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Reactions of [RuClH(CO)(PPh_3)$_3$] with 2-methyl-2-propen-1-ol. Reversible insertion/β-elimination, and reductive elimination on a 3-hydroxy-2-methylpropyl-C^1,O-ruthenium(II) complex☆

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Abstract

A hydridoruthenium complex [RuClH(CO)(PPh_3)$_3$] (**1**) reacts with 2-methyl-2-propen-1-ol at room temperature to give an insertion product, [Ru{$CH_2CH(CH_3)CH_2OH$}Cl(CO)(PPh_3)$_2$] (**2**), which undergoes β-elimination of 2-methyl-2-propen-1-ol reversibly in solution. The complex **1** reacts with 2-methyl-2-propen-1-ol under benzene refluxing conditions to produce 2-methylpropan-1-ol, 2-methylpropanal and 2-methyl-2-propenal catalytically in the presence of water. The production of 2-methylpropanal results in formation of two isomers of 2-methylpropanoato complex [RuCl{η^2-$(CH_3)_2CHCO_2$}(CO)(PPh_3)$_2$] (**3**). Heating **1** at 80°C in neat 2-methyl-2-propen-1-ol affords a novel ruthenium(O) complex [Ru{η^4-CH_2=C(CH_3)CH≡O}-(CO)(PPh_3)$_2$] (**7**) and a quaternary phosphonium salt [$Ph_3PCH_2CH(CH_3)CH_2OH$]Cl (**8**) via reductive elimination of 3-chloro-2methylpropan-1-ol from **2**. The molecular structures of **7** and **8** are determined by X-ray crystallography.

Keywords: [RuClH(CO)(PPh_3)$_3$]; Reversible insertion; Reductive elimination

1. Introduction

A large number of ruthenium complex-catalyzed reactions of allylic alcohols have been reported, such as isomerization of allylic alcohols [1–4] and ethers [5–7], redox fragmentation of allylic ethers [8], reshuffling of allylic alcohols [9], and condensation of allylic alcohols and 1-alkynes [10]. Hydridoruthenium complexes play essential roles in these catalytic reactions through coordination, activation, and transformation of the allylic alcohols on the ruthenium center. Therefore, detailed investigation on ruthenium species derived from the hydridoruthenium complexes and the allylic alcohols is needed to figure out how the ruthenium-complex catalysts work.

We have been working on reactions of a hydridoruthenium(II) complex [RuClH(CO)(PPh_3)$_3$] (**1**) and some allylic compounds such as allyl sulfides [11] and allylamines [12]. The allylic compounds generally inserted into the Ru–H bond of **1** to give the corresponding five-membered chelate rings. Sometimes the carbon–heteroatom bonds were cleaved; the allyl sulfides gave thiolato-bridged binuclear complexes accompanied by the liberation of propene [11]. The tertiary allylamines, in contrast, gave a π-allylruthenium complex in which the allyl moiety of the allylamines was combined to the ruthenium [12]. Here we report our recent study on reaction of the hydridoruthenium(II) complex **1** to 2-methyl-2-propen-1-ol (a 2-substituted allyl alcohol). Instead of the carbon–heteroatom

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bond cleavage, unexpected reductive elimination of 3-chloro-2-methyl-2-propan-1-ol follows the insertion of the allylic moiety to give a novel (η^4-enone)ruthenium(O) complex and a quaternary phosphonium salt. Furthermore, in the presence of water, carboxylato species, 2-methylpropanoatoruthenium(II) complexes are derived from **1** and 2-methyl-2-propen-1-ol.

