalities on their R^1 and R^2 substituents. Entries 1−5 show the suitability of this cyclization to alternation of the aryl R_2 and the alkynyl R_3 substituents with an alkyl group; the resulting chrysenes **7a**−**7e** were obtained in 66−79% yields. In this catalysis, species **6f**−**6g** bearing R_1 = OMe are more efficient than its analogue **6h** with R_2 = OMe, as shown by the yields of products **7f**−**7g** (81−83%) and **7h** (56%). This cyclization works well for substrates **6i**−**6k** bearing a fluoro at the R_1 or R_2 substituent, and the corresponding fluorochrysenes **7i**−**7k** were obtained with yields exceeding 59%. In the case of species **6l**, we obtained chrysene **7l** in low yield (27%) with HOAc solvent; herein, the use of wet 1,4-dioxane preferably gave 2,3-dimethylindenone **7n** (56% yield) in addition to chrysene **7l** in minor proportion (12% yield). This catalytic dimerization became less efficient for **6m** bearing a methylenedioxy group; the yield of chrysene products **7m** was only 29%.

The value of this cyclization is reflected by its applicability to the syntheses of novel and large polyaromatic compounds

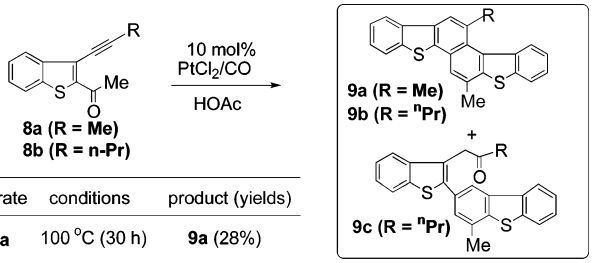
TABLE 2. Catalytic Synthesis of Chrysenes from 2-Alkynyl-1-acetylbenzenes



entry	substrate[a]	time / h	product (yields)[b]
1	R_1, R_2 = H, R_3 = C_4H_9 (**6a**)	15	**7a** (79%)
2	R_1 = H, R_2 = CH_3, R_3 = CH_3 (**6b**)	14	**7b** (71%)
3	R_1 = H, R_2 = CH_3, R_3 = C_4H_9 (6c)	16	**7c** (66%)
4	R_1 = H, R_2 = ^{t}Bu, R_3 = CH_3 (6d)	15	**7d** (79%)
5	R_1 = H, R_2 = ^{t}Bu R_3 = C_4H_9 (**6e**)	16	**7e** (74%)
6	R_1 = OCH_3, R_2 = H, R_3 = CH_3 (**6f**)	8	**7f** (81%)
7	R_1 = OCH_3, R_2 = H, R_3 = C_4H_9 (**6g**)	14	**7g** (83%)
8	R_1 = H, R_2 = OCH_3, R_3 = CH_3 (**6h**)	16	**7h** (56%)
9	R_1 = H, R_2 = F, R_3 = C_4H_9 (**6i**)	10	**7i** (78%)
10	R_1 = F, R_2 = H, R_3 = C_3H_7 (**6j**)	14	**7j** (73%)
11	R_1, R_2 = F, R_3 = C_4H_9 (**6k**)	16	**7k** (59%)
12	R_1 = H, R_2 = Br, R_3 = C_4H_9 (**6l**)	12	**7l** (27%)[c]
13	R_1, R_2 = OCH_2O R_3 = CH_3 (**6m**)	16	**7m** (29%)

[a] 10 mol % $PtCl_2$, CO (1 atm), 100 °C, [substrate] = 0.80−1.0 M. [b] Yields of products are given after separation using a silica column. [c] This reaction was run in HOAc solvent, and in the case of wet 1,4-dioxane, we obtained chrysene **7l** and 2,3-dimethylindenone **7n** in 12 and 56 yields, respectively.

SCHEME 2



substrate	conditions	product (yields)
(1) **8a**	100 °C (30 h)	**9a** (28%)
(2) **8b**	120 °C (60 h)	**9b** (31%), **9c** (12%)
(3) **8b**	100 °C (36 h)	**9b** (21%), **9c** (45%)
(4) **9c**	120 °C (49 h)	**9b** (67%), **9c** (15%)

9a and **9b** in respective yields of 28 and 31% from $PtCl_2$-catalyzed dimerization of benzothiophene analogues **8a** and **8b** in HOAc solvent (entries 1 and 2, Scheme 2); the thiophene group in these substrates is known to tolerate Pd(II) and Pt(II) catalysts.[17] In the cyclization of species **8b**, we isolated species **9c**, and its subsequent conversion to chrysene **9b** by $PtCl_2$/CO

