Cross-Coupling of Alkynes Catalyzed by Phebox−Rhodium Acetate Complexes

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Cross-coupling between terminal alkynes and dimethyl acetylenedicarboxylate (**3**) in the presence of 1 mol % bis(oxazolinyl)phenyl−rhodium acetate complex, (Phebox-R)Rh(OAc)$_2$(H$_2$O) (**1-ip**, R = ^{i}Pr), under 1 atm hydrogen atmosphere furnished alkynyl-substituted maleic acid dimethyl esters with high *Z*-selectivity. Rh−acetylide complexes (Phebox-R)Rh(OAc)(−C≡CPh) (**5-ip**, R = ^{i}Pr; **5-dm**, R = Me$_2$) were isolated on the reactions of **1-ip** and **1-dm** with phenylacetylene. Reactions of **5-ip** and **5-dm** with **3** provide the corresponding vinyl complexes (Phebox-R)Rh(OAc)(−C(CO$_2$Me)═C(CO$_2$Me)C≡CPh) (**6-ip**, R = ^{i}Pr; **6-dm**, R = Me$_2$) with *E*-configuration. Further reaction of **6-ip** with phenylacetylene resulted in the formation of an enyene **4a** accompanied by the formation of **5-ip**. The molecular structures of **5-dm** and **6-dm** were determined by X-ray diffraction.

Introduction

Catalytic dimerization of terminal alkynes by transition-metal complexes has received much attention, because it provides a versatile and efficient method to synthesize conjugated enynes, which have been applied in building blocks of natural compounds and organic materials.[1] Although such a dimerization reaction generally produces a mixture of linear and branched enynes, several transition-metal complexes have exhibited promising results in selective alkyne dimerization.[2] Recently, lanthanide alkyl complexes bearing cyclopentadienyl ligands have proven to be highly regio- and stereoselective catalysts in the homo-dimerization of alkynes to give head-to-head dimers.[3] In this context, cross-coupling between two different alkynes is also important to synthesize a variety of substituted enynes. Usually, addition of a terminal alkyne to an internal alkyne provides good selectivity.[4] For example, Trost et al. reported that Pd(OAc)$_2$ in the presence of bulky phosphine ligands was successfully used in the cross-coupling between terminal alkynes and acceptor alkynes with electron-withdrawing groups.[4b] Yi et al. reported cross-coupling of terminal alkynes with various internal alkynes catalyzed by ruthenium−acetylide complexes.[4c] Titanocene and vinylideneruthenium complexes have exhibited high efficiency for cross-coupling between two different terminal alkynes, such as aryl-, alkyl-, and silylalkynes.[5a,b]

During our investigation of Rh complexes bearing bis(oxazolinyl)phenyl (═Phebox) ligands, we recently found that C−H activation of various arenes was induced by the acetate ligands.[6,7] We therefore assumed that the acetate−Rh complex could activate a terminal C(sp)−H bond of an alkyne to generate a catalytically key intermediate of an acetylide−Rh species. Herein, we report a cross-coupling between terminal alkynes **2** and dimethyl acetylenedicarboxylate (**3**) catalyzed by the Phebox−Rh acetate complexes and acceleration of the reaction in the presence of molecular hydrogen.

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Scheme 1. Cross-Coupling of 2a with 3

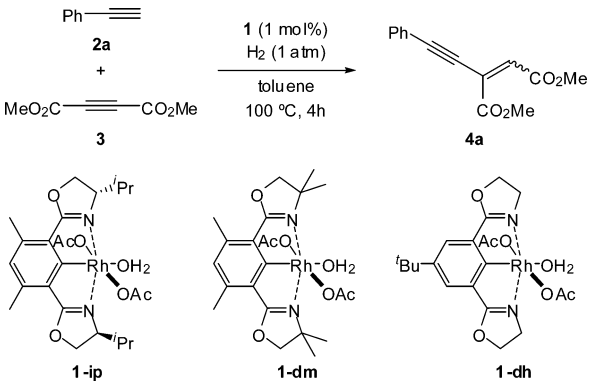


Table 1. Cross-Coupling of 2a with 3 Catalyzed by 1[a]

run	Rh cat.	condition	yield (%)[b]	*Z*:*E*[c]
1	**1-ip**	Ar (1 atm)	5	95:5
2	**1-ip**	H_2 (1 atm)	85	98:2
3	**1-ip**	Et_3SiH (10 mol %)[d]	0	
4	**1-ip**	H_2O (10 mol %)[d]	5	98:2
5	**1-ip**	AcOH (10 mol %)[d]	3	97:3
6	**1-ip**	MeOH (10 mol %)[d]	5	98:2
7	**1-ip**	HCOOH (10 mol %)[d]	37	97:3
8	**1-dm**	H_2 (1 atm)	17	100:0
9	**1-dh**	H_2 (1 atm)	27	96:4
10	none	H_2 (1 atm)	0	

[a] Reactions were carried out with 1.0 mmol of **2a**, 1.5 mmol of **3**, and 0.010 mmol of **1** in 4 mL of toluene. [b] Isolated yield. [c] Determined by ^{1}H NMR spectroscopy. [d] Reaction was carried out under 1 atm of argon.

