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Articles

C−C and C−H Bond Activation of Dialkylmethylenecyclopropane Promoted by Rhodium and Iridium Complexes. Preparation and Structures of M(η^1:η^2-$CH_2CR_2CH{=}CH_2$)(CO)(PPh_3)$_2$ and *trans*-M($CH{=}CHCMeR_2$)(CO)(PPh_3)$_2$ (M = Rh, Ir, R = CH_2CH_2Ph)

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2,2-Bis(2-phenylethyl)-1-methylenecyclopropane reacts with RhH(CO)(PPh_3)$_3$ at room temperature and with IrH(CO)(PPh_3)$_3$ at 70 °C to form the 3-butenyl complexes of these metals, M{η^1:η^2-$CH_2C(CH_2CH_2Ph)_2CH{=}CH_2$}(CO)($PPh_3$)$_2$ (**1**, M = Rh; **2**, M = Ir). Heating **1** at 55 °C liberates 1,1-bis(2-phenylethyl)-1,3-butadiene, while the thermal reaction of **2** at 110 °C forms a mixture of 3-methyl-3-vinyl-1,5-diphenyl-1-pentene (48% NMR yield) and 3-methyl-3-vinyl-1,5-diphenylpentane (15% NMR yield). The reactions of excess amounts of 2,2-bis(2-phenylethyl)-1-methylenecyclopropane with RhH(CO)(PPh_3)$_3$ at 55 °C and with IrH(CO)(PPh_3)$_3$ at 115 °C afford the alkenyl complexes *trans*-Rh{(*Z*)-$CH{=}CHC(CH_2CH_2Ph)_2CH_3$}(CO)($PPh_3$)$_2$ (**3**) and *trans*-Ir{(*E*)-$CH{=}CHC(CH_2CH_2Ph)_2CH_3$}(CO)($PPh_3$)$_2$ (**4**), respectively. The reaction mechanisms are discussed on the basis of the results of the reactions under different conditions. $HC{\equiv}CC(CH_2CH_2Ph)_2CH_3$ reacts with MH(CO)(PPh_3)$_3$ (M = Rh, Ir) to afford the alkynyl complexes *trans*-M{$C{\equiv}CC(CH_2CH_2Ph)_2CH_3$}(CO)($PPh_3$)$_2$ (**5**, M = Rh; **6**, M = Ir) via oxidative addition of the C(alkyne)−H bond to the metal center and subsequent elimination of H_2.

Introduction

Activation of C−C[1] and C−H[1a,2] bonds promoted by transition-metal complexes has been an important topic in organotransition-metal chemistry. Although the C−H bond is cleaved by transition metals more easily than the C−C bond in many cases, small-ring molecules undergo ring opening accompanied by C−C bond cleavage prior to the C−H bond cleavage. Methylenecyclopropanes have been used as the substrates of synthetic organic reactions catalyzed by transition-metal complexes because they are easily converted into acyclic compounds due to release of the ring strain caused by the reaction.[3] Recently, we reported the reaction of 2,2-diphenyl-1-methylenecyclopropane with RhH(CO)(PPh_3)$_3$, giving Rh(η^1:η^2-$CH_2CPh_2CH{=}CH_2$)(CO)(PPh_3)$_2$ and Rh(η^1:η^2-$C_6H_4C(Me)PhCH{=}CH_2$)(CO)(PPh_3)$_2$, depending on the conditions, as shown in Scheme 1.[4]

Formation of the former complex involves selective activation of the less sterically hindered C−C bond of the three-membered ring. The C−C bond cleavage

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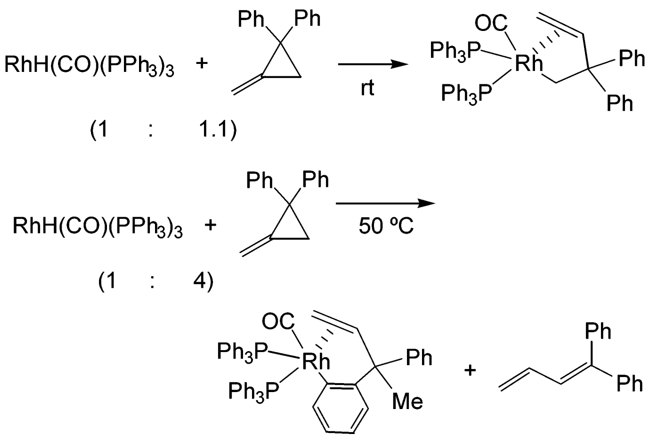
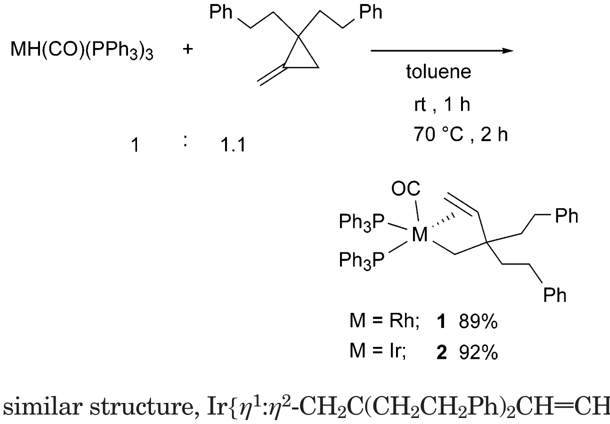
Scheme 1



proceeds via addition of an Rh−H bond to the C=C bond of the substrate, followed by β-alkyl elimination of the resulted cyclopropylmethyl complex. β-Alkyl elimination of strained or unstrained molecules by late-transition-metal complexes[5] has now become an important reaction for activating the C−C bond. Orthometalation of the produced 3-butenylrhodium complex leads to the latter complex. The hydrocarbon ligand of the initially formed Rh complex has no β-hydrogen and causes orthometalation to give the final product upon heating at high temperature. An analogous 3-butenylrhodium complex with alkyl substituents instead of the phenyl substituents at the β-position would produce different products, although there have been no reports of such complexes. In this paper we report the reactions of 2,2-bis(2-phenylethyl)-1-methylenecyclopropane with hydride complexes of Rh(I) and Ir(I) and the C−C and C−H bond activation of the substrates to afford new complexes of these metals.

Results and Discussion

Reactions of 2,2-Bis(2-phenylethyl)-1-methylenecyclopropane with MH(CO)(PPh$_3$)$_3$ (M = Rh, Ir). 2,2-Bis(2-phenylethyl)-1-methylenecyclopropane reacts with an almost equimolar amount of RhH(CO)(PPh$_3$)$_3$ at room temperature to form the 3-butenylrhodium complex Rh{η^1:η^2-$CH_2C(CH_2CH_2Ph)_2CH{=}CH_2$}(CO)(PPh$_3$)$_3$ (**1**), as shown in eq 1. An Ir complex with a similar structure, Ir{η^1:η^2-$CH_2C(CH_2CH_2Ph)_2CH{=}CH_2$}(CO)(PPh$_3$)$_3$ (**2**), is obtained from the reaction with IrH(CO)(PPh$_3$)$_3$ at 70 °C. The Ir complex **2** crystallizes from CH_2Cl_2−hexane to afford single crystals suitable for X-ray crystallography. Figure 1 shows the molecular structure of **2**, which contains the iridium center with a slightly distorted trigonal bipyramidal coordination having one of the PPh$_3$ ligands and a CH$_2$ group at the apical positions. The C=C bond of the 3-butenyl ligand (1.441(9) Å) is longer than the corresponding bonds of Rh(η^1:η^2-$CH_2CPh_2CH{=}CH_2$)(CO)(PPh$_3$)$_2$ (1.36(2) Å) and Ir(η^1:η^2-$CH_2C(H)PhCH{=}CH_2$)(CO)(PPh$_3$)$_2$ (1.33(2) Å).[4] Elongation of the bond compared with the C=C double bond of the organic molecule suggests strong π-back-donation of the ligand.



