CHEMISTRY
A European Journal

A Journal of
ChemPubSoc Europe

Accepted Article

Title: Room Temperature Decarboxylative and Oxidative [2+2+2] Annulation of Benzoic Acids with Alkynes Catalyzed by an Electron-Deficient Rhodium(III) Complex

Authors: Yusaku Honjo, Yu Shibata, Eiji Kudo, Tomoya Namba, Koji Masutomi, and Ken Tanaka

To be cited as: *Chem. Eur. J.* 10.1002/chem.201703928

Link to VoR: http://dx.doi.org/10.1002/chem.201703928

Supported by
ACES

WILEY-VCH

10.1002/chem.201703928

WILEY-VCH

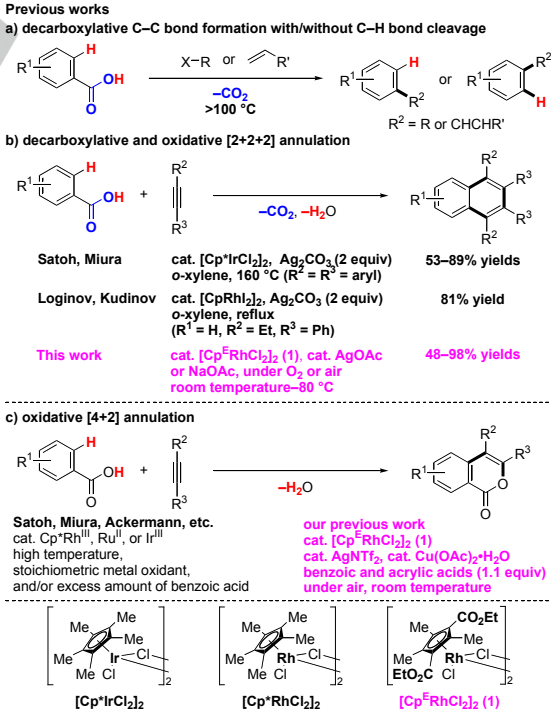
Room Temperature Decarboxylative and Oxidative [2+2+2] Annulation of Benzoic Acids with Alkynes Catalyzed by an Electron-Deficient Rhodium(III) Complex

Yusaku Honjo,[a] Yu Shibata,*[a] Eiji Kudo,[a] Tomoya Namba,[a] Koji Masutomi,[a] and Ken Tanaka*[a]

Abstract: It has been established that an electron-deficient (η^5-cyclopentadienyl)rhodium(III) [Cp^ERh^{III}] complex is capable of catalyzing the decarboxylative and oxidative [2+2+2] annulation of benzoic acids with alkynes to produce substituted naphthalenes at room temperature. The appropriate choice of the additive and the solvent is crucial for this transformation. This catalyst system allowed use of oxygen as a terminal oxidant and broadened the substrate scope including both aromatic and aliphatic alkynes. In this catalysis, the electron deficient nature of the Cp^ERh^{III} catalyst would cause the strong rhodium-π interaction, which accelerates the decarboxylation as well as the C–H bond cleavage.

Decarboxylative C–C bond forming reactions using carboxylic acids are highly efficient and economical due to ready availability of starting materials.[1–3] For example, the decarboxylative in situ generation of arylmetal species from arylcarboxylic acids and transition-metal catalysts eliminates the synthesis of expensive arylmetal compounds (Scheme 1a).[4] Alternatively, the transition-metal-catalyzed C–H bond functionalization at the *ortho* position of the carboxyl group followed by decarboxylation has also been developed (Scheme 1a).[2,5] By combining these two reactions, the decarboxylative double functionalization of the neighboring C–CO_2H and C–H bonds has been developed.[6–8] For example, Satoh and Miura reported the decarboxylative and oxidative [2+2+2] annulation of benzoic acids with diarylacetylenes catalyzed by a (η^5-pentamethyl-cyclopentadienyl)iridium(III) [Cp^*Ir^{III}] complex, which furnished substituted naphthalenes (Scheme 1b).[6] Loginov and Kudinov also reported that a $CpRh^{III}$ complex catalyzes the same reaction using an phenyl- and ethyl-substituted acetylene.[7] However, in sharp contrast to the decarboxylation of alkyl-, acyl-, β-keto-, or alkynyl-carboxylic acids giving highly stable radical or anion species,[3] that of arylcarboxylic acids giving the arylmetal species requires harsh reaction conditions (>100 °C).[9] Indeed, the above transition-metal-catalyzed decarboxylative [2+2+2] annulation reactions were conducted at 160 °C in *o*-xylene. Furthermore, a stoichiometric amount of a silver oxidant was required and applicable alkynes were largely limited to diarylacetylenes.

