Hydrido−Rhodium(I) and −Iridium(I) Complex Promoted Ring-Opening Isomerization of Unsymmetrically Substituted Methylenecyclopropanes into 1,3-Dienes. Structures of Intermediates and Reaction Pathways

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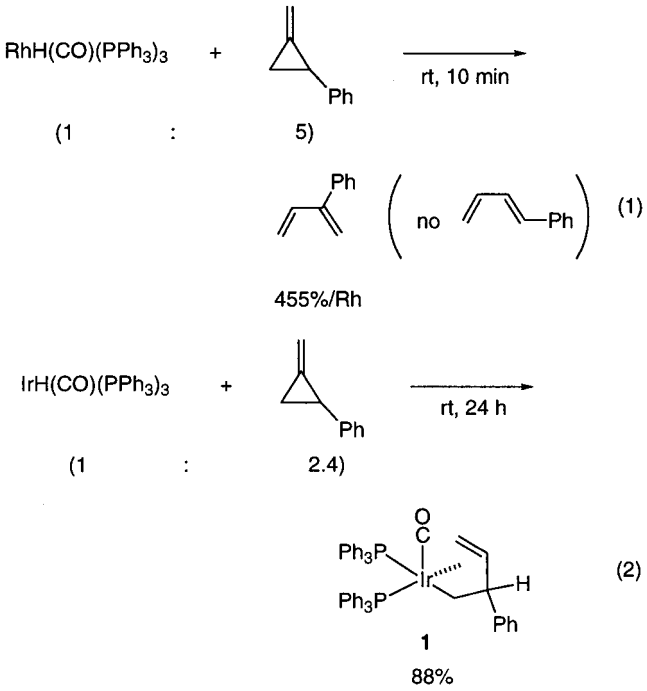
Summary: 2-Phenyl-1-methylenecyclopropane and 2,2-diphenyl-1-methylenecyclopropane react with MH(CO)-$(PPh_3)_3$ (M = Rh, Ir) to produce 1,3-dienes or the intermediate Rh and Ir complexes having a 3-butenyl ligand, depending on the conditions. The structures and chemical properties of the obtained complexes suggest plausible pathways for the ring-opening isomerization of the methylenecyclopropanes to the corresponding dienes.

Highly strained methylenecyclopropanes[1] undergo transition metal complex promoted ring opening to afford various products, depending on the kind of metal complex used and the reaction conditions. Rhodium(I) complexes promote ring-opening addition of methylenecyclopropane with alkenes,[2] hydrosilylation to give acyclic organosilanes,[3] and intramolecular phenylation of the cyclopropane via ring opening,[2] as well as isomerization to give 1,3-dienes or their Rh complexes.[4,5] Much less attention has been paid to the mechanism involved in the reactions and, in particular, the roles of the Rh complexes that promote C−C bond activation and subsequent bond formation reactions to produce the functionalized products. In this paper we report the reactions of substituted methylenecyclopropanes with $RhH(CO)(PPh_3)_3$ and $IrH(CO)(PPh_3)_3$, leading to their ring-opening isomerization into the corresponding 1,3-dienes, and the isolation of the intermediate organo−rhodium and −iridium complexes.

2-Phenyl-1-methylenecyclopropane reacts with $RhH(CO)(PPh_3)_3$ at room temperature to promote smooth ring-opening isomerization into 2-phenyl-1,3-butadiene (eq 1), while the reaction with $IrH(CO)(PPh_3)_3$ produces $Ir(\eta^1{:}\eta^2\text{-}CH_2CH(Ph)CH{=}CH_2)(CO)(PPh_3)_2$ (**1**) (eq 2).[6]



The molecular structure of **1**, shown in Figure 1, verifies the presence of a 2-phenyl-3-butenyl ligand derived from the C−C activation of a methylenecyclopropane ring.[7] The former reaction seems to involve an intermediate Rh complex, having a structure analogous to that of **1**, but it was not found in the products due to rapid formation of the 1,3-diene via β-hydrogen elimination. The lack of formation of 1-phenyl-1,3-butadiene in reaction 1 implies selective activation at the less substituted proximal C−C bond of the substrate.

The reaction of 2-phenyl-1-methylenecyclopropane with $IrH(CO)(PPh_3)_3$ at 50 °C in a 10:1 molar ratio gives a mixture of 2-phenyl- and 1-phenyl-1,3-buta-

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(6) Preparation of **1**: To a toluene (10 mL) solution of $IrH(CO)(PPh_3)_3$ (223 mg, 0.22 mmol) was added 2-phenyl-1-methylenecyclopropane (74 μL, 0.54 mmol) at room temperature. After 24 h the solvent was removed by evaporation. Addition of hexane (10 mL) to the yellow oily substance 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 $Ir(\eta^1{:}\eta^2\text{-}CH_2CH(Ph)CH{=}CH_2)(CO)(PPh_3)_2$ (**1**; 171 mg, 0.20 mmol, 88%). Complex **1** crystallizes from toluene at −20 °C as colorless crystals. Other complexes were obtained analogously from the reactions at room temperature or at 50 °C.