Results and Discussion

Catalytic Cross-Coupling of Alkynes. Initial experiments were carried out using a toluene solution of phenylacetylene (**2a**) and **3** (1.5:1.0) in the presence of 1 mol % of **1-ip** (Scheme 1). When the reaction of **2a** with **3** was performed under argon atmosphere at 100 °C for 4 h, the yield of an enyne **4a** was disappointingly very low (Table 1, run 1). However, under 1 atm of hydrogen gas instead of argon gas, the yield of **4a** was dramatically increased to 85% with high stereoselectivity of *Z*:*E* = 98:2 (run 2). Under the condition of run 2, only a trace amount of homo-dimerization products was observed. In contrast, addition of the catalytic amount of hydride or proton sources did not improve the yield of **4a** (runs 3−6). Use of formic acid as an additive slightly affected the yield (run 7). We also found that the chemical yield was strongly dependent on the substituent environment around the Rh active site. When the complex **1-dm** was employed as a catalyst, the yield of **4a** decreased to 17% (run 8). The complex **1-dh** was also less effective to give **4a** in 27% yield (run 9). In the case of **1-dh**, homo-dimerization products, *E*- and *Z*-1,4-diphenylbutenyne, were detected. This substituent effect cannot be explained clearly.

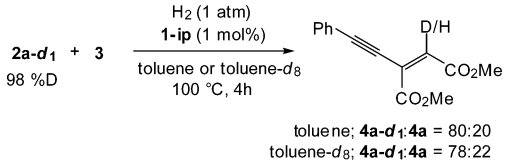
Under the standard condition, the scope and limitations of substrates for cross-coupling between various terminal alkynes **2** and **3** were examined. The results are summarized in Table 2. Use of aromatic alkynes, **2b** and **2c**, with electron-withdrawing groups, such as trifluoromethyl and bromo groups, at the *para*-position resulted in high yields with excellent stereoselectivity (runs 1 and 2). However, electron-donating substituents, methoxy and methyl groups, at the *para*-position decreased the yield (runs 3 and 4). In contrast to aromatic alkynes, reactions of aliphatic alkynes, ethynylcyclohexane (**2h**) and 1-octyne (**2i**), resulted in low yields (runs 7 and 8). The yield of **4i** was increased to 40% by using a 5 mol % loading of **1-ip** (run 9). Reactions of trimethylsilylacetylene (**2j**) and ethyl propionate (**2k**) resulted in low yields (runs 10 and 11).

Table 2. Cross-Coupling of Terminal Alkynes (2) with 3 Catalyzed by 1-ip[a]

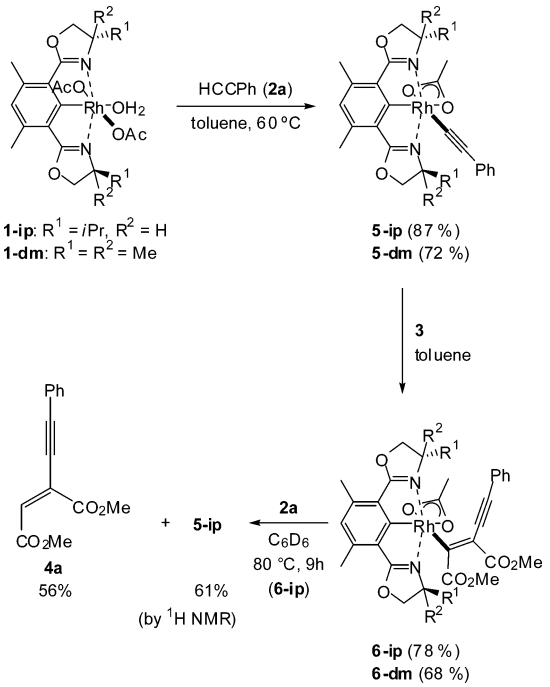
run	alkyne	product	yield (%)[b]	*Z*:*E*[c]
1	4-$CF_3C_6H_4$ (**2b**)	**4b**	79	98:2
2	4-BrC_6H_4 (**2c**)	**4c**	87	97:3
3	4-$OMeC_6H_4$ (**2d**)	**4d**	49	99:1
4	4-MeC_6H_4 (**2e**)	**4e**	66	99:1
5	2-MeC_6H_4 (**2f**)	**4f**	85	97:3
6	1-naphthyl (**2g**)	**4g**	74	96:4
7	Cy (**2h**)	**4h**	9	100:0
8	*n*-C_6H_{13} (**2i**)	**4i**	14	100:0
9[d]	*n*-C_6H_{13} (**2i**)	**4i**	40	98:2
10	Me_3Si (**2j**)	**4j**	26	99:1
11	EtO_2C (**2k**)	**4k**	3	100:0

[a] Reactions were carried out with 1.0 mmol of **2a**, 1.5 mmol of **3**, and 0.010 mmol of **1-ip** in 4 mL of toluene at 100 °C for 4 h under 1 atm of H_2. [b] Isolated yield. [c] Determined by ^{1}H NMR spectroscopy. [d] **1-ip** (5 mol %) was used.

