Synthesis H. Takahashi et al. Special Topic

Dienylation of Unfunctionalized Arenes with 1,6-Diynes via Rhodium-Catalyzed Directing-Group-Free C–H Bond Activation

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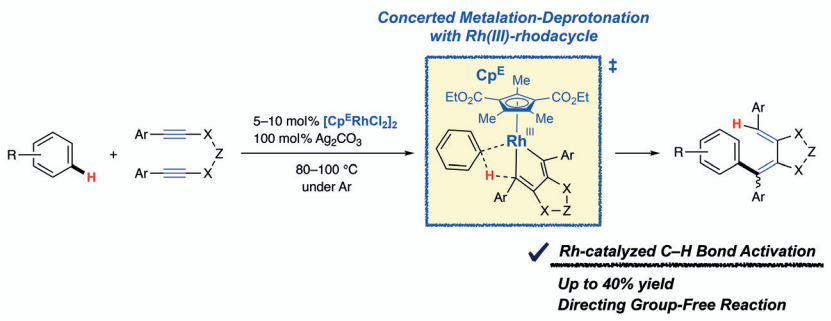

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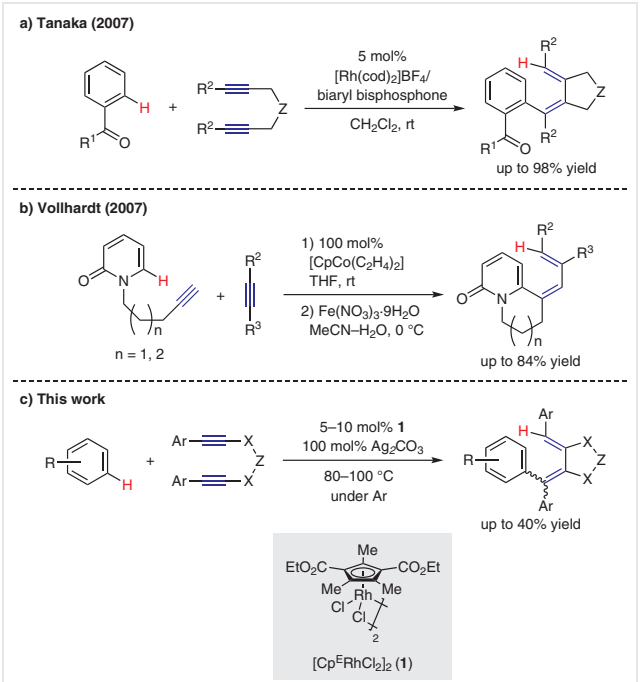
Abstract It has been established that the dienylation of unfunctionalized arenes with 1,6-diynes, possessing aryl groups at the diyne termini, proceeds to give the corresponding dienylated arenes in the presence of a catalytic amount of an electron-deficient cyclopentadienyl rhodium(III) complex, $[Cp^ERhCl_2]_2$, and a stoichiometric amount of silver carbonate. Experimental and theoretical mechanistic studies revealed that a $Cp^ERh(I)$ complex generated in situ might catalyze the present dienylation reaction.

Key words alkynes, dienylation, directing group-free C–H bond activation, rhodium, unfunctionalized arenes

The alkenylation reactions of arenes with alkynes via transition-metal-catalyzed sp^2 C–H bond cleavage is a useful transformation in organic synthesis.[1] This transformation has been reported in great numbers of examples.[1] In contrast, reports on the dienylation reactions of arenes with two alkynes via transition-metal-catalyzed sp^2 C–H bond cleavage have been quite limited.[2–4] Our research group[2] and the Shibata research group[3] independently reported the carbonyl-directed dienylation reactions of aryl ketones with internal 1,6-diynes by using cationic rhodium(I)/biaryl bisphosphine complexes as catalysts (Scheme 1a). The Vollhardt research group reported the directing-group-free dienylation reactions of 2-pyridones with pendant and external alkynes by using a cyclopentadienyl (Cp) cobalt(I) complex (Scheme 1b).[5] However, this reaction required a stoichiometric amount of the cobalt(I) complex, and available substrates were limited to 2-pyridones. Thus, the dienylation reaction of unfunctionalized arenes with two alkynes via transition-metal-catalyzed directing-free sp^2 C–H bond activation[6] has not been reported to date. In this paper, we disclose the first example of the directing-free dienylation reactions of unfunctionalized arenes with two alkynes by using a commercially available electron-deficient cyclopentadienyl rhodium(III) complex $[Cp^ERhCl_2]_2$ (**1**) as a catalyst[7] and diaryl-substituted 1,6-diynes as the two alkyne components (Scheme 1c).



Scheme 1 Transition-metal-mediated dienylation of arenes with two alkynes (cod = 1,5-cyclooctadiene)

Our research group reported the convenient synthesis of $[Cp^ERhCl_2]_2$ (**1**) by reductive complexation of a substituted silylfulvene with $RhCl_3$ in ethanol.[7] This complex showed high catalytic activity in [3+2],[7,8a] [4+2],[8b,c] [2+2+2],[8d–f] and [2+1+2+1][8g] annulation reactions through cleavage of sp^2 C–H bonds.[9] In the course of our recent study on the oxidative

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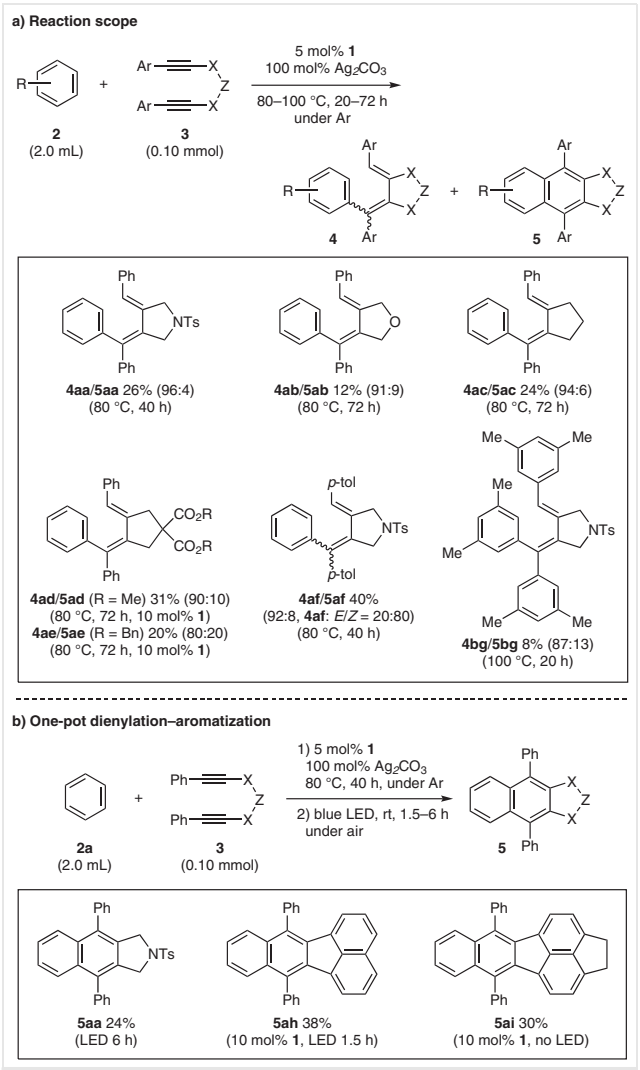
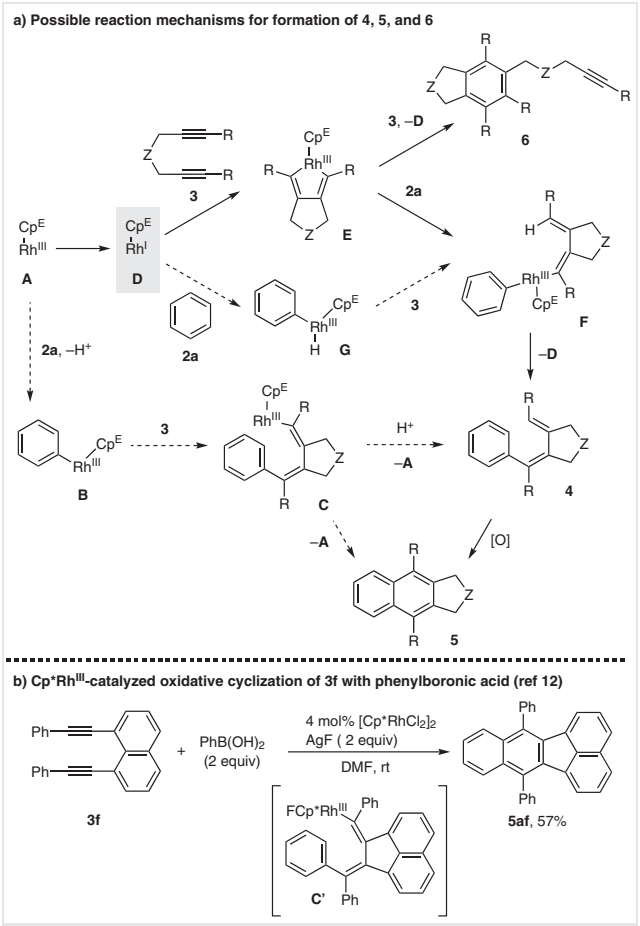
and decarboxylative [2+1+2+1] annulation reaction of benzoic acid with a diphenyl-substituted 1,6-diyne,[8g] we unexpectedly found that the dienylation of toluene, which is used as a solvent, with the 1,6-diyne, proceeds as a side reaction to give the corresponding dienylation products as an inseparable mixture of diastereomers and regioisomers (Scheme 2).[10]



