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Stereocontrolled Synthesis of Benzo[*k*]fluoranthenes—An Unexpected Isomerization Mediated by Rhodacyclopentadiene

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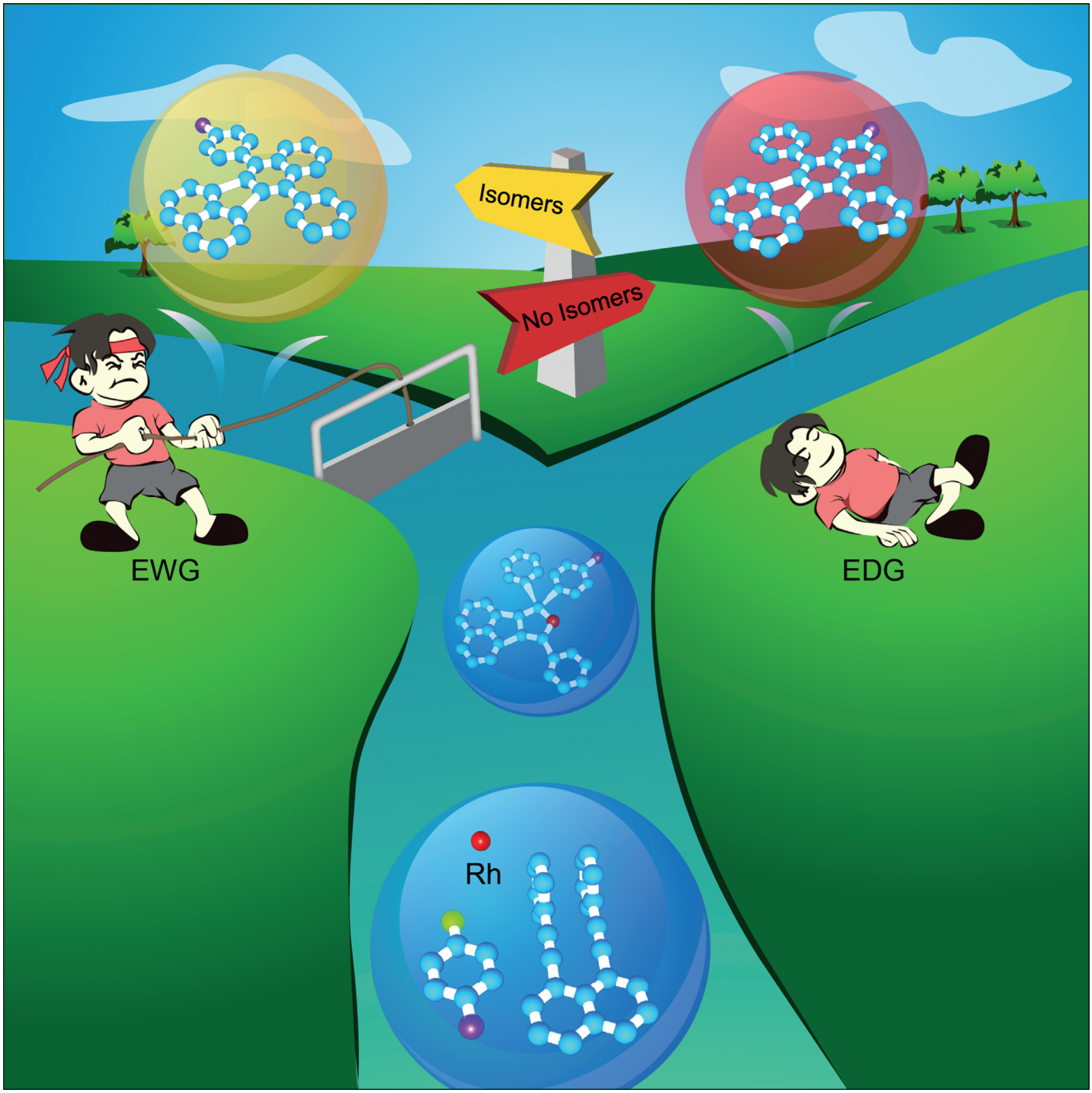
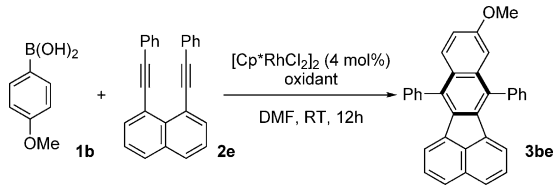


