Single and Multiple Insertion of Arylallene into the Rh−H Bond To Give (π-Allyl)rhodium Complexes

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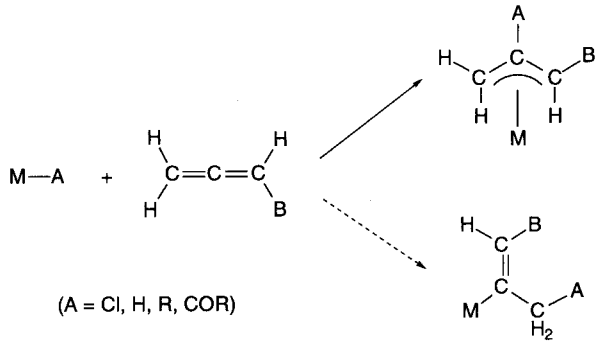
The reaction of $RhH(PPh_3)_4$ at room temperature with excess phenylallene, (4-methylphenyl)allene, (4-methoxyphenyl)allene, (4-*tert*-butylphenyl)allene, (4-chlorophenyl)allene, and (4-fluorophenyl)allene results in the insertion of four arylallene molecules into the Rh−H bond to afford $Rh\{\eta^3\text{-}CH_2C[CH(Ar)]C(=CHAr)CH_2C(=CHAr)CH_2CH_2CH=CHAr)\}(PPh_3)_2$ (**1**, Ar = C_6H_5; **2**, Ar = C_6H_4Me-*p*; **3**, Ar = C_6H_4OMe-*p*; **4**, Ar = C_6H_4-*t*-Bu-*p*; **5**, Ar = C_6H_4Cl-*p*; **6**, Ar = C_6H_4F-*p*), respectively. NMR (^1H, ^{13}C, and ^{31}P) spectroscopy was used to characterize the (π-allyl)rhodium(I) complexes. Reaction of (4-methoxyphenyl)allene with $RhD(PPh_3\text{-}d_{15})_4$ gives **3**-d_{31}, $Rh\{\eta^3\text{-}CH_2C[CH(Ar)]C(=CHAr)CH_2C(=CHAr)CH_2CH_2CD=CHAr)\}(PPh_3\text{-}d_{15})_2$ (Ar = C_6H_4OMe-*p*), whose vinylene hydrogen is deuterated selectively. Complexes **1** and **3** do not react further with arylallene at room temperature. Reaction of arylallenes with an equimolar amount of $RhH(CO)(PPh_3)_3$ leads to the insertion of a molecule into the Rh−H bond to give the (π-allyl)rhodium complexes $Rh(\eta^3\text{-}CH_2CHCHC_6H_4X\text{-}p)(CO)(PPh_3)_2$ (**9**, X = Me; **10**, X = OMe; **11**, X = F; **12**, X = Cl), while excess phenylallene reacts with the hydridorhodium complex to give a mixture of **1**, $Rh(\eta^3\text{-}CH_2CHCHPh)(CO)(PPh_3)_2$, and unreacted $RhH(CO)(PPh_3)_3$. A crystallographic study of **9** and ^1H NMR data for the complexes indicate that the aryl substituent has a syn orientation. The π-allyl complexes react with monosubstituted acetylenes to give *trans*-$Rh(C{\equiv}CZ)(CO)(PPh_3)_2$ (**13**, Z = Ph; **14**, Z = C_6H_4Me-*p*; **15**, Z = $SiMe_3$) accompanied by the generation of 1-arylpropene.

Introduction

The insertion of alkene and alkyne into Rh−H or Rh−C bonds[1] plays an important role in Rh-catalyzed organic reactions such as hydrogenation and hydroformylation of alkenes and oligomerization and polymerization of alkenes and alkynes.[2,3] Allene and substituted allenes were reported to undergo insertion of a C=C double bond into a M−X bond (M = transition metal, X = H, Cl, alkyl, acyl) to give π-allyl transition-metal complexes rather than 2-propenyl complexes, as shown in Scheme 1.[4]

Scheme 1



π-Allyl Ni(II) and Pd(II) complexes initiate the polymerization of allene and various substituted allenes to give polymers with unique structures and block copolymers with isocyanides.[5] The polymerization involves repeated insertion of allene into the bond between the metal center and the π-allyl-coordinated growing polymer (Scheme 2).

(1) (a) Pino, P.; Pacenti, F.; Bianci, M. In *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P. Eds.; Wiley: New York, 1977; Vol. 2, pp 43, 233. (b) *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum: New York, 1983. (c) Jardine, F. H. In *The Chemistry of the Metal−Carbon Bond*; Patai, S., Hartley, F. R., Eds.; Wiley: Chichester, U.K., 1987; Vol. 4, p 734.

(2) (a) Hauptman, E.; Sabo-Etienne, S.; White, P. S.; Brookhart, M.; Garner, J. M.; Fagan, P. J.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 8038. (b) Kaneko, Y.; Kanke, T.; Kiyooka, S.; Isobe, K. *Chem. Lett.* **1997**, 23.

(3) (a) Wang, L.; Lu, R. S.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1993**, *115*, 6999. (b) Tabata, M.; Yang, W.; Yokota, K. *Polym. J.* **1990**, *22*, 1105. (c) Tabata, M.; Yang, W.; Yokota, K. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 1113. (d) Tabata, M.; Sadahiro, Y.; Nozaki, Y.; Inaba, Y.; Yokota, K. *Macromolecules* **1996**, *29*, 6673. (e) Kishimoto, Y.; Eckerle, P.; Miyatake, T.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1994**, *116*, 12131. (f) Kishimoto, Y.; Itou, M.; Miyatake, T.; Ikariya, T.; Noyori, R. *Macromolecules* **1995**, *28*, 6662. (g). Kishimoto, Y.; Miyatake, T.; Ikariya, T.; Noyori, R. *Macromolecules* **1996**, *29*, 5054.

(4) (a) Powell, P. Synthesis of η^3-Allyl Complexes. In *The Chemistry of the Metal−Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1982; pp 355−357. (b) Schultz, R. G. *Tetrahedron Lett.* **1964**, 301, 2809. (c) Lupin, M. S.; Shaw, B. L. *Tetrahedron Lett.* **1965**, 883. (d) Deeming, A. J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1970**, 598. (e) Stevens, R. R.; Shier, G. D. *J. Organomet. Chem.* **1970**, *21*, 495. (f) Okamoto, T. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1353. (g) Chisholm, M. H.; Clark, H. C.; Hunter, D. H. *J. Chem. Soc. D* **1971**, 809. (h) Hughes, R. P.; Powell, J. *J. Organomet. Chem.* **1972**, *34*, C51. (i) Clark, H. C.; Milne, C. R. C.; Wong, C. S. *J. Organomet. Chem.* **1977**, *136*, 265. (j) Chisholm, M. H.; Johns, W. S. *Inorg. Chem.* **1975**, *14*, 1189. (k) Hegedus, L. S.; Kambe, N.; Tamura, R.; Woodgate, P. D. *Organometallics* **1983**, *2*, 1658. (l) Rülke, R. E.; Kliphuis, D.; Elsevier, C. J.; Fraanje, J.; Goubitz, K.; van Leeuwen, P. W. N. M.; Vrieze, K. *J. Chem. Soc., Chem. Commun.* **1994**, 1817. (m) Groen, J. H.; Elsevier, C. J.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1996**, *15*, 3445. (n) Delis, J. G. P.; Groen, J. H.; Vrieze, K.; van Leuuwen, P. W. N. M.; Veldman, N.; Spek, A. L. *Organometallics* **1997**, *16*, 551.

