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Rhodium-Catalyzed [2+1+2+1] Cycloaddition of Benzoic Acids with Diynes via Decarboxylation and C≡C Triple Bond Cleavage

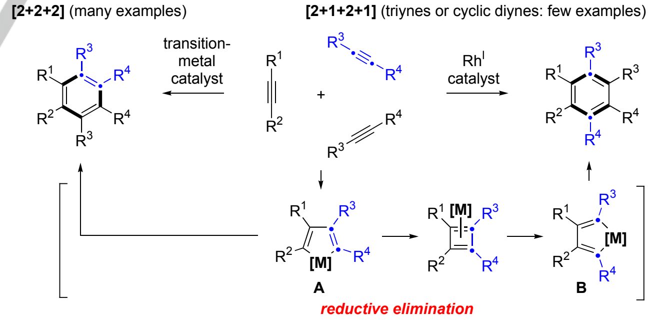
Yusaku Honjo, Yu Shibata,*,[a] and Ken Tanaka*,[a]

Abstract: It has been established that an electron-deficient cyclopentadienyl rhodium(III) (Cp^{E}Rh^{III}) complex catalyzes the oxidative and decarboxylative [2+1+2+1] cycloaddition of benzoic acids with diynes through C≡C triple bond cleavage, leading to fused naphthalenes. This cyclotrimerization is initiated by directed *ortho* C–H bond cleavage of a benzoic acid, and the subsequent regioselective alkyne insertion and decarboxylation produce a five-membered rhodacycle. The electron-deficient nature of the Cp^{E}Rh^{III} complex promotes reductive elimination giving a cyclobutadiene-rhodium(I) complex rather than the second *intermolecular* alkyne insertion. The oxidative addition of the thus generated cyclobutadiene to rhodium(I) (formal C≡C triple bond cleavage) followed by the second *intramolecular* alkyne insertion and reductive elimination give the corresponding [2+1+2+1] cycloaddition product. The synthetic utility of the present [2+1+2+1] cycloaddition was demonstrated in the facile synthesis of a donor-acceptor [5]helicene and a hemi-hexabenzocoronene by a combination with the chemoselective Scholl reaction.

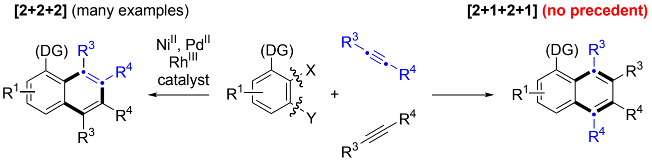
The transition-metal-catalyzed alkyne cyclotrimerization is one of the most useful and straightforward methods for the synthesis of substituted benzenes. Particularly, the [2+2+2] cycloaddition of three alkynes has been widely investigated by using various transition-metal catalysts for the synthesis of functional molecules such as polycyclic aromatic hydrocarbons (Scheme 1a, left).[1] In rare cases, the [2+1+2+1] cycloaddition of three alkynes that affords structurally isomeric benzenes through C≡C triple bond cleavage also proceeds by using cyclic diynes or electron-deficient and/or sterically demanding triynes as substrates and cationic rhodium(I) complexes as catalysts (Scheme 1a, right).[2,3] In this unusual cyclotrimerization, the reductive elimination of a cyclobutadiene from rhodacyclopentadiene **A**, generated by the oxidative cycloaddition of two alkynes and the cationic rhodium(I) complex, is a crucial step to give regioisomeric rhodacyclopentadiene **B** through the formal C≡C triple bond cleavage.

