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Rhodium-Catalyzed Oxidative Coupling of Triarylmethanols with Internal Alkynes via Successive C−H and C−C Bond Cleavages

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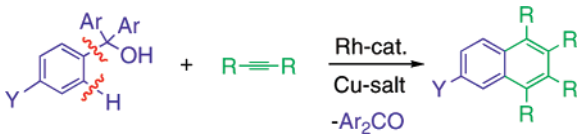
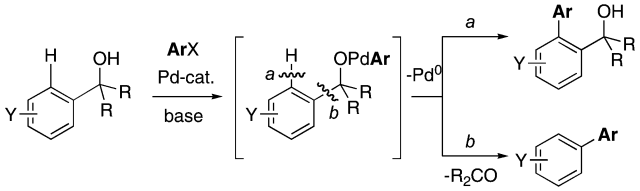


The rhodium-catalyzed oxidative coupling of triarylmethanols with internal alkynes effectively proceeds in a 1:2 manner via cleavage of C−H and C−C bonds to produce the corresponding naphthalene derivatives. Addition of tri- or tetraphenylcyclopentadiene as a ligand is crucial for the reaction to occur efficiently.

Transition-metal-catalyzed organic reactions via C−H[1] and C−C[1c,h,2] bond cleavage have attracted much attention from the atom-economic and chemoselective points of view, and various catalytic processes involving different modes to activate the relatively inert bonds have been developed. Among the most promising activation strategies is to utilize the proximate effect by coordination of a functional group in a given substrate to the metal center of a catalyst. As such examples, we recently reported that a number of α,α-disubstituted arylmethanols react with aryl chlorides and bromides in the presence of a palladium catalyst to give biaryls via cleavage of the ortho C−H or ipso C−C bond selectively depending on the substrates and catalysts employed, in which coordination of their alcoholic oxygen to the metal is the key (Scheme 1).[3] Furthermore, under appropriate conditions, the alcohols also couple with diphenylacetylene accompanied by C−C bond cleavage to form 1:1 coupling products, 1,1,2-triphenylethenes.[4] In the course of our further study of the catalytic intermolecular coupling of aromatic substrates with alkynes,[5] it has been revealed that the alcohols efficiently react with internal alkynes in a 1:2 manner under oxidative conditions using Rh as a principal catalyst[5a,d,6] in place of Pd to produce naphthalene derivatives via successive C−H and C−C bond cleavages. This represents a new example of aromatic homologation by the coupling of ArX and two alkyne molecules.[7] The findings are described herein.

SCHEME 1. Coupling of α,α-Disubstituted Arylmethanols with Aryl Halides via C−H or C−C Bond Cleavage



When triphenylmethanol (**1a**) (0.25 mmol) was treated with diphenylacetylene (**2a**) (0.5 mmol) in the presence of $[Cp^*RhCl_2]_2$ (0.005 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.5 mmol) in *o*-xylene at 170 °C (bath temperature) for 4 h under N_2, 1,2,3,4-tetraphenylnaphthalene (**3a**) was formed in 16% yield (entry 1 in Table

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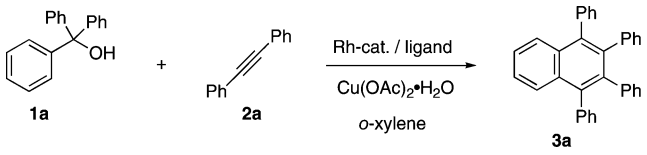
TABLE 1. Reaction of Triphenylmethanol (1a) with Diphenylacetylene (2a)[a]



entry	Rh catalyst	ligand	yield of **3a**[b]
1	$[Cp^*RhCl_2]_2$		16
2[c]	$RhCl_3 \cdot 3H_2O$		tr
3	$[RhCl(cod)]_2$		tr
4	$[Cp^*RhCl_2]_2$	$C_5H_2Ph_4$	56
5	$[Cp^*RhCl_2]_2$	$C_5H_3Ph_3$	53
6	$[Cp^*RhCl_2]_2$	C_5HPh_5	51
7	$[Cp^*RhCl_2]_2$	C_5HMe_5	10
8[d]	$[Cp^*RhCl_2]_2$	$C_5H_2Ph_4$	2
9[c]	$RhCl_3 \cdot 3H_2O$	$C_5H_2Ph_4$	2
10[c]	$Rh(acac)_3$	$C_5H_2Ph_4$	2
11	$[RhCl(C_2H_4)_2]_2$	$C_5H_2Ph_4$	22
12	$[RhCl(cod)]_2$	$C_5H_2Ph_4$	82
13[e]	$[Cp^*RhCl_2]_2$	$C_5H_2Ph_4$	79(77)
14[e]	$[RhCl(cod)]_2$	$C_5H_2Ph_4$	quant(99)