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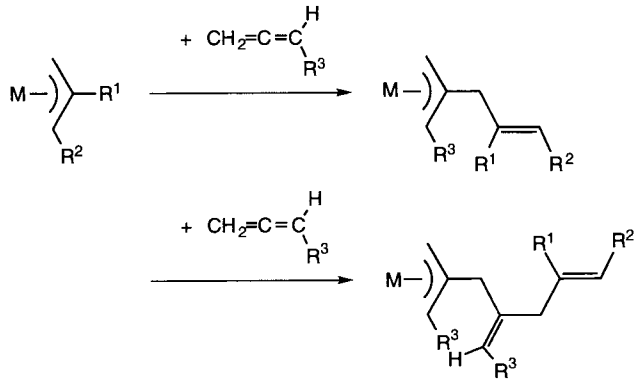
Scheme 2



A similar type of allene insertion into Pd−π-allyl bonds as well as into Pd−alkyl bonds was studied in detail.[6] On the other hand, Rh(I) complexes promote the polymerization of allene and phenylallene[7] or their cyclooligomerization,[8] depending on the auxiliary ligand. The cyclooligomerization involves several unique reactions such as cycloaddition of two allene molecules to the metal center to give metallacyclopentane[9] and insertion of allene into the metal−carbon σ-bond of the intermediate metallacycle complex. A detailed study of the insertion of allene into Rh−H, Rh−alkyl, and Rh−π-allyl bonds is significant with respect to the mechanisms of allene polymerization and cyclooligomerization. So far, there have been only a limited number of reports on such reactions.[7e,10] In this paper we report the reaction of arylallene with hydridorhodium complexes leading to the insertion of one or more arylallene molecules into the Rh−H bond. Chemical properties of the resulting π-allyl rhodium complexes are also presented. Part of this work has been reported in a preliminary form.[11]

Table 1. Yields and Analytical Data for the Complexes Rh{η^3-CH_2C[CH(Ar)]C(=CHAr)-CH_2C(=CHAr)CH_2CH_2CH=CHAr)}(PPh_3)$_2$ (1−6)

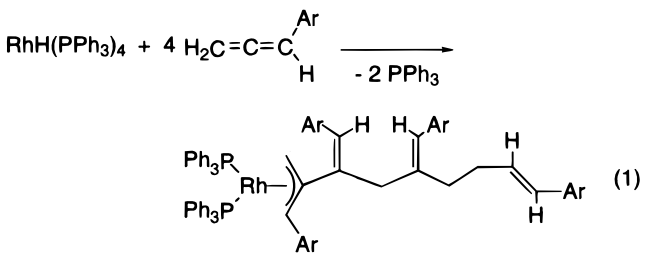
complex	M	Ar	color	yield (%)	anal.[a] C (%)	anal.[a] H (%)
1	Rh	C_6H_5	red	60	78.99 (79.11)	6.09 (5.81)
2	Rh	C_6H_4Me-*p*	red	72	79.09 (79.43)	6.62 (6.23)
3	Rh	C_6H_4OMe-*p*	red	85	74.71 (75.24)	5.99 (5.90)
4	Rh	C_6H_4-*t*-Bu-*p*	red	70	*b*	
5	Rh	C_6H_4Cl-*p*	red	72	69.84 (70.26)	5.03 (4.83)[c]
6	Rh	C_6H_4F-*p*	red	88	73.89 (74.22)	5.27 (5.10)

[a] Calculated values are given in parentheses. [b] Satisfactory results were not obtained, although the complex was spectroscopically pure. [c] Cl: 11.02 (11.52).

Results and Discussion

Preparation of Rh Complexes 1−6 Containing Arylallene Tetramer as the π-Allyl Ligand. Arylallenes, including phenylallene, (4-methylphenyl)allene, (4-methoxyphenyl)allene, (4-*tert*-butylphenyl)allene, (4-chlorophenyl)allene, and (4-fluorophenyl)allene, react with $RhH(PPh_3)_4$ in a 5:1 molar ratio at room temperature to give (π-allyl)rhodium(**I**) complexes, Rh{η^3-CH_2C[CH(Ar)]CHC(=CHAr)CH_2C(=CHAr)CH_2CH_2CH=CHAr)}(PPh_3)$_2$ (**1**, Ar = C_6H_5; **2**, Ar = C_6H_4Me-*p*; **3**, Ar = C_6H_4OMe-*p*; **4**, C_6H_4-*t*-Bu-*p*; **5**, Ar = C_6H_4Cl-*p*; **6**, Ar = C_6H_4F-*p*). The complexes were isolated in moderate to high yields, as summarized in Table 1.

Figures 1 and 2 depict respectively the ^{1}H and ^{13}C-{^{1}H} NMR spectra of **3**. The ^{1}H NMR spectrum of **3**-d_{31} obtained from the reaction of (4-methoxyphenyl)allene with $RhD(PPh_3\text{-}d_{15})_4$ is also included in Figure 1. The three ^{13}C{^{1}H} NMR resonances at δ 52.0, 71.9, and 116.8 exhibit splitting due to P−C and Rh−C coupling and are assigned to carbons bonded to the Rh center in an η^3 form. The H−C COSY technique was useful for assigning signals of three hydrogens attached to these carbons. The ^{1}H NMR signal at δ 4.93 and the ^{13}C NMR signal at δ 71.9 show a correlation peak, while peaks are observed at the intersection of the ^{13}C NMR signal at δ 52.0 and two ^{1}H NMR signals at δ 3.56 and 2.70. These results suggest coordination of the 1,2-disubstituted π-allylic ligand to the Rh center and are consistent with the crystallographic structure of **3** shown in eq 1.



1: Ar = C_6H_5; **2**: Ar = C_6H_4Me-*p*; **3**: Ar = C_6H_4OMe-*p*; **4**: Ar = C_6H_4Bu-*t*-*p*; **5**: Ar = C_6H_4Cl-*p*; **6**: Ar = C_6H_4F-*p*.

