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Catalytic [2 + 2 + 2] and Thermal [4 + 2] Cycloaddition of 1,2-Bis(arylpropiolyl)benzenes

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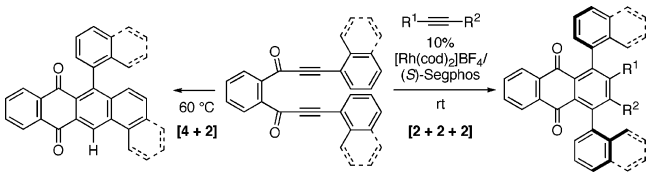

We have determined that a cationic rhodium(I)/Segphos complex catalyzes an enantio- and diastereoselective intermolecular [2 + 2 + 2] cycloaddition of 1,2-bis(arylpropiolyl)benzenes with various monoalkynes at room temperature to give axially chiral 1,4-teraryls possessing an anthraquinone structure in good yields with good enantio- and diastereoselectivities. We have also determined that a thermal intramolecular [4 + 2] cycloaddition of 1,2-bis(arylpropiolyl)benzenes proceeds at 60 °C to give aryl-substituted naphthacenediones in moderate to good yields.

Transition-metal-mediated [2 + 2 + 2] cycloaddition[1] of 1,2-bis(propiolyl)benzene derivatives with monoalkynes is a valuable transformation for the synthesis of substituted anthraquinones. Such a transformation was achieved by cycloadditions of isolated naphthoquinone-fused rhodacyclopentadiene complexes with monoalkynes[2] and of 1,2-bis(phenylpropiolyl)benzene with monoalkynes using a large excess of highly toxic $Ni(CO)_4$.[3] After these reports, several catalytic methods were developed. The first catalytic reaction was realized by using 5−25% $Ni(PPh_3)_2(CO)_2$ as a precatalyst at 60−130 °C.[4] $CpCo(CO)_2$[5] and $RhCl(PPh_3)_3$,[6] which are widely used for the [2 + 2 + 2] cycloadditions of α,ω-diynes with monoalkynes, were found to catalyze the [2 + 2 + 2] cycloaddition in refluxing *n*-octane[7] or refluxing ethanol,[8] respectively. However, these catalytic systems require high reaction temperature (60−130 °C), and the product yields were not satisfactory (5−77%). Recently, highly efficient Cp*RuCl(cod)-catalyzed [2 + 2 + 2] cycloaddition of terminal and methyl-substituted internal 1,2-bis(propiolyl)benzenes with monoalkynes was reported.[9] Although this catalyst system realized mild reaction conditions (room temperature) and high product yields (33−92%), 1,2-bis(phenylpropiolyl)benzene could not be employed as a result of the formation of a stable ruthenacycle.[9,10]

We reported previously that cationic rhodium(I)/modified-BINAP complexes are highly effective catalysts for chemo- and regioselective [2 + 2 + 2] cycloadditions.[11] These catalysts were further extended to enantioselective [2 + 2 + 2] cycloadditions for the construction of axial chiralities.[12] Herein, we describe a cationic rhodium(I)/(*S*)-Segphos [(4,4′-bi-1,3-benzodioxole)-5,5′-diylbis(diphenylphosphine)][13] complex-catalyzed enantio- and diastereoselective intermolecular [2 + 2 + 2] cycloaddition of 1,2-bis(arylpropiolyl)benzenes with monoalkynes at room temperature leading to axially chiral 1,4-teraryls possessing an anthraquinone structure. We also describe a thermal intramolecular [4 + 2] cycloaddition of 1,2-bis(arylpropiolyl)benzenes leading to aryl-substituted naphthacenediones.

We first examined various rhodium(I) and iridium(I) complexes [10% based on 1,2-bis(phenylpropiolyl)benzene (**1a**)] for their ability to catalyze the [2 + 2 + 2] cycloaddition of **1a** with internal monoalkyne **2a** as shown in Table 1. The use of Segphos and H_8-BINAP [2,2′-bis(diphenylphosphino)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl][14] as ligands, which