Scheme 2. Labeling Experiment



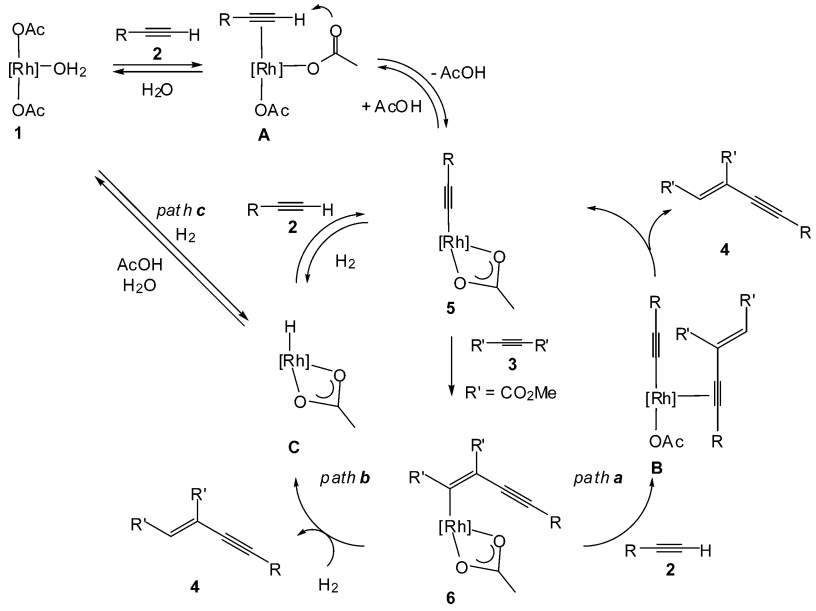
Scheme 3. Stoichiometric Reactions of 1-ip with the Alkynes 2a and 3



Because the presence of hydrogen accelerated the cross-coupling of alkynes, we tested the reaction of **2a**-d_1 (98% D) with **3** (Scheme 2). The ^{1}H NMR spectrum revealed 80% deuteration of the vinyl proton in **4a**-d_1. The reaction in toluene-d_8 gave the same result, indicating that the lower than expected deuteration results from the incorporation of hydrogen from the reaction atmosphere.

Stoichiometric Reactions of Rh Acetate Complexes with Alkynes. To investigate the mechanism, we performed stoichiometric reactions of **1-ip** and **1-dm** with alkynes (Scheme 3). Treatment of **1-ip** with **2a** in toluene at 60 °C for 12 h

Scheme 4. Proposed Mechanism



resulted in the formation of an acetylide κ^2-acetate complex **5-ip** in 87% yield. The ^{13}C NMR spectrum of **5-ip** showed the doublet signal of the acetylide carbon at δ 86.9 ppm (J_{RhC} = 53 Hz). Furthermore, **5-ip** reacted with **3** at room temperature to afford the corresponding vinyl complex **6-ip** in 78% yield. This step is significantly faster than the reaction of **1-ip** with **2a**. In the ^{13}C NMR spectrum of **6-ip**, the doublet signal of the α-vinyl carbon was observed at δ 175.5 ppm (J_{RhC} = 33 Hz).

Similarly, the related acetylide complex **5-dm** was obtained in 72% yield by reaction of **1-dm** with **2a**. The structure of **5-dm** shows that the acetylide moiety is placed almost perpendicular to the Phebox plane (Figure 1). The vinyl complex **6-dm**, which was obtained in 68% yield upon treatment of **5-dm** with **3**, was also analyzed by X-ray diffraction to clarify the maleic acid skeleton (Figure 2).

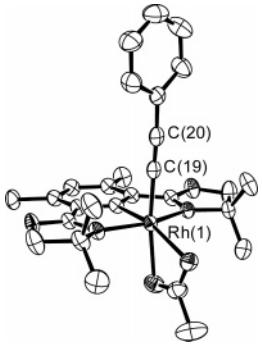


Figure 1. ORTEP drawing of **5-dm** using thermal ellipsoids at the 50% probability level. Selected bond lengths (Å): Rh(1)−C(19) 1.958(4), C(19)−C(20) 1.214(5).

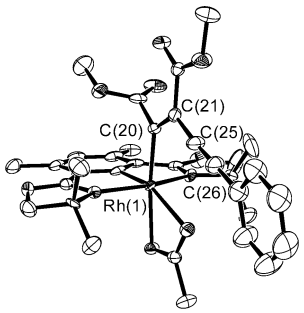


Figure 2. ORTEP drawing of **6-dm** using thermal ellipsoids at the 50% probability level. Selected bond lengths (Å): Rh(1)−C(20) 1.992(6), C(20)−C(21) 1.341(8), C(21)−C(25) 1.493(8), C(25)−C(26) 1.180(9).

To get further insight into the formation of **4a**, the C_6D_6 solution of **6-ip** was treated with 5 equiv of **2a** at 80 °C for 9 h. The ^{1}H NMR spectrum of the reaction mixture showed the formation of **4a** in 56% yield with the *Z*:*E* ratio of 95:5, accompanied by the formation of **5-ip** in 61% yield (Scheme 3). Under acidic condition of AcOH in C_6D_6 at 80 °C in the absence of **2a**, **6-ip** proved to be stable and was recovered.

Proposed Mechanism. On the basis of these results, we propose the mechanism of cross-coupling of alkynes outlined in Scheme 4.[8] C−H bond activation by deprotonation with the acetate ligand as a base takes place to produce the acetylide complex **5**. Subsequent insertion of internal alkyne **3** into the Rh−acetylide bond gives the vinyl complex **6**. As shown in path **a**, further reaction of **6** with a terminal alkyne produces the acetylide−enyne intermediate **B** followed by elimination of **4** to regenerate **5**. This pathway has been commonly proposed in a homo- and cross-coupling of alkynes.[2n,4b,5a] An alternative pathway could involve the reaction of **6** with H_2 to generate a hydride intermediate **C** and **4** (path **b**). Subsequent reactions of **C** with acetic acid and another alkyne **2** give **1** and **5**, respectively. The result of the labeling experiment described in Scheme 2 supports path **b** as a minor process. Formation of **4** resulting from protonation of **6** by acetic acid can be ruled out because addition of acetic acid did not facilitate the catalytic dimerization (Table 1, run 5).

