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Reaction of 1-aryl-2-methylenecyclopropanes with rhodium(I) complexes leading to ring opening isomerization and π co-ordination of the C=C double bond

Kohtaro Osakada,* Hisami Takimoto and Takakazu Yamamoto *

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

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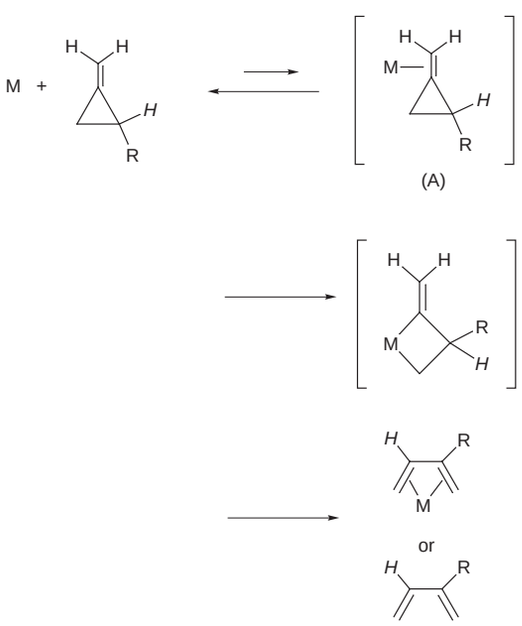
1-Aryl-2-methylenecyclopropanes reacted with $[RhCl(PPh_3)_3]$ at 50 °C to give $[RhCl(\eta^4\text{-}CH_2{=}CArCH{=}CH_2)(PPh_3)_2]$ (Ar = C_6H_5 **1a**, C_6H_4F-*p* **1b**, C_6H_4Me-*p* **1c** or C_6H_4OMe-*p* **1d**) *via* ring opening isomerization of the substrate and its subsequent co-ordination to Rh. The diene-co-ordinated rhodium complexes have been characterized by X-ray crystallography and NMR spectroscopy. Similar reaction at 0 °C afforded the rhodium(I) complexes with π-co-ordinated 1-aryl-2-methylenecyclopropane, $[RhCl(\eta^2\text{-}CH_2{=}\overline{CCH_2CH}Ar)(PPh_3)_2]$ (Ar = C_6H_5 **2a**, C_6H_4F-*p* **2b**, C_6H_4Me-*p* **2c** or C_6H_4OMe-*p* **2d**). Exchange of the ligand of **2a** with added 1-aryl-2-methylenecyclopropanes occurs reversibly at 30–45 °C with the thermodynamic parameters of the reactions **2a** + $CH_2{=}\overline{CCH_2CH}C_6H_4X$-*p* $\rightleftharpoons$ **2b** (or **2c**) + $CH_2{=}\overline{CCH_2CH}C_6H_5$ being $\Delta H° = -10.3$ kJ mol^{-1} and $\Delta S° = -32$ J K^{-1} mol^{-1} for X = F and $\Delta H° = 2.2$ kJ mol^{-1} and $\Delta S° = -2.6$ J K^{-1} mol^{-1} for X = Me, respectively, at 298 K. The structure of a PEt_3 co-ordinated analog, $[RhCl(\eta^2\text{-}CH_2{=}\overline{CCH_2CH}C_6H_4Me\text{-}p)(PEt_3)_2]$ **3c**, has been determined by X-ray crystallography. The reaction of 1-methylene-2-phenylcyclopropane with $[RhCl(PPh_3)_3]$ at 25 °C gave a mixture of **1a** and **2a**. Heating of a benzene solution of **2a** at 50 °C turned it into **1a** in low yield (<7%), while the reactions of 1-methylene-2-phenylcyclopropane with **2a** at the same temperature gave **1a** (10%) and 2-phenylbuta-1,3-diene (14%). The amounts of the products formed *via* ring opening isomerization in these reactions are much smaller than those in the reaction of 1-methylene-2-phenylcyclopropane with $[RhCl(PPh_3)_3]$ at 50 °C.

Methylenecyclopropane with a high strain energy (ΔH_f larger than that of cyclopropane by *ca.* 35 kcal mol^{-1})[1] has been regarded as a useful synthetic equivalent of butadiene and trimethylenemethane[2,3] since upon reaction with transition metal complexes it is easily turned into the ring-opened isomers that are free from the ring strain. The reactions of methylenecyclopropane and its derivatives with organotransition metal complexes give various products such as 1,3-diene (Sc),[4] trimethylenemethane-co-ordinated metal complexes (Fe, Mo),[5] and organometallic compounds formed *via* insertion of a C=C double bond into M–C or M–Cl bonds (Ti, Pd).[6,7]

Rhodium(I) complexes, which often cause C–C bond activation of small-membered ring molecules,[8] react also with methylenecyclopropanes to form 1,3-dienes[9,10] or organic products through formation of a trimethylenemethane-co-ordinated rhodium complex and its further reaction with olefins.[11] Complexes containing η^2-co-ordinated methylenecyclopropane were also prepared.[12] There have been few reports on elucidation of the detailed mechanism of the reactions. Ring opening isomerization of vinylcyclopropane and cyclopropene promoted by d^9 metal (Co, Ir) complexes was proposed to involve pre-co-ordination of the C=C double bond of the substrate and ensuing C–C bond cleavage of the three-membered ring of the molecule.[13,14] Cobalt and rhodium complex promoted reactions of methylenecyclopropane and its derivatives giving 1,3-dienes have also been believed to proceed *via* initial π co-ordination followed by C–C bond activation of the resulting intermediate (A) as shown in Scheme 1.[10,15] Although such an anchoring effect of the C=C double bond of methylenecyclopropanes may facilitate the ring-opening isomerization, no experimental results have been presented to support the above reaction pathway.

In this paper we report the reaction of 1-aryl-2-methylenecyclopropanes with $[RhCl(PPh_3)_3]$, leading to ring opening isomerization or η^2-co-ordination of a C=C double bond of the substrate depending on the conditions. The reaction pathway of the ring opening isomerization is discussed based on several reactions of rhodium complexes with and without π-co-ordinated 1-methylene-2-phenylcyclopropane. Part of this work was reported in a preliminary form.[16]



Scheme 1

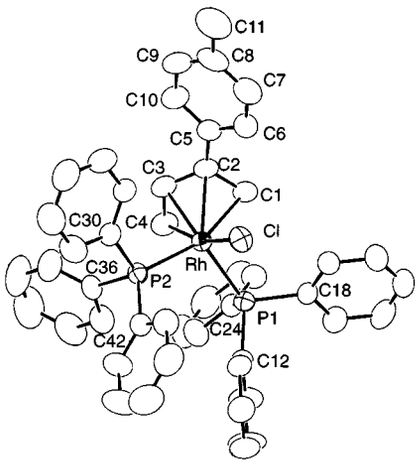


Fig. 1 An ORTEP[17] drawing of $[RhCl\{CH_2{=}C(C_6H_4Me\text{-}p)CH{=}CH_2\}(PPh_3)_2]\cdot 0.5C_6H_{14}$ **1c**·$0.5C_6H_{14}$ with 50% thermal ellipsoidal plotting. Atoms of the solvated hexane and hydrogen atoms were omitted for simplicity.

