JOC The Journal of Organic Chemistry

Featured Article

pubs.acs.org/joc

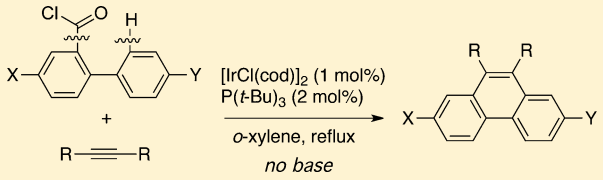
Iridium-Catalyzed Annulative Coupling of 2-Arylbenzoyl Chlorides with Alkynes: Selective Formation of Phenanthrene Derivatives

Tomoya Nagata, Koji Hirano, Tetsuya Satoh, and Masahiro Miura*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

Supporting Information

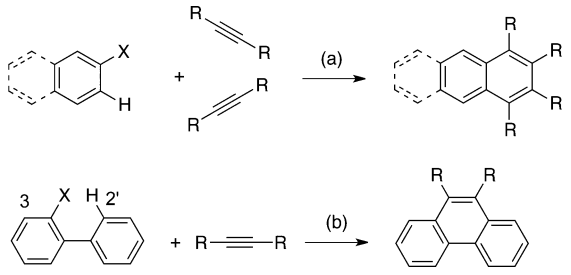
ABSTRACT: 2-Arylbenzoyl chlorides undergo annulative coupling with internal alkynes in the presence of a catalyst system of $[IrCl(cod)]_2/P(t\text{-}Bu)_3$ to selectively afford the corresponding phenanthrene derivatives accompanied by elimination of carbon monoxide and hydrogen chloride. The reaction occurs without addition of any external base. Deuterium-labeling experiments using 2-(d_5-phenyl)benzoyl chloride suggest that the rate-determining step does not involve the C2′−H bond cleavage. Formation of a $[(t\text{-}Bu)_3PH][(biphenyl\text{-}2,2'\text{-}diyl)Ir(CO)Cl_2]$ complex dimer, of which the structure was determined by single-crystal X-ray analysis, from a stoichiometric reaction at 60 °C without addition of alkyne also supports the facile C−H cleavage.



INTRODUCTION

The chemistry of polycyclic aromatic hydrocarbons (PAHs) has a long history,[1] and they have become increasingly important in recent years as the structural cores of various π-conjugated functional materials.[2] Thus, the selective synthesis of substituted PAHs even more attracts attention. Among potential and straightforward strategies to construct condensed aromatics is the transition-metal-catalyzed benzannulation of aromatic substrates with alkynes. For instance, the reaction of monofunctionalized benzenes and 2-functionalized naphthalenes with two alkyne molecules via *o*-C−H bond cleavage directly provides multiply substituted naphthalenes and anthracenes, respectively (Scheme 1a).[3] Using aliphatic alkynes may produce compounds having substantial solubilities. Meanwhile, the annulation reaction of 2-functionalized 1,1′-biphenyls with an alkyne through the activation of C2′−H bond appears to be a promising pathway for the synthesis of phenanthrene series of compounds (Scheme 1b).[4] This second type of coupling is, however, less explored compared with the 1:2 coupling, and there remains room for further development.

Scheme 1. Annulation of Monofunctionalized Arenes with Alkynes



As an early example of the phenanthrene formation (Scheme 1b), Heck reported the palladium-catalyzed reaction of 2-iodobiphenyl (X = I) with diphenylacetylene albeit with a low yield.[3d] Larock described that the reaction is significantly promoted by the addition of sodium acetate as base, and various arylalkynes can be employed.[4a] Glorius demonstrated that 2-phenylbenzoic acids (X = COOH) can be used as the starting substrates in place of 2-iodobiphenyl in the palladium-catalyzed reaction using silver carbonate as oxidant and base.[4b] Takahashi described the chromium-mediated reaction of 2-halo-1,1′-biphenyls.[4c] An iron-catalyzed annulation of 1,1′-biphenyl-2-yl-magnesium bromide (X = MgBr) was reported by Nakamura.[4d] Wu recently employed the Larock method (X = I) for the synthesis of [8]circulenes.[4e]

We previously reported that benzoyl and naphthoyl chlorides effectively undergo 1:2 coupling with alkynes in the presence of an iridium catalyst to afford the corresponding annulated products accompanied by elimination of hydrogen chloride and carbon monoxide (Scheme 1a, X = COCl).[3f,5] It may be conceived that if a similar catalyst system is used, the reaction of 2-phenylbenzoyl chloride leads to the corresponding phenanthrene (Scheme 1b, X = COCl). Indeed, we have found that the annulation via C2′−H cleavage proceeds selectively without involving any 1:2 coupling via C3−H cleavage. This reaction allows the use of dialkylacetylenes, which could not be employed in the palladium-catalyzed reactions,[4a,b] while it was also possible in the case with 2,2′-diiodobiaryls as substrates.[4f,g] It should also be noted that the reaction takes place without addition of any base as in the reaction of simple benzoyl chloride. This implies that the C2′−H cleavage during the annulation process can occur without assistance of an external base. Consequently, we have

Received: August 8, 2014
Published: September 13, 2014

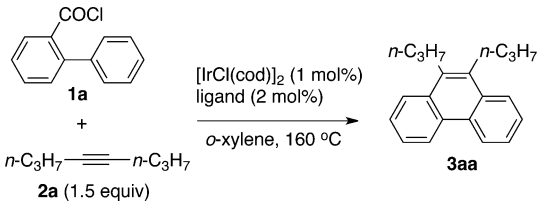
dx.doi.org/10.1021/jo501835u | J. Org. Chem. 2014, 79, 8960−8967

investigated the phenanthrene formation reaction with respect to the substrate scope and undertaken deuterium-labeling experiments using 2-(d_5-phenyl)benzoyl chloride and isolation of an intermediary complex from a stoichiometric reaction to provide mechanistic insights. The results are described herein.

RESULTS AND DISCUSSION

In an initial attempt, 2-phenylbenzoyl chloride (**1a**, 0.5 mmol) was treated with 4-octyne (**2a**, 0.75 mmol) in the presence of $[IrCl(cod)]_2$ (0.005 mmol) in refluxing *o*-xylene at 160 °C (bath temperature) for 24 h under nitrogen, and the expected 9,10-dipropylphenanthrene (**3aa**) was formed in 61% GC yield (Table 1, entry 1). Then, the reaction was carried out with the

Table 1. Reaction of 2-Phenylbenzoyl Chloride (1a) with 4-Octyne (2a)[a]



entry	ligand	time (h)	yield of **3aa**[b] (%)
1		24	(61)
2	PPh_3	9	(72)
3	$PPhCy_2$	9	(97)
4	P(*o*-tolyl)Cy_2	6	(18)
5	Ruphos	6	(40)
6	Xphos	9	(24)
7	Johnphos	9	(23)
8	P(*t*-Bu)$_3$	3	83 (>98)
9[c]	P(*t*-Bu)$_3$	24	47
10[d]		3	88 (>98)

[a]Reaction conditions: **1a** (0.50 mmol), **2a** (0.75 mmol), $[IrCl(cod)]_2$ (0.005 mmol), ligand (0.010 mmol), *o*-xylene (2.5 mL), under N_2. [b]Yield in parentheses was determined by GC with 1-methylnaphthalene as internal standard. [c]Reaction with $[RhCl(cod)]_2$ in place of $[IrCl(cod)]_2$. [d]Reaction with complex **6** (0.005 mmol) as catalyst.

addition of a number of phosphine ligands. The use of PPh_3 improved the yield of **3aa** to 72% (entry 2), and $PPhCy_2$ gave an excellent yield of 97% within 9 h (entry 3). However, related more bulky P(Ar)Cy_2-type phosphines, P(*o*-tolyl)Cy_2, Ruphos (2-(dicyclohexylphosphino)-2′,6′-diisopropoxy-1,1′-biphenyl), and Xphos (2-(dicyclohexylphosphino)-2′,4′,6′-triisopropyl-1,1′-biphenyl) were less effective (entries 4−6). While the reaction with Johnphos (2-(di-*tert*-butylphosphino)-1,1′-biphenyl) was sluggish (entry 7), P(*t*-Bu)$_3$ was found to be superior to $PPhCy_2$ and afforded **3aa** quantitatively within 3 h (entry 8, 83% after chromatographic purification). The use of $[RhCl(cod)]_2$/P(*t*-Bu)$_3$ in place of $[IrCl(cod)]_2$ gave only a moderate yield of **3aa** (entry 9). It is noted that in the absence of the alkyne **2a**, fluorenone (**4a**) was formed in 78% (24 h), whereas the formation of **4a** was not observed at all in the presence of **2a**.