On the other hand, replacing one alkyne with an aryne would afford a substituted naphthalene. To date, various aryne precursors and equivalents have been employed for the [2+2+2] cycloaddition,[4–11] while their preparation and reactions require harsh conditions. Alternatively, directed[12] or non-directed[13] functionalization of the adjacent two C–H bonds of benzenes with two alkynes is convenient and atom-economical, but the directing group remains in the former method and the harsh conditions require in the latter method (Scheme 1b, left). As a traceless directing group, a carboxy group was successfully employed in the pentamethylcyclopentadienyl (Cp*)-iridium(III)[14] or cyclopentadienyl (Cp)-rhodium(III)[15] complex-catalyzed decarboxylative and oxidative [2+2+2] cycloaddition of benzenes with two alkynes, which yields only water and carbon dioxide as by-products. However, these reactions required high temperatures (xylene, reflux to 160 °C) and stoichiometric amounts of metal oxidants. Very recently, our research group reported that the use of an electron-deficient Cp-rhodium(III) complex (Cp^{E}Rh^{III}) significantly mildened the reaction conditions (at RT–80 °C under air or O_2).[16] The highly Lewis acidic nature of the Cp^{E}Rh^{III} complex may accelerate the decarboxylation step as well as the C-H bond cleavage step[17] as a result of the strong π-rhodium interaction in their transition-states. Here, we have established that the Cp^{E}Rh^{III} complex catalyzes the oxidative and decarboxylative [2+1+2+1] cycloaddition of benzoic acids with acyclic diynes (Scheme 1b, right). The highly Lewis acidic nature of the Cp^{E}Rh^{III} complex may promote the reductive elimination to form a cyclobutadiene-rhodium(I) intermediate. Furthermore, it is worthy of note that this report is the first example of the [2+1+2+1] cycloaddition using the aryne or its equivalent and acyclic diynes.

(a) construction of benzene ring



(b) construction of naphthalene ring



Scheme 1. Transition-metal-catalyzed cyclotrimerization to construct benzene and naphthalene rings. [M] = transition-metal complex. DG = directing group.

As mentioned above, benzoic acid (**1a**) reacted with two internal monoynes in the presence of the Cp^{E}Rh^{III} complex to give oxidative and decarboxylative [2+2+2] cycloaddition products **C** in good yields without forming [2+1+2+1]

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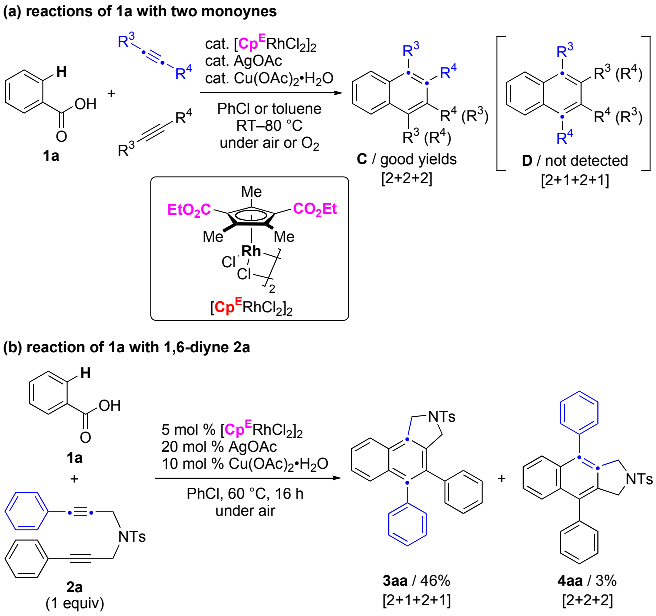
cycloaddition products **D** (Scheme 2a).[16] On the contrary, the reaction of **1a** with 1,6-diyne **2a** instead of two monoynes afforded [2+1+2+1] cycloaddition product **3aa** as a major product along with a small amount of [2+2+2] cycloaddition product **4aa** (Scheme 2b).