Table 1 Selected bond distances (Å) and angles (°) for complexes **1a** and **1c**

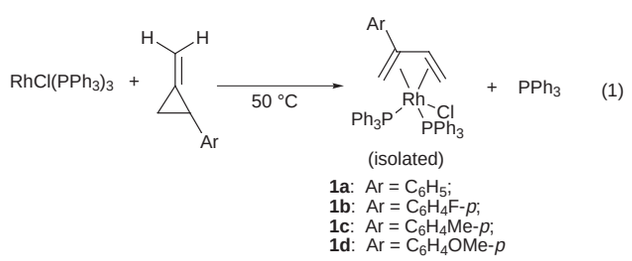
	1a[a]	**1c**[b]
Rh–Cl	2.459(3)	2.470(1)
Rh–P1	2.354(3)	2.339(2)
Rh–P2	2.368(3)	2.370(1)
Rh–Cl	2.159(10)	2.152(3)
Rh–C2	2.21(1)	2.212(3)
Rh–C3	2.144(9)	2.155(3)
Rh–C4	2.082(10)	2.111(3)
C1–C2	1.42(1)	1.423(5)
C2–C3	1.44(1)	1.411(5)
C2–C5	1.51(1)	1.492(5)
C3–C4	1.40(1)	1.414(4)
C1–Rh–P1	96.90(10)	97.12(3)
C1–Rh–P2	88.1(1)	87.82(4)
P1–Rh–P2	107.6(1)	108.27(5)
C1–C2–C3	114.(1)	115.0(3)
C1–C2–C5	127.0(7)	122.7(4)
C3–C2–C5	121.0(1)	122.0(3)
C2–C3–C4	118.1(10)	117.8(3)

[a] Taken from ref. 16. [b] This work.

Results and discussion

Preparation and characterization of the rhodium complexes

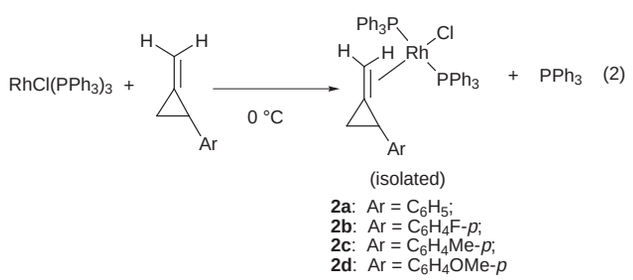
1-Methylene-2-phenylcyclopropane reacts with $[RhCl(PPh_3)_3]$ (5:1 molar ratio) at 50 °C to give $[RhCl(\eta^4\text{-}CH_2{=}CPhCH{=}CH_2)(PPh_3)_2]$ **1a** in 95% yield after 16 h. The reactions of 1-aryl-2-methylenecyclopropanes with $[RhCl(PPh_3)_3]$ give analogous complexes **1b**–**1d** as summarized in eqn. 1. Fig. 1 depicts the



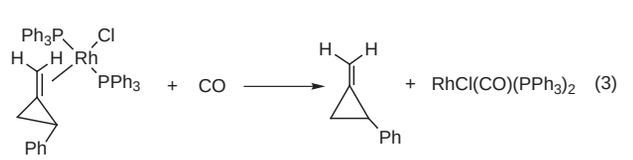
molecular structure of **1c** determined by X-ray crystallography. The molecule has a distorted piano-stool co-ordination around the Rh that is bonded to a η^4-2-(*p*-methylphenyl)buta-1,3-diene ligand and to Cl and PPh_3 ligands. The diene ligand adopts an *s-cis* conformation similarly to other rhodium(I) complexes with 1,3-diene ligands.[18] Table 1 summarizes selected bond distances and angles of **1c** and of the preliminarily reported **1a**.[16] The C2–C3 bond distances of the diene ligand [1.44(1) Å for **1a** and 1.411(5) Å for **1c**] are shorter than that of a single bond of an unco-ordinated 1,3-diene molecule. The above results as well as elongation of the C=C double bonds (C1=C2 and C3=C4) are consistent with partial contribution of a metallacyclopentene structure to co-ordination of the diene ligand as proposed for many transition metal diene complexes.[19]

Complexes **1a**–**1d** were characterized also by NMR (^1H, ^{13}C and ^{31}P) spectroscopy. The ^1H NMR spectra show two signals at δ 3.44–3.62 and 5.45–5.59 due to two hydrogens of the diene ligand. Signals of the other three hydrogens of the ligand appear at significantly higher magnetic field (δ −0.56 to −0.49, 0.56–0.58 and 0.77–0.82). The $^{13}C\text{-}\{^1H\}$ NMR spectrum of **1a** contains signals due to the diene carbons at δ 38.7, 48.3, 87.8 and 113.0. The two former signals of $=CH_2$ carbons are split by PC or RhC coupling. These ^1H and ^{13}C NMR signals were assigned by $^1H\text{–}^1H$ and $^1H\text{–}^{13}C$ COSY technique although the assignment of a part of the $=CH_2$ hydrogens is ambiguous. The molecular structures of **1a** and **1c** suggest close contact of three $=CH_2$ hydrogens (one attached to C1 and two to C4 in Fig. 1) to phenyl planes of the PPh_3 ligands. Thus, the high magnetic field positions of the three ^1H NMR signals can be attributed to a magnetic anisotropy effect of π electrons of the phenyl groups.