The signals due to two CH_2 hydrogens, H_f and H_g, appear as an AB quartet at δ 3.62 and 3.78, while the

(5) (a) Otsuka, S.; Mori, K.; Suminoe, T.; Imaizumi, F. *Eur. Polym. J.* **1967**, *3*, 73. (b) Krentsel, B. A.; Mushina, E. A.; Khar'kova, E. M.; Shinshkina, M. V. *Eur. Polym. J.* **1975**, *11*, 865. (c) Ghalamkar-Moazzam, M.; Jacobs, T. L. *J. Polym. Sci., Polym. Chem.* **1978**, *16*, 615. (d) Tomita, I.; Kondo, Y.; Takagi, K.; Endo, T. *Macromolecules* **1994**, *27*, 4413. (e) Tomita, I.; Abe, T.; Takagi, K.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 2487. (f) Tomita, I.; Kondo, Y.; Takagi, K.; Endo, T. *Acta Polym.* **1995**, *46*, 432. (g) Takagi, K.; Tomita, I.; Endo, T. *Chem. Lett.* **1997**, 1187. (h) Takagi, K.; Tomita, I.; Endo, T. *Macromolecules* **1997**, *30*, 7386. (i) Endo, T.; Takagi, K.; Tomita, I. *Tetrahedron* **1997**, *45*, 15187.

(6) (a) van Helden, R.; Kohll, C. F.; Medema, D.; Verberg, G.; Jonkhoff, T. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 961. (b) Medema, D.; van Heden, R.; Kohll, C. F. *Inorg. Chim. Acta* **1969**, *3*, 255. (c) Medema, D.; van Helden, R. *Recl. Trav. Chim. Pays-Bas* **1977**, *90*, 304. (d) Hughes, R. P.; Powell, J. *J. Organomet. Chem.* **1973**, *60*, 409. (e) May, C. J.; Powell, J. *J. Organomet. Chem.* **1980**, *184*, 385.

(7) (a) Otsuka, S.; Nakamura, A. *J. Polym. Sci., Part B: Polym. Lett. Ed.* **1967**, *5*, 973. (b) Scholten, J. P.; van der Ploeg, H. J. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 3067. (c) Scholten, J. P.; van der Ploeg, H. J. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 3205. (d) Leland, J.; Boucher, J.; Anderson, K. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2785. (e) Sóvágó, J.; Newton, M. G.; Mushina, E. A.; Ungváry, F. *J. Am. Chem. Soc.* **1996**, *118*, 9589. (f) Choi, J.-C.; Osakada, K.; Yamaguchi, I.; Yamamoto, T. *Appl. Organomet. Chem.* **1997**, *11*, 957.

(8) (a) Jones, F. N.; Lindsey, R. V. *J. Org. Chem.* **1968**, *33*, 3838. (b) Otsuka, S.; Nakamura, A.; Tani, K.; Ueda, S. *Tetrahedron Lett.* **1969**, 297. (c) Otsuka, S.; Nakamura, A.; Minamida, H. *J. Chem. Soc. D* **1969**, 191. (d) Scholten, J. P.; van der Ploeg, H. J. *Tetrahedron Lett.* **1972**, 1685.

(9) (a) Ingrosso, G.; Immirzi, A.; Porri, L. *J. Organomet. Chem.* **1973**, *60*, C35. (b) Ingrosso, G.; Porri, L.; Pantini, G.; Racanelli, P. *J. Organomet. Chem.* **1975**, *84*, 75. (c) Immirzi, A. *J. Organomet. Chem.* **1974**, *81*, 217. (d) Choi, J.-C.; Sarai, S.; Koizumi, T.; Osakada, K.; Yamamoto, T. *Organometallics* **1998**, *17*, 2037.

(10) (a) Brown, C. K.; Mowat, W.; Yagupsky, G.; Wilkinson, G. *J. Chem. Soc. A* **1971**, 850. (b) Osakada, K.; Choi, J.-C.; Koizumi, T.; Yamaguchi, I.; Yamamoto, T. *Organometallics* **1995**, *14*, 4962.

(11) Osakada, K.; Choi, J. C.; Yamamoto, T. *J. Am. Chem. Soc.* **1997**, *119*, 12390.

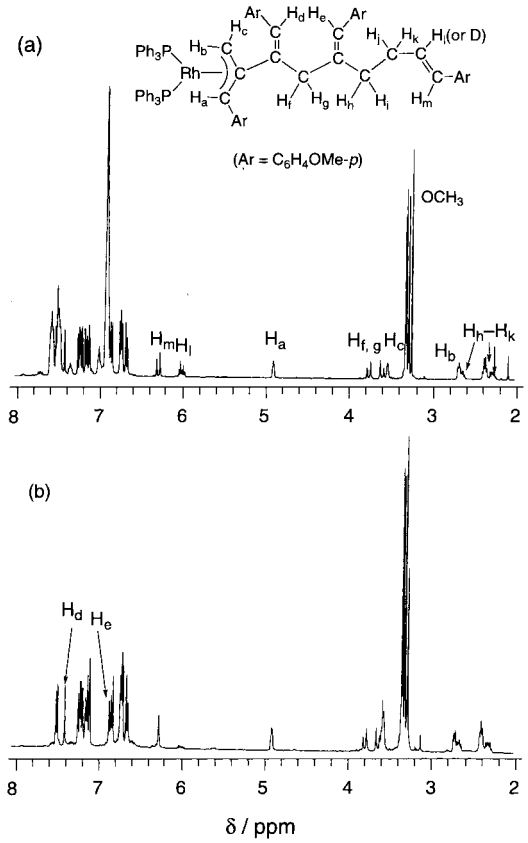


Figure 1. ^{1}H NMR spectra of (a) **3** and (b) **3**-d_{31} (400 MHz in benzene-d_6). Signals at δ 3.6 in the spectrum of **3**-d_{31} contain overlapping peaks of H_c, $H_{g'}$ and an impurity derived from the RhD(PPh_3-d_{15})$_4$ used.

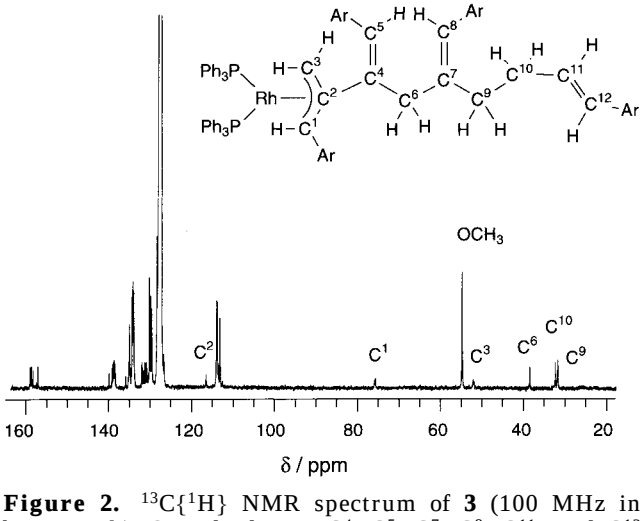


Figure 2. ^{13}C{^{1}H} NMR spectrum of **3** (100 MHz in benzene-d_6). Signals due to C^4, C^5, C^7, C^8, C^{11}, and C^{12} overlap with PPh_3 carbon signals. Positions of the signals due to C^5, C^8, C^{11}, and C^{12} were determined to appear at δ 132.0, 130.3, 128.6, and 130.5, respectively, on the basis of the H−C COSY spectrum.