It is well known that the decarboxylation proceeds via β-carbon elimination from the metal carboxylate with metal-π interaction.[10] Therefore, there is a good chance that electronically tuned catalysts facilitate the decarboxylation. As an example of the electronically tuned catalyst, we reported the synthesis of an electron-deficient Cp^ERh^{III} complex bearing two ester moieties on the Cp ring and its high catalytic activity toward various C–H bond functionalization reactions.[11,12] For example, the oxidative [4+2] annulation of benzoic acids with alkynes catalyzed by Rh^{III}, Ru^{II}, and Ir^{III} complexes required high temperature, stoichiometric amounts of metal oxidants, and/or excess amounts of benzoic acids (Scheme 1c).[13] Pleasingly, the use of the Cp^ERh^{III} catalyst solved all the above problems (Scheme 1c).[11g] We anticipated that this electrophilic Cp^ERh^{III} catalyst would accelerate the decarboxylation as well as the C–H bond cleavage as a result of the strong rhodium-π interaction. In this paper, we disclose the room temperature decarboxylative and oxidative [2+2+2] annulation of benzoic acids with alkynes catalyzed by the electron deficient Cp^ERh^{III} complex.



Scheme 1. Transition-metal-catalyzed C–C bond forming reactions of benzoic acids.

In the course of our study on the [4+2] annulation of benzoic acid (**2a**) with diphenylacetylene (**3a**) (Table 1, entry 1),[11g] the use of AgOAc in place of $AgNTf_2$ afforded not [4+2] annulation

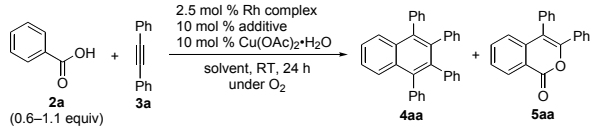
[a] Y. Honjo, Dr. Y. Shibata, E. Kudo, T. Namba, K. Masutomi, Prof. Dr. K. Tanaka
Department of Chemical Science and Engineering, Tokyo Institute of Technology
O-okayama, Meguro-ku, Tokyo 152-8550 (Japan)
E-mail: ktanaka@apc.titech.ac.jp
E-mail: yshibata@apc.titech.ac.jp
http://www.apc.titech.ac.jp/~ktanaka/
Supporting information for this article is given via a link at the end of the document

10.1002/chem.201703928

COMMUNICATION

product **5aa** but decarboxylative [2+2+2] annulation product **4aa** as a major product, although the reaction was sluggish (entry 2). The reaction under O_2 atmosphere slightly improved the yield of **4aa** (entry 3). Screening of solvents[14] revealed that the use of aromatic solvents (toluene or chlorobenzene) improved the yield of **4aa** (entries 4 and 5). Pleasingly, reducing the amount of **2a** to a slight excess relative to **3a** (0.6 equiv) further improved the yield of **4aa** (entry 6). Screening of additives revealed that Ag_2CO_3 and NaOAc work as well, while the yields of **4aa** decrease somewhat (entries 7 and 8). The use of cationic salts (SbF_6, NTf_2, and OTf) afforded exclusively **5aa** (entries 9–11) and no reaction was observed without additive (entry 12). Finally, prolonged reaction time (48 h) furnished **4aa** in the highest yield (entry 13). Importantly, under this optimized reaction conditions, Cp^*Rh^{III} and Cp^*Ir^{III} complexes failed to afford **4aa** (entries 14 and 15). Inexpensive NaOAc could be employed instead of AgOAc, while even longer reaction time (72 h) was required (entry 16). Although the yield decreased, **4aa** was obtained even in the absence of the Cu^{II} oxidant (entry 17).