The reactions of 1-aryl-2-methylenecyclopropanes with $[RhCl(PPh_3)_3]$ at 0 °C afforded complexes with π-co-ordinated 1-aryl-2-methylenecyclopropane, $[RhCl(\eta^2\text{-}CH_2{=}\overline{CCH_2}CHAr)(PPh_3)_2]$ **2a**–**2d**, which were separated from the solution during the reaction, eqn. (2). The complexes were characterized by



NMR spectroscopy. The $^{13}C\text{-}\{^1H\}$ NMR signal of the $=CH_2$ carbon of **2a** appears at high magnetic field (δ 34.2) with splitting due to RhC coupling (J 13 Hz). The signal due to the other vinylic carbon shows coupling with Rh also (δ 61.5, J 22 Hz), whereas the remaining two carbon signals of the cyclopropane ring are free from such coupling. These results indicate η^2 co-ordination of the double bond to Rh. Upfield shift of the ^1H NMR signals of two vinylic hydrogens (δ 2.18–2.34) from those of unco-ordinated 1-methylene-2-phenylcyclopropane (δ 5.50) also indicates co-ordination of the olefin group. The single $^{31}P\text{-}\{^1H\}$ NMR signal with J(RhP) of 133 Hz suggests a structure with PPh_3 ligands at mutually *trans* positions, similar to other $RhCl(olefin)(PR_3)_2$-type complexes.[20] Complexes **2b**–**2d** show quite similar NMR data to those of **2a** and are considered to have the same four-co-ordinated structure. Introduction of ambient pressure of CO to a solution of **2a** led to formation of quantitative amounts of 1-methylene-2-phenylcyclopropane and $[RhCl(CO)(PPh_3)_2]$ which were identified by GLC and by IR and NMR spectroscopy, respectively, eqn. (3). Recovery of



the organic product in a high yield indicates that the complex contains 1-methylene-2-phenylcyclopropane as the ligand.

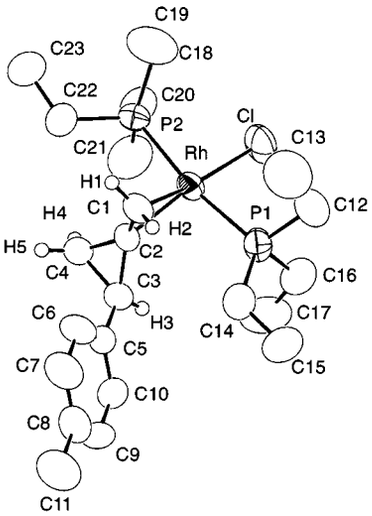
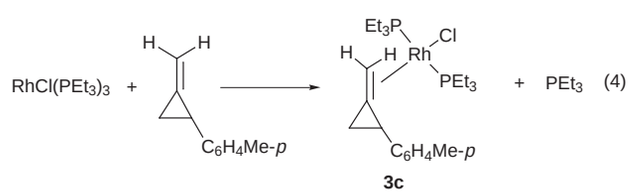


Fig. 2 An ORTEP drawing of [RhCl(CH_2=$\overline{CCH_2}$$\overline{CHC_6H_4Me\text{-}p}$)-($PEt_3$)$_2$] **3c** with 50% thermal ellipsoidal plotting. Hydrogen atoms except for those in vinyl and cyclopropyl groups were omitted for simplicity. Selected bond distances (Å) and angles (°): Rh–Cl 2.373(2), Rh–P1 2.323(2), Rh–P2 2.319(2), Rh–C1 2.105(7), Rh–C2 2.047(7), C1–C2 1.405(9), C2–C3 1.497(9), C2–C4 1.465(10) and C3–C4 1.528(10); Cl–Rh–P1 86.45(8), Cl–Rh–P2 86.31(8), P1–Rh–P2 171.18(7), C1–Rh–C2 39.5(3), Rh–C1–C2 68.0(4), Rh–C2–C1 72.4(4), C1–C2–C3 136.8(7), C1–C2–C4 136.5(7), C2–C3–C4 57.9(5), C2–C4–C3 60.0(5), C3–C2–C4 62.1(5), H1–C1–H2 107, C2–C1–H1 119 and C2–C1–H2 120.

Although X-ray crystallography of complexes **2a**–**2d** was not feasible due to insufficient quality of the crystals, the PEt_3-co-ordinated analogue, [RhCl(η^2-CH_2=$\overline{CCH_2}$$\overline{CHC_6H_4Me\text{-}p}$)-($PEt_3$)$_2$] **3c** was prepared from the reaction of 1-methylene-2-(*p*-methylphenyl)cyclopropane with [RhCl(PEt_3)$_3$] and characterized by X-ray crystallography. The reaction shown in eqn. (4)



(4)

does not give any other products *via* ring opening isomerization of the substrate. Fig. 2 depicts the molecular structure of **3c**. It reseals square-planar co-ordination around the Rh that is bonded to the η^2-olefinic group of the ligand. The *p*-methylphenyl group of the ligand is situated at the opposite side of the Rh. The C=C double bond is orientated perpendicular to the co-ordination plane and elongated from a typical C=C double bond [C1–C2 1.405(9) Å]. Deviation of the C=C double bond from the cyclopropane plane (*ca.* 135°) caused by back donation from Rh to the ligand seems to release a part of the strain energy of unco-ordinated 1-methylene-2-(*p*-methylphenyl)cyclopropane.

The NMR data of complex **3c** shown below indicate its similar structure to those of PPh_3 co-ordinated complexes **2a**–**2d**. The ^{13}C-{^{1}H} NMR signals of two vinylic carbons at δ 26.6 and 56.1 are accompanied by large *J*(RhC) (66 and 22 Hz, respectively). The vinylic hydrogen signals are observed at high magnetic field similarly to those of **2a**–**2d**, while the position of one of the signals was determined from the ^{1}H–^{13}C COSY spectrum due to their severe overlapping with the signals of phosphine ligands. The ^{31}P-{^{1}H} NMR spectrum of **3c** contains an AB pattern with *J*(PP) = 415 Hz as depicted in Fig. 3. Two P nuclei are magnetically inequivalent arising from η^2 co-ordination of unsymmetrically substituted methylenecyclopropane.

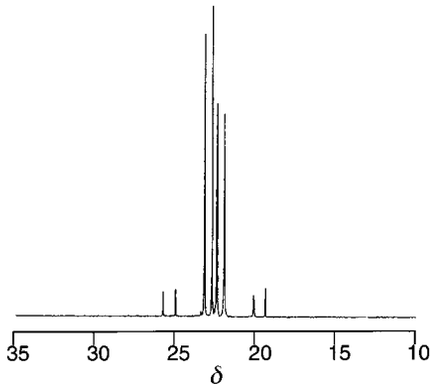


Fig. 3 The ^{31}P-{^{1}H} NMR spectrum of complex **3c** (160 MHz in C_6D_6) at room temperature. Chemical shifts are referenced to external H_3PO_4.

