Rhodium-Catalyzed Dimerization of Terminal Alkynes Assisted by MeI

Chrong-Ching Lee, Ying-Chih Lin,* Yi-Hung Liu, and Yu Wang

Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, Republic of China

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Dimerization of terminal arylalkynes at ambient temperature catalyzed by $Rh(CO)(PPh_3)_2Cl$ (**2**) in the presence of MeI leads to formation of enyne with high conversion and high regio- and stereoselectivity. A rhodium intermediate captured from oxidative addition of MeI was used for dimerization of alkyne with selectivity controlled by the use of solvents. In aprotic solvent (such as acetone, CH_2Cl_2, or THF) dimerization of terminal alkynes HC≡C(*p*-C_6H_4X) (**1**, X = H, **a**; NO_2, **b**; C(O)H, **c**; Me, **d**; CN, **e**; NMe_2, **f**; CF_3, **g**; F, **h**; Br, **i**; I, **j**) leads to the (*E*)-1,4-disubstituted enynes **6** (**a**−**k**) in high selectivity. However, when MeOH is used as a solvent, the dimerization of 1-arylalkynes containing an electron-withdrawing group affords selectively the (*Z*)-1,4-disubstituted enyne **8**. Requirement of the presence of MeI for this conversion indicates that the process presumably involves initially a six-coordinated rhodium methylacetylide intermediate. Oxidative addition of ICH_2CN to **2** yielded the catalytically inactive six-coordinated complex $Rh(CO)(PPh_3)_2(C{\equiv}CPh)(I)(CH_2CN)$ (**5a**). The analogous complex **5b** with a *p*-nitro group on the phenyl acetylide ligand is characterized by X-ray diffraction analysis.

Introduction

Alkyne-coupling reactions catalyzed by transition metals are of considerable current interest because these reactions afford unsaturated four-carbon compounds such as conjugated enynes, which are important building blocks[1] for synthetic organic chemistry and key units found in a variety of biologically active compounds. Many metal complexes including early, late transition metals and lanthanide series such as Sc,[2] Y,[3] Ce,[3] La,[3] Sm,[4] Zr,[5] Ti, Cr,[6] and Ru,[7] Rh,[8] Ni,[9] Pd,[10] and Cu[11] have been used in the dimerization reaction of terminal alkynes; however, in most cases a mixture of regio- and stereoisomeric enynes (*E*,*Z*-form and head-to-tail dimers) is obtained.

The factors that affect regio- and stereoselectivity depend mainly on the electronic effects and steric hindrance at the alkyne substituent and at the coordination sphere of the metal. Methods for selective construction of head-to-tail enynes in the presence of the Pd system were developed by Trost.[12] The homocoupling and cross-coupling of acetylenes were achieved

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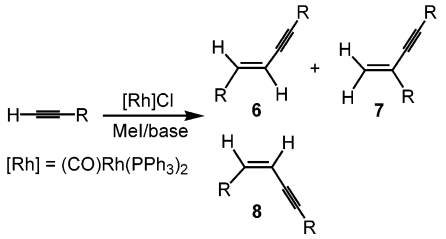

in high yield by using a Pd template.[13] Bianchini and Peruzzini reported the selective coupling of terminal alkynes to *Z*-1,4-disubstituted butenynes in a catalytic manner by using Ru complexes.[14] Another complex, $RuTp(py)_2Cl$ (Tp = trispyazolyborate, py = pyridine), was found to be an efficient catalyst for the selective coupling of HC≡CPh and allyl alcohol.[15] The catalytic coupling of HC≡CR (R = Ph, $SiMe_3$, *n*-Bu, and *t*-Bu) to 1,4- and 2,4-disubstituted butenynes with the aid of Ru complexes has been reported.[16] Recently, Miyaura reported the iridium-catalyzed dimerization of terminal alkynes[17] to give (*E*)-enyne, (*Z*)-enyne, or 1,2,3-butatriene derivatives in the presence of triethylamine. The reaction used a triarylphosphine complex selectively yielding linear (*E*)-enynes for silylethynes, while the tripropylphosphine complex provided linear (*Z*)-enynes for silylalkynes or 1,2,3-butatrienes for *tert*-alkylethynes, and formation of a head-to-tail dimer was not observed. Gevorgyan and Rubina discovered that a Pd system in the dimerization of terminal aryl acetylene produced not only the head-to-tail enyne but also a head-to-head *Z*-form enyne.[18] They synthesized a series of different ortho-substituted aryl alkynes and found that at least one ortho hydrogen in aryl acetylene is involved for a selective head-to-head dimerization reaction. It was proposed that an agostic interaction between the transition metal and ortho proton of the aromatic ring in the substrate is responsible for the observed unusual regioselectivity of the reaction.

Rhodium complexes[19] have also been used to catalyze the dimerization reaction of terminal alkynes. Rhodium(I) triphenylphosphine complexes are most commonly used as catalysts in these reactions. The selectivity for enyne formation is 65−75%, but alkyne trimerization also takes place. In 1990, Vinogradov and co-workers reported that $RhCl(PMe_3)_3$ catalyzed dimerization of aliphatic terminal alkynes to form enynes.[8d] However, the yield of enynes is low and the regio- and stereoselectivity of enynes is poor. For arylalkyne, under this reaction condition no dimer was obtained.

We are interested in exploring the chemical reactivity of various metal vinylidene complexes[20] commonly prepared by alkylation[21] of metal acetylide complexes. However, in the reaction of methyliodide with the rhodium phenylacetylide complex, oxidative addition takes place preferentially followed by a reductive elimination to give the 1-phenyl-1-propyne. Surprisingly a competing dimerization product from the reaction of the terminal acetylide ligand is also observed. This indicates that the intermediate generated in the process could be used to produce a different product. With careful control of the reaction conditions, the system is developed to take advantage of the intermediate formed from the oxidative addition as a catalyst[22] to catalyze the dimerization of alkynes. Herein, we describe the catalytic enyne formation reaction of terminal arylalkynes at ambient temperature that lead to high conversion and high regio- and stereoselectivity depending on the solvent used.

Results and Discussion

Stoichiometric Reactions of Rh Acetylide Complexes. The reaction of HC≡CPh (**1a**) with [Rh]-Cl (**2**, [Rh] = $Rh(CO)(PPh_3)_2$) in the presence of MeONa and CO results in the formation of the rhodium σ-acetylide complex [Rh]-C≡CPh (**3a**) in high yield. Complex [Rh]-C≡C(*p*-$C_6H_4NO_2$) (**3b**), where the terminal phenyl group on the acetylide ligand is substituted by a *p*-nitrophenyl group, was similarly obtained from HC≡C(*p*-$C_6H_4NO_2$) (**1b**) also in high yield. Addition of MeI to a CH_2Cl_2 solution of complex **3a** affords [Rh]-I (**2′**) and the organic compound MeC≡CPh (**4a**) in quantitative yield. Obviously the reaction proceeds via oxidative addition of CH_3I leading to an unobserved six-coordinated complex $Rh(CO)(PPh_3)_2(Me)I(C{\equiv}CPh)$ followed by reductive elimination to give [Rh]-I (**2′**) and **4a**. Alkylation at C_β of the acetylide ligand leading to the vinylidene complex was not observed.