(1)

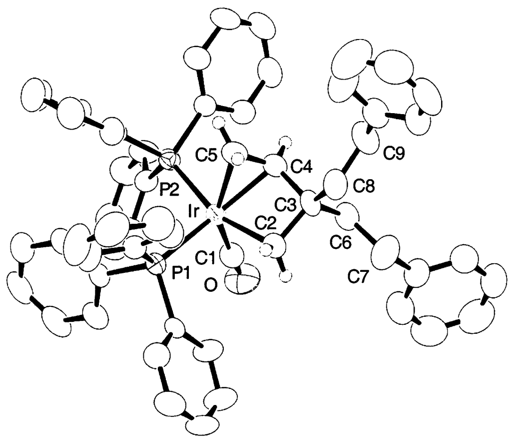


Figure 1. Structure of complex **2** determined by X-ray crystallography with 30% thermal ellipsoidal plotting. Hydrogen atoms at the aromatic rings were omitted for simplicity. Selected bond distances (Å) and angles (deg): Ir−P1 = 2.375(2), Ir−P2 = 2.353(2), Ir−C1 = 1.881(7), Ir−C2 = 2.162(6), Ir−C4 = 2.132(6), Ir−C5 = 2.157(6), C2−C3 = 1.534(8), C3−C4 = 1.520(8), C4−C5 = 1.441(9), O1−C1 = 1.146(7); P1−Ir−P2 = 102.49(6), P1−Ir−C1 = 100.3(2), P1−Ir−C2 = 93.4(2), P1−Ir−C4 = 142.1(2), P1−Ir−C5 = 109.4(2), P2−Ir−C1 = 94.7(2), P2−Ir−C2 = 161.9(2), P2−Ir−C4 = 97.3(2), P2−Ir−C5 = 87.5(2), C1−Ir−C2 = 90.9(3), C1−Ir−C4 = 110.0(3), C1−Ir−C5 = 149.0(3), C2−Ir−C4 = 64.6(2), C2−Ir−C5 = 78.9(2), C4−Ir−C5 = 39.3(2), Ir−C1−O1 = 178.2(6), Ir−C2−C3 = 96.6(4), C2−C3−C4 = 97.5(5), Ir−C4−C3 = 98.2(4), Ir−C4−C5 = 71.3(4), C3−C4−C5 = 117.0(6), Ir−C5−C4 = 69.4(4).

The ^{1}H NMR spectrum of **1** exhibits the signals of two olefinic hydrogens at δ 1.61 and 2.40 with a J(HH) value of 7.1 Hz. The coupling constant suggests a cis geometry for the C=C double bond of the ligand. The other olefinic hydrogen signal is overlapped with the signals at δ 1.86−2.00 due to the benzylic hydrogens. The ^{1}H−^{1}H COSY spectrum indicates correlation among the three olefinic hydrogen signals. The signals at δ −0.95 and 0.37 are assigned to the CH$_2$−Rh hydrogens, which also show a correlation peak in the ^{1}H−^{1}H COSY spectrum. The ^{31}P{^{1}H} NMR spectrum of **1** contains two signals at δ 38.8 and 26.9 with ^1J(RhP) values of 90 and 121 Hz, respectively. The ^{1}H NMR spectrum of **2** exhibits three vinyl resonances around δ 1.10−1.17, 1.34−1.43, and 2.05−2.14, which are overlapped with alkyl proton

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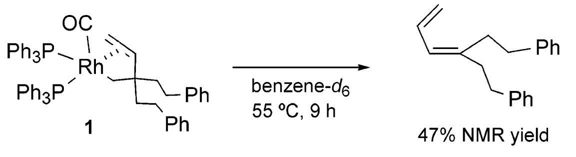
signals of the $PhCH_2CH_2$ group. The cross-peaks in the $^1H-^1H$ COSY spectrum confirm the presence of the olefinic hydrogens at the positions. The signals are positioned at higher magnetic field than the corresponding signals of Rh complex **1**. The $^{13}C\{^1H\}$ NMR spectrum of **2** shows a signal of the methylene carbon at δ −9.91 with a large coupling constant of J = 60.6 Hz. The resonances of the coordinated =CH and H_2C= carbons appeared at δ 36.58 and 29.44, respectively. A carbonyl carbon signal at δ 187.06 couples with two phosphorus nuclei with coupling constants of 16.6 and 7.3 Hz.

Complex **1** is stable in the solid state, but dissolution causes gradual decomposition of the complex at room temperature. Addition of 2,2-bis(2-phenylethyl)-1-methylenecyclopropane to a solution of **1** retards the decomposition. Heating **1** at 55 °C for 9 h give 1,1-bis(2-phenylethyl)-1,3-butadiene (47% NMR yield), while heating **2** at 110 °C for 2 h results in the formation of mixture of 3-methyl-3-vinyl-1,5-diphenyl-1-pentene (48% NMR yield) and 3-methyl-3-vinyl-1,5-diphenylpentane (15% NMR yield) (eqs 2 and 3).



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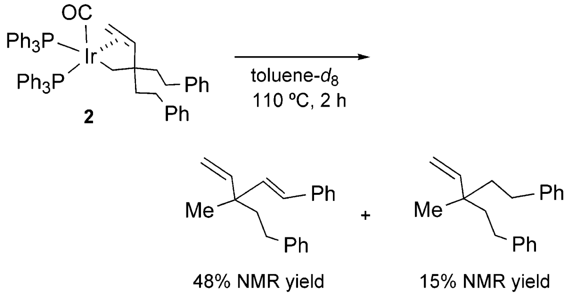
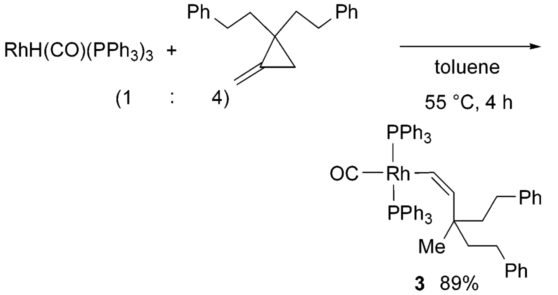


(3)

Reaction of excess 2,2-bis(2-phenylethyl)-1-methylenecyclopropane with $RhH(CO)(PPh_3)_3$ in toluene at 55 °C for 4 h afforded *trans*-Rh{(*Z*)-$CH=CHC(CH_2CH_2Ph)_2CH_3$}(CO)$(PPh_3)_2$ (**3**) in 89% yield (eq 4). Changes of the ^1H NMR spectra during the reaction revealed that **3** was gradually formed via complex **1** and that a mixture of dienes was generated as byproducts. An ORTEP drawing of **3** is shown in Figure 2, and selected bond distances and angles are listed in Table 1. Complex **3** contains typical square-planar coordination with two PPh_3 ligands at trans positions. The bond distances of Rh−C2(sp^2) and C=C bonds are 2.09(1) and 1.31(1) Å, respectively. Vinyl or alkenyl complexes of Rh(III)[6] and Rh(I)[7] show the Rh−C lengths ranging from 2.00 to 2.12 Å and the C=C lengths ranging from 1.25 to 1.36 Å. The σ-bonded 3,3-bis(2-phenylethyl)-1-butenyl ligand of **3** possesses a C=C bond with a *Z* configuration. The Rh−C=C angle of **3** (134.6(8)°) is larger than the reported Rh−C=C angles (121−130°).