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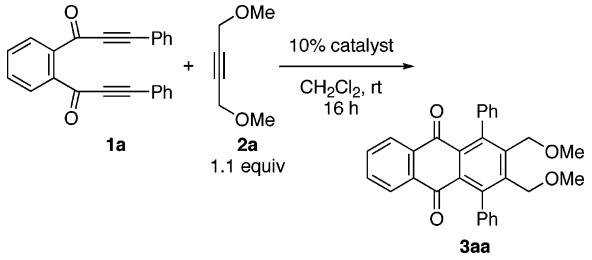
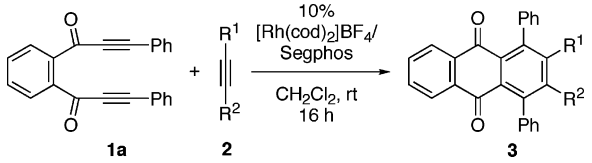
TABLE 1. Screening of Catalysts for [2 + 2 + 2] Cycloaddition of 1,2-Bis(phenylpropiolyl)benzene with Monoalkyne[a]



entry	catalyst	conv (%)	yield (%)[b]
1	$[Rh(cod)_2]BF_4$/Segphos	100 (46[c])	76 (33[c])
2	$[Rh(cod)_2]BF_4$/H_8-BINAP	100 (28[c])	77 (18[c])
3	$[Rh(cod)_2]BF_4$/BINAP	60	36
4	$[Rh(cod)_2]BF_4$/dppb	22	11
5	$[Rh(cod)_2]BF_4$/dppf	39	19
6	$[Rh(cod)Cl]_2$/Segphos	11	<5
7	$[Ir(cod)_2]BF_4$/Segphos	11	0

[a] Catalyst (0.015 mmol), **1a** (0.15 mmol), **2a** (0.165 mmol, 1.1 equiv), and CH_2Cl_2 (1.5 mL) were used. [b] Isolated yield. [c] Catalyst: 5%.

TABLE 2. Rhodium-Catalyzed [2 + 2 + 2] Cycloaddition of 1,2-Bis(phenylpropiolyl)benzene with Monoalkynes[a]



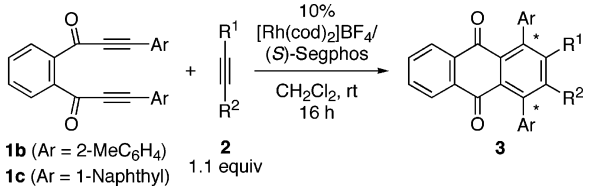
entry	2 (equiv)	R^1	R^2	3	yield (%)[b]
1	**2a** (1.1)	CH_2OMe	CH_2OMe	**3aa**	76
2	**2b** (1.1)	Me	CH_2OH	**3ab**	95
3	**2c** (1.1)	*n*-Pr	*n*-Pr	**3ac**	86
4	**2d** (1.1)	Me	CO_2Et	**3ad**	64
5[c]	**2e** (2.0)	H	CH_2OMe	**3ae**	82
6	**2f** (2.0)	H	*n*-Bu	**3af**	78
7	**2g** (2.0)	H	Ph	**3ag**	96

[a] $[Rh(cod)_2]BF_4$ (0.015 mmol), Segphos (0.015 mmol), **1a** (0.15 mmol), **2** (0.165 mmol, 1.1 equiv or 0.30 mmol, 2.0 equiv), and CH_2Cl_2 (1.5 mL) were used. [b] Isolated yield. [c] Reaction time: 24 h.

are effective for our previous [2 + 2 + 2] cycloaddition of electron-deficient alkynes with monoalkynes,[12] furnished the desired diphenyl-substituted anthraquinone **3aa** in good yields (entries 1 and 2). On the other hand, other conventional bidentate phosphine ligands (BINAP, dppb, and dppf) were found to be less effective (entries 3−5). The catalytic activities of cationic rhodium(I)/Segphos and H_8-BINAP complexes were examined with low catalyst loading (5%), which revealed that Segphos showed catalytic activity higher than that of H_8-BINAP (entries 1 and 2). Importantly, the use of a cationic rhodium(I) complex is essential for the present [2 + 2 + 2] cycloaddition. The use of neutral rhodium(I)/Segphos complex furnished **3aa** in <5% yield, and the cationic iridium(I)/Segphos complex did not catalyze this reaction at all (entries 6 and 7). Unfortunately, the [2 + 2 + 2] cycloaddition of methyl-substituted internal 1,2-bis(propiolyl)benzene with monoalkynes did not proceed under the present optimal reaction conditions.

A series of monoalkynes **2a**−**g** were subjected to the above optimal reaction conditions as shown in Table 2. Methoxymethyl-, hydroxymethyl-, alkyl-, and ethoxycarbonyl-substituted internal alkynes afforded the corresponding substituted anthraquinones **3aa**−**3ad** in good to high yields (entries 1−4). Not only internal alkynes but also terminal alkynes can be employed for this reaction. Methoxymethyl-, alkyl-, and phenyl-substituted terminal alkynes cleanly afforded the corresponding substituted anthraquinones **3ae**−**3ag** in high yields (entries 5−7).