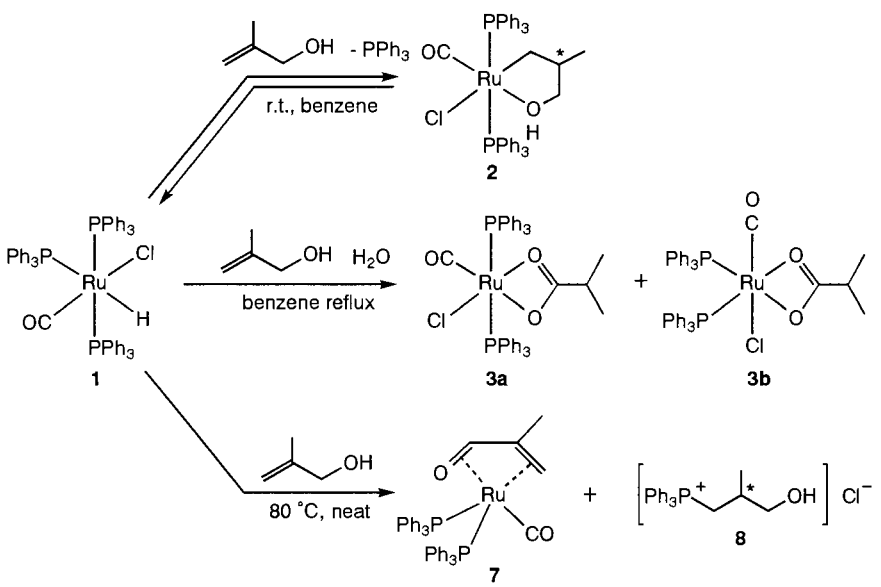
2. Results and discussion

2.1. Insertion of 2-methyl-2-propen-1-ol: formation of 3-hydroxy-2-methylpropyl-C^1,O-ruthenium(II) complex

When the hydridoruthenium(II) complex **1** is heated with a large excess amount of 2-methyl-2-propen-1-ol in benzene at room temperature for 120 h, the starting suspension turns into a yellow solution. The GLPC analysis of the reaction mixture shows no peak other than 2-methyl-2-propen-1-ol and benzene. Addition of hexane to the concentrated reaction mixture gives pale yellow precipitates of a crude insertion product $[Ru\{CH_2CH(CH_3)CH_2OH\}Cl(CO)(PPh_3)_2]$ (**2**). The infrared spectrum of the precipitates shows a strong band at 1890 cm^{-1} and a broad band near 3520 cm^{-1}, ascribable to ν(C≡O) and ν(O–H), respectively. The $^{31}P\{^1H\}$-NMR spectrum of the precipitates at −30°C exhibits two doublets at δ 34.8 and 42.6 with a remarkably large coupling constant (J_{PP} = 332.1 Hz) accompanied by a set of the signals of **1**, a triplet at δ 11.1 and a doublet at δ 39.0. The doublets with the large coupling constant are ascribed to two *trans*-coordinated triphenylphosphines in different chemical circumstances owing to a newly formed asymmetric carbon of the 3-hydroxy-2-methylpropyl-C^1,O-ligand. The ^{1}H-NMR spectrum of the precipitates shows a doublet of the methyl protons at δ 0.35 and five broad signals of the methylene and methine protons in the range of δ 1.4–3.2, which were ascribed to the 'RuCH^{a}H^{b}CH(CH$_3$)CH^{c}H^{d}O' moiety by means of ^{1}H-^{1}H-COSY. These spectroscopic data confirm the structure of **2** depicted in Scheme 1.

When the solution of the precipitates stands at room temperature, the $^{31}P\{^1H\}$- and ^{1}H-NMR spectra indicate a gradual increase of the starting complex **1**. In addition, the ^{1}H-NMR shows four signals assignable to 2-methyl-2-propen-1-ol. These results are interpreted together in the following manner: in the presence of an excess amount of 2-methyl-2-propen-1-ol, the allylic moiety inserts into the Ru–H bond to give **2**, whereas in the absence of 2-methyl-2-propen-1-ol, the allylic alcohol is gradually eliminated from the complex **2**.

As shown above, the insertion/β-elimination of 2-methyl-2-propen-1-ol on the ruthenium(II) center are reversible. In our previous study [11,12], alkyl allyl sulfides, primary and secondary allylamines irreversibly inserted into the Ru–H bond of **1**. Basicity of the heteroatom function explains the difference between 2-methyl-2-propen-1-ol and the other allylic compounds. The alcoholic hydroxy function of 2-methyl-2 propen-1-ol is a weak and hard base so that the hydroxy group is coordinated weakly to the ruthenium(II) center, a soft acid. That is, the 3-hydroxy-2-methylpropyl-C^1,O-ruthenium(II) five-membered chelate is rather unstable in comparison with 3-(alkylmercapto)-propyl-C^1,S- and 3-amino- or 3-(alkylamino)propyl-C^1,N-chelate structures. Because of the weak coordination of the hydroxy group, the ruthenium(II) center easily dissociates the hydroxy group to



Scheme 1. Products of reactions of 2-methyl-2-propen-1-ol with **1** under various conditions.

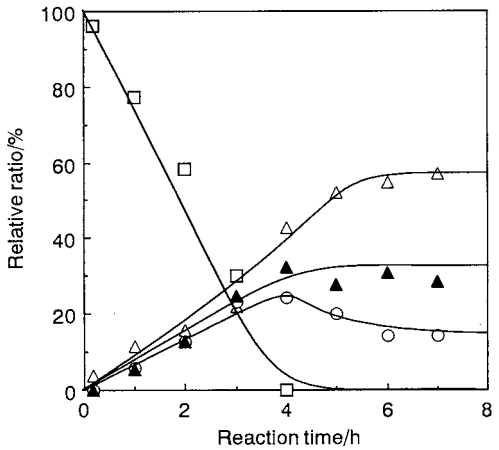


Fig. 1. Reaction time-conversion/yield curves of 2-methyl-2-propen-1-ol (□) and its derivatives: 2-methylpropanal (△), 2-methylpropan-1-ol (▲) and 2-methylpropenal (○).

produce a vacant site. The vacant site abstracts a β-hydrogen from the 3-hydroxy-2-methylpropyl ligand to bring about the β-elimination of 2-methyl-2-propen-1-ol.

2.2. Reaction of **1** with 2-methyl-2-propen-1-ol in the presence of water

When 2-methyl-2-propen-1-ol is employed as purchased (i.e. the presence of a small amount of water), **1** reacts with the allylic alcohol to give unexpected 2-methylpropanoatoruthenium(II) complexes, *P*,*P*′-*trans*-[RuCl{η^2-$(CH_3)_2CHCO_2$}(CO)$(PPh_3)_2$] (**3a**) and *P*,*P*′-*cis*-[RuCl{η^2-$(CH_3)_2CHCO_2$}(CO)$(PPh_3)_2$] (**3b**) in refluxing benzene (Scheme 1). Each complex is isolated by purification on a silica-gel column chromatography. The data of the elemental analyses, and the IR and NMR spectroscopic analyses of **3a** and **3b** are consistent with the *P*,*P*′-*trans*- and *cis*-structures, respectively, and are identical with those of the corresponding authentic samples derived from **1** and 2-methylpropanoic acid [13].