The mechanism discussed above does not include the acceleration effect of the catalytic cross-coupling by hydrogen. Although we have not obtained the experimental details, we have presumed that reversible formation of the hydride intermediate **C** generated by the direct reaction of **1** with H_2 is

(8) As for an alternative mechanism, producing enyne via reductive elimination of an acetylide−vinyl complex, see refs 2p and 4e and: (a) Werner, H.; Kukla, F.; Steiner, P. *Eur. J. Inorg. Chem.* **2002**, 1377. (b) Schäfer, M.; Wolf, J.; Werner, H. *Organometallics* **2004**, *23*, 5713. (c) Ghosh, F.; Zhang, X.; Achord, P.; Emge, T. J.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2007**, *129*, 853.

significant for an activation step of the catalytic precursor (path **c**). In this case, the intermediate **C** mediates the facial formation of **5** via the σ-bond metathesis of an alkyne with the Rh−H bond. Slight improvement of the yield by treatment of formic acid into the catalytic reaction also suggests the formation of **C**, which is formed by decomposition of a formate species generated in situ.[10]

In summary, we found that molecular hydrogen has a remarkable acceleration effect on the cross-coupling reaction of terminal alkynes and dimethyl acetylenedicarboxylate in the presence of the Phebox−Rh acetate complex. The reactions afforded various enynes with high *Z*-stereoselectivity. The stoichiometric reactions provided the mechanistic aspects involving the stepwise sequence of C−H activation and insertion of the second alkyne. X-ray diffraction revealed the structural information about catalytically key intermediates of the acetylide and the vinyl complexes. Further studies on substrate scope and mechanistic details for the role of H_2 gas are in progress.

Experimental Section

General Procedures. ^{1}H and ^{13}C NMR spectra were obtained at 25 °C on a Varian Mercury 300 spectrometer. ^{1}H NMR chemical shifts are reported in δ units, in ppm relative to the singlet at 7.26 ppm for chloroform. ^{13}C NMR spectra are reported in terms of chemical shift (δ, ppm) relative to the triplet at $\delta = 77.0$ ppm for $CDCl_3$ as an internal standard. Infrared spectra were recorded on a JASCO FT/IR-230 spectrometer. Complexes **1-ip**, **1-dm**, and **1-dh** were prepared according to the literature.[11]

Rhodium-Catalyzed Cross-Dimerization Reaction. To a mixture of **1-ip** (5.7 mg, 0.010 mmol) and alkyne **2** (1.5 mmol) in toluene (4 mL) was added **3** (142 mg, 1.0 mmol) at 100 °C under a hydrogen atmosphere. The mixture was stirred at 100 °C for 4 h. After concentration, the residue was purified by silica gel column chromatography with hexane/ethyl acetate (15:1) as an eluent to give the mixture of **4-*Z*** and **4-*E***. The *Z*:*E* ratio was determined by ^{1}H NMR spectroscopy.

Dimethyl 2-(Phenylethynyl)maleate (4a-*Z*) and the Corresponding Fumarate (4a-*E*).[12] 85% yield (*Z*:*E* = 98:2). **4a-*Z***: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.78 (s, 3H, CO_2Me), 3.92 (s, 3H, CO_2Me), 6.34 (s, 1H, CC*H*), 7.35−7.52 (m, 5H, C_6H_5). **4a-*E***: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.85 (s, 3H, CO_2Me), 3.90 (s, 3H, CO_2Me), 7.12 (s, 1H, CC*H*), 7.36−7.62 (m, 5H, C_6H_5).

Dimethyl 2-((4-(Trifluoromethyl)phenyl)ethynyl)maleate (4b-*Z*) and the Corresponding Fumarate (4b-*E*). 79% yield (*Z*:*E* = 98:2). **4b-*Z***: Colorless solid, mp 67.1−67.4 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.79 (s, 3H, CO_2Me), 3.92 (s, 3H, CO_2Me), 6.40 (s, 1H, CC*H*), 7.59 (d, $J = 9.0$ Hz, 2H, C_6H_4), 7.62 (d, $J = 9.0$ Hz, 2H, C_6H_4). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 52.2, 53.1, 85.5, 95.8, 123.3 (q, $J_{CF} = 269.8$ Hz), 124.8 (q, $J_{CF} = 1.1$ Hz), 125.0 (q, $J_{CF} = 4.0$ Hz), 128.7, 129.0, 130.8 (q, $J_{CF} = 32.5$ Hz), 132.0, 164.0, 164.1. IR (KBr, cm^{-1}) ν 2208, 1739, 1723. Anal. Calcd for $C_{15}H_{14}F_3O_4$: C, 57.70; H, 3.55. Found: C, 58.02; H, 3.58. **4b-*E***: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.85 (s, 3H, CO_2Me), 3.91 (s, 3H, CO_2Me), 7.18 (s, 1H, CC*H*), 7.62 (d, $J = 8.0$ Hz, 2H, C_6H_4), 7.70 (d, $J = 8.0$ Hz, 2H, C_6H_4).