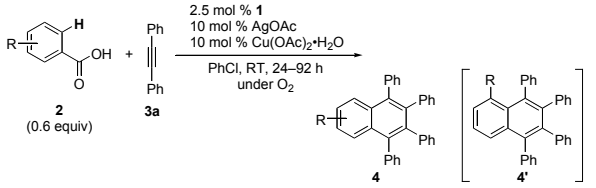
Table 1. Optimization of reaction conditions.[a]



Entry	Rh Complex	Additive	**2a** (equiv)	Solvent	Yield [%][b] **4aa**	**5aa**
1[c]	**1**	$AgNTf_2$	1.1	$(CH_2Cl)_2$	0	96
2[c]	**1**	AgOAc	1.1	$(CH_2Cl)_2$	6	<1
3	**1**	AgOAc	1.1	$(CH_2Cl)_2$	11	<3
4	**1**	AgOAc	1.1	toluene	42	0
5	**1**	AgOAc	1.1	PhCl	46	<3
6	**1**	AgOAc	0.6	PhCl	66	<3[d]
7	**1**	Ag_2CO_3[e]	0.6	PhCl	58	<3[d]
8	**1**	NaOAc[f]	0.6	PhCl	49	<3[d]
9	**1**	$AgSbF_6$	0.6	PhCl	0	28[d]
10	**1**	$AgNTf_2$	0.6	PhCl	0	72[d]
11	**1**	AgOTf	0.6	PhCl	0	8[d]
12	**1**	none	0.6	PhCl	0	0
13[g]	**1**	AgOAc	0.6	PhCl	81	<3[d]
14[g]	$[Cp^*RhCl_2]_2$	AgOAc	0.6	PhCl	0	35[d]
15[g]	$[Cp^*IrCl_2]_2$	AgOAc	0.6	PhCl	<1	0
16[h]	**1**	NaOAc[f]	0.6	PhCl	83	<3[d]
17[h,i]	**1**	NaOAc[f]	0.6	PhCl	74	<3[d]

[a] Rh complex (0.0050 mmol), additive (0.020 mmol), $Cu(OAc)_2•H_2O$ (0.020 mmol), **2a** (0.120–0.220 mmol), **3a** (0.200 mmol), and solvent (2.0 mL) were used. [b] Isolated yields based on **3a**. [c] Under air. [d] Based on **2a**. [e] Ag_2CO_3 (0.010 mmol) was used. [f] NaOAc (0.040 mmol) was used. [g] For 48 h. [h] For 72 h. [i] In the absence of $Cu(OAc)_2•H_2O$.

With optimized conditions in hand, we investigated the scope of benzoic acids **2** (Scheme 2). With regard to the substituent at the *para* position, the introduction of both electron donating (**2b**–**d**) and withdrawing (**2e**,**f**) groups was tolerable (entries 2–7), although the reaction of highly electron-deficient **2f** required higher catalyst loading (entry 6) or reaction temperature (entry 7). In entry 6, the use of NaOAc instead of AgOAc slightly decreased the yield of **4fa**. When using 4-methoxybenzoic acid (**2c**), not only **4ca** but also a trace amount of 5-substituted naphthalene **4ca'** was generated via the 1,3-shift of the rhodium center.[6] Although the introduction of the substituent at the *meta*-position (**2g**–**i**) decreased the reactivity (entries 8–12), the reactions at elevated temperature afforded the corresponding naphthalenes in good yields (entries 9, 11, 12). Interestingly, the reaction of 3-fluorobenzoic acid (**2i**) afforded 5-fluoro-substituted naphthalene **4ia'** as a major regioisomer, as a result of the preferred C–H bond cleavage at the *ortho*-position of the fluorine atom (entry 12). 3,4-Dimethylbenzoic acid (**2j**) reacted with **3a** at 80 °C to give the corresponding naphthalene **4ja** selectively (entry 13). 2-Methoxybenzoic acid (**2k**) reacted with **3a** to give rearranged product **4ca** as a major regioisomer via the 1,3-shift of the rhodium center (entry 14).[6]