Interestingly, when ICH_2CN is used to react with **3a**, the six-coordinated complex $Rh(CO)(PPh_3)_2(CH_2CN)I(C{\equiv}CPh)$ (**5a**) is obtained in high yield. Namely, the reductive elimination reaction is obstructed by the presence of the electron-withdrawing CN group even at

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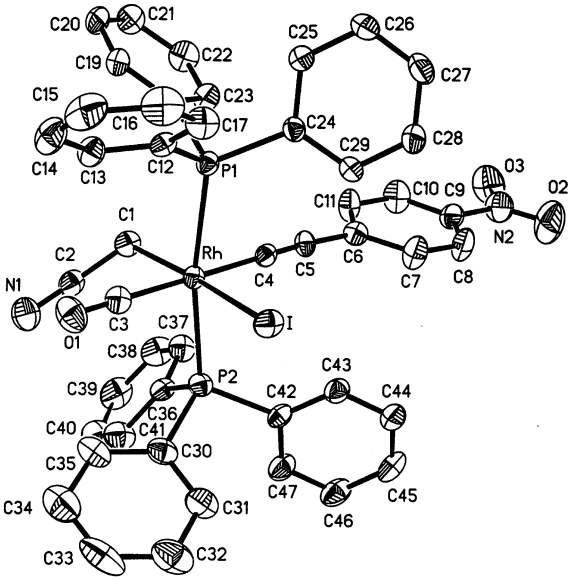


Figure 1. ORTEP drawing of **5b**.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) of 5b

Rh−I	2.7923(10)	Rh−P1	2.3912(23)
Rh−P2	2.3953(24)	Rh−C1	2.146(8)
Rh−C3	1.919(9)	Rh−C4	2.010(8)
C1−C2	1.428(12)	C2−N1	1.143(12)
C3−O1	1.121.(10)	C4−C5	1.189(11)
I−Rh−C1	170.36(24)	I−Rh−C3	80.65(25)
I−Rh−C4	101.56(22)	I−Rh−P1	87.77(6)
I−Rh−P2	89.55(6)	Rh−C1−C2	112.3(6)
Rh−C3−O1	178.6(7)	Rh−C4−C5	178.3(7)
C1−C2−N1	177.3(10)	C4−C5−C6	172.1(9)

60 °C. Complex $Rh(CO)(PPh_3)_2(CH_2CN)I(C{\equiv}C(p\text{-}C_6H_4\text{-}NO_2))$ (**5b**), where the terminal phenyl group is substituted by a *p*-nitrophenyl group, is similarly prepared from **3b** and fully characterized by an X-ray diffraction analysis. An ORTEP drawing of **5b** is shown in Figure 1, and selected bond lengths and angles are collected in Table 1. The coordination sphere of the Rh center can be described as octahedral with the cyanomethyl and the acetylide ligands in *cis* disposition and the cyanomethyl and iodide ligands in *trans* disposition. This kind of *cis* disposition should also be present in the reaction of **3a** with MeI; it is therefore not surprising to see rapid formation of **4a** via reductive elimination. Alkylation reaction of terminal acetylenes **1a** and **1b** with MeI in MeOH could be carried out catalytically in the presence of **2′** and the base MeONa at room temperature. The product **4a** is isolated in 88% yield in 6 h and $MeC{\equiv}C(p\text{-}C_6H_4NO_2)$ (**4b**) in 95% yield in 1 h.

Catalytic Dimerization of Alkyne. When the above-mentioned procedure was extended to the reaction of rhodium complexes with other terminal aryl alkynes, we observed dimerization of alkyne. From the aryl alkyne $HC{\equiv}C(p\text{-}C_6H_4CHO)$ (**1c**), in addition to the desired alkylation product **4c**, the (*E*)-1,4-disubstituted enyne **6c** (see Scheme 1) was also obtained in high yield. The stoichiometric reaction of **2** with **1c** was first carried out in the presence of MeI and K_2CO_3 in MeOH at room temperature. After 5 h, the ^1H NMR spectrum of the crude reaction mixture revealed the formation of the alkylation product **4c** in low yield possibly due to the reactive aldehyde group in **1c** in the presence of K_2CO_3 in MeOH. We modified the catalytic reaction by using THF. Interestingly, the reaction of **1c** with MeI in the presence of **2** and K_2CO_3/THF at room temperature for 24 h afforded **4c** and the dimerization product **6c** in a 1:2 ratio, which could be separated by chromatography, and **6c** was identified by ^1H and ^{13}C NMR and EI mass spectrum. The ^1H NMR spectrum of **6c** displays two doublet signals at δ 7.14 and 6.55 with $^3J_{H-H} = 16.2$ Hz, indicating the presence of two *trans* olefinic protons. Two singlet signals at δ 9.99 and 9.98 are assigned to two aldehyde protons. In the ^{13}C NMR spectrum of **6c**, two singlet resonances at δ 191.43 and 191.33 are assigned to two carbonyl carbons. The ^{13}C signals of the C=C group appear at δ 114.6 and 111.1.

Scheme 1

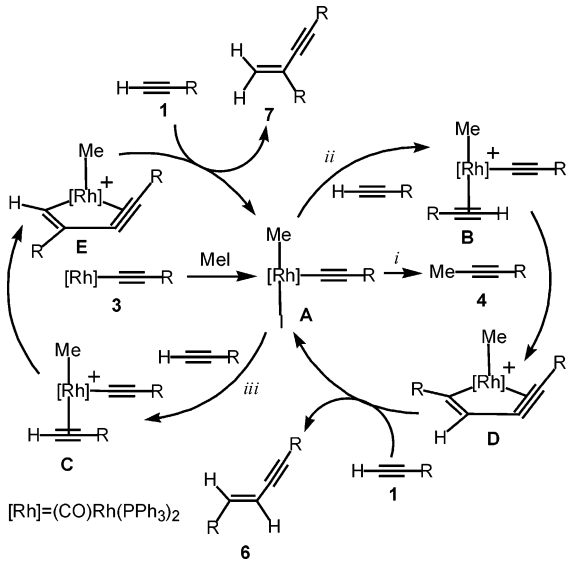


Table 2. Effect of the Solvent on Rhodium-Catalyzed Dimerization of 1a[a]

entry	solvent	**2** (mol %)	MeI (equiv)	ratio for **6a**:**7a**:**4a**	time (h)	conversion (%)	yield (%) for **6a**
1	MeOH	5	2	0:0:100	2	100	0[c]
2	THF	5	3	78:19:3	24	100	70[c]
3	CH_2Cl_2	1	0.5	81:18:1	18	100	75[c]
4	benzene	5	3	79:20:1	18	100	71[c]
5	ether	5	1	71:19:10	18	47	33[b]
6	acetone	5	3	79:20:1	18	100	70[c]
7	MeCN	5	1	5:5:90	18	100	5[b]

[a] Catalyst: $[Rh(CO)(PPh_3)_2Cl]/K_2CO_3$ (10 equiv). [b] NMR yield. [c] Isolated yield.

(*E*)-1,4-Disubstituted Enynes from Terminal Alkynes. In our optimization studies, phenyl-acetylene was used as the model substrate for the dimerization. The catalytic system consists of 5 mol % of **2** and 3 equiv of MeI with 10 equiv of K_2CO_3 as a base in THF. Most reactions were complete in 18 h. The ratio of (*E*)-1,4-disubstituted enyne **6a**, 1,3-disubstituted enyne **7a**, and the alkylation product **4a** is 78:19:3 from the reaction of **1a**, showing good chemo-, regio-, and stereoselectivity. The head-to-head dimeric product (*Z*)-1,4-disubstituted enyne was not obtained. The structure of **6a** was readily determined by the coupling constant between two olefinic protons ($J = 16.2$ Hz) for the (*E*)-enyne as compared to that ($J = 11.9$ Hz) of the (*Z*)-enyne. Table 2 lists our survey of various solvents for this system showing nearly complete dimerization and similar

Table 3. Dimerization of Terminal Alkynes to Enynes Catalyzed by the [Rh(CO)(PPh$_3$)$_2$Cl]/K$_2$CO$_3$/MeI System[a]

entry	R	**2** (mol %)	MeI (equiv)	ratio for **6**:**7**:**4**	time (h)	conversion (%)	yield (%) for **6**
1[e]	**1a**, Ph	1	0.5	81:18:1	18	100	75[c]
2	**1b**, *p*-C$_6$H$_4$NO$_2$	5	3	60:15:25	48	100	52[c]
3	**1c**, *p*- C$_6$H$_4$CHO	5	3	67:0:33	4	100	60[c]
4[d]	**1d**, *p*-C$_6$H$_4$Me	5	3	92:0:8	48	100	90[c]
5	**1e**, *p*-C$_6$H$_4$CN	1	0.1	83:3:14	48	84	54[c]; 69[b]
6[d]	**1f**, *p*-C$_6$H$_4$NMe$_2$	1	0.1	90:8:2	40	100	82[c]
7	**1g**, *p*-C$_6$H$_4$CF$_3$	5	3	97:0:3	24	100	90[c]
8[e]	**1h**, *p*-C$_6$H$_4$F	5	3		24		39[c]
9[e]	**1i**, *p*-C$_6$H$_4$Br	1.25	0.25	93:3:4	24	98	88[c]
10[e]	**1j**, *p*-C$_6$H$_4$I	1	0.1		14	100	77[c]
11	**1k**, *n*-Bu	5	3	10:90:0	18	100	*f*

[a] Catalyst: [Rh(CO)(PPh$_3$)$_2$Cl] (**2**)/K$_2$CO$_3$ (10 equiv)/THF (10 mL). [b]NMR yield. [c] Isolated yield. [d] 5 equiv of NaOMe as base. [e] 5 mL of CH$_2$Cl$_2$ as solvent. [f] **7k** in 72% isolated yield.