Dimethyl 2-((4-Bromophenyl)ethynyl)maleate (4c-*Z*) and the Corresponding Fumarate (4c-*E*). 87% yield (*Z*:*E* = 97:3). **4c-*Z***: Colorless solid, mp 35.3−35.8 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.78 (s, 3H, CO_2Me), 3.91 (s, 3H, CO_2Me), 6.35 (s, 1H, CC*H*), 7.34 (d, $J = 8.7$ Hz, 2H, C_6H_4), 7.49 (d, $J = 8.7$ Hz, 2H, C_6H_4). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 52.2, 53.1, 84.7, 96.8, 119.9, 124.0, 127.6, 129.6, 131.4, 133.0, 164.1, 164.2. IR (KBr, cm^{-1}) ν 2205, 1739, 1721. Anal. Calcd for $C_{14}H_{11}BrO_4$: C, 52.04; H, 3.43. Found: C, 51.84; H, 3.43. **4c-*E***: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.84 (s, 3H, CO_2Me), 3.91 (s, 3H, CO_2Me), 7.13 (s, 1H, CC*H*), 7.45 (d, $J = 8.7$ Hz, 2H, C_6H_4), 7.51 (d, $J = 8.7$ Hz, 2H, C_6H_4).

Dimethyl 2-((4-Methoxyphenyl)ethynyl)maleate (4d-*Z*) and the Corresponding Fumarate (4d-*E*). 49% yield (*Z*:*E* = 99:1). **4d-*Z***: Colorless solid, mp 70.3−70.8 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.77 (s, 3H, CO_2Me), 3.83 (s, 3H, O*Me*), 3.91 (s, 3H, CO_2Me), 6.28 (s, 1H, CC*H*), 6.87 (d, $J = 9.0$ Hz, 2H, C_6H_4), 7.43 (d, $J = 9.0$ Hz, 2H, C_6H_4). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 52.2, 53.2, 55.4, 83.2, 99.2, 113.2, 114.0, 125.9, 130.8, 133.6, 160.5, 164.7, 164.8. IR (KBr, cm^{-1}) ν 2198, 1738, 1717. Anal. Calcd for $C_{15}H_{14}O_5$: C, 65.69; H, 5.15. Found: C, 65.86; H, 5.14. **4d-*E***: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.84 (s, 3H), 3.85 (s, 3H), 3.90 (s, 3H), 6.89 (d, $J = 9.0$ Hz, C_6H_4), 7.06 (s, 1H, CC*H*), 7.55 (d, $J = 9.0$ Hz, C_6H_4).

Dimethyl 2-(*p*-Tolylethynyl)maleate (4e-*Z*) and the Corresponding Fumarate (4e-*E*). 4e-*Z*: 66% yield (*Z*:*E* = 99:1), colorless solid, mp 67.0−67.2 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.38 (s, 3H, *Me*), 3.78 (s, 3H, CO_2Me), 3.92 (s, 3H, CO_2Me), 6.31 (s, 1H, CC*H*), 7.16 (d, $J = 7.8$ Hz, 2H C_6H_4), 7.39 (d, $J = 7.8$ Hz, 2H, C_6H_4). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 21.6, 52.0, 53.0, 83.8, 98.8, 117.9, 126.4, 128.9, 130.4, 131.6, 139.9, 164.4, 164.5. IR (KBr, cm^{-1}) ν 2202, 1738, 1718. Anal. Calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46. Found: C, 69.56; H, 5.43. **4e-*E***: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.38 (s, 3H, *Me*), 3.85 (s, 3H, CO_2Me), 3.90 (s, 3H, CO_2Me), 7.09 (s, 1H, CC*H*), 7.17 (d, $J = 7.6$ Hz, 2H, C_6H_4), 7.49 (d, $J = 7.6$ Hz, 2H, C_6H_4).

Dimethyl 2-(*o*-Tolylethynyl)maleate (4f-*Z*) and the Corresponding Fumarate (4f-*E*). 4f-*Z*: 85% yield (*Z*:*E* = 97:3), colorless solid, mp 64.8−65.2 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.43 (s, 3H, *Me*), 3.79 (s, 3H, CO_2Me), 3.92 (s, 3H, CO_2Me), 6.34 (s, 1H, CC*H*), 7.14−7.31 (m, 3H C_6H_4), 7.44 (d, $J = 7.5$ Hz, 1H, C_6H_4). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 20.7, 52.3, 53.2, 87.7, 97.6, 120.9, 125.5, 126.8, 129.4, 129.6, 130.2, 132.1, 140.8, 164.6. IR (KBr, cm^{-1}) ν 2197, 1739, 1720. Anal. Calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46. Found: C, 70.00; H, 5.44. **4f-*E***: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.56 (s, 3H, *Me*), 3.85 (s, 3H, CO_2Me), 3.91 (s, 3H, CO_2Me), 7.11 (s, 1H, CC*H*), 7.15−7.32 (m, $J = 7.6$ Hz, 2H, C_6H_4), 7.55 (d, $J = 7.5$ Hz, 2H, C_6H_4).