We next carried out the annulation reactions using a number of 2-arylbenzoyl chlorides and alkynes under the conditions employed for entry 8 in Table 1 (Scheme 2). The reactions of **1a** with 6-dodecyne (**2b**), 8-hexadecyne (**2c**), 1-phenyl-1-hexyne (**2d**), and diphenylacetylene (**2e**) gave the corresponding 9,10-disubstituted phenanthrenes **3ab**−**ae**, with good yields, as in the case with **2a**. 4,4′-Dimethoxy-, dimethyl-, dichloro-, and di(trifluoromethyl)-substituted diphenylacetylenes **2f**−**i** also coupled with **1a** to give 9,10-diarylphenanthrenes **3af**−**ai**. It is noted that while these products were formed in more than 90% GC yields with the exception of **3ai** (ca. 60%), their lower yields are attributable to the isolation process by recrystallization to eliminate the residual acetylenes. The reaction of 1,2-bis(2-thienyl)acetylene (**2j**) with **1a** afforded 9,10-di(2-thienyl)phenanthrene (**3aj**) in excellent yield. Functionalized internal alkynes, ethyl 3-phenylpropynoate (**2k**) and [2-(trimethylsilyl)ethynyl]benzene (**2l**), and even terminal alkynes, 1-octyne (**2m**) and ethynylbenzene (**2n**), could also couple with **1a** to provide phenanthrenes **3ak**−**an**, albeit in moderate yields. 4′-Methyl-, 4′-fluoro-, and 4′-(trifluoromethyl)-substituted 2-phenylbenzoyl chlorides **1b**−**d** also reacted with **2a** to selectively produce phenanthrenes **3ba**, **3ca**, and **3da**. In contrast, the reaction of 2-(4-methoxyphenyl)benzoyl chloride (**1e**) with **2a** gave the expected **3ea** along with 2-methoxyfluorenone (**4e**). The reaction of 2-(2-naphthyl)-benzoyl chloride (**1f**) with **2a** similarly gave tetraphene **3fa** (an isomer was accompanied: **3fa**/isomer = 92:8, judged by ^{1}H NMR) and benzofluorenone **4f**. Note that **3fa** and **4f** are formed by the cleavage of C3′−H and C1′−H bonds, respectively. 4,4′-Dibromo-substituted 2-phenylbenzoyl chloride **1g** effectively underwent coupling with alkynes **3a** and **3c** to give 2,7-dibromo-9,10-dialkylphenanthrenes **3ga** and **3gc** in good yields, demonstrating that bromo functions that can be used further transformations are tolerable under the reaction conditions. It is worth citing that 2,7-dibromo-9,10-dialkylphenanthrenes are useful building blocks for the synthesis of π-conjugated polymers.[6] The reaction of 2-(3-methylphenyl)-benzoyl chloride (**1h**) reacted with **2a** to selectively afford the corresponding 3,9,10-trisubstituted phenanthrene **3ha**.

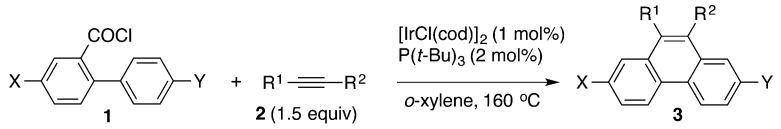
On the basis of literature information and our findings, we are tempted to assume the mechanism for the reaction of **1** with **2** as depicted in Scheme 3, in which neutral ligands are omitted.

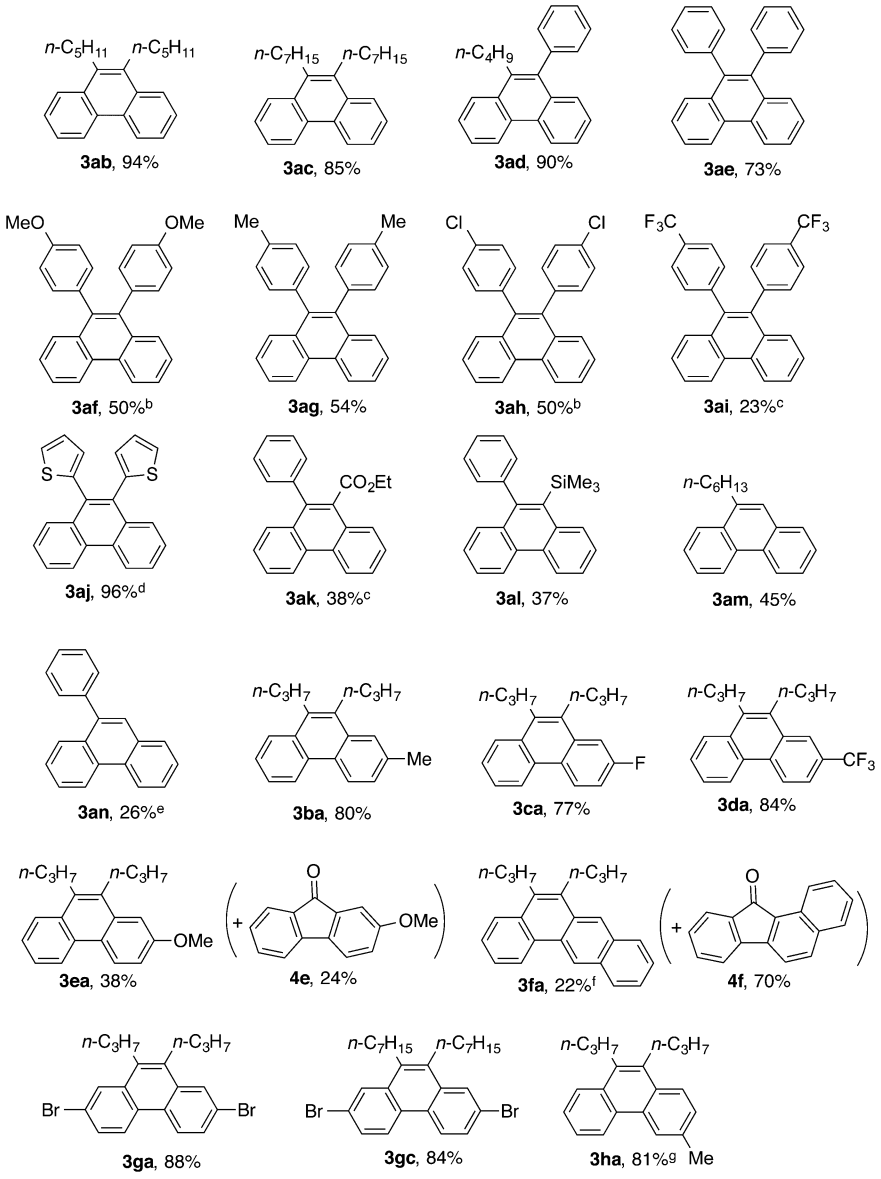
Oxidative addition of **1** to chloroiridium(I) gives aroyliridium(III) **A**, which undergoes decarbonylation to give aryliridium(III) **B**.[3f,5c,7] Then, there may be two pathways. (a) Insertion of alkyne **2** to **B** gives vinyliridium **C** and the subsequent iridation via cleavage of C2′−H bond yields seven-membered iridacycle **E**. (b) Alternatively, five-membered iridacycle **D** is formed before the insertion of **2**. In this case, the insertion occurs at both C2−Ir and C2′−Ir bonds to yield iridacycles **E** and **F**. Anyway, reductive elimination at **E** or **E**/**F** affords product **3**.[4j,8]

To provide further mechanistic information, we carried out deuterium-labeling experiments using 2-(d_5-phenyl)benzoyl chloride (**1a**-d_5) (Scheme 4). When the reaction of **1a**-d_5 with **2a** at 140 °C was stopped at 18 min and methanol was added, phenanthrene **3aa**-d_4 was formed together with methyl 2-(d_5-phenyl)benzoate (**5a**-d_5) (eq 1). ^{1}H NMR analysis of the isolated **3aa**-d_4 and **5a**-d_5 indicated that no D−H exchange took place. The reaction of **1a**-d_5 with the unsymmetrical alkyne **2d** gave a 1:1 mixture of the corresponding phenanthrenes **3ad**-d_4 and **3ad**-d_4′ (eq 2). As such an insertion of alkyl(aryl)acetylene to an aryl−metal bond usually occurs regioselectively to a greater or lesser extent,[9] this implies that pathway (b) in Scheme 3 leading to the 1:1 product mixture is predominantly involved in the catalytic cycle. No observation of 1:2 coupling product via pathway (a) followed by iridation at C3, which corresponds to Scheme 1a, is consistent with the

dx.doi.org/10.1021/jo501835u | J. Org. Chem. 2014, 79, 8960−8967

Scheme 2. Reaction of Various 2-Phenylbenzoyl Chlorides 1 with Alkynes 2[a]





