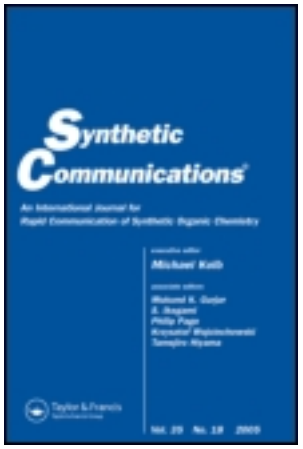

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Rhodium-Catalyzed Dimerization of Diaryl Acetylenes in the Presence of Grignard Reagents: Synthesis of 1,2,3-Triphenyl Naphthalene Derivatives

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RHODIUM-CATALYZED DIMERIZATION OF DIARYL ACETYLENES IN THE PRESENCE OF GRIGNARD REAGENTS: SYNTHESIS OF 1,2,3-TRIPHENYL NAPHTHALENE DERIVATIVES

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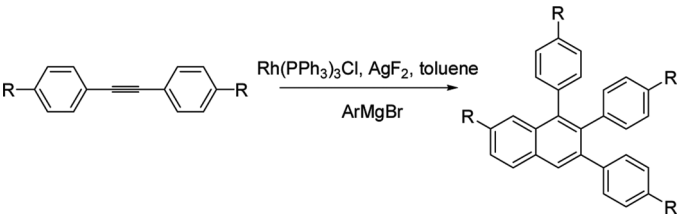
GRAPHICAL ABSTRACT



Abstract *An efficient Rh-catalyzed dimerization of diaryl acetylenes was achieved in the presence of Wilkinson catalyst, AgF_2, and 1.5 equivalent of PhMgBr in toluene, providing the 1,2,3-triaryl naphthalene derivatives in moderate to good yields.*

Supplemental materials are available for this article. Go to the publisher's online edition of Synthetic Communications *to view the free supplemental file.*

Keywords Diaryl acetylenes; dimerization; Grignard reagents; rhodium-catalyzed; 1,2,3-triaryl naphthalene

INTRODUCTION

In the past few years, much attention has been paid to rhodium catalysts in the formation of carbon–carbon bonds because the construction of carbon–carbon bonds is a central theme of research in organic synthesis.[1] Selective synthesis of substituted polycyclic aromatic hydrocarbons has become more important because of increasing application as conjugated functional materials.[2]

In recent years, the rhodium-catalyzed hydroarylation of alkynes has received much attention.[3] Recently, Zhang et al. developed a phosphine-free

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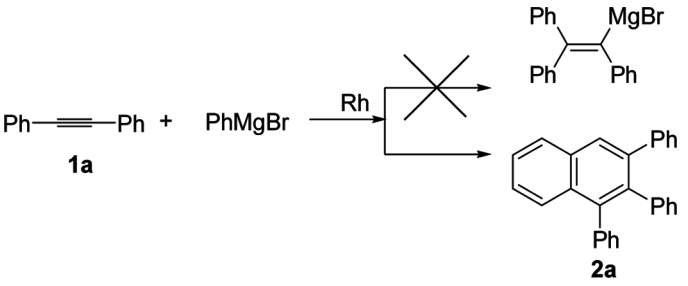
rhodium-catalyzed hydroarylation of alkynes with arylboronic acids, providing the triaryl ethenes in good to excellent yields.[4] Subsequently, Lin et al. reported rhodium–copper–TBAF-catalyzed hydroarylation of symmetrical and asymmetrical alkynes with aryl trimethoxysilanes.[5] Based on the aforementioned works, we envisioned the possibility of using cheap and abundant Grignard reagents with alkynes to access hydroarylation products (Scheme 1).