Dimethyl 2-(Naphthalen-1-ylethynyl)maleate (4g-*Z*) and the Corresponding Fumarate (4g-*E*). 74% yield (*Z*:*E* = 96:4). **4g-*Z***: Yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.82 (s, 3H, CO_2Me), 3.97 (s, 3H, CO_2Me), 6.47 (s, 1H, CC*H*), 7.41−7.99 (m, 6H, $C_{10}H_7$), 8.23 (m, 1H, $C_{10}H_7$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 52.3, 53.3, 88.6, 96.7, 118.7, 124.9, 125.5, 126.5, 127.1, 127.3, 128.2, 129.9, 130.2, 131.3, 132.8, 132.8, 164.53, 164.55. IR (KBr, cm^{-1}) ν 2193, 1742, 1720. Anal. Calcd for $C_{18}H_{14}O_4$: C, 73.46; H, 4.79. Found: C, 73.29; H, 4.73. **4g-*E***: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.90 (s, 3H, CO_2Me), 3.98 (s, 3H, CO_2Me), 7.18 (s, 1H, CC*H*), 7.45−7.91 (m, 6H, $C_{10}H_7$), 8.60 (m, 1H, $C_{10}H_7$).

Dimethyl 2-(Cyclohexylethynyl)fumarate (4h-*Z*). 9% yield, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.24−1.88 (s, 10H, C_6H_{11}), 2.57 (tt, $J = 5.1$, 9.0 Hz, 1H, C_6H_{11}), 3.74 (s, 3H, CO_2Me), 3.87 (s, 3H, CO_2Me), 6.17 (d, $J = 0.6$ Hz, 1H, CC*H*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 24.9, 25.9, 30.0, 32.0, 52.2, 53.1, 75.8, 105.1, 126.1, 131.2, 164.8, 165.1. IR (KBr, cm^{-1}) ν 2212, 1746, 1725. HR-MS: calcd for $C_{14}H_{19}O_4$ (M^+), 251.1278; found, 251.1283.

Dimethyl 2-(Oct-1-ynyl)maleate (4i-*Z*) and the Corresponding Fumarate (4i-*E*). 4i-*Z*: 14% yield, colorless oil. ^{1}H NMR (300

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MHz, $CDCl_3$) δ 0.90 (t, J = 6.9 Hz, 3H, *Me*), 1.21−1.61 (m, 8H, C*H*$_2$), 2.39 (t, J = 6.9 Hz, 2H, C*H*$_2$), 3.75 (s, 3H, CO_2*Me*), 3.87 (s, 3H, CO_2*Me*), 6.17 (s, 1H, CC*H*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 14.2, 19.9, 22.6, 28.1, 28.7, 31.3, 52.2, 53.1, 75.7, 101.5, 126.2, 131.1, 164.7, 165.0. IR (KBr, cm^{-1}) ν 2219, 1747, 1726. HR-MS: calcd for $C_{14}H_{21}O_4$ (M^+), 253.1434; found, 253.1440. **4i-*E***: ^1H NMR (300 MHz, $CDCl_3$) δ 2.51 (t, J = 7.1 Hz, 2H, C*H*$_2$), 3.81 (s, 3H, CO_2*Me*), 3.85 (s, 3H, CO_2*Me*), 7.04 (s, 1H, CC*H*) (signals of the cyclohexyl group cannot be distinguished from those of byproducts).

Dimethyl 2-((Trimethylsilyl)ethynyl)maleate (4j-*Z*) and the Corresponding Fumarate (4j-*E*). 4j-*Z*: 26% yield (*Z*:*E* = 99:1), colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 0.22 (s, J_{SiH} = 7.2 Hz, 9H, *Me*), 3.75 (s, 3H, CO_2*Me*), 3.87 (s, 3H, CO_2*Me*), 6.28 (s, 1H, CC*H*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ −0.3, 52.3, 53.2, 98.1, 105.5, 128.4, 130.0, 164.3, 164.4. IR (KBr, cm^{-1}) ν 2150, 1748, 1728. HR-MS: calcd for $C_{11}H_{17}O_4Si$ (M^+), 241.0891; found, 241.0896. **4j-*E***: ^1H NMR (300 MHz, $CDCl_3$) δ 0.28 (s, 9H, *Me*), 3.82 (s, 3H, CO_2*Me*), 3.86 (s, 3H, CO_2*Me*), 7.09 (s, 1H, CC*H*).

Dimethyl 2-(Ethoxycarbonylethynyl)maleate (4k-*Z*). 3% yield, yellow oil. ^1H NMR (300 MHz, $CDCl_3$) δ 1.34 (t, J = 7.2 Hz, 3H, *Et*), 3.81 (s, 3H, CO_2*Me*), 3.88 (s, 3H, CO_2*Me*), 4.29 (q, J = 7.2 Hz, 2H, *Et*), 6.59 (s, 1H, CC*H*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 14.2, 52.7, 53.5, 62.7, 78.7, 86.2, 125.1, 134.9, 152.5, 162.4, 163.7. IR (KBr, cm^{-1}) ν 2221, 1729, 1717. HR-MS: calcd for $C_{11}H_{13}O_6$ (MH^+), 241.0707; found, 241.0712.

Isotope Labeling Experiments. To a mixture of **2a-*d*$_1$** (155 mg, 1.5 mmol, 98%-*d*) and **1-ip** (5.7 mg, 0.010 mmol) in toluene (4.0 mL) or toluene-d_8 (1.0 mL) was added **3** (142 mg, 1.0 mmol) at 100 °C under a hydrogen atmosphere. The mixture was stirred at 100 °C for 4 h. After concentration, the residue was analyzed by ^1H NMR spectroscopy.