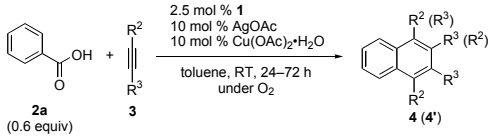
Entry	**2**	Time (h)	**4** / Yield (%)
1	**2a** (R = H)	48 (72[a])	**4aa** / 81% (83%[a])
2	**2b** (R = Me)	72	**4ba** / 98%
3	**2c** (R = OMe)	72	**4ca+4ca'** / 70% (95:5)
4	**2d** (R = OPh)	72	**4da** / 79%
5	**2e** (R = Cl)	72	**4ea** / 77%
6[b]	**2f** (R = CF_3)	72 (92[a])	**4fa** / 63% (55%[a])
7[c]	**2f** (R = CF_3)	24	**4fa** / 88%
8	**2g** (R = Me)	72	**4ba** / 29% (>50:1)
9[c]	**2g** (R = Me)	24	**4ba+4ba'** / 85% (95:5)
10[b]	**2h** (R = CF_3)	72	**4fa** / 49% (>50:1)
11[c]	**2h** (R = CF_3)	24	**4fa** / 90% (>50:1)
12[c]	**2i** (R = F)	24	**4ia+4ia'** / 71% (29:71)
13[c]	**2j**	24	**4ja** / 93%
14	**2k**	92	**4ca'+4ca** / 77% (12:88)

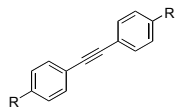
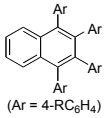
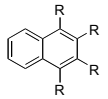
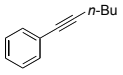
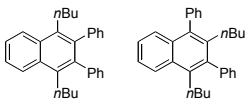
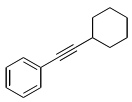
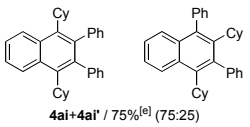
Scheme 2. Scope of benzoic acids. **1** (0.0050 mmol), AgOAc (0.020 mmol), $Cu(OAc)_2•H_2O$ (0.020 mmol), **2a** (0.120 mmol), **3a** (0.200 mmol), and PhCl (2.0 mL) were used. The structures of **4** and **4'** are shown on the left and right, respectively. Cited yields were of the isolated products. [a] NaOAc [0.040 mmol (entry 1) or 0.080 mmol (entry 6)] was used instead of AgOAc. [b] **1** (0.010 mmol), AgOAc (0.040 mmol) were used. [c] At 80 °C.

10.1002/chem.201703928

COMMUNICATION

The scope of alkynes **3** was also investigated (Scheme 3). Substituted diarylacetylenes **3b**–**e** reacted with **2a** to give the corresponding naphthalenes **4ab**–**ae** (entries 1–5). In the reactions of electron-rich alkynes **3b**–**d**, the use of toluene as a solvent improved the product yields (entries 1–4). In the reactions of highly electron-rich alkynes **3c** and **3d**, high catalyst loadings improved the product yields (entries 3 and 4). Pleasingly, previously unusable dialkylacetylenes **3f** and **3g** could be employed to give the corresponding tetraalkylnaphthalenes **4af** and **4ag** in good yields (entries 6 and 7). In entry 6, the use of NaOAc instead of AgOAc afforded **4af** in moderate yield, although prolonged reaction time (72 h) was required. Unsymmetrical alkyl-phenyl-substituted acetylenes **3h** and **3i** showed low reactivity (entry 8–10), but the desired cycloadducts were obtained in good yields with moderate regioselectivity at 80 °C (entries 9 and 10).

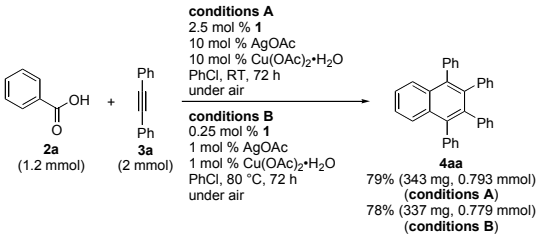


Entry	2	Time (h)	4 / Yield (%)
			 (Ar = 4-RC$_6$H$_4$)
1	**3b** (R = Me)	72	**4ab** / 60%
2	**3c** (R = *n*-C$_5$H$_{13}$)	72	**4ac** / 47%
3[a]	**3c** (R = *n*-C$_5$H$_{13}$)	72	**4ac** / 81%
4[a]	**3d** (R = OMe)	72	**4ad** / 48%
5[b]	**3e** (R = Cl)	72	**4ae** / 60%
			