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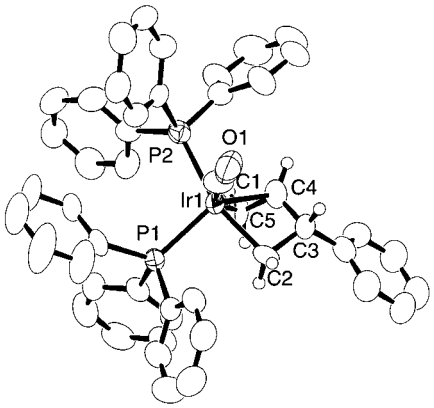
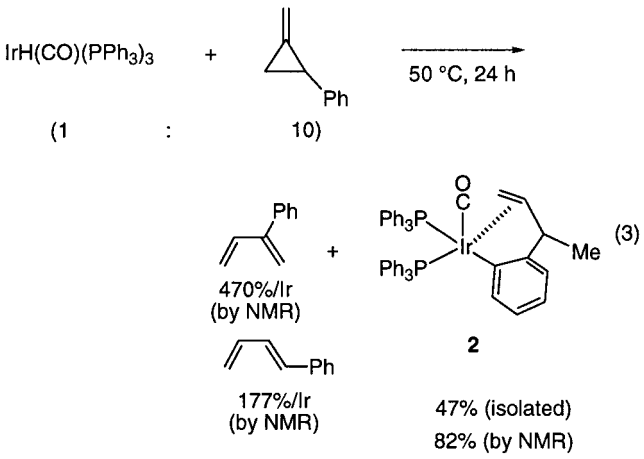


Figure 1. Structure of complex **1** determined by X-ray crystallography with 50% thermal ellipsoid plotting. Hydrogen atoms at the aromatic rings were omitted for simplicity. Selected bond distances (Å) and angles (deg): Ir1−P1 = 2.385(4), Ir1−P2 = 2.341(4), Ir1−C1 = 1.65(3), Ir1−C2 = 2.11(1), Ir1−C4 = 2.14(1), Ir1−C5 = 2.12(2), C2−C3 = 1.54(2), C3−C4 = 1.48(2), C4−C5 = 1.33(2); Ir1−C2−C3 = 94.7(9), C2−C3−C4 = 98(1), Ir1−C4−C3 = 95(1), Ir1−C4−C5 = 71(1), C3−C4−C5 = 120(2), Ir1−C5−C4 = 72(1).

dienes and Ir(η^1:η^2-$C_6H_4CH(Me)CH{=}CH_2$)(CO)(PPh_3)$_2$ (**2**) (eq 3). The molecular structure of complex **2** was



confirmed by X-ray crystallography (Figure 2).[8] 2-Phenyl-1,3-butadiene and complex **2** are formed via β-hydrogen elimination of **1** and via orthometalation of the phenyl group of **1**, respectively. At that temperature, the reaction produces 1-phenyl-1,3-butadiene from partial activation of the more highly substituted proximal bond of the substrate.

2,2-Diphenyl-1-methylenecyclopropane reacts with $RhH(CO)(PPh_3)_3$ at room temperature to give Rh(η^1:η^2-$CH_2CPh_2CH{=}CH_2$)(CO)(PPh_3)$_2$ (**3**) via cleavage of the

(7) X-ray data for **1**: monoclinic, $P2_1/c$ (No. 14), a = 14.128(3) Å, b = 18.584(3) Å, c = 15.013(3) Å, β = 100.62(2)°, V = 3874 Å^3, Z = 4, D_{calcd} = 1.502 g cm^{-3}, F(000) = 1752, μ(Mo Kα) = 3.57 mm^{-1} for monochromated Mo Kα radiation (λ = 0.71069 Å), R (R_w) = 0.058 (0.057) for 4246 reflections with $I > 3\sigma(I)$ among 9166 unique reflections (R_{int} = 0.044), 460 parameters, GOF = 1.87.

(8) X-ray data for **2**: monoclinic, $P2_1/c$ (No. 14), a = 13.214(4) Å, b = 21.397(3) Å, c = 14.678(2) Å, β = 93.71(2)°, V = 4141 Å^3, Z = 4, D_{calcd} = 1.479 g cm^{-3}, F(000) = 1852, μ(Mo Kα) = 3.35 mm^{-1} for monochromated Mo Kα radiation (λ = 0.710 69 Å), R (R_w) = 0.039 (0.034) for 5990 reflections with $I > 3\sigma(I)$ among 8695 unique reflections (R_{int} = 0.021), 476 parameters, GOF = 1.70.