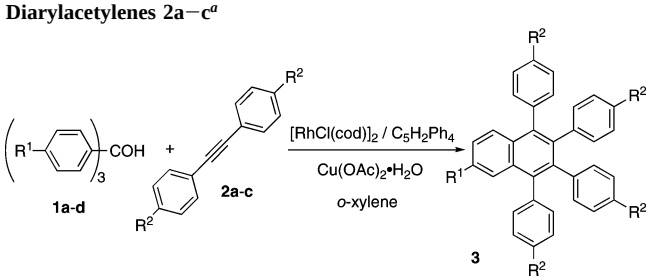
[a] Reaction conditions: [**1a**]/[**2a**]/[[Rh catalyst]/[ligand]/$[Cu(OAc)_2 \cdot H_2O]$ = 0.25:0.5:0.005:0.02:0.5 (in mmol), in *o*-xylene (2.5 mL) at 170 °C for 4 h under N_2. [b] GC yield based on the amount of **2a** used. Value in parentheses indicates yield after purification. [c] With Rh catalyst (0.01 mmol). [d] In DMAc (2.5 mL). [e] With **1a** (0.5 mmol).

1, Cp* = η^5-pentamethylcyclopentadienyl). Trace amounts of **3a** were obtained in the cases using $RhCl_3 \cdot H_2O$ and $[RhCl(cod)]_2$ (cod = 1,5-cyclooctadiene) in place of $[Cp^*RhCl_2]_2$. Interestingly, it was found that the addition of a multiply phenylated cyclopentadiene as a ligand (0.02 mmol) significantly improves the reaction efficiency. Thus, the reaction with a catalyst system of $[Cp^*RhCl_2]_2/C_5H_2Ph_4$ afforded **3a** in 56% yield (entry 4). While $C_5H_3Ph_3$ and C_5HPh_5 showed comparable effects (entries 5 and 6), use of C_5HMe_5 decreased the yield (entry 7). The reaction in a polar solvent such as DMAc was sluggish (entry 8). Even with $C_5H_2Ph_4$ as the ligand, $RhCl_3 \cdot H_2O$, $Rh(acac)_3$, and $[RhCl(C_2H_4)_2]_2$ showed low activities (entries 9−11). Finally, the combination of $[RhCl(cod)]_2$ with $C_5H_2Ph_4$ was found to be the catalyst system of choice, and the yield of **3a** was enhanced up to 82% (entry 12). Furthermore, under conditions using an excess amount of **1a** (0.5 mmol) in the presence of $[RhCl(cod)]_2/C_5H_2Ph_4$, **3a** was formed quantitatively (entry 14).

Table 2 summarizes the results for the coupling employing a series of triarylmethanols and diarylacetylenes with use of the $[RhCl(cod)]_2/C_5H_2Ph_4$ catalyst system. The reaction of alcohols **1b−d** with **2a** proceeded efficiently to produce 6-methoxy-, -methyl-, and -chloro-1,2,3,4-tetraphenylnaphthalenes **3b−d** in 61−88% yields (entries 1−3).[8] In the reaction of **1d** with **2a**, the catalyst system with $[Cp^*RhCl_2]_2$ gave a somewhat better result compared with that with $[RhCl(cod)]_2$. 4,4′-Disubstituted diphenylacetylenes **2b** and **2c** also reacted with **1a** to give the corresponding 1,2,3,4-tetraarylnaphthalenes **3e** and **3f** in good yields (entries 4 and 5). In contrast to these alkynes, bis(4-methoxyphenyl)acetylene (**2d**) was found to react with **1a** in a 1:1 manner with retaining the C−C bond of **1a** to give an

(8) Reactions of (4-methylphenyl)- and (4-fluorophenyl)diphenylmethanols with **2a** under similar conditions gave mixtures of 6-substituted and unsubstituted 1,2,3,4-tetraphenylnaphthalenes (6-Me/6-H = ca. 1:1, 6-F/6-H = ca. 1:4).