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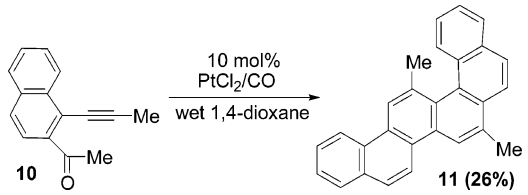
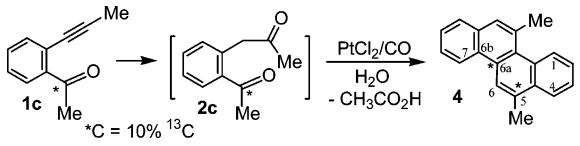
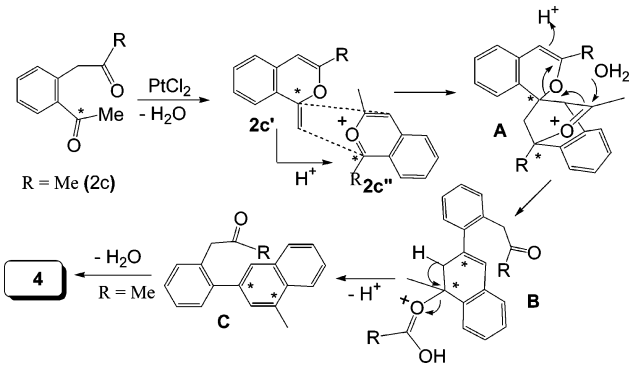
SCHEME 3



SCHEME 4



SCHEME 5



suggested that it is likely to be the reaction intermediate (entries 3 and 4). Scheme 3 shows an additional application for the synthesis of polyaromatic species **11** via dimerization of naphthyl derivative **10**; the corresponding yield was 26%. The molecular structure of compound **11** was confirmed by an X-ray diffraction study.[12]

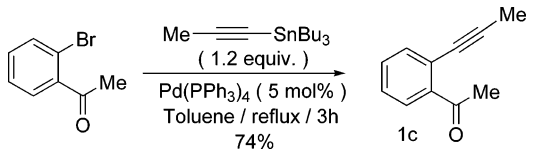
A ^{13}C-labeling experiment was performed to elucidate the mechanism because the chrysene synthesis involved complex structural organization. As depicted in Scheme 4, we prepared compound **1c** bearing 10% ^{13}C at the carbonyl carbon; the reaction using isotopically labeled **1c** and produced the desired chrysene **4** with ^{13}C enrichment at the tertiary C(5) and C(6a) carbons, identified by HMBC and HMQC NMR spectra.[18] This information indicates that the acetic acid byproduct arose from a hydrative cleavage of the propynyl triple bond. In this manner, the newly generated naphthalene core is constructed from two acetyl and one propynyl group, in addition to one cleaved carbide carbon. The organization verifies the hypothesis that ketone **9c** was the intermediate for chrysene **4**.

Scheme 5 shows a plausible mechanism to rationalize the formation of chrysene **4** via the dimerization of diketone species **2c**. In this four-ketone coupling process, the traditional aldol condensation alone fails to rationalize the observed chemoselectivity.[19] The preceding results in Scheme 2 support the intermediacy of species **C**, which loses an acetyl group before its formation. In the presence of $PtCl_2$, we envisage that diketone **2c** forms a dehydrated cyclized ether **2c′**, which also generates benzopyrylium species **2c″** in this acidic medium. A subsequent [4 + 2]-cycloaddition of this benzopyrylium species with cyclic ether **2c′** generates oxonium species **A**,[20] which is prone to loss of an acetyl group upon hydrolysis according to recent reports by Yamamoto.[21,22] The final aromatization reaction of resulting species **B** enables the formation of desired intermediate **C** with its ^{13}C labeling consistent with observation. This mechanism not only rationalizes the chemoselectivity of chrysene **4** but also explains the deacetylation reaction for intermediate **C**.

In summary, we report a novel $PtCl_2$-catalyzed dimerization of hydrative dimerization of 2-alkynyl-1-acetylbenzenes to give chrysenes, whereas, before this work, chrysenes were commonly prepared from tedious procedures.[8−10] The new tandem catalysis comprises an initial selective hydration of the alkyne, followed by chemoselective dimerization of diketone intermediates. The value of this cyclization is reflected by its extension to the synthesis of novel polyaromatic compounds including **9a**, **9b**, and **11**. Studies toward the synthesis of functionalized polycyclic molecules via $PtCl_2$-catalyzed condensation of multi-aldehyde and ketone groups are under current studies.

Experimental Section

(a) Typical Procedure for the Synthesis of 1-[2-(Prop-1-ynyl)-phenyl]ethanone (1c).

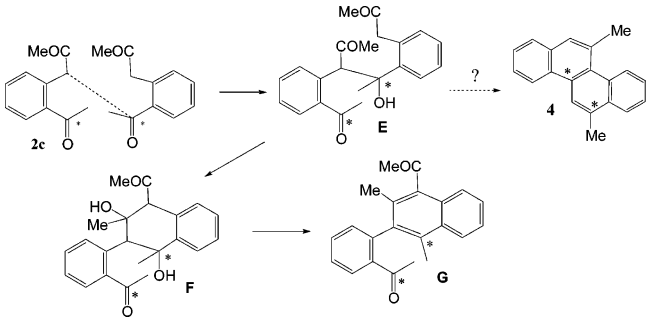


To a toluene solution of 2-bromoacetophenone (1.0 g, 5.02 mmol) was added $Pd(PPh_3)_4$ (290 mg, 0.251 mmol) at 25 °C, and the mixture was stirred for 10 min before addition of tributyltinpropyne (1.98 g, 6.03 mmol). The resulting mixture was refluxed at 110 °C for 3 h before it was cooled to 25 °C. To this solution was added KF solution, and the solution was extracted with ethyl acetate (50 mL), dried over $MgSO_4$, and concentrated under reduced pressure.