The production of the carboxylato complexes is caused by an aldehyde formed catalytically in the reaction mixture. The GLPC analysis of the reaction mixture reveals the catalytic conversion of the starting 2-methyl-2-propen-1-ol into 2-methylpropan-1-ol, 2-methylpropanal and 2-methyl-2-propenal. Typical time-conversion/yield curves of these compounds are shown in Fig. 1. Isomerization of 2-methyl-2-propen-1-ol into 2-methylpropanal catalyzed by **1** is known [14], whereas 2-methylpropan-1-ol and 2-methyl-2-propenal are considered as disproportionation products of 2-methyl-2-propen-1-ol via catalytic transfer hydrogenation. In the presence of water, **1** reacts with 2-methylpropanal under the benzene-reflux conditions to give the carboxylato complexes **3a** and **3b**. In a similar manner, **1** reacts with cyclohexanecarbaldehyde, benzaldehyde and 3-phenylpropanal to give the corresponding carboxylato complexes, *P*,*P*′-*trans*-[RuCl(η^2-RCO_2)(CO)$(PPh_3)_2$] (**4**–**6a**) and *P*,*P*′-*cis*-[RuCl(η^2-RCO_2)(CO)$(PPh_3)_2$] (**4**–**6b**) (**4a**,**b**: R = C_6H_{11}; **5a**,**b**: R = C_6H_5; **6a**,**b**: R = $C_6H_5C_2H_4$). These carboxylato complexes **4**–**6a**,**b** are identified by comparing their NMR spectra to those of the authentic samples derived from **1** and the carboxylic acids [13].

A considerable amount of 3-phenylpropan-1-ol is formed along with the carboxylato complexes **6a** and **6b** when the complex **1** reacts with 3-phenylpropanal starting with an initial ratio of 1:2.2, respectively. The GLPC analysis shows that a small amount of the starting aldehyde remains (1/5–1/6 of 3-phenylpropan-1-ol) and a trace amount of 3-phenylpropanoic acid is free in the reaction mixture. No other organic product is recognized. The formation of the alcohol and the carboxylato complexes from the aldehyde reminds us of the well known Cannizzaro reaction in the presence of aqueous base [15]. This ruthenium-promoted reaction is apparently not a mere Cannizzaro reaction because even the aldehydes with an α-hydrogen give their corresponding alcohols. This ruthenium-promoted Cannizzaro-type reaction is formulated as the following:

$$[RuClH(CO)(PPh_3)_3] + 3RCHO + H_2O \rightarrow P,P'\text{-}trans\text{- and }cis\text{-}[RuCl(\eta^2\text{-}RCO_2)(CO)(PPh_3)_2] + PPh_3 + 2RCH_2OH \quad (1)$$

There has previously been reported some other examples of ruthenium-promoted conversion of an aldehyde into a coordinating carboxylate. Cook et al. [16] reported that $[Ru_2(OH)_3(\eta^6\text{-}C_6Me_6)_2]PF_6$ and $[Ru_2Cl_4(\eta^6\text{-}p\text{-cymene})_2]$ catalyzed disproportionation of acetaldehyde into ethanol and acetic acid in the presence of water, and that the former complex was recovered as a carboxylato complex, $[Ru_2(OAc)_3(\eta^6\text{-}C_6Me_6)_2]PF_6$. Ito et al. [17] reported that $[RuH_2(PPh_3)_4]$ reacted with butanal in the presence of water at 0°C to afford a carboxylato complex, $[RuH(C_3H_7CO_2)(PPh_3)_3]$, which reacted with extra aldehyde molecules at over 75°C to give mono- and dicarbonyl dicarboxylato complexes, $[Ru(C_3H_7CO_2)_2(CO)(PPh_3)_2]$ and $[Ru(C_3H_7CO_2)_2(CO)_2(PPh_3)_2]$.

In the literature, Cook et al. [16] proposed two reaction paths for the catalytic disproportionation of aldehyde; oxidative addition of the RC(O)–H bond of the aldehyde and hydroxy-metallation on the C=O moiety of the aldehyde followed by β-hydrogen elimination. As for our reaction, both the starting **1** and the produced carboxylato complexes hold the carbonyl ligand, which generally stabilizes a low valent state but unstabilizes a high valent state such as ruthenium(IV). Accordingly, the hydroxy-ruthenation path is plausible

for our ruthenium-promoted Cannizzaro-type reaction of the aldehydes into the carboxylato complexes and the alcohols.

Taking this discussion into consideration, we propose a mechanism for the formation of the carboxylato complexes **3a**,**b** as shown in Scheme 2. Isomerization of 2-methyl-2-propen-1-ol into 2-methylpropanal via an olefin-inserted intermediate is a known process [2]. Insertion of the aldehyde into the Ru–H bond followed by proton-transfer from the coordinating water to the alkoxy ligand gives a hydroxyruthenium species and one molecule of the alcohol. The hydroxy-ruthenation of the second aldehyde occurs successively. The β-hydrogen elimination transfers the hydrogen to the third aldehyde and, finally, the hydroxy proton migrates onto the alkoxy ligand to produce the second alcohol molecule and the carboxylato ligand.