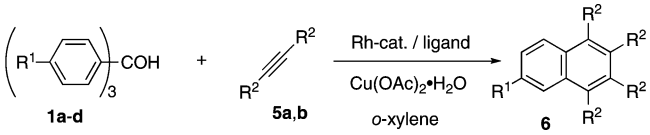
TABLE 2. Reaction of Triarylmethanols 1a−d with Diarylacetylenes 2a−c[a]



entry	**1**	R^1	**2**	R^2	product, % yield[b]
1[c]	**1b**	OMe	**2a**	H	**3b**, 88 (65)
2	**1c**	Me	**2a**	H	**3c**, (85)
3[d]	**1d**	Cl	**2a**	H	**3d**, 61 (58)
4	**1a**	H	**2b**	Me	**3e**, 87 (63)
5	**1a**	H	**2c**	Cl	**3f**, (86)

[a] Reaction conditions: [**1**]/[**2**]/[[$RhCl(cod)]_2$]/[$C_5H_2Ph_4$]/$[Cu(OAc)_2 \cdot H_2O]$ = 0.5:0.5:0.005:0.02:0.5 (in mmol), in *o*-xylene (2.5 mL) at 170 °C for 4 h under N_2. [b] GC yield based on the amount of **2** used. Value in parentheses indicates yield after purification. [c] For 6 h. [d] $[Cp^*RhCl_2]_2$ was used in place of $[RhCl(cod)]_2$.

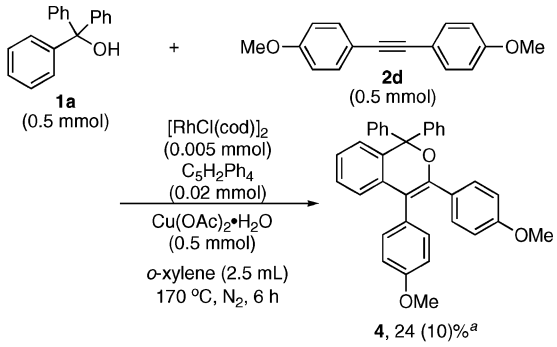
TABLE 3. Reaction of Triarylmethanols 1a−d with Dialkylacetylenes 5a,b[a]



entry	1	R^1	5	R^2	Rh catalyst	ligand	product, % yield[b]
1	**1a**	H	**5a**	C_7H_{15}	$[RhCl(cod)]_2$	$C_5H_2Ph_4$	**6a**, 45
2					$[RhCl(cod)]_2$	$C_5H_3Ph_3$	**6a**, 68
3					$[Cp^*RhCl_2]_2$	$C_5H_3Ph_3$	**6a**, 87 (63)
4	**1b**	OMe	**5a**	C_7H_{15}	$[Cp^*RhCl_2]_2$	$C_5H_3Ph_3$	**6b**, 57 (47)
5	**1c**	Me	**5a**	C_7H_{15}	$[Cp^*RhCl_2]_2$	$C_5H_3Ph_3$	**6c**, 68 (56)
6	**1d**	Cl	**5a**	C_7H_{15}	$[Cp^*RhCl_2]_2$	$C_5H_3Ph_3$	**6d**, 91 (89)
7	**1a**	H	**5b**	Pr	$[Cp^*RhCl_2]_2$	$C_5H_3Ph_3$	**6e**, 59 (57)

[a] Reaction conditions:[**1**]/[**5**]/[Rh catalyst]/[ligand]/$[Cu(OAc)_2 \cdot H_2O]$ = 0.5:0.5:0.005:0.02:0.5 (in mmol), in *o*-xylene (2.5 mL) at 170 °C for 4−6 h under N_2. [b] GC yield based on the amount of **5** used. Value in parentheses indicates yield after purification.

SCHEME 2. Reaction of Triphenylmethanol (1a) with Bis(4-methoxyphenyl)acetylene (2d)

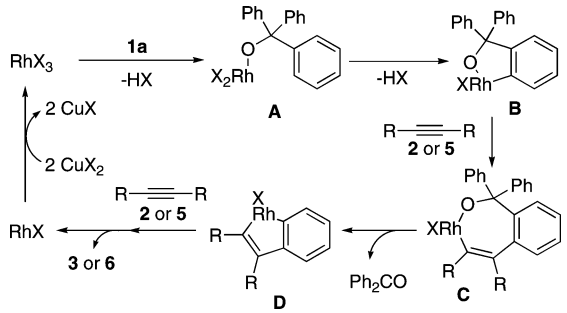


[a] GC yield. Value in parentheses indicates yield after purification.

isochromene derivative **4** in 24% yield, along with a small amount of the expected tetraarylnaphthalene (Scheme 2).

Under similar conditions using $[RhCl(cod)]_2/C_5H_2Ph_4$, **1a** also reacted with an aliphatic alkyne, 8-hexadecyne (**5a**) to afford 1,2,3,4-tetraheptylnaphthalene (**6a**) in 45% yield (entry 1 in Table 3). For this reaction, $C_5H_3Ph_3$ functioned as a more