Abstract: Herein, a Rh^{III}-catalyzed stereocontrolled synthesis of benzo[*k*]fluoranthenes is reported. It was found that the unexpected *E*/*Z* isomerization was highly sensitive to the electronic effects of the substituents on the aryl groups. Theoretical calculations revealed that this controllable stereochemistry originates from the mediation of rhodacyclopentadiene intermediates during the isomerization. The fact that similar stereochemistry was observed when using an Ir^{III} catalyst further suggests a certain generality of this discovery toward some other transition metals.

The transition-metal-catalyzed synthesis of cyclic compounds, which are core components in organic chemistry, materials science, and medicinal chemistry, is a crucial issue in modern organic chemistry.[1] In this regard, carborhodation of alkynes[2] followed by C–E bond formation (for example, E = C, Si, N, or O) has been developed into a powerful tool for the synthesis of carbocycles and heterocycles.[3] Distinct from their Pd counterparts,[4] the stereochemistry of the carborhodation of alkynes related to *E*/*Z* isomerization has rarely been reported[5] because the final products could always be afforded with the same configuration as the rhodium intermediates formed by an initial *syn* addition (Scheme 1a).[2,6] In most cases, *syn* adducts promptly proceeded to the next reaction step, such as 1,4-rhodium migration[2a,7] or the formation of a rhodacycle by C–H activation.[8] Rh^{III}-catalyzed synthesis of naphthalene derivatives from arylboronic acids and alkynes can be viewed as a typical example.[9] As shown in Scheme 1a, five-membered rhodacycles were formed quickly by means of C–H activation following the initial carborhodation of alkynes. Afterwards, the locked five- and seven-membered rhodacycles exclusively afforded naphthalenes by final reductive elimination without any isomer observed. Thus, it is of interest to investigate what will happen if the formation of the five-membered rhodacycles, after the initial carborhodation of alkynes, is hindered. Herein, we report that the Rh^{III}-catalyzed synthesis of benzo[*k*]fluoranthenes,[10] from arylboronic acids **1** and 1,8-bis(arylethynyl)-naphthalenes **2** (Scheme 1b), is a suitable model reaction because the intramolecular alkenylrhodium–alkyne complexation prevents rapid formation of a rhodacycle. Benzo[*k*]fluoranthene isomers **3** and **3′** were formed unexpectedly and their ratios were highly sensitive to the relative electron-withdrawing abilities of the two terminal substituents, R^1 and R^2. This finding can be correlated to their σ values in the Hammett equation.[11] From the theoretical mechanism investigations, we found that 1) for substrates with electron-withdrawing groups (EWGs), the isomers can be formed via a rhodacyclopentadiene intermediate (Scheme 1b); 2) thermodynamically, aryl groups with EWGs are more prone to locate at the 1*Z*,3*E*-position of the Rh species compared with those bearing electron-donating groups (EDGs); 3) kinetically, by bearing a lower isomerization barrier, aryl groups with EWGs are easier to isomerize than those with EDGs. We believe that this assay will stimulate a deeper understanding of the stereochemistry of transition-metal-catalyzed annulation reactions.