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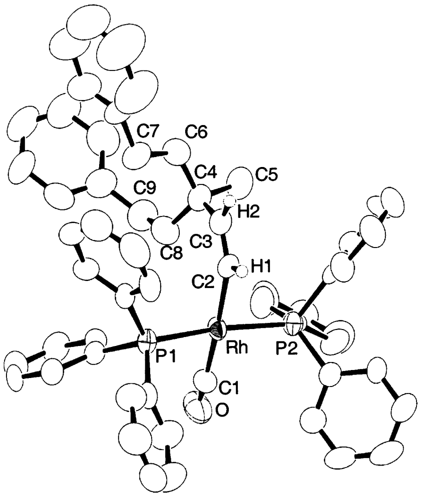

Figure 2. Structure of complex **3** determined by X-ray crystallography with 30% thermal ellipsoidal plotting. Hydrogen atoms at the aromatic rings were omitted for simplicity.

Table 1. Selected Bond Distances (Å) and Angles (deg) of 3−6

	3 (M = Rh)	**4** (M = Ir)	**5** (M = Rh)	**6** (M = Ir)
M(1)−P(1)	2.328(3)	2.288(3)	2.302(1)	2.306(1)
M(1)−P(2)	2.311(3)	2.295(2)	2.310(1)	2.308(1)
M(1)−C(1)	1.88(1)	1.89(1)	1.859(5)	1.844(6)
M(1)−C(2)	2.09(1)	2.108(8)	2.031(4)	2.027(5)
C(1)−O(1)	1.10(1)	1.12(1)	1.141(5)	1.158(6)
C(2)−C(3)	1.31(1)	1.30(1)	1.196(6)	1.206(6)
C(3)−C(4)	1.53(1)	1.54(1)	1.481(6)	1.488(7)
C(4)−C(5)	1.53(1)	1.53(1)	1.546(8)	1.540(9)
P(1)−M(1)−P(2)	169.2(1)	165.94(8)	170.27(4)	170.70(5)
P(1)−M(1)−C(1)	91.3(3)	91.6(3)	93.9(1)	93.4(2)
P(1)−M(1)−C(2)	89.9(3)	88.3(3)	85.8(1)	86.3(1)
P(2)−M(1)−C(1)	90.1(3)	96.4(3)	92.8(1)	92.5(2)
P(2)−P(1)−C(2)	89.8(3)	85.9(3)	88.4(1)	88.7(1)
C(1)−P(1)−C(2)	173.7(5)	169.1(4)	173.0(2)	172.9(2)
M(1)−C(1)−O(1)	171(1)	176(1)	175.3(5)	175.6(6)
M(1)−C(2)−C(3)	134.6(8)	136.0(7)	176.7(4)	176.7(5)
C(2)−C(3)−C(4)	130(1)	127.9(8)	177.9(5)	178.5(6)
C(3)−C(4)−C(5)	108.8(9)	111.5(7)	109.1(4)	109.0(5)

The ^1H and $^{13}C\{^1H\}$ NMR parameters for the alkenyl ligand of **3** are similar to those of LRh{(*Z*)-CH=CHMe}$_3$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane) and Rh{(*Z*)-C(C≡CPh)=CHPh}(CO){P(*i*-Pr)$_3$}$_2$.[8] The ^1H NMR spectrum of **3** shows the resonances of hydrogens

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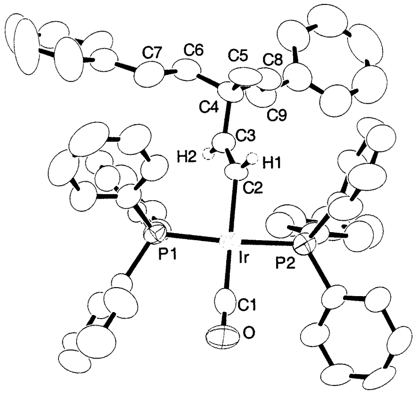
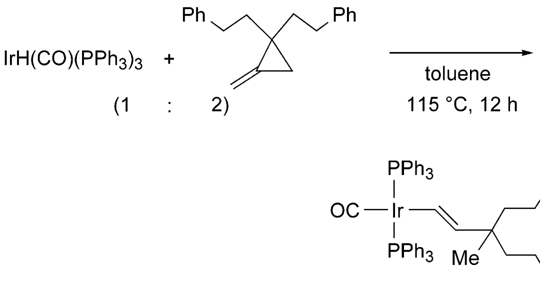


Figure 3. Structure of complex **4** determined by X-ray crystallography with 30% thermal ellipsoidal plotting. Hydrogen atoms at the aromatic rings were omitted for simplicity.

bonded to α- and β-carbons. The signal at δ 6.15 ($^3J_{cis}$(HH) = 12.8 Hz and ^3J(PH) = 5.2 Hz) is assigned to the former hydrogen, while the doublet at δ 5.91 ($^3J_{cis}$(HH) = 12.8 Hz) is due to the latter. The coupling constant is consistent with a cis geometry. The $^{13}C\{^1H\}$ NMR spectrum of **3** exhibits the signal of the vinyl β-carbons at δ 144.92 and that of the α-carbons at δ 159.21. The coupling constant of the latter signal, ^1J(RhC) = 23.2 Hz, is smaller than those of alkenylrhodium complexes (40−43 Hz).[7]

The reaction of 2,2-bis(2-phenylethyl)-1-methylenecyclopropane with IrH(CO)(PPh$_3$)$_3$ at 115 °C for 12 h produces *trans*-Ir{(*E*)-CH=CHC(CH$_2$CH$_2$Ph)$_2$CH$_3$}(CO)(PPh$_3$)$_2$ (**4**) in 88% yield (eq 5). The product from the



(5)

4 88%

reaction in toluene-d_8 does not contain deuterium derived from the solvent. Figure 3 displays the molecular structure of **4** determined by X-ray crystallography. The C=C bond of the ligand apparently possesses an *E* configuration. The Ir−C=C (136.0(7)°) and C=C−C (127.9(8)°) angles are larger than 120°, which reflects severe steric interaction between the 2-phenylethyl group of the ligand and the PPh$_3$ ligands. The ^{1}H NMR spectrum of **4** in CD$_2$Cl$_2$ shows a doublet at δ 4.40 and 6.66 with ^3J(HH) = 18.4 Hz. The large coupling constant attests to the trans relationship of the vinyl hydrogens. In the $^{13}C\{^1H\}$ NMR spectrum the IrCH= carbon atom appears at δ 147.56 (s, Ir*C*) as a singlet, while the IrCH=*C*HC carbon atom displays a singlet at δ 150.65.