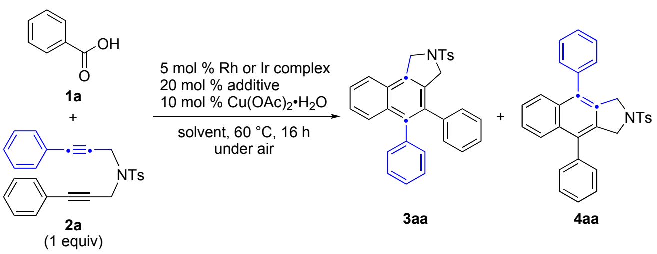


Scheme 2. Cp^{E}Rh^{III} complex-catalyzed oxidative and decarboxylative [2+2+2] and [2+1+2+1] cycloadditions of benzoic acid with alkynes.

To improve the yield of **3aa**, we conducted further investigations into the reaction conditions as shown in Table 1. With respect to the solvent (entries 1–3), the use of toluene that was a suitable solvent for our previously reported oxidative and decarboxylative [2+2+2] cycloaddition markedly decreased the yield (entry 2), but the use of $(CH_2Cl)_2$ improved the yield to 57% (entry 3). Lowering the reaction temperature to 40 °C led to an incomplete conversion of **2a** even for 72 hours (entry 4). Screening of additives revealed that AgOAc was the best one (entries 5–9), although the use of NaOAc instead of AgOAc still promote the desired reaction (entry 8). The use of moderately electron-deficient Ind^{E}Rh^{III}[18] and Cp^{A}Rh^{III}[19] complexes lowered the yields of **3aa** (entries 10 and 11). Importantly, the use of electron-rich Cp*Rh^{III} and Cp*Ir^{III} complexes failed to give **3aa** (entries 12 and 13), and no reaction was observed in the absence of the rhodium/iridium complex (entry 14).

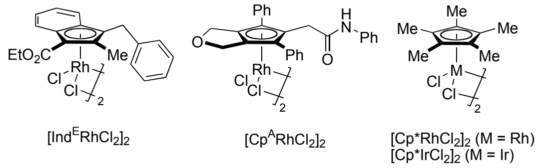
With the optimized conditions in hand, we investigated the substrate scope of the Cp^{E}Rh^{III} complex-catalyzed [2+1+2+1] cycloaddition (Scheme 3).[20] The investigation of the diyne termini revealed that not only non-substituted phenyl (**2a**) but also electron-withdrawing (**2b**) and donating (**2c**) phenyl groups are tolerable to afford **3ab** and **3ac**, although the product yields decreased. Unfortunately, the use of diyne **2d** possessing alkyl groups at the alkyne termini significantly decreased the product yields. Concerning tethers of the 1,6-diynes, oxygen-linked diyne **2e** reacted with **1a** to give **3ae** as a sole product, although its yield was moderate. Carbon-linked diynes **2f** and **2g** showed low reactivity even at 80 °C, especially, the use of malonate-linked diyne **2g** led to an incomplete conversion (ca. 40%). Importantly, the reaction of naphthalene-linked 1,6-diyne **2h** with **1a** afforded [2+2+2] cycloaddition product **4ah** as a predominant product. Concerning benzoic acids, introduction of electron-donating (**1b** and **1c**) and withdrawing (**1d**) groups at the 4-position was tolerable. Interestingly, in these reactions, regioisomeric products **3'** were not generated at all. Sterically demanding 3,4-dimethyl-substituted **1e** also reacted with **2a** to give the corresponding naphthalene **3ea**. Not only 1,6-diynes but biphenyl-linked 1,7-diyne **2i** also reacted with **1a** at 80 °C to give **3ai** in 36% yield along with a small amount of **4ai** (7%). In this reaction, lowering substrate concentration (0.01 M) improved the yield to 42%. Concerning substituents at the alkyne termini, the introduction of electron-donating (**2j**) and withdrawing (**2k**) groups was tolerable, and the structure of **3aj** was confirmed by the X-ray crystallographic analysis.[21] The introduction of electron-donating (**2l**) and withdrawing (**2m**) groups into the biphenyl-linker was also tolerable, while the use of **2m** afforded