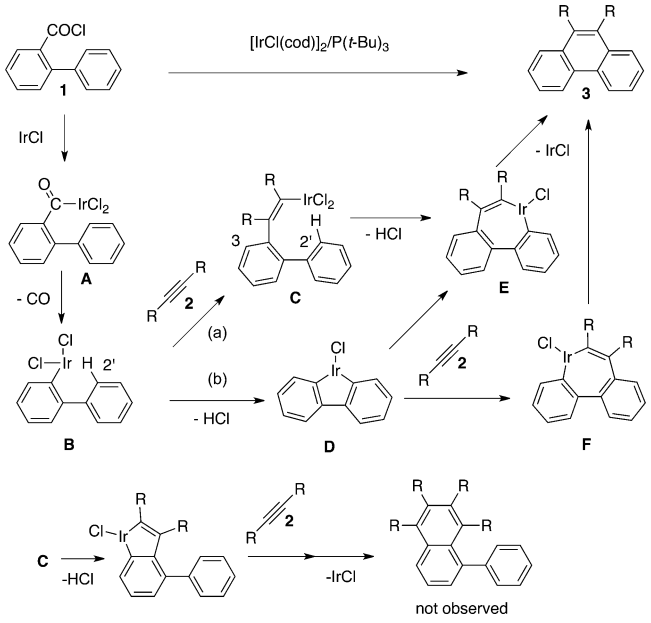
[a]Reaction conditions: **1** (0.50 mmol), **2** (0.75 mmol), $[IrCl(cod)]_2$ (0.005 mmol), P(*t*-Bu)$_3$ (0.010 mmol), *o*-xylene (2.5 mL), under N_2 for 3 h. [b]Reaction for 4 h. [c]Reaction for 5 h. [d]Reaction for 6 h. [e]Reaction for 22 h. [f]An isomer was contaminated (**3fa**/isomer = 92:8). [g]Reaction with 0.42 mmol of **1h** and 0.63 mmol of **2a**.

consideration. This is in marked contrast to the related palladium catalysis with 2-phenylbenzoic acids as substrates, in which preference for pathway (a)-type insertion was suggested.[4b] The precedence of pathway (b) may be attributed to the facile C2′−H bond cleavage under the present conditions. In connection with this, we carried out the competitive experiment with a 1:1 mixture of **1a** and **1a**-d_5 together with **2a**. The reaction proceeded even at 120 °C and gave a 1:1 mixture of **3aa** and **3aa**-d_4 at an early stage, suggesting that **1a** and **1a**-d_5 equally reacted. While the rate-determining step of the present catalytic cycle is not definitive at this stage, the observation leads us to deduce that it does not involve the C2′−H cleavage, which occurs without addition of any external base. This contrasts with the fact that in recently developed various Rh(III)-catalyzed direct coupling reactions of arenes with unsaturated compounds through C−H bond cleavage, the presence of a carboxylate species is usually required and substantial k_H/k_D values are often observed.[9,10]

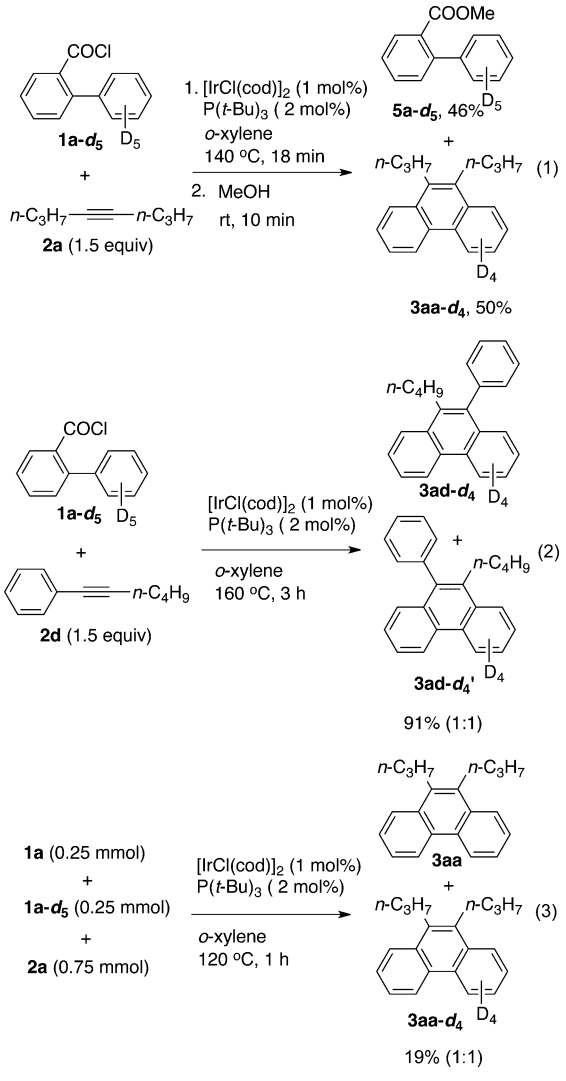
We also carried out the stoichiometric reaction of **1a**, $[IrCl(cod)]_2$, and P(*t*-Bu)$_3$ without adding alkyne as depicted

dx.doi.org/10.1021/jo501835u | J. Org. Chem. 2014, 79, 8960−8967

Scheme 3. Plausible Mechanism

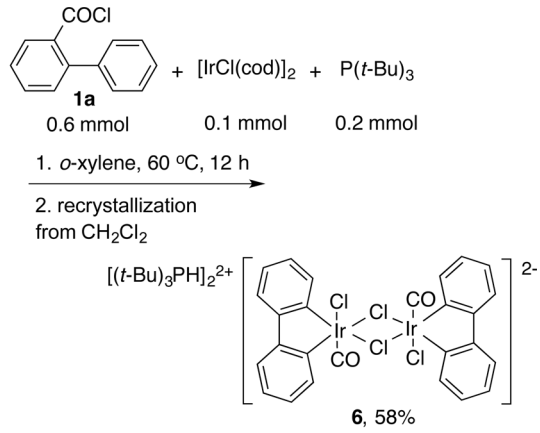


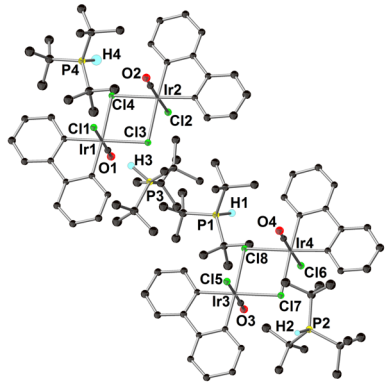
Scheme 4. Deuterium-Labeling Experiments



in Scheme 5. The reaction at 60 °C for 12 h gave an off-white solid. Dissolving it in dichloromethane and gradual evaporation

Scheme 5. Formation of Complex 6





(X-ray structure of 2 units)

of the solvent afforded a sample suitable for single-crystal X-ray analysis. Interestingly, it was found to be the dianionic iridium dimer complex **6** with the cation part of $[(t\text{-Bu})_3\text{PH}]_2^{2+}$ (Scheme 5). Its FT-IR spectrum showed two characteristic bands at 2345 (P−H) and 2019 (C═O) cm^{-1} as expected. It was confirmed that the FT-IR spectra before and after recrystallization are identical. The complex **6** may be considered as a $[(t\text{-Bu})_3\text{PH}]\text{Cl}$ adduct to the assumed intermediate **D**. Importantly, the reaction of **1a** with **2a** using **6** (1 mol %) as catalyst efficiently proceeded as in the case using $[\text{IrCl(cod)}]_2/\text{P}(t\text{-Bu})_3$ (Table 1, entry 10). The formation of **6** in the stoichiometric reaction may imply that the C2′−H cleavage that occurs even at 60 °C is likely promoted by $(t\text{-Bu})_3\text{P}$ as an internal base. It should be noted that the $^{31}\text{P}\{^1\text{H}\}$ NMR of CD_2Cl_2 solution of **6** unexpectedly showed two peaks at 50.14 and −13.96 ppm, which are assignable to $(t\text{-Bu})_3\text{PH}$ and $(t\text{-Bu})_3\text{PIr}$ species, respectively.[11] In accordance with this, the ^1H NMR of CD_2Cl_2 solution of **6** exhibited two doublets of *t*-Bu hydrogens coupled with the P atoms (J = 16 Hz) (see the Supporting Information). These NMR spectra may suggest that the complex **6** is in equilibrium with a $(t\text{-Bu})_3\text{PIr}$ species in CD_2Cl_2, while its exact structure is not definitive. On the basis of these results, it may be reasonable to consider that $(t\text{-Bu})_3\text{P}$ acts as both the internal base and ligand during the reaction.[11]