four CH_2 hydrogens H_h−H_k are observed at δ 2.28, 2.40, and 2.65 as complex signals due to H−H coupling. Two resonances at δ 6.03 and 6.32 are assigned to trans vinylene hydrogens H_l and H_m, respectively, on the basis of the splitting pattern caused by H−H coupling. The singlets at δ 3.34, 3.33, 3.30, and 3.27 are assigned to hydrogens of four OMe groups of the π-allylic ligand. The signals due to H_d and H_e and the aromatic hydrogens of the 4-methoxyphenyl groups overlap markedly with large peaks of PPh_3 hydrogens; in contrast, the ^{1}H NMR spectrum of **3**-d_{31}, having much smaller PPh_3 peaks, shows singlet signals for H_d and H_e at δ 7.44 and 6.87, respectively. The deuterium from the hydrido ligand is situated at the H_l position because the ^{1}H NMR spectrum of **3**-d_{31} does not contain the corresponding peak and shows the peak of H_m at δ 6.32 as a singlet. The correlation peaks in the H−C COSY NMR spectrum of **3** are consistent with the above assignment of ^{1}H NMR signals; ^{13}C NMR peak assignments are listed in Table 2. The ^{31}P{^{1}H} NMR spectrum of **3** exhibits two doublets of doublets due to two magnetically nonequivalent P nuclei arising from the coordination of the unsymmetric π-allyl ligand. Complexes **1**, **2**, and **4**−**6** show NMR peaks at positions similar to those of **3**, as summarized in Tables 2 and 3, and have similar 1,2-disubstituted π-allylic ligands, respectively, formed *via* the insertion of four molecules of the corresponding para-substituted phenylallene.

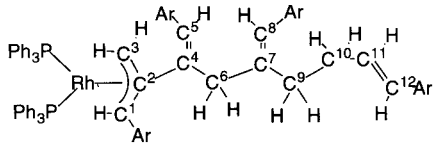
Reaction 1 in a 1:5 molar ratio gives complexes **1**−**6** selectively, among several other products such as Rh complexes with a coordinating arylallene tetramer with a structure different from **1**−**6** and complexes with a π-allylic ligand formed *via* the insertion of one, two, three, or five molecules of arylallene into the Rh−H bond. The reaction of phenylallene with RhH(PPh_3)$_4$ in a 3:1 molar ratio affords complex **1** in 35% yield after repeated recrystallization, while an equimolar reaction also gives **1**, but in a lower yield. These results suggest that isolation of complexes **1**−**6** is due not only to preferential crystallization of the products but also to their formation with high selectivity.

Scheme 3 depicts a plausible pathway for the formation of complexes **1**−**6**.

The insertion of an arylallene molecule into the Rh−H bond gives the (π-allyl)rhodium complex A, similar to an equimolar reaction of allene and phenylallene with RhH(CO)(PPh_3)$_3$.[10] Selective deuteration at the H_l position of **3**-d_{31} prepared from the reaction of (4-methoxyphenyl)allene with RhD(PPh_3-d_{15})$_4$ is consistent with the generation of the (π-allyl)rhodium intermediate A rather than the other 2-propenylrhodium complexes (M−C(=CHAr)CH_3 and M−C(=CH_2)CH_2Ar). Structure D found in the crystallographic study of **3** strongly indicates the presence of intermediates B and C, containing respectively a dimer and a trimer of arylallene as an η^1-bonded alkenyl ligand. The insertion of one arylallene molecule into the Rh−π-allyl bond of A gives the alkenylrhodium complex B, which undergoes further insertion of arylallene into the Rh−C bond to give an alkenyl group coordinated complex (C). The fourth arylallene molecule reacts with C to afford complex D, having the π-allylic-coordinated arylallene tetramer. We have no clear rationale for selective formation of product D, although steric demands of the oligomer bonded to the Rh center seem to influence the structure of the product and of the intermediate complexes. The formation of complex A involves an initial dissociation of a PPh_3 ligand to form RhH(PPh_3)$_3$, followed by the insertion of an arylallene molecule into the Rh−H bond.[12] Liberation of a second PPh_3 molecule, which may occur

(12) Yamamoto, T.; Miyashita, S.; Naito, Y.; Komiya, S.; Ito, T.; Yamamoto, A. *Organometallics* **1982**, *1*, 808.

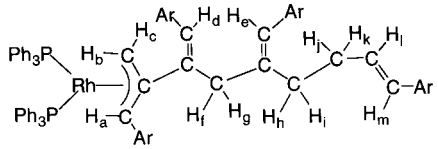
Table 2. ^{13}C and ^{31}P NMR Data for Complexes 1−6[a]



complex	$^{13}C\{^1H\}$ NMR	$^{31}P\{^1H\}$ NMR[b]
1	130.5 (C^{12}), 130.4 (C^{11}), 116.6 (C^2, J(CRh) = 7 Hz),76.1 (C^1, J(CRh) = 24 Hz, J(CP) = 7.3 Hz), 52.9 (C^3, J(CRh) = 29 Hz, J(CP) = 9.2 Hz), 38.7 (C^6), 32.2, 31.8 (C^9 and C^{10})	42.0 (193, 24), 39.8 (200, 24)
2	131.5 (C^{12}), 130.4 (C^{11}), 116.7 (C^2, J(CRh) = 6 Hz), 76.2 (C^1, J(CRh) = 24 Hz, J(CO) = 9 Hz), 52.4 (C^3, J(CRh) = 26 Hz, J(CO) = 7 Hz), 38.6 (C^6), 32.4, 31.8 (C^9 and C^{10}), 21.24, 21.20, 21.16 (CH_3)	42.4 (192, 24), 40.3 (200, 24)
3	135.44, 135.39, 135.3, 134.8, 134.6, 134.5, 132.4, 132.33, 132.28, 132.0, 131.7, 131.5, 131.4, 130.6 (C_6H_5 and C_6H_4), 130.5 (C_{12}), 130.3, 130.0 (C_6H_5 and C_6H_4), 128.6 (C_{11}), 116.8 (C_2, J(C_2Rh)=7.4 Hz), 114.5, 114.3, 114.2, 113.4 (C_6H_4), 71.9 (C_1, J(C_1Rh) = 23.9 Hz, J(C_1P) = 7.4 Hz)), 54.8, 54.74, 54.68 (OCH_3), 52.0 (C_3, J(C_3Rh) = 29.5 Hz, J(C_3P) = 9.2 Hz), 38.5 (C^6), 32.4 (C^{10}), 31.7 (C^9)	42.4 (193, 24), 40.5 (200, 24)
4	130.3 (C^{12}), 129.8 (C^{11}), 116.9 (C^2, J(CRh) = 7 Hz), 76.1(C^1, J(CRh) = 24 Hz, J(CP) = 7 Hz), 52.7 (C^3, J(CRh) = 26 Hz, J(CP) = 6 Hz), 38.8 (C^6), 31.9, 31.8 (C^9 and C^{10}), 31.64, 31.55 (CH_3)	42.4 (192, 24), 40.2 (200, 24)
5	130.0 (C^{12}), 129.5 (C^{11}), 115.8 (C^2, J(CRh) = 7 Hz), 74.3 (C^1, J(CRh) = 24 Hz, J(CP) = 9 Hz), 52.6 (C^3, J(CRh) = 26 Hz, J(CP) = 7 Hz), 38.6 (C^6), 31.8, 31.5 (C^9 and C^{10})	42.4 (192, 24), 40.5 (200, 24)
6	116.0 (C^2, J(CRh) = 7 Hz), 74.4(C^1, J(CRh) = 24 Hz, J(CP) = 7 Hz), 52.3 (C^3, J(CRh) = 28 Hz, J(CP) = 6 Hz), 38.4 (C^6), 31.9, 31.5 (C^9 and C^{10})	41.8 (193, 24), 39.8 (200, 24)