The Rh^{III}-catalyzed synthesis of benzo[*k*]fluoranthenes **3be** from (4-methoxyphenyl)boronic acid **1b** and 1,8-bis(phenylethynyl)naphthalene **2e** was optimized in *N*,*N*-dimethylformamide (DMF) at room temperature with the Rh^{III} catalyst $[Cp^*RhCl_2]_2$ ($Cp^* = \eta^5$-C_5Me_5) (Table 1). The use of AgF as an oxidant significantly improved the yield to 92%.[12] The scope of

Table 1. Optimization of reaction conditions.[a]



Entry	Oxidant	Yield [%][b]
1	$Cu(OOCCH_3)_2$	8
2	$Cu(OOCCF_3)_2$	50
3	$AgOOCCH_3$	10
4	$AgOOCCF_3$	36
5	AgF	92
6	CuF_2	57

[a] Reaction conditions: **1b** (0.40 mmol), **2e** (0.20 mmol), $[Cp^*RhCl_2]_2$ (4 mol% based on **2e**), oxidant (0.40 mmol), DMF (2 mL), RT, 12 h. [b] Isolated yield based on **2e**.

the cycloaromatization reaction between arylboronic acids **1** and bis(arylethynyl)naphthalenes **2** was examined under optimized reaction conditions (Table 2). Compounds **1a**–**1d** with *para*-EDGs gave benzo[*k*]fluoranthenes **3ae**–**3de** in excellent yields (82–92%) with the expected molecular structures (entries 1–4). In the case of 4-fluorophenylboronic acid, an unexpected mixture of **3fe** and **3fe′** was formed with a total yield of 72% (entry 6), and was unambiguously confirmed by single-crystal X-ray analysis (Figure 1),[13] which suggested the existence of a potential *E*/*Z* isomerization at some stage of the reaction. Arylboronic acid **1j**, with a stronger EWG (NO_2), could also react with diyne **2e** to give a mixture of **3je** and **3je′** with a high total yield of 96% (entry 10). The main product was identified to be the isomer **3je′** (Figure 1).[13] The isomer ratio

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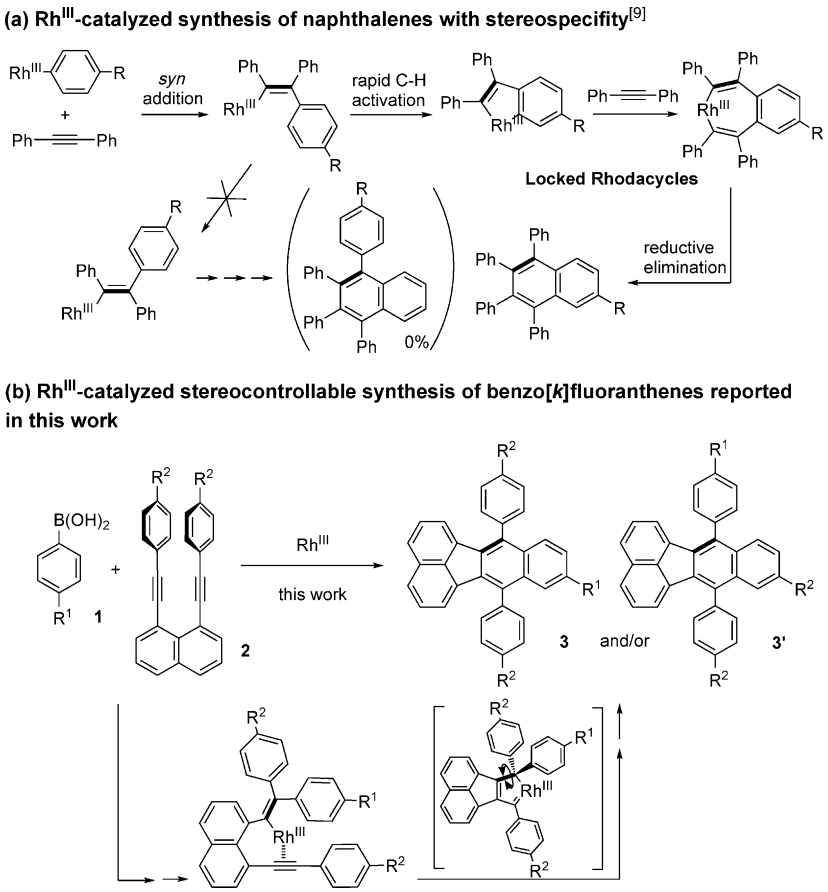


Scheme 1. Rh^{III}-catalyzed synthesis of polycyclic aromatic hydrocarbons (PAHs) between aromatic substrates and alkynes.