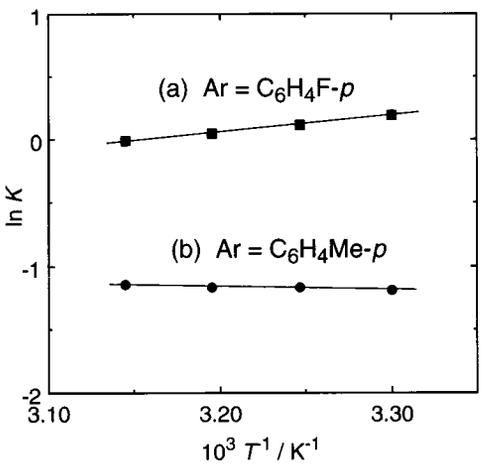
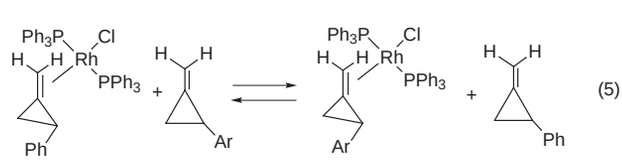


Fig. 4 Van't Hoff plots of the reactions (a) **2a** + CH_2=$\overline{CCH_2}$CH-C_6H_4F-*p* ⟶ **2b** + CH_2=$\overline{CCH_2}$$\overline{CHC_6H_5}$ and (b) **2a** + CH_2=$\overline{CCH_2}$CH-C_6H_4Me-*p* ⟶ **2c** + CH_2=$\overline{CCH_2}$$\overline{CHC_6H_5}$.

Associative exchange of π-co-ordinated ligand of complex 2a

Addition of 1-aryl-2-methylenecyclopropanes to a benzene-d_6 solution of complex **2a** caused partial conversion of the complex into **2b**–**2d** accompanied by liberation of 1-methylene-2-phenylcyclopropane. The ^{1}H NMR spectra of solutions containing **2a**, 1-methylene-2-phenylcyclopropane and a 1-aryl-2-methylenecyclopropane show reversible and rapid exchange between the olefin co-ordinated to Rh and that in solution as shown in eqn. (5). The equilibrium constants were obtained by



(5)

2b: Ar = C_6H_4F-*p*;
2c: Ar = C_6H_4Me-*p*;
2d: Ar = C_6H_4OMe-*p*

comparison of the ^{1}H NMR peak area ratios of the mixtures in the temperature range 30–45 °C. The temperature dependence of the equilibrium constants shown in Fig. 4 gives the thermodynamic parameters of the reactions, $\Delta H^\circ = -10.3$ kJ mol^{-1} and $\Delta S^\circ = -32$ J K^{-1} mol^{-1} for Ar = C_6H_4F-*p* and $\Delta H^\circ = 2.2$ kJ mol^{-1} and $\Delta S^\circ = -2.6$ J K^{-1} mol^{-1} for Ar = C_6H_4Me-*p*, respectively, at 298 K. Although the reaction of 1-(*p*-methoxyphenyl)-2-methylenecyclopropane with **2a** proceeds smoothly to result in exchange of the ligand, an accompanying ring opening isomerization of the substrate to give **1d** prevented determin-

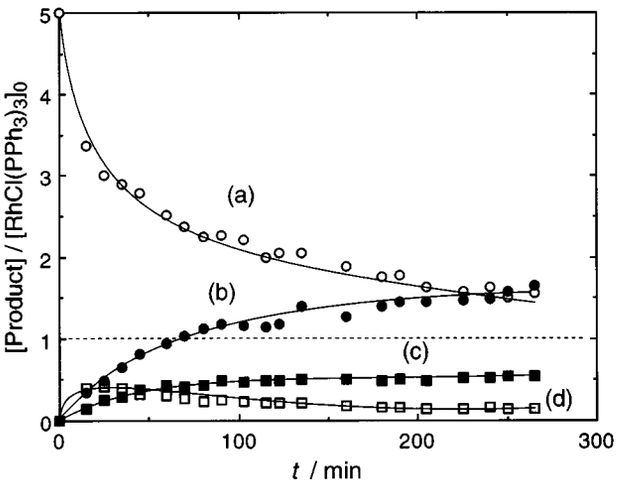


Fig. 5 Plots of the products of the reaction of 1-methylene-2-phenylcyclopropane with $[RhCl(PPh_3)_3]$ (5:1) at 50 °C. Relative amounts of (a) 1-methylene-2-phenylcyclopropane, (b) 2-phenylbuta-1,3-diene, (c) **1a**, and (d) **2a** to the initial amount of $[RhCl(PPh_3)_3]$ are shown.

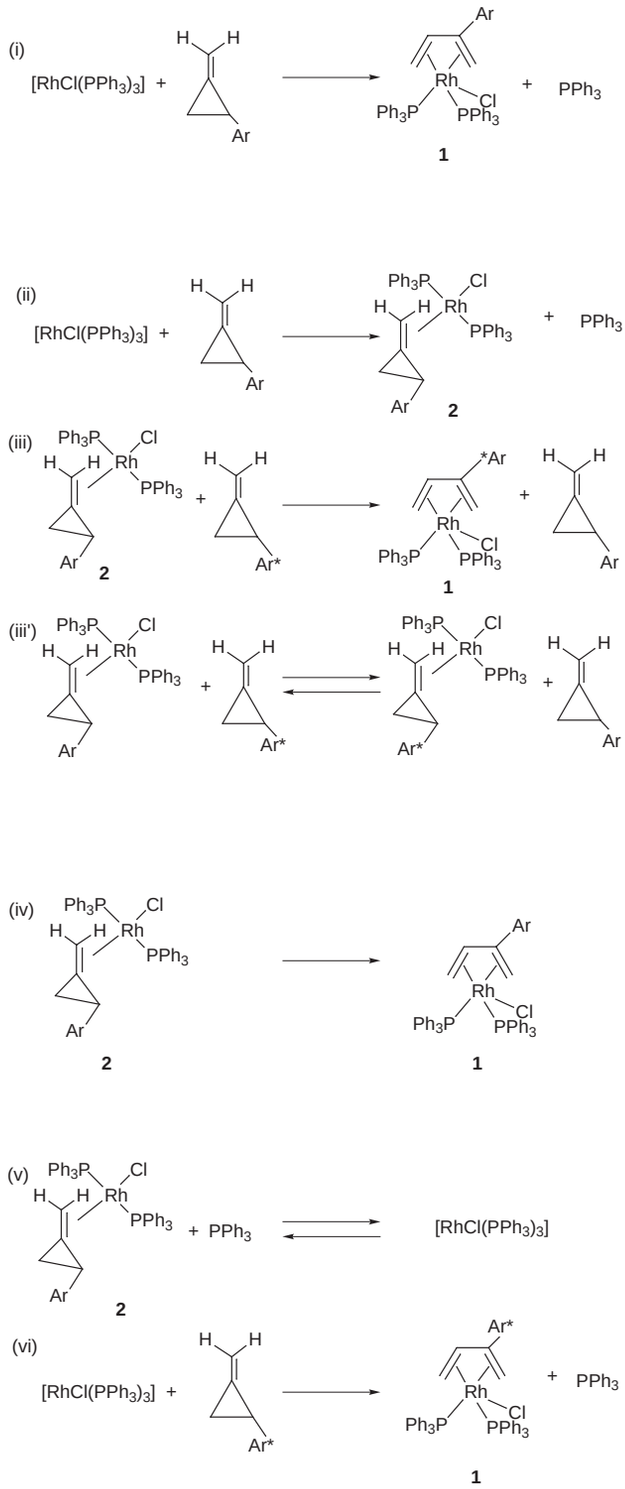
ation of the precise equilibrium constants. Comparison of ΔH° values of the two above reaction systems indicates that the η^2 co-ordination of 1-aryl-2-methylenecyclopropanes to Rh is stabilized by the presence of the electron withdrawing substituent on the aryl group.