[a] Peaks due to C11 and C12 are significantly overlapped with the phenyl carbon peaks. [b] J(RhP) and J(PP) (Hz) are in parentheses.

Table 3. ^1H NMR Data for Complexes 1−6[a]



complex	H_a	H_b	H_c	$H_{f,g}$	H_{h-k}	H_l	H_m	other[b]
1	4.89 (br)	2.60 (d, 5)	3.47 (br)	3.70, 3.58 (AB q, 17)	2.25 (3H), 2.52 (1H) (m)	6.01 (ddd, 16, 8, 8)	6.23 (d, 16)	
2	4.91 (br)	2.71 (d, 6)	3.52 (br)	3.75, 3.60 (AB q, 18)	2.28 (1H), 2.61 (2H), 2.71 (1H) (m)	6.08 (ddd, 16, 8, 8)	6.30 (d, 16)	2.09, 2.12, 2.13, 2.16 (CH_3)
3	4.93 (br)	2.70 (d, 4)	3.56 (br)	3.78, 3.62 (AB q, 18)	2.28 (1H), 2.40 (2H), 2.65 (1H) (m)	6.03 (ddd, 16, 8, 8)	6.32 (d, 16)	3.27, 3.30, 3.33, 3.34 (OCH_3)
4	4.98 (br)	2.77 (d, 8)	3.56 (br)	3.80, 3.62 (AB q, 18)	2.29 (1H), 2.35 (2H), 2.69 (1H) (m)	6.17 (ddd, 16, 8, 8)	6.36 (d, 16)	1.19, 1.25 (CH_3)
5	4.60 (br)	2.58 (d, 4)	3.33 (br)	3.52, 3.45 (AB q, 18)	2.10 (3H), 2.36 (1H) (m)	5.78 (ddd, 16, 8, 8)	6.00 (d, 16)	
6	4.67 (br)	2.57 (d, 4)	3.38 (br)	3.55, 3.48 (AB q, 18)	2.13 (3H), 2.40 (1H) (m)	5.79 (ddd, 16, 8, 8)	6.08 (d, 16)	

[a] Measured at 25 °C in C_6D_6 (400 MHz). Figures in parentheses are the coupling constants. [b] Aromatic hydrogen peaks are observed at δ 6.4−7.9. Aromatic hydrogens other than PPh_3 ligands are overlapped with those due to PPh_3. The hydrogens of complex **3** were analyzed by using PPh_3-d_{15} to show the peaks at 7.56, 7.25, 7.20, 6.89, 6.76, and 6.70 (d, J = 8 Hz).

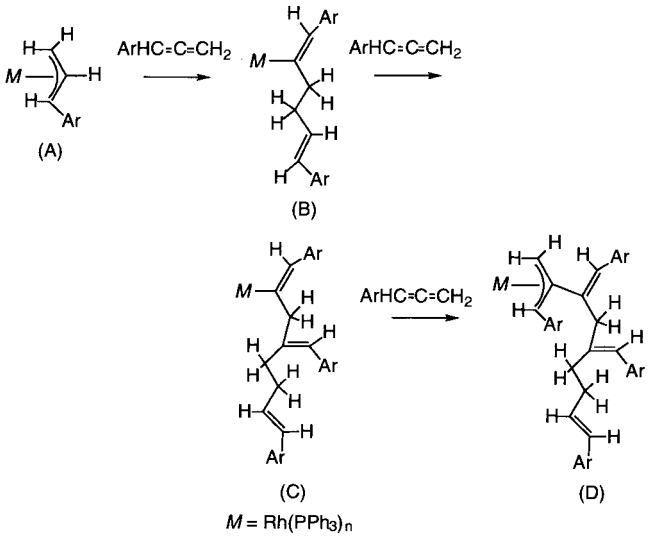
during the reactions shown in Scheme 3, involves the sequence η^3-allyl → alkenyl, alkenyl → alkenyl, and alkenyl → η^3-allyl.

Reaction of a large excess of phenylallene with $RhH(PPh_3)_4$ (10:1) at room temperature gives rise to isolation of **1** in high yield. Complexes **1** and **3** do not react further with arylallene at room temperature. The 1,2-disubstituted π-allylic ligand in **1** and **3** (structure D in Scheme 3) forms a more stable bond than the Rh−C σ bond of B and C and is more sterically demanding than the monosubstituted π-allyl group in A. These features of **1** and **3** prevent the complexes from further insertion of arylallene into the Rh−allyl bond. The poor reactivity of **1** and **3** toward insertion of arylallene into the Rh−C bond contrasts with the labile nature of the bond between Ni and the 1,2-disubstituted π-allylic ligand, which is found in the living polymer of monosubstituted allene promoted by Ni(II) complexes.[5]

The formation of **1**, even in the equimolar reaction of phenylallene and $RhH(PPh_3)_4$, suggests that the initial insertion of the substrate into the Rh−H bond to give A is much slower than the subsequent insertion of three arylallene molecules into the Rh−C bond. The reactant difference toward insertion of arylallene between $RhH(PPh_3)_4$ and intermediates A−C can be attributed to the requirement of PPh_3 dissociation from $RhH(PPh_3)_4$.

