Rhodium(I) Complexes with π-Coordinated Arylallene. Structures in the Solid State and in Solution and Reaction with Arylallene To Give Rhodacyclopentane

Jun-Chul Choi, Susumu Sarai, Take-aki Koizumi, Kohtaro Osakada,* and Takakazu Yamamoto*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

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Reactions of phenylallene and of (4-fluorophenyl)allene with $[Rh(\mu\text{-}Cl)(PMe_3)_2]_2$ (Rh: arylallene = 1:1) give Rh(I) complexes with π-coordinated arylallene, $RhCl(\eta^2\text{-}CH_2{=}C{=}CHAr)(PMe_3)_2$ (**1a**, Ar = C_6H_5; **1b**, Ar = C_6H_4F-*p*). X-ray crystallography of **1a**,**b** has established their square-planar coordination around the rhodium center, which is bonded to the 2,3-double bond of the arylallene. The aryl group of the ligand and the Rh center are situated on the same side of the uncoordinated 1,2-double bond. The position of an *ortho* hydrogen of the phenyl group in the ligand suggests an agostic interaction between the C−H group and the Rh center. Dissolution of **1a** in benzene results in equilibration with its isomer **3a**, which does not have a close contact between the *ortho* C−H group of the ligand and the Rh center. The ^{1}H NMR spectra of an equilibrated mixture in the temperature range 30−55 °C afford thermodynamic parameters for **3a**↔**1a** of $\Delta H° = -5.0$ kJ mol^{-1} and $\Delta S° = -8$ J mol^{-1} K^{-1}. The arylallenes react also with $RhCl(PMe_3)_3$ in a 1.2:1 molar ratio to yield pentacoordinated Rh(I)−arylallene complexes, $RhCl(\eta^2\text{-}CH_2{=}C{=}CHAr)(PMe_3)_3$ (**2a**, Ar = C_6H_5; **2b**, Ar = C_6H_4F-*p*). A crystallographic study of **2b** shows a distorted trigonal-bipyramidal coordination around the Rh center, which is bonded to equatorial Cl, PMe_3, and 2,3-η^2-$CH_2{=}C{=}CHAr$ ligands and to two apical PMe_3 ligands. The 4-fluorophenyl group of the ligand and the Rh center are situated on opposite sides of the uncoordinated C=C double bond. Complex **2a** is in equilibrium with its isomer **4a**, which shows dynamic NMR behavior on the NMR time scale. Reactions in a 3:1 molar ratio give rhodacyclopentanes, *mer*-$Rh[CH_2C(=CHAr)C(=CHAr)CH_2]Cl(PMe_3)_3$ (**5a**, Ar = C_6H_5; **5b**, Ar = C_6H_4F-*p*) as the main product. Complex **5a** is also obtained from reaction of phenylallene with **2a**. Reactions of (4-fluorophenyl)allene with $RhCl(PEt_3)_3$, $RhCl\{P(i\text{-}Pr)_3\}_2$, and $RhCl(PPh_3)_3$ proceed smoothly to give the corresponding Rh(I)−(4-fluorophenyl)allene complexes, $RhCl(\eta^2\text{-}CH_2{=}C{=}CHC_6H_4F\text{-}p)(PR_3)_2$ (**6**, R = Et; **7**, R = *i*-Pr; **8**, R = Ph). The ^{1}H NMR spectra of the complexes and X-ray crystallography of **8** indicate square-planar coordination around the Rh center, which is bonded to the 2,3-double bond of the arylallene.

Introduction

Rh(I) complexes catalyze polymerization or cyclooligomerization of 1,2-dienes depending on auxiliary ligands of the complexes and reaction conditions. Catalysts such as $RhCl(PPh_3)_3$, $[RhCl(CH_2{=}CH_2)_2]_2{-}PPh_3$ mixture, and $[RhCl(CO)_2]_2{-}PPh_3$ mixture lead to cyclooligomerization of 1,2-propadiene.[1] Chlorocarbonylrhodium(I) complexes, $[RhCl(CO)_2]_2$, $RhCl(CO)_3$, and $RhCl(CO)_2(PPh_3)$, have a tendency to initiate allene polymerization rather than cyclooligomerization.[2] Phenylallene undergoes polymerization in the presence of $[RhCl(CO)_2]_2$ to give the polymer formulated as $-[CH_2{-}C(=CHPh)]_n-$.[3] Use of $RhH(PPh_3)_4$ or $CoH(N_2)(PPh_3)_3$ as the catalyst improves the polymer yield.[4]

Detailed studies of the reaction of 1,2-dienes with chlororhodium(I) complexes in equimolar amounts or in low substrate/catalyst ratios could provide a clue to reactions that initiate the polymerization and oligomerization of 1,2-dienes. There seem to be several possible reactions of 1,2-dienes and chlororhodium(I) complexes in stoichiometric amounts: (i) π-coordination of a C=C double bond to Rh center, (ii) insertion of a double bond into the Rh−Cl bond, and (iii) 2:1 cycloaddition to give a five-membered rhodacyclopentane, as depicted in Scheme 1.

Insertion of allene into the Rh−Cl bond (ii) and

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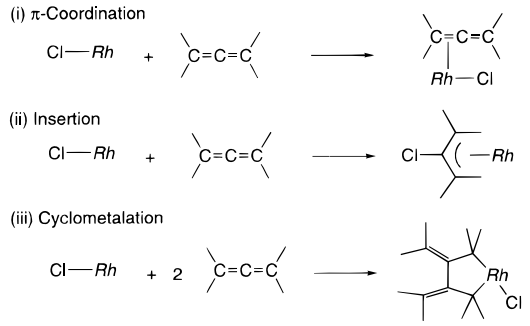
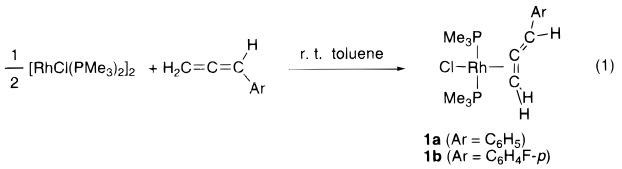
Scheme 1



cyclometalation (iii) would initiate the catalytic polymerization and cyclooligomerization, respectively. π-Coordination of allene or related cumulenes to transition metals is known for Ni(0), Pt(0), Fe(0), and Rh(I) complexes,[5] although it is less common than coordination of alkenes. The Ni(0)−allene complex is regarded as an intermediate in the reaction of allene with a Ni(0) complex with CO_2 and HOMe to give methyl methacrylate.[5f] Insertion of a double bond of allene into a Pd−Cl bond gives the corresponding π-allylic complex.[6] There have been fewer reports on metallacycle formation from the 2:1 reaction of allene and transition metal complexes[7] than on cyclometalation of alkenes and various transition metals such as Ti, Ta, Co, Ir, and Ni.[8] In this paper, we report preparation and structure of π-coordinated arylallene−Rh(I) complexes containing auxiliary phosphine ligands. Their further reaction with arylallene to give a rhodacyclopentane is also described. A part of this work has been reported in a preliminary form.[9]

Results

Rhodium(I) Complexes Having a π-Coordinated Arylallene Ligand. Reactions of phenylallene and of (4-fluorophenyl)allene with $[Rh(\mu\text{-}Cl)(PMe_3)_2]_2$ (Rh:arylallene = 1:1) give phenylallene-coordinated Rh(I) complexes, $RhCl(\eta^2\text{-}CH_2{=}C{=}CHAr)(PMe_3)_2$ (**1a**, Ar = C_6H_5; **1b**, Ar = C_6H_4F-*p*), as pale yellow crystals.