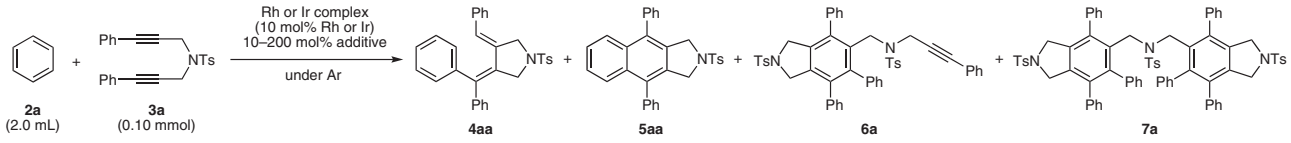
Scheme 2 Substrate scope for dienylation of arenes **2** with 1,6-diynes **3**. Complex **1** (0.0050–0.010 mmol), Ag_2CO_3 (0.10 mmol), **2** (2.0 mL), and **3** (0.10 mmol) were used. Cited yields are of the isolated products.

To avoid the formation of diastereomers and regioisomers, the reaction of benzene (**2a**) with diphenyl-substituted 1,6-diyne **3a** was conducted under the same conditions as in Scheme 2 except for argon atmosphere because the dienylation is a redox-neutral process. This reaction afforded the corresponding dienylation product **4aa** as a single diastereomer along with a trace amount of aromatized product **5aa** and [2+2+2] cycloaddition products **6a**/**7a** (Table 1, entry 1). $Cu(OAc)_2$ may not be necessary due to the redox-neutral nature of the formation of **4aa**, and thus the reaction in the absence of $Cu(OAc)_2$ also afforded **4aa** in 20% yield and significantly increased the yield of **6a**/**7a** (entry 2). The use of Ag_2CO_3 instead of AgOAc increased the selectivity of **4aa**, although the conversion of **3a** decreased to 57% (entry 3). Pleasingly, the use of a stoichiometric amount of Ag_2CO_3 gave **4aa** in higher yield than under the conditions detailed in entry 1 (entry 4). The use of Cs_2CO_3 (entry 5) and lowering the reaction temperature to 60 °C (entry 6) decreased the yield of **4aa**. Finally, prolonged reaction time (40 h) afforded **4aa** in the highest yield of 30% (entry 7). Even when using a catalytic amount (10 mol%) of Ag_2CO_3, further prolonged reaction time (72 h) afforded **4aa** in an improved yield of 29% (entry 8). Under the optimized reaction conditions, moderately electron-deficient $[CpRhI_2]_n$[11] and electron-rich $[Cp^*RhCl_2]_2$ were ineffective for the formation of **4aa** (entries 9 and 10). Diene **4aa** was not obtained at all by using $[Cp^*IrCl_2]_2$ (entry 11) or in the absence of the Rh or Ir complex (entry 12).



Scheme 3 Mechanistic considerations

Table 1 Optimization of Reaction Conditions for Dienylation of Benzene (**2a**) with 1,6-Diyne **3a**[a]



Entry	Rh or Ir complex	Additive (mol%)	Conditions	Conv. of **3a** (%)[b]	Yield (%) **4aa** + **5aa** (**4aa**/**5aa**)[b]	Yield (%) **6a** + **7a** (**6a**/**7a**)[b]
1	**1**	$[Cu(OAc)_2 \cdot H_2O]$ (20), AgOAc (20)	80 °C, 20 h	98	24 (94:6)	27 (88:12)
2	**1**	AgOAc (20)	80 °C, 20 h	>99	20 (95:5)	50 (78:22)
3	**1**	Ag_2CO_3 (10)	80 °C, 20 h	57	15 (100:0)	19 (60:40)
4	**1**	Ag_2CO_3 (100)	80 °C, 20 h	94	28 (100:0)	37 (72:28)
5	**1**	Cs_2CO_3 (100)	80 °C, 20 h	54	6 (100:0)	32 (85:15)
6	**1**	Ag_2CO_3 (100)	60 °C, 20 h	39	8 (100:0)	11 (68:32)
7	**1**	Ag_2CO_3 (100)	80 °C, 40 h	>99	30 (100:0)	42 (64:36)
8	**1**	Ag_2CO_3 (10)	80 °C, 72 h	96	29 (100:0)	38 (62:38)
9	$[CpRhI_2]_n$	Ag_2CO_3 (100)	80 °C, 40 h	54	0	23 (100:0)
10	$[Cp^*RhCl_2]_2$	Ag_2CO_3 (100)	80 °C, 40 h	76	<1	59 (92:8)
11	$[Cp^*IrCl_2]_2$	Ag_2CO_3 (100)	80 °C, 40 h	29	0	4 (100:0)
12	none	Ag_2CO_3 (100)	80 °C, 20 h	<5	0	0

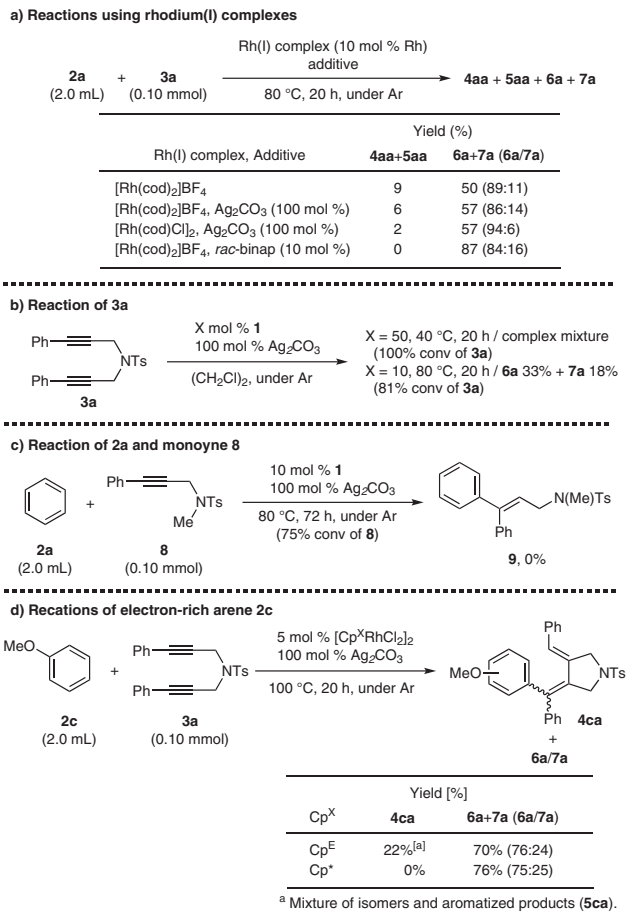
[a] Reaction conditions: Rh or Ir complex (0.010 mmol of Rh or Ir), additive (0.010–0.10 mmol), **2a** (2.0 mL), and **3a** (0.10 mmol) were used.
[b] Determined by ^{1}H NMR analysis using dimethyl terephthalate as internal standard.

