Selected Paper

Selective C–C Bond Activation of 2-Aryl-1-methylenecyclopropanes Promoted by Ir(I) and Rh(I) Hydrido Complexes. Mechanism of Ring-Opening Isomerization of the Strained Molecules

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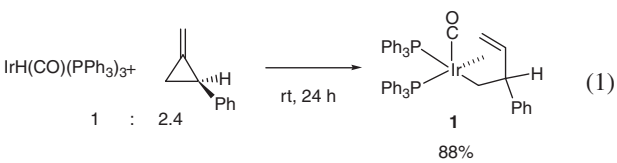
[IrH(CO)(PPh_3)$_3$] promotes ring opening of 2-phenyl-1-methylenecyclopropane at room temperature to produce the Ir complex with a chelating 2-phenyl-3-butenyl ligand, [Ir{η^2-$CH_2CH(Ph)CH{=}CH_2$-κC^1}(CO)(PPh_3)$_2$] (**1**). The reaction of excess 2-phenyl-1-methylenecyclopropane with [IrH(CO)(PPh_3)$_3$] at 50 °C yields [Ir{η^2-(*o*-C_6H_4)CH(Me)CH=CH_2-κC^1}(CO)(PPh_3)$_2$] (**2**), accompanied by the formation of 1-phenyl-1,3-butadiene and 2-phenyl-1,3-butadiene. 2,2-Diphenyl-1-methylenecyclopropane reacts with [IrH(CO)(PPh_3)$_3$] to afford [Ir{η^2-$CH_2CPh_2CH{=}CH_2$-κC^1}(CO)(PPh_3)$_2$] (**3**) at 50 °C and [Ir{η^2-(*o*-C_6H_4)CMe(Ph)CH=CH_2-κC^1}(CO)(PPh_3)$_2$] (**4**) at 100 °C. Heating a solution of **3** at 100 °C also forms **4** quantitatively. X-ray crystallography of **3** reveals a penta-coordinated structure around the Ir center bonded to a chelating 2,2-diphenyl-3-butenyl ligand. The reactions of 2,2-diphenyl-1-methylenecyclopropane and of 2,2-di(4-fluorophenyl)-1-methylenecyclopropane with [RhH(CO)(PPh_3)$_3$] at room temperature yield [Rh{η^2-$CH_2CAr_2CH{=}CH_2$-κC^1}(CO)(PPh_3)$_2$] (**5a**: Ar = Ph, **5b**: Ar = C_6H_4-F-4). The reactions at 50 °C cause ring opening of the substrate and orthometalation of the phenyl group to afford [Rh{η^2-(*o*-C_6H_4)CMe(Ph)CH=CH_2-κC^1}(CO)(PPh_3)$_2$] (**6a**) and [Rh{η^2-(*o*-C_6H_3-F-4)CMe(C_6H_4-F-4)CH=CH_2-κC^1}(CO)(PPh_3)$_2$] (**6b**), respectively. Formation of 1,1-diaryl-1,3-butadiene is observed during the reaction. Heating a solution of **5a** at 50 °C produces 1,1-diphenyl-1,3-butadiene and an allylrhodium complex, **8**, rather than **6a**, although the reaction of excess 2,2-diphenyl-1-methylenecyclopropane with **5a** at 50 °C affords **6a** in 60%. The mechanisms of the above reactions are discussed based on the products and reaction rates. Coordination of $P(OMe)_3$ to the Rh center of **5a** causes insertion of the CO ligand into the Rh–C bond to afford [Rh{η^2-CO-$CH_2CPh_2CH{=}CH_2$-κC^1}($P(OMe)_3$)$_3$] (**7**).

Methylenecyclopropanes, which have high strain energy (ΔH_f larger than that of cyclopropane by approximately 35 kcal mol^{-1}),[1,2] have been utilized as the substrates of synthetic organic reactions[3–23] and polymer synthesis[24–32] catalyzed by transition metal complexes. Reactions of methylenecyclopropanes with transition metal complexes lead to the formation of unique products such as 1,3-dienes via ring-opening isomerization (Ni and Sc),[33,34] cyclopropylmethyl complexes via insertion of C=C bond into hydride–metal bond (Pd),[35,36] and metallacycle via co-dimerization with olefin (Ti).[37,38] Previously we reported that 2-aryl-1-methylenecyclopropane reacted with [RhCl(PPh_3)$_3$] to produce the Rh complexes with π-coordinated methylenecyclopropanes, [RhCl(η^2-CH_2=$CCH(Ar)CH_2$)(PPh_3)$_2$], and that the complexes having a 1,3-diene ligand, [RhCl(η^2,η^2-CH_2=C(Ar)CH=CH_2)(PPh_3)$_2$], are formed via isomerization of the π-coordinated methylenecyclopropanes.[39,40] In this paper, we report the reactions of substituted 1-methylenecyclopropanes with hydride complexes of Rh and Ir, in which stepwise ring-opening isomerization takes place via selective C–C bond cleavage of the cyclopropane ring and the subsequent C–H bond activation of the ligand. A part of this work was reported in a preliminary form.[41]

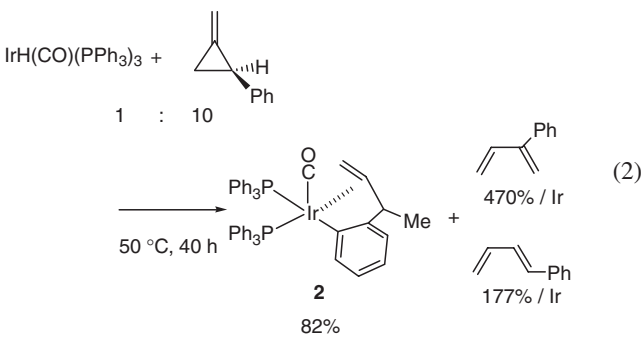
Results and Discussion

Reaction of 2-Phenyl-1-methylenecyclopropane with [IrH(CO)(PPh_3)$_3$]. The reaction of 2-phenyl-1-methylenecyclopropane with [IrH(CO)(PPh_3)$_3$] produces the 2-phenyl-3-butenyliridium(I) complex, [Ir{η^2-$CH_2CH(Ph)CH{=}CH_2$-κC^1}(CO)(PPh_3)$_2$] (**1**, 88%) at room temperature (Eq. 1).



(1)

The reaction of excess 2-phenyl-1-methylenecyclopropane at 50 °C gives a mixture of [Ir{η^2-(*o*-C_6H_4)CH(Me)CH=CH_2-κC^1}(CO)(PPh_3)$_2$] (**2**, 82%), 2-phenyl-1,3-butadiene (470%/Ir), and 1-phenyl-1,3-butadiene (177%/Ir) (Eq. 2).



(2)

Once isolated, **1** is stable in the solid state and in a solution containing 2-phenyl-1-methylenecyclopropane, but dissolution of it in benzene-d_6 results in partial isomerization into **2** even

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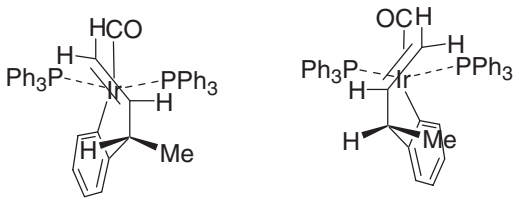
at room temperature.

Crystallographic structures of **1** and **2** were reported in the preceding communication.[41] Both complexes have distorted trigonal bipyramidal coordination around the Ir center. A chelating coordination of the 2-phenyl-3-butenyl ligand of **1** resembles that of the 2,2-di(phenylethyl)-3-butenyl ligand of [Rh{η^2-$CH_2C(CH_2CH_2Ph)_2CH{=}CH_2$-$\kappa C^1$}(CO)$(PPh_3)_2$].[42] The Ir–C bond distances of the vinylic group of the 2-phenyl-3-butenyl ligand are 2.14(1) Å and 2.12(2) Å. The C=C bond distance (1.33(2) Å) is close to the length of the corresponding bonds of the complexes with a tethered C=C functionality, (1.34–1.40 Å).[43,44] The C=C bond (1.439(9) Å) of **2** is elongated more significantly by the coordination, this is ascribed to the absence of a ligand at the coordination site trans to the vinyl ligand.

The ^{1}H NMR spectrum of **1** exhibits the Ir–CH_2 hydrogen signals at δ 0.11 and 1.70, the latter of which is overlapped with the signal of an olefinic hydrogen. The signals at δ 1.70, 1.81, and 2.96 are assigned to the hydrogens of the $CH{=}CH_2$ group based on the ^{1}H–^{1}H COSY spectrum. The vinyl hydrogen signals appear at higher magnetic field than those of $CH{=}CH_2$ group of organic molecules (δ 4.5–7.0), similarly to the olefin complexes of transition metals.[45] The CH hydrogen signal at δ 4.48 shows coupling with the two CH_2 hydrogens. The ^{13}C{^{1}H} NMR spectrum of **1** contains the signals at δ −12.4 and 28.2 due to the carbons of the Ir–CH_2–CH group. The resonances of the $=CH_2$ and CH= carbons at δ 31.2 and 28.2 are close to the positions expected for the carbons of a coordinated olefin (δ 40–85).[46] The presence of a carbonyl ligand is evidenced by the ^{13}C{^{1}H} NMR signal at low field position (δ 185.8) and by the IR band at a characteristic position (1939 cm^{-1}).

