JOC*Article*

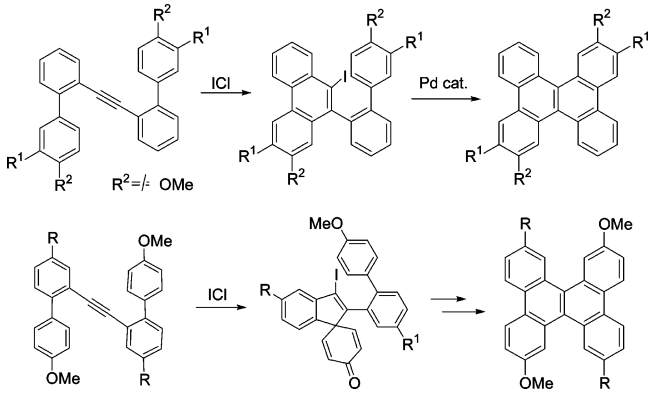
Synthesis of Dibenzo[*g,p*]chrysenes from Bis(biaryl)acetylenes via Sequential ICl-Induced Cyclization and Mizoroki−Heck Coupling

Chia-Wen Li,[†] Cheng-I Wang,[†] Hsin-Yi Liao,[‡] Rupsha Chaudhuri,[†] and Rai-Shung Liu*,[†]

Department of Chemistry, National Tsing-Hua University, Hsinchu, Taiwan, Republic of China, and Department of Science Education, National Taipei University of Education, Taipei, Taiwan, Republic of China

rsliu@mx.nthu.edu.tw

Received July 11, 2007



We report a facile synthesis of functionalized dibenzo[*g,p*]chrysenes via initial ICl-promoted cyclization of bis(biaryl)acetylenes, followed by the Mizoroki−Heck coupling reaction. This new approach works well for various bis(biaryl)acetylenes to afford dibenzo[*g,p*]chrysenes bearing various functionalities. With substrates of one special type including 4′-methoxy-2-ethynylbiphenyls, we found that the ICl treatment led to *ipso* cyclization to give bicyclic spirocyclohexadienones. In the presence of MeOH/H_2SO_4, these spiroketone products undergo rearrangement to give 9-iodophenanthrenes through a selective 1,2-alkenyl migration. We prepared various 4′-methoxy-2-ethynylbiphenyl compounds to show the generalization of such an *ipso* cyclization and 1,2-alkenyl shift. This *ipso*-cyclization approach can be extended to the preparation of dibenzo[*g,p*]chrysenes.

Introduction

Polycyclic aromatic hydrocarbons have widespread applications as functional materials in various electronic devices such as nonlinear optical,[1] photo- and electroluminescent,[2] and molecule-based sensory devices.[3] Dibenzo[*g,p*]chrysenes represent an interesting class of such compounds because of their attractive fluorescent properties such as high quantum yields, small Stoke shifts, and long-lived excited states.[4] Synthesis of dibenzo[*g,p*]chrysenes is generally plagued by long procedures prior to the advent of $SbCl_5$/MeOH oxidation of bis(biaryl)-acetylenes by Swager.[4] However, this method is limited to substrates of a special type (R^1 = OMe, eq 1) via the carbocation radical intermediate I. Iodine, ICl, and iodonium salt induced[5] intramolecular acetylene cyclization is synthetically useful as it provides alkenyl iodides, which can be further functionalized

[†] National Tsing-Hua University.
[‡] National Taipei University of Education.

(1) (a) Munn, R. W.; Ironside, C. N. *Principles and Application of Nonlinear Optical Materials*; Chapman & Hall: London, UK, 1993. (b) Nie, W. *Adv. Mater*. **1993**, *5*, 520. (c) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991.

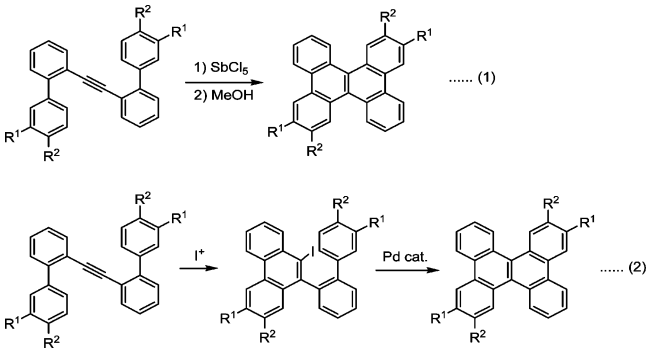
(2) (a) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628. (b) Schwoerer, M. *Phys. Bull*. **1994**, *50*, 52. (c) Gruner, J.; Hamer, P. J.; Friend, R. H.; Huber, H. J.; Scherf, U.; Holmes, A. B. *Adv. Mater*. **1994**, *6*, 748. (d) Braun, D.; Heeger, A. J. *Appl. Phys. Lett*. **1991**, *58*, 1982.

