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Short and Efficient Synthesis of Coronene Derivatives via Ruthenium-Catalyzed Benzannulation Protocol

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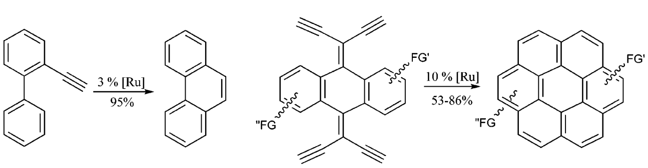
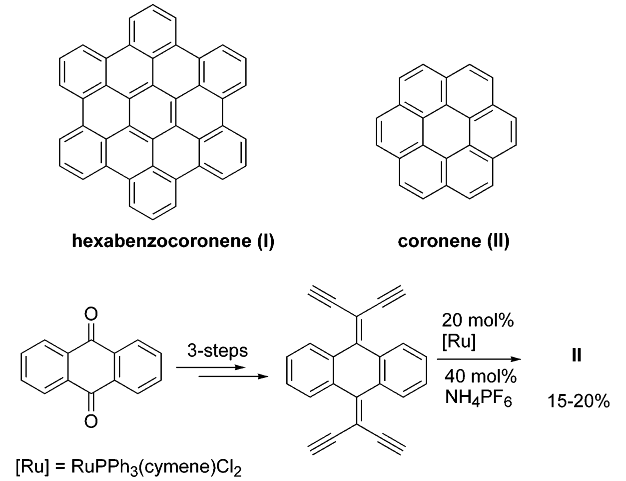


$TpRuPPh_3(CH_3CN)_2PF_6$ (3 mol %) was very active in catalytic benzannulation of 1-phenyl-2-ethynylbenzenes in dichloroethane (60 °C, 36 h) to afford phenanthrene in 95% yield. This method is applicable to the synthesis of various polycyclic aromatic hydrocarbons via two- and four-fold benzannulations, including various substituted coronene derivatives (53−86% yields) using this catalyst at a moderate loading (10 mol %).

Large polycyclic aromatic compounds such as hexabenzocoronene derivatives[1−3] (Scheme 1, eq 1) tend to form columnar liquid crystal mesophases via intermolecular $\pi-\pi$ stacking. This structural feature shows promising applications for organic transistors[4] and photovoltaic devices.[5] The facile and practical synthesis of hexabenzocoronene derivatives,[1−3] notably by the work of Müllen and co-workers, enhances the development of these materials for optoelectronic applications.[4,5] In contrast with hexabenzocoronenes, published methods for the synthesis of coronenes are plagued with long procedures and inefficiency,[6] typically including a pyrolysis step at high temperatures. Only persulfurated coronene derivatives were prepared directly from perchlorocoronene.[7] The lack of a convenient and efficient synthesis of coronenes impedes their progress in organic chemistry. Scott and co-workers[8] proposed a short synthesis of coronenes from metal-catalyzed cyclization of bis(1,1-ethynyl)alkene species, which was prepared conveniently in three steps from commercially available anthraquinone (Scheme 1, eq 2). This approach was, however, inefficient as it gave coronene in only 15−20% yield using 20 mol % $RuPPh_3(cymene)Cl_2$ catalyst; no additional coronene example was reported from the use of this catalytic approach. In this study, we sought to accomplish this catalytic transformation using $TpRuPPh_3(CH_3CN)_2PF_6$ catalyst.[9] This cationic species readily reacts with terminal alkynes to afford highly electrophilic ruthenium-vinylidenium intermediates and enables the realization of many interesting catalytic cyclizations.[9]

SCHEME 1



Catalytic transformations of 3,5-dien-1-ynes, 4-phenyl-3-en-1-ynes, and 1-phenyl-2-ethynylbenzenes into benzene derivatives have been studied by either chemical oxidation[10] or metal-catalyzed cyclization (Scheme 2).[11−13]

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(1) (a) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons*; Wiley-VCH: New York, 1997. (b) Sakurai, H.; Daiko, T.; Hirao, T. *Science* **2003**, *301*, 1878.