The ^{1}H NMR spectrum of **2** displays a doublet of the methyl hydrogens at δ 1.53 and the signals due to four hydrogens of the 1-methylallyl group at δ 1.79, 2.85, and 3.48. Small signals are observed at δ 2.97 and 3.69, which can be assigned to a minor isomer of **2** (vide infra). The ^{13}C{^{1}H} NMR signals of the coordinated vinyl group at δ 28.1 and 55.3 are split due to coupling with two phosphorus nuclei. The phenyl carbon signals of the 2-(1-methylallyl)phenyl ligand at δ 122.5, 124.5, 124.7, 141.2, 150.1, and 154.2 show small ^{31}P–^{13}C coupling constants (2–12 Hz). The ^{31}P{^{1}H} NMR spectrum of **2** exhibits two doublets at δ 0.36 and 3.31 (J(P–P) = 43.4 Hz) and another pair of doublets at δ 1.66 and 4.28 (J(P–P) = 40.1 Hz) in much smaller intensities, indicating the presence of a minor isomer in solution. Positions of the ^{13}C{^{1}H} NMR signals and of a part of the ^{1}H NMR signals are not determined unambiguously due to the low peak intensity and/or overlapping with other signals. The NMR spectra of the solution of **2**, which can be isolated as single crystals show the presence of the two isomers, which indicates isomerization of **2** in the solution. Scheme 1 depicts the structure of **2** determined by X-ray crystallography and that of its possible diastereomer **2′**. The two species observed in the solution may be attributed to these isomers.

Isomerization between **2** and **2′** should occur via decoordination of the vinyl group, rotation of the C–C bond of the ligand, and re-coordination of the vinyl group. Temperature dependent NMR spectra suggest fluxional behavior of the species, but this could not be interpreted by simple interconversion of the two species.



2 **2′**

Scheme 1.

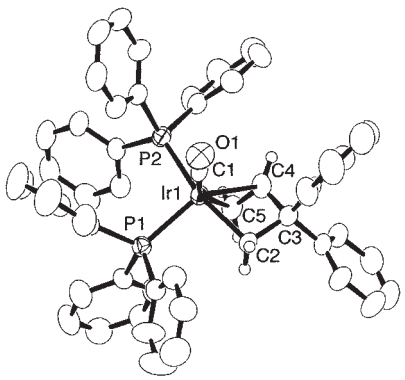
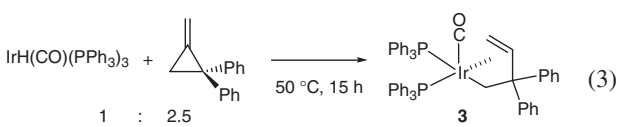
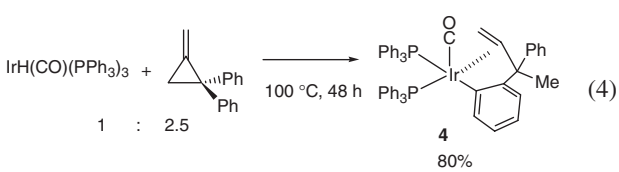


Fig. 1. Structure of complex **3** determined by X-ray crystallography with 50% thermal ellipsoidal plotting. Hydrogen atoms at the aromatic rings were omitted for simplicity.

Reaction of 2,2-Diphenyl-1-methylenecyclopropane with [IrH(CO)$(PPh_3)_3$]. Although the reaction of 2,2-diphenyl-1-methylenecyclopropane with [IrH(CO)$(PPh_3)_3$] does not occur at room temperature, heating the mixture to 50 °C forms [Ir{η^2-$CH_2CPh_2CH{=}CH_2$-κC^1}(CO)$(PPh_3)_2$] (**3**) in 78% yield after 15 h (Eq. 3). The reaction of 2,2-diphenyl-1-methylenecyclopropane with [IrH(CO)$(PPh_3)_3$] at 100 °C affords [Ir{η^2-(o-C_6H_4)CMe(Ph)CH=CH_2-κC^1}(CO)$(PPh_3)_2$] (**4**) in 80% yield (Eq. 4).



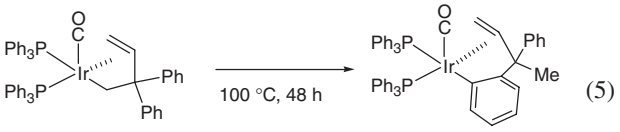


Complex **3** was characterized by X-ray crystallography and NMR spectroscopy. The molecular structure of **3** in Fig. 1 indicates a distorted trigonal bipyramidal coordination with PPh_3 and CH_2 groups at the apical sites.

The C=C double bond (C4–C5 = 1.434(9) Å) is elongated from uncoordinated C=C double bond. The ^{1}H NMR signals of **3** at δ 1.63, 1.75, and 3.00 are assigned to the olefinic hydrogens based on the ^{1}H–^{1}H COSY spectrum. The diastereotopic methylene protons of the CH_2 group bonded to iridium appear

at δ −0.70 and 1.93. The $^{13}C\{^1H\}$ NMR spectrum shows a signal of the CH_2 carbon at δ −7.0 with a large coupling constant (J(C–P) = 62.0 Hz). A carbonyl carbon signal at δ 184.9 couples with two phosphorus nuclei with coupling constants of 14.4 and 7.5 Hz.

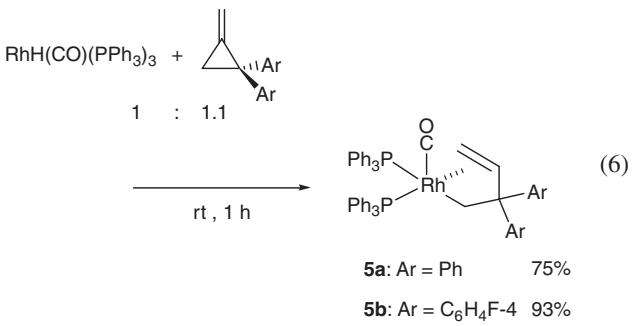
Complex **4** shows the ^1H NMR signals for three olefinic protons at δ 0.72, 1.43, and 2.73. The ^1H NMR (δ 1.94) and $^{13}C\{^1H\}$ NMR (δ 29.5) signals of the methyl group are observed at reasonable positions. The $^{13}C\{^1H\}$ NMR spectrum shows the signal of carbonyl carbon at δ 185.4 with J(C–P) = 12.2, 10.5 Hz. Heating a toluene solution of **3** at 100 °C leads to its clean conversion into **4** (Eq. 5).



3 **4** quant. (5)

Such a process indicates that formation of **4** in reaction (4) involves initial formation of **3** and its thermally induced C–H bond activation. The reaction is followed by a change of the ^1H NMR signal intensity, which indicates first-order kinetics with k_{obs} (s^{-1}) = 3.19×10^{-4} (358 K), 5.97×10^{-4} (363 K), 8.22×10^{-4} (368 K), and 1.52×10^{-3} (373 K). Figure 2 shows Arrhenius plots of the reaction, giving the activation energy of E_a = 111.2 kJ mol^{-1}.

Reactions of 2,2-Diaryl-1-methylenecyclopropanes with [RhH(CO)(PPh$_3$)$_3$]. The reactions of 2,2-diphenyl-1-methylenecyclopropane and of 2,2-di(4-fluorophenyl)-1-methylenecyclopropane with [RhH(CO)(PPh$_3$)$_3$] at room temperature give Rh(I) complexes with 2,2-diaryl-3-butenyl ligands, [Rh{η^2-$CH_2CPh_2CH{=}CH_2$-κC^1}(CO)(PPh$_3$)$_2$] (**5a**), and [Rh{η^2-$CH_2C(C_6H_4$-F-4$)_2CH{=}CH_2$-κC^1}(CO)(PPh$_3$)$_2$] (**5b**), respectively (Eq. 6).



5a: Ar = Ph 75%

5b: Ar = C_6H_4F-4 93% (6)

The reaction of 2,2-diphenyl-1-methylenecyclopropane with [RhD(CO)(PPh$_3$-d_{15})$_3$] gives complex **5a** containing deuterium at γ-position of the 2,2-diphenyl-3-butenyl ligand. Figure 3 shows the ^1H and ^2H NMR spectra of the product.

The ^1H NMR signal at δ 3.43 due to a vinyl hydrogen (=CH–) is much lower than the signals of other vinyl hydrogens (=CH_2). The ^2H NMR spectrum exhibits a broad signal at the same position owing to selective deuteration at the position. The content of the introduced deuterium is calculated as 87% from the ^1H NMR peak area ratio.

The molecular structure of **5a** was determined by X-ray crystallography.[41] Coordination of the chelating 3-butenyl ligand to the trigonal bipyramidal Rh center is similar to the structures of **1** and **3**. Table 1 compares the bond parameters of these complexes and of [Rh{η^2-$CH_2C(CH_2CH_2Ph)_2$-$CH{=}CH_2$-κC^1}(CO)(PPh$_3$)$_2$].[42] The ^1H NMR spectrum of **5a** exhibits resonances of the olefinic protons at δ 2.20, 2.36, and 3.43, which are at slightly lower magnetic field positions than the corresponding signals of **1** (δ 1.70, 1.81, and 2.96). The signals due to Rh–CH_2 hydrogens are observed at δ 0.52 and 1.87. The $^{13}C\{^1H\}$ NMR spectrum of **5a** shows the signal of the Rh–CH_2 carbon at δ 6.1. The signals of the olefinic carbons (δ 51.0 and 59.0) are shifted to lower field positions compared with **1** (δ 28.2 and 31.2). The IR spectrum demonstrates terminal carbonyl stretching (ν(CO) = 1952 cm^{-1}), which is consistent with the $^{13}C\{^1H\}$ NMR spectrum, showing a carbonyl carbon signal at δ 201.2 (J(Rh–C) = 71 Hz, J(C–P) = 16 and 12 Hz). Accordingly, 2,2-di(4-fluorophenyl)-1-methylenecyclopropane reacts with [RhH(CO)(PPh$_3$)$_3$] to yield [Rh{η^2-$CH_2C(C_6H_4$-F-4$)_2CH{=}CH_2$-κC^1}(CO)(PPh$_3$)$_2$] (**5b**) in 93% yield. The ^1H spectrum of **5b** at room temperature is very similar to that of **5a**, although facile isomerization of **5b** into the isomer with 2-allylphenyl ligand (vide infra) prevents measurement of its $^{13}C\{^1H\}$ NMR spectrum.