(3) (a) Swager, T. M.; Marsella, M. J. *Adv. Mater*. **1994**, *6*, 595. (b) Marsella, M. J.; Swager, T. M. *J. Am. Chem. Soc*. **1993**, *115*, 12214. (c) Marsella, M. J.; Carroll, P. J.; Swager, T. M. *J. Am. Chem. Soc*. **1994**, *116*, 9347. (d) Matsue, T.; Nishizawa, M.; Sawaguchi, T.; Uchida, I. *J. Chem. Soc., Chem. Commun*. **1991**, 1029. (e) Schuhmann, W.; Huber, J.; Mirlach, A.; Daub, J. *Adv. Mater*. **1993**, *5*, 124.

(4) Yamaguchi, S.; Swager, T. *J. Am. Chem. Soc*. **2001**, *123*, 12087.

10.1021/jo701504m CCC: $37.00
Published on Web 11/01/2007

by using palladium chemistry.[6] To prepare dibenzo[*g*,*p*]chrysenes bearing diverse substituents, we have designed a two-step transformation involving an initial ICl-promoted cyclization to give iodophenanthrene II, followed by Pd-catalyzed cyclization, as depicted in eq 2. Here we report our findings on various dibenzo[*g*,*p*]chrysene syntheses.

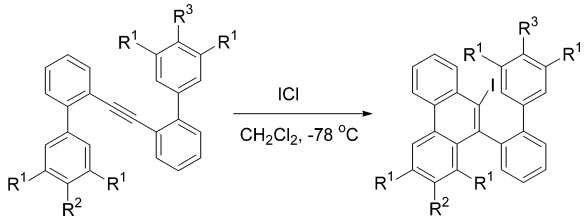


Results and Discussion

Bis(biaryl)acetylenes **1a**−**d** were prepared according to Swager's procedures.[4] $SbCl_5$/MeOH oxidation was unsuccessful in preparing dibenzo[*g*,*p*]chrysenes from compounds **1a** and **1b** because of the lack of an activating group (R^1 = OMe). When species **1a** was subjected to ICl-induced[7,8] cyclization, 9-iodophenanthrene **2a** was obtained in 90% yield via ortho cyclization. 3′,5′-Difluoro-2-ethynylbiphenyl **1b** and 3′,5′-dimethoxy-2-ethynylbiphenyl **1c** similarly afforded the corresponding iodophenanthrene derivatives **2b** and **2c** in 70% and 89% yields, respectively. This method was efficient for the cyclization of trimethoxy-substituted ethynyl biphenyl **1d**, as evident from the formation of 1,2,3-trimethoxy 9-iodophenanthrene **2d** in 95% yield. Although the R^3 substituent of resulting product **2c** was also iodinated by ICl (R^3 = I), this unexpected iodide was removable in the subsequent Pd-catalyzed cyclization (see Table 1).

When this cyclization was extended to 4′-methoxy-2-ethynylbiphenyls **3a**,**b**, as shown in Scheme 1, spiro[4.5]-cyclohexadienones **4a**,**b** were, however, obtained through *ipso*-cyclization in 87% and 88% yields, respectively; in these cases, we observed no corresponding phenanthrene derivatives. The distinct behavior of species **3a** and **3b** is attributed to the directing effect of the *p*-methoxy group to favor a 5-*endo*-*dig* cyclization. ICl-induced *ipso*-cyclization was reported for 4-(*p*-methoxyaryl)alk-1-ynes by Larock.[8,9] As spiro structural motifs are present frameworks in some natural products,[10] as well as some organic optoelectronic materials,[11] we proceeded to investigate this ICl-induced spiro cyclization in detail.

