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Ring-opening isomerization of methylenecyclopropanes catalyzed by hydridorhodium(I) complexes

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Abstract

2-Phenyl-1-methylenecyclopropane is isomerized into 2-phenyl-1,3-butadiene and 1-phenyl-1,3-butadiene in the presence of catalytic amounts of $RhH(CO)(PPh_3)_3$ and $RhH(PPh_3)_4$. The Rh-containing product of the reactions has a 2-phenyl-1-methylallyl (or 1-phenyl-1-methylallyl) ligand, and is formed also from the reaction of 2-phenyl-1,3-butadiene with $RhH(CO)(PPh_3)_3$. $RhH(CO)(PPh_3)_3$ promotes ring-opening isomerization of 4-phenyl-1-methylenespiro[2,2]pentane to afford $Rh[\eta^3\text{-anti-}CH_2C\{C(=CH_2)Ph\}CHCH_3](PPh_3)_2$ (**2**) at 50 °C and $Rh\{\kappa^1,\eta^2\text{-}CH_2CH(Ph)C(=CH_2)CH=CH_2\}(CO)(PPh_3)_2$ (**3**) at −35 °C. X-ray crystallography of **2** shows the π-allylic ligand having a methyl group at anti position. The mechanism for formation of **2** via intermediate **3** is discussed.

Keywords: Rhodium; C─C bond activation; Hydrido complex; Methylenecyclopropane; Diene

1. Introduction

Activation of C–C bond of organic molecules promoted by soluble transition metal complexes has attracted significant attention in homogeneous catalysis [1,2]. The reactions do not always take place smoothly because of high stability of the C–C bonds to be cleaved and the occurrence of the metal-promoted C–H bond activation that is kinetically more favorable than the C–C bond activation. Small-membered ring molecules often undergo facile C–C bond activation accompanied by ring opening owing to the release of the ring strain caused by the reactions [3–6]. Organic compounds having two small-membered rings with a spiro structure are expected to exhibit high reactivity toward the reactions involving the C–C bond cleavage. Murakami and Ito reported the selective conversion of a spiro ketone into the monocyclic substituted ketone promoted by Rh complexes, as shown in Scheme 1 [7].

The reaction involves stepwise C–C bond cleavage of the substrate via the metalacyclic intermediates.

Methylenecyclopropanes have high strain energy (ΔH_f larger than that of cyclopropane by approximately 35 kcal mol^{-1}) [8] and are easily converted into its thermodynamically stable diene isomers in the presence of transition metal complexes. Recently we reported the reaction of 2,2-diaryl- and 2,2-dialkyl-1-methylenecyclopropanes with $IrH(CO)(PPh_3)_3$ to afford the Ir complexes having a 2,2-disubstituted 3-butenyl ligand formed via ring opening of the substrate [9,10]. It is closely related to the ring-opening isomerization of methylenecyclopropanes promoted by the Ir complexes and by the complexes of other late transition metals. In this paper, we report the reaction of 2-phenyl-1-methylenecyclopropane and 4-phenyl-1-methylenespiro[2,2]pentane with hydridorhodium(I) complexes to produce the corresponding dienes or the Rh complexes with the ligands formed via ring-opening isomerization of the substrate. Results of the reaction of 2-phenyl-1-methyelenecyclopropane with $RhH(CO)(PPh_3)_3$ were partly reported in a preliminary communication [11].

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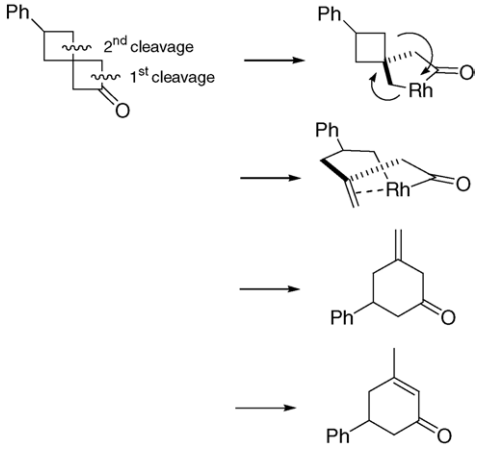
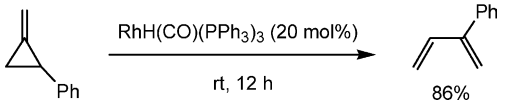


Scheme 1.