Mechanism of the ring opening isomerization

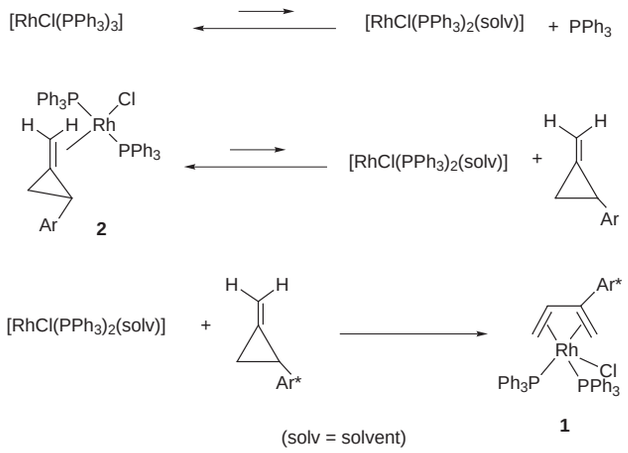
As shown above, the reactions of 1-aryl-2-methylenecyclopropanes with $[RhCl(PPh_3)_3]$ at 50 and at 0 °C gave the 2-arylbuta-1,3-diene- and the 1-aryl-2-methylenecyclopropane-co-ordinated rhodium complexes, respectively. 1-Methylene-2-phenylcyclopropane reacts with $[RhCl(PPh_3)_3]$ at 25 °C to give a mixture of **1a** and **2a** in a 47:53 molar ratio. Similar reaction of 1-(*p*-fluorophenyl)-2-methylenecyclopropane and of 1-(*p*-methoxyphenyl)-2-methylenecyclopropane with $[RhCl(PPh_3)_3]$ afforded a mixture of **1b** and **2b** (54:46) and **1d** and **2d** (55:45), respectively. Several additional experiments were conducted to elucidate detailed pathways of formation of these products.

The change in the amounts of organic and inorganic products during the reaction of 1-methylene-2-phenylcyclopropane with $[RhCl(PPh_3)_3]$ was monitored at 50 °C by ^1H NMR spectroscopy to obtain mechanistic insights into the ring opening isomerization pathway. Fig. 5 shows plots of the increase in **1a** and 2-phenylbuta-1,3-diene which reached 55 and 165% per Rh, respectively, after the reaction for 4.5 h. The ^1H and ^{31}P-$\{^1H\}$ NMR signals of $[Rh_2(\mu\text{-}Cl)_2(PPh_3)_4]$ and polymer of 2-phenylbuta-1,3-diene[21] were also observed during the reaction although the amounts were not included in Fig. 5. The reactions of **2a** at 50 °C were examined to compare its reactivity with $[RhCl(PPh_3)_3]$ toward 1,3-diene formation. Heating of a benzene solution of **2a** for 7 h at 50 °C led to the formation of **1a** in a low NMR yield (<7%) and a negligible amount of 2-phenylbuta-1,3-diene. The reaction of **2a** with 1-methylene-2-phenylcyclopropane (1:5 molar ratio) at 50 °C gave **1a** (10%) and 2-phenylbuta-1,3-diene (14% per Rh) after 6 h. The amounts of the products formed *via* ring-opening isomerization of the substrate are much smaller than those in the reaction of 1-methylene-2-phenylcyclopropane with $[RhCl(PPh_3)_3]$ under similar conditions (55 and 165%).

Scheme 2 summarizes several possible routes for the ring opening isomerization of 1-aryl-2-methylenecyclopropanes promoted by rhodium(I) complexes. Oxidative addition of a C–C bond of the substrate to $[RhCl(PPh_3)_3]$ (i) will give **1** directly. Reactions (ii) and (iii) involving initial co-ordination of the C=C double bond to Rh and the reaction of the 1-aryl-2-methylenecyclopropane with the formed **2** also account for formation of the product. The reaction (iii) should be accompanied by more rapid associative exchange of the ligand (iii′) because complex **2a** undergoes exchange of the π-co-ordinated ligand even at room temperature. Direct conversion of **2** into **1** *via* intramolecular C–C bond activation of the co-ordinated 1-aryl-2-methylenecyclopropane (iv) will provide the ring opening isomerization products. The reactions (ii)–(iv) are slower than (i) since heating of **2a** and of a mixture of **2a** and 1-methylene-2-phenylcyclopropane forms the 1,3-diene product in low yields. As suggested in Fig. 5, initially formed **2** is further converted into **1** or 2-phenylbuta-1,3-diene under the conditions. Another pathway involving regeneration of $[RhCl(PPh_3)_3]$ from the reaction of **2** and PPh_3 and its reaction with the substrate is also to be considered. However, addition of PPh_3 to the reaction mixture of **2a** and 1-methylene-2-phenylcyclopropane



Scheme 2



Scheme 3

at 50 °C caused inhibition of formation of **1a** and of 2-phenylbuta-1,3-diene. The mechanism in Scheme 3 accounts for all the above results. Dissociation of a PPh_3 ligand from $[RhCl(PPh_3)_3]$ and of 1-aryl-2-methylenecyclopropane ligand from **2** gives $[RhCl(PPh_3)_2(solv)]$ (solv = solvent) that is responsible for oxidative addition of a C–C bond of the substrate giving **1** or 2-phenylbuta-1,3-diene. Addition of PPh_3 to the reaction mixture will turn a labile $[RhCl(PPh_3)_2(solv)]$ species present into $[RhCl(PPh_3)_3]$ that shows much less reactivity toward the activation of the C–C bond.

The present study has revealed the reaction of 1-aryl-2-methylenecyclopropanes with $[RhCl(PPh_3)_3]$ to give the ring opening isomerization product or a complex having the substrate as the η^2-bonded ligand depending on the conditions. Ring opening isomerization occurs at higher temperature than simple π co-ordination of the substrate, but heating of the π-co-ordinated rhodium complex does not give the ring opened products.