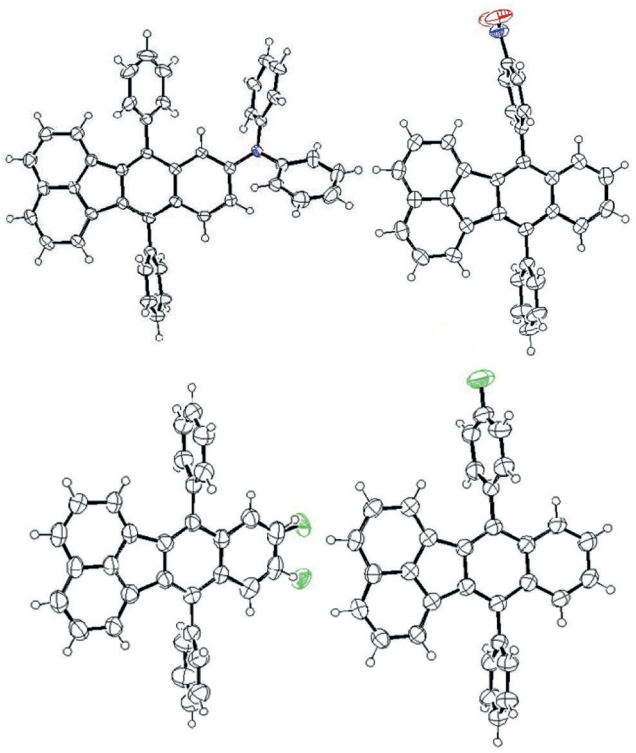
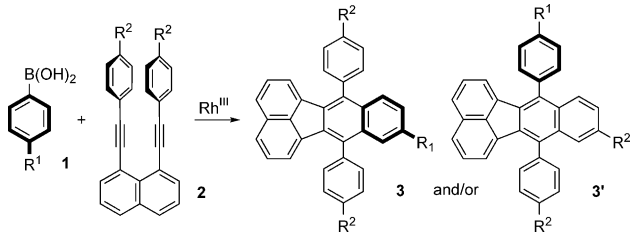


Figure 1. Single-crystal structures of compounds **3 ae** (top left), **3 je**′ (top right), **3 fe** (bottom left), and **3 fe**′ (bottom right).