TABLE 3. Rhodium-Catalyzed Enantio- and Diastereoselective [2 + 2 + 2] Cycloaddition of 1,2-Bis(arylpropiolyl)benzenes with Monoalkynes[a]



entry	1	2	R^1	R^2	3	% yield[b] (dr)	ee (%)[c]
1[d]	**1b**	**2h**	Et	Et	(+)-**3bh**	78 (4:1)	97
2	**1b**	**2c**	*n*-Pr	*n*-Pr	(+)-**3bc**	75 (6:1)	98
3	**1b**	**2i**	Me	n-C_5H_{11}	(+)-**3bi**	80 (8:1)	97
4	**1b**	**2a**	CH_2OMe	CH_2OMe	(-)-**3ba**	70 (2:1)	97
5	**1b**	**2b**	Me	CH_2OH	(*R*,*R*)-(-)-**3bb**	68 (3:1)	87
6	**1b**	**2d**	Me	CO_2Et	(-)-**3bd**	93 (3:1)	89
7[e]	**1c**	**2c**	*n*-Pr	*n*-Pr	(+)-**3cc**	71 (3:1)	85

[a] $[Rh(cod)_2]BF_4$ (0.015 mmol), Segphos (0.015 mmol), **1** (0.15 mmol), **2** (0.165 mmol, 1.1 equiv), and CH_2Cl_2 (1.5 mL) were used. [b] Isolated yield. [c] ee (%) of major diastereomers. [d] **2h** (0.30 mmol, 2 equiv) was used. [e] CH_2Cl_2 (3.0 mL) was used.

The [2 + 2 + 2] cycloaddition of 1,2-bis(propiolyl)benzenes, bearing an *ortho*-substituted phenyl group at both alkyne termini, with monoalkynes would install two axial chiralities during the formation of benzene rings.[15−18] Recently, Shibata et al. reported the highly efficient enantio- and diastereoselective synthesis of axially chiral 1,4-teraryl compounds via $[IrCl(cod)]_2$/MeDUPHOS [1,2-bis(2,5-dimethylphospholano)benzene]-catalyzed [2 + 2 + 2] cycloaddition of electron rich α,ω-diynes, bearing an *ortho*-substituted phenyl group at both alkyne termini, with electron-rich oxygen-functionalized monoalkynes.[18] However, our experiments revealed that iridium(I) complexes did not catalyze the [2 + 2 + 2] cycloaddition of electron-deficient diketodiyne substrates. As shown in Table 3, the reaction of 2-methylphenyl-substituted diketodiyne **1b** with 3-hexyne **2h** using $[Rh(cod)_2]BF_4$/(*S*)-Segphos furnished 1,4-teraryl **3bh** in 78% yield with good diastereoselectivity (*dl*-isomer was obtained as a major isomer, *dl*:*meso* = 4:1) and high enantioselectivity (97% ee, *dl*-isomer) (entry 1).[19] Interestingly, increasing the length of the alkyl chain improved the diastereoselectivities (entries 2 and 3). Not only unfunctionalized alkyl-substituted

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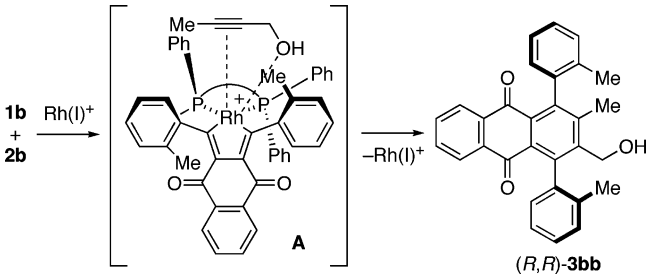
(19) The use of other BINAP-type ligands (BINAP, tol-BINAP, H_8-BINAP) gave a *meso*- or *cis*-isomer as a major product.

SCHEME 1



internal alkynes **2h**,**c**,**i** and 2-methylphenyl-substituted diketodiyne **1b** but also both electron-rich and electron-deficient oxygen-functionalized internal alkynes **2a**,**b**,**d** and 1-naphthyl-substituted diketodiyne **1c** can be employed for this reaction, although enantio- and/or diastereoselectivities decreased (entries 4−7). Importantly, good enantio- and diastereoselectivities were observed by using both symmetrical (entries 1, 2, 4, and 7) and unsymmetrical (entries 3, 5, and 6) monoalkynes. The absolute configuration of 4-bromobenzoate of (−)-**3bb** was determined to be the (*R*,*R*)-form by the anomalous dispersion method.