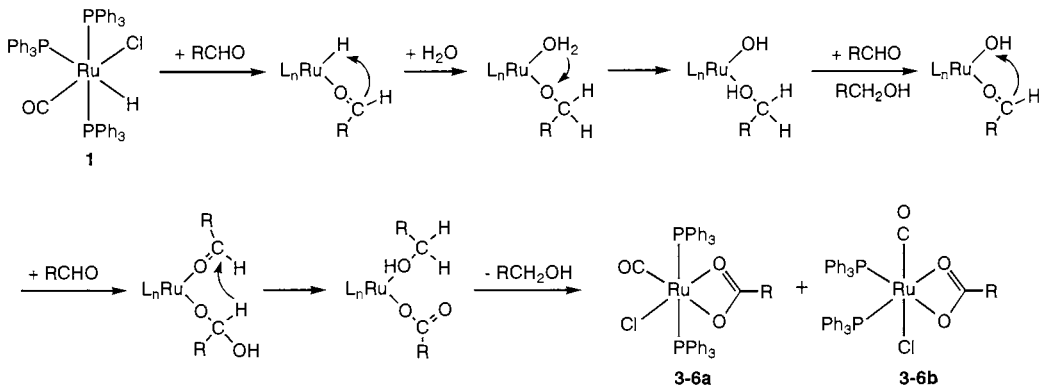
2.3. Reaction of *1* with 2-methyl-2-propen-1-ol at a high temperature

When the complex **1** is heated at 80°C for 48 h in dried 2-methyl-2-propen-1-ol, **1** is converted into an (η^4-enone)ruthenium(O) complex [Ru{η^4CH$_2$=C(CH$_3$)CH=O}(CO)(PPh$_3$)$_2$] (**7**) and a quaternary phosphonium salt [Ph$_3$PCH$_2$CH(CH$_3$)CH$_2$OH]Cl (**8**) almost quantitatively (Scheme 1). The ^{31}P{^{1}H}-NMR spectrum of the reaction mixture shows two doublets with a small coupling constant (J_{PP} = 2.0 Hz) at δ 31.0 and 40.7, which are ascribed to **7**, and another singlet of **8** at δ 21.2 in a intensity ratio of nearly 1:1:1. These products are isolated from the reaction mixture by silica-gel column chromatography. The η^4-enone complex **7** is eluted with hexane–diethyl ether (1:2) in 68% yield. The other product, the quaternary phosphonium salt **8** is eluted with chloroform–methanol (4:1) in 48% yield. Interestingly, the yields of **7** and **8** are significantly dependent on the solvent and on the ratio of the alcohol to **1**, as shown in Table 1. The conversion of **1** to **7** and **8** is almost quantitative in the neat alcohol, whereas the presence of benzene retards the reaction. Reaction rate decreases as the ratio of alcohol/**1** in benzene is reduced.

2.4. Molecular structure of the (η^4-enone)ruthenium(O) complex *7*

The NMR spectroscopic characteristics of **7**, i.e. the small J_{PP} value and the unusual high-field shift of vinyl protons, are common to some reported (η^4-enone)ruthenium(O) complexes [18,19]. A ^{13}C-doublet at δ 39.7 coupled with a phosphorus atom is attributed to the terminal methylene carbon showing an appropriate J value (J_{CP} = 31.3 Hz). This confirms the η^4-coordination of the 2-methylpropenal moiety. These spectroscopic data of **7** are consistent with the structure having an η^4-2-methylpropenal ligand, two phosphines and one carbonyl group around the ruthenium(O) center. To our knowledge, **7** is one of the rare examples of (η^4-enone)ruthenium(O) complexes having two phosphine and one CO ligands. Only Mawby and collaborators [19] has prepared a series of η^4-vinyl ketone complexes [Ru{η^4-RCH=CHC(C$_6$H$_4$X-4)=O}(CO)(PR$'_3$)$_2$] (R = Ph, C(CH$_3$)$_3$, CH$_3$ and H; X = H, Cl, CH$_3$ and OCH$_3$; PR$'_3$ = P(CH$_3$)$_2$Ph, P(CH$_3$)$_3$, P(OCH$_3$)$_2$Ph) by intramolecular combination of vinyl, aryl and carbonyl ligands in the ruthenium(II) complexes; but their X-ray structures have not been published. Therefore we tried the X-ray analysis on the (η^4-enone)ruthenium(O) complexes **7** having two phosphines and one carbonyl group.

The X-ray structure of **7** is depicted in Fig. 2. The selected bond distances and bond angles are summarized in Table 2. As expected, the structure of **7** is tripodal piano stool-like with the η^4-2-methylpropenal moiety; the bond lengths between the ruthenium atom and the atoms of the coordinating 2-methylpropenal fall within 2.165(5)–2.208(5) Å. The C(2)–C(3) length is 1.416(8) Å and shorter than a normal C–C single



Scheme 2. A plausible mechanism for the formation of the carboxylato complexes in the presence of water. **3a**,**b**: R = CH(CH$_3$)$_2$; **4a**,**b**: R = C$_6$H$_{11}$; **5a**,**b**: R = C$_6$H$_5$; **6a**,**b**: R = C$_6$H$_5$C$_2$H$_4$.