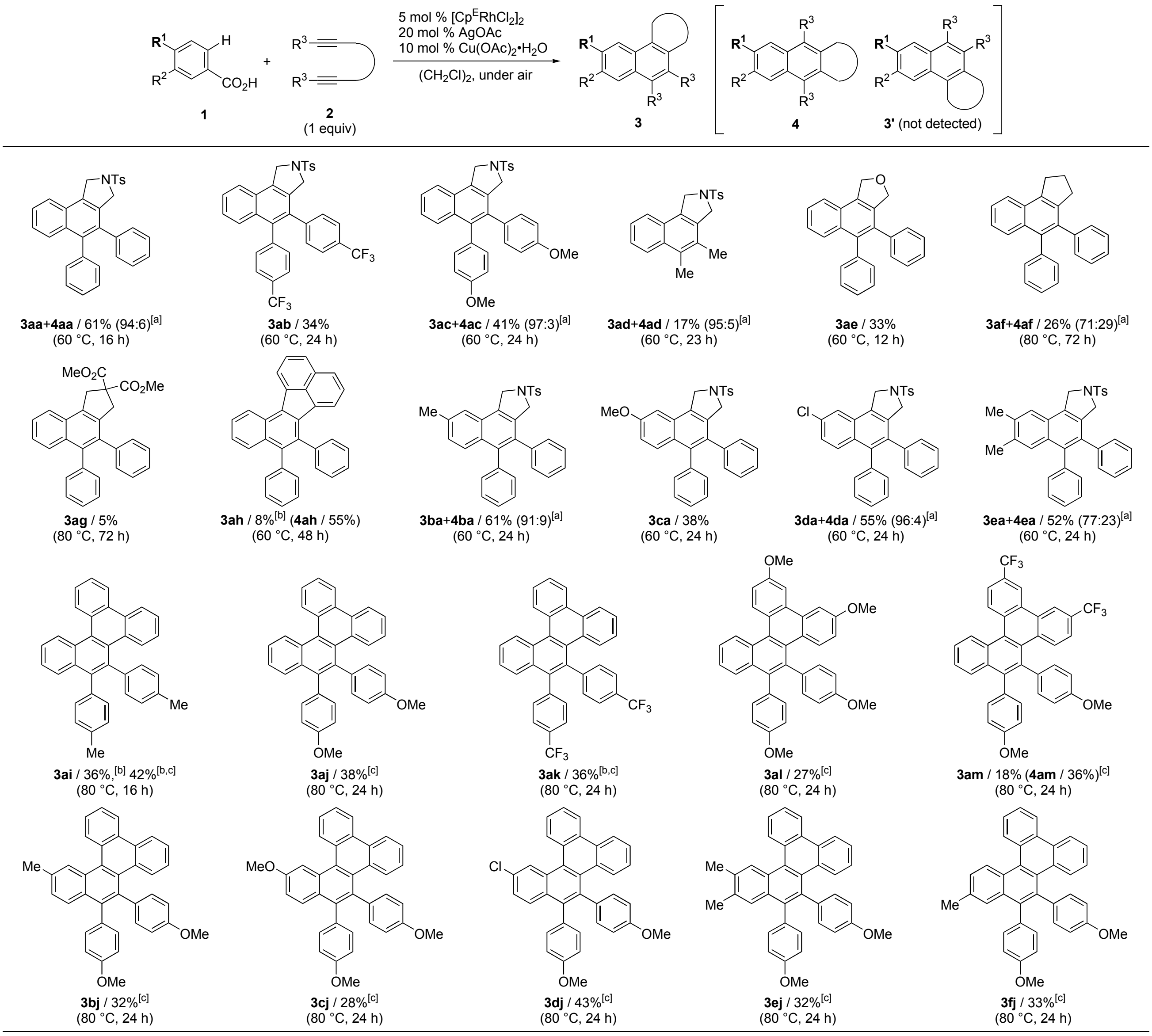
Table 1. Screening of reaction conditions.[a]



