Rhodium-Catalyzed Reaction of Aroyl Chlorides with Alkynes

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Aroyl chlorides react with terminal alkynes accompanied by decarbonylation in the presence of a catalytic amount of $[RhCl(cod)]_2$ and PPh_3 to give the corresponding vinyl chloride derivatives regio- and stereoselectively in good yields. The catalyst efficiency is a marked function of the ratio of PPh_3 to the rhodium species; satisfactory results are obtained by employing a PPh_3/Rh ratio of 1.0. The reaction may involve chlororhodation to the alkynes by the intermediary arylchlororhodium(III) species generated *in situ* followed by reductive elimination of the products, which are suggested by the results of some control experiments. In contrast to the reaction with terminal alkynes, that with some internal ones proceeds without decarbonylation to produce 2,3-disubstituted-1-indenones as the predominant products. The product structures suggest that, while the arylchlororhodium intermediate is also involved, arylrhodation to the alkynes, reinsertion of CO (coordinated to the metal), and intramolecular cyclization sequentially take place to give the indenones.

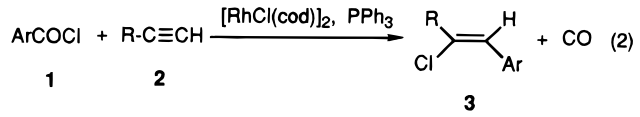
Introduction

Aroyl chlorides are known to smoothly react with low-valent transition-metal species, including rhodium and palladium complexes, to produce the corresponding aroylchlorometal complexes which may be further transformed into arylchlorometal complexes by decarbonylation at somewhat elevated temperatures.[1] The aroyl− and aryl−metal species may be expected to be synthetically versatile, and indeed, catalytic aroylation of alkenes[2] and alkynes[3] and arylation of alkenes[4] and dienes[5] with aroyl chlorides using palladium complexes have been successfully developed. While such catalytic reactions could also be realized by using rhodium species, they have been so far unexplored.

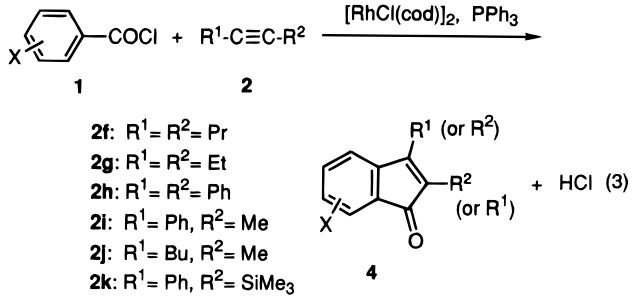
On the other hand, we have recently reported that benzoic anhydride smoothly reacts with styrene under a normal pressure of hydrogen in the presence of a tertiary amine and catalytic amounts of $[RhCl(cod)]_2$ and a phosphorus ligand to give 1,2-diphenyl-1-propanone together with its 1,3-diphenyl isomer (eq 1);[6] however, benzoyl chloride is ineffective for this reaction.

$$(ArCO)_2O + R\text{-}CH{=}CH_2 \xrightarrow[H_2,\ base]{[RhCl(cod)]_2,\ P(OPh)_3} Ar\text{-}C(=O)\text{-}CH(CH_3)\text{-}R + Ar\text{-}C(=O)\text{-}CH_2CH_2\text{-}R \quad (1)$$

In the context of our study of arylation and aroylation of unsaturated compounds by means of homogeneous catalysis,[7] we observed that aroyl chlorides can effectively react with terminal alkynes accompanied by decarbonylation in the presence of $[RhCl(cod)]_2$ and PPh_3 to give the corresponding vinyl chloride derivatives regio- and stereoselectively with good product yields (eq 2). Moreover, the reaction of aroyl chlorides with some internal alkynes in place of terminal ones has been found to proceed without decarbonylation to produce 2,3-disubstituted-1-indenones (eq 3).[8]



1a: Ar= Ph **2a**: R= Ph
1b: Ar= 4-ClC_6H_4 **2b**: R= $CH_3(CH_2)_5$
1c: Ar= 4-MeC_6H_4 **2c**: R= 1-cyclohexenyl
1d: Ar= PhCH=CH **2d**: R= $BuOCH_2$
1e: Ar= MeCH=CH **2e**: R= 5-hexynyl



Consequently, a detailed investigation has been carried

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(3) Tohda, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1977**, 777.

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(8) The relevant transition metal-mediated synthesis of indenones using aryl halides and alkynes: (a) Liebeskind, L. S.; South, M. S. *J. Org. Chem.*, **1980**, *45*, 5426. (b) Larock, R. C.; Doty, M. J.; Cacchi, S. *J. Org. Chem.*, **1993**, *58*, 4579 and references therein.

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Table 1. Effect of Ligands on the Reaction of Benzoyl Chloride (1a) with Phenylacetylene (2a)[a]

entry	ligand (equiv)[b]	% yield[c]
1	PPh_3 (1)	71
2[d]	PPh_3 (1)	92
3	PPh_3 (0)	2
4	PPh_3 (2)	7
5	PPh_3 (6)	1
6	PBu3 (1)	17
7	$P(OPh)_3$ (1)	21
8	dppb (1)	5
9	dppb (0.5)	10
10	dppp (0.5)	23
11[e]	PPh_3 (1)	23
12[f]	PPh_3 (1)	57
13[g]	PPh_3 (1)	68
14[h]	PPh_3 (1)	47
15[i]	PPh_3 (1)	33

[a] The reaction was carried out in octane at 140 °C for 20 h under N_2. [[RhCl(cod)]$_2$]:[ligand]:[**1a**]:[**2a**] = 0.01:0.02:2:2 (in mmol). [b] Relative to Rh metal. [c] GC yield based on **1a** used. [d] [**2a**] = 3 mmol. [e] Reaction at 100 °C. [f] Reaction at 120 °C. [g] Reaction in *o*-xylene. [h] Reaction in 2-methoxyethyl ether. [i] [[RhCl(cod)]$_2$] = 0.001 mmol, [**2a**] = 3 mmol.

out to elucidate the factors affecting these reactions. The results are described herein.