Initial studies of the reaction conditions were conducted by using the reaction of PhMgBr (0.3 mmol) with diphenyl acetylene **1a** (0.2 mmol) in the presence of Wilkinson catalyst (5 mol%) in toluene (3 mL) as the model reaction. To our surprise, it was not the arylmagnesiation of diphenylacetylene but the dimerization that occurred, and the dimerization product 1,2,3-triphenyl naphthalene **2a** was formed in 20% yield (Scheme 1). The structure of compounds **2a** was identified by ^{1}H NMR and ^{13}C NMR and unambiguously confirmed by single-crystal X-ray diffraction analysis (Figure 1).

Particularly, only some limited methods existed for the preparation of 1,2,3-triphenyl naphthalene. In 1928, Schlenk and Bergmann first reported the synthesis of 1,2,3-triphenyl naphthalene.[6] Subsequently, Bergmann et al. described a modified methodology to access 1,2,3-triphenyl naphthalene.[7] Recently, Goettmann et al. Thomas described mesoporous graphitic carbon nitride as a versatile, metal-free catalyst for the cyclolization of alkynes, producing the 1,2,3-triphenyl naphthalene in quantitative yield.[8] However, among the aforementioned studies, only diphenyl acetylene was reported as the substrate, and the reaction of the derivatives of diphenyl acetylene was not studied. In 1998, Huang et al. reported a rhodium-catalyzed cyclodimerization of arylalkynes for the synthesis of naphthalene derivatives in the presence of HCl.[9] However, the reaction was conducted under strong acidic conditions. Recently, Sakabe et al. developed an efficient rhodium/phosphine/amine · HBr catalyst system for highly selective cross-cyclodimerization as well as homodimerization of diarylacetylenes, leading to the multisubstituted naphthalenes ($T = 160\,^{\circ}C$).[10] Herein, we report a Rh-catalyzed dimerization reaction of diaryl acetylene in the presence of Grignard reagent and an additive, providing 1,2,3-triaryl naphthalene derivatives in moderate to excellent yields. This methodology would be a complemental method to that of Huang et al.

Encouraged by these results, we tested some other parameters such as rhodium source, oxidant, and additive in the reaction, as shown in Table 1. During the screening process, the Wilkinson catalyst was the best. $Rh(CO)_2(acac)$, Rh(cod)(acac), and



Scheme 1. Rhodium-catalyzed reaction of alkynes with ArMgBr.

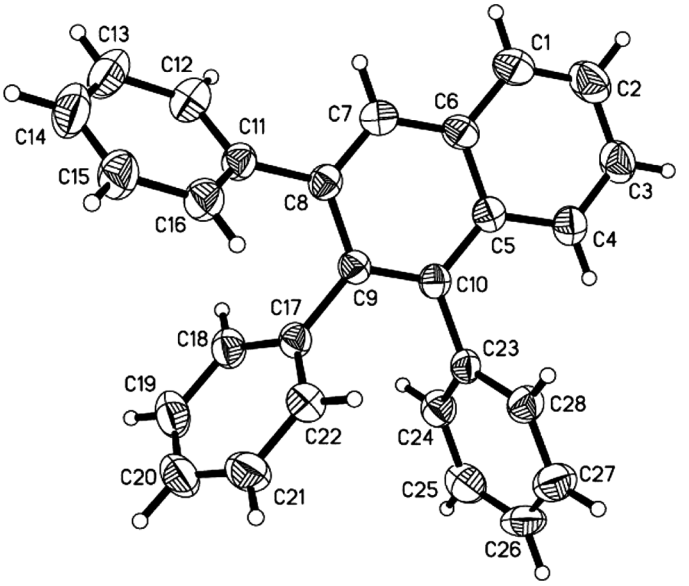


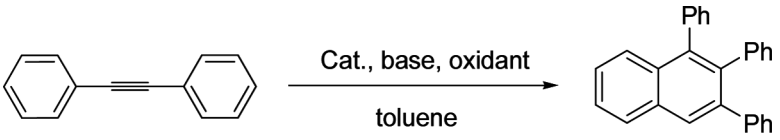
Figure 1. ORTEP diagram of the single-crystal X-ray structure of compound **2a**.