Meanwhile, the competitive formation of fluorenones **4e** and **4f** together with **3ea** and **3fa**, respectively, may be rationalized

dx.doi.org/10.1021/jo501835u | J. Org. Chem. 2014, 79, 8960−8967

by the mechanism that involves either intramolecular iridation at intermediary aroyliridium **A** or reinsertion of carbon monoxide at iridacycle **D**. It was confirmed that both **1e** and **1f** did not give the fluorenones without addition of the iridium catalyst under otherwise identical conditions. The fact that the formation of the fluorenones in the presence of alkyne **2a** was observed only in the case of the electron-rich substrates **1e** and **1f** may imply the competitive participation of iridation at aroyliridium **A**. The observation that in the reaction of **1f**, **3fa** and **4f** are formed through C−H cleavage on the different carbons, less hindered C3′ for **3fa** and hindered but relatively more electron-rich C1′ for **4f**, respectively, appears to be in harmony with the assumption.

In summary, we have demonstrated that 2-arylbenzoyl chlorides effectively undergoes annulative coupling on treatment with both aliphatic and aromatic alkynes in the presence of a catalyst system of $[IrCl(cod)]_2$/P(*t*-Bu)$_3$ to selectively give the corresponding phenanthrene derivatives. The reaction occurs without adding any external base and one of the major factors to this success may be attributed to the facile intramolecular iridation via C−H bond cleavage promoted by the phosphine ligand.

EXPERIMENTAL SECTION

Instrumentation and Chemicals. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, for $CDCl_3$ solutions. HRMS data were obtained by APCI using a TOF unless otherwise noted. GC analysis was carried out using a silicon OV-17 column (i.d. 2.6 mm × 1.5 m) or a CBP-1 capillary column (i.d. 0.5 mm × 25 m). Materials obtained from commercial suppliers were used without further purification. Acid chloride **1a** was prepared by the reaction of commercially available 1,1′-biphenyl-2-carboxylic acid with oxalyl chloride in the presence of DMF at 0 °C in dichloromethane according to the published procedure.[12] The carboxylic acids for the preparation of acid chlorides **1b**−**f**, **1h**, and **1a**-d_5 were synthesized by the nickel-catalyzed Suzuki−Miyaura-type coupling of methyl 2-iodobenzoate with the corresponding arylboronic acids followed by hydrolysis with potassium hydroxide in aqueous ethanol.[13] All of the 2-arylbenzoic acids (aryl = 4-MeC_6H_4,[14] 4-FC_6H_4,[15] 4-$CF_3C_6H_4$,[16] 4-MeOC_6H_4,[4b] 2-naphthyl,[4b] 3-MeC_6H_4,[4b] and C_6D_5[4b]) are known. 4,4′-Dibromo-1,1′-biphenyl-2-carboxylic acid was prepared from 2,7-dibromofluorenone by the published procedure.[17] The carboxylic acids were treated with oxalyl chloride as for the chlorination of 1,1′-biphenyl-2-carboxylic acid[12] to give **1b**−**h** and **1a**-d_5. The purity of the acid chlorides was confirmed by ^{1}H and ^{13}C NMR.

*2-Phenylbenzoyl chloride (**1a**):* colorless oil;[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.53 (m, 7H), 7.63 (dt, J = 7.6, 1.3 Hz, 1H), 8.03 (dd, J = 7.9, 1.1 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 127.6, 128.1, 128.6, 128.8, 131.2, 131.4, 133.2, 134.6, 139.8, 142.9, 168.5.

*2-(4-Methylphenyl)benzoyl chloride (**1b**):*[18] colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 7.23−7.27 (m, 4H), 7.41 (dd, J = 7.7, 0.9 Hz, 1H), 7.47 (dt, J = 7.7, 1.3 Hz, 1H), 7.61 (dt, J = 7.6, 1.4 Hz, 1H), 8.00 (dd, J = 7.9, 1.3 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 21.4, 127.3, 128.7, 129.4, 131.1, 131.4, 133.2, 134.7, 136.9, 138.0, 142.8, 168.6.

*2-(4-Fluorophenyl)benzoyl chloride (**1c**):*[19] orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08−7.16 (m, 2H), 7.27−7.33 (m, 2H), 7.38 (dd, J = 7.7, 1.4 Hz, 1H), 7.50 (dt, J = 7.7, 1.2 Hz, 1H), 7.63 (dt, J = 7.6, 1.4 Hz, 1H), 8.04 (dd, J = 7.9, 1.1 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 115.6 (d, J = 21.1 Hz), 127.8, 130.5 (d, J = 8.3 Hz), 131.4, 131.5, 133.4, 134.5, 135.8 (d, J = 3.6 Hz), 141.9, 162.8 (d, J = 245.9 Hz), 168.4.

*2-[4-(Trifluoromethyl)phenyl]benzoyl chloride (**1d**):*[20] colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, J = 7.6, 0.9 Hz, 1H), 7.44 (d, J = 8.0 Hz, 2H), 7.56 (dt, J = 7.7, 1.2 Hz, 1H), 7.64−7.72 (m, 3H), 8.12 (dd, J = 7.9, 1.1 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 124.2 (q, J = 269.0 Hz), 125.5 (q, J = 3.7 Hz), 128.4, 129.2, 130.2 (q, J = 32.5 Hz), 131.3, 131.9, 133.6, 134.1, 141.7, 143.6, 168.2.

*2-(4-Methoxyphenyl)benzoyl chloride (**1e**):*[21] colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 6.94−7.00 (m, 2H), 7.25−7.30 (m, 2H), 7.40 (dd, J = 7.7, 0.9 Hz, 1H), 7.45 (dt, J = 7.7, 1.3 Hz, 1H), 7.60 (dt, J = 7.6, 1.4 Hz, 1H), 7.98 (dd, J = 7.9, 1.0 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 55.4, 114.1, 127.2, 130.1, 131.1, 131.4, 132.1, 133.1, 134.6, 142.4, 159.7, 168.8.

*2-(2-Naphthyl)benzoyl chloride (**1f**):*[22] yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, J = 8.4, 1.7 Hz, 1H), 7.49−7.56 (m, 4H), 7.63−7.69 (m, 1H), 7.82 (s, 1H), 7.85−7.93 (m, 3H), 8.08 (d, J = 7.9 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 126.57, 126.61, 127.0, 127.7, 127.8, 127.9, 128.2, 128.3, 131.5, 131.7, 132.9, 133.3, 133.4, 134.6, 137.4, 142.9, 168.5.

4,4′-Dibromobiphenyl-2-carboxylic acid:[17] white solid; mp 212 °C; ^{1}H NMR (400 MHz, $(CH_3)_2SO$) δ 7.25−7.30 (m, 2H), 7.33 (d, J = 8.3 Hz, 1H), 7.57−7.63 (m, 2H), 7.78 (dd, J = 8.2, 2.2 Hz, 1H), 8.90 (d, J = 2.1 Hz, 1H), 13.20 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $(CH_3)_2SO$) δ 120.7, 121.0, 130.4, 131.1, 131.7, 132.5, 133.8, 133.9, 138.98, 139.03, 167.7.

*4,4′-Dibromobiphenyl-2-carbonyl chloride (**1g**):* pale yellow solid; mp 82−83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15−7.21 (m, 2H), 7.27−7.29 (s, 1H), 7.55−7.61 (m, 2H), 7.77 (dd, J = 8.2, 2.1 Hz, 1H), 8.16 (d, J = 2.0 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 121.9, 122.9, 130.3, 132.0, 132.7, 133.9, 135.8, 136.3, 137.6, 140.3, 167.2; HRMS (EI) m/z calcd for $C_{13}H_7Br_2ClO$ (M^+) 371.8552, found 371.8551.