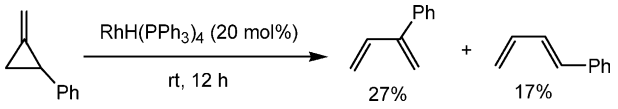
2. Results and discussion

2.1. Ring-opening isomerization of 2-phenyl-1-methylenecyclopropane by hydridorhodium complexes

2-Phenyl-1-methylenecyclopropane is isomerized into 2-phenyl-1,3-butadiene at room temperature in the presence of the $RhH(CO)(PPh_3)_3$ catalyst as shown in Eq. (1). Formation of 1-phenyl-1,3-butediene is not observed during the reaction.



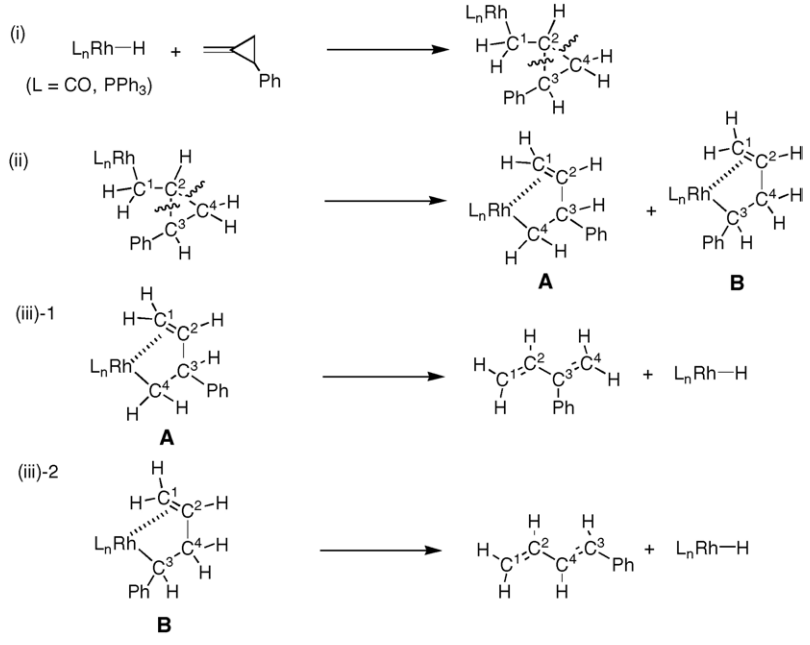
(1)



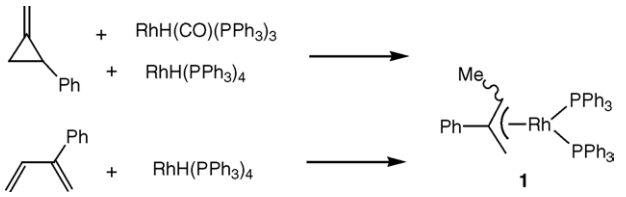
(2)

$RhH(PPh_3)_4$ also promotes ring-opening isomerization of 2-phenyl-1-methylenecyclopropane at room temperature to yield a mixture of 2-phenyl-1,3-butadiene and 1-phenyl-1,3-butadiene (Eq. (2)). The reaction of 2-phenyl-1-methylenecyclopropane with $IrH(CO)(PPh_3)_3$ was reported to produce a mixture of the phenyl-1,3-butadienes and the Ir complex having a 3-butenyl ligand formed via ring opening of 2-phenyl-1-methylenecyclopropane [10,11]. Scheme 2 displays the reaction pathway proposed based on the results of the reaction of $IrH(CO)(PPh_3)_3$. Insertion of a C=C bond of methylenecyclopropane into the Rh–H bond produces the cyclopropylmethylrhodium intermediate. Subsequent C–C bond cleavage of the three-membered ring by β-alkyl elimination leads to the formation of 3-butenylrhodium complexes, **A** and **B**, depending on the C–C bond to be cleaved by the Rh center. β-Hydrogen elimination of **A** and **B** results in formation of 2-phenyl-1,3-butadiene and 1-phenyl-1,3-butadiene, respectively, and regenerates the hydridorhodium species.

$RhH(CO)(PPh_3)_3$-catalyzed reaction of 2-phenyl-1-methylenecyclopropane produces 2-phenyl-1,3-butadiene exclusively, suggesting that the C–C bond cleavage in (ii) occurs selectively at the sterically less hindered C–C bond. The diene-forming reaction by $RhH(PPh_3)_4$ shows slower rate and lower selectivity than that by $RhH(CO)(PPh_3)_3$. Slow β-hydrogen elimination from the intermediate **A** without a CO ligand may result in the decrease in the



Scheme 2.