Experimental

General considerations, measurements and materials

Manipulations of the rhodium complexes were carried out under nitrogen or argon using standard Schlenk techniques. The NMR spectra (^1H, ^{13}C, and ^{31}P) were recorded on a JEOL EX-400 spectrometer at 25 °C unless otherwise stated; ^{31}P-{^1H} NMR peaks were referenced to external 85% H_3PO_4. Elemental analyses were carried out by a Yanaco MT-5 CHN autocorder. The complex $[RhCl(PPh_3)_3]$ and 1-aryl-2-methylenecyclopropanes were prepared according to the literature,[22] $[RhCl(PEt_3)_3]$ from the reaction of PEt_3 with $[\{RhCl(C_8H_{14})\}_2]$ (C_8H_{14} = cyclooctene).[23] 1-(*p*-Fluorophenyl)-2-methylenecyclopropane: δ_H (C_6D_6) 0.90 (1 H, dddd, *cyclo*-C_3H_3, *J* 2, 2, 5 and 10), 1.41 (1 H, dddd, *cyclo*-C_3H_3, *J* 2, 2, 9 and 10), 2.26 (1 H, dddd, *cyclo*-C_3H_3, *J* 2, 2, 5 and 9 Hz), 5.52 (m, 2 H, vinyl) and 6.72–6.83 (4 H, m, C_6H_4). 1-Methylene-2-(*p*-methylphenyl)cyclopropane: δ_H (C_6D_6) 1.05 (1 H, dddd, *cyclo*-C_3H_3, *J* 2, 2, 5, and 9), 1.47 (1 H, dddd, *cyclo*-C_3H_3, *J* 2, 2, 9 and 10), 2.11 (3 H, s, Me), 2.42 (dddd, 1 H, *cyclo*-C_3H_3, *J* 2, 2, 5 and 10 Hz), 5.52–5.55 (2 H, m, vinyl) and 7.02–7.04 (4 H, m, C_6H_4). 1-(*p*-Methoxyphenyl)-2-methylenecyclopropane: δ_H (C_6D_6) 1.05 (1 H, dddd, *cyclo*-C_3H_3, *J* 2, 2, 5, and 9), 1.46 (1 H, dddd, *cyclo*-C_3H_3, *J* 2, 2, 9 and 10), 2.41 (1 H, dddd, *cyclo*-C_3H_3, *J* 2, 2, 5 and 10 Hz), 3.31 (3 H, s, OMe), 5.52–5.55 (2 H, m, vinyl) and 6.73–7.04 (4 H, m, C_6H_4).

Preparations

Complexes 1a–1d. To a toluene (4 cm^3) solution of $[RhCl(PPh_3)_3]$ (193 mg, 0.21 mmol) was added 1-methylene-2-phenylcyclopropane (135 mg, 1.04 mmol) at 50 °C. The solution changed from red to orange during the reaction. After 16 h the solvent was removed by evaporation. Addition of hexane to the orange product led to separation of a yellow solid, which was collected by filtration and dried *in vacuo* to give complex **1a** (157 mg, 95%) (Found: C, 69.75; H, 5.95; Cl, 4.22. $C_{46}H_{40}ClP_2Rh$ requires C, 69.66; H, 5.08, Cl, 4.47%). δ_H (C_6D_6) −0.56 (1 H, br, H^d or H^e), 0.58 (1 H, br, H^b), 0.77 (1 H, br, H^e or H^d), 3.56 (1 H, br, H^a), 5.45 (1 H, br, H^c), 6.81–6.96 (21 H, m), 7.43 (6 H, t, *J* 8 Hz), 7.78 (6 H, br) and 8.08 (2 H, br). δ_C (C_6D_6) 38.7 (d, C^4, *J* 11), 48.3 (dd, C^1, *J* 53 and 11 Hz), 87.8 (s, C^3), 113.0 (s, C^2), 128.2, 128.7, 128.8, 129.1, 129.4, 131.8, 132.6, 132.7, 134.9, 135.7, 136.0, 137.5, 137.8 and 138.0. δ_P (C_6D_6) 23.1 [d, *J*(PRh) 121] and 35.1 [d, *J*(PRh) 180 Hz]. Coupling due to a small *J*(PP) (<8 Hz) was observed depending on the measurement conditions (Chart 1).

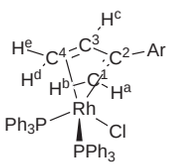


Chart 1 Numbering scheme of complexes **1a**–**1d**.

The reactions of 1-methylene-2-(*p*-methylphenyl)cyclopropane and of 1-(*p*-methoxyphenyl)-2-methylenecyclopropane with $[RhCl(PPh_3)_3]$ gave similar butadiene co-ordinated complexes **1c** and **1d** which were recrystallized from CH_2Cl_2–hexane. Complex **1b** was isolated from the reaction of 1-(*p*-fluorophenyl)-2-methylenecyclopropane with $[RhCl(PPh_3)_3]$ at 25 °C followed by repeated recrystallization of the product. Complex **1b** (yield 24%) (Found: C, 68.29; H, 5.43; Cl, 4.23; F, 2.16. $C_{46}H_{39}ClFP_2Rh$ requires C, 68.12; H, 4.85; Cl, 4.37; F, 2.34%): δ_H (C_6D_6) −0.56 (1 H, br, H^d or H^e), *ca*. 0.5 (1 H, br, H^b), *ca*. 0.8 (1 H, br, H^e or H^d), 3.44 (1 H, br, H^a), 5.34 (1 H, br, H^c), 6.83–7.12 (20 H, m), 7.41 (6 H, br) and 7.72–7.87 (8 H, br); δ_P (C_6D_6) 22.9 [d, *J*(PRh) 121] and 34.7 [d, *J*(PRh) 180 Hz]. Complex **1c** (yield 72%) (Found: C, 67.74; H, 5.39; Cl, 7.71. $C_{47}H_{42}ClP_2Rh{\cdot}0.5\ CH_2Cl_2$ requires C, 67.15; H, 4.99; Cl, 8.35%): δ_H −0.49 (1 H, br, H^d or H^e), 0.56 (1 H, br, H^b), 0.82 (1 H, br, H^e or H^d), 3.55 (3 H, s, Me), 3.59 (1 H, br, H^a), 5.48 (1 H, br, H^c), 6.84 (10 H, br), 6.86 (10 H, br), 7.45 (6 H, br), 7.78 (6 H, br) and 8.02 (2 H, br); δ_P (C_6D_6) 23.6 [d, *J*(PRh) 117] and 34.7 [d, *J*(PRh) 184 Hz]. Complex **1d** (yield 77%) (Found: C, 63.12; H, 5.02. $C_{47}H_{42}ClOP_2Rh{\cdot}CH_2Cl_2$ requires C, 63.49; H, 4.88%): δ_H −0.53 (1 H, br, H^d or H^e), 0.56 (1 H, br, H^b), 0.80 (1 H, br, H^e or H^d), 3.62 (1 H, br, H^a), 5.49 (1 H, br, H^c), 6.86–6.97 (20 H, m), 7.45 (6 H, t, *J* 7 Hz), 7.79 (6 H, br) and 8.02 (2 H, br); δ_P (C_6D_6) 24.9 [d, *J*(PRh) 121] and 36.4 [d, *J*(PRh) 180 Hz].