Table 1
Effect of the ratio of 2-methyl-2-propen-1-ol to **1**[a]

Run	**1** (mg)	Ratio of alcohol/**1**	Benzene (ml)	Time (h)	Yields (%)[b]		
					7	**8**	Free PPh_3
1[c]	600	190	–	48	99	83	Trace
2	300	200	5	24	41	44	Trace
3	100	100	10	48	16	12	Trace
4	100	25	10	48	12	Trace	26
5	100	5	10	48	5	Trace	38

[a] Reactions are carried out under benzene-refluxing conditions unless otherwise stated.
[b] Yields are calculated based on the integrated intensities of the ^{31}P-NMR peaks.
[c] Reaction is carried out at 80°C (see Section 3).

bond length, whereas the C(3)=C(4) length is 1.420(9) Å and longer than that of a normal C=C bond [20]. Especially, the C(2)–C(3) and C(3)=C(4) distances are almost the same within an error. Therefore the 2-methylpropenal moiety apparently bears delocalized π-electrons being coordinated in η^4-mode. These structural characteristics are quite similar to another (η^4-enone)ruthenium(O) complex, $[Ru(CH_3COCH{=}CHPh)(CO)_2(PPh_3)]$ that has one phosphine and two CO ligands [18].

2.5. Characterization of the phosphonium chloride **8**

The analytical and NMR spectroscopic data of **8** are consistent with the structure that is confirmed by single crystal X-ray analysis (Fig. 3). The selected bond distances and bond angles are summarized in Table 3. The quaternary phosphorus is attached to the terminal carbon of the 2-methyl-2-propen-1-ol, whereas the hydrogen is bound to the inner carbon making an asymmetric center. Four P–C bond distances are almost similar to one another (1.798 Å average) and fall within the range of those of $[Et_3PCMe_2OH]Br$ and a zwitterionic phosphonium salt $(MeO)CH(Ph)P^+Ph_2(C_6H_4SO_3^-)$ reported so far [21]. The Cl(1)···O(1) distance is 3.076(4) Å and it is reasonable to expect a hydrogen bond between the chloride anion and the alcoholic OH group in the solid state. In contrast, there is no close contact between the positively charged phosphorus atom and the negative centers such as Cl and O; all the distances between the phosphorus and those negative atoms are longer than 3.60 Å, showing negligible electrostatic attraction between them.

2.6. Mechanism of the formation of **7** and **8**

The ruthenium complex is essential to the formation of **8**. Actually, reaction between PPh_3 and an excess amount of aqueous HCl in refluxing 2-methyl-2-propen-1-ol without **1** affords no quaternary phosphonium salt. Hence a direct reaction of PPh_3 and 2-methyl-2-propen-1-ol with the aid of an acid can be denied [21].

Thc detailed $^{31}P\{^1H\}$-NMR analysis reveals that the insertion of 2-methyl-2-propen-1-ol occurs before the formation of **7** and **8** (Fig. 4). When the reaction mixture is kept at room temperature for 72 h, the insertion product **2** is produced in the mixture along with the starting **1** in a ratio of 3:10, respectively. After heating at 50°C for an additional 48 h, the ratio of 1:2 changes slightly to 4:10 and three ^{31}P-signals are observed at δ 21.2 (**8**), and 31.0 and 40.7 (**7**). Furthermore, the extra treatment of the mixture at 65°C for 70 h makes the products **7** and **8** dominant, whereas **1** and **2** disappear completely.

Based on these results, a reasonable route to generate a ruthenium(O) species is reductive elimination of 3-chloro-2-methylpropan-1-ol after the insertion of 2-methyl-2-propen-1-ol [22]. As shown in Scheme 3, the starting 2-methyl-2-propen-1-ol is catalytically converted into 2-methylpropenal during the reaction. Once the unsaturated ruthenium(O) species is generated, it has to be trapped by 2-methylpropenal to form **7**. Reaction of a dihydridoruthenium(II) complex $[RuH_2(CO)(PPh_3)_3]$ with 2-methylpropenal in refluxing toluene results in the formation of **7** [23]. The result confirms that the η^4-enone complex **7** arises when the ruthenium(O) species generated in situ [24] comes in contact with 2-methylpropenal. As to the released alkyl chloride, 3-chloro-2-methylpropan-1-ol reacts with the free PPh_3 to give **8**.

Castano et al. [25] reported that the closely related phosphonium salt $[Ph_3PCH{=}CHCO_2CH_3]Cl$ was formed in the reaction of **1** with methyl propiolate. They supposed that the direct reaction between the terminal alkyne and triphenylphosphine gave an alkenylphosphonium acetylide and that the substitution of the acetylide anion for the chloride ligand of an unidentified insertion product $[Ru(CH{=}CHCO_2CH_3)Cl(CO)(PPh_3)_2]$ followed to give the isolable product $[Ru(CH{=}CHCO_2CH_3)(C{\equiv}CCO_2CH_3)Cl(CO)(PPh_3)_2]$.