$[Rh(cod)_2Cl]_2$ were totally ineffective in the procedure (Table 1, entries 3–5). $Pd(OAc)_2$, $PdCl_2$, and $Ni(dppe)Cl_2$ inhibited the reaction (Table 1, entries 6–8). The oxidant was also crucial in this transformation. For example, the yields would increase to 55%, 62%, and 85% in the presence of CuO, CuF_2, and $CuCl_2$, respectively (Table 1, entries 9, 12, and 11). However, the addition of CuCN gave only a trace of product. Among the oxidants screened, $Cu(OTf)_2$ and AgF_2 were the best, and the yields would dramatically increased to 92% in both cases (Table 1, entries 13 and 14). Finally, we tested some other additives in the reaction. Surprisingly, only Grignard reagent was the proper one in the procedure, and other bases were totally ineffective in the reaction.

With the optimized conditions in hand, we then explored the scope of the dimerization reaction, as shown in Table 2. All the substrates ran smoothly in the procedure and produced the products in moderate to excellent yields. Both the electronic effect and hindrance on the substrates somewhat influenced the reaction. For example, **2c** and **2d** were obtained in only 63% and 45% yields, respectively (Table 2, entries 3 and 4). Having demonstrated the utility of dimerization reaction conditions on a number of symmetrical 4,4′-disubstituted aryl alkynes, we chose to test the generality of the addition to 3,3′-disubstituent aryl alkynes. As expected, the reaction proceeded smoothly, providing the products in good yields, whereas the regioselectivity was poor. For example, 72% of **2f** and 91% of **2 g** were isolated with 5:4 and 3:2 regioselectivity, respectively (Table 2, entries 6 and 7). It was noteworthy that **1e** [R = 4-(1,3-dioxolanyl)] was not compatible under Huang et al.'s procedure.[9] However, it ran smoothly under our procedure, albeit the yield was poor (Table 2, entry 5).

The rhodium-catalyzed dimerization reaction of d^{10}-diphenyl acetylene **1a′** was conducted. After the completion of the reaction, D_2O was added to quench the

Table 1. Screening for the optimum conditions[a]



Entry	Catalyst	Additive	Oxidant	Yield (%)[b]
1	$RhCl(PPh_3)_3$	PhMgBr	no	20
2	$RhCl_3 \cdot 3H_2O$	PhMgBr	no	11
3	$[Rh(cod)_2Cl]_2$	PhMgBr	no	<5
4	$Rh(CO)_2(acac)$	PhMgBr	no	<5
5	Rh(cod)(acac)	PhMgBr	no	<5
6	$PdCl_2$	PhMgBr	no	<5
7	$Pd(OAc)_2$	PhMgBr	no	<5
8	$NiCl_2(dppe)_2$	PhMgBr	no	<5
9	$RhCl(PPh_3)_3$	PhMgBr	CuO	55
10	$RhCl(PPh_3)_3$	PhMgBr	CuCN	<5
11	$RhCl(PPh_3)_3$	PhMgBr	$CuCl_2$	82
12	$RhCl(PPh_3)_3$	PhMgBr	CuF_2	65
13	$RhCl(PPh_3)_3$	PhMgBr	$Cu(OTf)_2$	92
14	$RhCl(PPh_3)_3$	PhMgBr	AgF_2	92
15	$RhCl(PPh_3)_3$	4-TolMgBr	AgF_2	91
16	$RhCl(PPh_3)_3$	n-BuMgCl	AgF_2	<5
17	$RhCl(PPh_3)_3$	n-BuLi	AgF_2	<5
18	$RhCl(PPh_3)_3$	NaH	AgF_2	<5
19	$RhCl(PPh_3)_3$	t-BuOK	AgF_2	<5

[a]All reactions were run with diphenyl acetylene (0.2 mmol), PhMgBr (0.6 mL of 0.5 M in THF, 0.3 mmol) or additive (0.3 mmol), catalyst (5 mol %), and oxidant (0.2 mmol) in dry toluene (3 mL) under N_2, 110 °C, 12 h.
[b]Isolated yield.