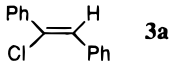
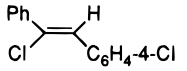
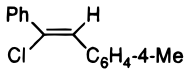
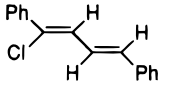
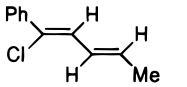
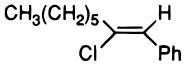
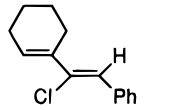
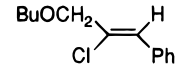
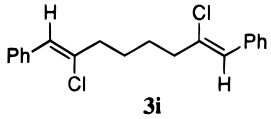
Results and Discussion

Reaction of Benzoyl Chloride (1a) with Phenylacetylene (2a). When the reaction of **1a** (2 mmol) with **2a** (2 mmol) in the presence of [RhCl(cod)]$_2$ (0.01 mmol, 1 mol %) and PPh_3 (0.02 mmol; P/Rh = 1.0) was carried out in octane at 140 °C (bath temperature) for 20 h under nitrogen, (*Z*)-1-chloro-1,2-diphenylethene (**3a**) was obtained in a yield of 71% (Table 1 and eq 1; Ar = R = Ph). The product yield was increased up to 92% (based on amount of **1a** used) by using 3 mmol of **2a**. Analysis of the reaction mixture by ^{1}H NMR and GC-MS confirmed that no (*E*)-1-chloro-1,2-diphenylethene was formed. The reaction was found to be very sensitive to the amount of the ligand added; the product yield was very low, when the PPh_3/Rh ratio was ≥2 or 0. Other phosphorus compounds, PBu_3, $P(OPh)_3$, dppb ($Ph_2P(CH_2)_4PPh_2$), and dppp ($Ph_2P(CH_2)_3PPh_2$) were examined as ligands; however, none of them was superior to PPh_3. At a lower reaction temperature of 100 or 120 °C, the product yield was considerably decreased. While *o*-xylene could be used as well as octane as solvent, $(CHCl_2)_2$, 2-methoxyethyl ether, and PhCN were less effective.

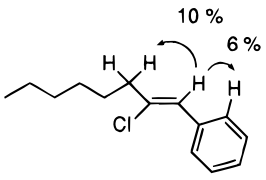
Reaction of Various Acid Chlorides with Terminal Alkynes. The reactions of 4-chloro- and 4-methylbenzoyl chlorides (**1b** and **1c**) with **2a** gave the corresponding vinyl chloride derivatives **3b** and **3c** in good yields, as did that of **1a** (Table 2). Cinnamoyl chloride (**1d**) and crotonoyl chloride (**1e**) also reacted with **2a** smoothly to afford chlorodienes **3d** and **3e**. 1-Octyne (**2b**), 1-ethynylcyclohexene (**2c**), and butyl propargyl ether (**2d**) could be used in place of **2a**, giving compounds **3f**−**h**. Reaction of **1a** (6 mmol) with 1,7-octadiyne (**2e**; 2 mmol) gave compound **3i**.

The configuration of each product was determined by ^{1}H NMR with the aid of NOE experiments. For example, NOE peak enhancements observed for products **3f** and **3g** were as follows. It should be noted that each product, with the exception of **3h** and **3i**, did not accompany other regio- and stereoisomers, which was confirmed by ^{1}H NMR and GC-MS. In the case of **3h** and **3i**, small amounts (≤5%) of the corresponding (*E*) and (*Z*,*E*) isomers, respectively, were contaminated. Reaction of benzoyl bromide (**1g**) with **2a** gave (*Z*)-1-bromo-1,2-diphenylethene (**3j**) (73%) along with its (*E*)-isomer **3j′** (3%) (Table 3).

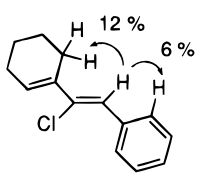
Table 2. Reaction of Various Acid Chlorides 1 with Terminal Alkynes 2[a]

substrates 1	substrates 2	product 3, % yield[b]		
1a	**2a**		**3a**	91
1b	**2a**		**3b**	94
1c	**2a**		**3c**	76
1d	**2a**		**3d**	91
1e	**2a**		**3e**	84
1a	**2b**		**3f**	74
1a	**2c**		**3g**	81
1a	**2d**		**3h**	(27)[c, d]
1a	**2e**		**3i**	(60)[d, e]

[a] The reaction was carried out in octane at 140 °C for 20 h under N_2.[[RhCl(cod)]$_2$]:[PPh_3]:[**1**]:[**2**]=0.01:0.02: 2 : 3 (in mmol). [b] Isolated yield based on **1** used. Value in parentheses was determined by GC. [c] [[RhCl(cod)]$_2$]:[PPh_3]=0.02:0.04. [d] The corresponding stereoisomer (≤5 %) was contaminated. [e] [**1**]:[**2**]=6:2.