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10.1021/jo0512599 CCC: $30.25

SCHEME 2

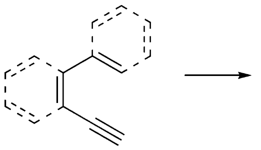
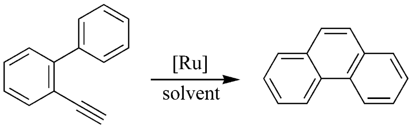


TABLE 1. Catalytic Cyclization of 1-Phenyl-2-ethynylbenzene

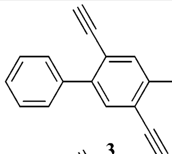
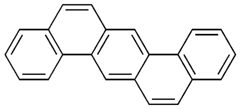
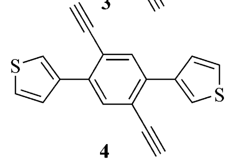
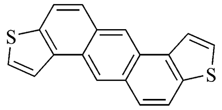
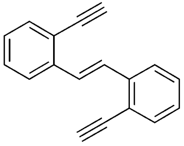
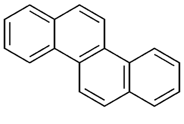
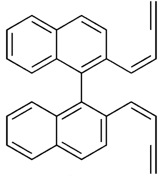
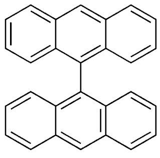
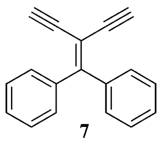
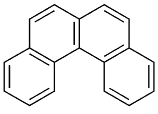
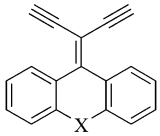
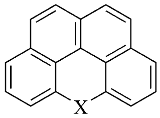
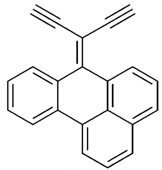
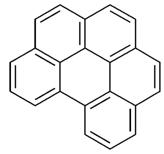


1 **2**

entry	mol %	solvents	conditions[a]	yields (%)
1	5.0	toluene	100 °C (18 h)	83
2	5.0	DCE	80 °C (10 h)	91
3	3.0	DCE	60 °C (36 h)	95
4	5.0	$CHCl_3$	80 °C (30 h)	72
5	5.0	3-pentanone	100 °C (12 h)	88
6	5.0	DME	90 °C (36 h)	13
7	5.0	CH_3CN	90 °C (36 h)	NR
8	5.0	DMF	100 °C (36 h)	NR

[a] [**1**] = 0.10 M. [b] The yields of phenanthrene **2** were given after separation from a silica column.

TABLE 2. Ruthenium-Catalyzed Cyclization via a Two-Fold Benzannulation[a]

entry	alkynes	products(yields)[b]
1	 **3**	 **11** (83%)
2	 **4**	 **12** (74%)
3	 **5**	 **13** (41%)
4	 **6**	 **14** (71%)
5	 **7**	 **15** (81%)
6	 X = O **8** X = S **9**	 X = O **16** (60%) X = S **17** (75%)
7	 **10**	 **18** (75%)

[a] [**3**−**10**] = 0.05 M, 10 mol % catalyst, DCE, 80 °C, 24 h. [b] Yields of products were given after separation from a silica column.