Entry	Rh or Ir complex	Additive	Solvent	Yield [%][b]	
				3aa	**4aa**
1	$[Cp^ERhCl_2]_2$	AgOAc	PhCl	46	3
2	$[Cp^ERhCl_2]_2$	AgOAc	toluene	25	2
3	$[Cp^ERhCl_2]_2$	AgOAc	$(CH_2Cl)_2$	57	4
4[c]	$[Cp^ERhCl_2]_2$	AgOAc	$(CH_2Cl)_2$	38	2
5	$[Cp^ERhCl_2]_2$	$AgNTf_2$	$(CH_2Cl)_2$	0	0
6	$[Cp^ERhCl_2]_2$	$AgSbF_6$	$(CH_2Cl)_2$	0	0
7	$[Cp^ERhCl_2]_2$	Ag_2CO_3[d]	$(CH_2Cl)_2$	49	4
8	$[Cp^ERhCl_2]_2$	NaOAc[e]	$(CH_2Cl)_2$	35	3
9	$[Cp^ERhCl_2]_2$	none	$(CH_2Cl)_2$	0	0
10	$[Ind^ERhCl_2]_2$	AgOAc	$(CH_2Cl)_2$	16	1
11	$[Cp^ARhCl_2]_2$	AgOAc	$(CH_2Cl)_2$	3	4
12	$[Cp^*RhCl_2]_2$	AgOAc	$(CH_2Cl)_2$	0	0
13	$[Cp^*IrCl_2]_2$	AgOAc	$(CH_2Cl)_2$	0	2
14	none	AgOAc	$(CH_2Cl)_2$	0	0

[a] $[Cp^ERhCl_2]_2$ (0.0050 mmol), AgOAc (0.020 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.010 mmol), **1a** (0.100 mmol), **2a** (0.100 mmol), and solvent (2.0 mL) were used. [b] Determined by ^1H NMR of the crude reaction mixture using dimethyl sulfone as an internal standard. [c] At 40 °C for 72 h. [d] Ag_2CO_3 (10 mol %) was used. [e] NaOAc (40 mol %) was used.