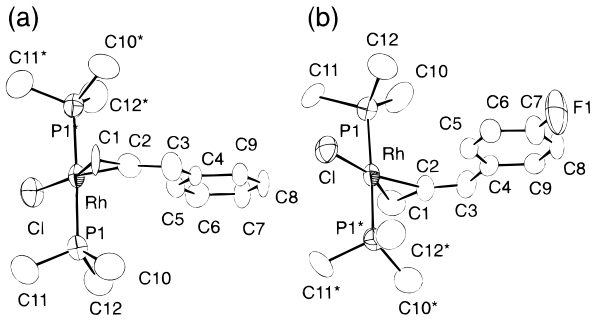
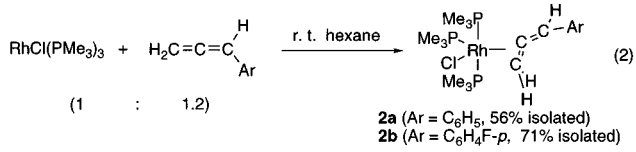


Figure 1. ORTEP drawing of (a) $RhCl(\eta^2\text{-}CH_2{=}C{=}CHPh)(PMe_3)_2$ (**1a**) and (b) $RhCl(\eta^2\text{-}CH_2{=}C{=}CHC_6H_4F\text{-}p)(PMe_3)_2$ (**1b**) at 50% probability level. Hydrogens are omitted for simplicity.

Figure 1 shows X-ray crystal structures of **1a**,**b**, which, as expected, are similar. Selected bond distances and angles are summarized in Table 1. The Rh center has a square-planar coordination, with two PMe_3 ligands at mutually trans positions. The molecules contain a crystallographic mirror plane including Rh, Cl, and carbon atoms of the coordinated arylallene molecule. The uncoordinated C=C double bond of **1a**,**b** has the phenyl group and the Rh center on the same side. Nonbonding distances between an *ortho* hydrogen of the phenyl group and the Rh center (**1a**, 2.75 Å; **1b**, 2.66 Å) are less than the expected sum of van der Waals radii of H and 4d transition metals and imply the presence of an agostic interaction between the C−H group and the metal center.[10]

$RhCl(PMe_3)_3$ reacts with equimolar arylallenes in hexane to give $RhCl(\eta^2\text{-}CH_2{=}C{=}CHAr)(PMe_3)_3$ (**2a**, Ar = C_6H_5; **2b**, Ar = C_6H_4F-*p*). The coordination geometry



of **2b** around the Rh center in Figure 2 can be rationalized as a distorted trigonal bipyramid containing phosphorus atoms (P1 and P3) occupying two apical positions. Carbon atoms bonded to the metal center (C1 and C2) are included in the equatorial coordination plane. Elongation of the C1−C2 bond (1.42 Å) compared to the C2−C3 bond (1.34 Å) and C=C double bonds of common organic molecules and bend in the C1=C2=C3 fragment (142°) suggest significant back-donation, which is common to most late transition metal complexes containing a π-coordinated C=C double bond. The 4-fluorophenyl

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Table 1. Selected Bond Distances (Å) and Angles (deg) of 1a, 1b, 2a, 2b, and 8

	1a	1b	2a[a]	2b	8
Rh−Cl	2.391(6)	2.386(4)	2.540(2)	2.549(4)	2.361(2)
Rh−P1	2.303(3)	2.308(2)	2.320(2)	2.320(5)	2.346(2)
Rh−P2			2.323(2)	2.336(4)	2.336(2)
Rh−P3			2.325(2)	2.308(4)	
Rh−C1	2.07(2)	2.08(1)	2.126(7)	2.15(1)	2.094(5)
Rh−C2	2.01(2)	1.99(1)	1.988(6)	1.97(2)	2.004(6)
C1−C2	1.35(2)	1.41(2)	1.406(9)	1.42(2)	1.384(4)
C2−C3	1.35(3)	1.31(1)	1.353(9)	1.34(2)	1.321(8)
C3−C4	1.46(2)	1.44(2)	1.477(10)	1.48(2)	1.460(7)
Cl−Rh−P1	87.5(2)	87.94(9)	84.79(7)	83.6(1)	88.88(6)
Cl−Rh−P2			97.80(7)	98.2(2)	90.33(7)
Cl−Rh−P3			83.36(7)	84.9(2)	
P1−Rh−P2			96.74(7)	97.0(2)	170.55(6)
P1−Rh−P3			162.98(7)	163.3(2)	
P2−Rh−P3			96.94(7)	96.6(2)	
P1−Rh−P1*	174.8(3)	175.8(2)			
Cl−Rh−C1	161.2(5)	161.2(5)	118.3(2)	117.6(4)	163.3(2)
Cl−Rh−C2	160.3(6)	158.2(3)	158.0(2)	157.4(5)	157.2(2)
C1−Rh−C2	38.5(7)	40.5(5)	39.8(3)	39.9(5)	39.4(2)
C1−C2−C3	152(1)	146(1)	142.1(7)	142(1)	152.2(6)
C2−C3−C4	131(1)	127(1)	126.9(7)	125(1)	124.3(5)
C3−C4−C5	123(1)	124(1)	122.3(7)	120(1)	123.5(6)

[a] Taken from ref 9.

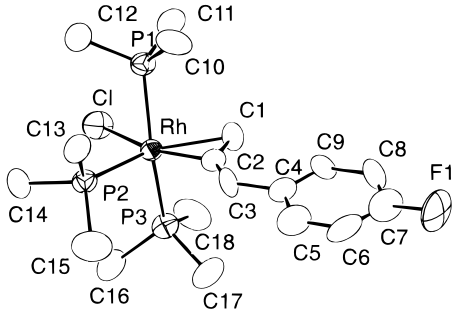


Figure 2. ORTEP drawing of $RhCl(\eta^2\text{-}CH_2{=}C{=}CHC_6H_4F\text{-}p)(PMe_3)_3$ (**2b**) at 50% probability level. Hydrogens are omitted for simplicity.

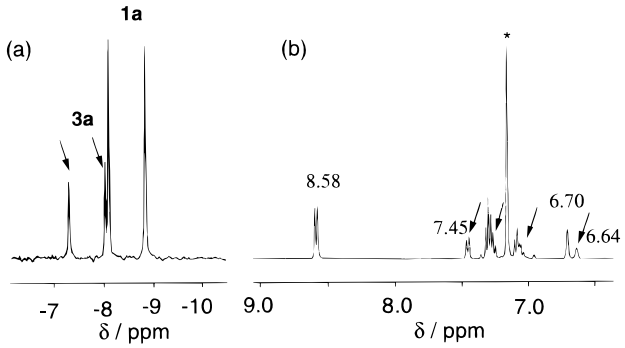


Figure 3. (b) ^1H (400 MHz) and (a) $^{31}P\{^1H\}$ (160 MHz) NMR spectra of a C_6D_6 solution of an equilibrated mixture of **1a** at 25 °C. Peaks with an arrow are due to **3a** generated in the solution through isomerization of **1a**. The solvent peak is marked with an asterisk.

group and Rh center exist on opposite sides of the uncoordinated C═C bond, thus reducing steric congestion between the aryl group and a PMe_3 ligand within the equatorial coordination plane. These crystallographic results of **2b** are similar to those of **2a** reported in a preliminary communication.[9]

Although **1a** and **2a** are isolated as crystals, the NMR spectra of the complexes in solution demonstrate the presence of an equilibration of the complexes with their isomers. Figure 3 shows the ^1H and $^{31}P\{^1H\}$ NMR spectra of a C_6D_6 solution of **1a**. The $^{31}P\{^1H\}$ NMR spectrum contains two pairs of signals with different intensities at δ −8.5 and −7.7, indicating the existence of two Rh complexes. The peak intensity ratio varies reversibly depending on temperature due to equilibrium between **1a** and its isomer. The ^1H NMR spectrum at 25 °C shows two signals due to a vinylic CH hydrogen of the phenylallene ligand at δ 6.70 and 6.64 in a 74:26 peak area ratio and those due to the *ortho* phenyl hydrogens at δ 8.58 and 7.45 in a similar ratio.[11] Peaks of the *meta* and *para* hydrogens of the two complexes are observed as two pairs of partly overlapped two triplet signals at δ 7.26−7.29 and 7.06−7.08, respectively. The $^{13}C\{^1H\}$ NMR spectrum also shows signals due to the two isomeric complexes. The signal of the *ortho* carbons of the major complex appears at a higher magnetic field position (δ 127.6) than that of the *meta* carbon signal (δ 128.4), while the minor complex shows the *ortho* and *meta* carbon signals at δ 128.8 and 125.7, respectively. The $^1J(CH)$ value of the C−H group at the *ortho* position of the major complex (157 Hz) is smaller than those of the *ortho* C−H group of the minor isomer (160 Hz) and of uncoordinated phenylallene (160 Hz). The $^{13}C\{^1H\}$ NMR data of the *ortho* C−H group, including the upfield shift of the peak and the relatively smaller $^1J(C{-}H)$ value, suggests that **1a** has a C−H··· Rh agostic interaction.[12] The minor isomer **3a** is assigned to a structure without an agostic interaction (Scheme 2), based on the $^1J(CH)$ value and NMR data similar to those of **1a**, except for the ^1H NMR peak position of the *ortho* hydrogens. The different structures of **1a** and **3a** arise from opposite coordination modes of the 2,3-double bond plane of the ligand. The Rh center

(11) Peak area of the ^1H NMR signal at δ 8.58 corresponds to two hydrogens of **1a** in the solution. Rotation of the C−C single bond between allenyl and phenyl groups seems to occur much faster than the NMR time scale.