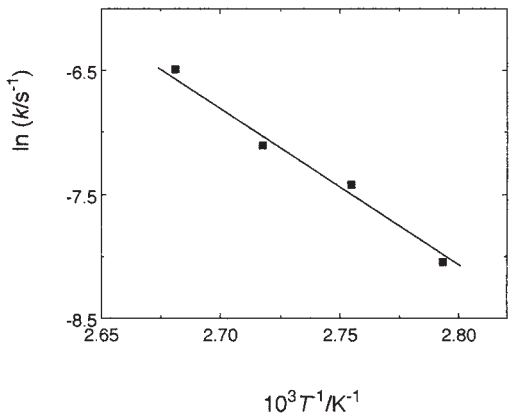


Fig. 2. Arrhenius plot of the first-order rates constant for thermal isomerization of **3** into **4**.

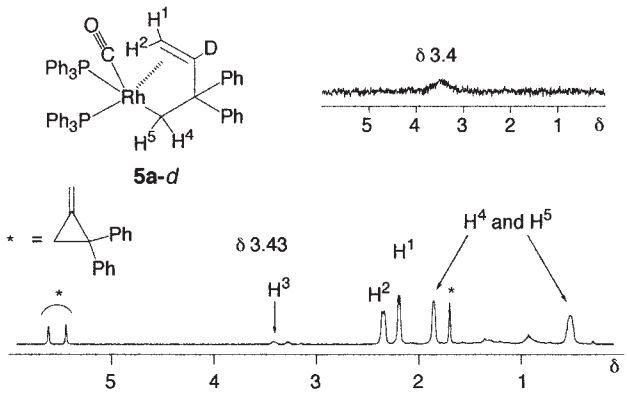
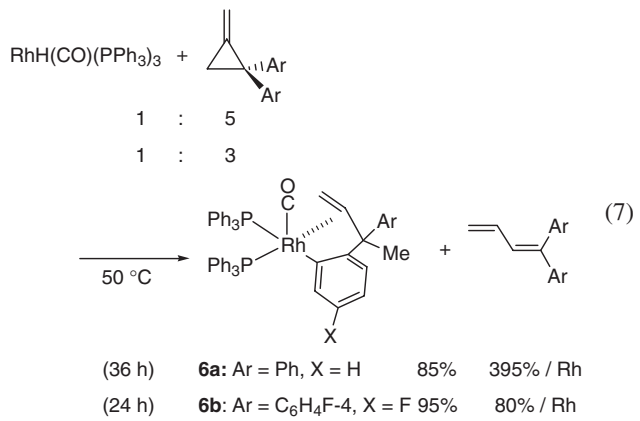


Fig. 3. ^1H NMR spectra of the reaction of 2,2-diphenyl-1-methylenecyclopropane with [RhD(CO)(PPh$_3$)$_3$] in benzene-d_6 after 1 h. Signals with an asterisk are assignable to 2,2-diphenyl-1-methylenecyclopropane. ^2H NMR spectra (in benzene) of the same sample (upper right).

Table 1. Selected Bond Distances (Å) and Angles (deg) for 2,2-Diaryl-3-butenyl Complexes

	1 (M = Ir)	**3** (M = Ir)	**5a** (M = Rh) [Rh(η^2-$CH_2CR_2CH{=}CH_2$)-$(CO)(PPh_3)_2$] (R: CH_2CH_2Ph)	
M–P1	2.385(4)	2.377(2)	2.408(4)	2.375(2)
M–P2	2.341(1)	2.361(2)	2.376(4)	2.353(2)
M–C1	1.65(3)	1.860(7)	1.89(1)	1.881(7)
M–C2	2.11(1)	2.155(6)	2.13(1)	2.162(6)
M–C4	2.14(1)	2.150(5)	2.12(1)	2.132(6)
M–C5	2.12(5)	2.162(6)	2.16(1)	2.157(6)
C2–C3	1.54(2)	1.565(8)	1.52(2)	1.534(8)
C3–C4	1.48(2)	1.592(9)	1.54(2)	1.520(8)
C4–C5	1.33(2)	1.434(9)	1.36(2)	1.441(9)
C1–O1	1.31(3)	1.148(7)	1.13(1)	1.146(7)
P1–M–P2	106.6(1)	101.04(6)	100.6(1)	102.49(6)
M–C1–O1	167(2)	178.4(6)	179(1)	178.2(6)
M–C2–C3	94.7(8)	95.8(4)	96.0(8)	96.6(4)
M–C4–C3	95(1)	95.2(4)	95.8(8)	98.2(4)
M–C4–C5	71(1)	71.0(4)	72.9(8)	71.3(4)
M–C5–C4	72(1)	70.1(3)	70.0(8)	98.2(4)
C2–C3–C4	98(1)	96.6(5)	97(1)	97.5(5)
C3–C4–C5	120(2)	117.1(6)	116(1)	117.0(6)
Ref.	41	this work	41	42

The reaction of 2,2-diphenyl-1-methylenecyclopropane and [$RhH(CO)(PPh_3)_3$] in a 5:1 molar ratio in toluene at 50 °C gives [Rh{η^2-(*o*-C_6H_4)CMe(Ph)CH=CH_2-κC^1}$(CO)(PPh_3)_2$] (**6a**) (Eq. 7).



(7)

NMR experiments in benzene-d_6 indicated that the resulting reaction mixture contained **6a** in 85% and 1,1-diphenyl-1,3-butadiene in 395%/Rh, respectively. The analogous complex with fluorophenyl groups, [Rh{η^2-(*o*-C_6H_3-F-4)CMe(C_6H_4-F-4)CH=CH_2-κC^1}$(CO)(PPh_3)_2$] (**6b**), is formed similarly. Figure 4 shows ORTEP diagram of **6b** which has a distorted trigonal bipyramidal structure, having a phosphorus atom (P1) and an ortho carbon of the phenyl ring at the apical positions and the other phosphorus atom (P2), a carbonyl group, and the vinyl group at the equatorial positions.

The coordination of **6b** is in sharp contrast with **2** that has a CO and the ortho phenyl carbon at the apical positions of the trigonal bipyramidal coordination (Table 2).

NMR spectra of **6a** indicate the presence of two isomers in solution, similarly to **2** (Scheme 1). The ^1H NMR spectrum of

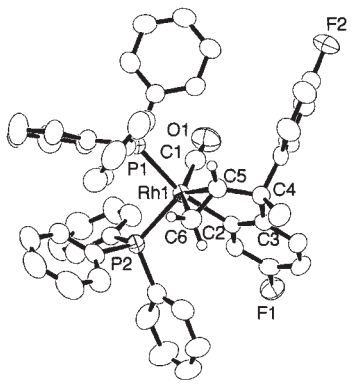


Fig. 4. Structure of **6b** determined by X-ray crystallography with 50% thermal ellipsoidal plotting. One of the two crystallographically independent molecules is shown. Hydrogen atoms at the aromatic rings and solvents were omitted for simplicity.

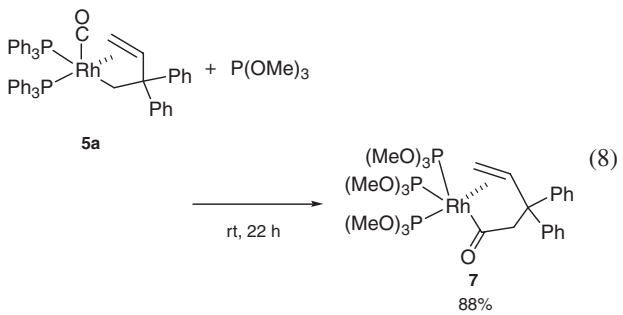
6a shows the hydrogens of the $CH{=}CH_2$ moiety at δ 1.87, 2.67, and 4.13 in 1:1:1 peak area ratio. The resonance at δ 2.07 is assigned to the methyl group hydrogens. A minor signal due to the methyl hydrogens is observed at δ 2.40. Since the peak area ratio between the two peaks due to methyl hydrogens varies reversibly with temperature, the two isomers are equilibrated in the solution. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance for the carbonyl carbon appears at δ 200.5. The $^{31}P\{^1H\}$ NMR spectrum of **6a** shows two sets of doublets of doublets at δ 28.9 and 31.6 arising from two inequivalent phosphorus atoms coupling to the rhodium center (J(Rh–P) = 113.5 and 78.3 Hz, respectively) and to each other (J(P–P) = 15.7 Hz). Another pair of doublets of doublets assigned to the minor isomer was observed at δ 28.4

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2-Allylphenyl Complexes

	2 (M = Ir)	**6b** (M = Rh)
M–P1	2.377(2)	2.386(3)
M–P2	2.358(2)	2.424(3)
M–C1	1.869(6)	1.85(1)
M–C2	2.126(6)	2.083(9)
M–C5	2.161(7)	2.158(9)
M–C6	2.144(7)	2.16(1)
C2–C3	1.408(8)	1.38(1)
C3–C4	1.505(9)	1.52(1)
C4–C5	1.509(9)	1.52(1)
C5–C6	1.439(9)	1.39(1)
C1–O1	1.163(7)	1.15(1)
P1–M–P2	113.10(6)	101.08(9)
M–C1–O1	172.9(7)	177(1)
M–C2–C3	115.4(5)	116.1(7)
M–C5–C4	111.4(5)	113.2(6)
M–C5–C6	69.8(4)	71.1(6)
M–C6–C5	71.1(4)	71.3(6)
C2–C3–C4	116.8(6)	119.3(8)
C3–C4–C5	104.5(6)	106.7(7)
C4–C5–C6	121.6(6)	121.4(9)
Ref.	41	this work

(J(Rh–P) = 116.5 and J(P–P) = 15.7 Hz) and 29.7 (J(Rh–P) = 78.3 and J(P–P) = 15.7 Hz).