*2-(3-Metylphenyl)benzoyl chloride (**1h**):*[4b] colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 7.11−7.19 (m, 2H), 7.20−7.25 (m, 1H), 7.32 (dd, J = 7.5, 7.5 Hz, 1H), 7.41 (dd, J = 7.7, 1.2 Hz, 1H), 7.48 (ddd, J = 7.7, 7.7, 1.3 Hz, 1H), 7.61 (ddd, J = 7.6, 7.6, 1.3 Hz, 1H), 8.01 (dd, J = 7.9, 1.3 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 21.6, 126.0, 127.5, 128.5, 128.9, 129.5, 131.1, 131.4, 133.1, 134.6, 138.3, 139.8, 143.0, 168.5.

Typical Procedure for Reaction of 1 with 2. The synthesis of **3aa** is representative: in a 20 mL two-necked flask were placed $[IrCl(cod)]_2$ (3.4 mg, 0.005 mmol) and P(*t*-Bu)$_3$ (2 mg, 0.01 mmol) in *o*-xylene (0.1 mL). The central neck of the flask was equipped with a reflux condenser having an N_2 balloon connected by a three-way cock at its top, and a rubber cap was inserted to the side neck. The flask was evacuated and filled with nitrogen (three times). A solution of acid chloride **1a** (108.3 mg, 0.5 mmol) and alkyne **2a** (82.7 mg, 0.75 mmol) in *o*-xylene (2.4 mL) was injected, and the resulting mixture was heated at 160 °C (bath temperature) with stirring for 3 h. After cooling, the solvent was evaporated, and the residue was fractionated by column chromatography on silica gel. Elution with hexane gave phenanthrene **3aa** (109 mg, 83%).

*9,10-Dipropylphenanthrene (**3aa**):*[4j] white solid; mp 97−98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, J = 7.4 Hz, 6H), 1.72−1.83 (m, 4H), 3.12−3.19 (m, 4H), 7.58−7.66 (m, 4H), 8.09−8.15 (m, 2H), 8.70−8.78 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 15.0, 24.2, 31.7, 123.1, 124.9, 125.5, 126.7, 130.0, 131.5, 134.0; HRMS m/z calcd for $C_{20}H_{23}$ ($M + H^+$) 263.1794, found 263.1794.

*9,10-Dipentylphenanthrene (**3ab**):*[23] purified by column chromatography with hexane as eluent (149 mg, 94%); white solid; mp 58−59 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, J = 7.2 Hz, 6H), 1.42−1.52 (m, 4H), 1.53−1.63 (m, 4H), 1.68−1.80 (m, 4H), 3.10−3.20 (m, 4H), 7.57−7.66 (m, 4H), 8.09−8.15 (m, 2H), 8.70−8.76 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.3, 22.8, 29.5, 30.6, 32.8, 123.1, 124.8, 125.5, 126.7, 130.0, 131.5, 134.1; HRMS m/z calcd for $C_{24}H_{31}$ ($M + H^+$) 319.2420, found 319.2420.

*9,10-Diheptylphenanthrene (**3ac**):* purified by column chromatography with hexane as eluent; white solid (159 mg, 85%); mp 33−34 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, J = 6.9 Hz, 6H), 1.33−1.50 (m, 12H), 1.55−1.65 (m, 4H), 1.70−1.80 (m, 4H), 3.13−3.20 (m, 4H), 7.58−7.67 (m, 4H), 8.10−8.16 (m, 2H), 8.71−8.77 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.3, 22.9, 29.4, 29.5, 30.6, 30.9, 32.1, 123.1, 124.8, 125.5, 126.7, 130.0, 131.5, 134.1; HRMS m/z calcd for $C_{28}H_{39}$ ($M + H^+$) 375.3046, found 375.3041.

dx.doi.org/10.1021/jo501835u | J. Org. Chem. 2014, 79, 8960−8967

*9-Butyl-10-phenylphenanthrene (**3ad**).* purified by column chromatography with hexane as eluent (140 mg, 90%); white solid; mp 119−120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (t, J = 7.4 Hz, 3H), 1.31 (sextuplet, J = 7.4 Hz, 2H), 1.56−1.65 (m, 2H), 2.82−2.89 (m, 2H), 7.30−7.35 (m, 3H), 7.39−7.61 (m, 5H), 7.65−7.71 (m, 2H), 8.14−8.20 (m, 1H), 8.70−8.76 (m, 1H), 8.77−8.83 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 13.9, 23.3, 30.4, 33.2, 122.4, 123.2, 125.4, 125.8, 126.2, 126.5, 126.9, 127.2, 127.7, 128.5, 129.5, 130.4, 130.6, 131.1, 132.6, 135.0, 137.0, 140.7; HRMS m/z calcd for $C_{24}H_{23}$ (M + H$^+$) 311.1794, found 311.1794.

*9,10-Diphenylphenanthrene (**3ae**):*[4i] purified by column chromatography with hexane/ethyl acetate (95:5, v/v) as eluent (120 mg, 73%); white solid; mp 238−239 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12−7.27 (m, 10H), 7.45−7.51 (m, 2H), 7.53−7.59 (m, 2H), 7.63−7.70 (m, 2H), 8.81 (d, J = 8.3 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 122.6, 126.5, 126.6, 126.8, 127.7, 128.0, 130.1, 131.2, 132.0, 137.3, 139.7; HRMS m/z calcd for $C_{26}H_{19}$ (M + H$^+$) 331.1481, found 331.1480.

*9,10-Bis(4-methoxyphenyl)phenanthrene (**3af**):*[4i] purified by recrystallization from toluene; white solid (98 mg, 50%); mp 263−264 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 6H), 6.80 (d, J = 8.8 Hz, 4H), 7.06 (d, J = 8.8 Hz, 4H), 7.48 (ddd, J = 8.1, 6.9, 1.2 Hz, 2H), 7.59 (dd, J = 8.3, 1.0 Hz, 2H), 7.65 (ddd, J = 8.3, 6.9, 1.4 Hz, 2H), 8.80 (d, J = 8.3 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 55.3, 113.2, 122.6, 126.4, 126.7, 128.0, 130.1, 132.1, 132.2, 132.5, 137.3, 158.1; HRMS m/z calcd for $C_{28}H_{23}O_2$ (M + H$^+$) 391.1693, found 391.1694.

*9,10-Bis(4-methylphenyl)phenanthrene (**3ag**):*[4j] purified by recrystallization from toluene; white solid (97 mg, 54%); mp 246 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 6H), 7.03−7.08 (m, 8H), 7.47 (ddd, J = 8.1, 6.8, 1.1 Hz, 2H), 7.56 (dd, J = 8.3, 1.3 Hz, 2H), 7.65 (ddd, J = 8.3, 6.8, 1.4 Hz, 2H), 8.80 (d, J = 8.2 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 21.4, 122.6, 126.4, 126.6, 128.0, 128.5, 130.1, 131.0, 132.3, 135.9, 136.8, 137.3; HRMS m/z calcd for $C_{28}H_{23}$ (M + H$^+$) 359.1794, found 359.1791.

*9,10-Bis(4-chlorolphenyl)phenanthrene (**3ah**):*[4b] purified by recrystallization from toluene and preparative GPC (100 mg, 50%); white solid; mp 251−252 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05−7.10 (m, 4H), 7.23−7.28 (m, 4H), 7.47−7.53 (m, 4H), 7.65−7.72 (m, 2H), 8.81 (d, J = 8.4 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 122.8, 126.9, 127.0, 127.7, 128.3, 130.2, 131.6, 132.4, 132.9, 136.3, 137.9; HRMS m/z calcd for $C_{26}H_{17}Cl_2$ (M + H$^+$) 399.0702, found 399.0714.

*9,10-Bis(4-(trifluoromethyl)phenyl)phenanthrene (**3ai**):* purified by recrystallization from toluene (54 mg, 23%); white solid; mp 287−288 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.0 Hz, 4H), 7.44 (d, J = 8.2 Hz, 2H), 7.49−7.57 (m, 6H), 7.72 (ddd, J = 8.3, 7.0, 1.2 Hz, 2H), 8.84 (d, J = 8.2 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 122.9, 124.2 (q, J = 270.5 Hz), 125.0 (q, J = 3.7 Hz), 127.2, 127.6, 129.3 (q, J = 32.0 Hz), 130.3, 131.2, 131.4, 136.1, 143.1 (one peak is overlapped); HRMS m/z calcd for $C_{28}H_{17}F_6$ (M + H$^+$) 467.1229, found 467.1230.