The former process normally requires stoichiometric amount (>1.0 equiv) of suitable oxidants such as I_2, ICl, or $SbCl_5$.[10] The metal-catalyzed pathway may involve either a metal-π-alkyne or metal-vinylidene intermediate.[11−13] Among these catalysts,[8,11,12] only $RuPPh_3(cymene)Cl_2$ was shown to be active in the 2-fold benzannulation of such functionalities, which can produce more complex polyaromatic hydrocarbons. For our experiments, we selected 1-phenyl-2-ethynylbenzenes to study because it gives a complicated phenanthrene framework. Table 1 shows the efficiency of $TpRuPPh_3(CH_3CN)_2PF_6$ catalyst in the cyclization of compound **1** in various solvents. This ruthenium catalyst (5 mol %) is very active in several solvents (entries 1−5) including toluene (83%), dichloroethane (DCE, 91%), chloroform (72%), and 3-pentanone (88%) but less active or inactive in dimethoxyethane (DME, 13%), acetonitrile (0%), and dimethylformide (DMF, 0%). The same catalytic efficiency is maintained in DCE at 60 °C (36 h) using a 3.0 mol % catalyst (entry 3). The efficiency of this catalyst appears superior to that of other metal catalysts including $PtCl_2$, $AuCl_3$, AuCl, $PtCl_2(PhCN)_2$, and $In(OTf)_3$, which requires at least 5 mol % catalyst to attain the same efficiency.[12b]

We extended this new approach to a 2-fold benzannulation to examine its applicability to a short synthesis of polyaromatic hydrocarbons; the results are shown in Table 2. Diyne substrates **3**−**10** are readily prepared in short steps from commercial sources; their synthetic procedures are provided in Supporting Information. This ruthenium catalyst (10 mol %) works well for the synthesis of dibenzo[*a.h*]anthracene (**11**), which was obtained in 83% yield (entry 1). We also obtained such an anthracene species (**12**) fused with two thiophene rings, for which the yield was 74% (entry 2). Tandem cyclization of diyne-ene species (**5**) with this ruthenium catalyst gave chrysene (**13**) in 41% yield (entry 3). Synthesis of 9,9′-bianthracene (**14**) was obtained in 71% yield from binaphthalene (**6**) bearing two enyne groups (entry 4). This cyclization is applicable to the synthesis of benzo[*c*]phenanthrene (**15**) and its oxa- and thia-bridged congeners (**16** and **17**); the yields were 60−81% (entries 5 and 6). Entry 7 shows a successful instance of this cyclization to the synthesis of benzo[*ghi*]perylene (**18**) with 75% yield. Among these examples, ribbon type compound **11** has been prepared efficiently (ca. 75%) using photochemical I_2-oxidation, which required a sto-

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(12) (a) Maeyama, K.; Iwasawa, N. *J. Org. Chem.* **1999**, *64*, 1344. (b) Mamane, V.; Hannen, P.; Fürstner, A. *Chem. Eur. J.* **2004**, *10*, 4556.

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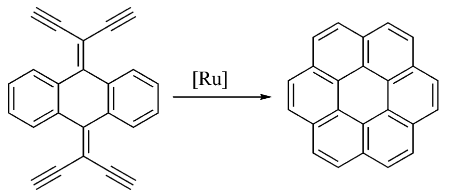
TABLE 3. Synthesis of Coronene under Various Conditions



entry	catalyst	condition[a]	yields (%)[b]
1	$TpRuPPh_3(CH_3CN)_2PF_6$	5 mol %, 1.0×10^{-4} M	86
2	$TpRuPPh_3(CH_3CN)_2PF_6$	5 mol %, 1.0×10^{-3} M	42
3	$TpRuPPh_3(CH_3CN)_2PF_6$	10 mol %, 1.0×10^{-3} M	67
4	$TpRuPPh_3(CH_3CN)_2PF_6$	10 mol %, 1.0×10^{-2} M	45
5	$TpRuPPh_3(CH_3CN)_2PF_6$	20 mol %, 1.0×10^{-2} M	66
6	$RuPPh_3(cymene)Cl_2$	20 mol %, 1.0×10^{-2} M + NH_4PF_6 (40 mol %)	15−20[c]

