π-Coordination vs Ring-Opening Isomerization of 2-Phenyl-1-methylenecyclopropane upon the Reaction with $RhCl(PPh_3)_3$

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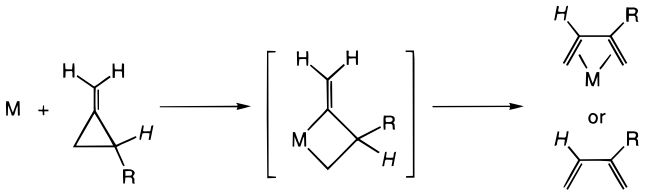
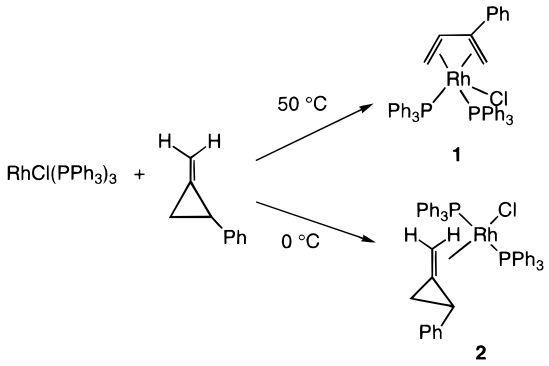
*Summary: The reactions of 2-phenyl-1-methylenecyclopropane with $RhCl(PPh_3)_3$ for 16 h at 50 °C and at 0 °C gave $RhCl(\eta^4\text{-}CH_2{=}CPhCH{=}CH_2)(PPh_3)_2$ (**1**) and $RhCl(\eta^2\text{-}CH_2{=}CCH_2CHPh)(PPh_3)_2$ (**2**) as respective isolated products. Heating of a benzene solution of **2** at 50 °C turned it into **1** in a low yield (<7%), while the reactions of 2-phenyl-1-methylenecyclopropane with $RhCl(PPh_3)_3$ and with **2** at the same temperature afforded **1** (10%) and 2-phenyl-1,3-butadiene (14%).*

The transition metal complex promoted C−C bond activation of small-membered ring molecules has been of significant interest for the past several decades. Methylenecyclopropane and its derivatives have high strain energy (ΔH_f larger than that of cyclopropane by approximately 35 kcal mol^{-1})[1] in their molecules and are employed as the substrates for synthetic organic reactions[2] and polymer synthesis[3] catalyzed by transition metals. The reactions of methylenecyclopropanes with organotransition metal complexes afforded various products such as 1,3-diene *via* ring-opening isomerization (Sc, Rh),[4] trimethylenemethane-coordinated metal complexes (Fe, Mo),[5] and organometallic compounds formed *via* the insertion of a C=C double bond to the M−C or M−Cl bond (Ti, Pd).[6] Rh(I) complexes, which were reported to cause C−C bond activation of small-membered ring molecules,[7] react also with methylenecyclopropanes to form a 1,3-diene[4c,8] and to generate a trimethylenemethane complex.[9] Rh complexes containing η^2-coordinated methylenecyclopropane were also reported.[10] The ring-opening isomerization most probably involves the initial oxidative addition of the C−C bond to the Rh center, followed by a 1,2-hydrogen shift to form a 1,3-diene, as shown in Scheme 1.

Scheme 1



Scheme 2



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(11) X-ray data of **1**: triclinic, $P\bar{1}$ (No. 2), a = 13.395(10) Å, b = 16.613(11) Å, c = 10.157(9) Å, α = 92.47(7)°, β = 103.29(7)°, γ = 71.17-(6)°, V = 2080 Å^3, Z = 2, D_{calc} = 1.335 g cm^{-3}, $F(000)$ = 866, μ(Mo Kα) = 5.84 cm^{-1} for monochromated Mo Kα radiation (λ = 0.710 69 Å). R (R_w) = 0.062 (0.046) for 3729 reflections with $I > 3\sigma(I)$ among 9554 unique reflections (R_{int} = 0.071), GOF = 1.83.