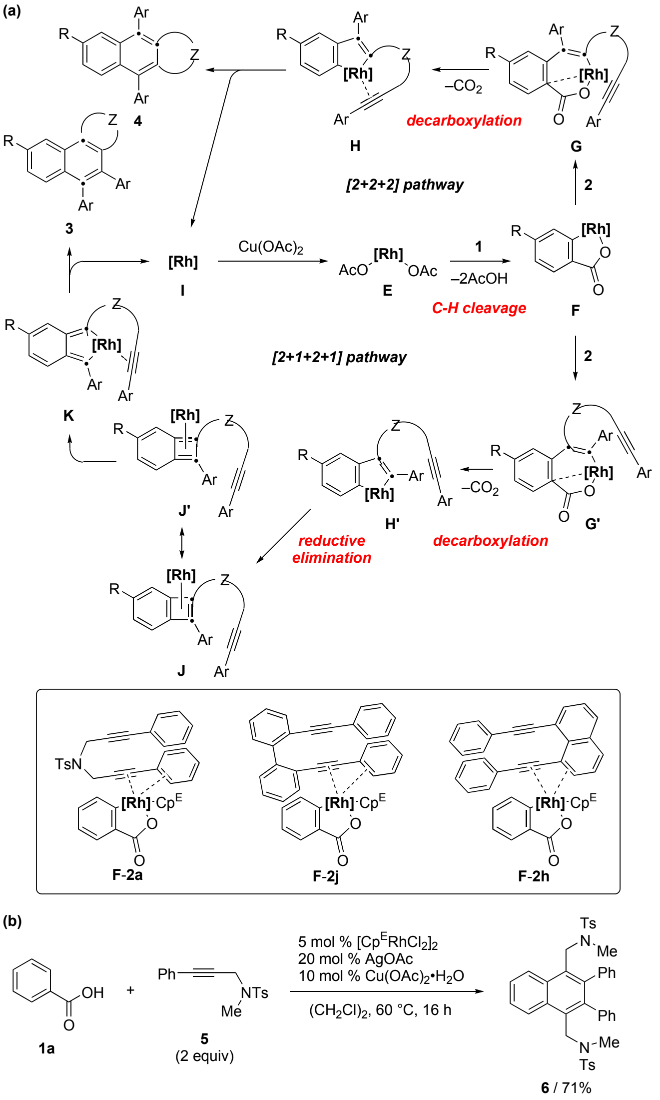




Scheme 3. Substrate scope. $[Cp^ERhCl_2]_2$ (0.0050 mmol), AgOAc (0.020 mmol), $Cu(OAc)_2$•H_2O (0.010 mmol), **1** (0.100 mmol), **2** (0.100 mmol), and $(CH_2Cl)_2$ (2.0 mL) were used. The cited yields are of the isolated products. [a] A mixture of **3** and **4** was isolated. The ratios were determined by ^1H NMR. [b] The yields were determined by ^1H NMR of the crude reaction mixture using dimethyl sulfone as an internal standard. Analytically pure compounds were isolated by sequentiual silica gel chromatography and/or gel permeation chromatography. See the Supporting Information for details. [c] $(CH_2Cl)_2$ (10 mL) was used.

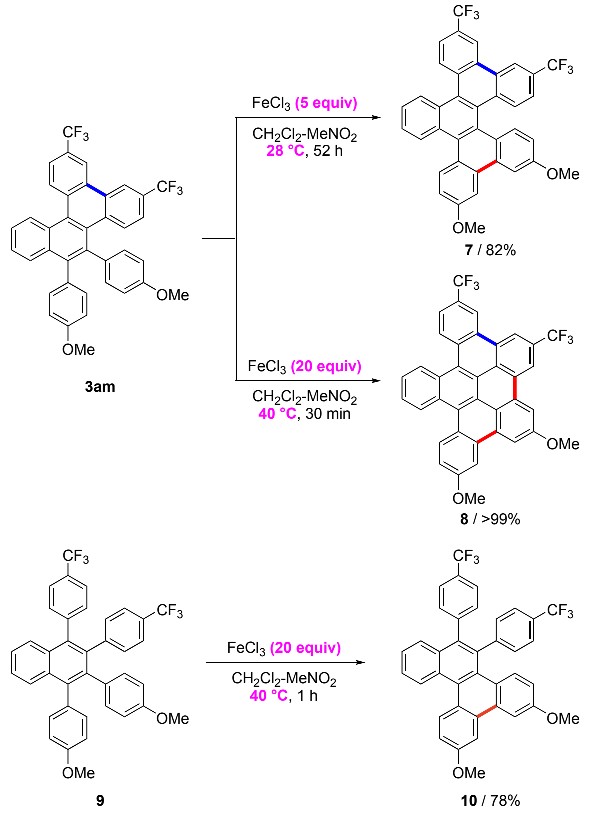
[2+2+2] cycloaddition product **4am** as a major product. As with 1,6-diyne **2a**, 1,7-diyne **2j** reacted with a series of substituted benzoic acids **1b–f** to furnish the corresponding [2+1+2+1] cycloaddition products **3bj–fj**.