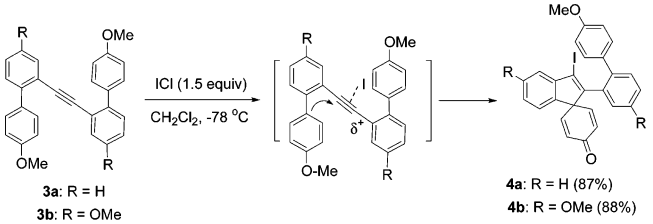
TABLE 1. ICl-Induced Iodocyclization



entry	ethynylarenes[a]	iodoarenes (% yield[b])
1	**1a** ($R^1 = R^2 = R^3$ = H)	**2a** ($R^1 = R^2 = R^3$ = H, 90%)
2	**1b** (R^1 = H, $R^2 = R^3$ = F)	**2b** (R^1 = H, $R^2 = R^3$ = F, 70%)
3	**1c** (R^1 = OMe, $R^2 = R^3$ = H)	**2c** (R^1 = OMe, R^2 = H, R^3 = I, 89%)
4	**1d** ($R^1 = R^2 = R^3$ = OMe)	**2d** ($R^1 = R^2 = R^3$ = OMe, 95%)

[a] [Substrate] = 0.1 M, ICl (1.5 equiv for entries 1, 2, and 4 and 2.5 equiv for entry 3. [b] Yields are given after column chromatography on a silica column.

SCHEME 1



We prepared various 4′-methoxy-2-alkynylbiphenyl compounds **5a**−**n** to examine the generality of this ICl-induced cyclization; our results are depicted in Table 2. Entries 1−8 show the variation of the alkynyl R substituent of substrates with phenyl (R = C_6H_5, 4-MeC_6H_4, and 4-$MeOC_6H_4$), heteroaryl (R = 2-furyl, 2-thienyl, 2-benzofuryl, and 2-benzo[*b*]-thienyl), and alkyl (R = *n*-C_6H_{13}) groups; the corresponding spirocyclohexadienones were obtained in yields exceeding 88%. Here we obtained no byproduct stemmed from iodination of the reactive furan or thiophene moieties. This ICl-induced *ipso*-cyclization also worked efficiently for substrates **5i**−**n** bearing methoxy at the bridging phenyl C(4) and C(5) positions; the desired spirocyclohexadienones **6i**−**n** were obtained in 88−94% yields. The crystal structure of compound **6j** was confirmed by an X-ray diffraction study.[12]

We also prepared 2′,4-dimethoxy-2-alkynylbiphenyl species **7**, which upon treatment with ICl produced 9-iodophenanthrene

(5) For selected examples, see: (a) Barluenga, J.; Trincado, M.; Rubio, E.; Gonzalez, J. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 2406. (b) Barluenga, J.; Gonzalez, J. M.; Campos, P. J.; Asensio, G. *Angew. Chem., Int. Ed.* **1988**, *27*, 1546. (c) Barluenga, J.; Llorente, I.; Alvarez-Garcia, L. J.; Gonzalez, J. M.; Compos, P. J.; Diaz, M. R.; Garcia-Granda, S. *J. Am. Chem. Soc.* **1997**, *119*, 6933. (d) Klein, T. R.; Bergemann, M.; Yehia, N. A. M.; Fanghanel, E. *J. Org. Chem.* **1998**, *63*, 4626. (e) Flynn, B. L.; Verdier-Pinard, P.; Hamel, E. *Org. Lett.* **2001**, *3*, 651. (f) Larock, R. C.; Yue, D. *Tetrahedron Lett.* **2001**, *42*, 6011. (g) Yue, D.; Larock, R. C. *J. Org. Chem.* **2002**, *67*, 1905. (h) Huang, Q.; Hunter, J. A.; Larock, R. C. *J. Org. Chem.* **2002**, *67*, 3437. (i) Arcadi, A.; Cacchi, S.; Di Giuseppe, S.; Fabrizi, G.; Marinelli, F. *Org. Lett.* **2002**, *4*, 2409. (j) Amjad, M.; Knight, D. W. *Tetrahedron Lett.* **2004**, *45*, 539.

(6) For selected reviews and examples, see: (a) Larock, R. C. *J. Organomet. Chem.* **1999**, *576*, 111. (b) Larock, R. C. *Palladium-Catalyzed Annulation* in *Perspectives in Organopalladium Chemistry for the XXI Century*; Tsuji, J., Ed.; Elsevier Press: Lausanne, Switzerland, 1999; pp 111−124. (c) Tsuji, J. *Palladium Reagents and Catalysts*; John Wiley & Sons: Chichester, UK, 1999. (d) Arcadi, A.; Cacchi, S.; Fabrizi, G.; Moro, L. *Eur. J. Org. Chem.* **1999**, 1137. (e) Campo, M. A.; Larock, R. C. *J. Org. Chem.* **2002**, *67*, 5616.

(7) Yao, T.; Campo, M. A.; Larock, R. C. *Org. Lett.* **2004**, *6*, 2677.

(8) Yao, T.; Campo, M. A.; Larock, R. C. *J. Org. Chem.* **2005**, *70*, 3511.