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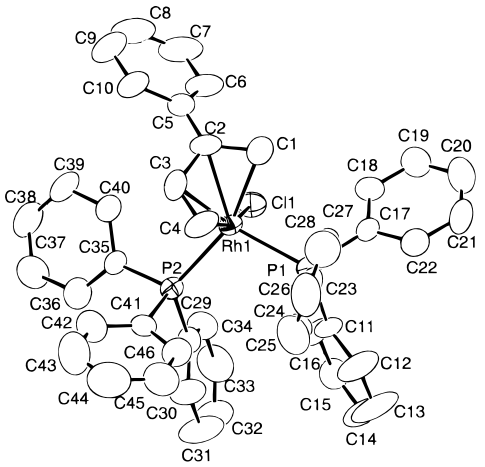


Figure 1. ORTEP drawing of $RhCl(CH_2{=}CHPhCH{=}CH_2)(PPh_3)_2$ (**1**) with 50% thermal ellipsoidal plotting. Selected bond distances (Å) and angles (deg): Rh1−Cl1 2.459(3), Rh1−P1 2.354(3), Rh1−P2 2.368(3), Rh1−C1 2.159(10), Rh1−C2 2.21(1), Rh1−C3 2.144(9), Rh1−C4 2.082(10), C1−C2 1.42(1), C2−C3 1.44(1), C2−C5 1.51(1), C3−C4 1.40(1), Cl1−Rh1−P1 96.90(10), Cl1−Rh1−P2 88.1(1), P1−Rh1−P2 107.6(1), C1−C2−C3 114(1), C1−C2−C5 127.0(7), C3−C2−C5 121(1), C2−C3−C4 118.1(10).

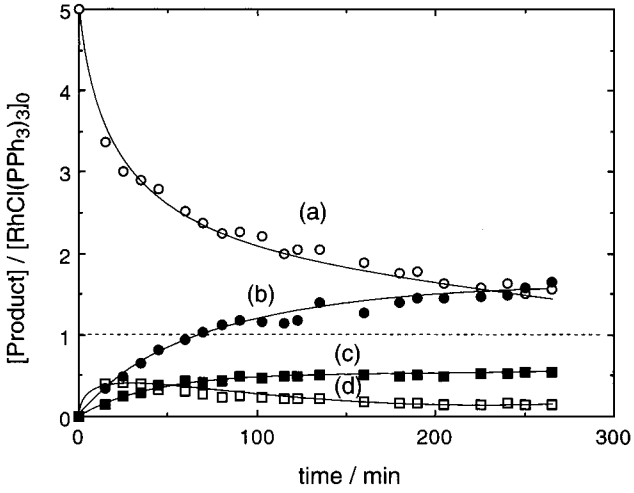


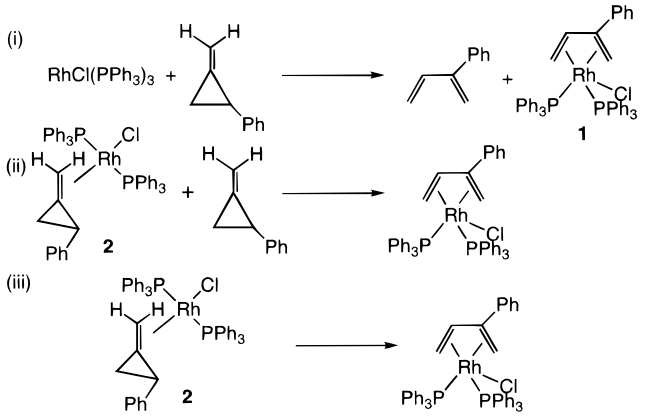
Figure 2. Plots of the products of the reaction of 2-phenyl-1-methylenecyclopropane with $RhCl(PPh_3)_3$ at 50 °C. Relative amounts of (a) 2-phenyl-1-methylenecyclopropane, (b) 2-phenyl-1,3-butadiene, (c) **1**, and (d) **2** to the initial amount of $RhCl(PPh_3)_3$ are shown. On cooling to 25 °C, the $^{31}P\{^1H\}$ NMR spectrum indicates the presence of **1** in a yield higher than 80%.

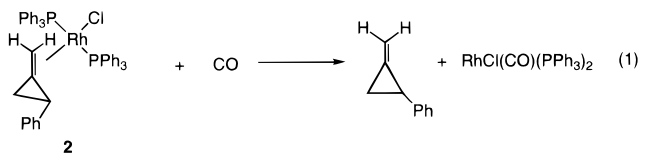
In this paper we report the reaction of 2-phenyl-1-methylenecyclopropane with $RhCl(PPh_3)_3$, leading to the ring-opening isomerization or the η^2-coordination of a C=C double bond of the substrate depending on the conditions as well as the mechanism for C−C bond activation.

2-Phenyl-1-methylenecyclopropane reacts with $RhCl(PPh_3)_3$ (5:1 molar ratio) at 50 °C to give $RhCl(\eta^4\text{-}CH_2{=}CPhCH{=}CH_2)(PPh_3)_2$ (**1**) in 95% yield after 16 h, while the reaction at 0 °C in toluene leads to isolation of $RhCl(\eta^2\text{-}CH_2{=}\overline{CCH_2CHPh})(PPh_3)_2$ (**2**) (Scheme 2). Complex **2** is sparingly soluble in toluene and separated from the solution during the reaction.