3f

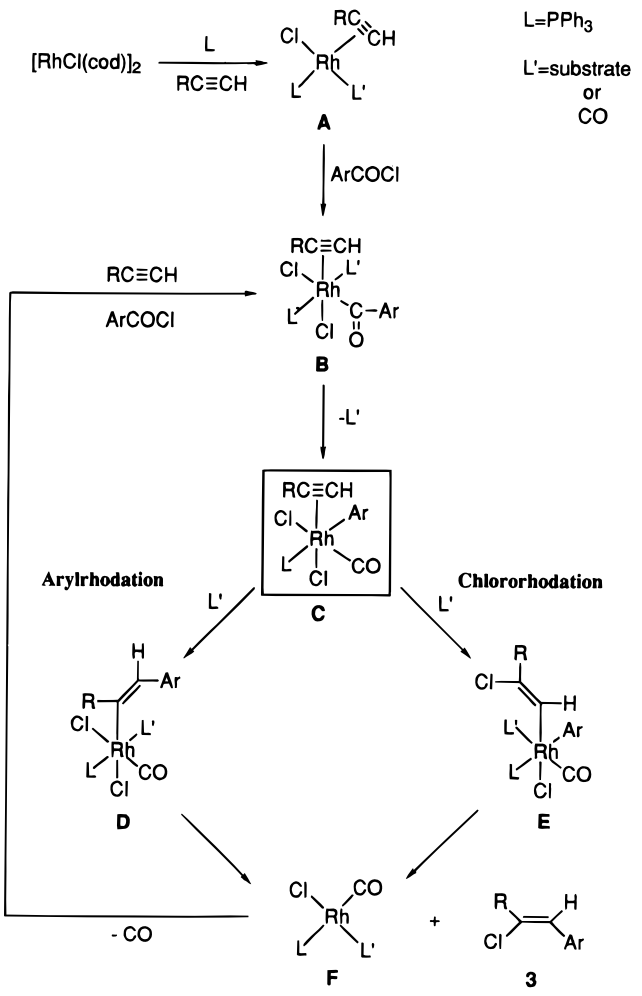


3g

Reaction Scheme for the Formation of 3. A plausible reaction mechanism, which may rationalize the regio- and stereoselective formation of **3** from **1** and **2**, is illustrated in Scheme 1.

The reaction may be considered to involve initial oxidative addition of aroyl chloride to a catalytically active rhodium(I) species **A** generated from [RhCl(cod)]$_2$ in the presence of PPh_3 and a terminal alkyne to form

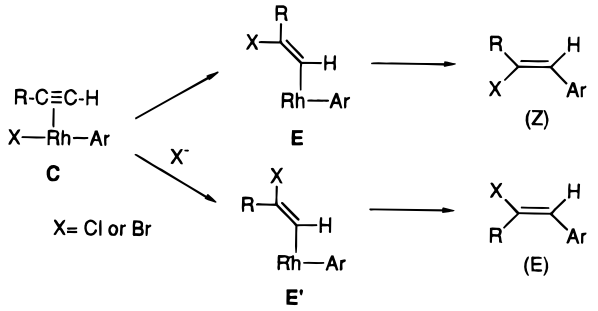
Scheme 1



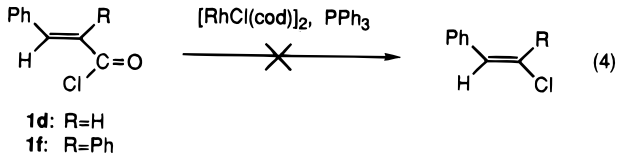
an aroylrhodium complex **B**. The subsequent decarbonylation gives intermediate **C**. Then, there may exist two possible pathways; the one is arylrhodation where the aryl moiety migrates to the coordinated alkyne in **C** to give complex **D**, and the other is chlororhodation where the chlorine migrates to the alkyne to give complex **E**. Whichever arylrhodation or chlororhodation, reductive elimination affords product **3** along with carbonylrhodium(I) species **F**. While the catalytic cycle proceeds, ligand L′ is possibly CO, since it is known that complete removal of CO from rhodium(I) species is rather difficult.[1,9] However, the second CO seems to be capable of being replaced by alkyne **2**. It should be noted that carbon monoxide exchange reaction in benzoyl chloride with ^{13}CO has been reported to occur in the presence of $RhCl(CO)(PPh_3)_2$ even at 90 °C.[10]

If the reaction proceeds *via* arylrhodation, it has to involve reductive elimination of the vinyl moiety with chlorine from **D**. Generally, reductive elimination of organic halides from haloorganometals usually requires high temperatures over 200 °C.[1,9,11] It is noted that decarbonylation of α,β-unsaturated acyl chlorides with a stoichiometric amount of $RhCl(PPh_3)_3$ has been reported to produce vinyl triphenylphosphonium salts, giving no vinyl chlorides.[12] It was also confirmed that

Scheme 2



treatment of cinnamoyl chloride (**1d**) and its α-phenyl derivative **1f** under the present catalytic conditions gave no trace of β-chlorostyrenes (eq 4). In the light of these results, the reaction sequence **C** → **D** → **F** seems to be unlikely involved.



While chlororhodation to alkynes is less common, a number of reactions, which involve chloropalladation to them, are known.[13,14] It has been recently reported that stereochemistry of alkyne chloropalladation is dependent on chloride ion concentration; at a low chloride concentration, *cis*-chloropalladation predominates, whereas at a high chloride concentration, *trans*-chloropalladation becomes to be favorable.[14] Consequently, we examined effect of addition of a quaternary ammonium chloride or bromide on the present reaction. When $PhCH_2NEt_3Cl$ (2 mmol) was added to the reaction of **1a** (2 mmol) with **2a** (3 mmol), a mixture of **3a** and its (*E*)-isomer **3a′** in a ratio of 19:13 was formed (eq 5 and Table 3). This is in marked contrast to the fact that without the chloride, the (*Z*)-isomer **3a** is exclusively produced. Addition of Bu_3NMeBr to the reaction of **1g** with **2a** also increased the product (*E*)/(*Z*) ratio. These results led us to deduce that the present haloarylation of terminal alkynes predominantly involves halorhodation reaction. The formation of the (*E*)-isomers **3a′** and **3f′** is attributable to the *anti*-addition of chloride and bromide added in intermediate **C** as shown in Scheme 2.