(9) For ICl-induced *ipso*-cyclization, see: (a) Appel, T. R.; Yehia, N. A. M.; Baumeister, U.; Hartung, H.; Kluge, R.; Strohl, D.; Fanghanel, E. *Eur. J. Org. Chem.* **2003**, 47. (b) Zhang, X.; Larock, R. C. *J. Am. Chem. Soc.* **2005**, *127*, 12230.

(10) (a) For a review, see: Heathcock, C. H.; Graham, S. L.; Pirrung, M. C.; Plavac, F.; White, C. T. In *The Total Synthesis of Natural Products*; Apsimon, J., Ed.; Wiley-Interscience: New York, 1983; Vol. 5, pp 264−313. (b) Sakamoto, K.; Tsuji, E.; Abe, F.; Nakanishi, T.; Yamashita, M.; Shigematsu, N.; Izumi, S.; Okuhara, M. *J. Antibiot.* **1996**, *49*, 37. (c) Gonzalez-Lopez de Turiso, F.; Curran, D. P. *Org. Lett.* **2005**, *7*, 151 and references cited therein.

(11) Saragi, T. P. I.; Spehr, T.; Siebert, A.; Fuhrmann-Lieker, T.; Salbeck, J. *Chem. Rev.* **2007**, *107*, 1011.

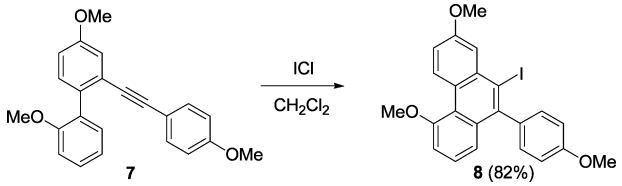
(12) X-ray data for compound **6j** are provided in the Supporting Information.

TABLE 2. ICl-Induced Synthesis of Spirocyclohexadienone Derivatives and Their Acid-Promoted Rearrangements

	alkynylarenes[a]	spiro compounds[b] (% yield)[c]	arenes (Yield%)[c]
(1)	**5a**: R = Ph	**6a** (92%)	**9a** (92%)
(2)	**5b**: R = 4-MeC_6H_4	**6b** (94%)	**9b** (94%)
(3)	**5c**: R = 4-MeOC_6H_4	**6c** (95%)	**9c** (93%)
(4)	**5d**: R = 2-furan	**6d** (91%)	**9d** (92%)
(5)	**5e**: R = 2-thiophene	**6e** (93%)	**9e** (93%)
(6)	**5f**: R = 2-benzofuran	**6f** (95%)	**9f** (95%)
(7)	**5g**: R = 2-benzo[*b*]thiophene	**6g** (94%)	**9g** (94%)
(8)	**5h**: R = *n*-C_6H_{13}	**6h** (88%)	**9h** (89%)
(9)	**5i**: R = Ph	**6i** (91%)	**9i** (94%)
(10)	**5j**: R = 4-MeOC_6H_4	**6j** (90%)	**9j** (95%)
(11)	**5k**: R = 2-furan	**6k** (89%)	**9k** (94%)
(12)	**5l**: R = 2-thiophene	**6l** (92%)	**9l** (94%)
(13)	**5m**: R = *n*-C_6H_{13}	**6m** (88%)	**9m** (90%)
(14)	**5n**: R = 4-MeOC_6H_4	**6n** (94%)	**9n** (94%)

[a] 0.1 M [substrate] in CH_2Cl_2, −78 °C for 2 h. [b] 0.1 M [substrate] in CH_2Cl_2/MeOH (1:1, v/v), H_2SO_4 (2.0 equiv), 0 to 23 °C, 6 h. [c] Yields are given after purification by column chromatography on silica gel.

SCHEME 2

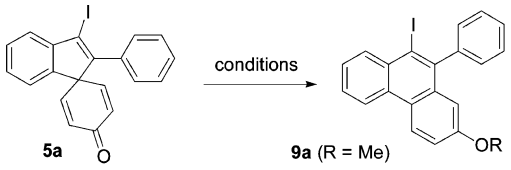


8 in an 82% yield (Scheme 2). The *ipso*-chemoselectivity is apparently limited to substrates bearing a *p*-methoxy-substituted phenyl ring.[13]