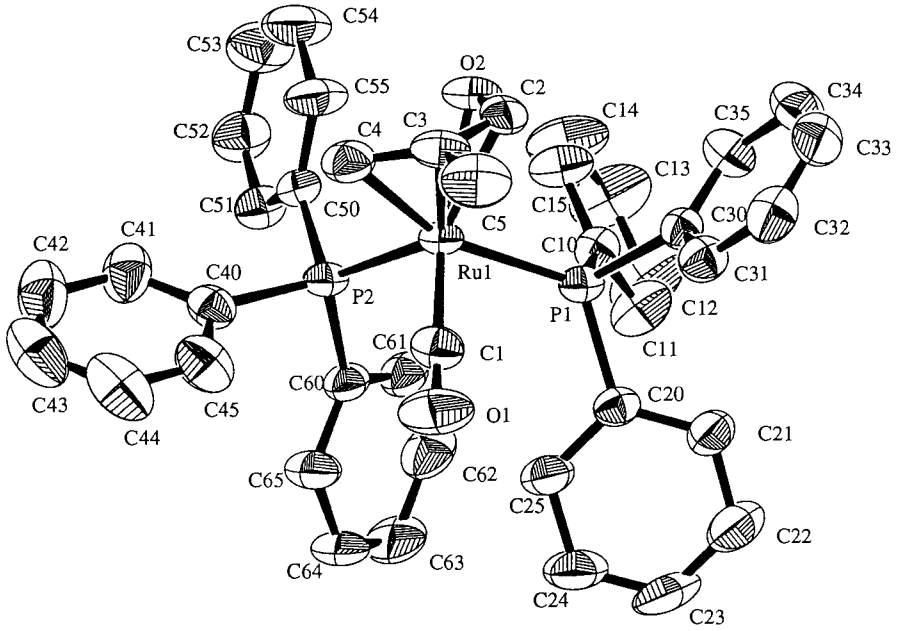


Fig. 2. Molecular structure of **7** showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

From our viewpoint, however, this formation of the alkenylphosphonium salt can be attributed to the result of the reductive elimination of methyl β-chloroacrylate. The reductive elimination is accompanied by the formation of the unsaturated ruthenium(*O*) species. When the ruthenium(*O*) species is formed, oxidative addition of the terminal C–H bond of the alkyne readily occurs on the ruthenium(*O*) center to give an alkynyl(hydrido)ruthenium(II) species. Successive insertion of the alkyne into the Ru–H bond forms the final product $[Ru(CH{=}CHCO_2CH_3)(C{\equiv}CCO_2CH_3)Cl(CO)(PPh_3)_2]$. Therefore, the formation of the ruthenium(*O*) species in the presence of the alkyne can be overlooked.

Our plausible mechanism explains well the regioselective formation of **8**. The structure of **8** in which the terminal carbon is attached to the phosphorus must be derived from 3-chloro-2-methylpropan-1-ol, an anti-Markownikov adduct of HCl and 2-methyl 2-propen-1-ol. The simple reductive elimination from the insertion product **2** affords the anti-Markownikov adduct in a single step. If HCl is added directly to 2-methyl-2-propen-1-ol, the addition should obey Markownikov rule to give 2-chloro-2-methylpropan-1-ol. It could only afford $[Ph_3PC(CH_3)_2CH_2OH]Cl$, an isomer of **8**.

This mechanism also explains the decrease in the yield of **7** as reducing the ratio of alcohol/**1** in benzene shown in the runs in Table 1. Scheme 3 implies that the catalytic isomerization and/or transfer hydrogenation and the formation of the ruthenium(*O*) species consume the 2-methyl-2-propen-1-ol competitively. When the ratio of alcohol/**1** is small, most of the alcohol must be consumed by the catalytic isomerization and/or transfer hydrogenation before the ruthenium(*O*) species is generated, because the reductive elimination proceeds rather slower than the catalytic reactions. When the reaction is carried out in the neat alcohol, the amount of alcohol is large enough for all the starting **1** to be converted into the ruthenium(*O*) species **7** (and also its accompanying product **8**) via the slow reductive elimination.

In this mechanism, the alkylchlororuthenium(II) species **2** releases the alkyl chloride in the presence of tertiary phosphine to afford ruthenium(*O*) species and alkylphosphonium chloride. From the viewpoint of the catalytic process, most of previous studies on the chlorohydridoruthenium(II) complex **1** have mentioned β-elimination from the insertion products [26], but

Table 2
Selected bond distances (Å), bond angles (°), and torsion angles (°) for **7**

Bond distances			
Ru(1)–P(1)	2.364(1)	Ru(1)–P(2)	2.360(1)
Ru(1)–C(1)	1.830(5)	Ru(1)–C(2)	2.165(5)
Ru(1)–C(3)	2.208(5)	Ru(1)–C(4)	2.192(6)
Ru(1)–O(2)	2.169(4)	O(1)–C(1)	1.152(6)
O(2)–C(2)	1.321(7)	C(2)–C(3)	1.416(8)
C(3)–C(4)	1.420(9)	C(3)–C(5)	1.508(8)
Bond angles			
P(1)–Ru(1)–P(2)	103.99(5)	P(1)–Ru(1)–C(1)	91.0(2)
P(2)–Ru(1)–C(1)	96.7(2)	Ru(1)–C(1)–O(1)	175.4(5)
O(2)–C(2)–C(3)	118.2(5)	C(2)–C(3)–C(4)	115.3(5)
C(2)–C(3)–C(5)	118.9(6)	C(4)–C(3)–C(5)	125.3(6)
Torsion angles			
O(2)–C(2)–C(3)–C(4)	3.2(7)	O(2)–C(2)–C(3)–C(5)	175.6(5)