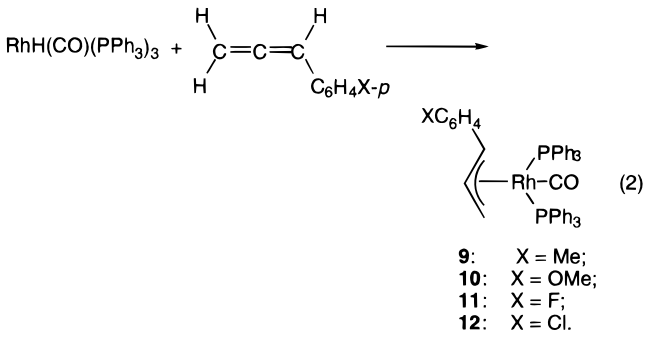
All these results are summarized as follows. $RhH(PPh_3)_4$ reacts with arylallene to give complexes **1**−**6**, containing the arylallene tetramer as the π-allylic ligand. Once an arylallene molecule has reacted with the Rh−H bond to give a (π-allyl)rhodium complex, the subsequent insertion of three arylallene molecules proceeds smoothly to give a product with the 1,2-disubstituted π-allylic ligand. The structure of the π-allylic ligand of the isolated major product does not depend on the substituent on the phenyl group and

Scheme 3



indicates a reaction route via (π-allyl)-, alkenyl-, and alkenylrhodium intermediates in that order to give the final product.

Preparation and Reaction of Rh(η^3-$CH_2CHCHAr$)(CO)(PPh_3)$_2$. Previously we reported that the equimolar reaction of phenylallene and of methoxyallene with $RhH(CO)(PPh_3)_3$ results in the single insertion of the substrate into the Rh−H bond to give Rh(η^3-$CH_2CHCHPh$)(CO)(PPh_3)$_2$ (**7**) and Rh(η^3-$CH_2CHCHOMe$)(CO)(PPh_3)$_2$ (**8**), respectively.[10] Reactions of the *p*-substituted phenylallenes with $RhH(CO)(PPh_3)_3$ also give the complexes Rh(η^3-$CH_2CHCHC_6H_4X$-*p*)(CO)(PPh_3)$_2$ (**9**, X = Me; **10**, X = OMe; **11**, X = F; **12**, X = Cl).



The complexes were characterized by NMR spectroscopy as well as X-ray crystallography of **9** (Figure 3), showing a syn orientation of the aryl substituent of the π-allylic ligand.

Multiple insertion of phenylallene into the Rh−H bond of $RhH(CO)(PPh_3)_3$ and into the Rh−π-allyl bond of **7** was examined. The former reaction at room temperature afforded mixtures of **1** and **7** along with unreacted $RhH(CO)(PPh_3)_3$, while the latter gave a mixture of **1** and **7** in a 23:77 molar ratio. No other Rh complexes were contained in the reaction mixture. In this reaction, insertion of phenylallene into the Rh−C bond occurs smoothly until the stable complex **1** is formed or does not occur at all. The monosubstituted π-allylic ligand in the above complexes shows higher reactivity than do **1** and **3**. The (π-allyl)rhodium complex **7** reacts with phenylacetylene at room temperature to give Rh(C≡CPh)(CO)(PPh_3)$_2$ (**13**), accompanied by the liberation of 1-phenylpropene in quantitative yield.

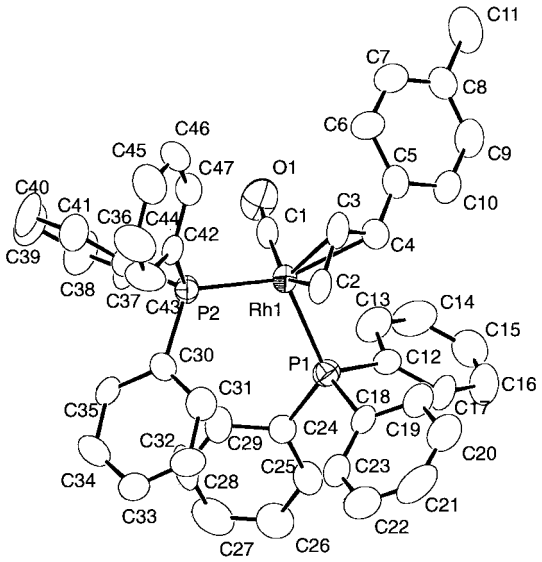


Figure 3. ORTEP drawing of Rh(η^3-$CH_2CHCHC_6H_4Me$-*p*)(CO)(PPh_3)$_2$ (**9**) with 50% probability atomic displacement ellipsoids. Hydrogen atoms were omitted for simplicity.

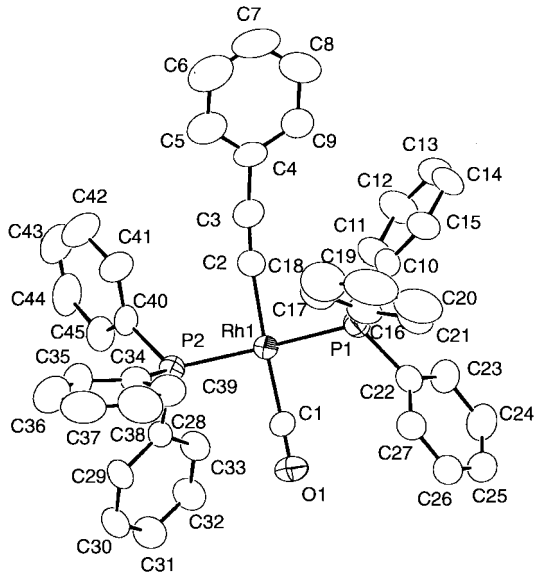
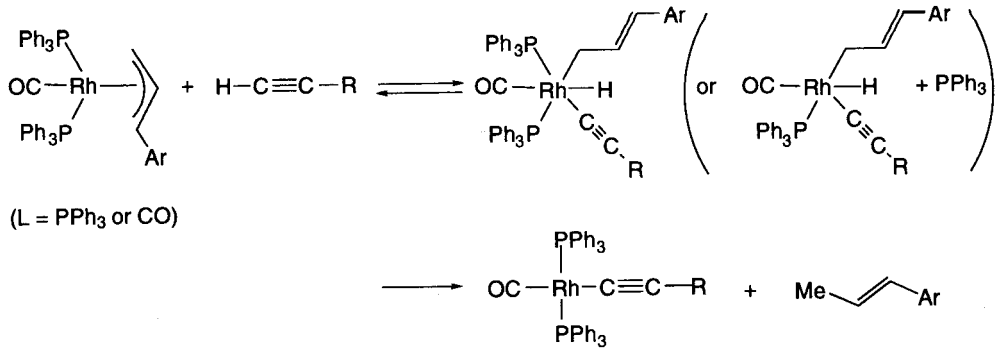


Figure 4. ORTEP drawing of *trans*-Rh(C≡CPh)(CO)(PPh_3)$_2$ (**13**) with 50% probability atomic displacement ellipsoids. Hydrogen atoms were omitted for simplicity.