Complex **5a** reacts with $P(OMe)_3$ to produce [Rh{η^2-CO-$CH_2CPh_2CH{=}CH_2$-κC^1}($P(OMe)_3$)$_3$] (**7**, 88%) (Eq. 8).



(8)

Migratory insertion of CO ligand into the Rh–C bond of **5a** ocurrs during the reaction. Figure 5 depicts the molecular structure of **7** determined by X-ray crystallography.

The complex has a distorted trigonal bipyramidal around the Rh center with a $P(OMe)_3$ ligand and the CO ligand at the apical positions. The C=C bond (1.426(7) Å) is comparable to **2** (1.439(9) Å) and **3** (1.434(9) Å). The ^{1}H NMR spectrum of **7** shows three hydrogen signals assigned to the CH=CH_2 group at δ 2.39, 2.67, and 4.56; these are shifted to downfield compared to those of the parent **5a** (δ 0.52, 1.87, and 3.43, respectively). The appearance of three sets of doublet of doublets of doublets in the ^{31}P{^{1}H} NMR spectrum of **7** indicates that the three $P(OMe)_3$ are magnetically inequivalent and do not undergo mutual exchange in solution. Jun demonstrated that the $P(OMe)_3$ promoted skeletal rearrangement of the 4-pentenylrhodium complex into cyclobutylmethyl complexes via a four-membered-ring recyclization.[47–50]

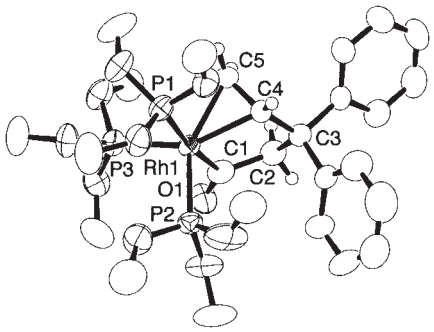
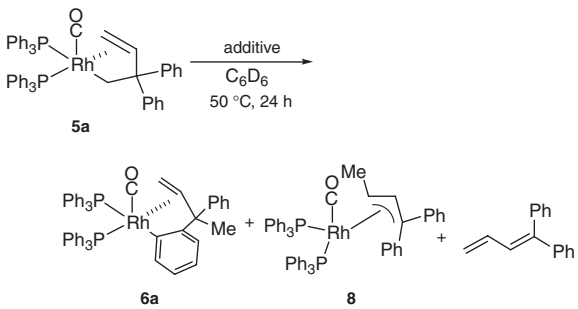


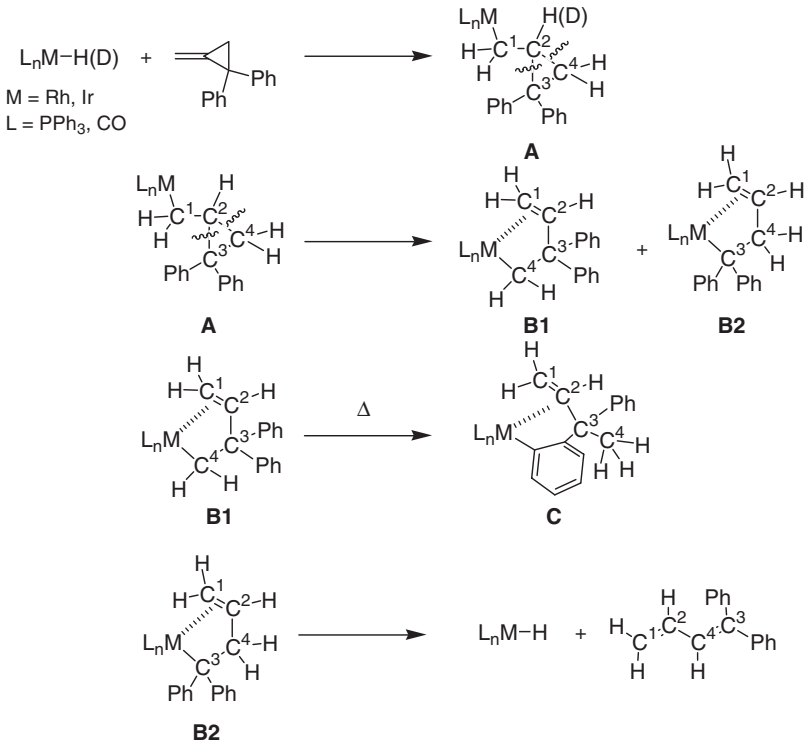
Fig. 5. Structure of **7** determined by X-ray crystallography with 50% thermal ellipsoidal plotting. Hydrogen atoms at the aromatic rings were omitted for simplicity. Selected bond distances (Å) and angles (°): Rh(1)–P(1) 2.347(2), Rh(1)–P(2) 2.291(2), Rh(1)–P(3) 2.286(2), Rh(1)–C(1) 2.066(6), Rh(1)–C(4) 2.169(5), Rh(1)–C(5) 2.152(6), O(1)–C(1) 1.206(6), C(1)–C(2) 1.532(8), C(2)–C(3) 1.535(8), C(3)–C(4) 1.521(7), and C(4)–C(5) 1.426(7); P(1)–Rh(1)–P(2) 93.18(7), P(2)–Rh(1)–P(4) 93.95(6), P(1)–Rh(1)–P(3) 102.92(6), Rh(1)–C(1)–O(1) 128.4(5), Rh(1)–C(1)–C(2) 114.6(4), O(1)–C(1)–C(2) 117.0(5), C(1)–C(2)–C(3) 113.8(5), C(2)–C(3)–C(4) 106.2(5), Rh(1)–C(4)–C(3) 114.0(4), Rh(1)–C(4)–C(5) 70.1(3), C(3)–C(4)–C(5) 119.1(5), and Rh(1)–C(5)–C(4) 71.4(3).

Thermally Induced Isomerization of 5a. As mentioned above, the isolated 2,2-diphenyl-3-butenyl Ir complex **3** undergoes clean thermal isomerization into **4**. The reaction of 2,2-diphenyl-1-methylenecyclopropane with [RhH(CO)(PPh_3)$_3$] at 50 °C produces **5a**, having a similar structure to **3**, accompanied by generation of 1,3-dienes. Heating the isolated 3-butenylrhodium complex **5a** at 50 °C does not produce the corresponding 2-allylphenylrhodium complex **6a** at all, as shown in Eq. 9, although the reaction of excess 2,2-diphenyl-1-methylenecyclopropane with [RhH(CO)(PPh_3)$_3$] affords **6a** in high yield (Eq. 7). The Rh-containing product of thermal reaction of **5a** is not isolated from the reaction mixture, and this is assigned tentatively to allylic rhodium complex **8** based on the ^{1}H NMR spectrum of the solution (vide infra). Formation of 1,1-diphenyl-1,3-butadiene in 44% yield is also noted.



(9)

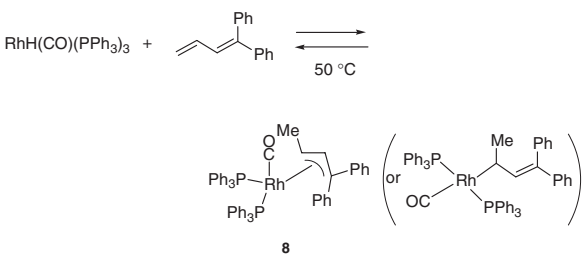
additive	NMR Yield (%) **6a**	**8**	butadiene
none	0	53	44
5 	60	0	439
PPh_3	24	0	59



Scheme 2.

Addition of 5 equiv of 2,2-diphenyl-1-methylenecyclopropane before heating the solution of **5a** produces **6a** in 60% yield, along with 1,1-diphenyl-1,3-butadiene in 439% yield based on Rh. Thermal reaction of **5a** in the presence of PPh_3 also yields **6a** (24%) and 1,1-diphenyl-1,3-butadiene (59%).

The Rh complex obtained from the thermal reaction of **5a** without the additives is not isolated from the reaction mixture. The reaction of 1,1-diphenyl-1,3-butadiene with [RhH(CO)-$(PPh_3)_3$] affords the same complex **8** (Eq. 10)



(10)

8

which is characterized in situ by the ^{1}H NMR spectroscopy. Heating a mixture of 1,1-diphenyl-1,3-butadiene and [RhH-$(CO)(PPh_3)_3$] in toluene-d_8 leads to generation of new signals at δ 1.14 (dd, $J = 3.9$, 6.3 Hz), 2.93 (m), and 5.61 (dd, $J = 2.0$, 12.7 Hz) in a 3:1:1 ratio, suggesting the formation of an allylic complex, although the present data are not sufficient to choose the coordination mode between π-allylic and σ-allylic[51,52] bond. Although we could not exclude the σ-allylrhodium structure for the complex, similar Rh and Ir complexes with π-allylic ligands were isolated and well characterized.[53–56] Interconversion between the σ-allyl and π-allyl Rh complex was discussed based on the results of copolymerization of substituted allenes with CO catalyzed by Rh complexes.[57]