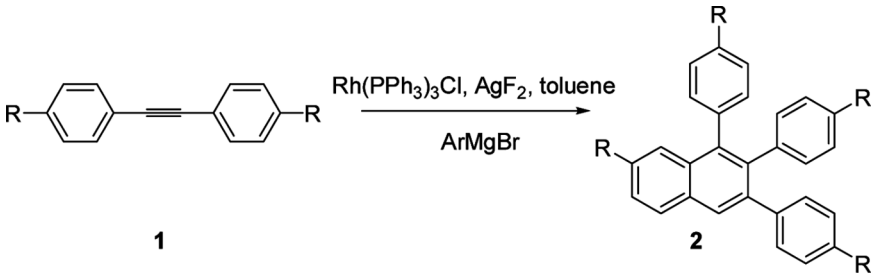
reaction, and **2a′** was isolated in 86% yield (Scheme 2). This result clearly showed that the H atom attached in the naphthalene was not derived from the exterior of the reaction system during the workup. Next, d^8-toluene was subjected to the standard reaction conditions. The 4-H of product **2a′** did not come from d^8-toluene as determined by ^1H NMR. However, the mechanism in detail is still unclear.

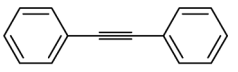
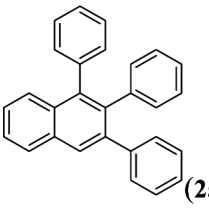
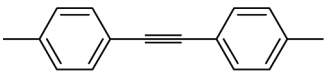
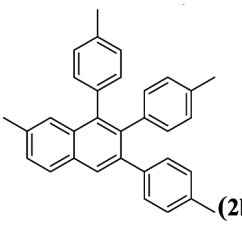
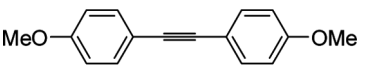
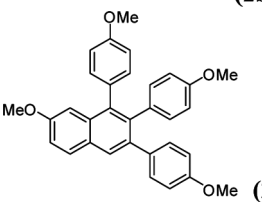
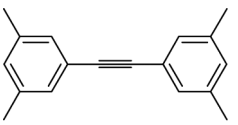
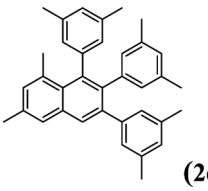
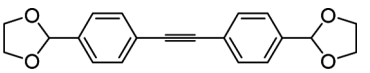
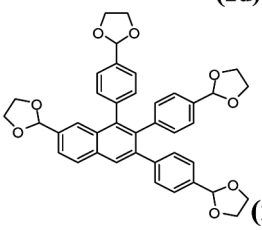
In conclusion, we have developed an efficient rhodium-catalyzed dimerization of diaryl acetylene that was achieved in the presence of 1.5 equivalent of PhMgBr and 1 equivalent of AgF_2, providing the 1,2,3-triaryl naphthalene derivatives in moderate to good yields. This mechanism study is currently ongoing in our laboratory.

EXPERIMENTAL

Chemicals were either purchased or purified by standard techniques without special instructions. ^1H NMR and ^{13}C NMR spectra were measured on a 300-MHz spectrometer (^1H 300 MHz, ^{13}C 75 MHz), using $CDCl_3$ as the solvent with