With the optimized reaction conditions in hand, we explored the scope of these dienylation reactions, as shown in Scheme 2a. Concerning 1,6-diynes, not only tosylamide (**3a**) but also oxygen and methylene-linked 1,6-diynes **3b** and **3c** could be employed for this transformation, although the product yields decreased. The use of malonate-linked 1,6-diynes **3d** and **3e** also afforded the corresponding dienylated products **4ad** and **4ae**, although high catalyst loadings were required. Although the reactions using dimethyl-substituted internal 1,6-diynes and terminal 1,6-diynes were also tested, dienylation products were not obtained due to the formation of homo-[2+2+2] cycloaddition products. Concerning unfunctionalized arenes, not only benzene (**2a**) but also sterically demanding *m*-xylene (**2b**) reacted with di-*m*-xylyl-substituted 1,6-diyne **3g** to give diene **4bg**, although the yield was low. In these reactions, aromatized products **5** were not observed in the crude reaction mixtures, but **5** was observed upon isolation under air and light. Thus, upon completion of the dienylation reaction, the reaction mixture was stirred at room temperature under air and blue LED irradiation to give the corresponding aromatized product **5aa** (Scheme 2b). Highly rigid naphthalene-linked 1,6-diynes **3h** and **3i** were also suitable substrates for this process, and dienylation products (diphenylfluoranthene) **4ah** and **4ai** were generated as the sole coupling product. However, isolation by preparative thin-layer chromatography (PTLC) gave a 1:1 mixture of **4ah** and aromatized product **5ah**. Pleasingly, **5ah** could be isolated in a pure form after blue LED irradiation; on the other hand, ethylene-bridged electron-rich diene **4ai** was aromatized to diphenylfluoranthene **5ai** on the PTLC without blue LED irradiation. The reactions using a biphenyl-linked 1,7-diyne[2,2′-bis(phenylethynyl)-1,1′-biphenyl] was also tested, but no reaction was observed.

Possible mechanisms for the formation of **4**, **5**, and **6** are shown in Scheme 3a. The C–H bond cleavage of **2a** with the $Cp^ERh(III)$ complex **A** would generate phenylrhodium **B**, which reacts with diyne **3** giving dienylrhodium **C**. Protodemetalation affords diene **4** and regenerates Rh(III) complex **A**. However, in the Cp*Rh(III) complex-catalyzed oxidative cyclization of naphthalene-linked 1,6-diyne **3f** with phenylboronic acid, the same dienylrhodium **C′** activates the adjacent arene sp^2 C–H bond to give exclusively aromatized product **5af** (Scheme 3b).[12] Thus, this mechanism is unlikely due to the selective formation of diene **4**. In situ generation of $Cp^ERh(I)$ complex **D** from $Cp^ERh(III)$ complex **A** well explains the formation of both diene **4** and [2+2+2] cycloaddition product **6**, although the reduction mechanism is not clear at the present stage.[13] Complex **D** reacts with **3** to give rhodacycle **E**. Electrophilic aromatic substitution with rhodium(III) complex **E** would afford phenylrhodium(III) complex **F**.[14] Reductive elimination affords diene **4** and regenerates the catalytically active $Cp^ERh(I)$ complex **D**. This mechanism well explains the selective formation of diene **4** without the formation of naphthalene **5** and competitive formation of [2+2+2] cycloaddition product **6**, which can be generated from common rhodacycle intermediate **E**. Alternatively, the C–H bond cleavage of **2a** with $Cp^ERh(I)$

complex **D** giving rhodium(III) hydride **G** followed by hydrorhodation of diyne **3** would also afford the same phenylrhodium(III) complex **F**. Oxidative aromatization of **4** during isolation under air and light affords aromatized product **5**.

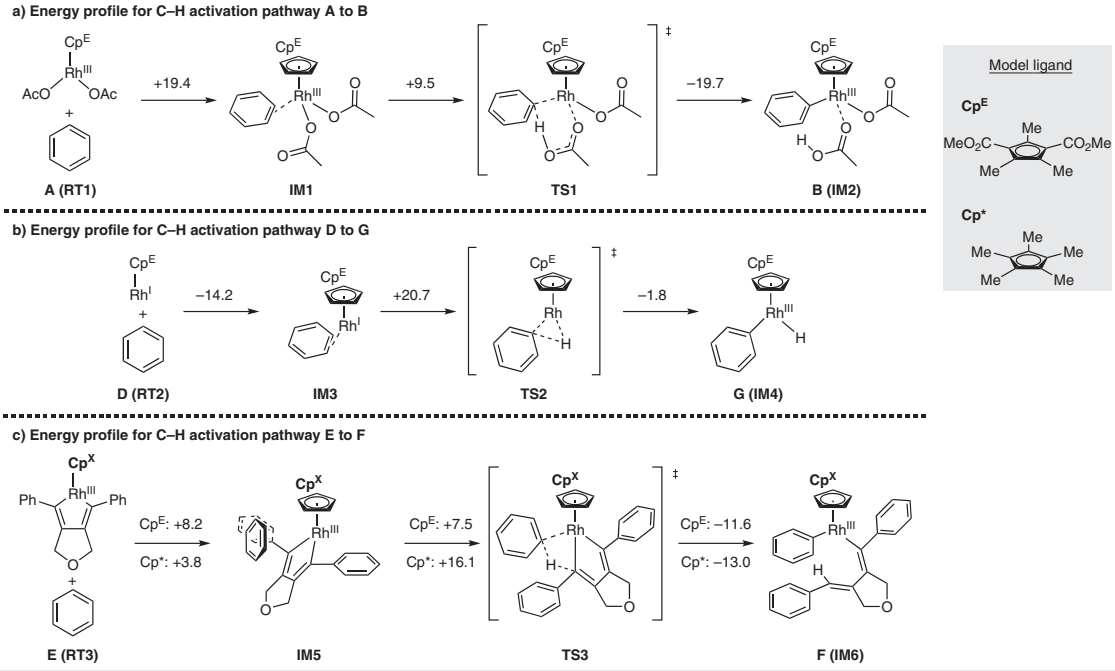
To confirm the participation of the $Cp^ERh(I)$ complex in this catalysis even in the presence of a stoichiometric amount of an oxidant (Ag_2CO_3),[15] several rhodium(I) complexes were tested in the reaction of **2a** and **3a**, as shown in Scheme 4a. A cationic rhodium(I)-cod complex $[Rh(cod)_2]BF_4$ could indeed catalyze this dienylation, although the product yield was low (9%). The addition of Ag_2CO_3 and the use of $[Rh(cod)Cl]_2$ instead of $[Rh(cod)_2]BF_4$ decreased the yield of **4aa**/**5aa** (6% and 2%, respectively), but slightly increased the yield of **6a**/**7a**. Importantly, the use of a cationic rhodium(I)/*rac*-binap complex, which was an effective catalyst for the dienylation reaction shown in Scheme 1a, catalyzed only the [2+2+2] cycloaddition of **3a**. Thus, a σ-donor ligand is ineffective for the present C–H activation. In the absence of **2a**, **3a** reacted with stoichiometric amounts of **1** and Ag_2CO_3 to give a complex mixture of products, but the use of a catalytic amount of **1** gave [2+2+2] cycloaddition products **6a** and **7a** (Scheme 4b).[16] No reaction was observed in the absence of **3a**, and the oxidative coupling of *o*-xylene giving biphenyl was not observed. These results might suggest the reduction of the $Cp^ERh(III)$ complex in situ into the $Cp^ERh(I)$ complex with diyne **3a**. The reaction of **2a** with monoyne **8** did not afford monoene **9** at all, which supports the formation of diene **4** via not rhodium hydride **G** but rhodacycle **E** (Scheme 4c). We anticipated that the electron-deficient nature of the $Cp^ERh(III)$ complex might be important to activate the C–H bond of electron-rich arenes in the present dienylation reaction. Thus, the reactions of a highly electron-rich arene [anisole (**2c**)] and **3a** using the $Cp^ERh(III)$ and $Cp^*Rh(III)$ complexes were examined, as shown in Scheme 4d. As expected, the $Cp^ERh(III)$ complex catalyzed the dienylation reaction to give diene **4ca** as a mixture of diastereomers and regioisomers; in contrast, the $Cp^*Rh(III)$ complex failed to catalyze the dienylation reaction. Additionally, both the $Cp^ERh(III)$ and $Cp^*Rh(III)$ complexes failed to catalyze the dienylation reaction of electron-deficient arenes (chlorobenzene and fluorobenzene) with **3a**.