Complexes 2a–2d. To a toluene (7 cm^3) solution of $[RhCl(PPh_3)_3]$ (860 mg, 0.93 mmol) was added 1-methylene-2-phenylcyclopropane (605 mg, 4.6 mmol) at 0 °C. Stirring the solution for 4 h at that temperature caused precipitation of a yellow solid. After 24 h the solid product was collected by filtration, washed with Et_2O and then with hexane, and dried *in vacuo* to give complex **2a** as a yellow microcrystalline solid (500 mg, 68%) (Found: C, 69.55 ; H, 5.15. $C_{46}H_{40}ClP_2Rh$ requires C, 69.66; H, 5.08%). δ_H (C_6D_6) 0.37 [1 H, dd, Hd, *J*(H^cH^d) 6, *J*(H^dH^e) 5], 1.89 [1 H, dd, H^c, *J*(H^cH^d) 6, *J*(H^cH^e) 9], 2.27 (1 H, br, H^a or H^b), 2.34 (1 H, br, H^a or H^b), 2.71 [1 H, dd, H^e, *J*(H^cH^e 9, *J*(H^dH^e) 5], 6.57–6.69 (2 H, m), 6.81–7.08 (21 H, m), 7.87 (6 H, t, *J* 8) and 8.01 (6 H, t, *J* 7 Hz). δ_C (C_6D_6) 27.2 [d, C^3, *J*(CRh) 6], 29.6 [d, C^4, *J*(CRh) 4], 34.2 [d, C^1, *J*(CRh) 13], 61.5 [d, C^2, *J*(CRh) 22], 124.8 (C_6H_5 of 1-methylene-2-phenylcyclopropane), 125.8 (d, *J* 33), 127.8, 128.5, 129.3 (C_6H_5 of 1-methylene-2-phenylcyclopropane), 129.8 (d, *J* 25), 133.0 (t, *J* 21 and 9), 133.3 (t, *J* 21 and 9), 135.6 (dd, *J* 9 and 4), 135.9 (dd, *J* 9 and 4 Hz), 137.8 (C_6H_5 of 1-methylene-2-phenylcyclopropane) and 144.7 (C_6H_5 of 1-methylene-2-phenylcyclopropane); δ_P

(C_6D_6) 33.1 and 36.7 [AB pattern, J(PRh) = 133, J(PP) = 426 Hz] (Chart 2).

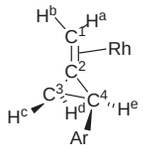


Chart 2 Numbering scheme of complexes **2a**–**2d** (Cl and PPh_3 are omitted.

Complex 2b (yield 80%) (Found: C, 68.40 ; H, 5.07; Cl, 4.19; F, 2.12. $C_{46}H_{39}ClFP_2Rh$ requires C, 68.12; H, 4.85; Cl, 4.37; F, 2.34%): δ_H (C_6D_6) 0.22 [1 H, dd, H^d, $J(H^cH^d)$ = 5, $J(H^dH^e)$ = 6], 1.83 [1 H, dd, H^c, $J(H^cH^d)$ = 6, $J(H^cH^e)$ = 9], 2.27 (1 H, br, H^a or H^b), 2.31 (1 H, br, H^a or H^b), 2.59 [1 H, dd, H^e, $J(H^cH^e)$ = 9, $J(H^dH^e)$ = 5], 6.34 (2 H, dd, J 8 and 6), 6.46 (2 H, t, J = 8), 6.95 (9 H, d, J 6), 7.08 (9 H, d, J 6), 7.84 (6 H, t, J 7) and 8.01 (6 H, t, J 7 Hz); δ_P(C_6D_6) 33.4 and 36.7 [AB pattern, J(PRh) = 133, J(PP) = 426 Hz]. Complex **2c** (yield 66%) (Found: C, 70.56; H, 5.46; Cl, 4.23. $C_{47}H_{42}ClP_2Rh$ requires C, 69.94; H, 5.24; Cl, 4.39%): δ_H (C_6D_6) 0.39 [1 H, dd, H^d, $J(H^cH^d)$ = 5, $J(H^dH^e)$ = 6], 1.90 [1 H, dd, H^c, $J(H^cH^d)$ = 5, $J(H^cH^e)$ = 7], 2.02 (3 H, s, Me) 2.18 (1 H, br, H^a or H^b), 2.19 (1 H, br, H^a or H^b), 2.70 [1 H, dd, H^e, $J(H^cH^e)$ = 9, $J(H^dH^e)$ = 5], 6.53 (2 H, d, J 8), 6.67 (2 H, d, J 8), 6.97 (9 H, d, J 8), 7.07 (9 H, d, J 6), 7.88 (6 H, t, J 8) and 8.01 (6 H, t, J 8 Hz); δ_P(C_6D_6) 34.7 and 35.3 [AB pattern, J(PRh) = 133, J(PP) = 426 Hz]. Complex **2d** (yield 79%) (Found: C, 68.68 ; H, 5.20; Cl, 4.31. $C_{47}H_{42}ClOP_2Rh$ requires C, 68.58; H, 5.14; Cl, 4.31%): δ_H (C_6D_6) 0.34 [1 H, dd, H^d, $J(H^cH^d)$ = 5, $J(H^dH^e)$ = 5], 1.87 [1 H, dd, H^c, $J(H^cH^d)$ = 5, $J(H^cH^e)$ = 9], 2.29 (1 H, br, H^a or H^b), 2.34 (1 H, br, H^a or H^b), 2.70 [1 H, dd, H^e, $J(H^cH^e)$ = 9, $J(H^dH^e)$ = 5], 3.26 (3 H, s, OMe), 6.44 (2 H, d, J 8), 6.50 (2 H, d, J 8), 6.98 (9 H, d, J 6), 7.08 (9 H, d, J 6), 7.88 (6H, t, J 7) and 8.02 (6 H, t, J 7 Hz); δ_P(C_6D_6) 33.0 and 36.7 [AB pattern, J(PRh) = 133, J(PP) = 426 Hz].