6	**3f** (R = *n*-C$_5$H$_{11}$)	24 (72[c])	**4af** / 70% (42%[c])
7	**3g** (R = *n*Bu)	72	**4ag** / 60%
			
8	**3h**	72	**4ah+4ah'** / 27% (78:22)
9[d]	**3h**	24	**4ah+4ah'** / 91% (75:25)
			
10[d]	**3i**	24	**4ai+4ai'** / 75%[e] (75:25)

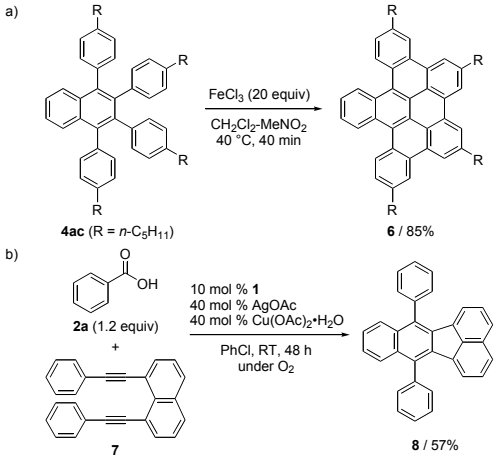
Scheme 3. Scope of alkynes. **1** (0.0050 mmol), AgOAc (0.020 mmol), $Cu(OAc)_2•H_2O$ (0.020 mmol), **2a** (0.120 mmol), **3a** (0.200 mmol), and toluene (2.0 mL) were used. The structures of **4** and **4'** are shown on the left and right, respectively. Cited yields were of the isolated products. Ratio of regioisomers were determined by ^{1}H NMR. [a] **1** (0.010 mmol) and AgOAc (0.040 mmol) were used. [b] PhCl was used instead of toluene. [c] NaOAc (0.040 mmol) was used instead of AgOAc. [d] At 80 °C. [e] Isolated with small amounts of impurities (ca. 5%).

This naphthalene synthesis could be conducted on a preparative scale (Scheme 4). The reaction on a >1 mmol scale under air proceeded to give **4aa** in 79% yield, which is comparable to the yield in a small scale under O_2 (81%: Scheme 2, entry 1). The catalyst loading could be reduced to 0.25 mol % without erosion of the product yield by conducting at 80 °C.

The present decarboxylative and oxidative [2+2+2] annulation is useful for the synthesis of π-conjugated molecules. For example, the Scholl reaction of the product tetraaryl naphthalene **4ac** with $FeCl_3$ afforded hemi-hexabenzocoronene[15] **6** in 85% yield (Scheme 5a). The use of diyne **7** afforded 7,12-diphenylbenzo[*k*]fluoranthene (**8**) in 57% yield (Scheme 5b).

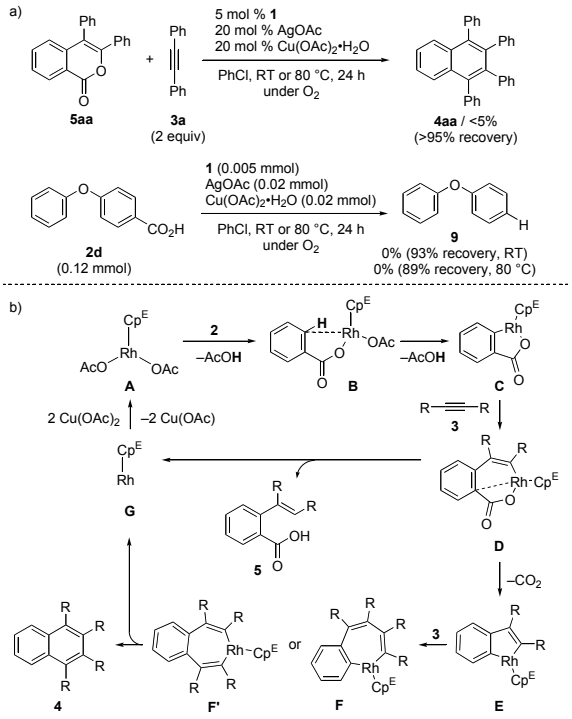


Scheme 4. Preparative scale reactions.