Reaction Mechanism. The reactions of 2,2-bis(2-phenylethyl)-1-methylenecylopropane with RhH(CO)(PPh$_3$)$_3$, which afford **1** at room temperature and the 1,3-diene at higher temperature, are explained by the reaction pathways shown in Scheme 2. Addition of an M−H bond to the C=C double bond of methylenecyclopropane[9] takes place more easily than the reaction of a simple olefin with the hydride complexes, because it releases a part of the ring strain of the substrate with an sp^2 carbon attached to the three-membered ring. The Rh complex with a cyclopropylmethyl ligand that is produced is converted into a thermodynamically more stable 3-butenylrhodium complex via C−C bond cleavage. β-Alkyl elimination accompanied by cleavage of the less sterically hindered C−C bond of the three-membered ring produces **1**, while the reaction that cleaves the more sterically hindered C−C bond results in the formation of the 1,3-diene and RhH(CO)(PPh$_3$)$_n$. The former reaction takes place at room temperature to produce **1**, which occurs much more easily than the latter reaction. Since the reactions between **1** and the cyclopropylrhodium intermediate are reversible above 55 °C, the reaction in eq 2 forms the diene via activation of the sterically more hindered C−C bond. Analogous reversible formation of the three-membered ring and its ring opening were proposed to account for the reactions of organometallic complexes having ligands with small-membered rings.[10]

Heating **2** at 110 °C, however, does not produce the 1,3-diene (eq 3). Complex **2** may not cause the formation of a three-membered ring via addition of an Ir−C bond to a C=C bond, which differs from the reaction of the Rh complex. Since **2** does not undergo β-hydrogen elimination either, the reaction at higher temperature produces the olefin or diene, whose formation is induced by γ-hydrogen elimination[11] of the 2,2-dialkyl-3-butenyl ligand, as shown in Scheme 3. γ-Hydrogen of a 2-phenylethyl group is abstracted by the Ir center to form the four-membered metallacycle including an Ir(III) center. Transfer of the hydride to the ligand, giving the 3-butenyliridium intermediate in Scheme 3, and subsequent β-hydrogen elimination of the ligand affords the diene product. Formation of the alkene as a minor compound in reaction 3 can be attributed to the hydrogen transfer to the 3-butenyliridium ligand in Scheme 3 from PPh$_3$ or solvent.

The stoichiometric reactions of 2,2-bis(2-phenylethyl)-1-methylenecyclopropane with MH(CO)(PPh$_3$)$_3$ (M = Rh, Ir) produce **1** and **2**, whereas the reaction of excess substrate affords the alkenyl complexes **3** and **4** at higher temperature. Scheme 4 depicts a possible pathway for the formation of complex **3**. Complex **1**, initially formed in the reaction mixture, is converted into the unsaturated five-membered metallacycle via intramolecular activation of the vinylic C−H bond. Transfer of

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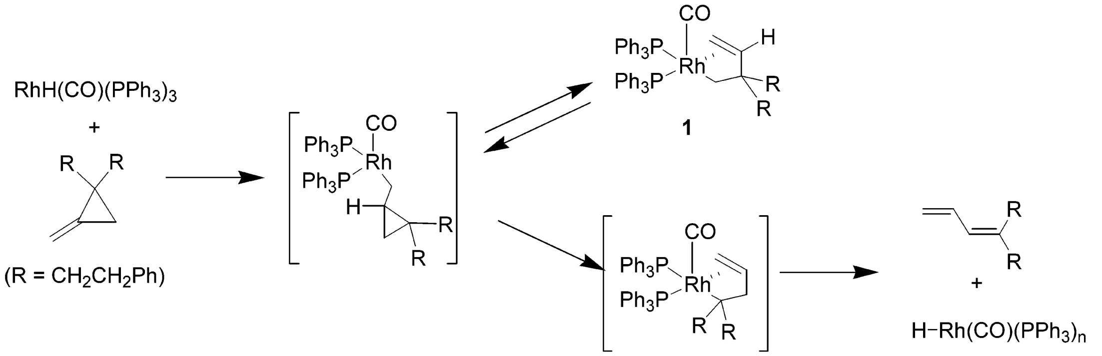
[9] (a) Green, M.; Hughes, R. P. *J. Chem. Soc., Chem. Commun.* **1974**, 686. (b) Green, M.; Howard, J. A. K.; Hughes, R. P.; Kellett, S. C.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1975**, 2007. (c) Goddard, R.; Green, M.; Hughes, R. P.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1976**, 1890.

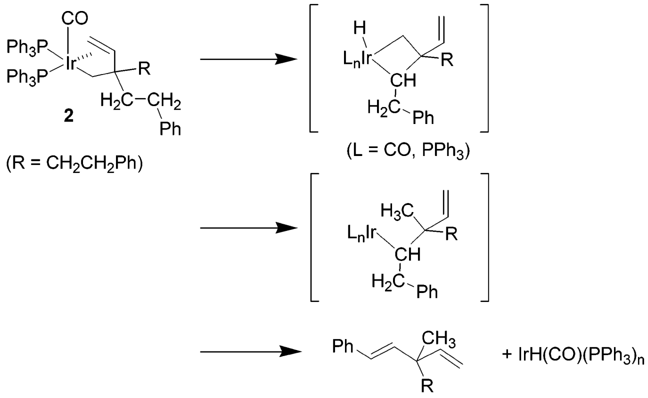
[10] (a) Flood, T. C.; Bitler, S. P. *J. Am. Chem. Soc.* **1984**, *106*, 6076. (b) Flood, T. C.; Statler, J. A. *Organometallics* **1984**, *3*, 1795. (c) Ermer, S. P.; Struck, G. E.; Bitler, S. P.; Richards, R.; Bau, R.; Flood, T. C. *Organometallics* **1993**, *12*, 2634. (d) Casey, C. P.; Hallenbeck, S. L.; Pollock, D. W.; Landis, C. R. *J. Am. Chem. Soc.* **1995**, *117*, 9770. (e) Jun, C.-H. *Organometallics* **1996**, *15*, 895.

[11] (a) Sharp, P. R.; Astruc, D.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *182*, 477. (b) Chang, B. H.; Tung, H. S.; Brubaker, C. H., Jr. *Inorg. Chim. Acta* **1981**, *51*, 143. (c) Hneihen, A. S.; Fermin, M. C.; Maas, J. J.; Bruno, J. W. *J. Organomet. Chem.* **1992**, *429*, C33. (d) Wu, Y.-D.; Peng, Z.-H.; Chan, K. W. K.; Liu, X.; Tuinman, A. A.; Xue, Z. *Organometallics* **1999**, *18*, 2081. (e) Park, J. W.; Jang, H. S.; Kim, M.; Sung, K.; Lee, S. S.; Chung, T.-M.; Koo, S.; Kim, C. G.; Kim, Y. *Inorg. Chem. Commun.* **2004**, *7*, 463.

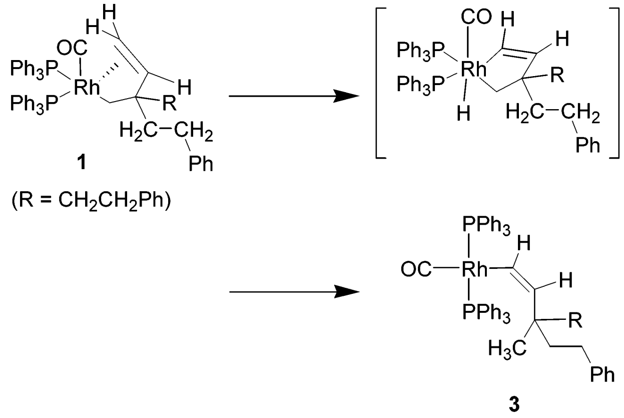
Scheme 2



Scheme 3



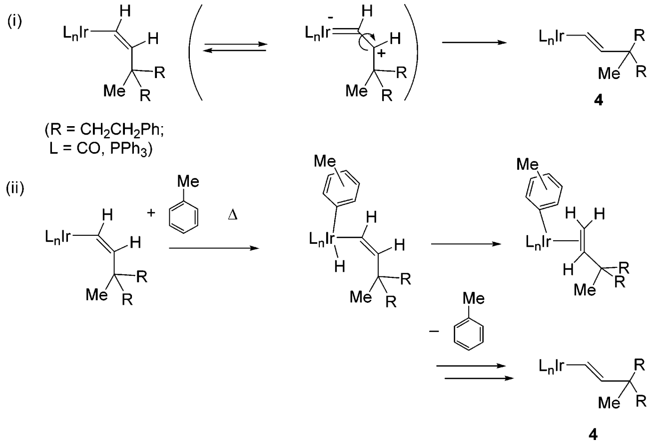
Scheme 4



the hydride to the CH_2 group bonded to Rh leads to the formation of complex **3** with a (*Z*)-alkenyl ligand. Formation of the *Z* isomer is due to exclusive abstraction of the vinylic hydrogen at a position cis to the CH_2 group. Complex **1**, formed by the reaction at room temperature, is converted both into 1,3-diene (reaction 2) and into complex **3** (Scheme 4). Since the former reaction regenerates $RhH(CO)(PPh_3)_n$, the final Rh-containing product of the reaction at high temperature is complex **3**.