The preceding spirocyclohexadienones **6a**−**n** are expected to undergo isomerization to give iodophenanthrene products through the dienone−phenol rearrangement, generally catalyzed by Brønsted acids.[14] As shown in Scheme 3, the organic acid *p*-TSA (10 mol %) or H_2SO_4 (2.0 equiv) gave no rearranged products even under refluxing in CH_2Cl_2 for 12 h. To our delight, the use of H_2SO_4 (2.0 equiv) in mixed CH_2Cl_2/MeOH (1:1, v/v) at 23 °C for 2 h afforded rearranged product **9a** in a 93% yield. The structure of compound **9a** was carefully elucidated from its ^1H NOE spectrum, which reveals that the acid-catalyzed rearrangement proceeds via a 1,2-migration of the alkenyl rather than the phenyl group. Scheme 4 shows an extension of this rearrangement to species **4a** and **4b**, which gave products **10a** and **10b** in 90% and 87% yields, respectively. Notably, the original protocol in eq 2 would have provided the same products **10a** and **10b** if the ICl-induced 6-*endo*-*dig* cyclization were applicable to initial substrates **3a** and **3b**.

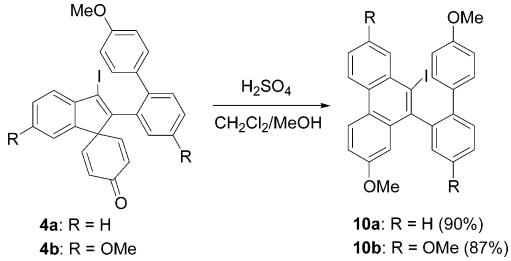
Using these optimum conditions, we further examined the generality of this acid-catalyzed 1,2-alkenyl migration by treating the remaining spirocyclohexadienones **6b**−**n** with H_2-

SCHEME 3

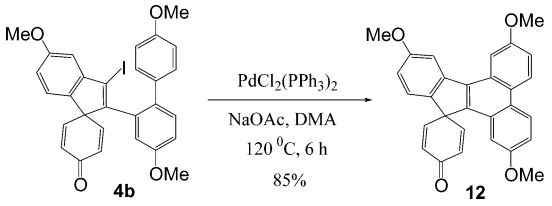


	solvent	condition	products
(1)	CH_2Cl_2	*p*-TSA (10%) reflux,12 h	NR
(2)	CH_2Cl_2	H_2SO_4 (2.0 equiv.), reflux, 12 h	NR
(3)	CH_2Cl_2/MeOH (1:1, v/v)	H_2SO_4 (2.0 equiv.), rt, 6 h	**9a**: R = Me (93%)

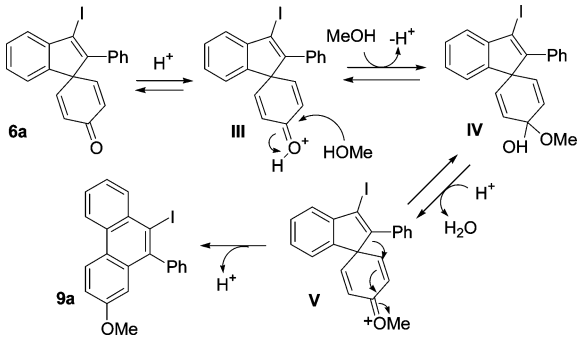
SCHEME 4



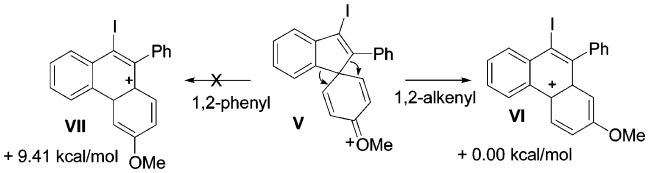
SCHEME 5



SCHEME 6



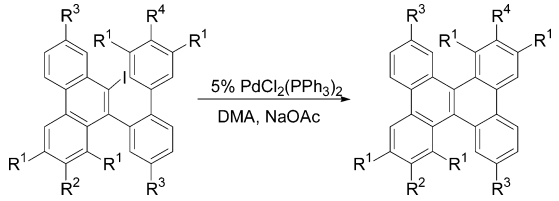
SCHEME 7



(13) We do not exclude the possibility that *ipso*-cyclization actually occurred for species **7** bearing an *o*-methoxy group, which underwent a rapid rearrangement under the reaction conditions.

(14) (a) Shine, H. J. In *Aromatic Rearrangements*; Elsevier: New York, 1967; pp 55−68. (b) Schultz, A. G.; Hardinger, S. A. *J. Org. Chem.* **1991**, *56*, 1105. (c) Zimmerman, H. E.; Cirkva, V. *J. Org. Chem.* **2001**, *66*, 1839.