Scheme 5. Synthetic applications.

To confirm the decaroboxylation step in the catalytic cycle, the following reactions were conducted (Scheme 6a). Isocoumarin **5aa** failed to react with **3a** under the standard conditions, which revealed that **5aa** was not the intermediate leading to **4aa**. The reaction of **2d** in the absence of **3a** under the standard conditions did not afford decarboxylated product **9**, which revealed that the direct decarboxylation of **2d** to form the corresponding arylrhodium species can be excluded. Furthermore, as the use of NaOAc instead of AgOAc was also effective for this reaction, the silver-mediated decarboxylation[9] can also be excluded. Therefore, we proposed the mechanism shown in Scheme 6b.[6] Rhodium acetate **A** generated from $[Cp^ERhCl_2]_2$ and AgOAc reacts with **2a** to give rhodium benzoate **B**. Subsequent C–H bond cleavage affords rhodacycle **C**. Insertion of **3** furnishes rhodacycle **D**, and the strong rhodium-π interaction would accelerate the decarboxylation to generate rhodacycle **E**. The second alkyne insertion affords rhodacycle **F** or **F'**, in which at least **F** is operative due to the formation of **8** from **7**. Reductive elimination furnishes **4** and Rh^I species **G**. Finally, reoxidation of **G** by Cu^{II} regenerates catalytically active Rh^{III} species **A**. The use of cationic silver salts instead of AgOAc might accelerate ionic reductive elimination of **D** to give **5** selectively. Hong suggested a similar counter anion effect in the Ru^{II} catalysis.[16]



Scheme 6. a) Mechanistic studies and b) plausible reaction mechanism.

In conclusion, we have established that an electron-deficient Cp^ERh^{III} complex is capable of catalyzing the decarboxylative and oxidative [2+2+2] annulation of benzoic acids with alkynes to produce substituted naphthalenes at room temperature. The appropriate choice of the additive and the solvent is crucial for this transformation. This catalyst system allowed use of oxygen as a terminal oxidant and broadened the substrate scope. In this catalysis, the electron deficient nature of the Cp^ERh^{III} catalyst might account for acceleration of the decarboxylation as well as the C–H bond cleavage as a result of the strong rhodium-π interaction. Future works will include further application of the Cp^ERh^{III} catalyst to the decarboxylative C–C bond formations.

Acknowledgements

This work was supported partly by ACT-C (No. JPMJCR1122YR) from JST (Japan), and Grants-in-Aid for Scientific Research (No. JP26102004), Research Activity Start-up (No. 15H06201), and Young Scientists (No. 17K14481) from JSPS (Japan). We thank Umicore for generous support in supplying $RhCl_3•nH_2O$.

Keywords: [2+2+2] Annulation • Cyclopentadienyl Complexes • C–H Functionalization • Decarboxylation • Rhodium

[1] For recent general reviews of decarboxylative coupling reactions, see: a) T. Patra, D. Maiti, *Chem. Eur. J.* **2017**, *23*, 7382; b) G. J. P. Perry, I. Larrosa, *Eur. J. Org. Chem.* **2017**, *2017*, 3517; c) H. Li, T. Miao, M. Wang, P. Li, L. Wang, *Synlett* **2016**, *27*, 1635; d) W. I. Dzik, P. P. Lange, L. J. Gooßen, *Chem. Sci.* **2012**, *3*, 2671; e) N. Rodriguez, L. J. Gooßen, *Chem. Soc. Rev.* **2011**, *40*, 5030.

[2] For recent reviews of decarboxylative coupling reactions with directed C–H bond cleavage, see: a) Y. Wei, P. Hu, M. Zhang, W. Su, *Chem. Rev.* **2017**, *117*, 8864; b) M. Font, J. M. Quibell, G. J. P. Perry, I. Larrosa, *Chem. Commun.* **2017**, *53*, 5584; c) M. Pichette Drapeau, L. J. Gooßen, *Chem. Eur. J.* **2016**, *22*, 18654; d) T. Satoh, M. Miura, *Synthesis* **2010**, 3395.