Table 4. Dimerization of Terminal Alkynes to (*Z*)-Enynes Catalyzed by the [Rh(CO)(PPh$_3$)$_2$Cl]/K$_2$CO$_3$/CH$_3$I System in MeOH[a]

entry	R	**2** (mol %)	MeI (equiv)	ratio for **6**:**8**:**4**	time (h)	conversion (%)	yield (%) for **8**
1	**1a**, Ph	1	0.1	13:82:5	16	100	82[b], 63[c]
2[e]	**1b**, *p*-C$_6$H$_4$NO$_2$	1	0.1		18		
3[e]	**1c**, *p*-C$_6$H$_4$CHO	1	0.1		18		
4[d,e]	**1d**, *p*-C$_6$H$_4$Me	1	0.1		48		
5	**1e**, *p*-C$_6$H$_4$CN	1	0.1	0:95:5	48	96	82[c]
6[d,e]	**1f**, *p*-C$_6$H$_4$NMe$_2$	1	0.1		40		
7	**1g**, *p*-C$_6$H$_4$CF$_3$	1	0.1	0:99.5:0.5	18	100	91[c]
8	**1h**, *p*-C$_6$H$_4$F	1	0.1		18		25[c]
9	**1i**, *p*-C$_6$H$_4$Br	1	0.1	0:97:3	18	100	90[c]
10	**1j**, *p*-C$_6$H$_4$I	1	0.1	0:80:20	14	57	35[c]

[a] Catalyst: [Rh(CO)(PPh$_3$)$_2$Cl] (**1a**)/K$_2$CO$_3$ (10 equiv)/MeOH (5 mL). [b]NMR yield. [c] Isolated yield. [d] 5 equiv of MeONa as base. [e] (*Z*)-Enynes were not observed.

product distribution in some aprotic solvents. Dimerization reaction of phenylacetylene was not observed in MeOH, as shown in entry 1. Low conversion in entry 5 could be due to the low solubility of rhodium complex **2** in ether. Acetonitrile appears to be an inappropriate solvent in the dimerization of phenylacetylene, presumably because of its coordinating nature (entry 7). Furthermore, as shown in Table 3, a survey of various terminal arylacetylenes for this system shows nearly complete dimerization and similar product distribution in a variety of solvents such as THF and CH$_2$Cl$_2$. All *E*-form enyne products **6** are characterized by ^{1}H and ^{13}C NMR and FAB mass spectroscopic data.

For the catalytic dimerization reaction of arylalkyne with electron-donating groups such as CH$_3$ (**1d**) and NMe$_2$ (**1f**) on the aryl ring, a stronger base such as MeONa is required (entries 4, 6). Substrate **1h** suffers from low yield (entry 8). For dimerization of **1j**, because of the low solubility of **6j**, the crude dimeric product ratio was not determined by ^{1}H NMR (entry 10). For alkyne **1c** (R = *p*-C$_6$H$_4$CHO), the (*E*)-enyne **6c** and alkylation product **4c** are formed in a ratio of 67:33% (**6c**:**4c**) with 100% conversion (entry 3). Finally, the aliphatic alkyne **1k** produces corresponding head-to-tail dimer **7k** as the major product (entry 11). Dimerization of **1h**, **1i**, **1j**, and **1c** to form enynyl products was not reported previously. This may be due to high affinity of the C−X bond of the aryl halide to the Pd catalyst.

(*Z*)-1,4-Disubstituted Enynes from Terminal Alkynes. The rhodium-catalyzed dimerization reaction of terminal alkynes in aprotic solvents such as THF, CH$_2$Cl$_2$, acetone, and benzene gives (*E*)-1,4-disubstituted enynes, but the corresponding *Z*-form isomer of 1,4-disubstituted enynes was not obtained. When MeOH is used, dimerization reactions of 1-alkynes catalyzed by **2** afforded (*Z*)-1,4-disubstituted enynes **8** at room temperature in excellent yield with high chemo-, regio-, and stereoselectivity. The catalytic system consisting of 1 mol % of **2** and 0.1 equiv of MeI with 10 equiv of K$_2$CO$_3$ as a base was tested in MeOH for the catalytic activity of the dimerization of various 1-alkynes (see Table 4). For the dimerization of **1a** (R = Ph), the reaction was complete in 16 h. The product ratio of (*E*)-1,4-disubstituted enyne **6a**, (*Z*)-1,4-disubstituted enyne **8a**, and the alkylation product **4a** is 13:82:5 (entry 1). The head-to-tail dimeric product 1,3-disubstituted enyne **7a** was not obtained. The structure of the (*Z*)-enyne was readily determined by the coupling constant between two olefinic *cis*-protons (J = 11.9 Hz). A number of other terminal arylacetylenes undergo nearly complete dimerization and give a similar product distribution in MeOH (Table 4). For the dimerization of HC≡C(*p*-C$_6$H$_4$CN) (**1e**), the reaction was complete in 48 h. The product ratio of **8e**:**4e** is 95:5 (entry 3). For **1g**, high conversion (100%) and excellent selectivity (99.5% in *Z*-isomer) are found for the catalytic dimerization reaction (entry 7). Dimerization of **1i** reveals similar selectivity and conversion (entry 9). In the case of **1j** (R = 4-C$_6$H$_4$I), the dimerization reaction results in lower selectivity and lower conversion (57%) (entry 10).

However, in cases of dimerization reaction of 1-arylalkynes, bearing Me$_2$N, NO$_2$, and Me groups at the para-position of the aryl group, neither (*E*)-enynes nor (*Z*)-enynes were obtained (Table 4). The reaction of **1b** with MeI in the presence of **2** and K$_2$CO$_3$ in MeOH afforded only the alkylation product **4b** in 10% NMR yield (entry

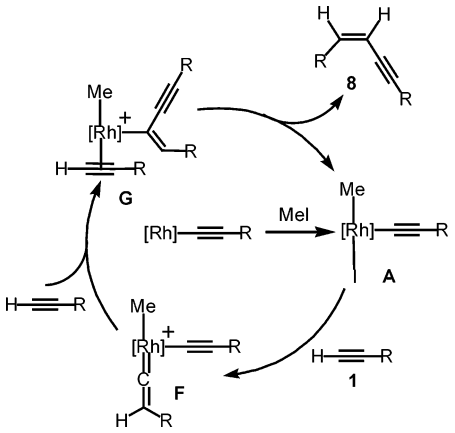
2). No dimeric (*E*)- or (*Z*)-enyne was obtained. This is clearly due to the presence of a para-NO_2 group at the phenyl group of **1b**. For HC≡C(*p*-C_6H_4Me) (**1d**), no *Z*-form enyne was observed in MeOH. Under catalytic conditions, the reaction of **1d** with MeI in MeOH affords the alkylation product **4d**, **3d**, and a trace amount of the *E*-form enyne **6d** (entry 4). For **1f**, only the alkylation product **4f** was obtained (entry 6). In the dimerization reaction of **1h** in MeOH the low yield of (*Z*)-enyne **8h** could be due to an unstable reaction intermediate (entry 8). Finally, the reaction of alkyne **1c** under catalytic conditions in MeOH affords a black, insoluble solid, which was not characterized (entry 3). We proposed that the black solid is derived from polymerization of **1c** in the presence of **2** and K_2CO_3/MeOH.[21] To the best of our knowledge, the transition metal-catalyzed dimerization of 1-arylalkyne with high regioselectivity to the head-to-head (*Z*)-enynes is rare.