Scheme 3.

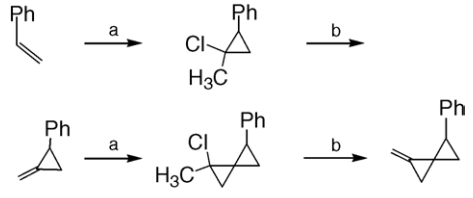
total reaction rate and form 1-phenyl-1,3-butadiene via intermediate **B** that is in rapid equilibrium with **A**.

Evaporation of the solvent from the product of reactions (1) and (2) and removal of the organic compounds by washing the solid product with solvent yielded the Rh-containing product which exhibits the $^{31}P\{^{1}H\}$ NMR signals as a pair of doublet of doublets at δ 42.7 and 44.5 due to two magnetically inequivalent phosphorous nuclei with reasonable coupling constants (J(P–P) = 24 Hz, J(RhP) = 207 and 196 Hz). Since the complex does not catalyze the ring-opening isomerization in Eqs. (1) and (2), its formation probably deactivates the catalyst. The reaction of 2-phenyl-1,3-butadiene with $RhH(PPh_3)_4$ also gives the product showing the $^{31}P\{^{1}H\}$ NMR signals at the same positions. These results indicate that formation of the complex in Eqs. (1) and (2) is ascribed to the reaction of once formed 2-phenyl-1,3-butadiene with the hydridorhodium complex in the reaction mixture. The structure of the complex was tentatively assigned to be $Rh(CH_2CPhCHMe)(PPh_3)_2$ (**1**) based on the NMR data and the results that the above three reactions produce the common complex as the major Rh-containing product (Scheme 3).

The ^{1}H NMR spectrum of **1** shows a signal at δ 1.32 due to the methyl hydrogens and broad signals at δ 2.53, 3.32 and 3.71, assigned to the hydrogens of the π-allylic ligand. Another structure of the complex with a 1-phenyl-1-methylallyl ligand may also be possible, although formation of the latter complex from 2-phenyl-1,3-butadiene requires insertion of sterically more hindered C=C bond into the Rh–H bond.

2.2. Ring-opening isomerization of 4-phenyl-1-methylenespiro[2,2]pentane

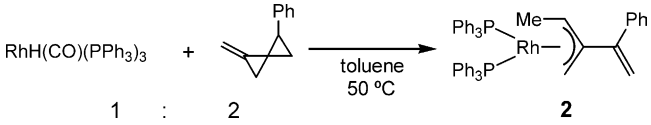
4-Phenyl-1-methylenespiro[2,2]pentane, having two three-membered rings with a spiro arrangement, is prepared according to the procedure shown in Scheme 4.



Reagents: (a) ^{n}BuLi, CH_3CHCl_2, Et_2O, -45 °C, 5 h.
(b) ^{t}BuOK, DMSO, rt,12 h.

Scheme 4.

Addition of chloro(methyl)carbene to 2-phenyl-1-methylenecyclopropane followed by base-promoted dehydrochlorination of the spiro compound formed affords the product. The new compound was characterized by NMR spectroscopy although satisfactory results for elemental analysis were not obtained. 4-Phenyl-1-methylenespiro[2,2]pentane reacts with $RhH(CO)(PPh_3)_3$ at 50 °C to produce $Rh[\eta^3\text{-}anti\text{-}CH_2C\{C(=CH_2)Ph\}CHMe](PPh_3)_2$ (**2**) in 67% as shown in Eq. (3).



(3)

Fig. 1 shows molecular structure of **2** determined by X-ray crystallography. The complex has a 16-electron Rh center bonded to the π-allylic ligand and two PPh_3 ligands. Three Rh–C bonds of the allylic ligand, 2.144(9)–2.187(9) Å, are similar to the π-allylic rhodium(I) complexes [12–14]. Carbonyl ligand of the starting complex is eliminated during the reaction, which is contrasted with the reaction of 1,3-diene and arylallene with $RhH(CO)(PPh_3)_3$, giving the π-allylrhodium complexes with an 18-electron metal center, $Rh(\pi\text{-allyl})(CO)(PPh_3)_2$ [15–17]. The methyl group of the allyl ligand is situated at anti position. Transition metal π-allylic complexes with the anti substituents were characterized by NMR and X-ray crystallography [18–20], although the number of such complexes was much smaller than the complexes with syn substituents at the allyl ligand.