Reaction of 1 with Phenylacetylene (2a). A mixture of **1-ip** (27.8 mg, 0.050 mmol) and **2a** (25.5 mg, 0.25 mmol) in toluene (2.0 mL) was stirred at 60 °C for 24 h under an argon atmosphere. After concentration of the solvent, the residue was purified by column chromatography on silica gel with hexane/ethyl acetate (1:1) as an eluent to give **5-ip** (25.7 mg, 0.044 mmol, 87%). The preparation procedure of **5-dm** was similar to that of **5-ip** (72%). **5-ip**: ^1H NMR (300 MHz, $CDCl_3$) δ 0.85 (d, J = 6.6 Hz, 3H, CH*Me*$_2$), 0.96 (d, J = 7.2 Hz, 3H, CH*Me*$_2$), 1.06 (d, J = 7.2 Hz, 3H, CH*Me*$_2$), 1.11 (d, J = 6.6 Hz, 3H, CH*Me*$_2$), 1.97 (s, 3H, O*Ac*), 1.97−2.51 (m, 2H), 2.53 (s, 3H, *Me*), 2.55 (s, 3H, *Me*), 4.08 (m, 1H), 4.37 (m, 1H), 4.53−4.78 (m, 4H), 6.70 (s, 1H), 6.96−7.09 (m, 5H, C$_6$*H*$_5$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 14.8, 16.5, 19.0, 19.1, 19.6, 24.0, 28.9, 30.5, 66.4, 67.3, 70.4, 71.7, 86.9 (d, J_{RhC} = 53 Hz, Rh−*C*CPh), 102.0 (d, J_{RhC} = 9.7 Hz, Rh−C*C*Ph), 124.4, 126.6, 126.6, 127.2, 127.8, 131.2, 140.2, 171.8 (d, J_{RhC} = 5.1 Hz), 172.5 (d, J_{RhC} = 5.1 Hz), 185.4, 186.6 (d, J_{RhC} = 25 Hz). IR (KBr, cm^{-1}) ν 2119. Anal. Calcd for $C_{30}H_{35}N_2O_4Rh$: C, 61.02; H, 5.97; N, 4.74. Found: C, 61.07; H, 6.03; N, 4.72. **5-dm**: ^1H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 6H, *Me*), 1.62 (s, 6H, *Me*), 1.93 (s, 3H, O*Ac*), 2.53 (s, 6H, *Me*), 4.45 (d, J = 8.4 Hz, 2H, C*H*$_2$), 4.55 (d, J = 8.4 Hz, 2H, C*H*$_2$), 6.67 (s, 1H), 6.94−7.09 (m 5H, C$_6$*H*$_5$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 19.0, 24.2, 26.7, 27.8, 65.0, 82.2, 86.5 (d, J_{RhC} = 52 Hz, Rh−*C*CPh), 102.7 (d, J_{RhC} = 9.2 Hz, Rh−C*C*Ph), 124.5, 127.0, 127.2, 127.4, 128.2, 131.1, 140.1, 170.9 (d, J_{RhC} = 5.2 Hz), 186.0, 186.8 (d, J_{RhC} = 26 Hz). IR (KBr, cm^{-1}) ν 2111. Anal. Calcd for $C_{28}H_{31}N_2O_4Rh$: C, 59.79; H, 5.56; N, 4.98. Found: C, 59.24; H, 5.50; N, 4.47.

Reaction of 5 with Dimethyl Acetylenedicarboxylate (3). A mixture of **5-ip** (54.3 mg, 0.090 mmol) and **3** (13.1 mg, 0.090 mmol) in toluene (2.0 mL) was stirred at room temperature for 4 h under an argon atmosphere. After concentration of the solvent, the residue was purified by column chromatography on silica gel with hexane/ethyl acetate (2:1) as an eluent to give **6-ip** (52.8 mg, 0.072 mmol, 78%). The preparation procedure of **6-dm** was similar to that of **6-ip**. A mixture of **5-dm** (28.1 mg, 0.050 mmol) and **3** (36.0 mg, 0.25 mmol) in toluene (2.0 mL) was stirred at 60 °C for 30 h. The mixture was purified by column chromatography on silica gel with methanol/ethyl acetate to give **6-dm** (23.8 mg, 0.034 mmol, 68%). **6-ip**: ^1H NMR (300 MHz, $CDCl_3$) δ 0.50 (brd, J = 5.4 Hz, 3H, CH*Me*$_2$), 0.72 (d, J = 6.9 Hz, 3H, CH*Me*$_2$), 0.89 (d, J = 6.9 Hz, 3H, CH*Me*$_2$), 1.07 (d, J = 6.9 Hz, 3H, CH*Me*$_2$), 1.99 (s, 3H, O*Ac*), 2.28−2.58 (m, 2H), 2.50 (s, 6H, *Me*), 2.94 (brs, 3H, CO_2*Me*), 3.69 (s, 3H, CO_2*Me*), 3.87 (m, 1H), 4.38−4.50 (m, 1H), 4.56−4.76 (m, 4H), 6.66 (s, 1H), 7.28−7.35 (m, 3H, C$_6$*H*$_5$), 7.86 (br, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 14.4, 17.1, 19.05, 19.09, 19.2, 20.6, 23.7, 29.0, 30.4, 50.2 (CO_2*Me*), 52.1 (CO_2Me), 67.1, 70.3, 72.2, 86.6, 91.6, 124.3, 126.5, 126.9, 127.2, 127.6, 131.8, 139.8, 140.2, 161.0, 171.5 (Rh−C═*C*), 171.7 (d, J_{RhC} = 4.6 Hz), 172.0 (d, J_{RhC} = 5.1 Hz), 175.5 (d, J_{RhC} = 33 Hz, Rh−*C*═C), 184.2, 189.3 (d, J_{RhC} = 29 Hz). IR (KBr, cm^{-1}) ν 1706. Anal. Calcd for $C_{36}H_{41}N_2O_8Rh$: C, 59.02; H, 5.64; N, 3.82. Found: C, 58.93; H, 5.77; N, 3.82. **6-dm**: ^1H NMR (300 MHz, $CDCl_3$) 1.42 (s, 6H, *Me*), 1.49 (s, 6H, *Me*), 1.91 (s, 3H, OCO*Me*), 2.54 (s, 6H, *Me*), 2.88 (s, 3H, CO_2*Me*), 3.68 (s, 3H, CO_2*Me*), 4.39 (d, J = 8.4 Hz, 2H, C*H*$_2$), 4.47 (d, J = 8.4 Hz, 2H, C*H*$_2$), 6.69 (s, 1H), 7.31−7.39 (m, 3H, C$_6$*H*$_5$), 8.00−8.04 (m, 2H, C$_6$*H*$_5$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 18.9, 23.8, 26.8, 49.9, 52.0, 65.4, 82.4, 87.1 (*C*CPh), 92.8 (C*C*Ph), 124.9, 127.1, 127.21, 127.22, 127.7, 132.1, 139.7, 161.0, 161.1, 170.8 (d, J_{RhC} = 4.5 Hz), 171.5 (Rh−C═*C*), 174.9 (d, J_{RhC} = 34 Hz, Rh−*C*═C), 184.8, 189.9 (d, J_{RhC} = 28 Hz). IR (KBr, cm^{-1}) ν 1712. Anal. Calcd for $C_{34}H_{37}N_2O_8Rh$: C, 57.96; H, 5.29; N, 3.98. Found: C, 57.82; H, 5.35; N, 3.51.