was further determined to be 14:86 (**3 je**/**3 je**′) by ^1H NMR analysis.[14] Arylboronic acids **1 g**–**1 i** with different EWGs similarly afforded the products (**3 ge**–**3 ie**) as mixtures in high total yields (85–93%) (entries 7–9). The isomer ratios (*E*/*Z*) decreased with the electron-withdrawing ability of the *para*-substituents: 73:27 (F, **3 fe**), 61:39 (COOMe, **3 ge**), 26:74 (CF_3, **3 he**), 17:83 (CN, **3 ie**), and 14:86 (NO_2, **3 je**), corresponding to the σ values: 0.15 (F), 0.45 (COOMe), 0.53 (CF_3), 0.70 (CN), and 0.81 (NO_2). The isomer ratio was also found to be solvent dependent. For the synthesis of compound **3 he**, the isomer ratio increased considerably in methanol, 57:43 (MeOH) versus 26:74 (DMF) (entry 8). Conversely, the reactions between phenylboronic acid **1 e** and diynes **2 b**, **2 d**, and **2 f**–**2 j** were also examined. Diynes **2 b** and **2 d**, with the EDGs OMe and Me, gave compounds **3 eb** and **3 ed** as single products in good yields of 60 and 88%, respectively (entries 11 and 12). However, isomers were formed from diynes **2 f**–**2 j** bearing EWGs, but in low ratios (7–12%, entries 13–17). No isomers were observed (entries 18–20) from the reaction of (4-methoxyphenyl)boronic acid **1 b** with diynes **2 f**, **2 g**, and **2 i**, which have EWGs with different electron-withdrawing abilities. Although the cycloaromatization reactions between **1 f** and diynes **2 b** with a weak EWG (F) gave a single product (**3 fb**) (entry 21), isomers were obtained by applying arylboronic acids with stronger EWGs, such as COOMe, and CN. The isomer ratios (*E*/*Z*) also depended on the electron-withdrawing abilities of R^1; 50:50 (**3 gb**) and 24:76 (**3 ib**) (entries 22 and 23). In agreement with the above observations, a mixture of compounds, **3 ig** and **3 ig**′, was obtained from (4-cyanophenyl)boronic acid **1 i** and dimethyl 4,4′-(naphthalene-1,8-diylbis(ethyne-2,1-diyl))dibenzoate **2 g** in 95% yield, with an isomer ratio of 33:67 because the electron-withdrawing ability of CN is stronger than that of COOMe (entry 24).[15]

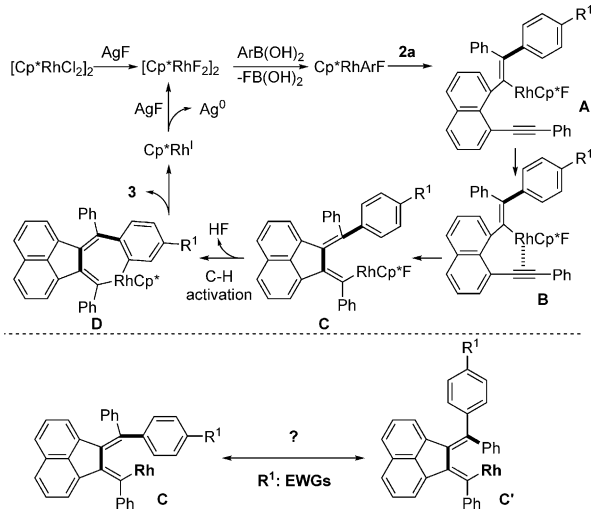
A plausible reaction mechanism for the cycloaromatization reaction of arylboronic acids and 1,8-bis(arylethynyl)naphthalenes is illustrated in Scheme 2. Substrates **1** and **2 a** are used for the mechanism discussion. The reaction was initiated by removing chloride from the catalyst ($[Cp^*RhCl_2]_2$) with Ag^I ions to afford the active catalyst, $[Cp^*RhF_2]_2$.[12] Benzo[*k*]fluoranthenes **3** were formed by the twofold alkyne insertions (generating intermediates **A** and **C**), C–H activation of **C**, and final reductive elimination of rhodabenzocycloheptatriene **D**. The Rh^{III}

Table 2. Rh^{III}-catalyzed cycloaromatization of arylboronic acids **1** and 1,8-bis(arylethynyl)naphthalenes **2**.[a]



Entry	Product (R)	Yield [%] (**3**:**3**′ ratio)[b]
1	**3ae** (NPh_2)	82 (100)
2	**3be** (OMe)	92 (100)
3	**3ce** (*t*Bu)	91 (100)
4	**3de** (Me)	89 (100)
5	**3ee** (H)	57 (–)
6	**3fe** (F)	72 (73:27)
7	**3ge** (COOMe)	93 (61:39)
8	**3he** (CF_3)	88 (26:74)
		40 (57:43)[c]
9	**3ie** (CN)	85 (17:83)
10	**3je** (NO_2)	96 (14:86)
11	**3eb** (OMe)	60 (100)
12	**3ed** (Me)	88 (100)
13	**3ef** (F)	77 (88:12)
14	**3eg** (COOMe)	93 (88:12)
15	**3eh** (CF_3)	94 (92:8)
16	**3ei** (CN)	99 (93:7)
17	**3ej** (NO_2)	94 (93:7)
18	**3bf** (OMe,F)[d]	95 (100)
19	**3bg** (OMe/COOMe)[d]	97 (100)
20	**3bi** (OMe/CN)[d]	95 (100)
21	**3fb** (F/OMe)[d]	56 (100)
22	**3gb** (COOMe/OMe)[d]	85 (50:50)
23	**3ib** (CN/OMe)[d]	86 (24:76)
24	**3ig** (CN/COOMe)[d]	95 (33:67)