The $^{31}P\{^{1}H\}$ NMR spectrum of **2** also contains a pair of doublet of doublets at δ 41.3 (dd, ^{1}J(P–Rh) = 204 Hz, ^{2}J(P–P) = 22 Hz) and 44.3 (dd, ^{1}J(P–Rh) = 193 Hz,

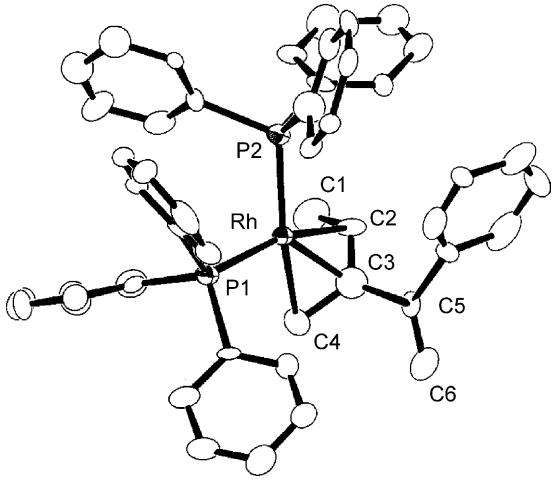


Fig. 1. ORTEP drawing of **2** with 30% thermal ellipsoidal plots. Selected bond distances (Å) and angles (°): Rh–P1 2.276(2), Rh–P2 2.270(2), Rh–C2 2.185(9), Rh–C3 2.144(9), Rh–C4 2.187(9), C1–C2 1.52(2), C2–C3 1.43(1), C3–C4 1.42(1), C3–C5 1.50(2), C5–C6 1.33(2), P1–Rh–P2 103.17(9), C2–Rh–C4 68.4(4), P2–Rh–C4 162.6(3), C2–C3–C4 119.1(9).

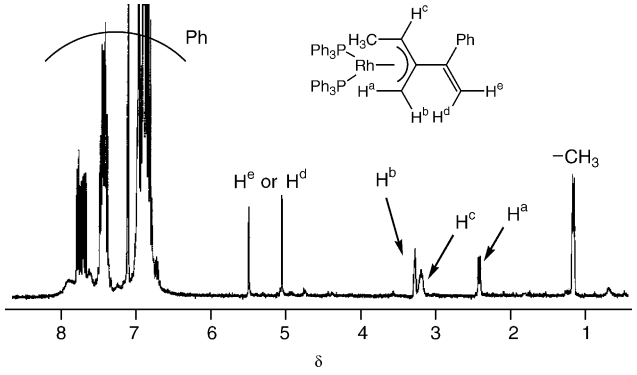
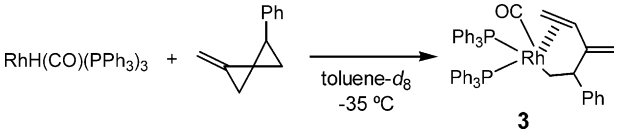


Fig. 2. ^{1}H NMR spectrum of Rh[η^3-anti-$CH_2C\{C(=CH_2)Ph\}CHMe$]$(PPh_3)_2$ (**2**) (C_6D_6, 25 °C).

^2J(P–P) = 22 Hz). Fig. 2 shows the ^{1}H NMR spectrum of **2**. Signal of methyl hydrogens of the allylic ligand is observed at δ 1.17. The signals of the other hydrogens of π-allylic ligand are assigned based on the ^{1}H–^{1}H COSY spectrum. Sharp signals due to vinylidene hydrogens appear at reasonable positions, δ 5.09 and 5.53. The hydrogens bonded to the same allylic carbon are observed at δ 2.43 and 3.21.

Reaction of 4-phenyl-1-methylenespiro[2,2]pentane with $RhH(CO)(PPh_3)_3$ at −35 °C produces Rh$\{\kappa^1,\eta^2$-$CH_2CHPhC(=CH_2)CH=CH_2\}(CO)(PPh_3)_2$ (**3**), as shown in Eq. (4).