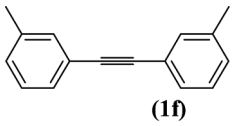
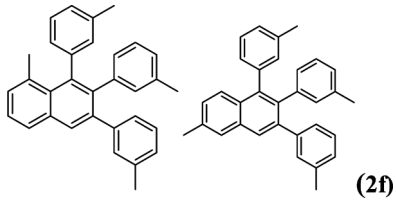
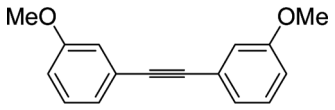
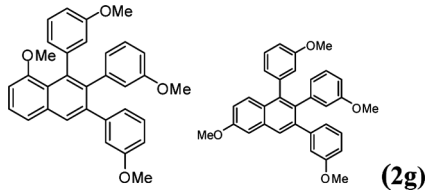
Table 2. Dimerization of diaryl acetylenes[a]



Entry	Substrate **1**	Product **2**	Yield (%)[b]
1	 **(1a)**	 **(2a)**	92
2	 **(1b)**	 **(2b)**	80[c]
3	 **(1c)**	 **(2c)**	63
4	 **(1d)**	 **(2d)**	45
5	 **(1e)**	 **(2e)**	31

(*Continued*)

Table 2. Continued

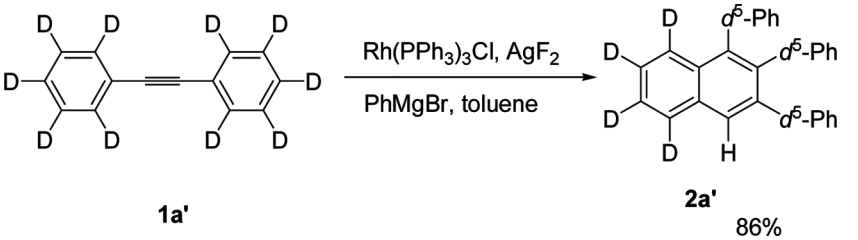
Entry	Substrate **1**	Product **2**	Yield (%)[b]
6	 **(1f)**	 **(2f)**	72 (5:4)[d]
7	 **(1g)**	 **(2g)**	91 (3:2)[d]

[a]Reaction conditions: diaryl acetylene (0.2 mmol), PhMgBr (0.6 mL of 0.5 M in THF, 0.3 mmol),$Rh(PPh_3)_3Cl$ (5 mol%), and AgF_2 (0.2 mmol) in dry toluene (3 mL) under N_2, 110 °C, 12 h.
[b]Isolated yield.
[c]4-TolMgBr (0.4 mL of 1.0 M in THF) was employed.
[d]The rations of the two isomers (in parentheses) were determined by ^1H NMR.

tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts (δ) are given in parts per million (ppm) relative to TMS, and the coupling constants (*J*) are given in hertz (Hz).

General Procedure

Under N_2, a reaction tube was charged with diaryl alkynes (0.2 mmol), phenylmagnesium bromide (ca. 0.3 mmol), or *p*-tolylmagnesium bromide (ca. 0.4 mmol), $RhCl(PPh_3)_3$ (9.3 mg, 5 mol%), AgF_2(0.2 mmol), and dry toluene (3 mL). The mixture was heated under N_2 at 110 °C for 12 h and then cooled to room temperature. The mixture was concentrated in vacuum, and the residue was purified by flash column chromatography on silica gel to give the product.



Scheme 2. Labeling study.

Characterization Data of All Products

1,2,3-Triphenylnaphthalene (2a)[8]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.95–7.94 (m, 2H), 7.93–7.52 (m, 2H), 7.49–7.40 (m, 1H), 7.25–7.14 (m, 10H), 6.95–6.92 (m, 3H), 6.87–6.84 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 142.0, 140.0, 139.9, 139.4, 132.7, 131.5, 131.2, 130.0, 128.7, 127.9, 127.5, 126.9, 126.9, 126.4, 126.2, 126.1, 126.1, 125.6.

7-Methyl-1,2,3-trip-tolylnaphthalene (2b)[9]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.83–7.78 (m, 2H), 7.32–7.30 (m, 2H), 7.06–6.95 (m, 8H), 6.74–6.73 (m, 4H), 2.39 (s, 3H), 2.33 (s, 3H), 2.28 (s, 3H), 2.16 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 139.6, 139.2, 138.4, 137.5, 136.8. 135.7, 135.7, 134.9, 132.5, 131.5, 131.3, 131.1, 130.1, 128.6, 128.4, 128.3, 127.9, 127.7, 125.9, 22.2, 21.5, 21.3.