Scheme 4 Experimental mechanistic studies

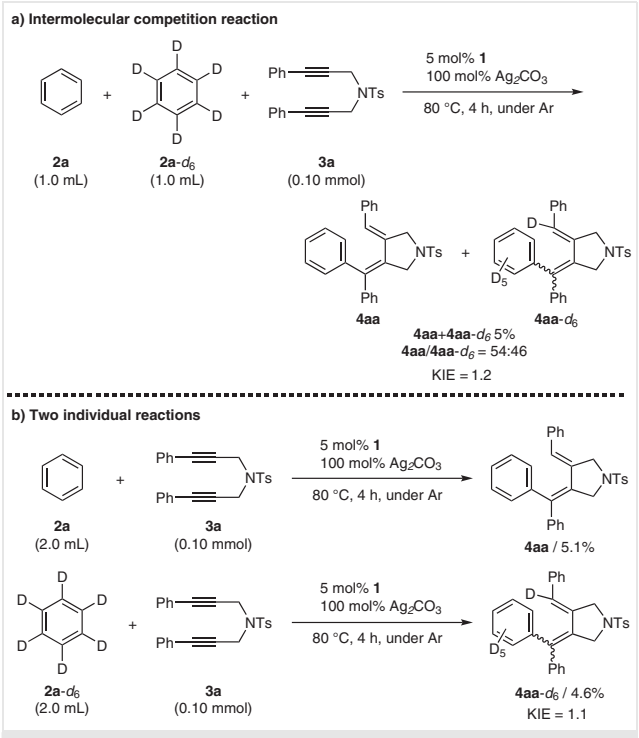
To gain more mechanistic insights, we conducted a computational study concerning each C–H activation pathway. The pathway for generating phenylrhodium **B (IM2)** from $Cp^ERh(III)$ complex **A (RT1)** requires a high activation energy (28.9 kcal mol^{-1}) due to the difficulty in approaching **A** to **2a** giving **IM1** (ΔG = 19.4 kcal mol^{-1}) without chelation assistance (Scheme 5a). Furthermore, considering that cationic $Cp^ERh(III)$ complex generated in situ by the addition of $AgSbF_6$ failed to catalyze the present dienylation, the direct C–H bond cleavage through electrophilic aromatic substitution pathway can be excluded. In sharp contrast, η^2 coordination of **2a** to the $Cp^ERh(I)$ complex greatly stabilizes **IM3** (ΔG = –14.2 kcal mol^{-1}), but high activation energy (20.7 kcal mol^{-1}) is required for the generation of rhodium(III) hydride **G (IM4)** from **IM3** via the non-directed C–H bond activation (Scheme 5b). The lowest activation energy (7.5 kcal mol^{-1}) is calculated for the generation of phenylrhodium Cp^E-**F (IM6)** from rhodacycle Cp^E-**E (RT3)** with the formation of **IM5** (ΔG = 8.2 kcal mol^{-1}) (Scheme 5c). In **IM1** and **IM3**, benzene is coordinated to rhodium, but in **IM5**, benzene is not coordinated to rhodium due to steric hindrance of the rhodacycle. Thus, the theoretically most favorable pathway is **E** to **F**. Furthermore, computational studies revealed that this pathway is not available for the Cp*Rh complex. The C–H bond activation from Cp^*-**E (RT3)** not only requires the higher activation energy (16.1 kcal mol^{-1}) but is thermodynamically unfavorable (ΔG = 3.1 kcal mol^{-1}).

Finally, a deuterium kinetic isotope effect (DKIE) of dienylation of **2a** with **3a** was measured. The intermolecular competition reactions between **2a** and **2a**-d_6 in the presence of **3a** revealed a DKIE value of 1.2 (Scheme 6a). A DKIE value, measured by comparing the initial rates obtained



Scheme 5 Theoretical mechanistic studies [ΔG (kcal mol^{-1}) values are absolute for the step depicted]

from two individual reactions of **2a** and **2a**-d_6 with **3a**, was 1.1 (Scheme 6b). These results indicate that the C–H bond cleavage is not the rate-limiting step in the present dienylation reactions, which is consistent with the low activation energy for the C–H bond activation, but high temperature is required for the present dienylation reaction.



Scheme 6 DKIE experiments

In conclusion, we have established that unfunctionalized arenes can be dienylated with 1,6-diynes, possessing aryl groups at the diyne termini, in the presence of a catalytic amount of an electron-deficient cyclopentadienyl rhodium(III) complex, $[Cp^ERhCl_2]_2$ (**1**), and a stoichiometric amount of silver carbonate to give the corresponding dienylated arenes, although the product yields were low. Experimental and theoretical mechanistic studies suggested that a $Cp^ERh(I)$ complex generated in situ might catalyze the present dienylation reaction. A low activation energy (15.7 kcal mol^{-1}) was calculated for the C–H bond activation of benzene with a rhodacyclopentadiene intermediate, derived from the $Cp^ERh(I)$ complex and the 1,6-diyne.

$(CH_2Cl)_2$ (No. 28,450-5), benzene (No. 401765), *o*-xylene (No. 294780), *m*-xylene (No. 296325) and anisole (No. 296295) were obtained from Aldrich and used as received. Benzene-d_6 (05080-96) was obtained from Kanto and used as received. Solvents for the synthesis of substrates were dried over molecular sieves 4Å (Wako) before use. $[Cp^ERhCl_2]_2$ was prepared from $RhCl_3{\cdot}nH_2O$ (ca. 39 wt% Rh) according to the literature.[7] Diynes **3a**,[17] **3b**,[17] **3c**,[17] **3d**,[17] **3e**,[18] **3f**,[19] **3g**,[20] **3h**,[12] **3i**[21] and monoynes **8**[22] were already reported. All other reagents were obtained from commercial sources and used as received. All reactions were carried out under nitrogen or argon in oven-dried glassware with magnetic stirring unless otherwise noted. ^1H and ^{13}C NMR data were collected with a Bruker Avance III HD 400 (400 MHz)

at ambient temperature. HRMS data were obtained with a Bruker micrOTOF Focus II.

Directing Group-Free Dienylation of Arenes with 1,6-Diynes; Typical Procedure (Scheme 2a)

To a Schlenk tube was added Ag_2CO_3 (27.6 mg, 0.10 mmol), **1** (4.3 mg, 0.0050 mmol), **3a** (40.0 mg, 0.100 mmol), and **2a** (2.0 mL) in this order. The mixture was stirred at 80 °C under Ar for 40 h. The resulting mixture was diluted with hexane, filtered through a silica gel pad, and washed with diethyl ether. The solvent was removed under reduced pressure, and the residue was purified by preparative thin-layer chromatography (PTLC, toluene/EtOAc = 30:1) to give a mixture of **4aa** and **5aa**[23] (12.4 mg, 0.0259 mmol, 26% yield, **4aa**/**5aa** = 96:4) as a pale-yellow solid, **6a** (8.6 mg, 0.0215 mmol, 22% yield) as a yellow solid, and **7a** (5.0 mg, 0.0125 mmol, 13% yield) as an orange solid.

(4*Z*)-3-(Diphenylmethylidene)-1-(4-methylbenzenesulfonyl)-4-(phenylmethylidene)pyrrolidine (4aa)

Mp 165.0–193.6 °C (dec.)

^{1}H NMR ($CDCl_3$, 400 MHz): δ (**4aa**) = 7.64 (d, *J* = 8.2 Hz, 2 H), 7.35–7.18 (m, 11 H), 7.04 (dd, *J* = 8.2, 1.6 Hz, 2 H), 6.96 (dd, *J* = 8.2, 1.6 Hz, 2 H), 6.89 (d, *J* = 7.4 Hz, 2 H), 5.96 (t, *J* = 2.4 Hz, 1 H), 4.34 (d, *J* = 2.4 Hz, 2 H), 4.11 (s, 2 H), 2.44 (s, 3 H); methylene and methyl protons of **5aa**: δ = 4.54 (s, 4 H), 2.38 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 143.8, 143.6, 142.3, 141.3, 138.0, 137.7, 136.5, 134.2, 133.8, 133.7, 133.6, 132.9, 132.3, 129.9, 129.8, 129.6, 129.5, 129.4, 128.9, 128.8, 128.7, 128.53, 128.51, 128.3, 128.1, 127.9, 127.8, 127.6, 127.4, 125.91, 125.86, 53.6, 52.9, 52.0, 21.54, 21.51.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for **4aa** $C_{31}H_{27}NNaO_2S$: 500.1655; found: 500.1636; *m*/*z* [M + Na]$^+$ calcd for **5aa** $C_{31}H_{27}NNaO_2S$: 498.1498; found: 498.1493.

4-Methyl-*N*-{[2-(4-methylbenzenesulfonyl)-4,6,7-triphenyl-2,3-dihydro-1*H*-isoindol-5-yl]methyl}-*N*-(3-phenylprop-2-yn-1-yl)benzene-1-sulfonamide (6a)

Mp 188.3–189.7 °C

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.65 (d, *J* = 8.2 Hz, 2 H), 7.50–7.38 (m, 3 H), 7.36–7.28 (m, 4 H), 7.20 (tt, *J* = 7.4, 1.6 Hz, 1 H), 7.17–7.08 (m, 8 H), 7.08–7.00 (m, 4 H), 6.93–6.84 (m, 4 H), 6.69 (dd, *J* = 8.4, 1.4 Hz, 2 H), 4.40 (s, 4 H), 4.23 (s, 2 H), 3.15 (s, 2 H), 2.43 (s, 3 H), 2.12 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 143.6, 143.0, 142.3, 138.8, 138.5, 138.4, 137.6, 136.6, 135.2, 135.0, 133.8, 132.9, 131.3, 131.1, 129.8, 129.23, 129.18, 129.0, 128.8, 128.0, 127.8, 127.7, 127.63, 127.56, 126.8, 126.6, 122.3, 85.0, 82.2, 54.3, 54.2, 47.1, 38.3, 21.5, 21.2.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{50}H_{42}N_2NaO_4S_2$: 821.2478; found: 821.2479.