Reaction of Aroyl Chlorides with Internal Alkynes. In order to examine applicability of internal alkynes to the present reaction, reaction of **1a** with 4-octyne (**2f**) was first carried out as the representative in *o*-xylene under the same conditions with those employed for the reactions with terminal alkynes. It was somewhat surprising that 2,3-dipropyl-1-indenone (**4a**)

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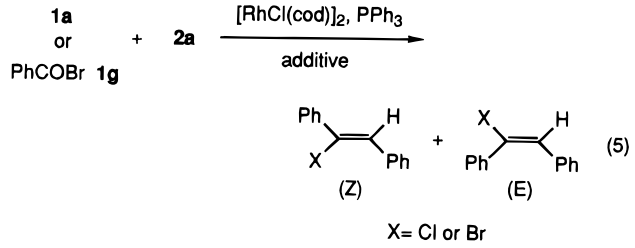
(14) Bäckvall, J.-E.; Nilsson, Y. I. M.; Gatti, R. G. P. *Organometallics* **1995**, *14*, 4242.

Table 3. Effect of Addition of Ammonium Halide on the Reaction of 1a or 1g with 2a[a]

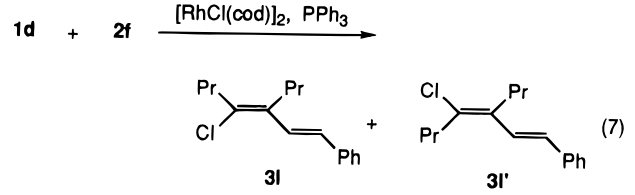
		3, % yield	
1	additive	(*Z*)	(*E*)
1a	none	92	0
1a	$PhCH_2NEt_3Cl$	19	13
1g	none	73	3
1g	Bu_3NMeBr	41	12

[a] Reaction was carried out in octane at 140 °C for 20 h under N_2. [[RhCl(cod)]$_2$]:[ligand]:[**1**]:[**2a**]:[additive] = 0.01:0.02:2:3:2 (in mmol).



was produced in 34% yield (14% in octane) as the single major product, no vinyl chloride derivative being detected (eq 3; X = H, R = Pr). By adding Na_2CO_3 as base to trap hydrogen chloride evolved and some modifications of the reaction conditions using 2 mol % of [RhCl(cod)]$_2$, the yield of **4a** was increased up to 76% based on amount of **2f** used (Table 4). The reactions of 4-substituted benzoyl chlorides **1b**, **1c**, and 3-methylbenzoyl chloride (**1h**) with **2f** also gave indenones **4b**−**d**. It was of quite interest that the carbonyl moiety in these products was found to be shifted to the neighboring position in the starting aroyl chlorides. The reaction of 2-naphthoyl chloride (**1i**) with **2f** predominantly gave 2,3-fused compound **4e** along with its 1,2-fused isomer **4e′**. Alkynes **2g**−**k** could react with **1a** to give the corresponding indenones, while the product yields were moderate to low. In the reactions using the unsymmetrical alkynes **2i**−**k**, two possible regioisomers were formed in each case. In contrast to the reactions with **2i**−**k**, treatment of **1a** with ethyl 2-heptynoate (**2l**) gave ethyl (*E*)-3-chloro-2-phenylheptenoate (**3k**) in a yield of 41% (eq 6), no indenone product being detected. Reaction of cinnamoyl chloride (**1d**) with **2f** afforded a

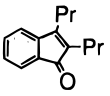
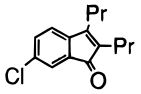
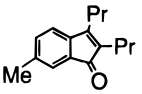
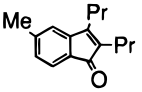
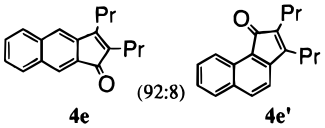
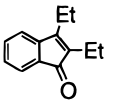
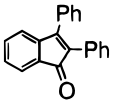
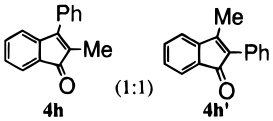
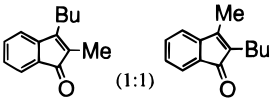
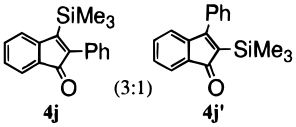
mixture of chlorodienes **3l** and **3l′** in a ratio of 77:23, the combined yield being 36% (eq 7). These results suggest that the precedence of the reaction courses leading to



vinyl chlorides and indenones depends on the structure of acid chlorides as well as that of alkynes.

It is noted that elaborated analysis of the reaction mixtures with **2f**−**k** by GC-MS suggested formation of

Table 4. Reaction of Aroyl Chlorides 1 with Internal Alkynes 2f−k[a]