Formation of complex **4** with an (*E*)-alkenyl ligand can be attributed to the initial formation of the ((*Z*)-alkenyl)-iridium complex and its isomerization into the thermodynamically more stable **4**. Scheme 5 depicts two possible pathways for the isomerization. The isomerization may take place via rotation of the C−C bond, which is facilitated by contribution of a carbenoid iridium character, as shown in path i in Scheme 5.

Scheme 5



Hydrosilylation of the terminal alkyne catalyzed by the Rh complex was reported to afford a product with an *E* structure also.[12] Path ii in Scheme 5 shows another possible pathway which involves an intermediate Ir complex with a π-coordinated olefin. Repetition of the oxidative addition of the C−H bond of the solvent and reductive elimination of olefin, forming a π-olefin complex, lead to the thermodynamically stable **4** with an *E* configuration.[13] This is less plausible because the reaction in toluene-d_8 does not introduce deuterium to **4**.

Reaction of $HC{\equiv}CC(CH_2CH_2Ph)_2CH_3$ with $MH(CO)(PPh_3)_3$ (M = Rh, Ir). The reaction of terminal alkynes with transition-metal hydride complexes causes oxidative addition to the metal center[14] or insertion of the C≡C bond into the M−H bond,[15] depending on the kind of metal centers and substituents of the alkyne. The latter reaction would form *cis*-alkenyl complexes, although insertion of alkyne into the Rh−H bond sometimes afforded the trans complexes.[16] Reactions of $HC{\equiv}CC(CH_2CH_2Ph)_2CH_3$ with $MH(CO)(PPh_3)_3$ (M = Rh, Ir) in toluene afforded the alkynyl complexes *trans*-

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[12] (a) Ojima, I.; Clos, N.; Donovan, R. J.; Ingalina, P. *Organometallics* **1990**, *9*, 3127. (b) Takeuchi, R.; Tanouchi, N.; *J. Chem. Soc., Chem. Commun.* **1993**, 1319.

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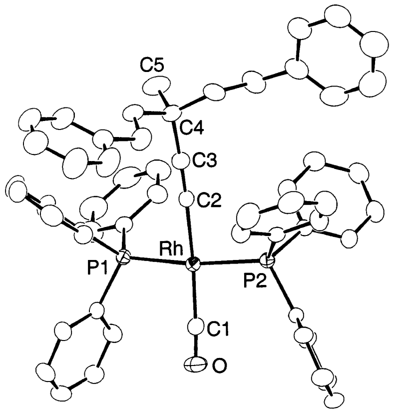


Figure 4. Structure of complex **5** determined by X-ray crystallography with 30% thermal ellipsoidal plotting. Hydrogen atoms at the aromatic rings were omitted for simplicity.

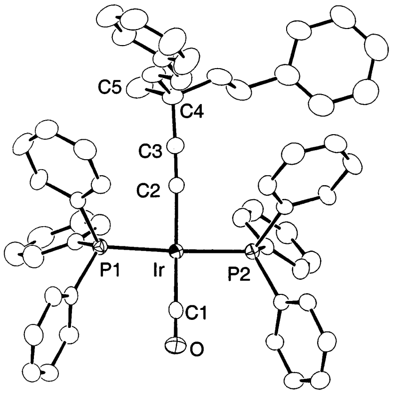
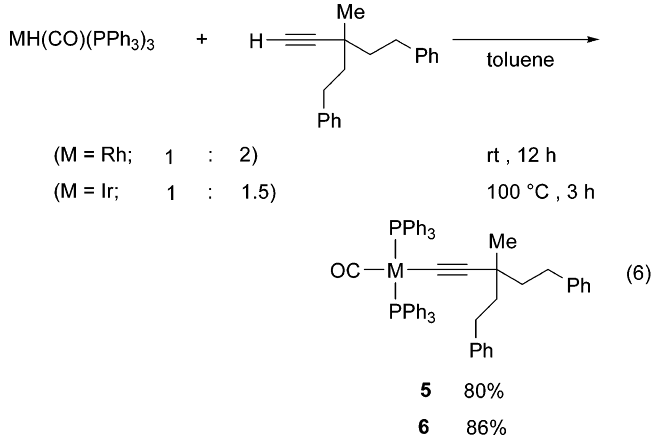


Figure 5. Structure of complex **6** determined by X-ray crystallography with 30% thermal ellipsoidal plotting. Hydrogen atoms at the aromatic rings were omitted for simplicity.

M{C≡CC(CH_2CH_2Ph)$_2$$CH_3$}(CO)($PPh_3$)$_2$ (**5**, M = Rh, **6**, M = Ir) in 80% and 86% yields (eq 6).



The structures of **5** and **6** revealed by X-ray crystallography are shown in Figures 4 and 5. Selected bond distances and angles in Table 1 are compared with those of **3** and **4**. Both complexes have square-planar structures with the two phosphine ligands in trans positions. Shorter M−CO bonds of **5** (1.859(5) Å) and **6** (1.844(6) Å) as compared to those of **3** (1.88(1) Å) and **4** (1.89(1) Å) are observed. The C(2)−C(3) bonds of the alkynyl complexes **5** and **6** (1.196(6) and 1.206(6) Å, respectively) are longer than the standard value of the C≡C bond (1.181 Å).[17,18] These structural parameters are reflected by a vinylene resonance form of the alkynyl complex having a strong π back-donation. The $^{13}C\{^1H\}$ NMR showed M−C$^{\alpha}$≡C$^{\beta}$ carbon signals at reasonable positions (**5**, δ 128.32 (C$^{\alpha}$), 135.27 (C$^{\beta}$); **6**, δ 110.91 (C$^{\alpha}$), 128.47 (C$^{\beta}$)). Complex **6** exhibits splitting due to coupling by two equivalent phosphorus nuclei (^2J(CP) = 18.3 Hz (C$^{\alpha}$); ^3J(CP) = 3.8 Hz (C$^{\beta}$)).

In summary, kinetically or thermodynamically favored products are obtained from the reaction of 2,2-dialkyl-1-methylenecyclopropane with the hydride complexes of Rh and Ir. β-Alkyl elimination accompanied by C−C bond cleavage of the three-membered ring occurs easily to form the 3-butenyl complexes as the initial products. The absence of β-hydrogens of the products led to cleavage and formation of C−H bonds at positions other than that of the β-carbon. The final products of the reactions of Rh and Ir complexes differ from each other.

Experimental Section

General Considerations. All manipulations were carried out under a nitrogen or an argon atmosphere using standard Schlenk techniques. Hexane and toluene were distilled from sodium and benzophenone prior to use or purchased from Kanto Chemicals Co. Ltd. The starting materials RhH(CO)(PPh_3)$_3$,[19] IrH(CO)(PPh_3)$_3$,[20] and 2,2-bis(2-phenylethyl)-1-methylenecyclopropane[21] were prepared according to the literature methods.