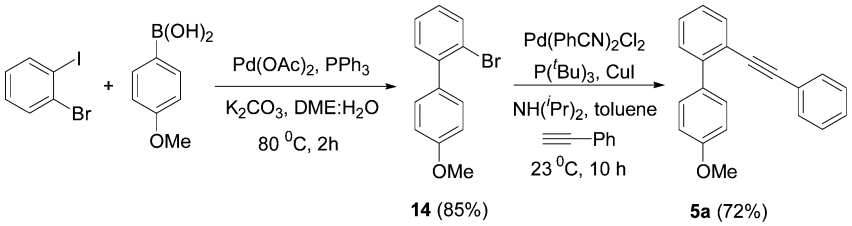
TABLE 3. Intramolecular Arylation of Iodophenanthrene



entry	ethynylarenes[a]	iodoarenes (% yield[b])
1	**2a** ($R^1 = R^2 = R^3 = R^4 = H$)	**11a** ($R^1 = R^2 = R^3 = R^4 = H$, 71%)
2	**2b** ($R^1 = R^3$, $R^2 = R^4 = F$)	**11b** ($R^1 = R^3 = H$, $R^2 = R^4 = F$, 72%)
3	**2c** ($R^1 = OMe$, $R^2 = R^3 = H$, $R^4 = I$)	**11c** ($R^1 = OMe$, $R^2 = R^3 = R^4 = H$, 69%)
4	**2d** ($R^1 = R^2 = R^4 = OMe$, $R^3 = H$)	**11d** ($R^1 = R^2 = R^4 = OMe$, $R^3 = H$, 68%)
5	**10b** ($R^1 = H$, $R^2 = R^3 = R^4 = OMe$)	**11e** ($R^1 = H$, $R^2 = R^3 = R^4 = OMe$, 85%)

[a] 0.05 M [substrate] in DMA, at 120 °C for 4 h with 5% $PdCl_2(PPh_3)_2$ and NaOAc (2.0 equiv). [b] Yields are given after purification by column chromatography on silica gel.

SCHEME 8



SO_4 in MeOH/CH_2Cl_2; the results are summarized in Table 2. The rearrangement occurred efficiently to generate the desired 9-iodophenanthrene products **9b**−**n**, with yields exceeding 89%. In these cases, we obtained no side product corresponding to a 1,2-phenyl migration. The diversity of substrates used demonstrates the scope and reliability of this rearrangement. The ^1H NMR spectral signals of all these products have a common singlet signal in the upfield region (δ 6.75−7.05 ppm), characteristic of the phenanthrene C-(1) proton resonance.

As shown in Table 3, we sought to accomplish the ultimate synthesis of dibenzo[*g*,*p*]chrysenes using 9-iodophenanthrenes **2a**−**d** and **10a**,**b**, via two distinctly different pathways, with the second cyclization being based on an intramolecular Mizoroki−Heck coupling.[15] Treatment of iodoarene **2a** with $PdCl_2(PPh_3)_2$ (5 mol %) and sodium acetate (2.0 equiv) in DMA (*N*,*N*-dimethylacetamide) at 120 °C for 4 h afforded the desired derivative **11a** in a 71% yield. This set of conditions was extendible to other 9-iodophenanthrenes **2b**, **2d**, and **10b**, giving the desired products **11b** and **11d**,**e** in 68−85% yields. Notably, the extra iodide ($R^4 = I$) of species **2c** was reduced in this cyclization to afford product **11c** (69%). Scheme 5 shows an alternative application of these spiroketone products; treatment of alkenyl species **4b** with catalyst $PdCl_2(PPh_3)_2$ and NaOAc in DMA afforded the cyclized product **12** in an 85% yield.

Scheme 6 depicts a plausible mechanism for the rearrangement of spirodienone **6a** to 9-iodophenanthrene **9a** promoted by MeOH/H_2SO_4. In this transformation, a proton initially enhances the addition of methanol at the ketone group of species **6a** to form species **IV**, which ultimately forms species **V** in the presence of excess MeOH. In contrast with species **III**, the methoxy group of species **V** is kinetically stable and stabilizes the oxonium center to induce a 1,2-alkenyl migration. We cannot exclude the possibility that because MeOH is more polar than CH_2Cl_2 it facilitates this migration.

As depicted in Scheme 7, we performed a calculation to estimate the relative stability of two carbocations **VI** and **VII**, corresponding to the 1,2-migration of an alkenyl and a phenyl group, respectively. According to the B3LYP/6-31+G* calculation (3-21G* for iodine atom since 6-31+G* in not available), carbocation **VI** has +9.41 kcal/mol less in energy than species **VII**; this result supports a 1,2-alkenyl migration.