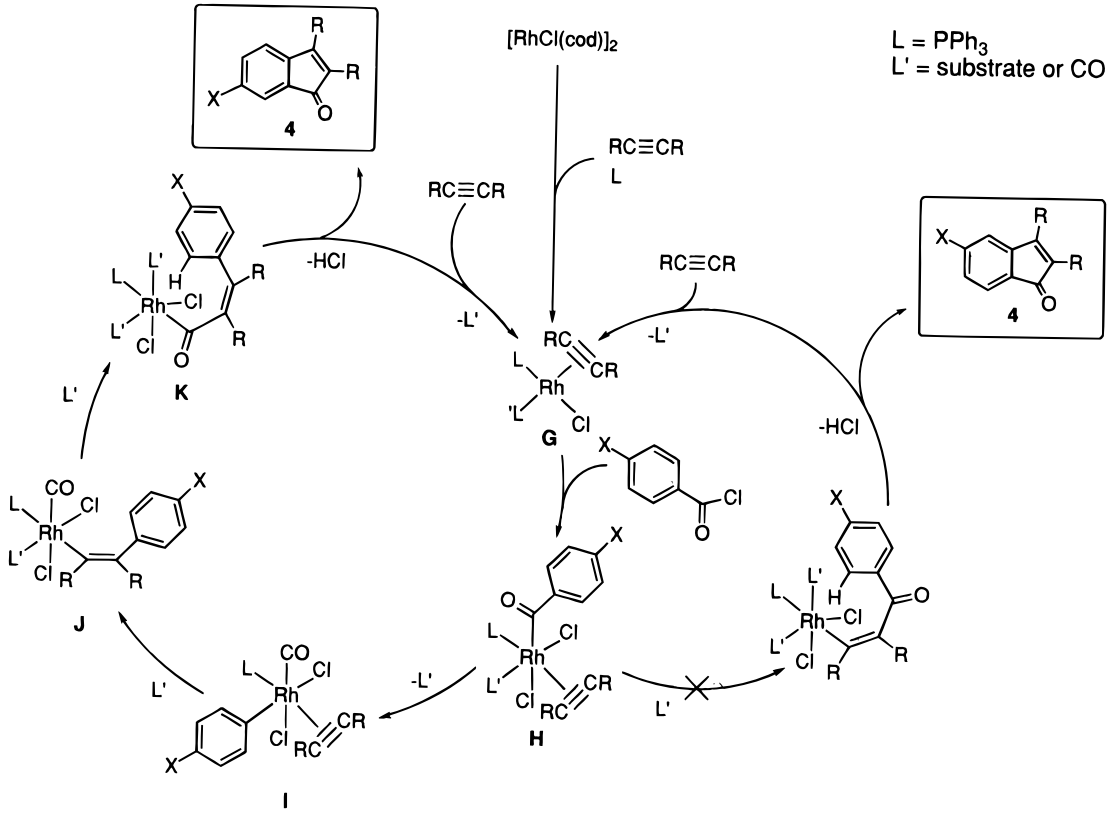
substrates				
1	**2**	product **4**, % yield[b]		
1a	**2f**		**4a**	76 (73)
1b	**2f**		**4b**	61 (57)
1c	**2f**		**4c**	67 (47)
1h[c]	**2f**		**4d**	88 (81)
1i[d]	**2f**	 **4e** (92:8) **4e'**		69 (59)
1a	**2g**[e]		**4f**	49
1a	**2h**		**4g**	13
1a	**2i**	 **4h** (1:1) **4h'**		27
1a	**2j**	 **4i** (1:1) **4i'**		36
1a	**2k**	 **4j** (3:1) **4j'**		23

[a] The reaction was carried out in *o*-xylene at 145 °C for 24 h under N_2. [[RhCl(cod)]$_2$]:[PPh_3]:[**1**]:[**2**]:[Na_2CO_3] = 0.02:0.04 : 3 : 2 : 2 (in mmol). [b] GC yield based on **2** used. Value in parentheses indicates yield after isolation. [c] 3-Methylbenzoyl chloride. [d] 2-Naphthoyl chloride. [e] Reaction was carried out in a sealed tube.

tetrasubstituted naphthalenes as byproducts in very low yields (≤4%). One of them produced from **1a** and **2f** was isolated and determined to be 1,2,3,4-tetrapropylnaphthalene (**5**). It was also obtained in 18% yield from the reaction in octane at a bath-temperature of 150 °C.

Reaction Scheme for the Formation of 4. A most plausible mechanism to account for the formation of indenones **4** based on the observed results is illustrated in Scheme 3. The key intermediate leading to **4** may be arylchlororhodium(III) species **I**, which is the equivalent to **C** in Scheme 1, formed *via* complexes **G** and **H**. Arylrhodation in **I** followed by reinsertion of carbon monoxide coordinated to the metal center affords complex **K**. The subsequent cyclization reaction accompanied by

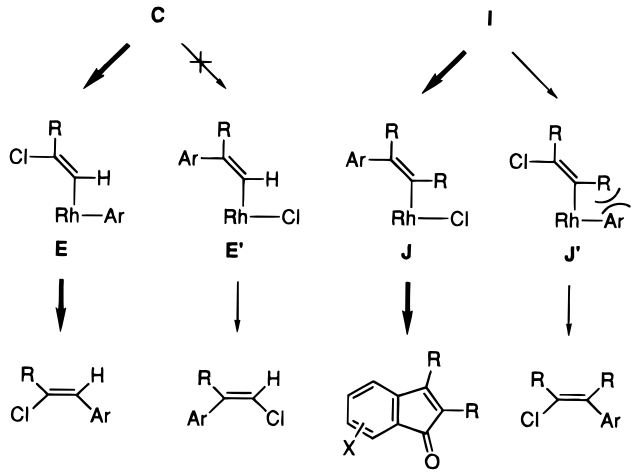
Scheme 3



regeneration of **G** and evolution of HCl gives product **4**. While aroylrhodation in **H** would lead to **4**, the route may be ruled out, since the structure of **4b**−**d** and **4e**′ is not consistent with it. The structures of **4d** and **4e** may suggest that each final cyclization step of **K** to **4** is sterically controlled; steric hindrance by the methyl group and the *peri*-hydrogen on the benzene and the naphthalene rings, respectively, may be the major reason for the selective formation of these products. The byproduct **5** may be formed *via* insertion of another alkyne molecule in complex **J** (L′ = **2**).