(17) Selected examples: (a) Zhao, C.; Zhang, Y.; Ng, M.-T. *J. Org. Chem.* **2007**, *72*, 8384. (b) Silva, N. O.; Abreu, A. S.; Ferreira, P. M. T.; Monteiro, L. S.; Queiroz, M.-J. R. P. *Eur. J. Org. Chem.* **2002**, 2524. (c) Wang, Z.; Elokdah, H.; McFarlane, G.; Pan, S.; Antane, M. *Tetrahedron Lett.* **2006**, *47*, 3365.

(18) HMBC, HMQC spectra of compound **4** are provided in Supporting Information.

(19) We envisage that the aldol reaction proceeds via an initial addition of the more enolizable Ar**C**H$_2$COMe to the less enolizable Ar**C**OMe, giving the aldol product **E**. In the manner, this reaction route is expected to give naphthalene species **G** ultimately as the major projects.



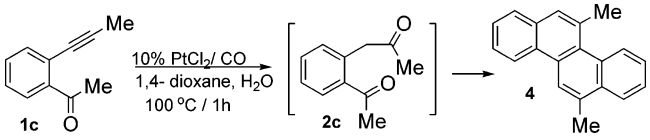
(20) (a) Asao, N.; Takahashi, K.; Lee, S.; Kasahara, T.; Yamamoto, Y. *J. Am. Chem. Soc.* **2002**, *124*, 12650. (b) Iwasawa, N.; Shido, M.; Kusama, H. *J. Am. Chem. Soc.* **2001**, *123*, 5814.

(21) (a) Asao, N.; Nogami, T.; Lee, S.; Yamamoto, Y. *J. Am. Chem. Soc.* **2003**, *125*, 10921. (b) Asao, N.; Aikawa, H. *J. Org. Chem.* **2006**, *71*, 5249.

(22) Acetic acid given from the production of chrysene **4** was identified by GC analysis using DB-WAX column (30 m × 0.32 mm i.d.).

The residue was eluted through a silica column to afford compound **1c** (589 mg, 3.71 mmol, 74%) as yellow liquid.

(b) Catalytic Operations.



A long-neck tube containing $PtCl_2$ (17 mg, 0.063 mmol) was dried in vacuo for 1 h, and vacuum was released with CO gas using a CO balloon before it was charged with 1-(2-(prop-1-ynyl)phenyl)-ethanone **1c** (100 mg, 0.63 mmol), water (0.068 mL, 3.78 mmol), and 1,4-dioxane (2.0 mL, 0.20 M). The mixture was stirred at 25 °C for 30 min and heated at 100 °C for 1 h. The solution was concentrated and eluted through a silica column (hexane/ethyl acetate) to afford compound **2c** (53.0 mg, 0.3 mmol, 48%), compound **4** (11 mg, 0.04 mmol, 13%, yellow oil), and starting compound **1c** (23 mg, 0.15 mmol, 23%).

Spectral Data for 1-[2-(Prop-1-ynyl)phenyl]ethanone (1c): Yellow oil, IR (neat, cm^{-1}) 3125(s), 2125(w), 1730(s), 770(s); ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, J = 7.6, 1.2 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.40−7.36 (m, 1H), 7.33−7.28 (m, 1H), 2.69 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 140.5, 133.4, 130.6, 127.8, 127.0, 121.9, 91.7, 78.4, 29.3, 4.0; HRMS calcd for $C_{11}H_{10}O$, 158.0732; found, 158.0735.

Spectral Data for 5,12-Dimethylchrysene (4): White solid, mp 108.5−109.7 °C; IR (neat, cm^{-1}) 3035(s), 2025(w), 1610(s), 885-(w); ^1H NMR (600 MHz, $CDCl_3$) δ 8.96 (d, J = 8.0 Hz, 1H), 8.71 (d, J = 8.2 Hz, 1H), 8.57 (s, 1H), 8.16 (d, J = 7.6 Hz, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.78 (s, 1H), 7.66−7.58 (m, 4H), 3.19 (s, 3H), 2.87 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 132.9, 132.8, 132.7, 131.8, 131.7, 129.8, 129.5, 129.2, 128.5, 127.9, 127.3, 126.3, 125.7, 125.6, 124.8, 124.4, 123.1, 122.2, 27.6, 20.4; HRMS calcd for $C_{20}H_{16}$, 256.1252; found, 256.1248.

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Supporting Information Available: Experimental procedures, spectral data, and NMR spectra of key compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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