(4)

The complex was not isolated due to facile conversion into other complexes such as **2** in the solution. Fig. 3 depicts the ^{1}H and ^{31}P$\{^1$H$\}$ NMR spectra of the complex. The signals at δ 4.39 and 5.32 are assigned to the vinylidene hydrogens uncoordinated to the Rh center. The peak positions indicate that Rh is bonded to the vinyl group (–CH=CH_2) rather than the vinylidene group (=C=CH_2). The vinyl hydrogen signals are observed at the positions, which are in the magnetically higher field than the signals of uncoordinated olefins (δ 3.35, 2.66, and 1.39). The ^{31}P$\{^1$H$\}$ NMR spectrum contains the major and minor signals. The complexes can be assigned to the diastereomers with regard to the configuration of asymmetric carbon of the ligand and face of the vinyl group coordinated to the Rh center.

Scheme 5 depicts the plausible pathways for formation of **3** as the initial product of the reaction of the spiro compound with $RhH(CO)(PPh_3)_3$ and its subsequent isomerization into the final product **2**. Insertion of a C=C double bond of the substrate into the Rh–H bond and β-alkyl elimination of the resultant cyclopropylmethylrhodium intermediate form the 3-butenylrhodium complex having cyclopropylidene group

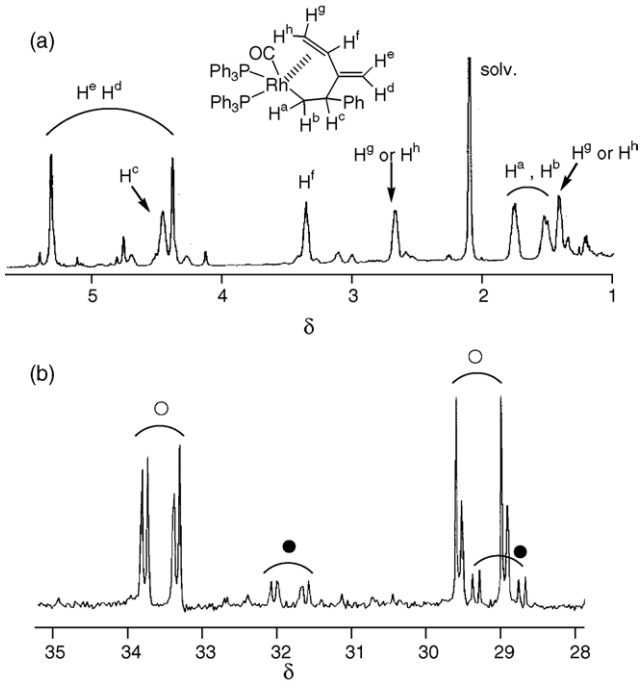


Fig. 3. (a) ^{1}H and (b) ^{31}P$\{^1$H$\}$ NMR spectra of Rh$\{\kappa^1,\eta^2$-$CH_2CH(Ph)C(=CH_2)CH=CH_2\}(CO)(PPh_3)_2$ (**3**) formed by the reaction of 4-phenyl-1-methylenespiro[2,2]pentane with $RhH(CO)(PPh_3)_3$ (toluene-d_8, −50 °C). Small signals in the ^{1}H NMR spectrum may be due to a minor diastereomer of **3** or organic impurities. Circles and dots in the ^{31}P$\{^1$H$\}$ NMR spectrum are assigned to major and minor diastereomers of **3**, respectively.

at the β-carbon. Analogous Rh and Ir complexes having aryl or alkyl substituents at the β-carbon were prepared and fully characterized in our studies [9–11]. The intermediate complex in this reaction undergoes second β-alkyl elimination of the three-membered ring due to severe ring strain, yielding complex **3**, which is characterized by NMR spectroscopy.