[a] General reaction conditions: **1** (0.40 mmol), **2** (0.20 mmol), $[Cp^*RhCl_2]_2$ (4 mol% based on **2**), AgF (0.40 mmol), DMF (2 mL) dark conditions, RT, 12 h. [b] Isomer ratios were determined by ^1H NMR measurements. [c] The reaction was performed in methanol. [d] R^1/R^2.



Scheme 2. Plausible reaction mechanism.

catalyst was recovered by the oxidation of Rh^I by the Ag^I ions. When the R^1 substituents, such as Me, *t*Bu, MeO, and Ph_2N, were electron donating, compounds **3** with the expected molecular configuration were obtained. However, when the R^1 substituents were EWGs, such as F, COOMe, CF_3, CN, and NO_2, an *E*/*Z* isomerization process appears possible before reaching the locked structure **D**, for example, the isomerization of **C** to **C**′, which results in the isomer **3**′ as observed experimentally, appears possible. Because isomers **3he**′–**3je**′ were obtained as the main products in the experimental studies, the formation of an isomerized intermediate such as **C**′ is expected to be preferred over **C** in the presence of strong EWGs. To shed more light on these mechanistic issues, theoretical calculations employing density functional theory (DFT) were conducted.

We first considered the typical EWG, NO_2, as R^1. Because the *E*/*Z* isomerization should occur at the initially formed double bond at some stage before reaching the locked structure **D**, we explored the reaction pathway from **A** to **C** and the possible *E*/*Z* isomerizations, the key findings of which are depicted in Figure 2. After the first alkyne insertion, generating **A**, the exothermic alkenylrhodium–alkyne complexation from **A** to **B**, as shown in Figure 2, prevents the rapid formation of a molecular configuration-locked five-membered rhodacycle from **A** by occupying the vacant metal coordinate site, leaving open the possibility for later *E*/*Z* isomerization. In principle, owing to their unlocked structures, 16-electron species of either **A** or **C** can be potential candidates accounting for *E*/*Z* isomerization.[16] However, our calculations demonstrate that compared

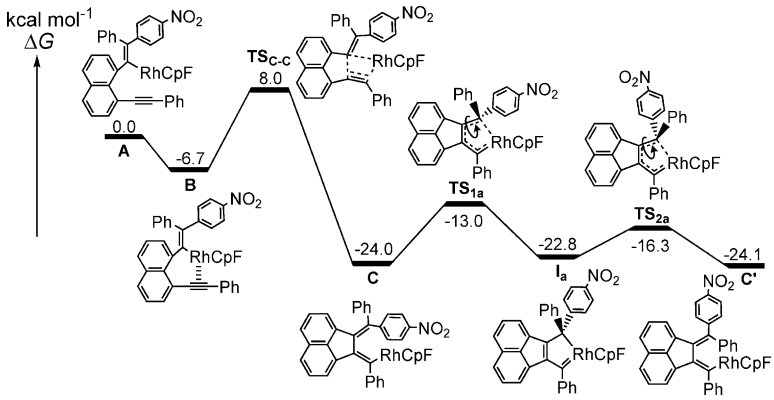


Figure 2. Relative energy profile from **A** to **C**, and the subsequent lowest-energy *E*/*Z* isomerization from **C** to **C**′ for $R^1 = NO_2$ calculated in DMF at 25 °C.