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(15) (a) Werner, H.; Esteruelas, M. A.; Otto, H. *Organometallics* **1986**, *5*, 2295. (b) Romero, A.; Santos, A.; Vegas, A. *Organometallics* **1987**, *6*, 1584. (c) Kundel, P.; Berke, H. *J. Organomet. Chem.* **1988**, *339*, 297. (d) Andriollo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Sanchez-Delgado, R. A.; Sola, E.; Valero, C.; Werner, H. *J. Am. Chem. Soc.* **1989**, *111*, 7431. (e) Echavarren, A. M.; Lopez, J.; Santos, A.; Romero, A.; Hermoso, J. A.; Vegas, A. *Organometallics* **1991**, *10*, 2371. (f) Le, T. X.; Merola, J. S. *Organometallics* **1993**, *12*, 3798. (g) Esteruelas, M. A.; Lahoz, F. J.; Onate, E.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 1662. (h) Schaefer, M.; Wolf, J.; Werner, H. *J. Organomet. Chem.* **1995**, *485*, 85. (i) Esteruelas, M. A.; Lahoz, F. J.; Onate, E.; Oro, L. A.; Rodriguez, L. *Organometallics* **1996**, *15*, 3670. (j) Zhao, C.-Q.; Han, L.-B.; Goto, M.; Tanaka, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 1929. (k) Ohtaka, A.; Kuniyasu, H.; Kinomoto, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2002**, *124*, 14324. (l) Liu, S. H.; Xia, H.; Wen, T. B.; Zhou, Z.; Jia, G. *Organometallics* **2003**, *22*, 737.

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(18) (a) Hoehn, A.; Otto, H.; Dziallas, M.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1987**, 852. (b) Werner, H.; Heohn, A.; Schulz, M. *J. Chem. Soc., Dalton Trans.* **1991**, 777. (c) Ilg, K.; Werner, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 1632. (d) Osakada, K.; Kimura, M.; Choi, J.-C. *J. Organomet. Chem.* **2000**, *602*, 144. (e) Werner, H.; Nurnberg, O.; Wolf, J. *Z. Anorg. Allg. Chem.* **2001**, *627*, 693.

NMR spectra (^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$) were recorded on JEOL EX-400 or Varian Mercury 300 spectrometers. Residual peaks of solvent were used as the reference for ^{1}H NMR (δ: benzene-d_6, 7.15; dichloromethane-d_2, 5.32; toluene-d_8, 2.09). For $^{13}C\{^{1}H\}$ NMR, solvent signals were used as the chemical shift reference, while 85% H_3PO_4 (δ 0) was used as the external reference for $^{31}P\{^{1}H\}$ NMR. 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.

Preparation of 1. To a toluene (6 mL) solution of $RhH(CO)(PPh_3)_3$ (142 mg, 0.155 mmol) was added 2,2-bis(2-phenylethyl)-1-methylenecyclopropane (45 mg, 0.171 mmol) at room temperature. The solution immediately turned from yellow to orange on stirring. After 1 h the volatiles were removed under reduced pressure. The resulting orange oily materials were washed with hexane repeatedly at −78 °C to give $Rh\{\eta^1{:}\eta^2\text{-}CH_2C(CH_2CH_2Ph)_2CH{=}CH_2\}(CO)(PPh_3)_2$ (**1**) as a pale orange powder (127 mg, 0.138 mmol, 89%). Dissolving the isolated **1** in a solvent at room temperature caused immediate formation of butadiene derivatives and $RhH(CO)(PPh_3)_3$. Attempts to obtain crystals of **1** suitable for X-ray analysis and elemental analyses were unsuccessful. ^{1}H NMR (400 MHz, dichloromethane-d_2, −40 °C): δ −0.95 (partially collapsed d, 1H, J = 16.6 Hz, H^4 or H^5), 0.37 (t, 1H, J = 5.4 Hz, H^5 or H^4), 0.91−0.98 (m, 1H, one of $PhCH_2CH_2$), 1.21−1.28 (m, 1H, one of $PhCH_2CH_2$), 1.61 (t, 1H, J = 7.1 Hz, H^2), 1.86−2.00 (m, 3H, H^1 and $PhCH_2CH_2$), 2.24−2.30 (m, 2H, $PhCH_2CH_2$), 2.40 (m, 1H, H^3), 2.44−2.56 (m, 2H, $PhCH_2CH_2$), 6.95−7.32 (m, 40H, Ph). $^{31}P\{^{1}H\}$ NMR (161.7 MHz, dichloromethane-d_2, −40 °C): δ 38.8 (dd, J(RhP) = 90 Hz, J(PP) = 20 Hz), 26.9 (dd, J(RhP) = 121 Hz, J(PP) = 20 Hz). IR (KBr, cm^{-1}):1937 (ν(CO)).

Preparation of 2. To a toluene (5 mL) solution of $IrH(CO)(PPh_3)_3$ (120 mg, 0.119 mmol) was added 2,2-bis(2-phenylethyl)-1-methylenecyclopropane (34 mg, 0.131 mmol) at room temperature. The resulting mixture was heated at 70 °C for 2 h, and the solution gradually turned from pale yellow to yellow on stirring. The volatiles were removed by evaporation. Addition of hexane (10 mL) to the resulting yellow oily substance led to the formation of a pale yellow powder, which was washed with 10 mL of hexane (four times), collected by filtration, and dried in vacuo to give $Ir\{\eta^1{:}\eta^2\text{-}CH_2C(CH_2CH_2Ph)_2CH{=}CH_2\}(CO)(PPh_3)_2$ (**2**; 111 mg, 0.110 mmol, 92%). Complex **2** crystallized from CH_2Cl_2−hexane at 0 °C as colorless crystals. ^{1}H NMR (400 MHz, dichloromethane-d_2, −40 °C): δ −0.66 (m, 1H, H^4 or H^5), 0.40 (m, 1H, H^5 or H^4), 1.10−1.17 (m, 2H, H^2 and one of $PhCH_2CH_2$), 1.34−1.43 (m, 2H, H^1 and one of $PhCH_2CH_2$), 2.05−2.14 (m, 3H, H^3 and $PhCH_2CH_2$), 2.14−2.36 (m, 2H, $PhCH_2CH_2$), 2.50−2.65 (m, 2H, $PhCH_2CH_2$), 7.05−7.36 (m, 40H, Ph). $^{31}P\{^{1}H\}$ NMR (161.7 MHz, dichloromethane-d_2, −40 °C): δ −7.66 (d, J(PP) = 8 Hz), 8.17 (d, J(PP) = 8 Hz). $^{13}C\{^{1}H\}$ NMR (100.4 MHz, dichloromethane-d_2, 25 °C): δ −9.91 (d, J = 60.6 Hz, IrC), 27.83 ($PhCH_2CH_2$), 29.44 (dd, J(CP) = 9.1, J(CP) = 3.6 Hz, C^5), 32.00 ($PhCH_2CH_2$), 36.58 (d, J(CP) = 23.9 Hz, C^4), 40.66 ($PhCH_2CH_2$), 49.16 (dd, J(CP) = 5.5, J(CP) = 3.7 Hz, C^3), 49.86 ($PhCH_2CH_2$), 125.55 (Ph para), 125.80 (Ph para), 127.59 (d, J(CP) = 9.1 Hz, PPh_3 ortho), 128.09 (d, J(CP) = 9.1 Hz, PPh_3 ortho), 128.48 (Ph), 128.74 (Ph), 128.90 (Ph, 2 carbons), 129.36 (PPh_3 para), 129.87 (PPh_3 para), 133.84 (d, J(CP) = 11.0 Hz, PPh_3 meta), 134.68 (d, J(CP) = 11.0 Hz, PPh_3 meta), 134.46 (dd, J(CP) = 40.4, J(CP) = 3.7 Hz, PPh_3 ipso), 136.91 (d, J(CP) = 36.7 Hz, PPh_3 ipso), 144.49 (Ph ipso), 144.76 (Ph ipso), 187.06 (dd, J(CP) = 16.6, J(CP) = 7.3 Hz, CO). IR (KBr, cm^{-1}):1941 (ν(CO)). Anal. Calcd for $C_{57}H_{53}OP_2Ir$: C, 67.90; H, 5.30. Found: C, 67.77; H, 5.21.