(12) The $^1J(CH)$ value is obtained as average of that of the two *ortho* C−H groups of the ligand. The coupling constants of the C−H groups with and without the agostic interaction are estimated as 154 and 160 Hz, respectively.

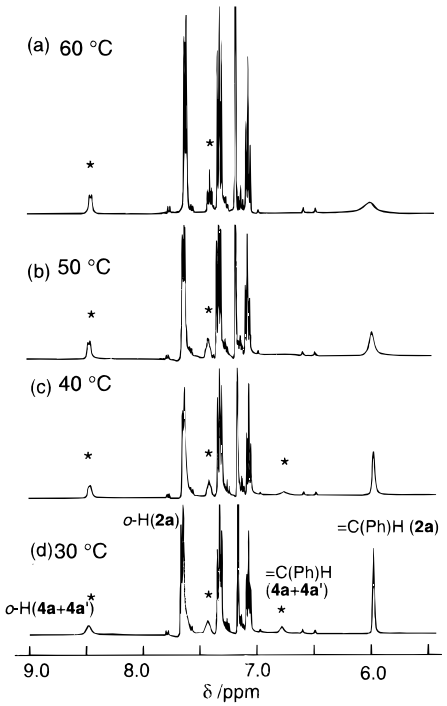
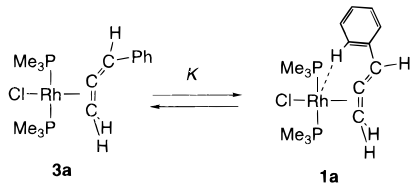


Figure 4. ^{1}H NMR spectra (400 MHz) of an equilibrated mixture of (**4a** + **4a′**) and **2a** at (a) 30, (b) 40, (c) 50, and (d) 60 °C. Peaks with an asterisk are due to the *ortho, meta,* and C(Ph)(H)═ hydrogens of **4a** and **4a′**. The peak due to the *para* hydrogen of **4a** is overlapped with the corresponding peak of **2a**.

Scheme 2



of **1a** faces the phenyl group, whereas it is at the reverse side of the C═C double bond in **3a**. Since the ratio of the two isomers reaches ca. 76:24 in a short period (<10 min) after dissolution of single crystals of **1a** in benzene-d_6 at room temperature and does not change further, rapid equilibrium exists between **1a** and **3a** (Scheme 2). A linear van't Hoff plot obtained from temperature-dependent changes in the relative peak area ratio of *ortho* hydrogens of **1a** and **3a** gives the thermodynamic parameters of the reaction, $\Delta H° = -5.0$ kJ mol^{-1} and $\Delta S° = -8$ J mol^{-1} K^{-1}.

The NMR spectrum of a solution of **2a** containing a small amount of added PMe_3 ([PMe_3]/[**2a**] = 0.1) shows the presence of **2a** as the sole Rh-containing species after 1 h below 0 °C. Dissolution of **2a** in benzene at 25 °C causes the appearance of new NMR signals. Figure 4 shows the temperature-dependent changes in the ^{1}H NMR spectra of the benzene-d_6 solution of **2a**; the new peaks indicated with asterisks. The intensity of the new peaks (δ 8.47 and 7.42) due to *ortho* and *meta* hydrogens of the newly formed complex increases, accompanied by peak sharpening on raising the temperature. One of the new peaks at δ 8.47 can be assigned to an *ortho* hydrogen of a complex containing an agostic interaction with the Rh center by comparing its position with that of **1a** (δ 8.58). The ^{31}P{^{1}H} NMR

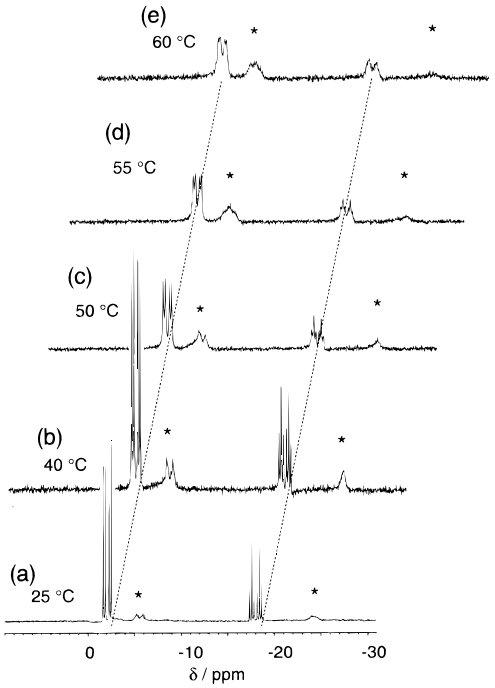
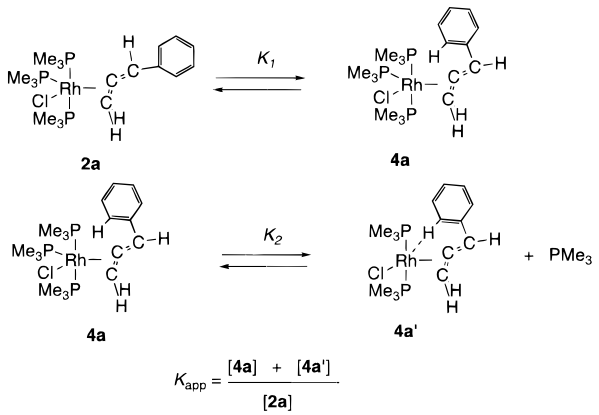


Figure 5. ^{31}P{^{1}H} NMR spectra (160 MHz) of an equilibrated mixture of **4a** and **2a** at (a) 25, (b) 40, (c) 50, (d) 55, and (e) 60 °C. Peaks with asterisks are due to **4a** and **4a′**.

Scheme 3



spectrum at 25 °C shows a doublet of doublets (δ −2.1) and a doublet of triplets (δ −18.1) due to the major complex **2a** and two new broad signals at δ −5.6 and −24.1 assigned to the newly formed complex **4a**, as shown in Figure 5. The breadth of the new peaks at δ −24.1 suggests exchange of the PMe_3 ligands on the NMR time scale at the newly formed complex. Raising the temperature causes a decrease in the relative intensity of the peak due to **2a**, accompanied by broadening of the new peaks. At 50−60 °C, the signal at δ −5.6 shows a significant increase in its intensity, whereas the signal at δ −24.1 becomes negligible.