In 1991, Bianchini and co-workers reported that the selective coupling of terminal alkynes to *Z*-1,4-disubstituted butenynes can be achieved catalytically by using either the Ru hydrido complex [(PP_3)Ru(H)(η^2-H_2)]-BPh_4 or the η^1-dinitrogen derivative [(PP_3)Ru(H)(N_2)]-BPh_4 (PP_3 = $P(CH_2CH_2PPh_2)_3$).[7b] When complex [(PP_3)-Ru(C≡CSiMe_3)]BPh_4 is reacted with excess HC≡CSiMe_3, catalytic production of (*Z*)-1,4-bis(trimethylsilyl)but-3-en-1-yne was observed.

Proposed Mechanism of Rhodium-Catalyzed Dimerization. There were only a few mechanistic studies on Rh(I)- and Pd(I)-catalyzed terminal alkyne dimerization reactions that provided direct evidence. It is generally accepted that the first step is the addition of the terminal alkyne to the transition metal catalyst to yield a metal acetylide complex intermediate (M = Rh, Pd).[13,18,21,23] Indeed, the reaction of 1-alkynes with **2** in the presence of base results in formation of Rh(I)-acetylide complexes. Further reaction of Rh(I)-acetylide complex with alkyl halide affords a six-coordinated Rh(III) complex by oxidative addition. In the absence of MeI, the reaction of alkyne **1** with **2** and a base affords only the Rh-acetylide complex. Thererore, formation of the metal acetylide should be derived from the reaction of rhodium chloride with the deprotonated terminal alkyne by base, instead of a direct oxidative addition. In the absence of a base, there is no reaction of the mixture of alkyne **1** and **2** in MeOH, THF, or CH_2Cl_2. The dimerization reaction of **1c** with 5 mol % of the Rh(III) complex Rh(CO)$(PPh_3)_2$(Cl)I_2, prepared by iodination of **2**, under catalytic conditions at room temperature affords the *E*-form disubstituted enyne **6c** in low yield due to poor catalytic activity of Rh(CO)$(PPh_3)_2$-(Cl)I_2.

On the basis of these observations, the proposed mechanism is depicted in the Schemes 1 and 2. The six-coordinated methyl acetylide Rh(III) complex (CO)Rh-$(PPh_3)_2$(C≡CR)(Me)(I) (**A**) is considered as the key intermediate. The catalytic cycle is initiated with formation of **A** from oxidative addition of MeI to **3**. Then coordination of the second terminal alkyne to the Rh atom affords two rhodium complexes, **B** and **C**, via two

Scheme 2



pathways, *ii* and *iii*, respectively.[24] Complex **A** could also undergo reductive elimination, affording the alkylation product MeC≡CR, **4**, via pathway *i*. To hamper the reductive elimination pathway, the amount of MeI was reduced. The reaction favored pathway *ii* for the alkyne substrate bearing an aryl group. In this pathway, a second terminal alkyne coordinates to the Rh atom, leading to the butenynyl intermediate **D**. Then further reaction of **D** with alkyne affords the product *E*-enynes **6**, regenerating **A**. However, for aliphatic alkyne such as 1-hexyne, the head-to-tail dimer **7** is formed more favorably than the head-to-head *E*-isomer **6** in the enyne formation reaction. The reaction may thus proceed through pathway *iii*.

Recently, Kirchner and co-workers reported that a TpRu acetylide complex reacts readily with stoichiometric amounts of HC≡CPh in benzene to give the alkyne coupling product featuring an (*E*)-1,4-enynyl ligand.[25] Head-to-head coupling with *E*- or *Z*-selectivity is, however, more frequently reported. In 1997, Jordan and Yoshida reported that the dicarbollide methyl complex (Cp*)(η^5-$C_2B_9H_{11}$)Hf(μ-η^2:η^3-$C_2B_9H_{11}$)Hf(Cp*)-Me_2 (Cp* = C_5Me_5) catalyzed the regioselective dimerization of terminal alkynes HC≡CR (R = Me, ^{n}Pr, ^{t}Bu) to 2,4-disubstituted 1-buten-3-ynes.[26]

In MeOH the reaction of 1-alkyne with an equal amount of MeI in the presence of 1−5 mol % of catalyst **2** and base results in alkylation product MeC≡CR (**4**). However, when the amount of MeI was reduced, the reaction leads to formation of the (*Z*)-1,4-disubstituted enyne **8** in MeOH. The proposed mechanism for the formation of enyne **8** is shown in Scheme 2 (pathway *iv*).[27] On the basis of the fact that a small amount of alkylation product **4** was always obtained in most enyne formation reactions, we propose that the six-coordinated complex **A** is also the intermediate in the dimerization

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reaction giving **8**. Further reaction of 1-alkyne with complex **A** in MeOH affords the cationic vinylidene complex **F**. Coupling of the σ-acetylide with the vinylidene group results in formation of (*Z*)-butenynyl rhodium complex **G**. Simple σ-bond metathesis of **G** and 1-alkyne discharges head-to-head (*Z*)-1,4-disubstituted enyne **8**, regenerating **A**. No dimerization reaction of alkyne **1d** or **1f** was observed in MeOH. Actually, there are few cases of the reaction of 1-alkyne, which bears an electron-donating group with the transition metal to form the vinylidene complex.[7b] The presence of the electron-donating group may hinder coupling of the vinylidene ligand with the acetylide ligand, thus prohibiting formation of the dimer product. The catalytic system requires the presence of MeI, which is known to react readily with PPh_3 to give phosphonium iodide. It is therefore less likely to have free dissociated PPh_3 from the catalyst in the reaction mixture. Intermediate complexes **B**, **C**, **D**, **F**, and **G** in Schemes 1 and 2 are thus proposed to be derived from the dissociation of iodide from the catalyst consequently bearing cationic charge.[24]

Concluding Remarks. A rhodium intermediate captured from oxidative addition of MeI was used for selective dimerization of alkyne. Using the rhodium complex as a catalyst, the dimerization of various terminal arylalkynes in aprotic solvents (such as CH_2Cl_2, THF, and acetone) resulted in formation of (*E*)-1,4-disubstituted enyne **6** in high stereoselectivity. However, when MeOH is used as a solvent, dimerization of 1-arylalkynes with an electron-withdrawing group gave the other stereoisomeric product (*Z*)-1,4-disubstituted enyne **8** in the presence of 0.1 equiv of MeI. With excess MeI, a competitive process, namely, oxidative additions of MeI and alkyne to the Rh metal center followed by reductive elimination, gave the alkylation product **4** of the terminal alkyne.