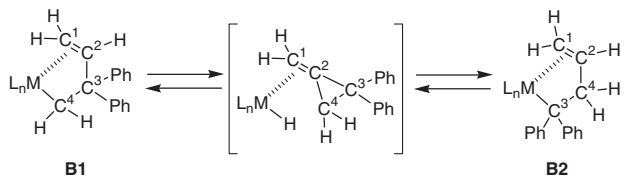
Reaction Mechanism. A plausible reaction mechanism for the reaction of 2,2-diaryl-1-methylenecyclopropanes is shown in Scheme 2. Insertion of the C=C double bond of 2,2-diaryl-1-methylenecyclopropane into a M–H bond forms the intermediate complex **A** having a cyclopropylmethyl ligand.[35,36] Cleavage of the C–C bond of the three-membered ring via β-alkyl elimination leads to the intermediate **B1** having a 2,2-diphenyl-3-butenyl ligand and **B2** having a 1,1-diphenyl-3-butenyl ligand. β-Alkyl elimination of alkyl transition metal complexes[58] has become common in the reactions of late transition metal complexes.[59–67] Cycloalkylmethyl complexes of transition metals undergo ring opening accompanied by C–C bond clevage, which is mentioned below. Isomerization between the Co complexes with 1-methyl-3-butenyl ligand and with 2-methyl-3-butenyl ligand involves an intermediate cyclopropylmethyl complex which undergoes cleavage of the C–C bond of the three-membered ring.[68,69] Casey reported the reaction of methylenecyclobutane with a yttrium hydrido complex to give a 4-pentenylyttrium complex via cyclobutylmethylyttrium intermediate.[70] Flood studied the reaction of 4-pentenylplatinum complexes in detail and proposed reversible formation of cyclobutylplatinum complex and its ring opening to account for the scrambling of labeled deuterium.[44,71,72] Similar reactions were proposed in the cyclization and ring opening of organic ligands catalyzed by Th and Pd complexes.[73,74]

Selectivity of the reactions in Scheme 3 is explained as follows. Cleavage of less sterically demanding C–C bond occurs easily to produce **B1**, while the sterically hindered C–C bond cleavage leads to the formation of **B2**. The complexes **3** (M = Ir) and **5a** (M = Rh), which correspond to **B1** in Scheme 3, are isolated from the reaction mixtures. The 1,1-diphenyl-3-butenyl complexes, having the structure of **B2**, were not obtained in the reactions in Eqs. 3, 4, 6, and 7. The reaction of 2,2-diphenyl-1-methylenecyclopropane with [RhH(CO)-

$(PPh_3)_3]$ (Eq. 6) accompanies formation of 1,1-diphenyl-1,3-butadiene, which is the product of β-hydrogen elimination of the complex **B2** (M = Rh). The complex **B2** that formed in the reaction with $[RhH(CO)(PPh_3)_3]$ is probably turned into $[RhH(CO)(PPh_3)_3]$ by β-hydrogen elimination of the 3-butenyl ligand to release 1,3-butadiene. The reaction with $[IrH(CO)(PPh_3)_3]$ (Eq. 4) does not form 1,3-diene nor the complex having the structure with a 1,1-diphenyl-3-butenyl ligand even at elevated temperature.

The absence of the intermediate **B2** or its product is explained by assuming the following equilibrium between the intermediates **B1** and **B2** (Scheme 3).

The Ir-containing complex with the 1,1-diphenyl-3-butenyl ligand does not undergo β-hydrogen elimination because the Ir–C bond is too stable to be cleaved by such a concerted reaction. Once formed via cleavage of the C–C bond which is more easily activated than the other C–C bond in the molecule, complex **B2** is converted into **B1** via γ-hydrogen elimination. Although the formation of three-membered ring is thermodynamically unfavorable, the complex having π-coordinated methylenecyclopropane is stabilized by strong coordination of the C=C double bond of the strained molecules. Similar repetition of ring-opening and formation of these type molecules by transition metal complexes was already reported.



Scheme 3.

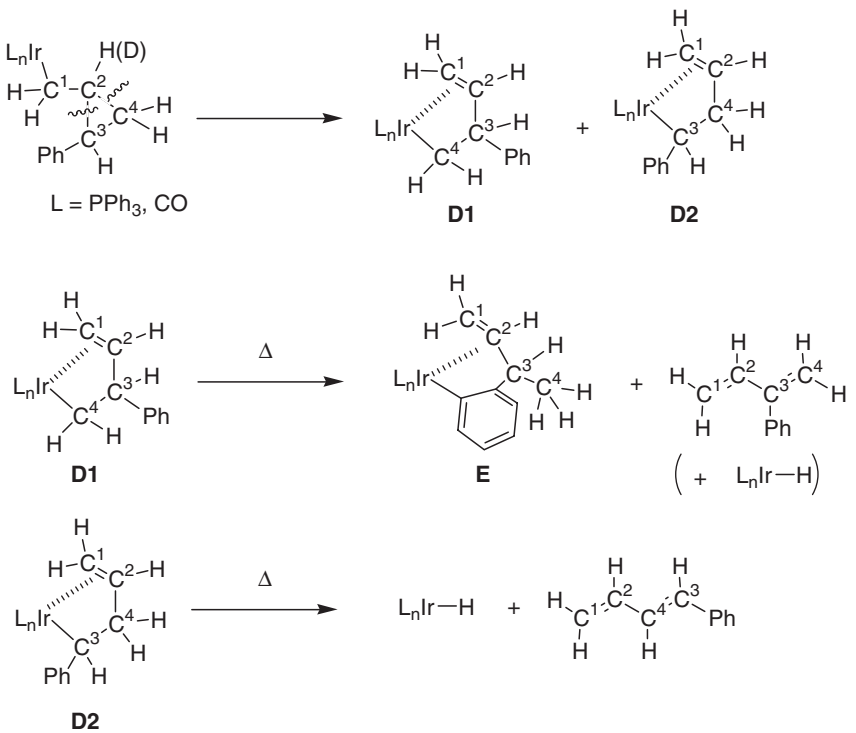
Several other rearrangements of cycloalkylmethyl-metal complexes, via concerted mechanisms have been reported.

The mechanism for the C–C bond activation of 2-phenyl-1-methylenecyclopropane is summarized in Scheme 4. C–C bond cleavage of the cyclopropylmethyl complexes of Ir, **D1** and **D2**, take place similarly to the reactions of 2,2-diphenyl-1-methylenecyclopropane with $[IrH(CO)(PPh_3)_3]$. **D1** undergoes thermally induced orthometalation of the 2-phenyl-3-butenyl ligand to produce **E** or undergoes β-hydrogen elimination of the ligand to give 2-phenyl-1,3-butadiene. The former product **E** corresponds to **2** in Eq. 2. β-Hydrogen elimination of **D2** releases 1-phenyl-1,3-butadiene. Hydrido iridium species formed by β-hydrogen elimination of **D1** and **D2** reacts further with 2-phenyl-1-methylenecyclopropane in the reaction mixture.

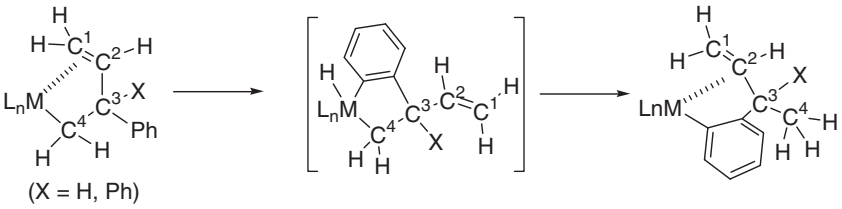
Both Scheme 3 and Scheme 5 include the thermal rearrangement of 2-phenyl or 2,2-diphenyl-3-butenyl ligands bonded to the metal center to 2-(1-methylallyl)phenyl ligand via orthometalation of the phenyl group of the ligand. The formation is considered to proceed via the pathway shown in Scheme 5.

Initial orthometalation of the phenyl group forms an intermediate five-membered metallacycle with the hydrido ligand. Reductive elimination giving a methyl group at the ligand results in the 2-(1-methylallyl)phenyl ligand.

In summary, the reactions of 2-phenyl-1-methylenecyclopropane and of 2,2-diaryl-1-methylenecyclopropane with hydrido complexes of Rh and Ir causes C–C bond cleavage of the three-membered ring. The bond cleavage occurs via β-alkyl elimination of the cyclopropylmethyl-metal intermediate. Sterically less hindered C–C bond is activated more easily, but the relative facility of the subsequent reaction of the intermediates changes relative amounts of the final products after isomerization.



Scheme 4.



Scheme 5.

Experimental

General. All manipulations of the complexes were carried out using standard Schlenk techniques under an argon or a nitrogen atmosphere. THF and toluene grade were distilled from sodium and benzophenone prior to use or were purchased from Kanto Chemicals Co., Ltd. [RhH(CO)(PPh_3)$_3$],[53,54] [IrH(CO)(PPh_3)$_3$],[75,76] 2-phenyl-1-methylenecyclopropane, 2,2-diphenyl-1-methylenecyclopropane, and 2,2-bis(4-fluorophenyl)-1-methylenecyclopropane,[77] 1-phenyl-1,3-butadiene, 2-phenyl-1,3-butadiene, and 1,1-diphenyl-1,3-butadiene,[78,79] were prepared according to the literature methods.

NMR spectra (^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H}) were recorded on JEOL EX-400 and Varian Mercury 300 spectrometers. The ^{1}H NMR peak positions were referenced with the residual peak of the solvent, while the ^{13}C{^{1}H} NMR peak positions were determined by using the solvent signals as the reference. An external standard (85% H_3PO_4, δ 0) was used in the ^{31}P{^{1}H} NMR measurement. The IR spectra were recorded on a Shimadzu FTIR-8100A spectrometer in KBr. Elemental analyses were carried out with a Yanaco MT-5 CHN autocorder.