*9,10-Di(thiophene-2-yl)phenanthrene (**3aj**):*[24] purified by column chromatography with hexane/ethyl acetate (98:2, v/v) as eluent (164 mg, 96%); white solid; mp 245 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (dd, J = 3.4, 1.2 Hz, 2H), 7.02 (dd, J = 5.1, 3.4 Hz, 2H), 7.34 (dd, J = 5.1, 1.2 Hz, 2H), 7.55 (ddd, J = 8.2, 7.0, 1.2 Hz, 2H), 7.70 (ddd, J = 8.3, 7.0, 1.3 Hz, 2H), 7.81 (dd, J = 8.3, 1.0 Hz, 2H), 8.78 (d, J = 8.2 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 122.6, 126.3, 126.5, 127.1, 127.3, 128.0, 129.4, 130.4, 132.3, 132.4, 139.9; HRMS m/z calcd for $C_{22}H_{15}S_2$ (M$^+$) 343.0610, found 343.0611.

*Ethyl 10-phenylphenanthrene-9-carboxylate (**3ak**):*[25] purified by column chromatography with hexane/ethyl acetate (95:5, v/v) as eluent and preparative GPC (62 mg, 38%); pale yellow solid; mp 128−129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, J = 7.1 Hz, 3H), 4.12 (q, J = 7.1 Hz, 2H), 7.42−7.55 (m, 6H), 7.62−7.75 (m, 4H), 7.94 (dd, J = 8.1, 1.3 Hz, 1H), 8.77 (d, J = 8.2 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 13.9, 61.3, 122.8, 123.0, 126.0, 127.0, 127.2, 127.56, 127.59, 127.9, 128.1, 128.2, 130.1, 130.5, 130.77, 130.81, 131.0, 136.6, 138.2, 169.4; HRMS m/z calcd for $C_{23}H_{19}O_2$ (M + H$^+$) 327.1380, found 327.1387.

*Trimethyl(9-phenylphenanthren-1-yl)silane (**3al**):*[4c] purified by column chromatography with hexane as eluent and preparative GPC (60 mg, 37%); pale yellow solid; mp 161−162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.29 (s, 9H), 5.96 (d, J = 8.0 Hz, 1H), 6.81 (ddd, J = 8.0, 7.4, 1.2 Hz, 1H), 7.05−7.11 (m, 2H), 7.18 (dt, J = 7.4, 1.0 Hz, 1H), 7.28−7.47 (m, 5H), 7.64 (d, J = 7.4 Hz, 1H), 7.72 (d, J = 7.4 Hz, 1H), 7.99 (d, J = 7.7 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 0.6, 119.1, 119.5, 125.7, 126.16, 126.22, 126.55, 126.64, 126.9, 127.9, 128.2, 129.0, 138.6, 139.0, 140.6, 141.3, 145.2, 145.8, 149.4; HRMS m/z calcd for $C_{23}H_{23}Si$ (M + H$^+$) 327.1564, found 327.1570.

*9-Hexylphenanthrene (**3am**):*[26] purified by column chromatography with hexane as eluent and preparative GPC (59 mg, 45%); white solid; mp 77−78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, J = 7.1 Hz, 3H), 1.30−1.43 (m, 4H), 1.45−1.55 (m, 2H), 1.78−1.88 (m, 2H), 3.12 (t, J = 7.7 Hz, 2H), 7.55−7.70 (m, 5H), 7.81−7.87 (m, 1H), 8.09−8.16 (m, 1H), 8.63−8.70 (m, 1H), 8.71−8.79 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.3, 22.8, 29.7, 30.4, 31.9, 33.6, 122.6, 123.3, 124.6, 126.0, 126.1, 126.2, 126.6, 126.7, 128.1, 129.7, 130.8, 131.5, 132.1, 137.2; HRMS m/z calcd for $C_{20}H_{23}$ (M + H$^+$) 263.1794, found 263.1802.

*9-Phenylphenanthrene (**3an**):*[25] purified by column chromatography with hexane as eluent and preparative GPC (32 mg, 25%); white solid; mp 104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.60 (m, 6H), 7.61−7.74 (m, 4H), 7.88−7.97 (m, 2H), 8.75 (dd, J = 8.1, 0.5 Hz, 1H), 8.80 (ddd, J = 8.3, 0.5, 0.5 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 122.7, 123.0, 126.58, 126.63, 126.7, 127.0, 127.1, 127.5, 127.6, 128.4, 128.8, 130.1, 130.2, 130.8, 131.3, 131.7, 138.9, 140.9; HRMS m/z calcd for $C_{20}H_{15}$ (M + H$^+$) 255.1168, found 255.1169.

*2-Methyl-9,10-dipropylphenanthrene (**3ba**):* purified by column chromatography with hexane as eluent (110 mg, 80%); white solid, mp 71−73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (t, J = 7.3 Hz, 3H), 1.21 (t, J = 7.3 Hz, 3H), 1.73−1.85 (m, 4H), 2.63 (s, 3H), 3.12−3.20 (m, 4H), 7.45 (dd, J = 8.4, 1.4 Hz, 1H), 7.57−7.64 (m, 2H), 7.90 (s, 1H), 8.09−8.15 (m, 1H), 8.63 (d, J = 8.5 Hz, 1H), 8.67−8.74 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 15.0 (2C), 22.2, 24.1, 24.2, 31.6, 31.7, 122.9, 123.0, 124.5, 124.8, 125.4, 126.2, 127.2, 127.8, 130.0, 131.1, 131.6, 133.7, 134.0, 136.2; HRMS m/z calcd for $C_{21}H_{25}$ (M + H$^+$) 277.1951, found 277.1950.

*2-Fluoro-9,10-dipropylphenanthrene (**3ca**):* purified by column chromatography with hexane as eluent (108 mg, 77%); white solid, mp 88−89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, J = 7.3 Hz, 3H), 1.19 (t, J = 7.4 Hz, 3H), 1.69−1.82 (m, 4H), 3.04−3.11 (m, 2H), 3.11−3.18 (m, 2H), 7.34 (ddd, J = 9.1, 7.8, 2.6 Hz, 1H), 7.58−7.65 (m, 2H), 7.73 (dd, J = 11.7, 2.6 Hz, 1H), 8.08−8.15 (m, 1H), 8.60−8.66 (m, 1H), 8.68 (dd, J = 9.2, 5.9 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.9, 15.0, 23.9, 24.1, 31.7, 31.8, 109.5 (d, J = 21.3 Hz), 114.3 (d, J = 23.4 Hz), 122.9, 125.0, 125.3 (d, J = 8.8 Hz), 125.9, 126.5, 126.6, 129.7, 131.0, 133.2 (d, J = 8.0 Hz), 133.4 (d, J = 3.7 Hz), 135.4, 161.8 (d, J = 242.7 Hz); HRMS m/z calcd for $C_{20}H_{22}F$ (M + H$^+$) 281.1700, found 281.1693.

*9,10-Dipropyl-2-(trifluoromethyl)phenanthrene (**3da**):* purified by column chromatography with hexane as eluent (139 mg, 84%); white solid, mp 106−107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, J = 7.4 Hz, 6H), 1.69−1.82 (m, 4H), 3.11−3.20 (m, 4H), 7.60−7.73 (m, 2H), 7.78 (dd, J = 8.7, 1.5 Hz, 1H), 8.14 (dd, J = 8.0, 1.3 Hz, 1H), 8.36 (s, 1H), 8.72 (dd, J = 8.0, 1.4 Hz, 1H), 8.80 (d, J = 8.7 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.86, 14.94, 24.1, 24.3, 31.5, 31.7, 121.3 (q, J = 3.2 Hz), 122.2 (q, J = 4.3 Hz), 123.5, 123.9, 124.8 (q, J = 270.7 Hz) 125.1, 126.1, 127.8, 128.3 (q, J = 31.8 Hz), 129.2, 131.0, 132.1, 132.2, 133.9, 135.7; HRMS m/z calcd for $C_{21}H_{22}F_3$ (M + H$^+$) 331.1668, found 331.1659.

*2-Methoxy-9,10-dipropylphenanthrene (**3ea**):* purified by column chromatography with hexane/ethyl acetate (98:2, v/v) as eluent (55 mg, 38%); pale yellow solid, mp 64−66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, J = 7.3 Hz, 3H), 1.19 (t, J = 7.3 Hz, 3H), 1.72−1.85 (m, 4H), 3.08−3.19 (m, 4H), 4.00 (s, 3H), 7.26 (dd, J = 9.1, 2.6 Hz, 1H), 7.51 (d, J = 2.6 Hz, 1H), 7.54−7.62 (m, 2H), 8.07−8.13 (m, 1H), 8.59−8.68 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.97, 15.02, 23.8, 24.2, 31.75, 31.80, 55.5, 106.5, 114.8, 122.6, 124.3, 124.7,

dx.doi.org/10.1021/jo501835u | J. Org. Chem. 2014, 79, 8960−8967

124.9, 125.6, 125.7, 130.0, 130.4, 132.9, 133.4, 134.7, 158.4; HRMS *m*/*z* calcd for $C_{21}H_{25}O$ (M + H$^+$) 293.1900, found 293.1907.