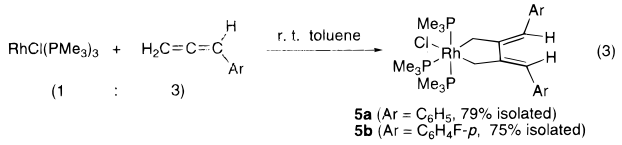
Scheme 3 depicts a plausible reaction scheme to account for the NMR results. Complex **2a** undergoes a reversible isomerization to **4a**, which is further equilibrated with **4a′** a stereoisomer of **1a** through partial liberation of PMe_3. The new ^{31}P{^{1}H} NMR peaks at δ −24.1 and −5.6 are assigned to the PMe_3 ligand coordinated to **4a** and **4a′** and are broadened due to the above dissociative exchange of PMe_3 ligands on the NMR time scale, whereas the peaks due to **2a** do not

show such broadening. More facile dissociation of PMe_3 from **4a** than that from **2a** is attributed to stabilization of **4a′** by an agostic interaction between an *ortho* C−H group and the Rh center. At 25 °C, the dissociation of PMe_3 from **4a** is less extensive, and the $^{31}P\{^1H\}$ NMR spectrum shows the peaks at δ −24.1 and δ −5.6 in ca. 2:1 area ratio. At higher temperature, broadening of the $^{31}P\{^1H\}$ NMR signals renders comparison of the relative peak intensity difficult, although dissociation of PMe_3 ligand would be more extensive than that at 25 °C. The ^{31}P NMR peak assigned to liberated PMe_3 is not detected.[13]

To confirm the liberation of PMe_3 from **4a**, the ^1H NMR peaks in the equilibrated mixture were compared at 25−60 °C. An apparent equilibrium constant, K_{app}, defined as ([**4a**] + [**4a′**])/[**2a**], is plotted against $1/T$, and the plots give a linear van't Hoff type correlation. The thermodynamic parameters calculated from K_{app} contain positive reaction enthalpy and entropy ($\Delta H°_{app}$ = 27.3 kJ mol^{-1} and $\Delta S°_{app}$ = 74 J mol^{-1} K^{-1} at 273 K), consistent with the equilibrium involving dissociation of PMe_3 (Scheme 3).

Complex **2b**, prepared from the reaction of (*p*-fluorophenyl)allene with $RhCl(PMe_3)_3$, also shows NMR spectra containing peaks of **4b** and **4b′** which are in equilibrium with **2b**.

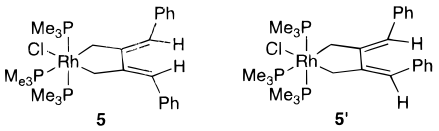
Reactions of Arylallene with $RhCl(PMe_3)_3$ To Give Rhodacyclopentane. Reactions of phenylallene and of (4-fluorophenyl)allene with $RhCl(PMe_3)_3$ in a 3:1 molar ratio result in isolation of *mer*-Rh[CH_2C(=CHAr)C(=CHAr)CH_2]Cl$(PMe_3)_3$ (**5a**, Ar = C_6H_5; **5b**, Ar = C_6H_4F-*p*) in 79% and 75% yields, as shown in eq 3.



(3)

X-ray crystallography of **5a** shows octahedral coordination around the Rh center with three PMe_3 ligands at meridional sites and the five-membered metallacycle having two phenylmethylidene substituents.[9] The $^{31}P\{^1H\}$ NMR spectrum of **5a** shows a doublet of doublets (δ −5.7) and a doublet of triplets (δ −20.8) in a 2:1 peak area ratio. The former signal is assigned to two mutually trans P nuclei and the latter to a P nucleus trans to a CH_2 group bonded to the Rh center. The ^1H NMR spectrum gives rise to two PMe_3 hydrogen signals in a 1:2 area ratio, the larger of which appears as an apparent triplet due to virtual coupling. The above NMR results are consistent with the meridional coordination of the PMe_3 ligands around the metal center. The $^{13}C\{^1H\}$ NMR spectrum shows signals due to the CH_2 carbons bonded to Rh at δ 22.13 and 13.67. The former peak, with a large J(CP) value (83 Hz), is assigned to the carbon bonded at the trans position of PMe_3 and the latter to the carbon trans to the Cl ligand. Based on the $^1H-^{13}C$ COSY NMR spectrum, the two

Chart 1



^1H NMR signals due to the CH_2 hydrogens at δ 3.02 and 2.11 are assigned respectively to the CH_2 group trans to PMe_3 and to that trans to Cl ligand. The $^{13}C\{^1H\}$ NMR spectrum shows the signals due to C(Ar)H= carbons and =C< carbons as two pairs of signals whose positions and coupling constants give reasonable assignment of each signal. That β-carbon signal of **5a** appears at a very low magnetic field position, which seems to reflect low electron density at the carbon, in analogy to the corresponding carbon of free allenes. These features imply that the carbon atoms of rhodacyclopentane have the character of unreacted allene. Complex **5b** gives NMR spectra similar to those of **5a** and is proposed to have the same five-membered metallacycle structure.

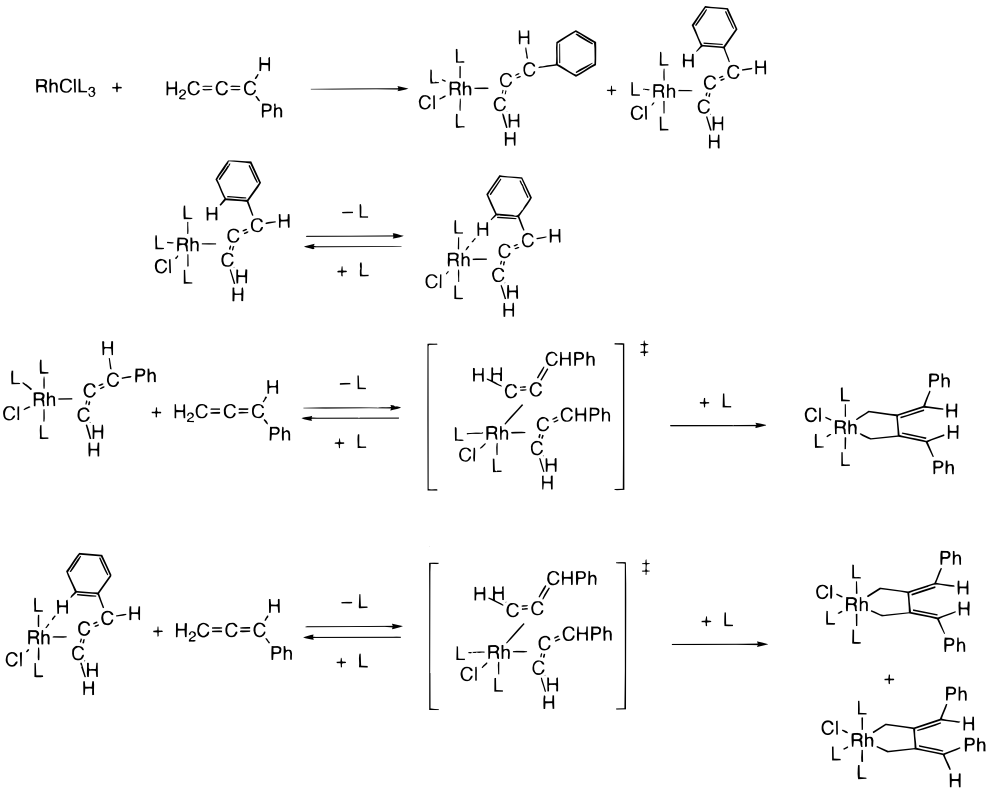
The reactions of phenylallene with $RhCl(PMe_3)_3$ shown in eqs 2 and 3 led to the isolation of **2a** and of **5a**, respectively. The results are rationalized by assuming that each reaction gives two Rh complexes, whose ratio depends on the relative amounts of phenylallene and $RhCl(PMe_3)_3$. NMR measurement of the reaction mixtures in several phenylallene/Rh ratios revealed the formation of several complexes, including **2a** and **5a**. Reaction of phenylallene with $RhCl(PMe_3)_3$ in a 0.5:1 molar ratio gave a mixture of Rh(I)−phenylallene complexes as the product, (**4a**:**2a** = 10:90 after 11 h). An equimolar reaction for 47 h afforded **4a**, **2a**, and **5a** in a 10:59:31 molar ratio. An increase in the amount of phenylallene to 2 and 3 equiv compared to the Rh complex caused a shift of the product ratio to 6:15:79 and 0:18:82, respectively.