Scheme 1 depicts a plausible mechanism for the selective formation of (*R*,*R*)-(−)-**3bb**. Both enantio- and diastereoselectivities are determined by preferential formation of intermediate **A**, due to the steric interaction between the two methyl groups of **1b** and the two axial PPh_2 groups of (*S*)-Segphos, and sterically less demanding coordination of monoalkyne **2b** to rhodium. Reductive elimination of rhodium gives (*R*,*R*)-(−)-**3bb** and regenerates the rhodium catalyst.

It is well-established that aryl alkynyl ketones exhibit enhanced reactivity toward thermal intramolecular [4 + 2] cycloaddition, and thus the reaction can be carried out at relatively lower temperature.[20,21] Indeed, when the rhodium-catalyzed cycloaddition of **1** with **2** was carried out at elevated temperature (60−80 °C), both intermolecular [2 + 2 + 2] cycloaddition of **1** with **2** and intramolecular [4 + 2] cycloaddition of **1** proceeded concurrently to give substituted anthraquinone **3** and substituted naphthacenedione **4**, respectively.[22]

The effect of reaction temperature and the scope of aryl-substituted diketodiyne substrates for this thermal intramolecular [4 + 2] cycloaddition were examined in the absence of rhodium catalysts as shown in Table 4. Increasing the reaction temperature decreased the yield of **4a**, although it shortened the reaction times (entries 1−3). The highest yield of **4a** was obtained at 60 °C for 48 h using $(CH_2Cl)_2$ as a solvent (entry 3). Under this optimal reaction conditions, 2-methylphenyl- and 1-naphthyl-substituted diketodiynes **1b** and **1c** also furnished the corresponding substituted naphthacenediones **4b** and **4c** in 52% and 59% isolated yields, respectively (entries 4 and 5).

TABLE 4. Thermal [4 + 2] Cycloaddition of 1,2-Bis(arylpropiolyl)benzenes[a]

entry	1	condition	4	yield (%)[b]
1	**1a** (R = H)	140 °C, 5 h	**4a**	43[c]
2	**1a** (R = H)	80 °C, 20 h	**4a**	58[c]
3	**1a** (R = H)	60 °C, 48 h	**4a**	77 (80[c])
4	**1b** (R = Me)	60 °C, 24 h	**4b**	52
5	**1c**	60 °C, 3 h	**4c**	59

[a] Reactions were conducted using **1** (0.10 mmol) in $(CH_2Cl)_2$ (60−80 °C) or xylene (140 °C) (2.0 mL). [b] Isolated yield. [c] NMR yield.

In conclusion, we have established that a cationic rhodium(I)/Segphos complex catalyzes an enantio- and diastereoselective intermolecular [2 + 2 + 2] cycloaddition of 1,2-bis(arylpropiolyl)benzenes with various monoalkynes at room temperature to give axially chiral 1,4-teraryls possessing the anthraquinone structure in good yields with good enantio- and diastereoselectivities. We have also established that a thermal intramolecular [4 + 2] cycloaddition of 1,2-bis(arylpropiolyl)benzenes proceed at 60 °C to give aryl-substituted naphthacenediones in moderate to high yields. These [2 + 2 + 2] and [4 + 2] cycloadditions of 1,2-bis(arylpropiolyl)benzenes represent a versatile new method for the preparation of aryl-substituted anthraquinone and naphthacenedione structures.

Experimental Section

Representative Procedure for Catalytic [2 + 2 + 2] Cycloadditions of 1,2-Bis(arylpropiolyl)benzenes with Monoalkynes (Table 2, entry 1). Under an Ar atmosphere, a CH_2Cl_2 (0.5 mL) solution of Segphos (9.2 mg, 0.015 mmol) was added to a CH_2Cl_2 (0.5 mL) solution of $[Rh(cod)_2]BF_4$ (6.1 mg, 0.015 mmol) at room temperature, and the mixture was stirred for 5 min. The resulting solution was stirred under H_2 (1 atm) at room temperature for 0.5 h, concentrated to dryness, and dissolved in CH_2Cl_2 (0.5 mL). To this solution was added a CH_2Cl_2 (0.5 mL) solution of 1,2-bis(phenylpropiolyl)benzene[10] (**1a**, 50.1 mg, 0.15 mmol) and 1,4-dimethoxy-2-butyne (**2a**, 18.8 mg, 0.165 mmol), and remaining substrates were washed away by using CH_2Cl_2 (0.5 mL). The solution was stirred at room temperature for 16 h. The resulting solution was concentrated and purified by silica gel chromatography (hexane/Et_3N = 15:1), which furnished 2,3-dimethoxymethyl-1,4-diphenylanthraquinone (**3aa,** 51.3 mg, 0.114 mmol, 76% yield) as a yellow solid.