Thus, it may be reasonable to consider that the present rhodium-catalyzed reaction of **1** with **2** involve arylchlororhodium(III)−alkyne complexes such as **C** and **I** as the common intermediates; chlororhodation and arylrhodation in them lead to vinyl chlorides **3** and indenones **4**, respectively. One of the major factors determining the reaction routes and the product structures may be steric repulsion in the vinylrhodium intermediates from **C** and **I** (Scheme 4). Of the two possible intermediates **J** and **J′** from **I**, there seems to be considerable steric repulsion between the R group and the rhodium moiety in **J′** and hence, arylrhodation to give **J** predominates. The steric interaction in **E** from **C** appears to be small and therefore, in the case of terminal alkynes, chlororhodation may be the favorable path. The repulsion in **J′** in the reactions of **1a** with **2l** (Ar = Ph, R = COOEt) and of **1d** with **2f** (Ar = PhCH=CH-, R = Pr) may be relatively small to produce vinyl chlorides **3k** and **3l**. Consequently, chlororhodation may be considered to be the energetically favorable route relative to arylrhodation, when steric hindrance dose not intervene.

Scheme 4



Experimental Section

^{1}H NMR spectra were recorded at 400 MHz for $CDCl_3$ solutions. MS data were obtained by EI. GC analysis was carried out using a silicone OV-17 glass column (∅ 2.6 mm × 1.5 m) or a CBP-1 capillary column (∅ 0.5 mm × 25 m). (*E*)-1,2-Diphenyl-2-propenoyl chloride[15] (**1f**), 3-butoxy-1-propyne[16] (**2e**), and ethyl 2-heptynoate[17] (**2l**) were prepared by the methods reported previously. Other starting materials were commercially available. The following experimental details given below may be regarded as typical in methodology and scale.

Reaction of Benzoyl Chloride (1a) with Phenylacetylene (2a). To a flask containing $[RhCl(cod)]_2$ (4.9 mg, 0.01 mmol) and PPh_3 (5.2 mg, 0.02 mmol) under nitrogen (with a balloon) was added a solution of **1a** (281 mg, 2 mmol), **2a** (306 mg, 3 mmol), and 1-methylnaphthalene (ca. 100 mg) as an

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internal standard in octane (5 mL), and the resulting mixture was stirred at 140 °C for 20 h. GC and GC-MS analyses of the mixture confirmed formation of **3a** (439 mg, 92%). Product **3a** (434 mg, 91%) was also isolated by column chromatography on silica gel using hexane as eluent.

Reaction of Benzoyl Chloride (1a) with 4-Octyne (2f). To a flask containing $[RhCl(cod)]_2$ (9.8 mg, 0.02 mmol), PPh_3 (10.4 mg, 0.04 mmol) and Na_2CO_3 (212 mg, 2 mmol) under nitrogen (with a balloon) was added a solution of **1a** (422 mg, 3 mmol), **2f** (220 mg, 2 mmol), and 1-methylnaphthalene (ca. 100 mg) as an internal standard in *o*-xylene (5 mL), and the resulting mixture was stirred at 145 °C for 24 h. GC and GC-MS analyses of the mixture confirmed formation of **4a** (325 mg, 76%). Product **4a** (312 mg, 73%) was also isolated by column chromatography on silica gel using hexane-dichloromethane (9:1, v/v) as eluent.

Products. Compounds **3a**,[18] **3a′**,[19] **3e**,[20] **3j**,[21] **3j′**,[21] **4a**,[8b] **4f**,[8a] **4g**,[8a] **4h**,[8a] **4h′**,[8a] and **4j′**[8b] are known and were compared with those authentic specimens. The analytical data of other products **3**, **4**, and **5** are as follows.

(*Z*)-1-Chloro-2-(4-chlorophenyl)-1-phenylethene (3b): mp 60.0−60.5 °C; ^{1}H NMR δ 7.00 (s, 1H), 7.35−7.43 (m, 5H), 7.67−7.70 (m, 4H); MS *m*/*z* 248, 250, 252 (M^+). Anal. Calcd for $C_{14}H_{10}Cl_2$: C, 67.49; H, 4.05; Cl, 28.46. Found: C, 67.69; H, 4.05; Cl, 28.36.

(*Z*)-1-Chloro-2-(4-methylphenyl)-1-phenylethene (3c): mp 45.5−46.0 °C; ^{1}H NMR δ 2.38 (s, 3H), 7.04 (s, 1H), 7.21 (d, 2H, *J* = 8.1 Hz), 7.33−7.42 (m, 3H), 7.64−7.71 (m, 4H); MS *m*/*z* 228, 230 (M^+). Anal. Calcd for $C_{15}H_{13}Cl$: C, 78.77; H, 5.73; Cl, 15.50. Found: C, 78.81; H, 5.92; Cl, 15.45.

(*Z*,*E*)-2-Chloro-1,4-diphenyl-1,3-butadiene (3d): mp 111−112 °C; ^{1}H NMR δ 6.80 (d, 1H, *J* = 7.9 Hz), 6.94 (d, 1H, *J* = 5.3 Hz), 7.25−7.40 (m, 7H), 7.49−7.52 (m, 2H), 7.67−7.69 (m, 2H); MS *m*/*z* 240, 242 (M^+). Anal. Calcd for $C_{16}H_{13}Cl$: C, 79.83; H, 5.44; Cl, 14.73. Found: C, 79.52; H, 5.70; Cl, 14.38.