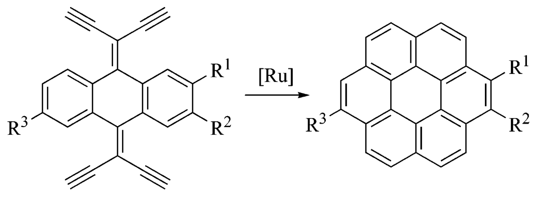
[a] DCE, 80 °C, 36 h. [b] Yields were given after separation from a silica column. [c] Data were taken from ref 8.

ichiometric amount of oxidant.[10b] Polyaromatic hydrocarbons **15**−**17** were previously studied by $RuPPh_3(cymene)Cl_2$ (20 mol %) and NH_4PF_6 (40 mol %), and the respective yields were 60%, 10%, and 95%.[8] The acidic nature of NH_4PF_6 is thought to cause the low yield of product **16**.

Table 3 shows our efforts to achieve a short synthesis of coronene **20** from bis(1,1-ethynyl)alkene species **19** under various conditions. The cyclization efficiency is highly dependent on the concentration of alkyne **19**. A dilute solution is catalytically more efficient (entries 1−5); this condition is expected to weaken the $\pi-\pi$ stacking of anthracene **19** to avoid an intermolecular dimerization catalyzed by this ruthenium catalyst.[14] A dilute solution (10^{-2} to 10^{-3} M) is more suitable for the catalytic transformation because the starting bis(1,1-ethynyl)alkene species **19** is sparingly soluble in DCE at 80 °C. A high catalytic efficiency is attained at 10^{-4} M using 5 mol % catalyst, at 10^{-3} M with 10 mol %, and at 10^{-2} M with 20 mol %. We also studied the catalytic activities of various metal catalysts including $AuCl_3$, $PtCl_2$, $PtCl_2(PhCN)_2/2AgBF_4$, $GaCl_3$, $In(OTf)_3$, and $InCl_3$, which were all inactive at [**19**] = 10^{-3} M with 10 mol % loading. Scott and co-workers[8] used $RuPPh_3(cymene)Cl_2$ (20 mol %) and NH_4PF_6 (40 mol %) catalyst to give coronene **20** in 15−20% at [**19**] = 10^{-2} M.

This new catalytic reaction provides a short synthesis of various functionalized coronenes via a 4-fold benzannulation of 3,5-dien-1-ynes. We prepared various bis(1,1-ethynyl)alkenes **21**−**26** to examine the generality of this cyclization. These substrates were readily prepared in short steps from commercially available anthraquinone. The catalytic reactions were performed with 10 mol % catalyst at a substrate concentration of 10^{-3} M; the results are summarized in Table 4. Entries 1 and 2 demonstrate successful synthesis of monosubstituted coronene **27** and **28** bearing a methyl or chloro substituent; the yields were 53−75%. This catalytic reaction is compatible with tetracene species **23** (entry 3), which gave its cyclized coronene derivative **29** in 78% yield. This cyclization is successfully extended to the synthesis of disubstituted coronenes **30**−**32** with 63−68% yields (entries 4−6).

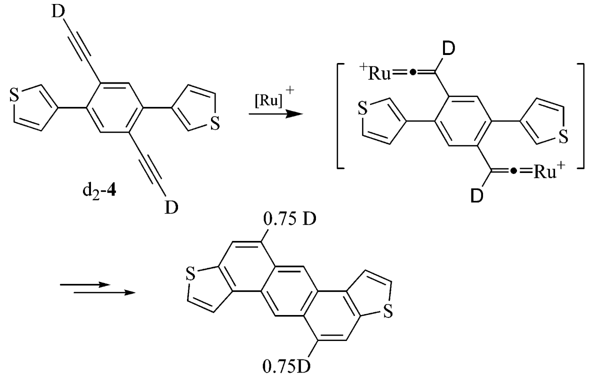
TABLE 4. Ruthenium-Catalyzed Synthesis of Various Coronenes via a Four-Fold Benzannulation



entry	alkynes[a]	coronene (yield, %)[b]
1	R^1 = Me, R^2 = R^3 = H (**21**)	**27** (75)
2	R^1 = Cl, R^2 = R^3 = H (**22**)	**28** (53)
3	R^1, R^2 = $(CH{=}CH)_2$; R^3 = H (**23**)	**29** (78)
4	R^1 = R^3 = n-C_8H_{17}; R^2 = H (**24**)	**30** (68)
5	R^1 = R^3 = $O^nC_4H_9$; R^2 = H (**25**)	**31** (63)
6	R^1 = R^3 = Ph; R^2 = H (**26**)	**32** (63)