Experimental Section

General Procedures. All manipulations were performed under nitrogen using vacuum-line, drybox, and standard Schlenk techniques. CH_2Cl_2 and CH_3CN were distilled from CaH_2 and THF and diethyl ether from Na/diphenylketyl. All other solvents and reagents were of reagent grade and were used without further purification. The NMR spectra were recorded on a Bruker AC-200 or a Bruker AM-300WB FT-NMR spectrometer at room temperature (unless stated otherwise) and are reported in δ units with residual protons in the solvent as an internal standard ($CDCl_3$, δ 7.24; CD_3CN, δ 1.93; C_2D_6CO, δ 2.04). FAB mass spectra were recorded on a JEOL SX-102A spectrometer. X-ray diffraction studies and elemental analyses were carried out at the Regional Center of Analytical Instrument at National Taiwan University. Complexes $Rh(CO)(PPh_3)_2Cl$ (**2**) and $[Rh(CO)_2Cl]_2$ were prepared from $RhCl_3$ according to the method reported in the literature.[28]

Synthesis of $Rh(CO)(PPh_3)_2C{\equiv}CPh$ (3a). Carbon monoxide was slowly bubbled through a mixture of **2** (500 mg, 0.72 mmol) and HC≡CPh (**1a**, 80 mg, 0.79 mmol) in MeONa/MeOH (ca. 240 mg of MeONa). After 1.5 h bubbling was ceased and the reaction was allowed to proceed under a CO atmosphere for 18 h to yield a yellow powder, which was collected, washed with methanol, and identified as **3a** (45 mg, 82% yield). Spectroscopic data of **3a**: ^{1}H NMR (*d*-acetone): δ 7.80, 7.71−7.49, 7.44 (m, Ph). ^{31}P NMR (*d*-acetone): δ 28.77 (br). IR (C_6H_6, cm^{-1}): 1979 (s, $\nu_{C\equiv O}$), 2122 (w, $\nu_{C\equiv C}$). MS (FAB, NBA, *m/z*): 757 ($M^+ + 1$), 728 ($M^+ - CO$), 655 ($M^+ - C{\equiv}CC_6H_5$), 627 ($M^+ - CO - C{\equiv}CC_6H_5$). Anal. Calcd for $RhP_2C_{45}H_{35}O$: C, 71.43; H, 4.66. Found: C, 71.41; H, 4.77. Complex $Rh(CO)(PPh_3)_2C{\equiv}C(p\text{-}C_6H_4NO_2)$ (**3b**, 510 mg, 85% yield) was similarly prepared from **2** (520 mg, 0.75 mmol) and **1b** in 4 h under CO. Spectroscopic data of **3b**: ^{1}H NMR (C_6D_6): δ 7.90 (m, Ph), 7.62 (d, J_{H-H} = 8.68 Hz, Ph, 2H), 7.05 (m, Ph), 6.33 (d, J_{H-H} = 8.68 Hz, Ph, 2H). ^{31}P NMR (C_6D_6): δ 33.9 (d, $^1J_{Rh-P}$ = 134.9 Hz). ^{13}C NMR (C_6D_6): δ 194.2 (d, $^1J_{Rh-C}$ = 59.1 Hz, *C*O), 122.07 (d, $^2J_{Rh-C}$ = 11.2 Hz, C_β), 144.9, 135.2, 135.0, 130.8, 130.0, 123.0 (Ph). IR (CH_2Cl_2, cm^{-1}): 1982 (s, $\nu_{C\equiv O}$), 2089 (w, $\nu_{C\equiv C}$). MS (FAB^+, NBA, *m/z*): 801 (M^+), 773 ($M^+ - CO$), 655 ($M^+ - C{\equiv}CC_6H_4 - NO_2$), 627 ($M^+ - CO - C{\equiv}CC_6H_4NO_2$). Anal. Calcd for $RhP_2C_{45}H_{34}NO_3$: C, 67.42; H, 4.28; N, 1.75. Found: C, 67.40; H, 4.37; N, 1.79.

Synthesis of $[Rh(CO)(PPh_3)_2(C{\equiv}CPh)(CH_2CN)I]$ (5a). To complex **3a** (115 mg, 0.15 mmol) in CH_2Cl_2 (15 mL) was added dropwise ICH_2CN (29 mg, 0.165 mmol) at room temperature under nitrogen. After the reaction mixture was stirred for 18 h, the color changed from yellow to orange-red, and the solvent was evaporated under vacuum. Purification by recrystallization from CH_2Cl_2/hexane (1:10) gave a pale orange powder, **5a** (115 mg, 83% yield). Spectroscopic data of **5a**: ^{1}H NMR (*d*-acetone): δ 8.30, 8.11, 7.66, 7.37 (m, Ph), 1.91 (m, CH_2). ^{31}P NMR (*d*-acetone): δ 16.8 (d, J_{Rh-P} = 88.4 Hz). ^{13}C NMR ($CDCl_3$): δ 184.5 (dt, $^1J_{Rh-C}$ = 47.0 Hz, $^2J_{P-C}$ = 8.1 Hz, *C*O), 114.3 (dt, $^2J_{Rh-C}$ = 7.8 Hz, $^3J_{P-C}$ = 3.5 Hz, C_β), 95.8 (dt, $^1J_{Rh-C}$ = 35.8 Hz, $^2J_{P-C}$ = 19.8 Hz, C_α), −6.3 (dt, $^1J_{Rh-C}$ = 23.8 Hz, $^2J_{P-C}$ = 3.78 Hz, *C*H_2), 134.8 (t, J = 4.9 Hz), 128.1 (t, J = 4.9 Hz), 132.1, 131.8, 131.4, 130.6, 130.2, 126.0 (s, *C*N). IR (benzene, cm^{-1}): 2206 (w, $\nu_{C\equiv N}$), 2123 (w, $\nu_{C\equiv C}$), 2088 (s, $\nu_{C\equiv O}$). MS (FAB, NBA, *m/z*): 924 ($M^+ + 1$), 855 ($M^+ - CO - CH_2CN$), 768 ($M^+ - I - CO$), 627 ($M^+ - I - CO - CH_2CN - C{\equiv}CC_6H_5$). Anal. Calcd for $RhP_2C_{47}H_{37}NOI$: C, 61.12; H, 4.04; N, 1.52. Found: C, 61.20; H, 4.07; N, 1.59. Complex **5b** (185 mg) was similarly prepared from the reaction of **3b** (175 mg, 0.22 mmol) with ICH_2CN (42.5 mg, 0.24 mmol) in 87% yield. Spectroscopic data of **5b**: ^{1}H NMR ($CDCl_3$): δ 8.04, 7.39 (m, Ph), 7.01 (d, J_{H-H} = 8.76 Hz, Ph, 2H), 1.85 (m, CH_2, 2H). ^{31}P NMR ($CDCl_3$): δ 17.8 (d, J_{Rh-P} = 88.8 Hz). ^{13}C NMR ($CDCl_3$): δ 184.38 (dt, J_{Rh-C} = 47 Hz, J_{P-C} = 8.2 Hz, *C*O), 145.8, 134.8 (t, J = 5 Hz), 133.7 (s, *C*N), 131.7, 131.4, 131.1, 130.9, 130.6, 128.2 (t, J = 5 Hz) 123.7, 113.5 (dt, J_{Rh-C} = 8 Hz, J_{P-C} = 3.4 Hz, C_β), 108.5 (dt, J_{Rh-C} = 36.5 Hz, J_{P-C} = 19.7 Hz, Rh−C_α), −5.98 (dt, J_{Rh-C} = 23.7 Hz, J_{P-C} = 4.0 Hz *C*H_2). IR (C_6H_6, cm^{-1}): 2206 (w, ν_{CN}), 2123 (w, ν_{CC}), 2088 (s, ν_{CO}). MS (FAB, NBA, *m/z*): 969 ($M^+ + 1$), 900 ($M^+ - CO - CH_2CN$), 813 ($M^+ - I - CO$), 627 ($M^+ - I - CO - CH_2CN - C{\equiv}CC_6H_4NO_2$). Anal. Calcd for $RhP_2C_{47}H_{36}N_2O_3I$: C, 58.28; H, 3.75; N, 2.89. Found: C, 58.30; H, 3.78; N, 2.91. Single crystals of **5b** were grown by slow diffusion of hexane into a dichloromethane solution, giving yellow crystals suitable for X-ray diffraction analysis.

Rhodium-Catalyzed Coupling of MeI and Terminal Alkyne. A flask was charged with **1a** (80 mg, 0.79 mmol), **2** (28 mg, 0.04 mmol), MeI (116 mg, 0.82 mmol), and MeOH (15 mL) in the presence of the base MeONa (140 mg). The reaction mixture was stirred for 10 h, and then the solvent was evaporated under vacuum. The residue was extracted into 20 mL of CH_2Cl_2, which was filtered to remove **2**, NaCl, excess MeONa, and other insoluble solids. The solvent was dried under vacuum and the product purified by column chromatography on silica gel eluted with ether/hexane (1:9), affording organic compound **4a** (81 mg, 88%). Spectroscopic data of **4a**: ^{1}H NMR ($CDCl_3$): δ 7.10−6.81 (m, Ph), 2.03 (s, CH_3). MS (EI, *m/z*): 116.1 (M^+).