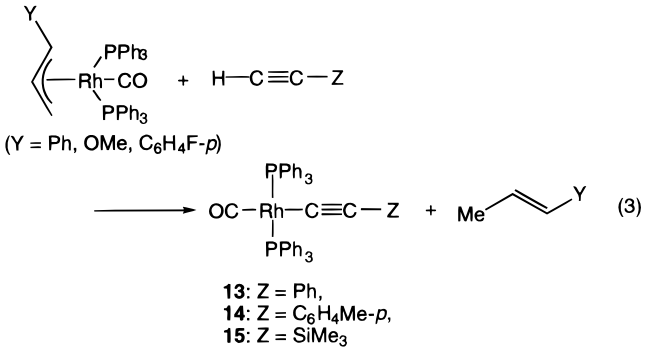
Analogous alkynylrhodium and -iridium(I) complexes were prepared from the reaction of phenylacetylene with alkoxido complexes.[13] Complex **13** has a trans coordination around the Rh center, as depicted in Figure 4. The alkynyl ligand bonded to the Rh center shows negligible elongation of the C≡C triple bond or shortening of the Rh−C bond, indicating only a small contribution from a vinylidene structure for the ligand (M^-=C=C^+−Ph). Similar reactions of (π-allyl)rhodium complexes with terminal alkynes produce the alkynyl-

(13) Fernández, M. J.; Esteruelas, M. A.; Covarrubias, M.; Oro, L. A. *J. Organomet. Chem.* **1990**, *381*, 275. For other alkynylrhodium complexes, see: Abu Salah, O. M.; Bruce, M. I. *J. Chem. Soc., Chem. Commun.* **1974**, 688. Abu Salah, O. M.; Bruce, M. I. *Aust. J. Chem.* **1977**, *30*, 2639.

Scheme 4



rhodium(I) complexes with CO and PPh_3 ligands, as shown in eq 3. The reaction of the π-allylic rhodium



complex with 18 electron metal center can be explained by a reaction path that involves the initial formation of 16 electron species through η^3 to η^1 conversion of the allylic ligand or dissociation of a PPh_3 ligand, followed by oxidative addition of C−H bond of the terminal alkyne (Scheme 4). Reductive elimination of 1-arylpropene from the Rh(III) intermediate seems to occur more rapidly than that of the terminal alkyne.

The present study has disclosed that arylallene smoothly reacts with hydridorhodium complexes to result in single or quadruple insertion of the unsaturated molecule into the Rh−H bond at room temperature. The 1,2-disubstituted (π-allyl)rhodium complexes show poor reactivity toward insertion of the arylallene molecule into their Rh−π-allyl bond. These results may be related to the low efficiency of hydridorhodium complexes as the initiators of arylallene polymerization.[7d,f]

Experimental Section

General Considerations, Measurement, and Materials. Manipulation of the Rh complexes was carried out under nitrogen or argon using standard Schlenk techniques. $RhH(PPh_3)_4$, $RhD(PPh_3\text{-}d_{15})_4$, $RhH(CO)(PPh_3)_3$, arylallenes, and complex **7** were prepared according to the literature.[10b,14] NMR spectra (^1H, ^{13}C, and ^{31}P) were recorded on a JEOL EX-400 spectrometer. $^{31}P\{^1H\}$ NMR peak positions were referenced to external 85% H_3PO_4. Elemental analyses were carried out using a Yanaco MT-5 CHN autocorder.

Preparation of 1−6. To a toluene (10 mL) solution of $RhH(PPh_3)_4$ (570 mg, 0.50 mmol) was added (4-methoxyphenyl)allene (362 mg, 2.5 mmol) at room temperature. The initial orange solution turned red on stirring. After 2 h the solvent was reduced to ca. 1 mL under vacuum. Slow addition of hexane to the solution caused the separation of an orange solid, which was collected by filtration, washed twice with hexane, and dried *in vacuo* to give **1** as an orange-red microcrystalline solid (510 mg, 85%). The complex thus obtained was analytically pure but can be recrystallized from acetone to give red single crystals (80% yield).

Preparation of **2**−**6** was carried out analogously.

Preparation of 9−12. To a toluene (10 mL) solution of $RhH(CO)(PPh_3)_3$ (327 mg, 0.36 mmol) was added (4-methylphenyl)allene (56 mg, 0.43 mmol) at room temperature. After 14 h, the solvent was evaporated to dryness. Addition of hexane to the resulting brown paste caused separation of a yellow solid, which was collected by filtration and recrystallized from THF−hexane to give **9** as yellow crystals (180 mg, 64%). Anal. Calcd for $C_{47}H_{41}OP_2Rh$: C, 71.76; H, 5.25. Found: C, 71.52; H, 5.26. ^1H NMR (400 MHz, in C_6D_6): δ 1.7 (br, 2H, *syn* and *anti*), 2.14 (s, 3H, CH_3), 3.79 (d, 1H, J = 9 Hz, *anti*), 5.20 (dddd, 1H, J = 9, 7, 7, and 2 Hz, central), 7.09−7.50 (m, 34H, aromatic).

Complexes **10**−**12** were prepared analogously. Data for **10** are as follows. Yield: 48%. Anal. Calcd for $C_{47}H_{41}O_2P_2Rh$: C, 70.33; H, 5.15. Found: C, 70.71; H, 5.40. ^1H NMR (400 MHz, in C_6D_6): δ 1.7 (br, 2H, *syn* and *anti*), 3.35 (s, 3H, OCH_3), 3.82 (d, 1H, J = 9 Hz, *anti*), 5.14 (dddd, 1H, J = 9, 7, 7, and 2 Hz, central), 7.51−6.85 (m, 34H, aromatic). IR (KBr) ν(C≡O): 1943 cm^{-1}. Data for **11** are as follows. Yield: 62%. Anal. Calcd for $C_{46}H_{38}FOP_2Rh$: C, 69.88; H, 4.84. Found: C, 69.72; H, 5.14. ^1H NMR (400 MHz in C_6D_6): δ 1.5 (br, 2H, *syn* and *anti*), 3.65 (d, 1H, J = 10 Hz, *anti*), 5.08 (dddd, 1H, J = 10, 7, 7, and 2 Hz, central), 6.85−7.46 (m, 34H, aromatic). IR (KBr): ν(C≡O), 1951 cm^{-1}. Data for **12** are as follows. Yield: 61%. Anal. Calcd for $C_{46}H_{38}COP_2Rh$: C, 68.45; H, 4.74. Found: C, 67.70; H, 4.74. ^1H NMR (400 MHz at 25 °C, in CD_2Cl_2): δ 1.7 (br, 2H, *syn* and *anti*), 3.25 (d, 1H, J = 10 Hz, *anti*), 4.81 (dddd, 1H, J = 10, 7, 7, and 2 Hz, central), 7.15−7.46 (m, 34H, aromatic). ^1H NMR (400 MHz at −70 °C, in CD_2Cl_2): δ 0.55 (dd, 1H, J = 22 and 8 Hz, *anti*), 1.55 (dd, 1H, J = 11 and 6 Hz, *syn*), 3.08 (ddd, 1H, J = 15, 9, and 7 Hz, *anti*), 4.58 (br, 1H, central), 6.98−7.66 (m, 34H, aromatic). $^{31}P\{^1H\}$ NMR (160 MHz at −40 °C in CD_2Cl_2): δ 21.9 (dd, J = 141 and 35 Hz), 41.4 (dd, J = 157 and 35 Hz). IR (KBr): ν(C≡O), 1948 cm^{-1}.