[a] 10 mol % catalyst, [alkynes] = 10^{-3} M, 80 °C, 36 h. [b] Yields were given after separation from a silica column.

SCHEME 3



The success of $TpRuPPh_3(CH_3CN)_2PF_6$ in the preceding cyclizations relies on its strong preference for the *6-endo-dig* cyclization, and we obtained no byproducts arising from the *5-endo-dig* mode. We prepared a deuterium-labeled sample d_2-**4** to elucidate the origin of this chemoselectivity (Scheme 3); the resulting product d_2-**12** showed a 1,2-deuterium shift during the cyclization. This feature is characteristic of the involvement of ruthenium-vinylidene intermediate.[15] NMR signals of polyaromatic species **12** were made on the basis of ^1H-NOE spectra.[16]

In summary, we have demonstrated that $TpRuPPh_3(CH_3CN)_2PF_6$ (3 mol %) catalyst was very active in catalytic cyclization of 1-phenyl-2-ethynyl-benzenes in dichloroethane (60 °C, 36 h) and gave phenanthrene efficiently. This catalyst maintains a great efficiency in the two- and four-fold benzannulation of such 4-aryl-3-en-1-yne functionalities and gives good yields of various polyaromatic

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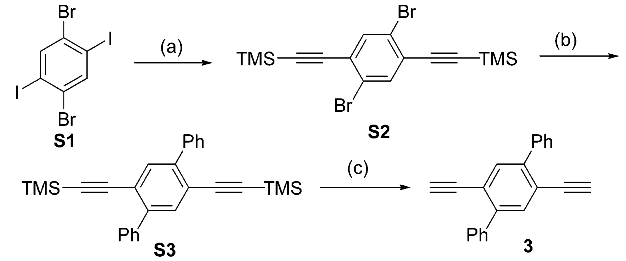
(14) In a separate experiment, we found that phenylacetylene was catalyzed by $TpRuPPh_3(CH_3CN)_2PF_6$ (10 mol %) via a dimerization reaction; the yields of the resulting enyne were 76% and 45% at a phenylacetylene concentration of 0.4 and 0.04 M, respectively.

(15) (a) Trost, B. M. *Acc. Chem. Res.* **2002**, *35*, 695. (b) Bruneau, C.; Dixneuf, P. *Acc. Chem. Res.* **1999**, *32*, 311. (c) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev.* **1999**, *193*−*195*, 977.

(16) The ^1H NOE map of compound **12** is provided in Supporting Information.

SCHEME 4[a]



[a] (a) Trimethylsilylacetylene, $PdCl_2(PPh_3)_2$, CuI, $HNEt_2$, rt, 8 h, 89%. (b) $PhB(OH)_2$, $Pd(PPh_3)_4$, $Ba(OH)_2$, THF, 65 °C, 24 h, 73%. (c) TBAF, THF, 0 °C, 2 h, 93%.

hydrocarbons including various substituted coronene derivatives. This method employs a short and convenient synthesis of coronene derivatives.

Experimental Section

General Sections. 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. $TpRuPPh_3(CH_3CN)_2PF_6$ catalyst was prepared by heating $TpRu(PPh_3)_2Cl$ with $LiPF_6$ in CH_3CN.[9] The diyne substrates **7**−**10** and tetraynes **19** were prepared according to the procedures described by Scott and co-workers.[8] Other tetraynes **21**−**26** were prepared from the corresponding anthraquinones according to the same protocol.