Typical Procedure for Dimerization of Arylacetylene. To a flask charged with **2** (20 mg, 0.029 mmol), K_2CO_3 (4.0 g,

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29 mmol), and MeI (208 mg, 1.49 mmol) in CH_2Cl_2 (15 mL) was added **1a** (302 mg, 2.9 mmol) by a syringe. The reaction mixture was stirred for 18 h at room temperature, and the solvent was removed under vacuum. The residue was extracted into 20 mL of CH_2Cl_2, which was filtered to remove organometallic compounds, salt, and K_2CO_3. The solution was dried under vacuum and the residue purified by column chromatography eluted by ether/hexane (1:9). The solution was dried under vacuum, and the major product was identified as **6a** (226 mg, 75% yield). Minor products **7a** and **4a** are identified by NMR and are not isolated. Spectroscopic data for **6a**: ^{1}H NMR ($CDCl_3$): δ 7.45−7.38, 7.35−7.29 (m, Ph, 10H), 7.05 (d, =CH, $^3J_{H-H}$ = 16.2 Hz), 6.39 (d, =CH, $^3J_{H-H}$ = 16.2 Hz). ^{13}C NMR ($CDCl_3$): δ 141.2 (s, *C*−Ar), 108.1 (s, −*C*=C−Ar), 91.7 (s, Ar−*C*≡C−), 88.9 (s, Ar−C≡*C*−), 136.3, 131.5, 128.7, 128.6, 128.3, 128.1, 126.3, 123.4 (all singlet, phenyl). MS (FAB, *m/z*): 204.1 (M^+).

Dimerization of 1b to 6b. A similar reaction using **2** (20 mg, 0.029 mmol), K_2CO_3 (800 mg, 5.8 mmol), THF (10 mL), HC≡C(*p*-$C_6H_4NO_2$) (**1b**, 85 mg, 0.58 mmol), and MeI (246 mg, 1.74 mmol) gave a mixture of **6b**, **7b**, and **4b** in a 60:15:25 ratio. Compound **6b** (44.2 mg) was obtained in 52% isolated yield. Spectroscopic data for **6b**: ^{1}H NMR ($CDCl_3$): δ 8.23 (d, $^3J_{H-H}$ = 8.7 Hz), 8.22 (d, $^3J_{H-H}$ = 8.7 Hz), 7.62 (d, $^3J_{H-H}$ = 8.7 Hz), 7.58 (d, $^3J_{H-H}$ = 8.7 Hz), 7.17 (d, =CH, $^3J_{H-H}$ = 16.2 Hz), 6.56 (d, =CH, $^3J_{H-H}$ = 16.2 Hz). ^{13}C NMR ($CDCl_3$): δ 142.5 (s, −C=*C*−Ar), 112.5 (s, −*C*=C−Ar), 93.5 (s, Ar−*C*≡C−), 92.7 (s, Ar−C≡*C*−), 148.4, 147.8 141.1, 132.9, 130.2, 127.6, 124.8, 124.3 (all singlet, phenyl). MS (FAB, *m/z*): 294.0 (M^+).

A similar reaction using **2** (10 mg, 0.0145 mmol), K_2CO_3 (2.0 g, 14.5 mmol), CH_2Cl_2 (5 mL), **1e** (184 mg, 1.45 mmol), and MeI (20 mg, 0.145 mmol) gave **6e** (99 mg) in 54% yield. Spectroscopic data for **6e**: ^{1}H NMR ($CDCl_3$): δ 7.63 (d, $^3J_{H-H}$ = 6.2 Hz), 7.62 (d, $^3J_{H-H}$ = 6.2 Hz), 7.54 (d, $^3J_{H-H}$ = 8.5 Hz), 7.51 (d, $^3J_{H-H}$ = 8.5 Hz), 7.08 (d, =CH, $^3J_{H-H}$ = 16.2 Hz), 6.50 (d, =CH, $^3J_{H-H}$ = 16.2 Hz). ^{13}C NMR ($CDCl_3$): δ 140.7 (s, −C=*C*−Ar), 111.1 (s, −*C*=C−Ar), 92.2 (s, Ar−*C*≡C−), 92.0 (s, Ar−C≡*C*−), 118.5 (CN), 118.3 (CN), 140.1, 133.0, 132.6, 132.2, 132.1, 132.0, 127.2, 126.8, 112.1, 111.8 (all singlet, phenyl). MS (FAB, *m/z*): 255.2 (M^+ + 1).

Compound **6d** (63 mg) was obtained from **2** (20 mg, 0.029 mmol), MeONa (156 mg, 2.9 mmol), THF (10 mL), MeI (250 mg, 1.74 mmol), and **1d** (70 mg, 0.58 mmol) in 90% yield. Spectroscopic data for **6d**: ^{1}H NMR ($CDCl_3$): δ 7.36 (d, $^3J_{H-H}$ = 8.0 Hz), 7.32 (d, $^3J_{H-H}$ = 8.0 Hz), 7.15 (d, $^3J_{H-H}$ = 7.75 Hz), 7.13 (d, $^3J_{H-H}$ = 7.75 Hz), 7.00 (d, =CH, $^3J_{H-H}$ = 16.2 Hz), 6.33 (d, =CH, $^3J_{H-H}$ = 16.2 Hz), 2.34 (s, CH_3, 6H). ^{13}C NMR ($CDCl_3$): δ 140.9 (s, −C=*C*−Ar), 107.2 (s, −*C*=C−Ar), 91.6 (s, Ar−*C*≡C−), 88.4 (s, Ar−C≡*C*−), 21.5 (s, CH_3), 21.3 (s, CH_3), 138.6, 138.2, 133.7, 131.6, 129.4, 129.1, 126.2, 120.4, 119.4 (all singlet, phenyl). MS (FAB, *m/z*): 232.1 (M^+).

Compound **6f** (172 mg) was obtained from **2** (10 mg, 0.0145 mmol), MeONa (391 mg, 7.25 mmol), CH_2Cl_2 (5 mL), **1f** (210 mg, 1.45 mmol), and MeI (20 mg, 0.145 mmol) in 82% yield. Spectroscopic data for **6f**: ^{1}H NMR ($CDCl_3$): δ 7.33 (d, $^3J_{H-H}$ = 9.2 Hz), 7.30 (d, $^3J_{H-H}$ = 9.2 Hz), 6.67 (d, $^3J_{H-H}$ = 9.1 Hz), 6.64 (d, $^3J_{H-H}$ = 9.1 Hz), 6.90 (d, $^3J_{H-H}$ = 16.2 Hz), 6.18 (d, $^3J_{H-H}$ = 16.2 Hz). ^{13}C NMR ($CDCl_3$): δ 139.8 (s, −C=*C*−Ar), 103.8 (s, −*C*=C−Ar), 91.5 (s, Ar−*C*≡C−), 87.8 (s, Ar−C≡*C*−), 40.3 (NMe_2), 40.2 (NMe_2), 150.4, 149.8, 139.8, 132.4, 127.3, 112.2, 111.9, 110.8 (all singlet, phenyl). MS (FAB, *m/z*): 290.1 (M^+).

Compound **6g** (182.7 mg) was prepared from **2** (40 mg, 0.058 mmol), K_2CO_3 (1.6 g, 11.6 mmol), THF (10 mL), MeI (492 mg, 3.48 mmol), and **1g** (203 mg, 1.16 mmol) in 90% yield. Spectroscopic data for **6g**: ^{1}H NMR ($CDCl_3$): δ 7.68−7.46 (m, phenyl, 8H), 7.11 (d, $^3J_{H-H}$ = 16.2 Hz), 6.47 (d, $^3J_{H-H}$ = 16.2 Hz). ^{13}C NMR ($CDCl_3$): δ 140.1 (s, −C=*C*−Ar), 110.2 (s, −*C*=C−Ar), 91.5 (s, Ar−*C*≡C−), 90.5 (s, Ar−C≡*C*−), 139.4, 137.0, 134.2, 132.0, 131.8, 130.8, 130.3, 129.9, 129.7, 128.4, 127.1, 126.8, 125.8 (q, J_{FC} = 3.7 Hz), 125.4 (q, J_{FC} = 3.7 Hz). MS (FAB, *m/z*): 340.0 (M^+).