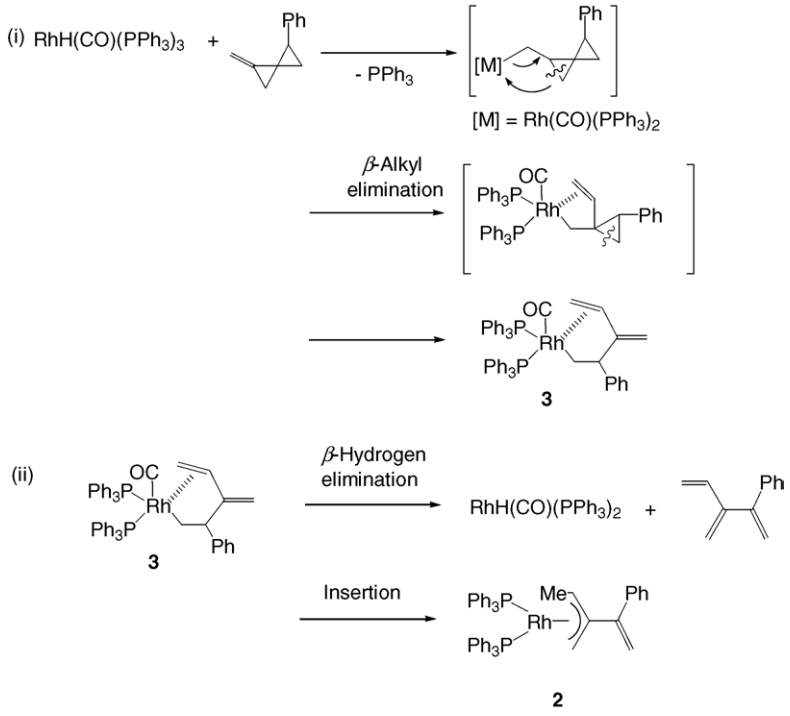
Complex **3** is stable in the solution at low temperature, although it is not isolated as crystals. Warming the solution to room temperature leads to formation of π-allylic rhodium complex **2**. β-Hydrogen elimination of the 4-pentenyl ligand of **3** and reinsertion of the C=C double bond of the vinyl group (–CH=CH_2) of the triene into the Rh–H bond produce **2**.

This paper presents organic and inorganic products of the C–C bond activation of the strained molecules promoted by hydridorhodium complexes. The reaction takes place selectively in spite of the high reactivity of the substrate with the strained structure.

3. Experimental

3.1. General

All manipulations of the complexes were carried out using standard Schlenk techniques under an argon or a



Scheme 5.

nitrogen atmosphere. THF and toluene grade were distilled from sodium and benzophenone prior to use or purchased from Kanto Chemicals Co. Ltd. The starting materials $RhH(PPh_3)_4$ [21,22], $RhH(CO)(PPh_3)_3$ [23,24], 2-phenyl-1-methylenecyclopropane, 1-phenyl-1,3-butadiene, and 2-phenyl-1,3-butadiene [25,26] were prepared according to the literature methods. NMR spectra (^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$) were recorded on JEOL EX-400 or Varian Mercury 300 spectrometers. H_3PO_4 (85%, δ 0) was used as the external reference for $^{31}P\{^1H\}$ 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.

3.2. Reaction of 2-phenyl-1-methylenecyclopropane with hydridorhodium(I) complexes

To a benzene-d_6 (0.6 mL) solution of $RhH(CO)(PPh_3)_3$ (27.6 mg, 0.030 mmol) was added 2-phenyl-1-methylenecyclopropane (20 mg, 0.15 mmol) at room temperature. The ^1H NMR spectrum after 10 min indicates consumption of 2-phenyl-1-methylenecyclopropane and formation of 2-phenyl-1,3-butadiene (91% based on 2-phenyl-1-methylenecyclopropane) without the formation of 1-phenyl-1,3-butadiene. The major Rh complex in the solution is $RhH(CO)(PPh_3)_3$ at this stage. After 12 h, the amount of 2-phenyl-1,3-butadiene decreased to 86%. The reaction using the $RhH(PPh_3)_4$ catalyst was carried out similarly.

After the reaction using the $RhH(PPh_3)_4$ catalyst, the solvent was removed by evaporation and the resulting solid was washed with hexane to remove the organic products. The NMR results shown below suggest the formation of $Rh(\eta^3\text{-}CH_2CPhCHMe)(PPh_3)_2$ (**1**). Isolation of the complex was not feasible because it undergoes decomposition in the solution in the absence of 2-phenyl-1,3-butadiene. ^1H NMR (400 MHz, benzene-d_6, 25 °C): δ 1.32 (dd, 3H, J = 2.6 Hz, J = 4.3 Hz), 2.53 (dd, ^1H, J = 1.6 Hz, J = 6.8 Hz), 3.32 (m, ^1H), 3.71 (m, ^1H), 6.2–8.1 (m, 35H); $^{31}P\{^1H\}$ NMR (160 MHz, benzene-d_6, 25 °C): δ 42.7 (dd, J(Rh–P) = 207 Hz, J(P–P) = 24 Hz), 44.5 (dd, J(Rh–P) = 196 Hz, J(P–P) = 24 Hz).