*5,6-Dipropyltetraphene (**3fa**):* purified by column chromatography with hexane/ethyl acetate (98:2, v/v) as eluent (34 mg, 22%); pale yellow solid, mp 105−107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (t, *J* = 7.4 Hz, 3H), 1.23 (t, *J* = 7.3 Hz, 3H), 1.74−1.91 (m, 4H), 3.10−3.18 (m, 2H), 3.20−3.27 (m, 2H), 7.51−7.57 (m, 2H), 7.61−7.67 (m, 2H), 8.05−8.13 (m, 3H), 8.55 (s, 1H), 8.85−8.91 (m, 1H), 9.20 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.99, 15.04, 23.94, 23.96, 31.8 (2C), 121.8, 123.26, 123.31, 125.0, 125.6, 125.7, 125.9, 127.2, 128.2, 128.3, 128.9, 130.27, 130.32, 131.2, 131.8, 132.2, 133.78, 133.84; HRMS *m*/*z* calcd for $C_{24}H_{25}$ (M + H$^+$) 313.1951, found 313.1950.

*2,7-Dibromo-9,10-dipropylphenanthrene (**3ga**):* purified by column chromatography with hexane as eluent (185 mg, 88%); white solid, mp 82−83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (t, *J* = 7.3 Hz, 6H), 1.65−1.77 (m, 4H), 3.02−3.09 (m, 4H), 7.66 (d, *J* = 8.7 Hz, 2H), 8.18 (d, *J* = 1.8 Hz, 2H), 8.47 (d, *J* = 8.8, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.9, 24.0, 31.6, 121.5, 124.7, 127.5, 128.2, 129.0, 133.0, 134.5; HRMS *m*/*z* calcd for $C_{20}H_{20}Br_2$ (M$^+$) 417.9932, found 417.9926.

*2,7-Dibromo-9,10-diheptylphenanthrene (**3gc**):* purified by column chromatography with hexane as eluent (225 mg, 84%); white solid, mp 62−64 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, *J* = 6.9 Hz, 6H), 1.30−1.47 (m, 12H), 1.51−1.61 (m, 4H), 1.61−1.73 (m, 4H), 3.00−3.09 (m, 4H), 7.65 (dd, *J* = 8.8, 1.8 Hz, 2H), 8.18 (d, *J* = 1.9 Hz, 2H), 8.44 (d, *J* = 8.8 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.3, 22.9, 29.2, 29.4, 30.4, 30.7, 32.0, 121.5, 124.7, 127.5, 128.2, 128.9, 133.0, 134.6; HRMS *m*/*z* calcd for $C_{28}H_{36}Br_2$ (M$^+$) 530.1184, found 530.1187.

*3-Methyl-9,10-dipropylphenanthrene (**3ha**):* purified by column chromatography with hexane as eluent (94 mg, 81%); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, *J* = 7.3 Hz, 6H), 1.71−1.84 (m, 4H), 2.63 (s, 3H), 3.10−3.19 (m, 4H), 7.46 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.56−7.65 (m, 2H), 8.02 (d, *J* = 8.5 Hz, 1H), 8.08−8.14 (m, 1H), 8.53 (s, 1H), 8.70−8.77 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 15.0, 22.0, 24.15, 24.20, 31.6, 31.7, 122.9, 123.0, 124.79, 124.84, 125.3, 126.5, 128.4, 129.4, 129.7, 130.0, 131.7, 133.0, 133.9, 135.0; HRMS *m*/*z* calcd for $C_{21}H_{25}$ (M + H$^+$) 277.1951, found 277.1947.

*2-Methoxy-9H-fluoren-9-one (**4e**):*[27] purified by column chromatography with hexane/ethyl acetate (98:2, v/v) as eluent (25 mg, 24%); yellow solid, mp 74−76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 3H), 6.97 (dd, *J* = 8.2, 2.4 Hz, 1H), 7.16−7.22 (m, 2H), 7.37−7.46 (m, 3H), 7.57−7.62 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 55.9, 109.5, 119.7, 120.4, 121.5, 124.5, 128.0, 134.4, 135.0, 136.0, 137.1, 145.0, 161.0, 194.0; HRMS *m*/*z* calcd for (M + H$^+$) 211.0754, found 211.0768.

*11H-Benzo[a]fluoren-11-one (**4f**):*[28] purified by column chromatography with hexane/ethyl acetate (98:2, v/v) as eluent (81 mg, 70%); orange solid, mp 130−132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21−7.28 (m, 1H), 7.37−7.46 (m, 3H), 7.54−7.61 (m, 3H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 8.93 (d, *J* = 8.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 118.2, 120.0, 123.9, 124.4, 126.5, 126.9, 128.6, 129.3, 129.5, 130.3, 134.3, 134.5, 134.7, 136.0, 144.0, 146.2, 195.5; HRMS *m*/*z* calcd for $C_{17}H_{11}O$ (M + H$^+$) 231.0804, found 231.0800.

Preparation of Complex 6. In a 20 mL two-necked flask were placed $[IrCl(cod)]_2$ (67.2 mg, 0.1 mmol) and P(*t*-Bu)$_3$ (40.5 mg, 0.2 mmol) in *o*-xylene (0.5 mL). The central neck of the flask was equipped with a reflux condenser having an N_2 balloon connected by a three-way cock at its top, and a rubber cap was inserted to the side neck. The flask was evacuated and filled with nitrogen (three times). A solution of acid chloride **1a** (130 mg, 0.6 mmol) in *o*-xylene (1.5 mL) was injected and the resulting mixture was heated at 60 °C with stirring for 12 h. After cooling, the solvent was evaporated and the residue was washed with diethyl ether and hexane to give an off-white solid (108 mg). Dissolving it in dichloromethane (ca. 15 mL) and gradual evaporation of the solvent afforded the analytical sample of complex **6** (75 mg, 58%). The structure was confirmed by single-crystal X-ray (Mo Kα) diffraction (Scheme 5 and the Supporting Information, CCDC 1018164): FT-IR (KBr) 2345, 2019 cm^{-1}. Anal. Calcd for $C_{50}H_{72}Cl_4Ir_2O_2P_2$: C, 46.43; H, 5.61. Found: C, 46.14; H, 5.47.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra for compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: miura@chem.eng.osaka-u.ac.jp.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by Grants-in-Aid for Scientific Research from the MEXT and JSPS, Japan. We thank Dr. M. Ohashi of Osaka University for X-ray analysis and helpful discussions.

■ REFERENCES

(1) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons*; Wiley-VCH: New York, 1996.

(2) (a) Watanabe, M.; Chen, K.-Y.; Chang, Y. J.; Chow, T. J. *Acc. Chem. Res.* **2013**, *46*, 1606. (b) Anthony, J. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 452. (c) Wu, J.; Pisula, W.; Müllen, K. *Chem. Rev.* **2007**, *107*, 718. (d) Murphy, A. R.; Fréchet, J. M. J. *Chem. Rev.* **2007**, *107*, 1066. (e) Sergeyev, S.; Pisula, W.; Geerts, Y. H. *Chem. Soc. Rev.* **2007**, *36*, 1902. (f) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028. (g) Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891. (h) Watson, M. D.; Fechtenkötter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267.