Compound **6h** (55 mg) was synthesized from **2** (40 mg, 0.058 mmol), K_2CO_3 (1.6 g, 11.6 mmol), CH_2Cl_2 (5 mL), MeI (492 mg, 3.48 mmol), and **1h** (142 mg, 1.16 mmol) in 39% yield. Spectroscopic data for **6h**: ^{1}H NMR ($CDCl_3$): δ 7.44−7.34 (m, Ph, 4H), 7.04∼6.94 (m, Ph, 4H), 7.00 (d, =CH, $^3J_{H-H}$ = 16.2 Hz), 6.28 (d, =CH, $^3J_{H-H}$ = 16.2 Hz). ^{13}C NMR ($CDCl_3$): δ 140.0 (s, −C=*C*−Ar), 107.7 (s, −*C*=C−Ar), 90.1 (s, Ar−*C*≡C−), 88.3 (s, Ar−C≡*C*−), 164.6 (d, $^1J_{F-C}$ = 36.6 Hz), 161.3 (d, $^1J_{F-C}$ = 37.6 Hz), 133.4 (d, $^3J_{F-C}$ = 8.3 Hz), 132.5 (d, J_{F-C} = 3.3 Hz), 128.0 (d, $^3J_{F-C}$ = 8.2 Hz), 119.5 (d, J_{F-C} = 3.5 Hz), 115.9 (d, $^2J_{F-C}$ = 21.8 Hz), 115.8 (d, $^2J_{F-C}$ = 22.0 Hz). MS (FAB, *m/z*): 240.0 (M^+).

Compound **6i** (369.2 mg) was prepared from **2** (20 mg, 0.029 mmol), K_2CO_3 (3.2 g, 23.2 mmol), CH_2Cl_2 (10 mL), **1i** (420 mg, 2.32 mmol), and MeI (83 mg, 0.58 mmol) in 88% yield. Spectroscopic data for **6i**: ^{1}H NMR ($CDCl_3$): δ 7.47 (d, $^3J_{H-H}$ = 8.5 Hz), 7.46 (d, $^3J_{H-H}$ = 8.5 Hz), 7.32 (d, $^3J_{H-H}$ = 8.0 Hz), 7.28 (d, $^3J_{H-H}$ = 8.0 Hz), 6.99 (d, =CH, $^3J_{H-H}$ = 16.2 Hz), 6.36 (d, =CH, $^3J_{H-H}$ = 16.2 Hz). ^{13}C NMR ($CDCl_3$): δ 140.3 (s, −C=*C*−Ar), 108.6 (s, −*C*=C−Ar), 91.2 (s, Ar−*C*≡C−), 89.7 (s, Ar−C≡*C*−), 135.1, 132.9, 131.9, 131.6, 127.7, 122.7, 122.6, 122.2 (all singlet, phenyl). MS (FAB, *m/z*): 362.9 (M^+ + 1).

Compound **6j** (254 mg) was prepared from **2** (10 mg, 0.0145 mmol), K_2CO_3 (2 g, 14.5 mmol), CH_2Cl_2 (5 mL), HC≡C(*p*-C_6H_4I) **1j** (330 mg, 1.45 mmol), and MeI (20 mg, 0.145 mmol) in 77% yield. Spectroscopic data for **6j**: ^{1}H NMR ($CDCl_3$): δ 7.67 (d, $^3J_{H-H}$ = 8.4 Hz), 7.66 (d, $^3J_{H-H}$ = 8.4 Hz), 7.17 (d, $^3J_{H-H}$ = 8.4 Hz), 7.14 (d, $^3J_{H-H}$ = 8.4 Hz), 6.96 (d, =CH, $^3J_{H-H}$ = 16.2 Hz), 6.36 (d, =CH, $^3J_{H-H}$ = 16.2 Hz). ^{13}C NMR ($CDCl_3$): δ 140.5 (s, −C=*C*−Ar), 108.7 (s, −*C*=C−Ar), 91.5 (s, Ar−*C*≡C−), 90.0 (s, Ar−C≡*C*−), 137.9, 137.6, 135.6, 132.9, 127.9, 122.7, 94.3, 94.2 (all singlet, phenyl). MS (FAB, *m/z*): 455.8 (M^+).

Compound **6c** (44 mg) was prepared from **2a** (20 mg, 0.029 mmol), K_2CO_3 (800 mg, 5.8 mmol), THF (10 mL), **1c** (74 mg, 0.585 mmol), and MeI (166 mg, 1.16 mmol) in 60% yield. Spectroscopic data for **6c**: ^{1}H NMR ($CDCl_3$): δ 10.0 (s, COH, 1H), 9.99 (s, COH, 1 H), 7.87 (d, $^3J_{H-H}$ = 8.1 Hz), 7.86 (d, $^3J_{H-H}$ = 8.1 Hz), 7.62 (d, $^3J_{H-H}$ = 8.4 Hz), 7.58 (d, $^3J_{H-H}$ = 8.4 Hz), 7.14 (d, =CH, $^3J_{H-H}$ = 16.2 Hz), 6.56 (d, =CH, $^3J_{H-H}$ = 16.2 Hz). ^{13}C NMR ($CDCl_3$): δ 141.7 (s, −C=*C*−Ar), 111.3 (s, -*C*=C−Ar), 92.7 (s, Ar−*C*≡C),92.3 (s, Ar−C≡*C*−), 191.4 (s, COH), 191.3 (s, COH), 141.1, 136.3, 135.6, 132.1, 130.2, 129.8, 129.6, 126.9 (all singlet, phenyl). MS (FAB, *m/z*): 261.1 (M^+ + 1).

Compound **7k** (176 mg) was prepared in 72% yield from **2** (20 mg, 0.029 mmol), K_2CO_3 (1.6 g, 11.6 mmol), CH_2Cl_2 (5 mL), **1k** (245 mg, 2.9 mmol), and MeI (1.23 g, 8.7 mmol). Spectroscopic data for **7k**: ^{1}H NMR ($CDCl_3$): δ 5.18 (d, $^2J_{H-H}$ = 2.06 Hz), 5.01 (d, $^2J_{H-H}$ = 2.06 Hz), 2.28 (d, $^3J_{H-H}$ = 6.72 Hz, 2H), 2.09 (d, $^3J_{H-H}$ = 7.44 Hz, 2H), 1.50−1.27 (m, 8H), 0.93−0.84 (m, 6H). MS (FAB, *m/z*): 164.0 (M^+).

Preparation of 8a. A flask was charged with **2** (20 mg, 0.029 mmol), K_2CO_3 (4.0 g, 29 mmol), and MeOH (10 mL), and then MeI (40 mg, 0.29 mmol) and **1a** (302 mg, 2.9 mmol) were added by a syringe. The reaction mixture was stirred at room temperature, and the solvent was removed under vacuum. The residue was extracted into 20 mL of CH_2Cl_2, which was filtered to remove organometallic compounds, salt, and K_2CO_3. The solution was dried under vacuum and the residue purified by column chromatography eluted by ether/hexane (1:9). The solution was dried under vacuum, and the major product was identified as **8a** (190 mg) in 63% yield. Spectroscopic data for **8a**: ^{1}H NMR ($CDCl_3$): δ 7.93 (d, $^3J_{H-H}$ = 8.7 Hz, 2 H), 7.48 (m, Ph, 2 H), 7.46−7.00 (m, Ph, 5 H), 6.71 (d, $^3J_{H-H}$ = 12.0 Hz, =CH), 5.93 (d, $^3J_{H-H}$ = 12.0 Hz, =CH). ^{13}C NMR ($CDCl_3$): δ 141.8 (s, C=*C*Ar), 108.0 (s, *C*=CAr), 96.4 (s, Ar*C*≡C), 88.8 (s, ArC≡*C*), 139.3, 137.1, 132.0, 129.4, 129.0, 129.0, 128.9, 128.8 (all singlet, phenyl). MS (FAB, *m/z*): 204.0 (M^+).