Reaction of 2-Phenyl-1-methylenecyclopropane with [IrH(CO)(PPh_3)$_3$] at Room Temperature. To a solution of [IrH(CO)(PPh_3)$_3$] (223 mg, 0.22 mmol) in 10 cm^3 of toluene was added 2-phenyl-1-methylenecyclopropane (0.074 cm^3, 0.54 mmol) at room temperature. After 24 h the solvent was removed by evaporation. Addition of hexane (10 cm^3) to the yellow oily substance led to the formation of a pale yellow solid, which was washed with 10 cm^3 of hexane (4 times), collected by filtration, and dried in vacuo to give [Ir{η^2-$CH_2CH(Ph)CH{=}CH_2$-κC^1}(CO)(PPh_3)$_2$] (**1**) as a colorless solid (171 mg, 0.20 mmol, 88%). Recrystallization from toluene at -20 °C gave colorless crystals. ^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ 0.11 (m, 1H), ca. 1.70 (overlapped m, 2H), 1.81 (m, 1H), 2.96 (m, 1H), 4.48 (m, 1H), 6.85–7.73 (m, 35H, Ph). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 25 °C): δ -4.93 (d, J(P–P) = 8.9 Hz), 8.14 (d, J(P–P) = 8.9 Hz). ^{13}C{^{1}H} NMR (75.3 MHz, CD_2Cl_2, 25 °C): δ -12.4 (d, J = 63.2 Hz), 28.2 (dd, J(C–P) = 20.9, J(C–P) = 14.8 Hz), 31.2 (dd, J(C–P) = 7.9 Hz, J(C–P) = 2.8 Hz), 51.8 (brs), 125.3 (Ph), 125.7 (Ph), 127.7 (Ph), 127.9 (d, J(C–P) = 9.2 Hz, PPh_3-*ortho*), 127.9 (d, J(C–P) = 9.2 Hz, PPh_3-*ortho*), 129.3 (d, J(C–P) = 1.5 Hz, PPh_3-*para*), 129.8 (d, J(C–P) = 1.7 Hz, PPh_3-*para*), 133.7 (d, J(C–P) = 10.9 Hz, PPh_3-*meta*), 134.3 (dd, J(C–P) = 34.9, J(C–P) = 2.4 Hz, PPh_3-*ipso*), 134.5 (d, J(C–P) = 11.4 Hz, PPh_3-*meta*), 136.8 (dd, J(C–P) = 36.5, J(C–P) = 2.3 Hz, PPh_3-*ipso*), 155.3 (dd, J(C–P) = 6.9, J(C–P) = 6.3 Hz, C^6), 185.8 (dd, J(C–P) = 16.4, J(C–P) = 7.1 Hz, CO). IR (KBr): 1939 cm^{-1}, ν(CO). Anal. calcd for $C_{47}H_{41}OP_2Ir$: C, 64.44; H, 4.72%. Found: C, 64.60; H, 4.72%.

Reaction of 2-Phenyl-1-methylenecyclopropane with [IrH(CO)(PPh_3)$_3$] at 50 °C. To a toluene (10 cm^3) solution of [IrH(CO)(PPh_3)$_3$] (222 mg, 0.22 mmol) was added 2-phenyl-1-methylenecyclopropane (285 mg, 2.2 mmol) at room temperature. Stirring the solution at 50 °C caused the change of the solution from pale yellow to dark yellow. After 24 h the volatiles were removed under reduced pressure. Addition of 10 cm^3 of hexane to the yellow oily residue at -78 °C led to the formation of a pale yellow solid, which was washed with 10 cm^3 of hexane (4 times), collected by filtration, and dried in vacuo to give a pale yellow powder of [Ir{η^2-(o-C_6H_4)CH(Me)CH=CH_2-κC^1}(CO)(PPh_3)$_2$] (**2**) (91 mg, 0.11 mmol, 47%). NMR yield of **2** was 82%. Complex **2** crystallizes from toluene–hexane at -20 °C as colorless crystals. ^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ 1.53 (d, J = 6.6 Hz, 3H, Me), 1.79 (m, 1H), 2.85 (m, 2H), 3.48 (m, 1H), 6.35–7.62 (m, 34H, Ph). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 25 °C): δ 0.36 and 3.31 (d, J(P–P) = 43.4 Hz, major), 1.66 and 4.28 (d, J(P–P) = 40.1 Hz, minor). ^{13}C{^{1}H} NMR (75.3 MHz, CD_2Cl_2, 25 °C): δ 23.5 (d, J(C–P) = 8.1 Hz, Me), 28.1 (dd, J(C–P) = 27.0, J(C–P) = 6.9 Hz), 44.4 (s), 55.3 (dd, J(C–P) = 25.3, J(C–P) = 4.6 Hz), 122.5 (d, J(C–P) = 3.1 Hz, Ph), 124.5 (t, J(C–P) = 2.5 Hz, Ph), 124.7 (d, J(C–P) = 1.3 Hz, Ph), 127.8 (d, J(C–P) = 9.2 Hz, PPh_3-*ortho*), 128.0 (d, J(C–P) = 9.2 Hz, PPh_3-*ortho*), 129.5 (d, J(C–P) = 1.7 Hz, PPh_3-*para*), 129.6 (d, J(C–P) = 1.7 Hz, PPh_3-*para*), 134.1 (d, J(C–P) = 10.9 Hz, PPh_3-*meta*), 134.2 (d, J(C–P) = 11.4 Hz, PPh_3-*meta*), 136.5 (dd, J(C–P) = 40.2, J(C–P) = 2.3 Hz, PPh_3-*ipso*), 137.5 (dd, J(C–P) = 37.4, J(C–P) = 2.3 Hz, PPh_3-*ipso*), 141.2 (dd, J(C–P) = 11.8, J(C–P) = 3.2 Hz), 150.1 (dd, J(C–P) = 12.2, J(C–P) = 9.0 Hz), 154.2 (dd, J(C–P) = 5.2, J(C–P) = 2.5 Hz), 179.6 (dd, J(C–P) = 8.6, J(C–P) = 5.2 Hz, CO). IR (KBr): 1977 cm^{-1}, ν(CO). Anal. calcd for $C_{47}H_{41}OP_2Ir$: C, 64.44; H, 4.72%. Found: C, 64.85; H, 4.70%.

NMR Experiment for the Reaction of 2-Phenyl-1-methylenecyclopropane with [IrH(CO)(PPh_3)$_3$] at 50 °C. To a solution of [IrH(CO)(PPh_3)$_3$] (20 mg, 0.020 mmol) in 0.6 cm^3 of benzene-d_6 was added 2-phenyl-1-methylenecyclopropane (0.027 cm^3, 0.20 mmol) at room temperature. The mixture was heated at 50 °C and the ^{1}H NMR spectrum after 40 h revealed formation of **2** (82%), 2-phenyl-1,3-butadiene (470% based on Ir), and 1-phenyl-1,3-butadiene (177% based on Ir).

Reaction of 2,2-Diphenyl-1-methylenecyclopropane with [IrH(CO)(PPh_3)$_3$] at 50 °C. To a solution of [IrH(CO)(PPh_3)$_3$] (223 mg, 0.22 mmol) in 10 cm^3 of toluene was added 2,2-diphenyl-1-methylenecyclopropane (0.134 cm^3, 0.54 mmol) at ambient temperature. The reaction mixture was heated to 50 °C and stirred for 15 h. The resulting pale yellow solution was subjected to evaporation to give yellow oily substances, which were washed with 10 cm^3 of hexane (4 times). The complete removal of hexane furnished [Ir{η^2-$CH_2CPh_2CH{=}CH_2$-κC^1}(CO)(PPh_3)$_2$] (**3**) (164 mg, 0.17 mmol, 78%) as a white powder. Recrystallization from toluene–hexane gave colorless prismatic crystals. ^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ -0.70 (ddd, J = 13.5, 8.4, 4.8 Hz, 1H, Ir–CH_2), 1.63 (m, 1H), 1.75 (m, 1H), 1.93 (dd, J = 8.4, 3.3 Hz, 1H), 3.00 (m, 1H), 6.79–7.84 (m, 40H, Ph). ^{31}P{^{1}H} NMR

(121.5 MHz, CD_2Cl_2, 25 °C): δ −4.38 (d, J(P–P) = 6.7 Hz), 6.78 (d, J(P–P) = 6.7 Hz). $^{13}C\{^1H\}$ NMR (75.3 MHz, CD_2Cl_2, 25 °C): δ −7.0 (d, J(C–P) = 62.0 Hz), 30.8 (dd, J(C–P) = 8.3, J(C–P) = 2.6 Hz), 32.9 (d, J(C–P) = 25.3 Hz), 61.4 (d, J(C–P) = 1.7 Hz), 124.6 (Ph-*para*), 125.2 (Ph-*para*), 125.3 (Ph-*ortho*), 125.6 (Ph-*ipso*), 127.1 (Ph-*ortho*), 127.6 (Ph-*meta*), 127.9 (Ph-*meta*), 127.9 (d, J(C–P) = 9.2 Hz, PPh_3-*ortho*), 128.1 (d, J(C–P) = 9.2 Hz, PPh_3-*ortho*), 128.5 (Ph-*ipso*), 129.3 (d, J(C–P) = 1.7 Hz, PPh_3-*para*), 129.8 (d, J(C–P) = 2.3 Hz, PPh_3-*para*), 133.7 (d, J(C–P) = 10.9 Hz, PPh_3-*meta*), 134.0 (dd, J(C–P) = 41.9, J(C–P) = 2.3 Hz, PPh_3-*ipso*), 134.5 (d, J(C–P) = 11.5 Hz, PPh_3-*meta*), 136.7 (dd, J(C–P) = 37.3, J(C–P) = 2.3 Hz, PPh_3-*ipso*), 184.9 (dd, J = 14.4, 7.5 Hz, CO). IR (KBr): 1945 cm^{-1}, ν(CO). Anal. calcd for $C_{53}H_{45}OP_2Ir$: C, 66.86; H, 4.76%. Found: C, 66.43; H, 5.15%.