Conclusion

We have achieved a facile synthesis of functionalized dibenzo[*g*,*p*]chrysenes via initial ICl-promoted cyclization of bis(biaryl)acetylenes, followed by Pd-catalyzed annulation of the resulting 9-iodophenanthrene intermediates. For substrates of one particular type, such as 4′-methoxy-2-ethynylbiphenyls, we found that this ICl treatment leads to *ipso* cyclization to give bicyclic spirocyclohexadienones, which are potentially useful intermediates in organic synthesis. In the presence of MeOH/H_2SO_4, these spirocyclohexadienones undergo rearrangement to give 9-iodophenanthrenes through a selective 1,2-migration of the alkenyl group. The feasibility of this migration is supported by calculation.

Experimental Sections

(1) Representative Synthesis of 2-Ethynyl Biphenyls: Synthesis of 4′-Methoxy-2-(phenylethynyl)biphenyl (5a). (a) Synthesis of 2-Bromo-4′-methoxybiphenyl (14). To a solution of $Pd(OAc)_2$ (101 mg, 0.45 mmol), PPh_3 (354 mg, 1.35 mmol), and K_2CO_3 (2.76 g, 20.0 mmol) in DME (30 mL) and H_2O (10 mL) near 23 °C was added 4-methoxyphenylboronic acid (1.67 g, 11.0 mmol);[16,17] the resulting mixture was stirred for 10 min. To this

(15) (a) Ames, D. E.; Opalko, A. *Tetrahedron* **1984**, *40*, 1919. (b) For a recent review on aryl−aryl bond formation, see: Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174.

(16) Karig, G.; Moon, M.-T.; Thasana, N.; Gallagher, T. *Org. Lett.* **2002**, *4*, 3115.

solution was added 2-iodo-1-bromobenzene (2.83 g, 10.0 mmol), and the mixture was heated to 80 °C for 2 h. The resulting solution was cooled to 23 °C before addition of saturated ammonium chloride solution and extraction with ethyl acetate. The extracts were washed with brine solution, dried over $MgSO_4$, filtered, and concentrated. The mixtures were eluted through a silica column to give bromobiaryl species **14** (2.24 g, 8.5 mmol, 85%) as a yellow oil.

(b) Synthesis of 4′-Methoxy-2-(phenylethynyl)biphenyl (5a). To $Pd(PhCN)_2Cl_2$ (195 mg, 0.509 mmol) and CuI (99 mg, 0.509 mmol) was added dry toluene (20 mL), P(*t*-Bu)$_3$ (206 mg 1.02 mmol), HN(*i*-Pr)$_2$ under N_2, and bromo derivative **14** (2.24 g, 8.5 mmol), and the mixture was stirred at 23 °C before addition of phenyl acetylene (1.23 g, 12.21 mmol). After 10 h, the reaction mixture was treated with hexane (40 mL), filtered through a small silica pad, concentrated, and purified by flash chromatography, which yielded the desired product **5a** (1.74 g, 72%) as a viscous oil. Spectral data for compound **5a**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.60−7.62 (m, 3H), 7.34−7.40 (m, 4H), 7.26−7.28 (m, 4H), 6.98 (dd, 2H, J = 8.8, 0.8 Hz), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.1, 143.4, 133.0, 132.9, 131.3, 130.5, 129.3, 128.5, 128.2, 128.0, 126.6, 123.5, 121.4, 113.3, 92.1, 89.6, 55.3; HRMS (EI) calcd for $C_{21}H_{16}O$ (M^+) 284.1201, found 284.1209.

(2) Representative Procedure for ICl-Induced *Ipso* Cyclization: Synthesis of Spirocyclohexadienone 6a. A solution of compound **5a** (500 mg, 1.76 mmol) in dry CH_2Cl_2 (18 mL) was maintained at −78 °C with an acetone−liquid N_2 bath. To this solution was added ICl (3.51 mL, 1 M solution in CH_2Cl_2), using a standard syringe. The reaction was maintained at the same temperature, and monitored by TLC. After the completion of the reaction, it was quenched with a saturated sodium thiosulfate solution and warmed to 22 °C. The reaction mixture was extracted with CH_2Cl_2 (2 × 20 mL); the combined extracts were washed with brine solution, dried over $MgSO_4$, concentrated, and chromatographed through a silica column to yield product **6a** (642 mg, 1.62 mmol, 92%) as a yellow solid (mp 206.3−208.5 °C). Spectral data for compound **6a**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44 (d, 2H, J = 2.4 Hz), 7.29−7.33 (m, 6H), 7.08 (d, 1H, J = 7.6 Hz), 6.41−6.50 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 185.7, 150.0, 147.0, 145.8, 140.0, 134.7, 131.0, 129.1, 128.7, 128.3, 128.2, 127.8, 123.8, 123.2, 99.8, 62.3; HRMS (EI) calcd for $C_{20}H_{13}IO$ (M^+) 396.0011, found 396.0007.