4-Methyl-*N*,*N*-bis({[2-(4-methylbenzenesulfonyl)-4,6,7-triphenyl-2,3-dihydro-1*H*-isoindol-5-yl]methyl})benzene-1-sulfonamide (7a)

Mp 170.1–172.5 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.59 (d, *J* = 8.2 Hz, 4 H), 7.43 (br, 6 H), 7.27 (d, *J* = 6.8 Hz, 6 H), 7.22–6.51 (br, 6 H), 7.14 (t, *J* = 7.2 Hz, 3 H), 7.05 (br, 9 H), 6.66 (br, 2 H), 6.61 (d, *J* = 8.0 Hz, 4 H), 6.03 (d, *J* = 8.2 Hz, 2 H), 4.46–3.86 (br, 12 H), 2.38 (s, 6 H), 2.29 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 143.6, 141.9, 141.5, 139.1, 138.4, 137.6, 136.0, 134.6, 134.3, 133.7, 131.3, 129.8, 129.7, 129.0, 128.6, 128.1, 127.7, 127.6, 127.5, 126.9, 126.7, 126.5, 54.2, 54.1, 49.9, 21.5, 21.2.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{75}H_{63}N_3NaO_6S_3$: 1220.3771; found: 1220.3778.

(4*Z*)-3-(Diphenylmethylidene)-4-(phenylmethylidene)oxolane (4ab)[24]

The title compounds were isolated as a mixture of **4ab** and **5ab**.

Yield: 4.0 mg (0.0120 mmol, 12%); **4ab**/**5ab** = 91:9; yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ (**4ab**) = 7.56–7.22 (m, 10 H), 7.17 (d, *J* = 7.4 Hz, 1 H), 7.12 (dd, *J* = 8.4, 1.6 Hz, 2 H), 6.88 (d, *J* = 7.4 Hz, 2 H), 6.02 (t, *J* = 2.4 Hz, 1 H), 4.81 (d, *J* = 2.4 Hz, 2 H), 4.57 (s, 2 H); methylene protons of **5ab**: δ = 5.08 (s, 4 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 142.7, 141.5, 138.3, 137.7, 137.2, 136.3, 136.1, 135.9, 132.4, 132.1, 129.8, 129.6, 128.9, 128.8, 128.7, 128.5, 128.4, 128.1, 127.7, 127.5, 127.4, 127.0, 125.9, 125.7, 125.6, 77.3, 77.2, 77.0, 76.7, 73.5, 72.3, 71.7.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{21}O$: 325.1587; found: 325.1574.

{[(1*E*)-2-(Diphenylmethylidene)cyclopentylidene]methyl}benzene (4ac)

The title compounds were isolated as a mixture of **4ac** and **5ac**.[25]

Yield: 7.9 mg (0.0244 mmol, 24%); **4ac**/**5ac** = 94:6; pale-yellow solid; mp 108.5–121.8 °C (dec.).

^{1}H NMR ($CDCl_3$, 400 MHz): δ (**4ac**) = 7.36–7.12 (m, 12 H), 7.11 (t, *J* = 7.4 Hz, 1 H), 7.04 (d, *J* = 7.4 Hz, 2 H), 6.04 (t, *J* = 2.0 Hz, 1 H), 2.74 (td, *J* = 7.2, 2.0 Hz, 2 H), 2.55 (t, *J* = 7.2 Hz, 2 H), 1.78 (tt, *J* = 7.2, 7.2 Hz, 2 H); methylene protons of **5ac**: δ = 2.88 (t, *J* = 8.0 Hz, 4 H), 2.00 (quin, *J* = 8.0 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 144.2, 143.4, 142.0, 141.7, 141.1, 139.7, 138.5, 135.8, 134.2, 131.9, 131.6, 130.2, 130.1, 129.6, 128.63, 128.56, 128.3, 128.1, 127.8, 127.3, 127.0, 126.6, 126.5, 126.2, 125.9, 124.7, 34.5, 33.0, 32.1, 25.7, 24.4.

HRMS (APCI): *m*/*z* [M] calcd for $C_{25}H_{22}$: 322.1722; found: 322.1738.

1,1-Dimethyl (4*E*)-3-(diphenylmethylidene)-4-(phenylmethylidene)cyclopentane-1,1-dicarboxylate (4ad)

The title compounds were isolated as a mixture of **4ad** and **5ad**.

Yield: 13.4 mg (0.0307 mmol, 31%); **4ad**/**5ad** = 90:10; yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ (**4ad**) = 7.35–7.11 (m, 13 H), 7.03 (d, *J* = 7.4 Hz, 2 H), 6.06 (t, *J* = 2.4 Hz, 1 H), 3.70 (s, 6 H), 3.35 (d, *J* = 2.4 Hz, 2 H), 3.12 (s, 2 H); methylene protons of **5ad**: δ = 3.67 (s, 6 H), 3.55 (s, 4 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 171.9, 171.8, 143.4, 142.6, 138.8, 137.9, 137.6, 137.4, 137.1, 136.7, 134.6, 132.3, 131.7, 130.02, 129.96, 129.8, 129.5, 129.0, 128.7, 128.60, 128.56, 128.4, 128.34, 128.28, 128.2, 128.0, 127.9, 127.6, 127.4, 127.3, 127.01, 126.99, 126.7, 125.93, 125.86, 125.2, 60.2, 58.1, 53.1, 52.9, 52.8, 41.1, 40.5, 39.1.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for **4ad** $C_{29}H_{26}NaO_4$: 461.1723; found: 461.1723; *m*/*z* [M + Na]$^+$ calcd for **5ad** $C_{29}H_{24}NaO_4$: 459.1567; found: 459.1583.

1,1-Dibenzyl (4*E*)-3-(diphenylmethylidene)-4-(phenylmethylidene)cyclopentane-1,1-dicarboxylate (4ae)

The title compounds were isolated as a mixture of **4ae** and **5ae**.

Yield: 11.5 mg (0.0195 mmol, 20%); **4ae**/**5ae** = 80:20; yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ (**4ae**) = 7.35–7.08 (m, 23 H), 7.01 (d, *J* = 7.4 Hz, 2 H), 6.04 (t, *J* = 2.4 Hz, 1 H), 5.12 (d, *J* = 12.4 Hz, 2 H), 5.06 (d, *J* = 12.4 Hz, 2 H), 3.38 (d, *J* = 2.4 Hz, 2 H), 3.18 (s, 2 H); methylene, protons of **5ae**: δ = 5.06 (s, 4 H), 3.55 (s, 4 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 171.0, 143.3, 142.6, 138.7, 137.9, 137.6, 137.4, 136.9, 136.7, 135.4, 135.3, 134.7, 132.3, 130.0, 129.9, 129.5, 128.7, 128.6, 128.52, 128.49, 128.47, 128.2, 128.02, 127.92, 127.32, 126.97, 126.96, 126.7, 125.9, 125.2, 67.32, 67.28, 60.7, 58.4, 41.1, 40.4, 39.2.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for **4ae** $C_{41}H_{34}NaO_4$: 613.2349; found: 613.2381; *m*/*z* [M + Na]$^+$ calcd for **5ae** $C_{41}H_{32}NaO_4$: 611.2193; found: 611.2231.

(4*Z*)-1-(4-Methylbenzenesulfonyl)-3-[(4-methylphenyl)(phenyl)methylidene]-4-[(4-methylphenyl)methylidene]pyrrolidine (4af)

The title compounds were isolated as a mixture of **4af** and **5af**.

Yield: 20.4 mg (0.0404 mmol, 40%); **4af**/**5af** = 92:8, **4af**: *E*/*Z* = 20:80; pale-yellow solid; mp 153.8–160.9 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ (*Z*)-**4af** = 7.63 (d, *J* = 7.6 Hz, 2 H), 7.35–7.18 (m, 6 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 7.10–7.01 (m, 2 H), 6.94–6.90 (m, 2 H), 6.82 (t, *J* = 7.6 Hz, 1 H), 6.78 (d, *J* = 7.6 Hz, 2 H), 5.91 (t, *J* = 2.4 Hz, 1 H), 4.33 (br, 2 H), 4.12 (s, 2 H), 2.43 (s, 3 H), 2.37 (s, 3 H), 2.30 (s, 3 H); a part of aromatic protons and vinyl, methylene, and methyl protons of (*E*)-**4af**: δ = 7.63 (d, *J* = 7.6 Hz, 2 H), 6.01 (t, *J* = 2.4 Hz, 1 H), 4.33 (br, 2 H), 4.08 (s, 2 H), 2.43 (s, 3 H), 2.31 (s, 3 H), 2.29 (s, 3 H); methylene and methyl protons of **5af**: δ = 4.54 (s, 4 H), 2.48 (s, 6 H), 2.38 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 143.7, 143.6, 142.6, 141.5, 139.5, 138.3, 137.7, 137.6, 137.4, 137.0, 134.7, 133.79, 133.76, 133.7, 133.6, 133.4, 133.3, 132.9, 132.7, 132.51, 132.46, 129.81, 129.75, 129.7, 129.52, 129.48, 129.33, 129.25, 129.0, 128.93, 128.88, 128.8, 128.6, 128.48, 128.46, 128.3, 127.84, 127.81, 127.7, 127.6, 127.3, 125.9, 125.7, 53.7, 53.0, 52.9, 52.0, 21.53, 21.49, 21.3, 21.24, 21.2, 21.18.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for **4af** $C_{33}H_{32}NO_2S$: 506.2148; found: 506.2196; *m*/*z* [M + H]$^+$ calcd for **5af** $C_{33}H_{30}NO_2S$: 504.1992; found: 504.2041.