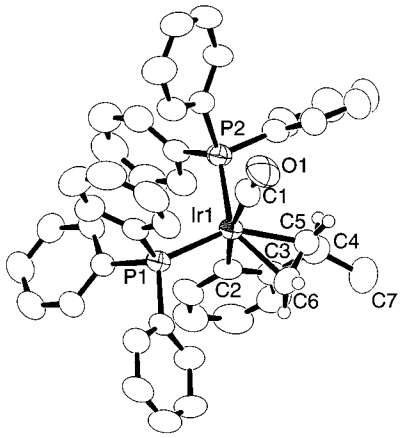
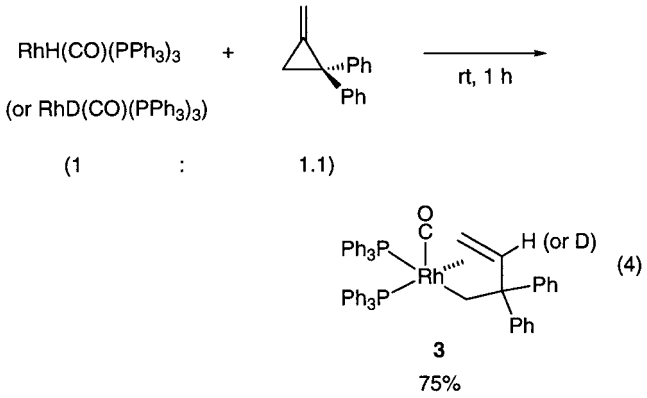


Figure 2. Structure of complex **2** determined by X-ray crystallography with 50% thermal ellipsoid plotting. Hydrogen atoms at the aromatic rings and solvated toluene molecules were omitted for simplicity. Selected bond distances (Å) and angles (deg): Ir1−P1 = 2.377(2), Ir1−P2 = 2.358(2), Ir1−C1 = 1.869(6), Ir1−C2 = 2.126(6), Ir1−C5 = 2.161(7), Ir1−C6 = 2.144(7), C2−C3 = 1.408(8), C3−C4 = 1.505(9), C4−C5 = 1.509(9), C4−C7 = 1.52(1), C5−C6 = 1.439(9); Ir1−C2−C3 = 115.4(5), C2−C3−C4 = 116.8-(6), C3−C4−C5 = 109.5(6), C3−C4−C7 = 116.0(6), C5−C4−C7 = 111.1(7), Ir1−C5−C4 = 111.4(5), Ir1−C5−C6 = 69.8(4), C4−C5−C6 = 121.6(6), Ir1−C6−C5 = 71.1(4).

proximal C−C bond (eq 4, Figure 3).[9] Use of RhD(CO)-



(PPh_3-d_{15})$_3$ results in selective deuteration at the γ-position of the ligand. The C−C bond activation appears to involve the initial insertion of the C=C double bond into the Rh−H bond and an ensuing β-alkyl elimination[10] of the resulting cyclopropylmethyl rhodium complex (Scheme 1).

(9) X-ray data for **3**: monoclinic, $C2/c$ (No. 15), a = 28.705(6) Å, b = 20.170(4) Å, c = 22.962 (4) Å, β = 122.77(1)°, V = 11179 Å^3, Z = 8, D_{calcd} = 1.200 g cm^{-3}, F(000) = 4208, μ(Mo Kα) = 0.402 mm^{-1} for monochromated Mo Kα radiation (λ = 0.710 69 Å), R (R_w) = 0.072 (0.105) for 4727 reflections with $I > 3\sigma(I)$ among 13 210 unique reflections (R_{int} = 0.065), 528 parameters, GOF = 2.45.

(10) β-Alkyl elimination of late-transition-metal complexes: (a) Thompson, S. K.; Young, G. B. *Organometallics* **1989**, *8*, 2068. (b) Alkianiec, B.; Christou, V.; Hardy, D. T.; Thompson, S. K.; Young, G. B. *J. Am. Chem. Soc.* **1994**, *116*, 9963. (c) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2717. (d) McNeill, K.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 11244. (e) Kaplan, A. W.; Bergman, R. G. *Organometallics* **1997**, *16*, 1106. (f) Thomas, B. J.; Noh, S. K.; Schulte, G. K.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* **1991**, *113*, 893. (g) Takemori, T.; Suzuki, H.; Tanaka, M. *J. Am. Chem. Soc.* **1994**, *116*, 10779. See also: Rybtchinski, B.; Vigalok, A.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 12406.