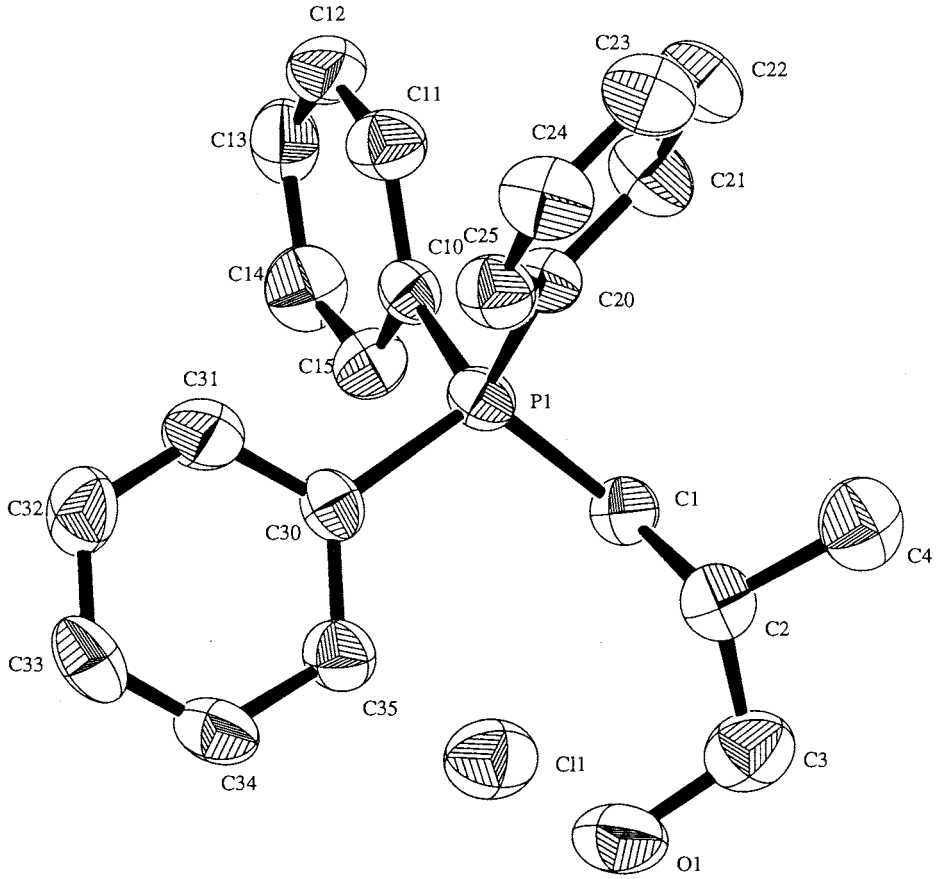


Fig. 3. Molecular structure of **8** showing the atom numbering scheme. Hydrogen atoms arc omitted for clarity.

rarely reductive elimination. Our case is the first example that confirms the reductive elimination of the alkyl chloride forming the ruthenium(*O*) species.

3. Experimental details

All the reactions were carried out by means of the ordinary Schlenk-tube techniques under a nitrogen atmosphere. However, special precautions were taken to exclude air and moisture during the column-chromatography process and the spectroscopic measurements, since most of the complexes were air-stable as solids and stable for a short period in solution.

IR spectra were recorded on a JASCO A-100 spectrophotometer with KBr disks. GLPC analyses were carried out on a Hitachi model 263-30 equipped with a flame ionization detector and a 5 mm$\varnothing \times 3$ m stainless-steel column (SE-30 or PEG 20M). Elemental analyses and NMR (400 MHz for ^{1}H, 101 MHz for ^{13}C and 162 MHz for ^{31}P) measurements were carried out at the Center for Instrumental Analysis, Nagasaki University, with a Yanaco MT-3 CHN Corder and a JEOL GX-400 spectrometer, respectively. Single crystal X-ray structure analyses were performed at the same institute.

Complex **1** was prepared according to the literature [27]. Dried 2-methyl-2-propen-1-ol was distilled slowly after careful treatment with a small amount of sodium. All the aldehydes and the carboxylic acids were used as purchased. Solvents were dried with usual methods and distilled prior to use.