(4*Z*)-3-[Bis(3,5-dimethylphenyl)methylidene]-4-[(3,5-dimethylphenyl)methylidene]-1-(4-methylbenzenesulfonyl)pyrrolidine (4bg)

The title compounds were isolated as a mixture of **4bg** and **5bg**.

Yield: 4.7 mg (0.0084 mmol, 8%); **4bg**/**5bg** = 87:13; yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ **4bg** = 7.61 (d, *J* = 8.4 Hz, 2 H), 7.29 (d, *J* = 8.4 Hz, 2 H), 6.92 (s, 1 H), 6.84 (s, 1 H), 6.83 (s, 1 H), 6.63 (s, 2 H), 6.49 (br, 4 H), 5.88 (t, *J* = 2.4 Hz, 1 H), 4.33 (d, *J* = 2.4 Hz, 2 H), 4.08 (s, 2 H), 2.45 (s, 3 H), 2.30 (s, 6 H), 2.27 (s, 3 H), 2.20 (s, 3 H); a part of aromatic protons and methylene and methyl protons of **5bg**: δ = 7.64 (d, *J* = 8.4 Hz, 2 H), 4.46 (s, 2 H), 4.37 (s, 2 H), 2.40 (s, 9 H), 2.36 (s, 6 H), 2.29 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 143.5, 142.5, 141.1, 138.3, 138.1, 137.9, 137.6, 136.8, 134.7, 134.22, 134.05, 132.2, 131.9, 129.8, 129.7, 129.4, 129.2, 129.03, 128.96, 128.9, 127.9, 127.8, 127.6, 127.1, 127.0, 126.8, 126.5, 126.2, 54.3, 53.2, 52.2, 21.6, 21.44, 21.37, 21.3.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for **4bg** $C_{37}H_{40}NO_2S$: 562.2774; found: 562.2805; *m*/*z* [M + H]$^+$ calcd for **5bg** $C_{37}H_{38}NO_2S$: 560.2618; found: 560.2669.

One-Pot Dienylation and Aromatization; Typical Procedure (Scheme 2b)

To a Schlenk tube was added Ag_2CO_3 (27.6 mg, 0.10 mmol), **1** (4.3 mg, 0.0050 mmol), **3a** (40.0 mg, 0.10 mmol), and **2a** (2.0 mL) in this order. The mixture was stirred at 80 °C under Ar for 40 h. The mixture was then irradiated with blue LED light at r.t. under air for 6 h. Then, the mixture was diluted with hexane, filtered through a silica gel pad, and washed with diethyl ether. The solvent was removed under reduced pressure, and the residue was purified by PTLC (toluene/EtOAc = 30:1) to give **5aa** (10.9 mg, 0.0229 mmol, 23% yield) as a colorless solid.

2-(4-Methylbenzenesulfonyl)-4,9-diphenyl-1*H*,2*H*,3*H*-benzo[*f*]isoindole (5aa)[22]

Mp 232.8–234.6 °C (dec.).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.69 (d, *J* = 8.4 Hz, 2 H), 7.63–7.59 (m, 2 H), 7.56–7.46 (m, 6 H), 7.37–7.27 (m, 8 H), 4.54 (s, 4 H), 2.39 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 143.7, 137.7, 133.8, 133.6, 132.9, 132.3, 129.8, 129.5, 128.8, 127.9, 127.6, 125.91, 125.87.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{31}H_{25}NNaO_2S$: 498.1498; found: 498.1499.

7,12-Diphenylbenzo[*k*]fluoranthene (5ah)[21]

Yield: 15.5 mg (0.0384 mmol, 38%); yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.71–7.55 (m, 14 H), 7.39 (dd, *J* = 6.4, 3.3 Hz, 2 H), 7.32 (t, *J* = 7.6 Hz, 2 H), 6.61 (d, *J* = 7.1 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 138.9, 136.6, 135.6, 134.9, 134.8, 132.9, 130.1, 130.0, 129.2, 128.0, 127.8, 126.8, 125.9, 125.8, 122.2.

5,10-Diphenyl-1,2-dihydrobenzo[*k*]cyclopenta[*cd*]fluoranthene (5ai)[21]

Yield: 13.0 mg (0.0302 mmol, 30%); yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.71–7.58 (m, 12 H), 7.39 (dd, *J* = 6.4, 3.3 Hz, 2 H), 7.14 (t, *J* = 7.1 Hz, 2 H), 6.65 (d, *J* = 7.1 Hz, 2 H), 3.42 (s, 4 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 145.1, 139.3, 136.7, 136.2, 134.8, 134.2, 132.4, 132.3, 130.2, 129.1, 127.8, 126.7, 125.5, 123.8, 120.9, 32.1.

Experimental Mechanistic Studies (Scheme 4)

Procedure for $[Rh(cod)_2]BF_4$ (Scheme 4a)

To a Schlenk tube was added Ag_2CO_3 (27.6 mg, 0.10 mmol), $[Rh(cod)_2]BF_4$ (4.1 mg, 0.0101 mmol), **3a** (40.0 mg, 0.100 mmol), and **2a** (2.0 mL) in this order. The mixture was stirred at 80 °C under Ar for 20 h. The resulting mixture was diluted with hexane, filtered through a silica gel pad, and washed with diethyl ether. The solvent was removed under reduced pressure to give **4aa** (6% yield) and **6a** (49% yield). The yields were determined by ^{1}H NMR analysis using dimethyl terephthalate as an internal standard.

Procedure for $[Rh(cod)Cl]_2$ (Scheme 4a)

To a Schlenk tube was added Ag_2CO_3 (27.6 mg, 0.10 mmol), $[Rh(cod)Cl]_2$ (2.5 mg, 0.00507 mmol), **3a** (40.0 mg, 0.100 mmol), and **2a** (2.0 mL) in this order. The mixture was stirred at 80 °C under Ar for

20 h. The resulting mixture was diluted with hexane, filtered through a silica gel pad, and washed with diethyl ether. The solvent was removed under reduced pressure to give **4aa** (2% yield) and **6a** (53% yield). The yields were determined by ^{1}H NMR analysis using dimethyl terephthalate as an internal standard.

Procedure for [Rh(cod)$_2$]BF$_4$/*rac*-binap System (Scheme 4a)

rac-Binap (6.2 mg, 0.0100 mmol) and [Rh(cod)$_2$]BF$_4$ (4.1 mg, 0.0101 mmol) were dissolved in CH_2Cl_2 (2 mL), and the mixture was stirred at r.t. for 10 minutes. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at r.t. for 30 minutes, the resulting mixture was concentrated to dryness. To the residue was added **3a** (40.0 mg, 0.100 mmol), and **2a** (2.0 mL) in this order. The mixture was stirred at 80 °C under Ar for 20 h. The resulting mixture was diluted with hexane, filtered through a silica gel pad, and washed with diethyl ether. The solvent was removed under reduced pressure to give **6a** (73% yield) and **7a** (14% yield). The yields were determined by ^{1}H NMR analysis using dimethyl terephthalate as an internal standard.

Procedure for Scheme 4b

To a Schlenk tube was added Ag_2CO_3 (27.6 mg, 0.10 mmol), **1** (8.5 mg, 0.0100 mmol), **3a** (40.0 mg, 0.100 mmol), and $(CH_2Cl)_2$ (2.0 mL) in this order. The mixture was stirred at 80 °C under Ar for 20 h. The resulting mixture was diluted with hexane, filtered through a silica gel pad, and washed with diethyl ether. The solvent was removed under reduced pressure, and the residue was purified by a preparative TLC (toluene/EtOAc = 30:1) to give **6a** (13.0 mg, 0.0325 mmol, 33% yield) and **7a** (7.3 mg, 0.0184 mmol, 18% yield).