Using the same procedure compound **8e** (151 mg) was obtained in 82% yield from **1e** (184 mg, 1.45 mmol). Spectro-

scopic data for **8e**: ^{1}H NMR ($CDCl_3$): δ 7.94 (d, $^3J_{H-H}$ = 8.46 Hz), 7.67 (d, $^3J_{H-H}$ = 8.06 Hz), 7.65 (d, $^3J_{H-H}$ = 8.06 Hz), 7.53 (d, $^3J_{H-H}$ = 8.46 Hz), 6.80 (d, =CH, $^3J_{H-H}$ = 12.0 Hz), 6.10 (d, =CH, $^3J_{H-H}$ = 12.0 Hz). ^{13}C NMR ($CDCl_3$): δ 140.3 (s, C=*C*Ar), 112.0 (s, *C*=CAr), 95.5 (s, Ar*C*≡C), 91.2 (s, ArC≡*C*), 118.6 (CN), 118.2 (CN), 138.2, 132.2, 132.1, 132.0, 129.1, 127.5, 112.2, 111.9, 110.3 (all singlet, Ph). MS (FAB, *m/z*): 254.0 (M^+). Compound **8g** (224 mg) was similarly obtained in 91% yield from **1g** (246.7 mg, 1.45 mmol). Spectroscopic data for **8g**: ^{1}H NMR ($CDCl_3$): δ 7.99 (d, $^3J_{H-H}$ = 8.2 Hz), 7.65−7.54 (m, Ph, 6H), 6.80 (d, =CH, $^3J_{H-H}$ = 11.9 Hz), 6.06 (d, =CH, $^3J_{H-H}$ = 11.9 Hz). ^{13}C NMR ($CDCl_3$): δ 139.5 (s, −C=*C*−Ar), 109.4 (s, −*C*=C−Ar), 95.2 (s, Ar−*C*≡C−), 89.6 (s, Ar−C≡*C*−), 138.1, 131.7, 130.6 (d, J_{F-C} = 6.18 Hz), 130.1 (d, J_{F-C} = 6.18 Hz), 128.8, 127.7, 125.6 (m), 125.3, 122.2 (d, J_{F-C} = 12.7 Hz). MS (FAB, *m/z*): 340.0 (M^+). Compound **8h** (44.3 mg) was similarly obtained in 25% yield from **1h** (177.5 mg, 1.45 mmol). Spectroscopic data for **8h**: ^{1}H NMR ($CDCl_3$): δ 7.89 (m, phenyl, 2H), 7.41 (m, Ph, 2H), 7.05 (m, Ph, 4H), 6.66 (d, =CH, $^3J_{H-H}$ = 11.9 Hz), 5.87 (d, =CH, $^3J_{H-H}$ = 11.9 Hz). MS (FAB, *m/z*): 240.0 (M^+). Compound **8i** (235.8 mg) was similarly obtained in 90% yield from **1i** (262 mg, 1.45 mmol). Spectroscopic data for **8i**: ^{1}H NMR ($CDCl_3$): δ 7.76 (d, $^3J_{H-H}$ = 8.5 Hz), 7.51 (d, $^3J_{H-H}$ = 8.6 Hz), 7.49 (d, $^3J_{H-H}$ = 8.6 Hz), 7.32 (d, $^3J_{H-H}$ = 8.5 Hz), 6.67 (d, =CH, $^3J_{H-H}$ = 11.9 Hz), 5.93 (d, =CH, $^3J_{H-H}$ = 11.9 Hz). ^{13}C NMR ($CDCl_3$): δ 137.7 (s, −C=*C*−Ar), 107.9 (s, −*C*=C−Ar), 95.3 (s, Ar−*C*≡C−), 88.9 (s, Ar−C≡*C*−), 135.3, 132.8, 131.7, 131.5, 130.2, 122.8, 122.5, 122.1 (all singlet, phenyl). MS (FAB, *m/z*): 361.8 (M^+). Compound **8j** (115 mg) was similarly obtained in 35% yield from **1j** (330 mg, 1.45 mmol). Spectroscopic data for **8j**: ^{1}H NMR ($CDCl_3$): δ 7.71 (d, $^3J_{H-H}$ = 8.14 Hz), 7.69 (d, $^3J_{H-H}$ = 8.35 Hz), 7.61 (d, $^3J_{H-H}$ = 8.35 Hz), 7.17 (d, $^3J_{H-H}$ = 8.14 Hz), 6.63 (d, $^3J_{H-H}$ = 11.9 Hz), 5.91 (d, $^3J_{H-H}$ = 11.9 Hz). ^{13}C NMR ($CDCl_3$): δ 137.8 (s, −C=*C*−Ar), 108.1 (s, −*C*=C−Ar), 95.7 (s, Ar−*C*≡C−), 89.3 (s, Ar−C≡*C*−), 137.6, 137.4, 135.8, 132.8, 130.3, 122.6, 94.6, 94.3 (all singlet, phenyl). MS (FAB, *m/z*): 455.8 (M^+).

X-ray Analysis of 5b. Single crystals of **5b** suitable for an X-ray diffraction study were grown by the methods described in the previous section. The diffraction data were collected on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo Kα (λ = 0.71037 Å) radiation. Crystallographic computations were carried out using the NRCC-SDP-VAX structure determination package.[29] A suitable single crystal of **5b** was mounted on the top of a glass fiber with glue. Initial lattice parameters were determined from 25 accurately centered reflections in the range from 15.70° to 23.74°. Cell constants and other pertinent data are collected in Table 5. Data were collected using the $\theta-2\theta$ scan method. The final scan speed for each reflection was determined from the net intensity gathered during an initial prescan and ranged from 2 to 8 deg min^{-1}. Merging equivalent and duplicate reflections gave a total of 8309 unique measured data in which 5787 were considered observed, $I > 2\sigma(I)$. The structure was first solved by using the heavy atom method (Patterson synthesis), which revealed the positions of metal atoms. The remaining atoms were found in a series of alternating difference Fourier maps and least-squares refinements. The quantity minimized by the least-squares program was $w(|F_o| - |F_c|)^2$, where w is the weight of a given operation. The analytical forms of the scattering factor tables for the neutral atoms were used. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculations in their expected positions on the basis of idealized bonding geometry but were not refined in least squares.

Table 5. Crystal Data and Structure Refinement for 5b

empirical formula	$C_{49}H_{40}Cl_4IN_2O_3P_2Rh$	
fw	1138.38	
temperature	295(2) K	
wavelength	0.71073 Å	
cryst syst	triclinic	
space group	$P\bar{1}$	
unit cell dimens	a = 12.915(2) Å	α = 77.06(2)°
	b = 13.210(3) Å	β = 71.678(13)°
	c = 15.975(3) Å	γ = 66.88(2)°
volume, Z	2363.9(7) Å^3, 2	
density (calcd)	1.599 Mg/m^3	
absorp coeff	1.352 mm^{-1}	
F(000)	1136	
cryst size	0.35 × 0.30 × 0.20 mm	
θ range for data collection	1.69 to 24.97°	
limiting indices	$-13 < h < 15$, $0 < k < 15$, $-18 < l < 18$	
no. of independent reflns	8309 [$I > 2\sigma(I)$: 5787]	
max. and min. transmn	0.7785 and 0.6829	
refinement method	full-matrix least-squares on F^2	
no. of data/restraints/params	8309/0/522	
goodness-of-fit on F^2	0.943	
final R indices [$I > 2\sigma(I)$]	R1 = 0.0454, wR2 = 0.1301	
R indices (all data)	R1 = 0.0738, wR2 = 0.1475	
largest diff peak and hole	1.065 and −0.809 e/Å^3	

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Supporting Information Available: Tables of crystal data collection, refinement parameters, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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