The reaction mixtures contain several minor products that were removed from the product during the recrystallization process. ^1H NMR peaks at δ 5.42(s), 5.29(s), 3.64 (m), and 2.32 (m) and $^{31}P\{^1H\}$ NMR peaks at δ −9.1 (dd, J(PRh) = 112 Hz, J(PP) = 31 Hz) and −23.0 (dt, J(PRh) = 87 Hz, J(PP) = 31 Hz) in the bulk reaction product were observed with small peak intensities (<5% of the Rh complexes). The similarlity of the peak pattern to that of **5a** suggests that the signals are due to a structural isomer of **5a**. Chart 1 depicts a possible structure of the isomer **5a′** containing an *E* double bond and a *Z* double bond in the metallacycle part. The other possible rhodacyclopentane with two *Z* double bonds would be highly congested around the *s*-cis diene unit.

The reaction of phenylallene with **2a** was examined to obtain insight on the mechanism of reactions 2 and 3. Figure 6 shows changes in the amount of the complexes in the reaction with a 2:1 molar ratio. The initial reaction mixture contains complexes **2a** and **4a**, the latter of which is formed through isomerization of **2a**. The amount of **5a** increases gradually to 80% of all the Rh complexes and does not change further. A similar reaction, with addition of a small amount of PMe_3, ([PMe_3]/[**2a**] = 0.2), does not form the rhodacyclopentane, even after 14 h.[14] The rhodacyclopentane formation probably involves initial ligation of phenyl-

(13) The absence of the $^{31}P\{^1H\}$ NMR peaks of free PMe_3 and of **4a′** can be accounted for by a small amount of the complex in the reaction mixture or its rapid equilibrium with **4a**. It is not clear whether **4a′** has a similar structure to **1a** or not because comparison of the ^{31}P NMR peak positions of **1a** and of **4a′** is not feasible.

Scheme 4



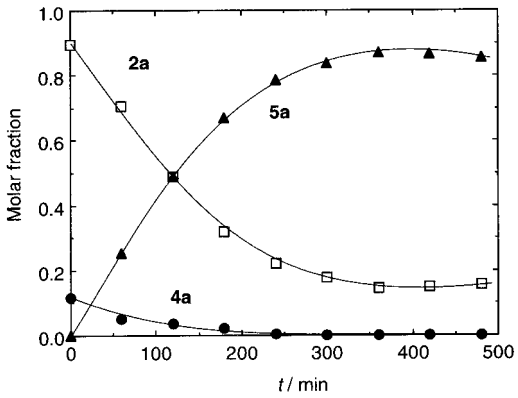
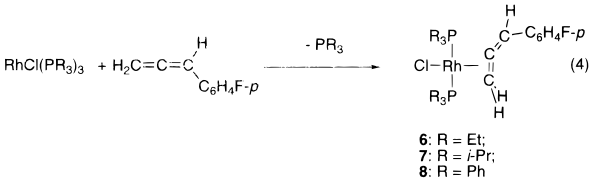


Figure 6. Time course of the reaction of **2a** and phenylallene in a 1:2 molar ratio in benzene-d_6 at 25 °C.

allene to $RhCl(PMe_3)_3$ to give complexes **4a** and **2a**, followed by reaction of another phenylallene molecule to the Rh complexes, leading to cyclometalation, as depicted in Scheme 4. Inhibition of the metallacycle formation by PMe_3 suggests that the reaction requires dissociation of PMe_3 to allow π-coordination of the second phenylallene ligand. The agostic interaction of a phenyl C−H group with the Rh center in **4a** may help to dissociate a PMe_3 from the complex and enhance the metallacycle formation.

Preparation of Rh(I)−Arylallene Complexes with Other Phosphine Ligands. Chlororhodium(I) complexes with other phosphine ligands, $RhCl(PEt_3)_3$, $RhCl[P(i\text{-}Pr)_3]_2$, and $RhCl(PPh_3)_3$, react with (4-fluorophenyl)allene to give Rh(I) complexes containing a π-coordinated phenylallene molecule, **6**, **7**, and **8**, respectively, as shown in eq 4. Complex **7** was prepared from the



reaction of $CH_2{=}C{=}CHC_6H_4F\text{-}p$ with $RhCl(H)(SiPh_3)[P(i\text{-}Pr)_3]_2$, accompanied by elimination of the hydrosilylation product of the arylallene. Reaction 4 does not give any other inorganic products including rhodacyclopentane, even when excess (4-fluorophenyl)allene is used. Figure 7 shows the X-ray structure of the square-planar complex **8** with Rh and the aryl group on opposite sides of the uncoordinated C=C double bond, as with **3a**. The appearance of the CH_2 hydrogens of coordinated allene molecule at high magnetic field positions (δ 1.4−2.5) in **6**, **7**, and **8** indicates coordination of the 2,3-C=C double bond rather than the 1,2-C=C double bond. The ^{1}H NMR peaks due to the phenyl hydrogens of **6**−**8** appear at positions similar to those found for **3a**.

Discussion

Reactions of arylallene with Rh(I) complexes give several types of products, depending on the conditions and auxiliary phosphine ligands. Both π-coordination and metallacycle formation occur at the 2,3-C=C double bond of the substrates, probably because it is sterically less hindered than the 1,2-C=C double bond and

(14) In the preliminary communication (ref 9), we reported that reaction of phenylallene with **2a** does not give the rhodacyclopentane **5a**. Further investigation has revealed that it is due to contamination of PMe_3 that hampers the metallacycle formation. Reaction using the complex purified by repeated recrystallization gives **5a** at room temperature, as shown in the present paper, while addition of PMe_3 stops formation of **5a**. Results of measurement of the equilibrium constant of PMe_3 dissociation from **2a** in the previous report are also unreliable.

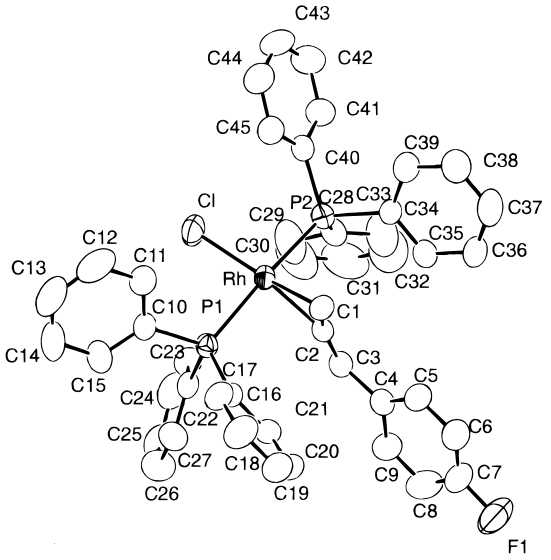


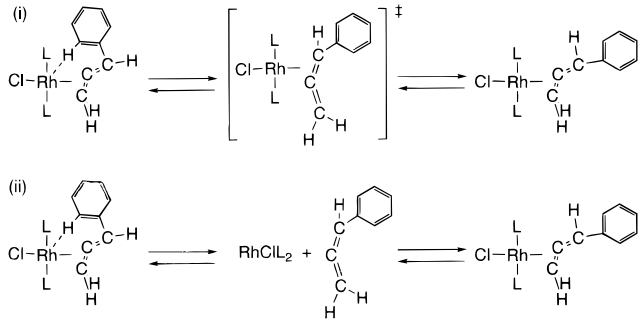
Figure 7. ORTEP drawing of $RhCl(\eta^2\text{-}CH_2{=}C{=}CHPh)(PPh_3)_2{\cdot}THF$ (**8**·THF) at 30% probability level. Hydrogen atoms and atoms of the solvent molecule are omitted for simplicity.