Reaction of Alkynes with (π-Allyl)rhodium Complexes 7, 8, and 11. A mixture of **7** (555 mg, 0.72 mmol) and phenylacetylene (183 mg, 1.8 mmol) was dissolved in toluene (10 mL) at room temperature. After 1 h, formation of 1-phenylpropene in a quantitative yield was confirmed by GC analysis. The solvent was evaporated to dryness. Addition of hexane to the resulting oily product caused the separation of a yellow solid, which was collected by filtration and recrystallized from Et_2O to give **13** as yellow crystals (81%). Anal. Calcd for $C_{45}H_{35}OP_2Rh$: C, 71.44; H, 4.66. Found: C,

(14) (a) Levinson, J. J.; Robinson, S. D. *J. Chem. Soc. A* **1970**, 2497. (b) Strauss, S. H.; Diamond, S. E.; Mares, F.; Shriver, D. F. *Inorg. Chem.* **1978**, *17*, 3064. (c) Jardin, F. H. *Polyhedron* **1982**, *1*, 569 and references therein. (d) Osakada, K.; Matsumoto, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1985**, *4*, 857. (e) Moore, W. R.; Ward, H. R. *J. Org. Chem.* **1962**, *27*, 4179.

70.93; H, 4.71. ^{1}H NMR (400 MHz, in C_6D_6): δ 6.67 (d, 2H, J = 8 Hz, *ortho*), 6.78 (t, 1H, J = 8 Hz, *para*), 6.87 (t, 2H, J = 8 Hz, *meta*), 7.05 and 7.99 (m, 30H, C_6H_5). ^{13}C{^{1}H} NMR (100 MHz, in CD_2Cl_2): δ 123.7 (d, *C*≡CPh, J(RhC) = 11 Hz), 125.1 (C≡*C*Ph), 127.6, 127.9, 129.8, 131.1, 135.0, 135.1, 194.1 (d, *C*O, J(RhC) = 59 Hz). ^{31}P{^{1}H} NMR (160 MHz in CD_2Cl_2) δ 34.0 (d, J(RhP) = 121 Hz). IR (KBr): ν(C≡C), 2336 cm^{-1}; ν(C≡O), 1968 cm^{-1}.

Similar reaction of phenylacetylene with **7** in a 1:1 molar ratio gave **13** in 80% yield. Reaction of phenylacetylene with **11** in a 3:1 molar ratio did not occur at room temperature, whereas reactions of (4-methylphenyl)acetylene and of (trimethylsilyl)acetylene with **11** (3:1 molar ratio) gave **14** (83%) and **15** (90%), respectively. Data for **14** are as follows. Anal. Calcd for $C_{46}H_{37}OP_2Rh$: C, 71.69; H, 4.84. Found: C, 70.40; H, 4.96. ^{1}H NMR (400 MHz in C_6D_6): δ 1.95 (s, 3H, CH_3), 6.60 (d, 2H, J = 8 Hz, *meta*), 6.69 (d, 1H, J = 8 Hz, *meta*), 7.05 (m, 18H, C_6H_5), 8.02 (d, 12H, J = 7 Hz, C_6H_5). ^{13}C{^{1}H} NMR (100 MHz, in CD_2Cl_2): δ 21.2, 122.1 (d, *C*≡CPh, J(RhC) = 40 Hz), 123.8 (d, C≡*C*Ph, J(PC) = 11 Hz), 126.1, 127.9, 128.4, 129.8, 131.1, 134.4, 134.8, 135.1, 194.1 (d, *C*O, J(RhC) = 59 Hz). ^{31}P{^{1}H} NMR (160 MHz in CD_2Cl_2): δ 33.7 (br). Data for **15** are as follows. Anal. Calcd for $C_{42}H_{39}OP_2SiRh$: C, 67.02; H, 5.22. Found: C, 66.48; H, 5.21. ^{1}H NMR (400 MHz, in C_6D_6): δ −0.17 (s, 9H, CH_3), 7.12 (m, 18H, C_6H_5), 7.96 (d, 12H, J = 7 Hz, C_6H_5). ^{13}C{^{1}H} NMR (100 MHz, in CD_2Cl_2): δ 0.94, 128.1, 129.0 (d, C≡*C*Si, J(PC) = 9 Hz), 129.8, 135.2, 144.9 (d, *C*≡CSi, J(RhC) = 39 Hz), 194.1 (d, *C*O, J(RhC) = 59 Hz). ^{31}P{^{1}H} NMR (160 MHz in CD_2Cl_2): δ 33.5 (br).

X-ray Crystallographic Study. Crystals of **9** and **13** suitable for crystallography were obtained by recrystallization from Et_2O at −20 °C. The data were collected on a Rigaku AFC5R diffractometer at ambient temperature (23 °C) using the ω scan mode ($2\theta \leq 50°$). Correction for Lorentz and polarization effects and an empirical absorption correction (Ψ scan) were applied. Atomic scattering factors were taken from the literature.[15] The structure was solved by a combination of direct methods and subsequent Fourier techniques. The positional and thermal parameters of non-hydrogen atoms were refined anisotropically, while hydrogen atoms were located by assuming an ideal geometry.

X-ray data for **9**: monoclinic, $P2_1/c$ (No. 14), a = 9.576(3) Å, b = 18.477(9) Å, c = 21.752(4) Å, β = 91.78(2)°, V = 3847 Å^3, Z = 4, D_{calc} = 1.358 g cm^{-3}, F(000) = 1624, μ(Mo Kα) = 5.61 cm^{-1} for monochromated Mo Kα radiation (λ = 0.710 69 Å). R (R_w) = 0.056 (0.040) for 3992 reflections with $I > 3\sigma(I)$ among 7216 unique reflections (R_{int} = 0.055). GOF = 2.40. X-ray data for **13**: monoclinic, $P2_1/a$ (No. 14), a = 12.295(2) Å, b = 18.635(5) Å, c = 17.673(5) Å, β = 103.86(2)°, V = 3930 Å^3, Z = 4, D_{calc} = 1.278 g cm^{-3}, F(000) = 1552, μ(Mo Kα) = 5.47 cm^{-1} for monochromated Mo Kα radiation (λ = 0.710 69 Å). R (R_w) = 0.052 (0.049) for 3460 reflections with $I > 3\sigma(I)$ among 8773 unique reflections (R_{int} = 0.214). GOF = 1.28.

Acknowledgment. This work was financially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Culture, and Sports of Japan.

Supporting Information Available: Tables giving crystallographic data for complexes **9** and **13** (17 pages). Ordering information is given on any current masthead page.

OM9801711

(15) *International Tables for X-ray Crystallography;* Kynoch: Birmingham, U.K., 1974; Vol. IV.