(3) X = $CrPh_2$: (a) Whitesides, G. M.; Ehmann, W. J. *J. Am. Chem. Soc.* **1970**, *92*, 5625. (b) Herwig, W.; Metlesics, W.; Zeiss, H. *J. Am. Chem. Soc.* **1959**, *81*, 6203. X = I: (c) Kawasaki, S.; Satoh, T.; Miura, M.; Nomura, M. *J. Org. Chem.* **2003**, *68*, 6836. (d) Wu, G.; Rheingold, A. L.; Feib, S. L.; Heck, R. F. *Organometallics* **1987**, *6*, 1941. (e) Sakakibara, T.; Tanaka, Y.; Yamasaki, T.-I. *Chem. Lett.* **1986**, 797. X = COCl: (f) Yasukawa, T.; Satoh, T.; Miura, M.; Nomura, M. *J. Am. Chem. Soc.* **2002**, *124*, 12680. X = CO_2H: (g) Yamashita, M.; Horiguchi, H.; Hirano, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2009**, *74*, 7481. (h) Yamashita, M.; Hirano, K.; Satoh, T.; Miura, M. *Org. Lett.* **2009**, *11*, 2337. (i) Ueura, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2007**, *72*, 5362. X = $B(OH)_2$: (j) Fukutani, T.; Hirano, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2011**, *76*, 2867. X = CR_2OH: (k) Uto, T.; Shimizu, M.; Ueura, K.; Tsurugi, H.; Satoh, T.; Miura, M. *J. Org. Chem.* **2008**, *73*, 298. X = H: (l) Umeda, N.; Hirano, K.; Satoh, T.; Shibata, N.; Sato, H.; Miura, M. *J. Org. Chem.* **2011**, *76*, 13. (m) Umeda, N.; Tsurugi, H.; Satoh, T.; Miura, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 4019. (n) Wu, Y.-T.; Huang, K.-H.; Shin, C.-C.; Wu, T.-C. *Chem.—Eur. J.* **2008**, *14*, 6697. (o) Pham, M. V.; Cramer, N. *Angew. Chem., Int. Ed.* **2014**, *53*, 3484.

(4) (a) Larock, R. C.; Doty, M. J.; Tian, Q.; Zenner, J. M. *J. Org. Chem.* **1997**, *62*, 7536. (b) Wang, C.; Rakshit, S.; Glorius, F. *J. Am. Chem. Soc.* **2010**, *132*, 14006. (c) Kanno, K.; Liu, Y.; Iesato, A.; Nakajima, K.; Takahashi, T. *Org. Lett.* **2005**, *7*, 5453. (d) Matsumoto, A.; Ilies, L.; Nakamura, E. *J. Am. Chem. Soc.* **2011**, *133*, 6557. (e) Feng, C.-N.; Kuo, M.-Y.; Wu, Y.-T. *Angew. Chem., Int. Ed.* **2013**, *52*, 7791. With 2,2′-dihalobiphenyls: (f) Watanabe, H.; Kumagai, J.; Tsurugi, H.; Satoh, T.; Miura, M. *Chem. Lett.* **2007**, *36*, 1336. (g) Lin, Y.-D.; Cho, C.-L.; Ko, C.-W; Pulte, A.; Wu, Y.-T. *J. Org. Chem.* **2012**, *77*, 9979. (h) Mandal, A. B.; Lee, G.-H.; Liu, Y.-H.; Peng, S.-M.; Leung, M.-K. *J. Org. Chem.* **2010**, *65*, 332. (i) Shimizu, M.; Nagao, I.; Tomioka, Y.; Kadowaki, T.; Hiyama, T. *Tetrahedron* **2011**, *67*, 8014. With biphenylene: (j) Krotvička, A.; Císařová, I.; Roithová, J.; Kotora, M. *Chem.—Eur. J.* **2012**, *18*, 4200.

(5) Related Rh-catalyzed chloroarylation and annulation of alkynes with aroyl chlorides to give 2-chrolostyrenes and indenones: (a) Kokubo, K.; Matsumasa, K.; Miura, M.; Nomura, M. *J. Org. Chem.* **1996**, *61*, 6941. Ir-catalyzed chloroaroylation: (b) Iwai, T.; Fujihara, T.; Terao, J.; Tsuji, Y. *J. Am. Chem. Soc.* **2009**, *131*, 6668. (c) Iwai, T.; Fujihara, T.; Terao, J.; Tsuji, Y. *J. Am. Chem. Soc.* **2012**, *134*, 1268. Fe-catalyzed chroloaroylation: (d) Wang, B.; Wang, S.; Li, P.; Wang, L. *Chem. Commun.* **2010**, *46*, 5891. (e) Gandeepan, P.; Parthasarathy, K.; Su, T.-H.; Chen, C.-H. *Adv. Synth. Catal.* **2012**, *354*, 457.

(6) (a) Yang, C.; Schreiber, H.; List, E. J. W.; Jacob, J.; Müllen, K. *Macromolecules* **2006**, *39*, 5213. (b) Büsing, A.; Heun, S.; Türk, S.; Leske, C. Patent WO2005104264, Nov 3, 2005. (c) Tokimitsu, R.; Koizumi, T.; Yamamoto, T. *Chem. Lett.* **2011**, *40*, 282.

(7) (a) Kubota, M.; Blake, D. M. *J. Am. Chem. Soc.* **1971**, *93*, 1368. (b) Blum, J.; Kraus, S.; Pickholtz, Y. *J. Organomet. Chem.* **1971**, *33*, 227.

(8) Lu, Z.; Jun, C.-H.; de Gala, S. R.; Sigalas, M. P.; Eisenstein, O.; Crabtree, R. H. *Organometallics* **1995**, *14*, 1168.

(9) (a) Satoh, T.; Miura, M. *Chem. —Eur. J.* **2010**, *16*, 11212. (b) D. A. Colby, D. A.; Tsai, A. S.; Bergman, R. G.; Ellman, J. A. *Acc. Chem. Res.* **2012**, *45*, 814. (c) Patureau, F. W.; Wencel-Delord, J.; Glorius, F. *Aldrichimica Acta* **2012**, *45*, 31. (d) Song, G.; Wang, F.; Li, X. *Chem. Soc. Rev.* **2012**, *41*, 3651.

(10) Carr, K. J. T.; Davies, D. L.; Macgregor, S. A.; Singh, K.; Villa-Marcos, B. *Chem. Sci.* **2014**, *5*, 2340.

(11) Barrios-Landeros, F.; Carrow, B. P.; Hartwig, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 5842.

(12) Branca, M.; Pena, S.; Guillot, R.; Gori, D.; Alezra, V.; Kouklovsky, C. *J. Am. Chem. Soc.* **2009**, *131*, 10711.

(13) Percec, V.; Golding, G. M.; Smidrkal, J.; Weichold, O. *J. Org. Chem.* **2004**, *69*, 3447.

(14) Asachenko, A. F.; Sorochkina, K. R.; Dzhevakov, P. B.; Topchiy, M. A.; Nechaev, M. S. *Adv. Synth. Catal.* **2013**, *355*, 3553.

(15) Li, Y.; Ding, Y.-J.; Wang, J.-Y.; Su, Y.-M.; Wang, X.-S. *Org. Lett.* **2013**, *15*, 2574.

(16) Tao, B.; Goel, S. C.; Singh, J.; Boykin, D. W. *Synthesis* **2002**, 1043.

(17) Bradsher, C. K.; Beavers, L. E.; Tokura, N. *J. Am. Chem. Soc.* **1956**, *78*, 3196.

(18) Matsuhisa, A.; Kikuchi, K.; Sakamoto, K.; Yatsu, T.; Tanaka, A. *Chem. Pharm. Bull.* **1999**, *47*, 329.

(19) Priepke, H.; Hauel, N.; Thomas, L.; Mark, M.; Dahmann, G. *PCT Int. Appl.* WO 2002004403 A1 20020117, 2002.

(20) Fink, C. A.; Ksander, G. M.; Kukkola, P. J.; Wallace, E. M.; Prashad, M. US 6197798 B1 Mar 06, 2001.

(21) Swenton, J. S.; Ikeler, T. J.; Smyser, G. L. *J. Org. Chem.* **1973**, *38*, 1157.

(22) Cook, J. W.; Schoental, R. *J. Chem. Soc.* **1945**, 288.

(23) Yoshikawa, E.; Radhakrishnan, K. V.; Yamamoto, Y. *J. Am. Chem. Soc.* **2000**, *122*, 7280.

(24) He, B.; Tian, H.; Geng, Y.; Wang, F.; Müllen, K. *Org. Lett.* **2008**, *10*, 773.

(25) Xiao, T.; Dong, X.; Tang, Y.; Zhou, L. *Adv. Synth. Catal.* **2012**, *354*, 3195.

(26) Sugimoto, A.; Hiraoka, R.; Yasueda, K. M.; Mukae, H.; Mizuno, K. *Tetrahedron* **2004**, *60*, 10883.

(27) Shi, Z.; Glorius, F. *Chem. Sci.* **2013**, *4*, 829.

(28) Zhao, Y.-B.; Mariampillai, B.; Candito, D. A.; Laleu, B.; Li, M.; Lautens, M. *Angew. Chem., In. Ed.* **2009**, *48*, 1849.