2,3-Dimethoxymethyl-1,4-diphenylanthraquinone (3aa). Yellow solid; mp 160.0−160.8 °C; IR (neat) 2875, 1670, 1320, 1250, 1090 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.98 (dd, J = 5.7 and

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(22) Saá and co-workers reported that attempted intramolecular [4 + 2] cycloadditions of diketodiyne **1a** under thermal or catalyzed conditions led to its decomposition; see: Rodríguez, D.; Castedo, L.; Domínguez, D.; Saá, C. *Org. Lett.* **2003**, *5*, 3119−3121.

3.3 Hz, 2H), 7.63 (dd, J = 5.7 and 3.3 Hz, 2H), 7.42−7.54 (m, 6H), 7.20−7.31 (m, 4H), 4.20 (s, 4H), 3.16 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 183.9, 144.7, 142.8, 140.0, 133.9, 133.6, 132.8, 128.2, 127.8, 126.9, 126.7, 68.0, 58.8; HRMS (FAB) calcd for $C_{30}H_{25}O_4$ $[M + H]^+$ 449.1753, found 449.1759.

(+)-2,3-Dipropyl-1,4-di-*o*-tolylanthraquinone [(+)-3bc, *dl*:*meso* = 6:1]. Pale yellow solid; mp 132.5−135.4 °C; $[\alpha]^{25}_D$ +83.7° [$CHCl_3$, *c*2 .19, *dl*:*meso* = 6:1, 98% ee (*dl*-isomer)]; IR (neat) 2900, 1670, 1310, 1250, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.91−8.02 (m, 2H), 7.55−7.64 (m, 2H), 7.22−7.43 (m, 6H), 6.99−7.11 (m, 2H), 2.38−2.58 (m, 2H), 2.14−2.32 (m, 2H), 2.03 (m, 6H), 1.19−1.42 (m, 4H), 0.72 (t, J = 7.2 Hz, 6H), methyl protons of *meso*-**3bc**: 2.00 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 184.34, 184.28, 147.8, 147.6, 142.1, 140.93, 140.85, 135.2, 135.0, 134.1, 134.0, 133.2, 130.7, 129.6, 129.5, 127.93, 127.86, 127.0, 126.5, 126.4, 125.6, 125.5, 32.7, 32.5, 24.0, 23.6, 20.2, 20.0, 14.72, 14.66; HRMS (FAB) calcd for $C_{34}H_{33}O_2$ $[M + H]^+$ 473.2481, found 473.2458; CHIRALPAK AD-H, hexane/2-PrOH = 98:2, 0.8 mL/min, t_R 4.48 min (minor *dl*-isomer), 6.07 min (*meso*-isomer), and 6.75 min (major *dl*-isomer).

Representative Procedure for Thermal Intramolecular [4 + 2] Cycloadditions of 1,2-Bis(arylpropiolyl)benzenes (Table 4, entry 3). Under an Ar atmosphere, a $(CH_2Cl)_2$ (2.0 mL) solution of 1,2-bis(phenylpropiolyl)benzene (**1a**, 33.4 mg, 0.10 mmol) was stirred at 60 °C for 48 h. The resulting solution was concentrated and purified by silica gel chromatography (hexane/CH_2Cl_2 = 2:1), which furnished 6-phenylnaphthacene-5,12-dione (**4a**, 25.7 mg, 0.077 mmol, 77% yield) as an orange solid.

6-Phenylnaphthacene-5,12-dione (4a).[22] Yellow solid; mp 282.2−282.8 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.01 (s, 1H), 8.31−8.41 (m, 1H), 8.08−8.23 (m, 2H), 7.41−7.84 (m, 8H), 7.18−7.34 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 183.4, 183.2, 144.2, 139.7, 136.2, 135.7, 134.6, 134.2, 133.6, 130.2, 130.1, 129.3, 129.1, 128.9, 128.5, 128.4, 127.7, 127.2, 126.9.

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Supporting Information Available: Experimental procedure for the synthesis of diynes (**1a**, **1b**, and **1c**), compound characterization data (**1a**, **1b**, **1c**, **3ab**, **3ac**, **3ad**, **3ae**, **3af**, **3ag**, **3ba**, **3bb**, **3bd**, **3bh**, **3bi**, **3cc**, 4-bromobenzoate of (*R*,*R*)-(−)-**3bb**, **4b**, and **4c**), ^{1}H NMR spectra of all compounds, and X-ray crystallographic files for 4-bromobenzoate of (*R*,*R*)-(−)-**3bb** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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