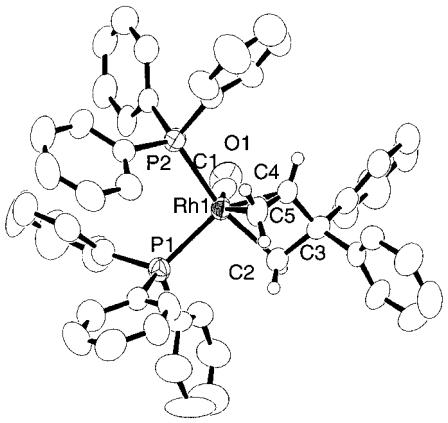
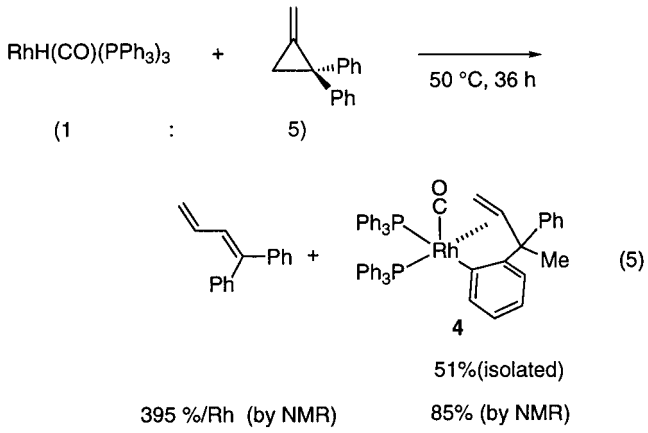


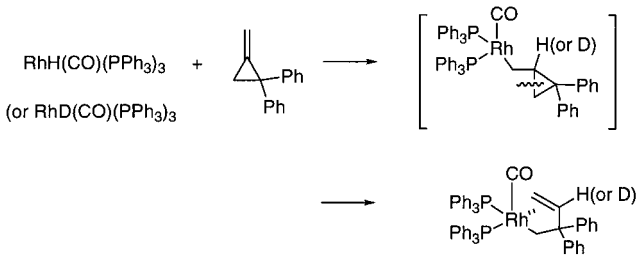
Figure 3. Structure of complex **3** determined by X-ray crystallography with 50% thermal ellipsoid plotting. Hydrogen atoms at the aromatic rings and solvated molecules were omitted for simplicity. Selected bond distances (Å) and angles (deg): Rh1−P1 = 2.408(4), Rh1−P2 = 2.376(4), Rh1−C1 = 1.89(1), Rh1−C2 = 2.13(1), Rh1−C4 = 2.12(1), Rh1−C5 = 2.16(1), C2−C3 = 1.52(2), C3−C4 = 1.54(2), C4−C5 = 1.36(2); Rh1−C2−C3 = 96.0(8), C2−C3−C4 = 97(1), Rh1−C4−C3 = 95.8(8), Rh1−C4−C5 = 72.9(8), C3−C4−C5 = 116(1), Rh1−C5−C4 = 70.0(8).

The reaction of 2,2-diphenyl-1-methylenecyclopropane with $RhH(CO)(PPh_3)_3$ at 50 °C leads to its ring-opening isomerization into 1,1-diphenyl-1,3-butadiene accompanied by formation of $Rh(\eta^1{:}\eta^2\text{-}C_6H_4C(Me)PhCH{=}CH_2)(CO)(PPh_3)_2$ (**4**) (eq 5). To elucidate the role of complex

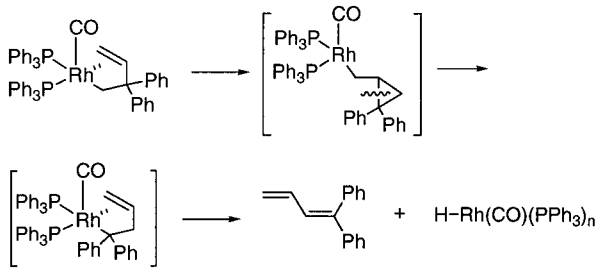


3 in the above reaction, chemical properties of the complexes were examined. Once isolated, complex **4** does not produce the 1,3-diene at elevated temperatures. Heating **3** at 50 °C causes the liberation of 1,1-diphenyl-1,3-butadiene in 44% yield. Since the direct elimination

Scheme 1



Scheme 2



of the diene from the ligand is not plausible, the reaction probably involves skeletal rearrangement and C−C bond formation of the 2,2-diphenyl-3-butenyl ligand to regenerate a cyclopropane ring[11] followed by its C−C activation, as shown in Scheme 2. Complex **3**, which is formed as the kinetic product of C−C activation of reaction 5, would be transformed into the diene via a similar pathway and regenerate the hydridorhodium complex that promotes further ring-opening isomerization.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas, "Molecular Physical Chemistry", from the Ministry of Education, Science, Culture, and Sports of Japan (No. 11166221).

Supporting Information Available: Text and tables giving experimental procedures and crystallographic data for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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