(*Z*)-2-Chloro-1-phenyl-1-octene (3f): oil; ^{1}H NMR δ 0.90 (t, 3H, *J* = 6.8 Hz), 1.30−1.37 (m, 6H), 1.65 (quintet, 2H, *J* = 7.3 Hz), 2.48 (t, 2H, *J* = 7.3 Hz), 6.46 (s, 1H), 7.23−7.27 (m, 1H), 7.32−7.36 (m, 2H), 7.58−7.59 (m, 2H); MS *m*/*z* 222, 224 (M^+). Anal. Calcd for $C_{14}H_{19}Cl$: C, 75.49; H, 8.60; Cl, 15.92. Found: C, 75.69; H, 8.73; Cl, 15.84.

(*Z*)-1-Chloro-1-(1-cyclohexenyl)-2-phenylethene (3g): oil; ^{1}H NMR δ 1.60−1.68 (m, 2H), 1.72−1.78 (m, 2H), 2.22−2.27 (m, 2H), 2.34−2.39 (m, 2H), 6.50−6.52 (m, 1H), 6.69 (s, 3−7.37 (m, 2H), 7.63 (d, 2H, *J* = 7.3 Hz); MS *m*/*z* 218, 220 (M^+). Anal. Calcd for $C_{14}H_{15}Cl$: C, 76.88; H, 6.91; Cl, 16.21. Found: C, 76.63; H, 6.96; Cl, 16.09.

(*Z*)- and (*E*)-3-Butoxy-2-chloro-1-phenyl-1-propene (3h and 3h′; 85:15): oil; ^{1}H NMR δ 0.93 (t, 3H, *J* = 7.6 Hz), 1.38−1.44 (m, 2H), 1.57−1.65 (m, 2H), 3.45 (t, 2H, *J* = 6.6 Hz; **3h′**), 3.52 (t, 2H, *J* = 6.6 Hz; **3h**), 4.17 (s, 2H; **3h**), 4.21 (s, 2H; **3h′**), 6.74 (s, 1H; **3h**), 6.94 (s, 1H; **3h′**), 7.24−7.29 (m, 1H), 7.32−7.37 (m, 2H), 7.63 (d, 2H, *J* = 7.3 Hz); MS *m*/*z* 224, 226 (M^+). HRMS *m*/*z* (M^+) Calcd for $C_{13}H_{17}OCl$: 224.0968. Found: 224.0960.

(*Z*,*Z*)-2,7-Dichloro-1,8-diphenyl-1,7-octadiene (3i): mp 58.5−59.5 °C; ^{1}H NMR δ 1.71−1.75 (m, 4H), 2.51−2.55 (m, 4H), 6.49 (s, 2H), 7.23−7.27 (m, 2H), 7.32−7.36 (m, 4H), 7.58−7.60 (m, 4H); MS *m*/*z* 330, 332, 334 (M^+). Anal. Calcd for $C_{20}H_{20}Cl_2$: C, 72.51; H, 6.09; Cl, 21.40. Found: C, 72.47; H, 6.11; Cl, 21.32.

Ethyl (*Z*)-3-chloro-2-phenyl-2-heptenoate (3k): oil; ^{1}H NMR δ 0.96 (t, 3H, *J* = 7.3 Hz), 1.23 (t, 3H, *J* = 7.1 Hz), 1.42 (sextet, 2H, *J* = 7.3 Hz), 1.67−1.75 (m, 2H), 2.79 (t, 2H, *J* = 7.7 Hz), 4.19 (q, 2H, *J* = 7.1 Hz), 7.25−7.38 (m, 5H); MS *m*/*z* 266, 268 (M^+). HRMS *m*/*z* (M^+) Calcd for $C_{15}H_{19}O_2Cl$: 266.1073. Found: 266.1077.

(*E*,*Z*)- and (*E*,*E*)-4-Chloro-1-phenyl-3-propyl-1,3-heptadiene (3l and 3l′; 3:1): oil; ^{1}H NMR δ 0.93−1.01 (m, 6H), 1.49−1.69 (m, 4H), 2.38−2.63 (m, 4H), 6.59 (d, 1H, *J* = 15.8 Hz; **3l′**), 6.60 (d, 1H, *J* = 15.8 Hz; **3l**), 7.00 (d, 2H, *J* = 15.8 Hz), 7.21−7.48 (m, 10H); MS *m*/*z* 248, 250 (M^+). HRMS *m*/*z* (M^+) Calcd for $C_{15}H_{19}O_2Cl$: 248.1332. Found: **3l**; 248.1332, **3l′**; 248.1329.

6-Chloro-2,3-dipropyl-1-indenone (4b): yellow solid, mp 50.5−50.7 °C; ^{1}H NMR δ 0.93 (t, 3H, *J* = 7.3 Hz), 1.03 (t, 3H, *J* = 7.3 Hz), 1.49 (sextet, 2H, *J* = 7.5 Hz), 1.63 (sextet, 2H, *J* = 7.7 Hz), 2.23 (t, 2H, *J* = 7.6 Hz), 2.51 (t, 2H, *J* = 7.8 Hz), 6.96 (d, 1H, *J* = 7.7 Hz), 7.28 (dd, 1H, *J* = 7.7, 2.0 Hz), 7.32 (d, 1H, *J* = 2.0 Hz); MS *m*/*z* 248, 250 (M^+); IR (KBr): 1707.2 (C═O) cm^{-1}. Anal. Calcd for $C_{15}H_{17}ClO$: C, 72.43; H, 6.89; Cl, 14.25. Found: C, 72.26; H, 6.93; Cl, 14.10.