Synthesis of 1,4-Diethynyl-2,5-diphenylbenzene (3). Synthesis of diyne **3** is shown in Scheme 4. To a diethylamine (35 mL) solution of compound **S1** (970 mg, 2.00 mmol) were added $PdCl_2(PPh_3)_2$ (147 mg, 0.209 mmol), copper(I) iodide (74 mg, 0.39 mmol), and trimethylsilylacetylene (470 mg, 4.80 mmol), and the mixture was stirred at 25 °C for 8 h. To this solution was added an aqueous NH_4Cl solution, and the mixture was concentrated and extracted with diethyl ether. The ether extract was evaporated and chromatographed through a silica colum (5% ethyl acetate/95% hexane) to give product **S2** as a colorless oil (761 mg, 89%).

To a THF (10 mL) solution of compound **S2** (428 mg, 1.00 mmol) were added $Pd(PPh_3)_4$ (170 mg, 0.15 mmol), K_2CO_3 (1.38 g, 10.0 mmol), and $PhB(OH)_2$ (360 mg, 3.00 mmol), and the mixture was stirred at 65 °C for 24 h. To this solution was added an aqueous NH_4Cl solution, and the mixture was concentrated and extracted with diethyl ether. The ether extract was evaporated and chromatographed through a silica column (hexane) to give **S3** (616 mg, 73%) as a colorless oil.

To a THF (20 mL) solution of compound **S3** (422 mg, 1.00 mmol) was added *n*-tetrabutylammonium fluoride (1.0 M, THF, 3.0 mL, 3.00 mmol) at 0 °C, and the resulting solution was stirred at 0 °C for 2 h. Column chromatography of the crude product on a silica column with hexane gave diyne 1,4-diethynyl-2,5-diphenylbenzene **3** as a colorless oil (258 mg, 93%).

Typical Procedure for Catalytic Operation. A long tube containing $TpRuPPh_3(CH_3CN)_2PF_6$ (41.1 mg, 0.05 mmol) was dried in vacuo for 2 h before it was charged with compound **3** (150 mg, 0.54 mmol) and 1,2-dichloroethane (10.8 mL). The mixture was heated at 80 °C for 24 h before cooling to room temperature. The so1ution was concentrated and eluted through a silica column to afford dibenzo[*a.h*]anthracene **11** (124.5 mg, 0.45 mmol, 83%) as a light yellow solid.

Spectral Data for 1,4-Diethynyl-2,5diphenylbenzene (3). IR (Nujol, cm^{-1}): 3296 (m), 3078 (s), 2210 (m), 1613 (s), 1475 (m). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62 (m, 6 H), 7.44 (m, 4 H), 7.40 (m, 2 H), 3.11 (s, 2 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 142.9, 138.9, 134.9, 129.1, 128.1, 127.9, 121.1, 82.5, 81.8. HRMS (EI, *m/z*) calcd for $C_{12}H_{14}$ 278.1096, found 278.1095.

Spectral Data for Dibenzo[*a.h*]anthracene (11). IR (Nujol cm^{-1}): 3292 (m), 3076 (s), 1614 (s), 1471 (m). ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.13 (s, 2 H), 8.85 (d, J = 7.8 Hz, 2 H), 7.99 (d, J = 7.8 Hz, 2 H), 7.89 (d, J = 7.8 Hz, 2 H), 7.68 (m, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 132.0, 130.8, 130.2, 129.1, 128.6, 127.5, 127.2, 127.0, 126.8, 122.9, 122.2. HRMS (EI, *m/z*) calcd for $C_{22}H_{14}$ 278.1096, found 278.1099.

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Supporting Information Available: Synthetic procedures for other starting alkynes **5** and **6**, ^{1}H NMR and ^{13}C NMR spectra, and spectral data of compounds **1**−**32**. This material is available free of charge via the Internet at http://pubs.acs.org.

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