Chart 2

because the resulting products contain efficient π-conjugation between the aryl group and the uncoordinated 1,2-double bond. The results of the structural study of **1a**, including close contact of an *ortho* hydrogen of aryl group with Rh in the crystal structure and smaller ^1J(CH) of the *ortho* C−H group than that of **3a** and uncoordinated phenylallene, indicate the presence of an agostic interaction both in the solid state and in solution. The 16-electron Rh center with square-planar coordination is conductive to the approach of the C−H group at the apical position. The geometry of the C−H group and metal center in **1a** is closer to an end-on type interaction than to a side-on type (Chart 2).[10c] The much smaller $\Delta H°$ for isomerization from **3a** to **1a** (−5.0 kJ mol^{-1}) than already reported formation enthalpies of metal alkane complexes with a side-on type coordination mode[10d] indicates that the agostic interaction shown in this system is thermodynamically favored to a limited extent. The shift of the ^{1}H NMR peak to a low magnetic field position does not agree with previously reported C−H···M interactions, which often result in a peak shift to high magnetic field positions due to its partial hydrido character. Elucidation of the reason for the uncommon ^{1}H NMR peak shift related to the weak agostic interaction of the aromatic C−H group in the present study would require further study.[15]

Rapid and reversible isomerization between **1a** and **3a** is observed above room temperature. Scheme 5

Scheme 5



depicts two possible mechanisms for the isomerization. The smooth conversion between the isomers is accounted for by reversible change of the coordination side of the 2,3-double bond through an intramolecular pathway involving a transition state whose Rh center is coordinated to the 1,2-double bond of the ligand (i). Another pathway, involving dissociation of phenylallene ligand (ii), is less plausible because the three-coordinated Rh(I) complex with compact PMe_3 ligands would be extremely unstable.

The Rh center of complex **4a** with 18 electrons undergoes partial dissociation of a PMe_3 ligand, triggered by agostic interaction of an *ortho* hydrogen of the phenylallene ligand to afford **4a′**. The labile Rh−P bond caused by the agostic interaction may be an important factor to promote the reaction of **2a** with phenylallene to give the metallacycle **5a**. Both the agostic interaction and rhodacyclopentane formation are unique to PMe_3 ligands because the reaction of arylallene with Rh(I) complexes with more bulky phosphine ligands $RhCl(PR_3)_3$ (R = Et, *i*-Pr, Ph) gives only Rh(I) complexes, with structure similar to that of **3a**.

Experimental Section

General Considerations, Measurement, and Materials. Manipulations of the Rh complexes were carried out under nitrogen or argon using standard Schlenk techniques. $RhCl(PMe_3)_3$, $[Rh(\mu\text{-}Cl)(PMe_3)_2]_2$, $RhCl(PPh_3)_3$, $RhCl[P(i\text{-}Pr)_3]_2$, $RhClH(SiPh_3)[P(i\text{-}Pr)_3]_2$, and arylallenes were prepared according to the literature.[16] NMR spectra (^{1}H, ^{13}C, and ^{31}P) were recorded on a JEOL EX-400 spectrometer. $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4. Elemental analyses were carried out by using a Yanaco MT-5 CHN autocorder.

Preparation of 1a and 1b. To a toluene (5 mL) solution of $[Rh(\mu\text{-}Cl)(PMe_3)_2]_2$ (282 mg, 0.98 mmolRh) was added phenylallene (113 mg, 0.97 mmol) at room temperature. The solution changed color from orange red to yellow on stirring. After 10 h, the solvent was evaporated to dryness. The resulting oily product was washed with hexane repeatedly to give a yellow solid (328 mg, 83%). Recrystallization from a THF−hexane mixture afforded **1a** as pale yellow crystals (198 mg, 50%). Anal. Calcd for $C_{15}H_{26}ClP_2Rh$: C, 44.30; H, 6.44. Found: C, 44.21; H, 6.54.

The NMR spectra of a solution of **1a** shows the signals of an equilibrated mixture of **1a** and **3a**. ^{1}H NMR (400 MHz in C_6D_6): δ 0.91 (apparent triplet due to virtual coupling, 18H,

(15) Previous reports on hydrogen bond of OH and NH groups of organic molecule and metal center of several organotransition metal complexes have shown downfiled shift of the ^{1}H NMR peaks of O−H and N−H hydrogen. See: Brammer, L.; Zhao, D.; Ladipo, F. T.; Braddock-Wilking, J. *Acta Crystallogr.* **1995**, *B51*, 632. Zhao, D.; Ladipo, F. T.; Braddock-Wilking, J.; Brammern L.; Sherwood, P. *Organometallics* **1996**, *15*, 1441 and references therein. The polar metal−hydrido interaction seems to be not related to the interaction of C−H group and Rh−PMe_3 complexes in the present study.

(16) (a) Price, R. T.; Andersen, R. A.; Muetterties, E. L. *J. Organomet. Chem.* **1989**, *376*, 407. (b) Jones, R. A.; Real, F. M.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 511. (c) Werner, H.; Wolf, J.; Höhn, A. *J. Organomet. Chem.* **1985**, *287*, 395. (d) Moore, W. R.; Ward, H. R. *J. Org. Chem.* **1962**, *27*, 4179. (e) Osakada, K.; Koizumi, T.; Yamamoto, T. *Organometallics* **1997**, *16*, 2063.

P(CH_3)$_3$), 2.26 (m, CH_2= (**3a**)), 2.32 (m, CH_2= (**1a**)), 6.64 (m, =CH− (**3a**)), 6.70 (m, =CH− (**1a**)), 7.06 (t, J = 7 Hz, *para* (**3a**), 7.08 (t, J = 7 Hz, *para* (**1a**), 7.26 (t, J(HH) = 7 and 8 Hz, *meta* (**3a**)), 7.29 (t, J(HH) = 7 and 8 Hz, *meta* (**1a**)), 7.45 (d, J(HH) = 7 Hz, *ortho* (**3a**)), 8.58 (d, J(HH) = 7 Hz, *ortho* (**1a**)). ^{31}P{^{1}H} NMR (160 MHz in C_6D_6) δ −8.5 (d, **1a**, J(RhP) = 117 Hz), −7.7 (d, **3a**, J(RhP) = 117 Hz). ^{13}C{^{1}H} NMR (100 MHz in CD_2Cl_2): δ 12.0 (apparent triplet due to virtual coupling, P(CH_3)$_3$ (**3a**)), 12.5 (apparent triplet due to virtual coupling, P(CH_3)$_3$ (**1a**)), 14.0 (CH_2= (**3a**)), 14.6 (CH_2= (**1a**)), 110.3 (CH= (**3a**)), 110.6 (d, J(RhC) = 4 Hz, CH= (**1a**)), 125.1 (^1J(CH) = 161 Hz, *para* (**3a**)), 125.7 (^1J(CH) = 161 Hz, *para* (**1a**) and *meta* (**3a**)), 127.6 (^1J(CH) = 157 Hz, *ortho* (**1a**)), 128.4 (^1J(CH) = 160 Hz, *meta* (**1a**)), 128.8 (^1J(CH) = 160 Hz, *ortho* (**3a**)), 137.2 (*ipso* (**3a**)), 140.0 (*ipso* (**1a**)), 170.8 (=C= (**3a**)), 174.5 (d, J(RhC) = 25 Hz, =C= (**1a**)).

The equilibrium constants between **1a** and **3a** were determined by comparison of the ^{1}H NMR peak area ratio of *ortho* hydrogens of the phenylallene ligand of **1a** and **3a** as follows. K = [**1a**]/[**3a**] = 2.69 (303 K), 2.62 (308 K), 2.45 (318 K), 2.36 (323 K), and 2.33 (328 K).

Complex **1b** was prepared analogously (45% after recrystallization). Anal. Calcd for $C_{15}H_{25}ClFP_2Rh$: C, 42.43; H, 5.93. Found: C, 42.30; H, 6.22. The NMR spectra of a solution of **1b** shows the signals of an equilibrated mixture of **1b** and **3b**. ^{1}H NMR (400 MHz in C_6D_6): δ 0.90 (apparent triplet due to virtual coupling, 18H, P(CH_3)$_3$), 2.16 (m, CH_2= (**3b**)), 2.29 (m, CH_2= (**1b**)), 6.51 (m, =CH− (**3b**)), 6.57 (m, =CH− (**1b**)), 6.93 (m, *meta* (**1b** and **3b**)), 7.22 (br, *ortho* (**3b**)), 8.41 (dd, J(HH) = J(HF) = 7 Hz, *ortho* (**1b**)). ^{31}P{^{1}H} NMR (160 MHz in C_6D_6): δ −8.6 (d, J(RhP) = 117 Hz, (**1b**)), −7.7 (d, J(RhP) = 117 Hz (**3b**)).