Thermal Reaction of 1. A benzene-d_6 (0.6 mL) solution of **1** (17.2 mg, 0.02 mmol) in an NMR tube was heated at 55 °C. After 9 h the ^{1}H NMR measurements revealed that 1,1-bis(2-phenylethyl)-1,3-butadine was obtained in 47% yield, based on tetramethylsilane as an internal standard.

Thermal Reaction of 2. A toluene-d_8 (0.6 mL) solution of isolated **2** (30.2 mg, 0.03 mmol) in an NMR tube was sealed and heated at 110 °C. After 2 h, 3-methyl-3-vinyl-1,5-diphenyl-1-pentene and 3-methyl-3-vinyl-1,5-diphenylpentane were obtained in NMR yields of 48% and 15%, respectively. The yields were determined by ^{1}H NMR based on **2** using diphenylmethane as an internal standard. ^{1}H NMR (300 MHz, toluene-d_8, 25 °C): 3-methyl-3-vinyl-1,5-diphenyl-1-pentene, δ 1.17 (s, 3H, Me), 1.72 (m, 2H, CH_2), 2.52 (m, 2H, CH_2), 5.04 (dd, J = 2, 17 Hz, 1H, CH_2CH), 5.06 (dd, J = 2, 11 Hz, 1H, CH_2CH), 5.84 (dd, J = 11, 17 Hz, 1H, CH_2CH), 6.18 (d, ^{3}J = 17 Hz, 1H, CH), 6.37 (d, ^{3}J = 17 Hz, 1H, CH); 3-methyl-3-vinyl-1,5-diphenylpentane, δ 0.98 (s, 3H, Me), 1.54 (m, 4H, CH_2), 2.45 (m, 4H, CH_2), 4.94 (dd, J = 2, 17 Hz, 1H, CH_2CH), 5.06 (dd, J = 2, 11 Hz, 1H, CH_2CH), 5.67 (dd, J = 11, 17 Hz, 1H, CH_2CH).

Preparation of 3. To a solution of $RhH(CO)(PPh_3)_3$ (202 mg, 0.220 mmol) in toluene (7 mL) was added 2,2-bis(2-phenylethyl)-1-methylenecyclopropane (231 mg, 0.880 mmol). The solution gradually turned from orange to reddish orange on stirring at 55 °C. After 4 h the volatiles were removed under vacuum to give dark red oily substances, which were washed with hexane at −78 °C repeatedly to give *trans*-$Rh\{(Z)\text{-}CH{=}CHC(CH_2CH_2Ph)_2CH_3\}(CO)(PPh_3)_2$ (**3**) as an orange solid (180 mg, 0.196 mmol, 89%). Recrystallization of **3** from CH_2Cl_2−hexane gave yellow crystals suitable for X-ray analysis. ^{1}H NMR (400 MHz, dichloromethane-d_2, 25 °C): δ 0.85 (s, 3H, CH_3), 1.19−1.52 (m, 2H, $PhCH_2CH_2$), 1.28−1.36 (m, 2H, $PhCH_2CH_2$), 2.12−2.16 (m, 4H, $PhCH_2CH_2$), 5.91 (d, J(HH) = 12.8 Hz, 1H, RhCH=CH), 6.15 (dt, J(HH) = 12.8 Hz, J(PH) = 5.2 Hz, 1H, RhCH), 6.98−7.51 (m, 28H, Ph), 7.57−7.74 (m, 12H, Ph). $^{31}P\{^{1}H\}$ NMR (161.7 MHz, dichloromethane-d_2, 25 °C): δ 30.84 (d, J(RhP) = 168.0 Hz). $^{13}C\{^{1}H\}$ NMR (100.4 MHz, dichloromethane-d_2, 25 °C): δ 25.52 (CH_3), 31.15 ($PhCH_2CH_2$), 39.12 (CCH_3), 42.41 ($PhCH_2CH_2$), 125.42 (Ph para), 128.05 (t, J(C−P) = 5.0 Hz, PPh_3 ortho), 128.33 (Ph ortho), 128.76 (Ph meta), 129.79 (PPh_3 para), 134.95 (t, J(CP) = 6.6 Hz, PPh_3 meta), 135.64 (t, J(CP) = 19.0 Hz, PPh_3 ipso), 144.62 (Ph ipso), 144.92 (t, J(CP) = 4.1 Hz, RhCH = CH), 159.21 (dt, J(RhC) = 23.2 Hz, J(CP) = 16.6 Hz, RhC), the signal for a carbonyl carbon was not observed. IR (KBr, cm^{-1}): 1960 (ν(CO)). Anal. Calcd for $C_{57}H_{53}OP_2Rh$: C, 74.51; H, 5.81. Found: C, 74.79; H, 6.16.

Preparation of 4. To a toluene (5 mL) solution of $IrH(CO)(PPh_3)_3$ (83 mg, 0.082 mmol) was added 2,2-bis(2-phenylethyl)-1-methylenecyclopropane (44 mg, 0.168 mmol) at room temperature. Stirring the solution at 115 °C caused the solution to change from pale yellow to orange. After 12 h the volatiles were removed under reduced pressure. Addition of 10 mL of hexane to the resulting dark yellow oily residue at −78 °C led to the formation of a pale yellow solid, which was washed with 10 mL of hexane (four times), collected by filtration, and dried in vacuo to give a pale yellow powder of *trans*-$Ir\{(E)\text{-}CH{=}CH\text{-}\{C(CH_2CH_2Ph)_2CH_3\}(CO)(PPh_3)_2$ (**4**; 73 mg, 0.072 mmol, 88%). Complex **4** crystallizes from dichloromethane−hexane at −20 °C as pale yellow crystals. ^{1}H NMR (400 MHz, dichloromethane-d_2, 25 °C): δ 0.24 (s, 3H, CH_3), 0.84−0.88 (m, 4H, $PhCH_2CH_2$), 1.76−1.80 (m, 4H, $PhCH_2CH_2$), 4.40 (d, J(HH) = 18.4 Hz, 1H, IrCH=CH), 6.66 (d, J(HH) = 18.4 Hz, 1H, IrCH), 6.71−6.73 (m, 4H, Ph), 7.06−7.17 (m, 6H, Ph), 7.31−7.38 (m, 18H, Ph), 7.68−7.69 (m, 12H, Ph). $^{31}P\{^{1}H\}$ NMR (161.7 MHz, dichloromethane-d_2, 25 °C): δ 5.19 (s). $^{13}C\{^{1}H\}$ NMR (100.4 MHz, dichloromethane-d_2, 25 °C): δ 23.47 (CH_3), 30.81 ($PhCH_2CH_2$), 41.84 (CCH_3), 42.94 ($PhCH_2CH_2$), 125.28 (Ph

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Table 2. Crystal Data and Details of the Structure Refinement of 2–6