3.3. Preparation of 1-chloro-1-methyl-4-phenylspiro[2,2]pentane

To an Et_2O (150 mL) solution of 2-phenyl-1-methylenecyclopropane (7.81 g, 60 mmol) was added 1,1-dichloroethane (25 mL, 300 mmol) at −45 °C. After stirring the solution at that temperature, *n*-BuLi (1.6 M hexane solution, 225 mL, 360 mmol) was added dropwise over 1 h. The solution was gradually warmed to room temperature and stirred for 30 min at that temperature. The solution was washed with aqueous NH_4Cl and brine in this order. The organic layer was dried over $MgSO_4$. Column chromatography (silica gel, hexane, R_f = 0.29) and bulb-to-bulb distillation (110–120 °C / 5 Torr) yielded 1-chloro-1-methyl-4-phenylspiro[2,2]-pentane as colorless

oil (9.15 g, 79%). The ^{1}H NMR spectrum indicated the presence of two diastereomers in 52:48 ratio.

Analysis calcd. for $C_{12}H_{13}Cl$:C, 74.80; H, 6.80%. Found: C, 76.87; H, 7.26%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.09 (d, J(H–H) = 5.4 Hz, 1H), 1.18 (t, J(H–H) = 4.8 Hz, 1H), 1.25 (d, J(H–H) = 5.7 Hz, 1H), 1.28 (t, J(H–H) = 4.8 Hz, 1H), 1.35 (d, J(H–H) = 5.7 Hz, 1H), 1.53 (d, J(H–H) = 5.7 Hz, 1H), 1.64 (s, 3H), 1.66 (partially overlapped by methyl proton, 1H), 1.71 (dd, J(H–H) = 4.8, 8.4 Hz, 1H), 2.43 (dd, J(H–H) = 4.8, 8.4 Hz, 1H), 2.47 (dd, J(H–H) = 5.4, 8.4 Hz, 1H), 7.06–7.09 (m, 2H), 7.13–7.15 (m, 2H), 7.18–7.22 (m, 2H), 7.25–7.32 (m, 4H). ^{13}C{^{1}H} NMR (75.3 MHz, $CDCl_3$, 25 °C): δ = 16.89, 17.61, 21.13, 21.16, 23.08, 23.64, 25.47, 25.62, 30.96, 31.15, 45.15, 45.80, 125.80 (2C), 125.99, 126.39, 128.24, 128.28, 141.04, 141.25.

3.4. Preparation of 4-phenyl-1-methylenespiro[2,2]pentane

To a DMSO (150 mL) solution of 1-chloro-1-methyl-4-phenylspiro[2,2]-pentane (9.15 g, 47.5 mmol) was added KO^{t}Bu (8.1 g, 72 mmol) at room temperature. After stirring the reaction mixture overnight, the black solution was washed with aqueous NH_4Cl (200 mL), water (500 mL), and brine (200 mL), in this order, and dried over $MgSO_4$. Purification by column chromatography (silica gel, hexane, R_f = 0.40) and bulb-to-bulb distillation (75 °C/3 Torr) yielded 4-phenyl-1-methylenespiro[2,2]pentane as colorless oil (6.3 g, 85%).

Analysis calcd. for $C_{12}H_{12}$:C, 92.26; H, 7.74%. Found: C, 90.90; H, 8.31%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.30 (d, J(HH) = 8.1 Hz, 1H), 1.49 (t, J(H–H) = 4.8 Hz, 1H), 1.54 (d, J(H–H) = 8.1 Hz, 1H), 1.76 (dd, J(H–H) = 4.5, 8.1 Hz, 1H), 2.51 (dd, J(H–H) = 5.4, 8.1 Hz, 1H), 5.25 (t, J(H–H) = 2.4 Hz, 1H), 5.33 (s, 1H), 7.16–7.23 (m, 3H), 7.32 (m, 2H). ^{13}C{^{1}H} NMR (75.3 MHz, $CDCl_3$, 25 °C): δ = 9.02, 19.81, 20.34, 25.94, 98.39, 125.64, 126.14, 128.18, 136.24, 141.27.