2,3-Dipropyl-6-methyl-1-indenone (4c): yellow oil; ^{1}H NMR δ 0.92 (t, 3H, *J* = 7.3 Hz), 1.01 (t, 3H, *J* = 7.3 Hz), 1.47 (sextet, 2H, *J* = 7.4 Hz), 1.63 (sextet, 2H, *J* = 7.5 Hz), 2.21 (t, 2H, *J* = 7.6 Hz), 2.30 (s, 3H), 2.49 (t, 2H, *J* = 7.8 Hz), 6.90 (d, 1H, *J* = 7.3 Hz), 7.08 (dt, 1H, *J* = 7.3, 1.0 Hz), 7.18 (d, 1H, *J* = 1.0 Hz); MS *m*/*z* 228 (M^+); IR (neat): 1707.2 (C═O) cm^{-1}. HRMS *m*/*z* (M^+) Calcd for $C_{16}H_{20}O$: 228.1514. Found: 228.1512.

2,3-Dipropyl-5-methyl-1-indenone (4d): yellow oil; ^{1}H NMR δ 0.93 (t, 3H, *J* = 7.3 Hz), 1.03 (t, 3H, *J* = 7.3 Hz), 1.48 (sextet, 2H, *J* = 7.3 Hz), 1.63 (sextet, 2H, *J* = 7.3 Hz), 2.22 (t, 2H, *J* = 7.8 Hz), 2.38 (s, 3H), 2.50 (t, 2H, *J* = 7.8 Hz), 6.83 (s, 1H), 6.93 (d, 1H, *J* = 7.3 Hz), 7.26 (d, 1H, *J* = 7.3 Hz); MS *m*/*z* 228 (M^+); IR (neat): 1705.3 (C═O) cm^{-1}. HRMS *m*/*z* (M^+) Calcd for $C_{16}H_{20}O$: 228.1514. Found: 228.1529.

2,3-Dipropylbenz[*d*]-1-indenone (4e): yellow solid, mp 46.0−46.5 °C; ^{1}H NMR δ 0.97 (t, 3H, *J* = 7.3 Hz), 1.08 (t, 3H, *J* = 7.3 Hz), 1.54 (sextet, 2H, *J* = 7.3 Hz), 1.73 (sextet, 2H, *J* = 7.3 Hz), 2.32 (t, 2H, *J* = 7.8 Hz), 2.63 (t, 2H, *J* = 7.8 Hz), 7.32 (s, 1H), 7.41 (t, 1H, *J* = 7.8 Hz), 7.48 (t, 1H, *J* = 7.8 Hz), 7.73 (d, 1H, *J* = 7.8 Hz), 7.80 (d, 1H, *J* = 7.8 Hz), 7.81 (s, 1H); MS *m*/*z* 264 (M^+); IR (KBr): 1699.5 (C═O) cm^{-1}. Anal. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.23; H, 7.62.

2,3-Dipropylbenz[*e*]-1-indenone (4e′): red solid, mp 43.5−44.5 °C; ^{1}H NMR δ 0.96 (t, 3H, *J* = 7.3 Hz), 1.06 (t, 3H, *J* = 7.3 Hz), 1.54 (sextet, 2H, *J* = 7.6 Hz), 1.69 (sextet, 2H, *J* = 7.3 Hz), 2.25 (t, 2H, *J* = 7.6 Hz), 2.56 (t, 2H, *J* = 7.6 Hz), 7.26 (d, 1H, *J* = 8.3 Hz), 7.31 (t, 1H, *J* = 8.3 Hz), 7.47 (t, 1H, *J* = 8.3 Hz), 7.69 (d, 1H, *J* = 8.3 Hz), 7.85 (d, 1H, *J* = 8.3 Hz), 8.69 (d, 1H, *J* = 8.3 Hz); MS *m*/*z* 264 (M^+); IR (KBr): 1693.7 (C═O) cm^{-1}. HRMS *m*/*z* (M^+) Calcd for $C_{19}H_{20}O$: 264.1514. Found: 264.1516.

3 (or 2)-Butyl-2 (or 3)-methyl-1-indenone (4i and 4i′; 1:1): yellow oil; ^{1}H NMR δ 0.89−0.98 (m, 6H), 1.30−1.46 (m, 6H), 1.56−1.60 (m, 2H; **4i**), 1.80 (s, 3H; **4i′**), 2.11 (s, 3H; **4i**), 2.27 (t, 2H, *J* = 7.5 Hz; **4i′**), 2.53 (t, 2H, *J* = 7.5 Hz), 7.00−7.02 (m, 2H), 7.13−7.17 (m, 2H), 7.26−7.37 (m, 4H); MS *m*/*z* 200 (M^+); IR (neat): 1709.1 (C═O) cm^{-1}. HRMS *m*/*z* (M^+) Calcd for $C_{14}H_{16}O$: 200.1201. Found: 200.1203.

2-Phenyl-3-(trimethylsilyl)-1-indenone (4j): yellow solid, mp 111.5−112.0 °C; ^{1}H NMR δ 0.08 (s, 9H), 7.10−7.42 (m, 9H); MS *m*/*z* 278 (M^+); IR (KBr): 1705.3 (C═O) cm^{-1}. Anal. Calcd for $C_{18}H_{18}OSi$: C, 77.65; H, 6.52. Found: C, 77.75; H, 6.56.

1,2,3,4-Tetrapropylnaphthalene (5): oil; ^{1}H NMR δ 1.08−1.13 (m, 12H), 1.56−1.71 (m, 8H), 2.71−2.75 (m, 4H), 2.98−3.03 (m, 4H), 7.38−7.41 (m, 2H), 7.97−8.00 (m, 2H); MS *m*/*z* 296 (M^+); HRMS *m*/*z* (M^+) Calcd for $C_{22}H_{32}$: 296.2504. Found: 296.2501.

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Supporting Information Available: ^{1}H NMR spectra for **3h** (+**3h′**), **3k**, **3l** (+**3l′**), **4c**, **4d**, **4e′**, **4i** (+**4i′**), and **5** (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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