(3) Representative Procedure for Acid-Mediated Rearrangements: Synthesis of Iodophenanthrene 9a. Compound **6a** (500 gm, 1.26 mmol) was dissolved in a mixture of CH_2Cl_2 and MeOH (12.5 mL, v/v, 1:1) and cooled to 0 °C with an ice water bath. At this temperature, H_2SO_4 (247 mg, 2.52 mmol) was added dropwise with use of a glass dropper for 10 min; the reaction was warmed to 22 °C, stirred for 6 h, and monitored with thin-layer chromatography. After completion, the reaction mixture was treated with water and extracted with CH_2Cl_2 (3 × 20 mL). The organic layers were washed with brine solution and dried over $MgSO_4$. The organic layer was filtered, concentrated, and purified by using column chromatography, which delivered the product **9a** (481 mg, 1.17 mmol, 93%) as a yellow solid (mp 137.2−138.5 °C). Spectral data for compound **9a**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.58 (d, 1H, J = 8.8 Hz), 8.52 (d, 1H, J = 8.0 Hz), 8.42 (d, 1H, J = 8.0 Hz), 7.49−7.64 (m, 5H), 7.24−7.28 (m, 3H), 6.75 (d, 1H, J = 2.4 Hz), 3.66 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.2, 145.4, 144.7, 134.6, 133.7, 131.4, 130.5, 129.8, 128.5, 127.8, 127.5, 127.0, 124.6, 124.1, 122.1, 116.8, 109.7, 109.1, 55.1; HRMS (EI) calcd for $C_{21}H_{15}IO$ (M^+) 410.0168, found 410.0166.

(4) Representative Procedure for ICl-Induced Cyclization: Synthesis of Iodophenanthrene 8. Compound **8** was obtained in a 82% yield by treatment of biphenyl species **7** with ICl in cold CH_2Cl_2 (−78 °C); the procedure was similar to that of species **6a**. Yellow solid (mp 112.3−113.5 °C); IR (neat, cm^{-1}) 3075, 3025, 2832, 1607, 1243; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.64 (d, 1H, J = 9.6 Hz), 7.96 (d, 1H, J = 2.8 Hz), 7.24−7.29 (m, 2H), 7.12−7.17 (m, 3H), 7.04−7.05 (m, 3H), 4.11 (s, 3H), 4.00 (s, 3H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.1, 158.6, 157.7, 145.5, 139.2, 134.5, 133.9, 131.0, 130.5, 125.6, 124.8, 121.9, 121.2, 116.8, 115.8, 113.8, 109.1, 108.8, 56.0, 55.4, 55.3; HRMS calcd for $C_{23}H_{19}IO_3$ (M^+) 470.0379, found 470.0375.

(5) Representative Procedure for Intramolecular Mizoroki−Heck Coupling: Synthesis of Dibenzo[*g*,*p*]chrysene 11a. A two-necked flask was charged with iodophenanthrene **2a** (200 mg, 0.44 mmol), $PdCl_2(PPh_3)_2$ (15 mg, 0.022 mmol), and CH_3COONa (72 mg, 0.88 mmol) under a nitrogen atmosphere, followed by addition of DMA (9 mL). The resulting solution was heated at 120 °C for 4 h, then cooled to 22 °C and HCl solution (100 mL, 1 M) was added. The resulting mixture was extracted with dichloromethane, and the organic layers were combined, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed on a silica column to afford **11a** (102 mg, 0.31 mmol, 71%) as a yellow solid (mp 210.5−213.4 °C). Spectral data for compound **11a**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.68−8.70 (m, 8H), 7.60−7.69 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 130.7, 129.1, 128.8, 127.4, 126.4, 123.5 (one peak merged); HRMS (EI) calcd for $C_{26}H_{16}$ (M^+) 328.1252, found 328.1256.

Acknowledgment. The authors wish to thank the National Science Council, Taiwan for supporting this work.

Supporting Information Available: Experimental procedures for the preparation of **1a**, X-ray data of compound **6j**, spectral data, and copies of NMR spectra of key compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JO701504M

(17) Blake. A. J.; Cooke, P. A.; Doyle, K. J.; Gair, S.; Simpkins, N. *Tetrahrdron Lett.* **1998**, *39*, 9093.