Based on the previous reports concerning the oxidative and decarboxylative [2+2+2] cycloaddition of benzoic acids with two alkynes,[14–16] and the [2+1+2+1] cycloaddition of three alkynes,[2,3] mechanisms for the formation of **3** and **4** are proposed as shown in Scheme 4a. Rhodium(III) acetate **E**, generated by the reaction of $[Cp^ERhCl_2]_2$ with AgOAc, reacts with **1** to give rhodacycle **F** via directed *ortho* C-H bond cleavage. Subsequently, insertion of one alkyne unit of diyne **2** affords regioisomeric seven-membered rhodacycle **G** or **G'**. Decarboxylation from **G** furnishes five-membered rhodacycle **H**, and intramolecular alkyne insertion and reductive elimination generate [2+2+2] cycloaddition product **4** and rhodium(I) complex **I**.[14–16] On the other hand, decarboxylation from **G'** affords **H'**, in which intramolecular alkyne insertion cannot proceed. Thus, reductive elimination furnishes cyclobutadiene-rhodium(I) complex **J**, and the subsequent oxidative addition of tautomeric cyclobutadiene **J'** (dearomatized form) to rhodium(I) generates rhodacycle **K**. Subsequent alkyne insertion and reductive elimination generate [2+1+2+1] cycloaddition product **3** and rhodium(I) complex **I**. Finally, oxidation of **I** by the copper(II) co-catalyst regenerates rhodium(III) complex **E**. This mechanism is consistent with the observed complete regioselectivity (absence of regioisomers **3'** in Scheme 3) in the reactions of substituted benzoic acids. According to the above mechanism, the chemoselectivity between **3** and **4** depends on the regioselectivity of the first alkyne insertion step giving **G** or **G'**. The phenyl group of **2a** rather than the tosylamide group may prefer to locate on the rhodium side (**F**-**2a**) giving **G'** as a result of the coordination of the phenyl group to rhodium. In the reaction of biphenyl-linked 1,7-diynes **2j**, the phenyl group rather than the biphenyl group may prefer to locate on the rhodium side (**F**-**2j**) giving **G'** as a result of the steric repulsion between the biphenyl group and the ligand.[22,23] On the contrary, the naphthalene moiety of **2h** may prefer to locate to the rhodium side (**F**-**2h**) giving **G** presumably due to the stronger interaction between the rhodium center and the π-electron of naphthalene than benzene,[10b,24] and thus the [2+2+2] cycloaddition product **4ah** was generated as a major product. Consistent with the above mechanism, the reaction of **1a** with monoyne **5** under the standard conditions furnished 2,3-diarylnaphthalene **6** as a major regioisomer (Scheme 4b).[25] The electron-deficient nature of the Cp^{E}Rh^{III} complex may accelerate the reductive elimination to form cyclobutadiene-rhodium(I) complex **J**.[26] Additionally, the intramolecular coordination of the arylacetylene moiety to rhodium in intermediate **H'** may deter the intermolecular reaction.



Scheme 4. (a) Proposed mechanisms for formation of **3** and **4**. [Rh] = Cp^{E}Rh complex. (b) Intermolecular reaction of **1a** with **5**.

A combination of the present [2+1+2+1] cycloaddition and the chemoselective Scholl reaction enabled the facile synthesis of a donor-acceptor [5]helicene and a hemi-hexabenzocoronene as shown in Scheme 5. The Scholl reaction of partially fused tetraarylnaphthalene **3am** with iron(III) chloride at room temperature promoted the selective dehydrogenation between the electron-rich aryl groups to give donor-acceptor [5]helicene **7** in good yield. The use of a large excess amount of iron(III) chloride at the elevated temperature (40 °C) enabled complete dehydrogenation to give hemi-hexabenzocoronene **8** in quantitative yield. Whereas, the Scholl reaction of none-fused tetraarylnaphthalene **9**[27] under the same conditions furnished partially fused tetraarylnaphthalene **10**, in which only the electron-rich aryl groups were dehydrogenated.



Scheme 5. Synthetic application.