Preparation of 2a and 2b. To a hexane (8 mL) dispersion of RhCl(PMe$_3$)$_3$ (115 mg, 0.31 mmol) was added phenylallene (44 mg, 0.38 mmol) at room temperature to dissolve the complex. Stirring the solution caused gradual separation of a yellow solid. After 26 h, the solid product was collected by filtration and dried in vacuo (119 mg, 78%). Recrystallization from a THF−hexane mixture afforded **2a** as yellow crystals (85 mg, 56%). Anal. Calcd for $C_{18}H_{35}ClP_3Rh$: C, 44.78; H, 7.31. Found: C, 44.39; H, 7.31.

The NMR spectra of a solution of **2a** show the signals of an equilibrated mixture of **2a** and **4a**. ^{1}H NMR (400 MHz in C_6D_6 at 25 °C): δ 1.09 (apparent triplet due to virtual coupling, 18H, P(CH_3)$_3$), 1.14 (d, 9H, J(PH) = 7 Hz, P(CH_3)$_3$), 1.86 (ddd, 2H, CH_2), 5.94 (s, CH (**2a**)), 6.78 (br, CH (**4a** + **4a′**)), 7.06 (t, 1 H, J(HH) = 7 Hz, *para*), 7.32 (t, J(HH) = 7 Hz, *meta* (**2a**)), 7.42 (br, *meta*, (**4a** + **4a′**)), 7.66 (d, J(HH) = 7 Hz, *ortho* (**2a**)), 8.47 (br, *ortho* (**4a** + **4a′**)). ^{13}C{^{1}H} NMR (100 MHz in CD_2Cl_2 at 25 °C): δ 9.8 (dt, CH_2Rh, J = 50 and 5 Hz), 15.0 (apparent triplet due to virtual coupling, P(CH_3)$_3$), 20.1 (d, J = 17 Hz), P(CH_3)$_3$), 114.2 (d, J = 11 Hz, CHPh=C), 124.2 (*para*), 125.7 (*ortho*), 128.5 (*meta*), 139.7 (*ipso*), 167.9 and 168.1 (CCH_2Rh). The ^{13}C NMR peaks due to the minor isomer **4a** were either not observed due to low solubility of the complex or overlapped with the peaks of **2a**. ^{31}P{^{1}H} NMR (160 MHz in C_6D_6 at 25 °C): δ −2.1 (dd, J(PRh) = 104 Hz, J(PP) = 37 Hz, (**2a**)), −5.6 (br, (**4a** + **4a′**)), −18.1 (dt, J(PRh) = 133 Hz, J(PP) = 37 Hz (**2a**)), −24.1 (br, (**4a** + **4a′**)).

Apparent equilibrium constants between **2a** and a mixture of **4a** and **4a′** were determined by comparison of the ^{1}H NMR signals of =CHPh hydrogen of **2a** with that of *ortho* hydrogens of **4a** and **4a′**. K_{app} = ([**4a**] + [**4a′**])/[**2a**] = 0.149 (303 K), 0.178 (308 K), 0.212 (313 K), 0.248 (318 K), 0.295 (323 K), 0.331 (328 K), and 0.403 (333 K).

Complex **2b** was prepared analogously (71% after recrystallization). Anal. Calcd for $C_{18}H_{34}ClFP_3Rh$: C, 43.18; H, 6.84. Found: C, 43.25; H, 7.16. The NMR spectra of a solution of **2b** shows the signals of an equilibrated mixture of **2b** and **4b**. ^{1}H NMR (400 MHz in C_6D_6 at 25 °C): δ 1.08 (apparent triplet due to virtual coupling, 18H, P(CH_3)$_3$), 1.14 (d, 9H, P(CH_3)$_3$, J(PH) = 7 Hz), 1.76 (ddd, 2H, CH_2), 5.81 (s, 1H, CH), 6.99 (t, 2H, J(HH) = J(HF) = 7 Hz, *meta*), 7.43 (dd, J(HH) = 8 Hz, J(HF) = 5 Hz, *ortho* (**2b**)), 8.36 (br, *ortho* (**4b** + **4b′**)). ^{31}P{^{1}H} NMR (160 MHz in C_6D_6 at 25 °C): δ −2.1 (dd, J(PRh) = 102 Hz, J(PP) = 37 Hz(**2b**)), −5.5 (br, (**4b** + **4b′**)), −17.9 (dt, J(PRh) = 129 Hz, J(PP) = 37 Hz, (**2b**)) −24.4 (br (**4b** + **4b′**)).

Preparation of 5a and 5b. To a toluene (8 mL) solution of RhCl(PMe$_3$)$_3$ (158 mg, 0.43 mmol) was added phenylallene (150 mg, 1.3 mmol) at room temperature. The solution changed color from pale yellow to pale brown, which was accompanied by deposition of an off-white solid. After 8 h, the solid product was collected by filtration and dried in vacuo to give **5a** as colorless crystals (203 mg, 79%). Anal. Calcd for $C_{27}H_{43}ClP_3Rh$: C, 54.15; H, 7.24. Found: C, 54.18; H, 7.20. ^{1}H NMR (400 MHz in C_6D_6 at 25 °C): δ 0.93 (d, 9H, P(CH_3)$_3$, J(PH) = 6 Hz), 1.10 (apparent triplet due to virtual coupling, 18H, P(CH_3)$_3$), 2.11 (m, 2H, CH_2 trans to Cl), 3.02 (td, 2H, CH_2 trans to P, J(PH) [or J(RhH)] = 9 and 9 Hz), 6.48, (s, 1H, CH trans to Cl), 6.59 (s, 1H, CH trans to PMe$_3$), 7.06 (t, 2H, *para*, J(HH) = 7 Hz), 7.26 (t, 4H, *meta*, J(HH) = 7 Hz), 7.59 (d, 2H, *ortho* trans to Cl, J(HH) = 7 Hz), 7.81 (d, 2H, *ortho* trans to PMe$_3$, J(HH) = 7 Hz). ^{13}C{^{1}H} NMR (100 MHz in CD_2Cl_2 at 25 °C): δ 13.67 (ddt, CH_2−Rh trans to Cl, J = 26, 6, and 6 Hz), 14.39 (apparent triplet due to virtual coupling, P(CH_3)$_3$), 13.67 (d, P(CH_3)$_3$, J(CP) = 17 Hz), 22.13 (m, CH_2Rh trans to PMe$_3$, J(CP) = 83 Hz), 115.81 (d, CH=CCH_2Rh, trans to PMe$_3$, J = 6 Hz), 118.07 (s, CH=CCH_2Rh, trans to Cl), 125.45 (*para*, trans to Cl), 125.62 (*para*, trans to PMe$_3$), 128.25 (*meta*, trans to Cl), 128.43 (*meta*, trans to PMe$_3$), 129.53 (*ortho*, trans to Cl), 129.59 (*ortho*, trans to PMe$_3$), 139.92 (*ipso*, trans to Cl), 140.45 (*ipso*, trans to PMe$_3$), 159.56 (d, CCH_2Rh trans to Cl, J = 7 Hz), 160.01 (d, CCH_2Rh trans to PMe$_3$, J = 13 Hz). ^{31}P-{^{1}H} NMR (160 MHz in C_6D_6 at 25 °C): δ −5.7 (dd, J(PRh) = 110 Hz, J(PP) = 31 Hz), −20.8 (dt, J(PRh) = 86 Hz, J(PP) = 31 Hz).