with the second alkyne insertions through transition state $\mathbf{TS_{C-C}}$ from **A** (Figure 2), *E*/*Z* isomerization from **A** are disfavored in energy by approximately 18 kcal mol^{-1}.[14] Thus, **A** can be excluded as an isomerization intermediate and the only remaining potential isomerization intermediate is **C**. We discovered that a rhodacyclopentadiene intermediate, $\mathbf{I_a}$, mediates the *E*/*Z* isomerization from **C** to **C**′, which only needs to overcome activation energy barriers up to 11 kcal mol^{-1}. Concerning the necessity of mediation of $\mathbf{I_a}$ in isomerization, we recall that **C** is a 16-electron species. By forming the five-membered rhodacyclopentadiene intermediate $\mathbf{I_a}$ from **C**, a stabilized 18-electron configuration of Rh can be generated, in which the C=C rotation can be viewed as being half-way. Compared with the isomerization from **A** via the necessary rhodacyclopropene intermediate with large reaction barriers of approximately 26 kcal mol^{-1},[14] this isomerization pathway, via rhodacyclopentadiene, is much more favored. This reactivity advantage of rhodacyclopentadiene over rhodacyclopropene is mainly due to the larger strain of the three-membered ring in the latter species compared to that of the five-membered ring in the former species. Therefore, rhodacyclopentadiene is more stable than rhodacyclopropene. Based on these results, we propose that in the current Rh system, *E*/*Z* isomerization is mediated by rhodacyclopentadiene species, which differs from the ruthenacyclopropene mechanism previously proposed for the *E*/*Z* isomerization in Ru systems.[17] To the best of our knowledge, this is the first time that the metallacyclopentadiene-mediated *E*/*Z* isomerization mechanism is proposed.

Having clarified the *E*/*Z* isomerization pathway, we compared the effects of the typical EWG, NO_2, and the typical EDG, OMe, as R^1 on the isomerization process. The distribution of intermediates **C** and **C**′ from isomerization would determine the stereochemical outcomes of the reaction. As shown in Figure 3, our comparative calculations demonstrate that for **C** with R^1 = OMe, the *Z* isomer **C** is more stable than the *E* isomer **C**′ by 1.0 kcal mol^{-1}, whereas for **C** with $R^1 = NO_2$, the relative stability of **C** and **C**′ is reversed and **C**′ becomes slightly more stable than **C**.[18] Thus, there is no thermodynamic driving force for isomerization with EDGs, such as OMe. Having shown the thermodynamic aspect of *E*/*Z* isomerization, we then turned to the kinetic aspect. Comparing the highest-energy isomerization transition states (**TS**s) with $R^1 = NO_2$ and OMe, one can see that the TS with the OMe group ($\mathbf{TS_{2b}}$) is higher in energy than that with the NO_2 group ($\mathbf{TS_{1a}}$) by approximately 3.8 kcal mol^{-1}. Therefore, our calculations indicate that isomerization with an NO_2 substituent on the aryl group is kinetically more favorable than that with an OMe substituent on the aryl group. Together, our calculations show *E*/*Z* isomerization in the presence of EDGs is disfavored both thermodynamically and kinetically compared with that of EWGs. These calculations are in good accordance with the experiments described above, demonstrating that isomerization is preferable in the presence of EWGs.

It is interesting to explore whether this *E*/*Z* isomerization process also exists for other transition metals.[19] Thus, we examined the synthesis of benzo[*k*]fluoranthenes by utilizing the iridium catalyst,[20] $[Cp^*IrCl_2]_2$, which is a congener of Rh. We used exactly the same reaction conditions as that of $[Cp^*RhCl_2]_2$ for comparison. To our delight, we found that **3 be** was also obtained as a single product, and isomers **3 he** and **3 he**′ were obtained in a 38:62 ratio,[21] suggesting that the stereochemistry described in this assay might have certain generality for other transition metals. Although the isomer ratio of **3 he** and **3 he**′ was slightly different from that with Rh catalyst (26:74), we conjectured that a similar isomerization process occurred for the Ir catalyst.