SCHEME 3. Plausible Mechanism for the Reaction of 1a with 2 or 5



efficient ligand rather than $C_5H_2Ph_4$ to improve the yield of **6a** to 68% (entry 2). Moreover, $[Cp^*RhCl_2]_2$ showed higher activity than $[RhCl(cod)]_2$ in combination with $C_5H_3Ph_3$. Thus, with the catalyst system of $[Cp^*RhCl_2]_2/C_5H_3Ph_3$, **6a** was obtained in 87% yield (entry 3). Other alcohols **1b**−**d** reacted with **5a** in the presence of $[Cp^*RhCl_2]_2/C_5H_3Ph_3$ to afford the corresponding naphthalenes **6b**−**d** in good to excellent yields (entries 4−6). Under similar conditions, 4-octyne (**5b**) also underwent the coupling with **1a** to form 1,2,3,4-tetrapropylnaphthalene (**6e**) (entry 7).[9]

A plausible mechanism for the reaction of triphenylmethanol (**1a**) with alkyne **2** or **5** is illustrated in Scheme 3, in which neutral ligands are omitted. Coordination of the alcoholic oxygen to a $Rh(III)X_3$ species gives a rhodium(III) alcoholate **A**. Then, *ortho*-rhodation to form a rhodacycle intermediate **B**, alkyne insertion, and β-carbon elimination successively occur to produce a rhodacycle **D** with libration of Ph_2CO. The subsequent second alkyne insertion and reductive elimination take place to form naphthalene **3** or **6**. The resulting Rh(I)X species may be oxidized in the presence of the copper(II) salt to regenerate $Rh(III)X_3$. While the stoichiometric[10] and catalytic reactions[5c,f,6] involving β-carbon elimination in Rh(I) alcoholates have been reported, the process via that in Rh(III) alcoholates is very rare. In the reaction of **1a** with **2d** (R = 4-$MeOC_6H_4$) (Scheme 2), C−O reductive elimination from the seven-membered rhodacycle intermediate **C**[5a,d] may be faster than β-carbon elimination to release isochromene **4** rather than the expected naphthalene.

In summary, we have demonstrated that the oxidative coupling of triarylmethanols with internal alkynes can be performed in the presence of a rhodium catalyst, a tri- or tetraphenylcyclopentadiene ligand, and a copper oxidant to selectively give the corresponding 1:2 coupling products, naphthalene derivatives accompanied by successive C−H and C−C bond cleavages. Rh-catalyst systems for oxidative C−C coupling reactions have been less explored than those with Pd.[5a,d,11,12] The present catalyst systems and related ones are expected to be applicable to other coupling reactions. Work is underway toward further development of the catalysis.

Experimental Section

General Procedure for Oxidative Coupling of Triarylmethanols with Internal Alkynes. To a 20 mL two-necked flask were added triarylmethanol **1** (0.25 or 0.5 mmol), internal alkyne **2** or **5** (0.5 mmol), Rh catalyst (0.005 or 0.01 mmol), ligand (0.02 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.5 mmol, 100 mg), 1-methylnaphthalene (ca. 50 mg) as internal standard, and *o*-xylene or DMAc (2.5 mL). The resulting mixture was stirred under N_2 at 170 °C (bath temperature) for 4−6 h. GC and GC−MS analyses of the mixtures confirmed formation of **3**, **4**, or **6**. The product was also isolated by evaporation of solvents in vacuo and chromatography on silica gel using hexane−ethyl acetate.

1,2,3,4-Tetraphenylnaphthalene (3a) (Entry 14 in Table 1). Following the general procedure allowed the product to be isolated as a slightly yellow solid (107 mg, 99%): mp 206−208 °C (lit.[5h] mp 209−210 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82−6.86 (m, 10H), 7.17−7.32 (m, 10H), 7.38−7.40 (m, 2H), 7.63−7.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.3, 125.8, 126.4, 126.5, 127.0, 127.5, 131.3 (overlapped), 132.0, 138.4, 138.9, 139.6, 140.5; MS *m*/*z* 432 (M^+).

1,2,3,4-Tetraheptylnaphthalene (6a) (Entry 3 in Table 3). Following the general procedure allowed the product to be isolated as a colorless oil (82 mg, 63%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.99−7.97 (m, 2H), 7.40−7.38 (m, 2H), 3.02−2.99 (m, 4H), 2.74−2.72 (m, 4H), 1.68−1.25 (m, 40H), 0.93−0.89 (m, 12H); ^{13}C NMR δ 136.9, 134.2, 131.1, 124.5, 124.4, 31.92, 31.89, 31.6, 31.3, 30.52, 30.46, 30.4, 30.3, 29.2, 29.1, 22.7 (overlapped), 14.13, 14.11; HRMS *m*/*z* (M^+) calcd for $C_{38}H_{64}$ 520.5008, found 520.4996.

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Supporting Information Available: Standard experimental procedure and characterization data of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Ir-Catalyzed reactions of benzoic acid with **5a** and **5b** gave the corresponding tetraalkylnaphthalenes in low yields (10−20%). See reference 5a.

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