3.5. Reaction of 4-phenyl-1-methylenespiro[2,2]pentane with RhH(CO)(PPh$_3$)$_3$

To a toluene (4 mL) solution of $RhH(CO)(PPh_3)_3$ (230 mg, 0.25 mmol) was added 4-phenyl-1-methylenespiro[2,2]pentane (100 μL, 0.60 mmol) at room temperature. Stirring the mixture for 1 h at 50 °C caused change of color from yellow to red. Solvent was removed under reduced pressure. The resulted dark orange oil was washed with hexane at −40 °C to afford Rh[*anti*-η^3-$CH_2C\{C(=CH_2)Ph\}CHMe](PPh_3)_2$ (**2**) as an orange solid (126 mg, 67%). Analysis calcd. for $C_{48}H_{43}P_2Rh$:C, 73.47; H, 5.52%. Found: C, 73.72; H, 5.80%. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 1.17 (m, 3H), 2.43 (d, J = 6.9 Hz, 1H), 3.21 (m, 1H), 3.29 (m, 1H), 5.09 (d, J = 1.8 Hz, 1H), 5.53 (d, J = 1.8 Hz, 1H), 6.72–7.94 (m, 35H). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 25 °C): δ = 41.3 (dd, ^1J(P–Rh) = 204 Hz, ^2J(P–P) = 22 Hz), 44.3 (dd, ^1J(P–Rh) = 193 Hz, ^2J(P–P) = 22 Hz).

3.6. Reaction of 4-phenyl-1-methylenespiro[2,2]pentane with RhH(CO)(PPh$_3$)$_3$ at low temperature

A toluene-d_8 (0.70 mL) solution of $RhH(CO)(PPh_3)_3$ (92 mg, 0.10 mmol) in an NMR tube sealed with a rubber septum was cooled at −78 °C. 4-Phenyl-1-methylenespiro[2,2]pentane (20 μL, 0.12 mmol) was added to the solution through septum. The reaction was monitored by NMR spectra at −35 °C. After 3 h, the ^{1}H, ^{31}P{^{1}H} and ^{1}H–^{1}H COSY spectra of the solution indicated the presence of $Rh\{\kappa^1,\eta^2\text{-}CH_2CH(Ph)C(=CH_2)CH=CH_2\}(CO)(PPh_3)_2$ (**3**) and its stereoisomer. ^{1}H NMR (500 MHz, toluene-d_8, −50 °C): δ = 1.39 (1H, H^g or H^h), 1.51 (1H, H^a or H^b), 1.75 (1H, H^a or H^b), 2.66 (1H, H^g or H^h), 3.35 (1H, H^f), 4.39 (1H, H^e or H^d), 4.46 (1H, H^c), 5.32 (1H, H^e or H^d). ^{31}P{^{1}H} NMR (202 MHz, toluene-d_8, −20 °C): δ = 29.0 (dd, ^1J(P–Rh) = 123 Hz, ^2J(P–P) = 19 Hz, minor), 29.2 (dd, ^1J(P–Rh) = 123 Hz, ^2J(P–P) = 19 Hz, major), 31.8 (dd, ^1J(P–Rh) = 86 Hz, ^2J(P–P) = 19 Hz, minor), 33.5 (dd, ^1J(P–Rh) = 86 Hz, ^2J(P–P) = 19 Hz, major).

3.7. X-Ray diffraction study

Single crystals of **2** suitable for X-ray diffraction studies were obtained by recrystallization from hexane at −20 °C. Intensities were collected for Lorentz and polarization effects on a Rigaku AFC-5R or AFC-7R automated four-cycle diffractiometer by using Mo Kα radiation λ = 0.7107 Å) and ω–2θ scan method, and an empirical absorption correction (ψ scan) was applied. Calculations were carried out by using a program package teXsan for Windows. The structure was solved by the Patterson method. A full matrix least-square refinement was used for the non-hydrogen atoms with anisotropic thermal parameters. All non-hydrogen atoms were refined with anisotropic thermal parameters, whereas all hydrogen atoms were located by assuming the ideal geometry and included in the structure calculation without further refinement of the parameters [27]. Crystal data: orange prisms, $C_{48}H_{43}P_2Rh$, formula weight 784.72, crystal system triclinic, space group $P\bar{1}$ (No. 2), a 12.441(1) Å, b 18.450(2) Å, c 11.608(1) Å, α 106.275(4)°, β 109.448(8)°, γ 74.306(2)°, V 2365.0(4) Å^3, Z 2, μ 0.455 mm^{-1}, F(0 0 0) 812.00, d_{calcd} 1.102 g cm^{-3}, crystal size 0.17 mm × 0.15 mm × 0.12 mm, unique reflections 9249, used reflections ($F^2 > 2.0\sigma(F^2)$) 5358, variables 503, R 0.0710, wR 0.1130, GOF 2.042.

Crystallographic data (excluding structural factors) have been deposited with the Cambridge Crystallographic Data Center as supplemental publication no. CCDC 265899. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44

1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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