Reaction of 2,2-Diphenyl-1-methylenecyclopropane with [IrH(CO)(PPh$_3$)$_3$] at 100 °C. To a solution of [IrH(CO)(PPh_3)$_3$] (223 mg, 0.22 mmol) in 10 cm^3 of toluene was added 2,2-diphenyl-1-methylenecyclopropane (0.134 cm^3, 0.54 mmol). Heating of the resulting mixture at 100 °C for 48 h furnished a pale yellow solution, which was subjected to evaporation to give yellow oily substances. Washing with 10 cm^3 of hexane (4 times) at −78 °C and removal of hexane gave [Ir{η^2-(*o*-C_6H_4)CMe(Ph)CH=CH_2-κC^1}(CO)(PPh_3)$_2$] (**4**) (169 mg, 0.18 mmol, 80%) as a colorless solid. ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): δ 0.72 (m, 1H), 1.43 (m, 1H), 1.94 (s, 3H, Me), 2.73 (m, 1H), 6.13–7.68 (m, 39H, Ph). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 25 °C): δ 2.54 (d, J(P–P) = 6.7 Hz), 4.52 (d, J(P–P) = 6.7 Hz). $^{13}C\{^1H\}$ NMR (75.3 MHz, CD_2Cl_2, 25 °C): δ 29.5 (d, J(C–P) = 6.9 Hz, Me), 30.9 (d, J(C–P) = 5.8 Hz), 57.3 (dd, J(C–P) = 5.0, J(C–P) = 3.5 Hz), 61.9 (d, J(C–P) = 24.7 Hz), 124.4 (d, J(C–P) = 5.8 Hz, Ph), 125.6 (Ph), 125.7 (Ph-*para*), 126.5 (d, J(C–P) = 2.9 Hz, Ph), 127.7 (Ph-*ortho*), 127.9 (d, J(C–P) = 9.3 Hz, PPh_3-*ortho*), 128.1 (d, J(C–P) = 9.2 Hz, PPh_3-*ortho*), 128.2 (Ph-*meta*), 129.4 (PPh_3-*para*), 129.8 (PPh_3-*para*), 134.3 (d, J(C–P) = 10.3 Hz, PPh_3-*meta*), 136.0 (d, J(C–P) = 39.6 Hz, PPh_3-*ipso*), 142.7 (dd, J(C–P) = 8.1, J(C–P) = 3.5 Hz), 153.2 (Ph-*ipso*), 157.2 (d, J(C–P) = 5.7 Hz, Ir–C), 185.4 (dd, J(C–P) = 12.2, J(C–P) = 10.5 Hz, CO). IR (KBr): 1956 cm^{-1}, ν(CO). Anal. calcd for $C_{53}H_{45}OP_2Ir$: C, 66.86; H, 4.76%. Found: C, 66.71; H, 4.87%.

Thermal Reaction of 3. A solution of **3** (14 mg, 0.015 mmol) in toluene-d_8 (0.6 cm^3) was placed in an NMR tube with a Teflon cap. The sample was heated at constant temperature in an oil bath, and the ^1H and $^{31}P\{^1H\}$ spectra were recorded at room temperature after cooling the solution quickly. The amount of **4** formed in the solution was monitored by the change of the peak area compared to a signal of anisole (δ 3.39) added as an internal standard. Experiments were carried out at 358, 363, 368, and 373 K.

Reaction of 2,2-Diphenyl-1-methylenecyclopropane with [RhH(CO)(PPh$_3$)$_3$] at Room Temperature. To a toluene (10 cm^3) solution of [RhH(CO)(PPh_3)$_3$] (707 mg, 0.77 mmol) was added 2,2-diphenyl-1-methylenecyclopropane (175 mg, 0.85 mmol) at room temperature. The color of the solution was immediately turned from yellow to orange on stirring. After 1 h the volatiles were removed under reduced pressure. The resulting oily materials were washed with hexane repeatedly to give [Rh{η^2-CH_2CPh_2CH=CH_2-κC^1}(CO)(PPh_3)$_2$] (**5a**) as a pale yellow solid (500 mg, 0.58 mmol, 75%). ^1H NMR (400 MHz, benzene-d_6, 25 °C): δ 0.52 (m, 1H), 1.87 (s, 1H), 2.20 (t, J = 7 Hz, 1H), 2.36 (t, J = 9 Hz, 1H), 3.43 (m, 1H), 6.80–7.75 (m, 40H, Ph). $^{31}P\{^1H\}$ NMR (160 MHz, benzene-d_6, 25 °C): δ 38.1 (dd, J(Rh–P) = 90 Hz, J(P–P) = 16 Hz), 27.3 (dd, J(Rh–P) = 121 Hz, J(P–P) = 16 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 25 °C): δ 6.1 (dd, J(Rh–C) = 66 Hz, J(C–P) = 12 Hz), 48.3 (s), 51.0 (dd, J(Rh–C) = 21 Hz, J(C–P) = 5 Hz), 59.0 (t, J = 3 Hz), 124.7 (Ph), 125.7 (Ph), 125.7 (Ph), 127.1 (Ph), 127.9–128.3 (PPh_3-*ortho*), 128.8–129.1 (PPh_3-*para*), 133.6–134.5 (PPh_3-*meta*), 135.2 (d, J(C–P) = 31.0 Hz, PPh_3-*ipso*), 137.3 (d, J(C–P) = 24.7 Hz, PPh_3-*ipso*), 150.6 (Ph), 157.6 (Ph), 201.2 (ddd, J(Rh–C)=71 Hz, J(C–P) = 16 Hz, J(C–P) = 12 Hz, CO). IR (KBr): 1952 cm^{-1}, ν(CO). Anal. calcd for $C_{53}H_{45}OP_2Rh$: C, 73.78; H, 5.26%. Found: C, 73.58; H, 5.72%.

The reaction of 2,2-di(4-fluorophenyl)-1-methylenecyclopropane was carried out in an NMR sample scale as follows. To a benzene-d_6 (0.6 cm^3) solution of [RhH(CO)(PPh_3)$_3$] (18.4 mg, 0.020 mmol) in an NMR tube was added 2,2-di(4-fluorophenyl)-1-methylenecyclopropane (0.0058 cm^3, 0.024 mmol) at room temperature. The initial orange solution was immediately turned into red. Monitoring the reaction by ^1H NMR revealed formation of [Rh{η^2-$CH_2C(C_6H_4$-F-4)$_2CH$=CH_2-κC^1}(CO)(PPh_3)$_2$] (**5b**) in 93% yield. ^1H NMR (300 MHz, benzene-d_6, 25 °C): δ 0.37 (m, 1H), 1.61 (s, 1H), 2.19 (t, J = 7 Hz, 1H), 2.24 (t, J = 10 Hz, 1H), 3.16 (m, 1H), 6.64 (t, J = 8 Hz, 2H), 6.87–7.02 (m, 24H, aromatics), 7.32–7.45 (m, 12H, aromatics). $^{31}P\{^1H\}$ NMR (121.5 MHz, benzene-d_6, 25 °C): δ 38.1 (dd, J(Rh–P) = 90 Hz, J(P–P) = 19 Hz), 26.7 (dd, J(Rh–P) = 121 Hz, J(P–P) = 19 Hz). IR (KBr): 1954 cm^{-1}, ν(CO). Isomerization of **5b** into **6b** at room temperature in solution prevented $^{13}C\{^1H\}$ NMR measurement of **5b**.

Reaction of 2,2-Diphenyl-1-methylenecyclopropane with [RhD(CO)(PPh$_3$-*d*$_{15}$)$_3$]. To a benzene-d_6 (0.60 cm^3) solution of [RhD(CO)(PPh_3-d_{15})$_3$] (19 mg, 0.020 mmol) was added 2,2-diphenyl-1-methylenecyclopropane (0.0050 cm^3, 0.025 mmol) at room temperature. The color of the solution was immediately turned from yellow to orange on stirring. After 1 h ^1H NMR was measured. The results reveal that the signal at δ 3.43 assigned as D attached to the γ-alkenyl carbon of the 3-butenyl ligand disappeared (13% integration compared to that of **6a**), indicating 87% D contents, instead a broad signal at the same chemical shift was observed in the ^2H NMR spectrum in benzene.

Reaction of 2,2-Diaryl-1-methylenecyclopropane with [RhH(CO)(PPh$_3$)$_3$] at 50 °C. To a toluene (6 cm^3) solution of [RhH(CO)(PPh_3)$_3$] (206 mg, 0.22 mmol) was added 2,2-diphenyl-1-methylenecyclopropane (227 mg, 1.1 mmol). During the reaction at 50 °C, the color of the solution changed from yellow to reddish orange. After 24 h the volatiles were evaporated to dryness and the resulting oily materials were washed with hexane repeatedly at 0 °C to give [Rh{η^2-(*o*-C_6H_4)CMe(Ph)CH=CH_2-κC^1}(CO)(PPh_3)$_2$] (**6a**) as a pale orange solid (100 mg, 0.12 mmol, 52%). NMR yield of **6a** was 85%. Recrystallization from CH_2Cl_2–hexane gave pale yellow crystals. ^1H NMR (400 MHz, benzene-d_6, 25 °C): δ 1.87 (q, 1H, J = 7.6 Hz), 2.07 (s, 3H, Me), 2.67 (q, 1H, J = 8.4 Hz), 4.13 (m, 1H), 6.50–7.44 (m, 39H, Ph). $^{31}P\{^1H\}$ NMR (121.5 MHz, benzene-d_6, 25 °C): major: δ 28.9 (dd, J(Rh–P) = 113.5 Hz, J(P–P) = 15.7 Hz), 31.6 (dd, J(Rh–P) = 78.3 Hz, J(P–P) = 15.7 Hz), minor: δ 28.4 (dd, J(Rh–P) = 116.5, J(P–P) = 15.7 Hz), 29.7 (dd, J(Rh–P) = 78.3, J(P–P) = 15.7 Hz). $^{13}C\{^1H\}$ NMR (100.4 MHz, CD_2Cl_2, 25 °C): δ 32.2 (Me), 46.5 (s), 54.4 (s), 82.1 (d, J = 14.7 Hz), 122.6 (Ph), 124.1 (d, J = 7.3 Hz, Ph), 128.1–128.3 (PPh_3-*ortho* and -*para*), 128.5 (Ph-*ipso*), 128.9 (d, J = 11.0 Hz, Ph), 134.3 (PPh_3-*meta*), 135.1 (br, PPh_3-*ipso*), 137.0 (d, J = 25.7 Hz, PPh_3-*ipso*), 142.2 (Ph), 153.2 (s), 157.0 (s), 200.5 (ddd, J(Rh–C) = 73.5 Hz, J(C–P) = 25.7, 7.3 Hz, CO). IR (KBr): 1966 cm^{-1}, ν(CO). Anal. calcd for $C_{53}H_{45}OP_2Rh$: C, 73.78; H, 5.26%. Found: C, 73.54; H, 5.55%.