Complex **1** has a distorted piano-stool coordination around the Rh center that is bonded to a η^4-2-phenyl-1,3-butadiene ligand and to Cl and PPh_3 ligands, as shown in Figure 1.[11] The ligand adopts an s-cis conformation similarly to other reported Rh(I) complexes with 1,3-diene ligands.[12] Complex **2** was characterized based on NMR spectra. The much higher magnetic field positions of the ^1H NMR signals of two vinylic hydrogens (δ 2.27 and 2.34) than that of uncoordinated 2-phenyl-1-methylenecyclopropane (δ 5.58) and the $^{13}C\{^1H\}$ NMR signals of vinylic carbons (δ 61.5 and 34.2) with large J(RhC) values (13 and 22 Hz, respectively) are crucial to the assignment of the structure containing 2-phenyl-1-methylenecyclopropane, whose C=C double bond is bonded to the Rh center in a η^2-fashion. The J(RhP) value (133 Hz) suggests a structure with PPh_3 ligands at mutually trans positions, similarly to other $RhCl(olefin)(PR_3)_2$-type complexes.[13] The reaction of CO (1 atm) with **2** to give quantitative amounts of 2-phenyl-1-methylenecyclopropane and $RhCl(CO)(PPh_3)_2$ (eq 1) also supports the proposed structure.

Scheme 3





The change in the amounts of organic and inorganic products during the reaction of 2-phenyl-1-methylenecyclopropane with $RhCl(PPh_3)_3$ was monitored by ^1H NMR spectroscopy. Figure 2 shows the plots of the increase in **1** and 2-phenyl-1,3-butadiene, which reached 55% and 165%/Rh, respectively, after the reaction for 4.5 h. The reactions of **2** at 50 °C were conducted to compare

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its reactivity with $RhCl(PPh_3)_3$ toward 1,3-diene formation. Heating of a benzene solution of **2** for 7 h at 50 °C led to the formation of **1** in a low NMR yield (<7%) and a negligible amount of 2-phenyl-1,3-butadiene. The reaction of **2** with 2-phenyl-1-methylenecyclopropane (1:5 molar ratio) at 50 °C gave **1** (10%) and 2-phenyl-1,3-butadiene (14%/Rh) after 6 h. Equimolar reaction of **2** and $RhCl(PPh_3)_3$ under similar conditions led to formation of **1** in less than 5% of **2**.

The above results provide the relative rates of the possible reactions involved in forming 2-phenyl-1,3-butadiene or its Rh complex, as summarized in Scheme 3. The reaction of 2-phenyl-1-methylenecyclopropane with $RhCl(PPh_3)_3$ to give 2-phenyl-1,3-butadiene or **1** (i) occurs more rapidly than its reaction with **2** (ii). The intramolecular C−C bond cleavage of the 2-phenyl-1-methylenecyclopropane ligand of **2** (iii) is slower than the above two reactions and is not operative in its ring-opening isomerization promoted by $RhCl(PPh_3)_3$ at 50 °C.

The present study has demonstrated the reaction of 2-phenyl-1-methylenecyclopropane with $RhCl(PPh_3)_3$ to give the ring-opening isomerization product and the complex having the substrate as the η^2-bonded ligand. The latter product undergoes intramolecular C−C bond activation of the ligand to a limited extent in the absence and presence of 2-phenyl-1-methylenecyclopropane.[14] This contrasts with the previously reported ring-opening reactions of 2,2-dimethylcyclopropene and allenylcyclopropane promoted by Co or Ir complexes *via* an initial coordination of a C=C double bond followed by an intramolecular C−C bond cleavage.[15]

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Supporting Information Available: Experimental procedure and spectroscopic and crystallographic data of the complexes and related reactions of 2-aryl-1-methylenecyclopropane with $RhCl(PPh_3)_3$ (12 pages). Ordering information is given on any current masthead page.

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(14) Reaction ii in Scheme 3 involves oxidative addition of 2-phenyl-1-methylenecyclopropane to the Rh center of **2**. More rapid exchange between coordinated and uncoordinated 2-phenyl-1-methylenecyclopropane occurs at room temperature *via* an associative pathway since addition of 2-(4-fluorophenyl)-1-methylenecyclopropane to a solution of **2** causes its conversion into $RhCl(\eta^2\text{-}CH_2{=}\overline{CCH_2CHC_6H_4F\text{-}p})(PPh_3)_2$ (**3**). Complexes **2** and **3** are equilibrated in the presence of 2-phenyl-1-methylenecyclopropane and 2-(4-fluorophenyl)-1-methylenecyclopropane with the thermodynamic parameters $\Delta H° = -10.3$ kJ mol^{-1} and $\Delta S° = -32$ J mol^{-1} deg^{-1}.

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