3-[(Methoxyphenyl)(phenyl)methylidene]-1-(4-methylbenzenesulfonyl)-4-(phenylmethylidene)pyrrolidine (4ca, Scheme 4d)

The title compounds were isolated as a mixture of **4ca** and **5ca**. The regio- and stereochemistries of **4ca** could not be determined.

Yield: 11.1 mg (0.0219 mmol, 22%); **4ca**/**5ca** = 92:8, **4ca**/isomer ratio = 75:25; yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ **4ca** = 7.63 (d, *J* = 8.0 Hz, 2 H), 7.36–7.24 (m, 8 H), 7.02 (dd, *J* = 8.4, 2.0 Hz, 2 H), 6.94 (d, *J* = 7.6 Hz, 2 H), 6.88 (d, *J* = 8.4 Hz, 2 H), 6.77 (d, *J* = 8.8 Hz, 2 H), 6.11 (t, *J* = 2.4 Hz, 1 H), 4.34 (d, *J* = 2.4 Hz, 2 H), 4.08 (s, 2 H), 3.77 (s, 3 H), 2.43 (s, 3 H); a part of aromatic, vinyl, methylene, and methyl protons of another isomer of **4ca**: δ = 7.63 (d, *J* = 8.0 Hz, 2 H), 7.05 (dd, *J* = 8.4, 2.0 Hz, 2 H), 6.03 (t, *J* = 2.4 Hz, 1 H), 4.33 (d, *J* = 2.4 Hz, 2 H), 4.10 (s, 2 H), 3.70 (s, 3 H), 2.44 (s, 3 H); methylene and methyl protons of **5ca**: δ = 4.51 (s, 2 H), 4.49 (s, 2 H), 3.68 (s, 3 H), 2.39 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 160.0, 158.9, 143.8, 143.7, 142.7, 142.6, 142.1, 137.7, 136.6, 136.5, 134.5, 134.1, 133.7, 133.6, 133.5, 132.8, 132.4, 130.9, 129.9, 129.83, 129.75, 129.4, 129.0, 128.8, 128.53, 128.52, 128.34, 128.29, 128.2, 127.8, 127.7, 127.6, 127.42, 127.35, 121.9, 115.2, 114.0, 112.8, 55.24, 55.21, 52.94, 52.86, 51.9, 23.8, 21.6.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for **4ca,** $C_{32}H_{29}NNaO_3S$: 530.1760; found: 530.1709.

Theoretical Mechanistic Studies (Scheme 5)

All calculations were carried with the Gaussian 16 program package.[26] The hybrid density functional method based on M06[27] with a standard 6-31g* basis set (LANL2DZ basis set for Rh) was used for geometry optimizations and calculation of the single-point energies. Geometry optimization and vibrational analysis were performed at the same level. All stationary points were optimized without any symmetry assumptions, and characterized by normal coordinate analysis at the same level of theory (number of imaginary frequencies, NIMAG, 0 for minima and 1 for TSs). The intrinsic reaction coordinate (IRC) method was used to track minimum energy paths from transition structures to the corresponding local minima.[28]

DKIE Measurements (Scheme 6)

Intermolecular Competition Reaction (Scheme 6a)

To a Schlenk tube was added Ag_2CO_3 (27.6 mg, 0.10 mmol), **1** (4.3 mg, 0.0050 mmol), **3a** (40.0 mg, 0.10 mmol), **2a** (1.0 mL), and **2a**-d_6 (1.0 mL) in this order. The mixture was stirred at 80 °C under Ar for 4 h. The resulting mixture was diluted with hexane, filtered through a silica gel pad, and washed with diethyl ether. The solvent was removed under reduced pressure and the residue was purified by PTLC (toluene/EtOAc/dichloromethane = 30:1:1) to give **4aa** and **4aa**-d_6 (2.3 mg, 0.0049 mmol, 5% yield, **4aa**/**4aa**-d_6 = 54:46).

Two Individual Reactions (Scheme 6b)

To a Schlenk tube was added Ag_2CO_3 (27.6 mg, 0.10 mmol), **1** (4.3 mg, 0.0050 mmol), **3a** (40.0 mg, 0.10 mmol), and **2a** (2.0 mL) in this order. The mixture was stirred at 80 °C under Ar for 4 h. The resulting mixture was diluted with hexane, filtered through a silica gel pad, and washed with diethyl ether. The solvent was removed under reduced pressure. To another Schlenk tube was added Ag_2CO_3 (27.6 mg, 0.10 mmol), **1** (4.3 mg, 0.0050 mmol), **3a** (40.0 mg, 0.10 mmol), and **2a**-d_6 (2.0 mL) in this order. The mixture was stirred at 80 °C under Ar for 4 h. The resulting mixture was diluted with hexane, filtered through a silica gel pad, and washed with diethyl ether. The solvent was removed under reduced pressure. Then, the two residues were mixed and purified by PTLC (toluene/EtOAc/dichloromethane = 30:1:1) to give **4aa** and **4aa**-d_6 (4.7 mg, 0.0097 mmol, 9.7% yield, **4aa**/**4aa**-d_6 = 53:47).

(3*Z*)-1-(4-Methylbenzenesulfonyl)-3-[phenyl(^{2}H)methylidene]-4-{phenyl[(2,3,4,5,6-$^2H_5$)phenyl]methylidene}pyrrolidine (4aa-d_6)

To a Schlenk tube was added Ag_2CO_3 (27.6 mg, 0.10 mmol), **1** (4.3 mg, 0.0050 mmol), **3a** (40.0 mg, 0.10 mmol), and **2a**-d_6 (2.0 mL) in this order. The mixture stirred at 80 °C under Ar for 40 h. The resulting mixture was diluted with hexane, filtered through a silica gel pad, and washed with diethyl ether. The solvent was concentrated under reduced pressure and the residue was purified by preparative TLC (toluene/EtOAc/dichloromethane = 30:1:1) to give **4aa**-d_6 and **5aa**-d_6 (14.3 mg, 0.0296 mmol, 30% yield, **4aa**-d_6/**5aa**-d_6 = 92:8, **4aa**-d_6, *E*/*Z* = 81:29) as a pale-yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ (*E*)-**4aa**-d_6 = 7.64 (d, *J* = 8.0 Hz, 2 H), 7.36–7.16 (m, 8 H), 7.04 (dd, *J* = 8.0, 1.6 Hz, 2 H), 6.89 (d, *J* = 7.6 Hz, 2 H), 4.34 (s, 1 H), 4.11 (s, 2 H), 2.43 (s, 3 H); (*Z*)-**4aa**-d_6: δ = 7.64 (d, *J* = 8.0 Hz, 2 H), 7.36–7.16 (m, 8 H), 6.96 (dd, *J* = 8.0, 1.6 Hz, 2 H), 6.89 (d, *J* = 7.6 Hz, 2 H), 4.34 (s, 2 H), 4.11 (s, 2 H), 2.43 (s, 3 H); methylene and methyl protons of **5aa**-d_6: δ = 4.54 (s, 4 H), 2.38 (s, 3 H).

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/a-1328-6436.

References

(1) For selected recent reviews, see: (a) Boyarskiy, V. P.; Ryabukhin, D. S.; Bokach, N. A.; Vasilyev, A. V. *Chem. Rev.* **2016**, *116*, 5894. (b) Yamamoto, Y. *Chem. Soc. Rev.* **2014**, *43*, 1575. (c) De Haro, T.; Nevado, C. In *Comprehensive Organic synthesis, 2nd ed*; Knochel, P., Ed.; Elsevier: Amsterdam, **2014**, 1621. (d) Kitamura, T. In *Transition-Metal-Mediated Aromatic Ring Construction*, *Chap. 13*; Tanaka, K., Ed.; Wiley: Hoboken, **2013**, 457. (e) Kitamura, T. *Eur. J. Org. Chem.* **2009**, 1111. (f) Shen, H. C. *Tetrahedron* **2008**, *64*, 3885. (g) Nevado, C.; Echavarren, A. *Synthesis* **2005**, 167.

(2) Tanaka, K.; Otake, Y.; Wada, A.; Hirano, M. *Org. Lett.* **2007**, *9*, 2203.

(3) Tsuchikama, K.; Kuwata, Y.; Tahara, Y.; Yoshinami, Y.; Shibata, T. *Org. Lett.* **2007**, *9*, 3097.

(4) For the reactions of aryketones with 1,6-enynes, see: (a) Tanaka, K.; Otake, Y.; Sagae, H.; Noguchi, K.; Hirano, M. *Angew. Chem. Int. Ed.* **2008**, *47*, 1312; see also ref. 3. (b) For the reactions of aryamides and acrylamides with 1,6-diynes, see: Shibata, Y.; Otake, Y.; Hirano, M.; Tanaka, K. *Org. Lett.* **2009**, *11*, 689.