[3] For recent reviews of decarboxylative coupling reactions using photoredox catalysts, see: a) Y. Jin, H. Fu, *Asian J. Org. Chem.* **2017**, *6*, 368; b) P. Liu, G. Zhang, P. Sun, *Org. Biomol. Chem.* **2016**, *14*, 10763.

[4] For selected examples of decarboxylative coupling reactions of arylcarboxylic acids, see: a) A. G. Myers, D. Tanaka, M. R. Mannion, *J. Am. Chem. Soc.* **2002**, *124*, 11250; b) L. J. Gooßen, G. Deng, L. M. Levy, *Science* **2006**, *313*, 662; c) R. Shang, Y. Fu, Y. Wang, Q. Xu, H.-Z. Yu, L. Liu, *Angew. Chem. Int. Ed.* **2009**, *48*, 9350; *Angew. Chem.* **2009**, *121*, 9514; d) C. Wang, I. Piel, F. Glorius, *J. Am. Chem. Soc.* **2009**, *131*, 4194; e) P. Hu, M. Zhang, X. Jie, W. Su, *Angew. Chem. Int. Ed.* **2012**, *51*, 227; *Angew. Chem.* **2012**, *124*, 231; f) B. Song, T. Knauber, L. J. Gooßen, *Angew. Chem. Int. Ed.* **2013**, *52*, 2954; *Angew. Chem.* **2013**, *125*, 3026.

[5] For selected examples of decarboxylation of arylcarboxylic acids with directed C–H bond functionalizations, see: a) M. Shimizu, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.* **2009**, *74*, 3478; b) S. Mochida, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2010**, *12*, 5776; c) J. Cornella, M. Righi, I. Larrosa, *Angew. Chem. Int. Ed.* **2011**, *50*, 9429; *Angew. Chem.* **2011**, *123*, 9601; d) S. Mochida, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.* **2011**, *76*, 3024; e) Y. Zhang, H. Zhao, M. Zhang, W. Su, *Angew. Chem. Int. Ed.* **2015**, *54*, 3817; *Angew. Chem.* **2015**, *127*, 3888; f) J. Zhang, R. Shrestha, J. F. Hartwig, P. Zhao, *Nat. Chem.* **2016**, *8*, 1144.

[6] K. Ueura, T. Satoh, M. Miura, *J. Org. Chem.* **2007**, *72*, 5362.

[7] a) D. A. Loginov, A. O. Belova, A. R. Kudinov, *Russ. Chem. Bull.* **2014**, *63*, 983; b) D. A. Loginov, D. V. Muratov, Y. V. Nelyubina, J. Laskova, A R. Kudinov, *J. Mol. Catal. A: Chem.* **2017**, *426*, 393.

[8] a) A. A. Cant, L. Roberts, M. F. Greaney, *Chem. Commun.* **2010**, *46*, 8671; b) C. Wang, S. Rakshit, F. Glorius, *J. Am. Chem. Soc.* **2010**, *132*, 14006.

[9] Although the room temperature decarboxylative coupling reactions of arylcarboxylic acids was reported, the substrates were limited to 2,6-dimethoxybenzoic acids and pentafluorobenzoic acid. See: A. Hossian, S. K. Bhunia, R. Jana, *J. Org. Chem.* **2016**, *81*, 2521.

[10] For mechanistic studies of decarboxylation, see: a) S.-L. Zhang, Y. Fu, R. Shang, Q.-X. Guo, L. Liu, *J. Am. Chem. Soc.* **2010**, *132*, 638; b) R. Shang, Q. Xu, Y.-Y. Jiang, Y. Wang, L. Liu, *Org. Lett.* **2010**, *12*, 1000; c) A. Fromm, C. van Wuellen, D. Hackenberger, L. J. Gooßen, *J. Am. Chem. Soc.* **2014**, *136*, 10007.