In conclusion, we have established that an electron-deficient Cp^{E}Rh^{III} complex catalyzes the oxidative and decarboxylative [2+1+2+1] cycloaddition of benzoic acids with 1,6- and 1,7-diynes through C≡C triple bond cleavage, which produces fused unsymmetric naphthalenes. In this cyclotrimerization, the electron-deficient nature of the Cp^{E}Rh^{III} complex may facilitate reductive elimination giving a cyclobutadiene-rhodium(I) complex that is a key intermediate of this [2+1+2+1] cycloaddition. The present Cp^{E}Rh^{III}-catalyzed [2+1+2+1] cycloaddition of benzoic acid with a biphenyl-linked donor-acceptor 1,7-diyne was successfully applied to the facile synthesis of a donor-acceptor [5]helicene and a hemi-hexabenzocoronene by a combination with the chemoselective Scholl reaction using iron(III) chloride.

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Keywords: C≡C Triple Bond Cleavage • C-H Bond Functionalization • Cyclopentadienyl Rhodium Complexes • Decarboxylation • [2+1+2+1] Cycloaddition

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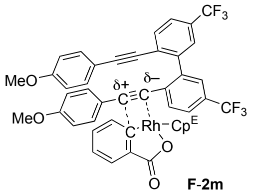
[20] In the reactions listed in Scheme 3, [2+2+2] cycloaddition products **4** were detected in the crude reaction mixtures as minor products (trace to ca. 25% yield) unless otherwise noted.

[21] CCDC 1901383 (**3aj**) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[22] a) T. K. Hyster, T. Rovis, *J. Am. Chem. Soc.* **2010**, *132*, 10565; b) D. R. Stuart, P. Alsabeh, M. Kuhn, K. Fagnou, *J. Am. Chem. Soc.* **2010**, *132*, 18326.

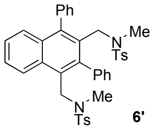
[23] In diyne **2m**, the biphenyl group may prefer to locate on the rhodium side (**F**-**2m**) giving **G** as a result of the charge-bias of the alkyne carbons shown below.



F-2m

[24] a) S. Rakshit, F. W. Patureau, F. Glorius, *J. Am. Chem. Soc.* **2010**, *132*, 9585; b) F. W. Patureau, T. Besset, N. Kuhl, F. Glorius, *J. Am. Chem. Soc.* **2011**, *133*, 2154.

[25] A small amount (ca. 15%) of regioisomer **6'** was also detected, although this compound could not be isolated in a pure form.



6'

[26] In the rhodium(I)-catalyzed cyclotrimerization of triynes, the introduction of the electron-withdrawing substituents at the triyne termini significantly increased the yields of the [2+1+2+1] cycloaddition products. See: ref 2d.

[27] Tetraarylnaphthalene **9** was prepared by the cross-[2+2+2] cycloaddition of **1a** with two different alkynes. See the Supporting Information for details.

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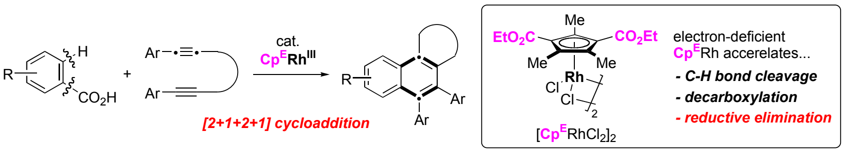
COMMUNICATION



It has been established that an electron-deficient Cp^{E}Rh^{III} complex catalyzes the oxidative and decarboxylative [2+1+2+1] cycloaddition of benzoic acids with diynes through C≡C triple bond cleavage. The electron-deficient nature of the Cp^{E}Rh^{III} complex may facilitate reductive elimination giving the key cyclobutadiene-rhodium(I) intermediate. The combination of the present [2+1+2+1] cycloaddition and the chemoselective Scholl reaction enabled the facile synthesis of a donor-acceptor [5]helicene and a hemi-hexabenzocoronene.

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Rhodium-Catalyzed [2+1+2+1] Cycloaddition of Benzoic Acids with Diynes via Decarboxylation and C≡C Triple Bond Cleavage