(5) (a) Aubert, C.; Betschmann, P.; Eichberg, M. J.; Gandon, V.; Heckrodt, T. J.; Lehmann, J.; Malacria, M.; Masjost, B.; Paredes, E.; Vollhardt, K. P. C.; Whitener, G. D. *Chem. Eur. J.* **2007**, *13*, 7443. (b) Aubert, C.; Gandon, V.; Geny, A.; Heckrodt, T. J.; Malacria, M.; Paredes, E.; Vollhardt, K. P. C. *Chem. Eur. J.* **2007**, *13*, 7466.

(6) For selected recent examples of the transition-metal-catalyzed and non-directed sp^2 C–H bond olefination of unfunctionalized arenes, see: (a) Ghosh, K.; Mihara, G.; Nishii, Y.; Miura, M. *Chem. Lett.* **2019**, *48*, 148. (b) Chen, H.; Wedi, P.; Meyer, T.; Tavakoli, G.; Van Gemmeren, M. *Angew. Chem. Int. Ed.* **2018**, *57*, 2497. (c) Wang, P.; Verma, P.; Xia, G.; Shi, J.; Qiao, J. X.; Tao, S.; Cheng, P. T. W.; Poss, M. A.; Farmer, M. E.; Yeung, K.-S.; Yu, J.-Q. *Nature* **2017**, *551*, 489. (d) Vora, H. U.; Silvestri, A. P.; Engelin, C. J.; Yu, J.-Q. *Angew. Chem. Int. Ed.* **2014**, *53*, 2683. (e) Kubota, A.; Emmert, M. H.; Sanford, M. S. *Org. Lett.* **2012**, *14*, 1760. (f) Patureau, F. W.; Nimphius, C.; Glourius, F. *Chem. Asian J.* **2012**, *7*, 1208.

(7) Shibata, Y.; Tanaka, K. *Angew. Chem. Int. Ed.* **2011**, *50*, 10917.

(8) (a) Hoshino, Y.; Shibata, Y.; Tanaka, K. *Adv. Synth. Catal.* **2014**, *356*, 1577. (b) Fukui, M.; Hoshino, Y.; Satoh, T.; Miura, M.; Tanaka, K. *Adv. Synth. Catal.* **2014**, *356*, 1638. (c) Kudo, E.; Shibata, Y.; Yamazaki, M.; Masutomi, K.; Miyauchi, Y.; Fukui, M.; Sugiyama, H.; Uekusa, H.; Satoh, T.; Miura, M.; Tanaka, K. *Chem. Eur. J.* **2016**, *22*, 14190. (d) Fukui, M.; Shibata, Y.; Hoshino, Y.; Sugiyama, H.; Uekusa, H.; Noguchi, K.; Tanaka, K. *Chem. Asian J.* **2016**, *11*, 2260. (e) Honjo, Y.; Shibata, Y.; Kudo, E.; Namba, T.; Tanaka, K. *Chem. Eur. J.* **2018**, *24*, 317. (f) Terasawa, J.; Shibata, Y.; Fukui, M.; Tanaka, K. *Molecules* **2019**, *23*, 3325. (g) Honjo, Y.; Shibata, Y.; Tanaka, K. *Chem. Eur. J.* **2019**, *25*, 9427.

(9) For applications of **1** in C–H bond functionalizations other than annulation reactions, see: (a) Morimoto, K.; Itoh, M.; Hirano, K.; Satoh, T.; Shibata, Y.; Tanaka, K.; Miura, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 5359. (b) Itoh, M.; Hirano, K.; Satoh, T.; Shibata, Y.; Tanaka, K.; Miura, M. *J. Org. Chem.* **2013**, *78*, 1365. (c) Baars, H.; Unoh, Y.; Okada, T.; Hirano, K.; Satoh, T.; Tanaka, K.; Bolm, C.; Miura, M. *Chem. Lett.* **2014**, *43*, 1782. (d) Takahama, Y.; Shibata, Y.; Tanaka, K. *Chem. Eur. J.* **2015**, *21*, 9053. (e) Shibata, Y.; Kudo, E.; Sugiyama, E.; Uekusa, H.; Tanaka, K. *Organometallics* **2016**, *35*, 1547. (f) Takahama, Y.; Shibata, Y.; Tanaka, K. *Org. Lett.* **2016**, *18*, 2934. (g) Takahama, Y.; Shibata, Y.; Tanaka, K. *Chem. Lett.* **2016**, *45*, 1177. (h) Yoshimura, R.; Shibata, Y.; Tanaka, K. *J. Org. Chem.* **2019**, *84*, 13164.

(10) Unfortunately, analytically pure dienylation products could not be isolated in this reaction.

(11) For examples of the CpRh(III) complex-catalyzed C–H bond functionalization, see: (a) Lin, W.; Li, W.; Lu, D.; Su, F.; Wen, T.-B.; Zhang, H.-J. *ACS Catal.* **2018**, *8*, 8070. (b) Yoshimura, R.; Tanaka, K. *Chem. Eur. J.* **2020**, *26*, 4969.

(12) Xu, S.; Chen, K.; Chen, H.; Yao, J.; Zhu, X. *Chem. Eur. J.* **2014**, *20*, 16442.

(13) The $RhCl_3$/*i*-Pr_2NEt catalyzed [2+2+2] cycloaddition of alkynes, in which $RhCl_3$ would be reduced by *i*-Pr_2NEt to afford a rhodium(I) complex, was reported, see: (a) Yoshida, K.; Morimoto, I.; Mitsudo, K.; Tanaka, H. *Tetrahedron* **2008**, *64*, 5800. (b) Yoshida, K.; Morimoto, I.; Mitsudo, K.; Tanaka, H. *Tetrahedron Lett.* **2008**, *49*, 2363. (c) Yoshida, K.; Morimoto, I.; Mitsudo, K.; Tanaka, H. *Chem. Lett.* **2007**, *36*, 998.

(14) The sp^2 C–H bond cleavage with a cobaltacyclopentadiene is proposed in the $CpCo^I$-catalyzed dienylation reaction shown in Scheme 1b; see ref. 5.

(15) The rhodium(I)-catalyzed [2+2+2] cycloaddition proceeded even in the presence of a stoichiometric amount of Ag_2CO_3, see: Li, Y.; Zhu, J.; Zhang, L.; Wu, Y.; Gong, Y. *Chem. Eur. J.* **2013**, *19*, 8294.

(16) Other than **5a** and **6a**, an unidentified complex mixture of products was generated.

(17) Lian, J.-J.; Chen, P.-C.; Lin, Y.-P.; Ting, H.-C.; Liu, R.-S. *J. Am. Chem. Soc.* **2006**, *128*, 11372.

(18) Shibata, T.; Yamashita, K.; Katayama, E.; Takagi, K. *Tetrahedron* **2002**, *58*, 8661.

(19) Bao, M.; Lu, W.; Su, H.; Qiu, L.; Xu, X. *Org. Biomol. Chem.* **2018**, *16*, 3258.

(20) Xu, T.; Yang, Q.; Ye, W.; Jiang, Q.; Xu, Z.; Chen, J.; Yu, Z. *Chem. Eur. J.* **2011**, *17*, 10547.

(21) Kung, Y.-H.; Cheng, Y.-S.; Tai, C.-C.; Liu, W.-S.; Shin, C.-C.; Ma, C.-C.; Tsai, Y.-C.; Wu, T.-C.; Kuo, M.-Y.; Wu, Y.-T. *Chem. Eur. J.* **2010**, *16*, 5909.

(22) Aikawa, H.; Tago, S.; Umetsu, K.; Haginiwa, N.; Asao, N. *Tetrahedron* **2009**, *65*, 1774.

(23) Hu, Y.-M.; Lin, X.-G.; Zhu, T.; Wan, J.; Sun, Y.-J.; Zhao, Q.-S.; Yu, T. *Synthesis* **2010**, 3467.

(24) Nguefack, J.; Bolitt, V.; Sinou, D. *Tetrahedron Lett.* **1996**, *37*, 5527.

(25) Hsieh, J. C.; Cheng, C. H. *Chem. Commun.* **2008**, 2992.

(26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.;

Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A. Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16, Revision A.03*; Gaussian, Inc: Wallingford CT, **2016**.

(27) (a) Beche, A. D. *Phys. Rev. A: At., Mol., Opt. Phys.* **1988**, *38*, 3098. (b) Beche, A. D. *J. Chem. Phys.* **1993**, *98*, 1372. (c) Beche, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (d) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785.

(28) (a) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363. (b) Ishida, K.; Morokuma, K.; Komornicki, A. *J. Chem. Phys.* **1977**, *66*, 2153. (c) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154. (d) Schlegel, H. B.; Gonzalez, C. *J. Phys. Chem.* **1990**, *94*, 5523.