Complex **5b** was prepared analogously (75%). Anal. Calcd for $C_{27}H_{41}ClF_2P_3Rh$: C, 51.08; H, 6.51. Found: C, 51.13; H, 6.41. ^{1}H NMR (400 MHz in C_6D_6 at 25 °C): δ 0.92 (d, 9H, P(CH_3)$_3$, J(PH) = 7 Hz), 1.08 (apparent triplet due to virtual coupling, 18H, P(CH_3)$_3$), 1.96 (m, 2H, CH_2 trans to Cl), 2.87 (td, 2H, CH_2 trans to P, J(PH) [or J(RhH)] = 9 and 9 Hz), 6.31, (s, 1H, CH trans to Cl), 6.41 (s, 1H, CH trans to PMe$_3$), 6.89 (t, 4H, *meta*, J(HH) = J(HF) = 8 Hz), 7.35 (dd, 2H, *ortho* trans to Cl, J(HH) = 9 Hz, J(HF) = 6 Hz), 7.58 (d, 2H, *ortho* trans to PMe$_3$, J(HH) = 7 Hz). ^{31}P{^{1}H} NMR (160 MHz in C_6D_6 at 25 °C): δ −5.6 (dd, J(PRh) = 110 Hz, J(PP) = 31 Hz), −17.9 (dt, J(PRh) = 86 Hz, J(PP) = 31 Hz).

Preparation of 6. To a pentane (5 mL) solution of RhCl(PEt$_3$)$_3$ (147 mg, 0.42 mmol) was added (4-fluorophenyl)allene (67 mg, 0.50 mmol) at room temperature. A yellow solid was soon separated from the solution. After 1 h, the solid product was collected by filtration and dried in vacuo (145 mg). Recrystallization from a toluene−pentane mixture afforded **6** as yellow crystals (57 mg, 27%). Anal. Calcd for $C_{21}H_{37}ClFP_2Rh$: C, 49.57; H, 7.32; Cl, 6.96. Found: C, 49.41; H, 7.45; Cl, 6.64. ^{1}H NMR (400 MHz in C_6D_6) δ 0.94 (apparent triplet due to virtual coupling, 18H, CH_3), 1.50 (m, 12H, PCH_2), 2.24 (m, 2H, =CH_2), 6.50 (m, 1H, C=CH), 6.92 (dd, 2H, J(HH) = J(HF) = 9 Hz), 7.20 (dd, 2H, J(HH) = 9 Hz, J(HF) = 6 Hz). ^{31}P{^{1}H} NMR (160 MHz in C_6D_6): δ 18.7 (d, J(RhP) = 117 Hz).

Preparation of 7. To a hexane (5 mL) suspension of RhCl(H)(SiPh$_3$)[P(*i*-Pr)$_3$)]$_2$ (145 mg, 0.20 mmol) was added (4-fluorophenyl)allene (135 mg, 1.01 mmol) at room temperature. The solution soon changed color from purple to yellow, which was accompanied by deposition of a yellow solid. After evaporation of the solvent under vacuum, the resulting yellow solid was recrystallized from a THF−hexane mixture to give **7** as yellow crystals (57 mg, 48%). Anal. Calcd for $C_{27}H_{49}ClFP_2Rh$: C, 54.68; H, 8.32; Cl, 5.97. Found: C, 55.08; H, 8.55; Cl, 5.44. ^{1}H NMR (400 MHz in C_6D_6): δ 1.24 (apparent triplet due to virtual coupling, 36H, CH_3), 2.30 (br, 6H, PCH), 2.51

Table 2. Crystal Data and Details of Structure Refinement of 1a, 1b, 2b, and 8

compound	**1a**	**1b**	**2b**	**8**·THF
formula	$C_{15}H_{26}ClP_2Rh$	$C_{15}H_{25}ClFP_2Rh$	$C_{18}H_{34}ClFP_3Rh$	$C_{49}H_{45}ClFP_2RhO$
mol wt	406.68	424.66	500.74	869.20
cryst syst	orthorhombic	orthorhombic	orthorhombic	monoclinic
space group	*Pnma* (No. 62)	*Pnma* (No. 62)	$P2_12_12_1$ (No. 19)	$P2_1/n$ (No. 14)
a (Å)	13.238(5)	13.362(6)	12.823(6)	17.522(7)
b (Å)	13.474(7)	13.530(7)	15.964(4)	10.514(9)
c (Å)	10.311(4)	10.466(5)	11.518(4)	23.41(1)
β (deg)				99.24(4)
U (Å^3)	1839	1892	2357	4253
Z	4	4	4	4
μ (cm^{-1})	12.32	12.09	10.46	5.79
F(000)	832	864	1032	1792
D_{calcd} (g cm^{-3})	1.469	1.491	1.411	1.357
cryst size (mm^3)	0.4 × 0.5 × 0.5	0.2 × 0.4 × 0.4	0.3 × 0.4 × 0.4	0.3 × 0.5 × 0.7
2θ range (deg)	5.0−55.0	5.0−55.0	5.0−55.0	5.0−55.0
no. of unique reflns	2415	2484	3065	10 324
no. of used reflns	747	1067	1259	5585
no. of variables	103	113	217	496
R	0.059	0.051	0.050	0.054
R_w[a]	0.030	0.035	0.035	0.049
GOF	1.93	2.11	1.33	2.25

[a] Weighting scheme $[\sigma(F_o)^2]^{-1}$.

(br, 2H, =CH_2), 6.60 (br, 1H, =C*H*), 6.90 (d, 2H, *meta*, *J*(HH) = *J*(HF) = 9 Hz), 7.17 (d, 2H, *ortho*, *J*(HH) = 9 Hz, *J*(HF) = 6 Hz). $^{31}P\{^1H\}$ NMR (160 MHz in C_6D_6): δ 32.6 (d, *J*(RhP) = 117 Hz).

Preparation of 8. To a toluene (10 mL) dispersion of $RhCl(PPh_3)_3$ (310 mg, 0.34 mmol) was added (4-fluorophenyl)allene (54 mg, 0.40 mmol) at room temperature. The solution gradually changed color from purple to yellow. After 17 h, the solvent was evaporated to dryness. Addition of hexane to the resulting yellow product caused separation of a yellow solid, which was recrystallized from a CH_2Cl_2−hexane mixture to afford **8** as yellow crystals (190 mg, 71%). Anal. Calcd for $C_{45}H_{37}ClFP_2Rh$: C, 67.81; H, 4.68. Found: C, 67.50; H, 4.99. ^1H NMR (400 MHz in CD_2Cl_2): δ 1.42 (br, 2H, CH_2=), 6.36 (br, 1H, =CH), 6.60 (d, 2H, *ortho*, *J*(HH) = 7 Hz), 6.77 (dd, 2H, *J*(HH) = *J*(HF) = 7 Hz), 7.3 (m, 18H, C_6H_5), 7.7 (m, 12H, C_6H_5). $^{31}P\{^1H\}$ NMR (160 MHz in CD_2Cl_2): δ 27.7 (d, *J*(RhP) = 125 Hz). Single crystals for X-ray crystallography were obtained in a THF solvated form from further recrystallization of the complex from THF−hexane.

Crystal Structure Determination. Crystals were mounted in glass capillary tubes under argon. The unit cell parameters were obtained by least-squares refinement of 2θ values of 25 reflections with 25° ≤ 2θ ≤ 35°. Intensities were collected on a Rigaku AFC-5R automated four-cycle diffractometer by using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) and the ω−2θ method. Empirical absorption correction (ψ scan method) of the collected data was applied. Table 2 summarizes crystal data and details of data refinement. Calculations were carried out by using the teXsan program package on a VAX-II computer. Atomic scattering factors were taken from the literature.[17] A full-matrix least-squares refinement was used for non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms, except for vinyl hydrogen of the ligands of **3a**, were located by assuming ideal positions (*d* = 0.95 Å) and were included in the structure calculation without further refinement of the parameters. Positions of the hydrogens of phenylallene molecule of **3a** were determined by D-Fourier map and were not refined further.

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Supporting Information Available: Crystallographic data of the complexes **1a**, **1b**, **2b**, and **8** (21 pages). Ordering information is given on any current masthead page.

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(17) *International Tables for X-ray Crystallography;* Kynoch: Birmingham, England, 1974; Vol. IV.