[Rh{η^2-(*o*-C_6H_3-F-4)CMe(C_6H_4-F-4)CH=CH_2-κC^1}(CO)-(PPh_3)$_2$] (**6b**) was prepared in 95% yield (211 mg, 0.24 mmol) by a similar reaction of 2,2-di(4-fluorophenyl)-1-methylenecyclopropane (0.179 cm^3, 0.74 mmol) with [RhH(CO)(PPh_3)$_3$] (227 mg, 0.25 mmol) at 50 °C. Recrystallization of from CH_2Cl_2–hexane gave pale yellow crystals suitable for X-ray analysis (**6b**·CH_2Cl_2·H_2O). ^{1}H NMR (400 MHz, benzene-d_6, 25 °C): δ 1.87 (dd, 1H, J = 15, 7 Hz), 1.90 (s, 3H, Me), 2.53 (dd, 1H, J = 17, 8 Hz), 3.99 (s, 1H). ^{31}P{^{1}H} NMR (162 MHz, benzene-d_6, 25 °C): δ 28.8 (dd, J(Rh–P) = 113 Hz, J(P–P) = 16 Hz), 31.8 (dd, J(Rh–P) = 74 Hz, J(P–P) = 16 Hz). IR (KBr): 1968 cm^{-1}, ν(CO). Anal. calcd for $C_{53}H_{43}F_2OP_2Rh$: C, 70.83; H, 4.82%. Found: C, 70.59; H, 5.21%.

Reaction of P(OMe)$_3$ with 5a. To a 7 cm^3 of toluene solution of **5a** (180 mg, 0.21 mmol) was added P(OMe)$_3$ (0.071 cm^3, 0.60 mmol) at room temperature. After 22 h the volatiles were removed by evaporation. Addition of hexane gave white precipitates, which were collected by filtration to yield [Rh{η^2-CO-CH_2CPh_2CH=CH_2-κC^1}(P(OMe)$_3$)$_3$] (**7**) (130 mg, 0.18 mmol, 88%). Recrystallization from hexane yielded colorless crystals suitable for X-ray analysis. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 2.39 (m, 1H), 2.50 (d, J = 16.8 Hz, 1H), 2.67 (m, 1H), 3.20 (d, J = 11.2 Hz, 9H, P(OMe)$_3$), 3.51 (d, J = 10.0 Hz, 9H, P(OMe)$_3$), 3.59 (d, J = 10.8 Hz, 9H, P(OMe)$_3$), 3.60–3.65 (overlapped, 1H), 4.56 (m, 1H), 7.05–7.09 (m, 2H, Ph), 7.16–7.22 (m, 4H, Ph), 7.31 (d, J = 7.6 Hz, 2H, Ph), 7.56 (d, J = 7.6 Hz, 2H, Ph). ^{31}P{^{1}H} NMR (162 MHz, benzene-d_6, 25 °C): δ 143.6 (ddd, J(Rh–P) = 143 Hz, J(P–P) = 74 Hz, J(P–P) = 66 Hz), 147.8 (ddd, J(Rh–P) = 228 Hz, J(P–P) = 74 Hz, J(P–P) = 33 Hz), 152.1 (ddd, J(Rh–P) = 214 Hz, J(P–P) = 66 Hz, J(P–P) = 33 Hz). ^{13}C{^{1}H} NMR (100.4 MHz, CD_2Cl_2, 25 °C): δ 33.9 (ddt, J(Rh–C) = 34 Hz, J(C–P) = 9 Hz, J(C–P) = 6 Hz, CH=CH_2), 51.0 (d, J(C–P) = 2 Hz, OCH_3), 51.9 (d, J(C–P) = 6 Hz, OCH_3), 52.6 (d, J(Rh–C) = 34 Hz), 64.0 (dt, J(Rh–C) = 41 Hz, J(C–P) = 4 Hz, CH_2), 68.7 (dddd, J(Rh–C) = 40 Hz, J(C–P) = 12 Hz, J(C–P) = 8 Hz, J(C–P) = 2 Hz), 125.0 (s, Ph-*para*), 125.2 (s, Ph-*para*), 127.56 (s, Ph-*ortho*), 127.63 (s, Ph-*ortho*), 128.5 (s, Ph-*meta*), 128.6 (s, Ph-*meta*), 152.8 (s, Ph-*ipso*), 153.0 (s, Ph-*ipso*). The carbonyl carbon was not detected due to low intensity. IR (KBr): 1638 cm^{-1}, ν(CO). Anal. calcd for $C_{26}H_{42}O_{10}P_3Rh$: C, 43.96; H, 5.96%. Found: C, 43.80; H, 6.28%.

Thermal Reaction of 5a. A benzene-d_6 (0.6 cm^3) solution of **5a** (17 mg, 0.020 mmol) in an NMR tube was heated at 50 °C. After 9 h the ^{1}H NMR measurement revealed that 1,1-diphenyl-1,3-butadiene was formed in 44% yield, based on tetramethylsilane as an internal standard. Formation of complex **8** (53%) was also noted.

NMR Study of the Reaction of 2,2-Diphenyl-1-methylenecyclopropane with 4. To a benzene-d_6 (0.6 cm^3) solution of **5a** (17.2 mg, 0.020 mmol) was added 0.040 cm^3 (0.20 mmol) of 2,2-diphenyl-1-methylenecyclopropane in an NMR tube at 50 °C. After 36 h the ^{1}H NMR measurement revealed that 1,1-diphenyl-1,3-butadiene in 439% and **6a** in 60% yield, respectively, based on tetramethylsilane as an internal standard.

Reaction of 1,1-Diphenyl-1,3-butadiene with [RhH(CO)-(PPh$_3$)$_3$] at Room Temperature. To a solution of [RhH(CO)-(PPh_3)$_3$] (18 mg, 0.020 mmol) in 0.6 cm^3 of toluene-d_8 was added 1,1-diphenyl-1,3-butadiene (8.3 mg, 0.040 mmol) at room temperature. After 24 h the ^{1}H NMR spectra indicate the formation of **8** in 20% yield. ^{1}H NMR (400 MHz, toluene-d_8, 25 °C): δ 1.14 (dd, 3H, J = 3.9 Hz, J = 6.3 Hz), 2.93 (m, 1H), 5.61 (dd, 1H, J = 2.0 Hz, J = 12.7 Hz).

X-ray Crystallography. Single crystals of **3**, **6b**, and **7**, suitable for X-ray diffraction studies, were obtained by recrystallization and were sealed in capillary tubes under argon. Crystallographic data and details of refinement are summarized in Table 3. Intensities were collected for Lorentz and polarization effects on a Rigaku AFC-5R or AFC-7R automated four-cycle diffractome-

Table 3. Crystallographic Data and Details of Structure Refinement

	3	**6b**	**7**
Formula	$C_{53}H_{45}OP_2Ir$·(C_7H_8)$_2$	$C_{53}H_{45}OP_2F_2Rh$·CH_2Cl_2·H_2O	$C_{26}H_{42}O_{10}P_3Rh$
Formula weight	1136.39	1900.49	710.44
Crystal system	monoclinic	triclinic	monoclinic
Space group	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
a/Å	28.627(7)	19.556(4)	18.020(3)
b/Å	20.053(5)	22.248(5)	9.704(5)
c/Å	23.017(6)	11.112(2)	19.332(3)
α/°	90	101.62(2)	90
β/°	122.69(2)	99.51(1)	108.82(1)
γ/°	90	100.20(2)	90
V/Å^3	11120(5)	4558(2)	3299(1)
Z	8	2	4
μ(Mo Kα)/mm^{-1}	2.507	0.550	0.733
F(000)	4624	1952	1472
D_c/g cm^{-3}	1.357	1.385	1.475
Crystal size/mm^3	0.50 × 0.30 × 0.05	0.43 × 0.25 × 0.05	0.30 × 0.20 × 0.05
2θ range/°	5.0–55.0	5.0–55.0	5.0–55.0
No. of unique reflns	13133	16292	7793
No. of used reflns	8187	10482	5697
No. of variables	570	1079	361
R	0.042	0.061	0.053
R_w[a)]	0.034	0.074	0.069
GOF	1.82	3.18	4.03

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

ter by using Mo Kα radiation ($\lambda = 0.7107$ Å) and ω-2θ scan method, and an empirical absorption correction (ψ scan) was applied.

Calculations were carried out by using a program package teXsan for Windows. The structures were all solved by the Patterson method. A full matrix least-square refinement was used for the non-hydrogen atoms with anisotropic thermal parameters. All non-hydrogen atoms were refined with anisotropic thermal parameters, whereas all hydrogen atoms were located by assuming the ideal geometry and included in the structure calculation without further refinement of the parameters.[80]

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk) and copies can be obtained on request, free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, by quoting the publication citation and the deposition number 264236–264238.

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