[11] For the C–H bond functionalization catalyzed by the Cp^ERh^{III} complex, see: a) Y. Shibata, K. Tanaka, *Angew. Chem. Int. Ed.* **2011**, *50*, 10917; *Angew. Chem.* **2011**, *123*, 11109; b) M. Fukui, Y. Hoshino, T. Satoh, M. Miura, K. Tanaka, *Adv. Synth. Catal.* **2014**, *356*, 1638; c) Y. Hoshino, Y. Shibata, K. Tanaka, *Adv. Synth. Catal.* **2014**, *356*, 1577; d) Y. Takahama, Y. Shibata, K. Tanaka, *Chem. Eur. J.* **2015**, *21*, 9053; e) M. Fukui, Y. Shibata, Y. Hoshino, H. Sugiyama, K. Teraoka, H. Uekusa, K. Noguchi, K. Tanaka, *Chem. Asian J.* **2016**, *11*, 2260; f) E. Kudo, Y. Shibata, M. Yamazaki, K. Masutomi, Y. Miyauchi, M. Fukui, H. Sugiyama, H. Uekusa, T. Satoh, M. Miura, K. Tanaka, *Chem. Eur. J.* **2016**, *22*, 14190; g) Y. Takahama, Y. Shibata, K. Tanaka, *Chem. Lett.* **2016**, *45*, 1177.

[12] For electronical properties of the Cp^ERh^{III} complex, see: T. Piou, F. Romanov-Michailidis, M. Romanova-Michaelides, K. E. Jackson, N. Semakul, T. D. Taggart, B. S. Newell, C. D. Rithner, R. S. Paton, T. Rovis, *J. Am. Chem. Soc.* **2017**, *139*, 1296.

[13] For selected examples of the oxidative [4+2] annulation of benzoic acids with alkynes, see: a) K. Ueura, T. Satoh, M. Miura, *Org. Lett.* **2007**, *9*, 1407; b) D. A. Frasco, C. P. Lilly, P. D. Boyle, E. A. Ison, *ACS Catal.* **2013**, *3*, 2421; c) Y. Yu, L. Huang, W. Wu, H. Jiang, *Org. Lett.* **2014**, *16*, 2146; d) S. Warratz, C. Kornhaaß, A. Cajaraville, B. Niepoetter, D. Stalke, L. Ackermann, *Angew. Chem. Int. Ed.* **2015**, *54*, 5513; *Angew. Chem.* **2015**, *127*, 5604.

[14] See the Supporting Information.

[15] A. K. Dutta, A. Linden, L. Zoppi, K. K. Baldridge, J. S. Siegel, *Angew. Chem. Int. Ed.* **2015**, *54*, 10792; *Angew. Chem.* **2015**, *127*, 10942.

10.1002/chem.201703928

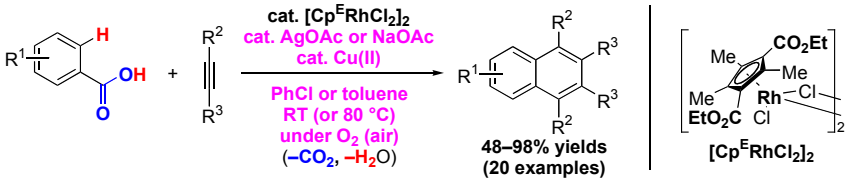
[16] J.-L. Yu, S.-Q. Zhang, X. Hong, *J. Am. Chem. Soc.* **2017**, *139*, 7224.

10.1002/chem.201703928

COMMUNICATION

Entry for the Table of Contents (Please choose one layout)

COMMUNICATION



It has been established that an electron-deficient (η^5-cyclopentadienyl)rhodium(III) [Cp^ERh^{III}] complex is capable of catalyzing the decarboxylative and oxidative [2+2+2] annulation of benzoic acids with alkynes to produce substituted naphthalenes at room temperature. This catalyst system allowed use of oxygen as a terminal oxidant and broadened the substrate scope including both aromatic and aliphatic alkynes.

Yusaku Honjo, Yu Shibata, Eiji Kudo, Tomoya Namba, Koji Masutomi, and Ken Tanaka**

Page No. – Page No.

Room Temperature Decarboxylative and Oxidative [2+2+2] Annulation of Benzoic Acids with Alkynes Catalyzed by an Electron-Deficient Rhodium(III) Complex