Reaction of 6-ip with Phenylacetylene (2a). An NMR sample tube was charged with **6-ip** (2.0 mg, 0.0028 mmol), **2a** (1.4 mg, 0.014 mmol), and C_6Me_6 (0.2 mg) as an internal standard with C_6D_6 (0.6 mL). The tube was heated at 80 °C for 9 h. The ^1H NMR spectrum showed the formation of **4a** and **5-ip** in 56% and 61% yield, respectively.

X-ray Diffraction Study. Single crystals of **5-dm** and **6-dm** suitable for X-ray diffraction study were obtained from $CHCl_3$/ether solution at room temperature. The diffraction data were collected on a Brucker SMART APEX CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction was applied by using SADABS. The structure was solved by direct method and refined by full-matrix least-square on F^2 using SHELXTL. All non-hydrogen atoms of the rhodium complex were refined with anisotropic displacement parameters. All hydrogen atoms were located on calculated positions and refined as rigid groups. CCDC-642228 and 642229 contain the supplementary crystallographic data for complexes **5-dm** and **6-dm**, respectively. Refinement details for **5-dm**: empirical formula $C_{32.50}H_{45.25}Cl_3N_2O_{4.50}Rh$; M_r = 745.22; temperature 173(2) K; crystal system triclinic; space group $P2_1/n$; a = 17.272(11), b = 9.691(6), c = 20.140(12) Å, β = 94.441(13)°, V = 3361(4) Å^3, Z = 4, ρ_{calcd} = 1.473 Mg/m^3, μ = 0.787 mm^{-1}, F(000) = 1545, crystal size = 0.40 × 0.40 × 0.10 mm^3, θ range = 2.33−27.47°; index ranges, $-18 \le h \le 22$, $-12 \le k \le 12$, $-26 \le l \le 26$; reflections collected 22 252; independent reflections 7592 [R(int) = 0.0611]; completeness to θ = 27.47°, 98.6%; max/min transmission 1.000000/0.668673; data/restraints/parameters 7592/0/404; goodness-of-fit on F^2 1.061; final R indices [$I > 2\sigma(I)$], R1 = 0.0543, wR2 = 0.1197; R indices (all data), R1 = 0.0789, wR2 = 0.1295; largest diff. peak/hole 0.840 and −0.850 e Å^{-3}. Refinement details for **6-dm**: empirical formula $C_{37}H_{44}N_2O_8Rh$; M_r = 747.65; temperature 173(2) K; crystal system triclinic; space group P-1; a = 9.437(10), b = 9.469(11), c = 19.68(2) Å, α = 89.08(2)°, β = 84.11(3)°, γ = 86.76(2)°, V = 1746(3) Å^3, Z = 2, ρ_{calcd} = 1.422

Mg/m^3, μ = 0.543 mm^{-1}, F(000) = 778, crystal size = 0.30 × 0.30 × 0.05 mm^3, θ range = 2.31−27.74°; index ranges, $-12 \le h \le 9$, $-12 \le k \le 11$, $-26 \le l \le 12$; reflections collected 9498, independent reflections 7659 [R(int) = 0.0622], completeness to θ = 28.04°, 90.4%; max/min transmission 0.973/0.846; data/restraints/parameters 7659/0/443; goodness-of-fit on F^2 1.110; final R indices [$I > 2\sigma(I)$], R1 = 0.0850, wR2 = 0.1923; R indices (all data), R1 = 0.1103, wR2 = 0.2045; largest diff. peak/hole 1.828 and −2.109 e Å^{-3}.

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Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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