In summary, we have revealed and rationalized the controllable stereochemistry in the Rh^{III}-catalyzed synthesis of benzo[*k*]-fluoranthenes. The experimental results combined with theoretical mechanism investigations suggested that the unexpected *E*/*Z* isomerization process occurs for those substrates with EWGs and that the reaction is mediated by the rhodacyclopentadiene intermediates. To the best of our knowledge, such C=C isomerization processes, controlled by the electronic properties of the substituents, was demonstrated for the first time in transition-metal-catalyzed annulation reactions. This work also unravels the importance of the locked rhodacycles on the stereochemical specificity of Rh^{III}-catalyzed annulation reactions. These findings also have a certain generality for transition metals besides Rh, as exemplified by an Ir catalyst.

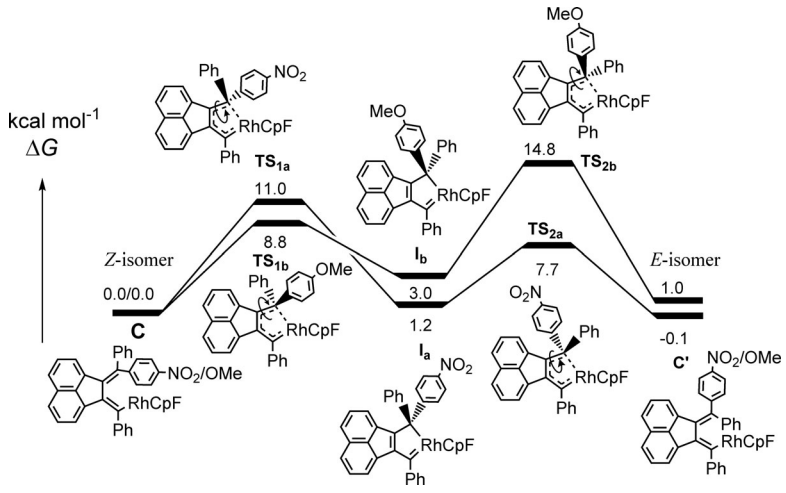


Figure 3. Relative energy profiles of the lowest-energy *E*/*Z* isomerization between **C** and **C**′ for $R^1 = NO_2$ and OMe calculated in DMF at 25 °C.

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Keywords: alkynes · benzo[*k*]fluoranthene · computational chemistry · rhodium · stereochemistry

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[13] CCDC-1008191 (**3 ae**), 1008193 (**3 fe**), 1008192 (**3 fe′**), 1008190 (**3 je′**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[14] See the Supporting Information for details.

[15] The complete orthogonal experiments between the representative arylboronic acids **1** and 1,8-bis(arylethynyl)naphthalenes **2** were examined and are indicated in Table S1 (see the Supporting Information).

[16] It should be noted that the 18-electron species **B** with $R^1 = NO_2$ lacks the prerequisite thermodynamic driving force for *E*/*Z* isomerization (the *Z* isomer is more stable than the *E* isomer by 0.4 kcal mol^{-1}). On the contrary, **B** with $R^1 =$ OMe has the thermodynamic driving force for *E*/*Z* isomerization (the *Z* isomer is less stable than the *E* isomer by 0.5 kcal mol^{-1}). These inconsistencies with the experimental observations indicate that **B** is not likely to be the intermediate for *E*/*Z* isomerization. In addition, 18-electron species **B** cannot form metallacyclopropene, and our trials to locate the transition state of rotation around the C=C bond without involving the metallacyclopropene species turned out to be unsuccessful for **B**.

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[21] The reaction was slow at room temperature (≈20% yields for a two-day reaction), but could be significantly accelerated at 100 °C.

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