	2	**3**	**4**	**5**	**6**
formula	$C_{57}H_{53}OP_2Ir$	$C_{57}H_{53}OP_2Rh$	$C_{57}H_{53}OP_2Ir$	$C_{57}H_{51}OP_2Rh$	$C_{57}H_{51}OP_2Ir$
mol wt	1008.21	918.90	1008.21	916.88	1006.20
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$C2/c$ (No. 15)
a (Å)	10.750(2)	12.275(3)	10.837(5)	48.726(5)	48.811(4)
b (Å)	28.200(3)	21.191(6)	24.909(4)	9.180(6)	9.156(3)
c (Å)	15.413(2)	10.029(3)	18.244(5)	23.832(8)	23.799(3)
α (deg)	90	102.78(2)	90	90	90
β (deg)	99.44(1)	113.40(2)	103.76(3)	117.36(1)	117.337(8)
γ (deg)	90	91.96(3)	90	90	90
V (Å^3)	4609(1)	2313(1)	4783(2)	9467(6)	9448(3)
Z	4	2	4	8	8
μ (mm^{-1})	3.014	0.477	2.904	0.466	2.941
$F(000)$	2040	956	2040	3808	4064
D_{calcd} (g cm^{-3})	1.453	1.319	1.400	1.286	1.415
cryst size (mm)	0.40 × 0.30 × 0.08	0.50 × 0.50 × 0.25	0.30 × 0.30 × 0.22	0.10 × 0.20 × 0.35	0.15 × 0.20 × 0.35
2θ range (deg)	5.0–50.0	5.0–55.0	5.0–50.0	5.0–55.0	5.0–55.0
no. of unique rflns	10 788	8145	11 248	11 471	11 518
no. of rflns used	6205	3086	4680	6134	7599
no. of variables	550	550	550	550	550
R	0.037	0.051	0.043	0.044	0.036
R_w[a]	0.029	0.052	0.039	0.048	0.035
GOF	1.17	1.20	1.33	1.30	1.35

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

para), 128.14 (Ph ortho), 128.15 (Ph meta), 128.51 (PPh_3 ortho), 130.12 (PPh_3 para), 134.23 (br, PPh_3 ipso), 134.95 (PPh_3 meta), 144.43 (Ph ipso), 147.56 (s, Ir*C*), 150.65 (s, IrCH=*C*H), 189.59 (s, *C*O). IR (KBr, cm^{-1}): 1975 (ν(CO)). Anal. Calcd for $C_{57}H_{53}OP_2Ir$: C, 67.90; H, 5.30. Found: C, 67.64; H, 5.33.

Preparation of 5. To a solution of $RhH(CO)(PPh_3)_3$ (202 mg, 0.220 mmol) in 3 mL of toluene was added $HC\equiv CC(CH_2CH_2Ph)_2CH_3$ (115 mg, 0.438 mmol). Stirring of the resulting mixture at room temperature for 12 h furnished a clear orange solution. Evaporation of the solvent under reduced pressure gave an orange oily substance, which was washed with 10 mL of hexane (three times) at −78 °C and dried in vacuo to give *trans*-$Rh\{C\equiv CC(CH_2CH_2Ph)_2CH_3\}(CO)(PPh_3)_2$ (**5**; 161 mg, 0.176 mmol, 80%) as a bright yellow solid. Recrystallization from CH_2Cl_2–hexane gave yellow crystals suitable for X-ray analysis. ^{1}H NMR (400 MHz, dichloromethane-d_2, 25 °C): δ 0.55 (s, 3H, CH_3), 1.01–1.18 (m, 4H, CH_2), 2.04–2.14 (m, 4H, CH_2), 6.78–6.81 (m, 4H, Ph), 7.11–7.14 (m, 2H, Ph), 7.18–7.21 (m, 4H, Ph), 7.36–7.38 (m, 18H, Ph), 7.87 (m br, 12H, Ph). $^{31}P\{^1H\}$ NMR (161.7 MHz, dichloromethane-d_2, 25 °C): δ 32.06 (d, J(RhP) = 132.9 Hz). $^{13}C\{^1H\}$ NMR (100.4 MHz, dichloromethane-d_2, 25 °C): δ 26.86 (*C*H_3), 31.53 ($PhCH_2$*C*H_2), 36.90 (C^4), 44.46 (Ph*C*H_2CH_2), 125.40 (Ph para), 128.32 (Rh*C*C), 128.78 (Ph), 130.04 (PPh_3 para), 135.27 (RhC*C*), 144.34 (Ph ipso), 193.44 (d, J(CP) = 60.6 Hz, CO). IR (KBr, cm^{-1}): 1985 (ν(CO)). Anal. Calcd for $C_{57}H_{51}OP_2Rh$: C, 74.67; H, 5.61. Found: C, 74.61; H, 5.79.

Preparation of 6. To a toluene (3 mL) solution of $IrH(CO)(PPh_3)_3$ (302 mg, 0.300 mmol) was added $HC\equiv CC(CH_2CH_2Ph)_2CH_3$ (115 mg, 0.438 mmol). During the reaction at 100 °C, the solution changed from pale yellow to reddish orange. After 3 h the volatiles were evaporated to dryness and the resulting oily materials were washed with 30 mL of hexane repeatedly to give *trans*-$Ir\{C\equiv CC(CH_2CH_2Ph)_2CH_3\}(CO)(PPh_3)_2$ (**6**; 260 mg, 0.258 mmol, 86%) as a yellow solid. Recrystallization from CH_2Cl_2–hexane gave orange crystals. ^{1}H NMR (400 MHz, dichloromethane-d_2, 25 °C): δ 0.57 (s, 3H, CH_3), 1.02–1.19 (m, 4H, CH_2), 2.03–2.12 (m, 4H, CH_2), 6.78–6.80 (m, 4H, Ph), 7.10–7.14 (m, 2H, Ph), 7.19–7.21 (m, 4H, Ph), 7.37–7.38 (m, 18H, Ph), 7.84–7.98 (m, 12H, Ph). $^{31}P\{^1H\}$ NMR (161.7 MHz, dichloromethane-d_2, 25 °C): δ 21.98 (s). $^{13}C\{^1H\}$ NMR (100.4 MHz, dichloromethane-d_2, 25 °C): δ 26.95 (*C*H_3), 31.51 ($PhCH_2$*C*H_2), 36.83 (C^4), 44.51 (Ph*C*H_2CH_2), 110.91 (t, J(CP) = 18.3 Hz, Ir*C*C), 125.45 (Ph para), 128.21 (vt, J(CP) = 5.5 Hz, PPh_3 ortho), 128.47 (t, J(CP) = 3.8 Hz, IrC*C*), 128.76 (Ph ortho and meta), 130.04 (PPh_3 para), 134.76 (vt, J(CP) = 27.5 Hz, PPh_3 ipso), 135.33 (vt, J(CP) = 7.3 Hz, PPh_3 meta), 144.22 (Ph ipso), 186.72 (vt, J(CP) = 9.2 Hz, CO). IR (KBr, cm^{-1}): 1970 (ν(CO)). Anal. Calcd for $C_{57}H_{51}OP_2Ir$: C, 68.04; H, 5.11. Found: C, 67.82; H, 5.34.

X-ray Diffraction. Crystallographic data and details of refinement are summarized in Table 2. The crystals were sealed in glass capillary tubes and mounted on a Rigaku AFC-5R or AFC-7R automated four-cycle diffractometer. Intensities were collected for Lorentz by using the diffractometer and $\omega-2\theta$ scan method, and an empirical absorption correction (ψ scan) was applied. The intensities of 3 standard reflections, measured every 150 reflections, were monitored throughout the data collection. Calculations were carried out using the program package teXsan for Windows. The structures were solved by the Patterson method. A full-matrix least-squares 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.[22]

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Supporting Information Available: Text giving the preparation procedures of the organic substrates and tables giving crystallographic data and all non-hydrogen and the selected hydrogen parameters, bond lengths and angles, calculated hydrogen atom parameters, anisotropic thermal parameters, and intermolecular contacts for **2**–**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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