Complex 3c. To a toluene (4 cm^3) solution of [$RhCl(PEt_3)_3$] (369 mg, 0.75 mmol) was added 1-methylene-2-(*p*-methylphenyl)cyclopropane (257 mg, 1.78 mmol) at 0 °C. The reaction mixture was warmed to room temperature gradually. After 22 h the solvent was removed under vacuum. The residue was recrystallized from Et_2O to afford complex **3c** as orange crystals (263 mg, 68%) (Found: C, 52.82; H, 8.18; Cl, 6.92. $C_{23}H_{42}ClP_2Rh$ requires C, 53.24; H, 8.16; Cl, 6.83%). δ_H(C_6D_6) 0.88 (1 H, br, H^c or H^d), 0.90–1.05 (18 H, m, PCH_2CH_3), 1.41–1.69 (13 H, m, PCH_2 and H^c (or H^d)), 2.15 (3 H, s, Me), 2.37–2.41 (3 H, br, H^a, H^b and H^e) and 7.03 (4 H, s, C_6H_4). δ_C(C_6D_6) 8.47 (s, CH_3), 8.52 (s, CH_3), 13.4 (dd, CH_2, J 16 and 5), 13.8 (dd, CH_2, J 16 and 7), 21.0 (s, *p*-Me), 26.3 (s, C^4), 26.6 [d, C^1 J(CRh) = 66], 30.8 (s, C3), 56.1 [d, C^2 J(CRh) = 22 Hz], 125.7, 129.3, 134.4 and 141.7. δ_P(C_6D_6) 21.2 and 24.3 [AB pattern, J(RhP) 121, J (PP) 415 Hz] (Chart 3).

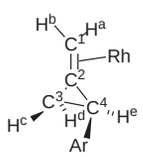


Chart 3 Numbering scheme of complex **3c** (Cl and PEt_3 are omitted).

Reaction of CO with complex 2a

A Schlenk flask was charged with a THF (2 cm^3) solution of complex **2a** (43 mg). After one freeze–pump–thaw cycle the solution was contacted with CO (1 atm = 101.325 Pa) at room temperature. The solution changed from orange to pale yellow. Evaporation of the solvent to *ca.* 1 cm^3 caused separation of an off-white solid which was collected by filtration and dried *in vacuo*. The IR spectrum of the solid product was identical with that of authentic [$RhCl(CO)(PPh_3)_2$]. The ^{1}H NMR analyses of the filtrate showed formation of 1-methylene-2-phenylcyclopropane in a quantitative amount.

Table 2 Crystallographic data for complexes **1c** and **3c**

	1c[a]	**3c**
Formula	$C_{50}H_{49}ClP_2Rh$	$C_{23}H_{42}ClP_2Rh$
M	850.24	518.89
Dimensions/mm	1.0 × 0.3 × 0.2	0.8 × 0.3 × 0.2
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a/Å	13.582(9)	12.856(5)
b/Å	16.643(5)	11.455(4)
c/Å	10.100(2)	18.717(6)
α/°	94.94(2)	
β/°	104.42(3)	101.51(3)
γ/°	73.21(4)	
V/Å^3	2116(1)	2700(1)
Z	2	4
D_c/g cm^{-3}	1.334	1.276
F(000)	882	1088
μ(Mo-Kα)/mm^{-1}	0.573	0.854
Reflections measured	9286	6764
Unique reflections	8864 (R_{int} = 0.026)	6485 (R_{int} = 0.181)
Used reflections [$I > 3.0\ \sigma(I)$]	6094	2985
Variables	487	244
$R(R')$	0.036 (0.029)	0.045 (0.049)

[a] Hexane solvated form.

Reaction of 1-aryl-2-methylenecyclopropanes with [$RhCl(PPh_3)_3$] at 25 °C

To a toluene (4 cm^3) solution of [$RhCl(PPh_3)_3$] (141 mg, 0.15 mmol) was added 1-methylene-2-phenylcyclopropane (99 mg, 0.76 mmol) at 25 °C. The solution changed from red to orange. After 20 h the solvent was removed under vacuum. Addition of hexane to the product led to separation of a yellow solid (132 mg) whose ^{1}H NMR spectrum indicated the presence of complexes **1a** and **2a** in a 47 : 53 ratio. Similar reaction of 1-(*p*-fluorophenyl)-2-methylenecyclopropane and of 1-(*p*-methoxyphenyl)-2-methylenecyclopropane with [$RhCl(PPh_3)_3$] afforded a mixture of **1b** and **2b** (54 : 46) and **1d** and **2d** (55 : 45), respectively.

Equilibrium constant measurement

To a benzene-d_6 (0.426 g) solution of complex **2a** (19.4 mg, 0.024 mol) were added 1-methylene-2-phenylcyclopropane (29.8 mg, 0.23 mmol) and 1-(*p*-fluorophenyl)-2-methylenecyclopropane (38.3 mg, 0.26 mmol) in an NMR sample tube. Then the NMR spectra were recorded at 30, 35, 40 and 45 °C. The molar ratio of **2a** and **2b** in the equilibrium mixtures was determined by comparison of the peak area of cyclopropane ring hydrogens (δ 2.59 and 2.71). Equilibrium constants between **2a** and **2c** were obtained from the peak intensity of the methyl hydrogens of **2c** and the other signals. The equilibrium constants at each temperature in the reaction of 1-(*p*-fluorophenyl)-2- methylenecyclopropane and of 1-methylene-2-(*p*-methylphenyl)cyclopropane with **2a** shown in eqn. (5) were 1.206 (30), 1.118 (35), 1.048 (40) and 0.988 (45) and 0.303 (30), 0.310 (35), 0.312 (40) and 0.317 (45 °C), respectively.

NMR study of the reaction of 1-methylene-2-phenylcyclopropane with [$RhCl(PPh_3)_3$]

To a benzene-d_6 (*ca.* 0.5 cm^3) solution of [$RhCl(PPh_3)_3$] (31.8 mg, 0.034 mmol) was added 1-methylene-2-phenylcyclopropane (22.6 mg, 0.17 mmol) at 0 °C. The NMR spectra were recorded every 10 min at 50 °C.

Crystallography

Recrystallization of complex **1c** from a THF–hexane mixture gave single crystals in a hexane solvated form, **1c**·0.5 C_6H_{14}. Orange single crystals of **3c** were obtained by recrystallization from Et_2O. The crystals were sealed in a glass capillary tube under argon and applied to data collection at 25 °C. Full-matrix least squares refinement was carried out with all the non-hydrogen atoms anisotropic. Vinyl hydrogens of **3c** were located in the final electron density map, while other hydrogens were situated at calculated positions. The hydrogens were included in the structure calculation without further refinement of the positional parameters. Crystal data and details of refinement are summarized in Table 2.

CCDC reference number 186/1335.

See http://www.rsc.org/suppdata/dt/1999/853/ for crystallographic files in .cif format.

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