7-Methoxy-1,2,3-tris(4-methoxyphenyl)naphthalene (2c)[9]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.82–7.79 (m, 2H), 7.17–7.14 (m, 1H), 7.07–7.03 (m, 4H), 6.89–6.88 (m, 1H), 6.81–6.70 (m, 6H), 6.52–6.50 (m, 2H), 3.80 (s, 3H), 3.77 (s, 3H), 3.70 (s, 3H), 3.68 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 157.8, 157.6, 157.2, 138.5, 137.5, 134.8, 133.4, 132.8, 132.5, 132.1, 132.0, 131.0, 129.3, 128.3, 128.2, 118.3, 113.1, 113.0, 112.4, 105.5, 55.1, 55.1, 54.9.

1,2,3-Tris(3,5-dimethylphenyl)-6,8-dimethylnaphthalene (2d). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.76 (s, 1H), 7.54 (s, 1H), 7.06 (s, 1H), 6.78–6.70 (m, 6H), 6.47 (s, 1H), 6.41 (s, 2H), 2.46 (s, 3H), 2.16 (s, 6H), 2.15 (s, 6H), 1.93 (s, 6H), 1.54 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 142.5, 142.0, 140.1, 139.3, 136.3, 135.8, 135.5, 135.0,134.7, 32.3, 129.6, 129.6, 128.5, 127.9, 127.5, 127.2, 126.4, 126.3, 29.7, 24.8, 21.1, 21.1, 20.9. IR (KBr, cm^{-1}): 3016, 2920, 2854, 1646, 1600, 909. MS (EI): m/z 468 $(M)^+$. Anal. calcd. for $C_{36}H_{36}$: C, 92.26; H, 7.74. Found: C, 92.12; H, 7.49.

2,2′,2″-(4,4′,4″-(7-(1,3-Dioxolan-2-yl)naphthalene-1,2,3-triyl)tris(benzene-4,1-diyl)) tris(1,3-dioxolane) (2e). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.97–7.89 (m, 2H), 7.66–7.59 (m, 2H), 7.37–7.30 (m, 4H), 7.18–7.13 (m, 4H), 7.05 (d, $J = 8.1$ Hz, 2H), 6.86 (d, $J = 7.5$ Hz, 2H), 5.87 (s, 1H), 5.75 (s, 1H), 5.75 (s, 1H), 5.64 (s, 1H), 4.17–3.94 (m, 16H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 142.7, 140.5, 139.9, 139.9, 139.2, 137.8, 136.0, 135.5, 133.2, 132.1, 132.0, 131.4, 131.2, 130.0, 129.0, 128.6, 128.5, 125.8, 125.3, 123.9, 104.2, 103.7, 103.6, 103.5, 65.4, 65.2, 65.2, 64.9. IR (KBr, cm^{-1}): 2920, 2852, 1698, 1649, 1514, 1460, 1081, 912. MS (EI): m/z 644 $(M)^+$, Anal. calcd. for $C_{40}H_{36}O_8$: C, 74.52; H, 5.63. Found: C, 74.72; H, 5.38.

8-Methyl-1,2,3-trim-tolylnaphthalene and 6-methyl-1,2,3-trim-tolylnaphthalene (2f). ^{1}H NMR ($CDCl_3$, 300 MHz): See the Supporting Information, available online.

8-Methoxy-1,2,3-tris(3-methoxyphenyl)naphthalene and 6-methoxy-1,2,3-tris(3-methoxyphenyl)naphthalene (2g). ^{1}H NMR ($CDCl_3$, 300 MHz) See the Supporting Information, available online.

ACKNOWLEDGMENTS

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