Table 3
Selected bond distances (Å) and angles (°) for **8**

Bond distances			
P(1)–C(1)	1.798(5)	P(1)–C(10)	1.789(5)
P(1)–C(20)	1.789(5)	P(1)–C(30)	1.799(4)
C(1)–C(2)	1.545(7)	C(2)–C(3)	1.518(8)
C(2)–C(4)	1.515(8)	C(3)–O(1)	1.426(7)
Bond angles			
C(1)–P(1)–C(10)	108.1(2)	C(1)–P(1)–C(20)	111.6(2)
C(1)–P(1)–C(30)	111.9(2)	C(10)–P(1)–C(20)	109.7(2)
C(10)–P(1)–C(30)	106.4(2)	C(20)–P(1)–C(30)	109.0(2)
P(1)–C(1)–C(2)	118.7(3)	C(1)–C(2)–C(3)	110.1(4)
C(1)–C(2)–C(4)	110.5(5)	C(3)–C(2)–C(4)	110.4(5)
C(2)–C(3)–O(1)	113.9(5)		

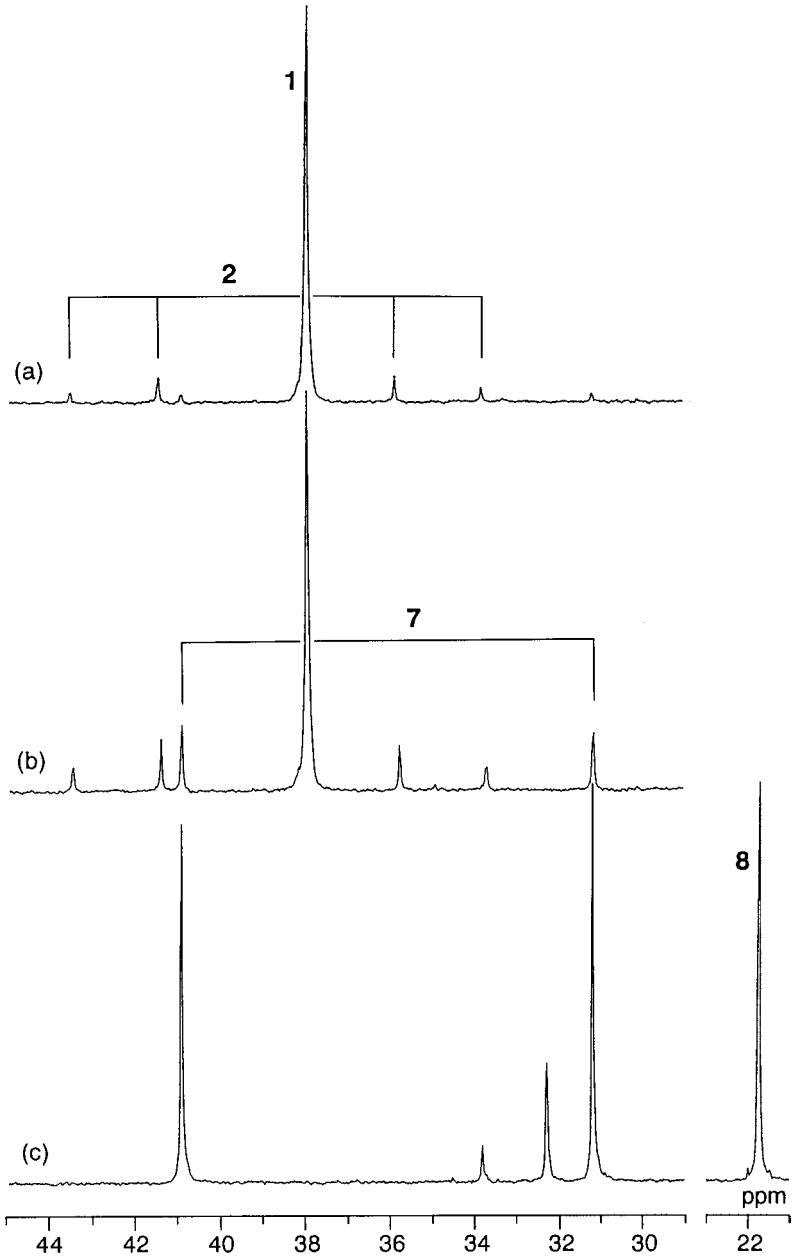


Fig. 4. Time-programmed $^{31}P\{^{1}H\}$-NMR spectra of the reaction of **1** with neat 2-methyl-2-propen-1-ol: (a) after 72 h at room temperature; (b) after the treatment at 50°C for an additional 48 h (total 120 h); (c) after an extra 70 h at 65°C (total 190 h).

*3.1. Reaction of **1** with 2-methyl-2-propen-1-ol at room temperature*

A benzene solution (20 ml) containing **1** (190 mg, 0.20 mmol) and 2-methyl-2-propen-1-ol (288 mg, 4.0 mmol) was stirred at room temperature for 120 h. The reaction mixture was concentrated under a reduced pressure. Addition of hexane to the mixture solidified the complex. The resulting yellow precipitates were washed with hexane and dried under a reduced pressure to give yellow solids of $[Ru\{CH_2CH(CH_3)CH_2OH\}Cl(CO)(PPh_3)_2]$ (**2**) (112 mg, 74%). Anal. Found: C, 65.24; H, 5.32. Calc. for $C_{41}H_{39}ClO_2P_2Ru$: C, 64.61; H, 5.16%. M.p. 166°C (dec.). IR (cm^{-1}): ν(OH) 3520br, ν(C≡O) 1890vs, ν(C–OH) 1090s. ^{1}H-NMR ($CDCl_3$, −30°C): δ 0.35 (d, $J = 5.1$ Hz, 3H, CH_3), 1.41 (br, 1H, CH), 1.52 (br, 1H, $RuCH^aH^b$), 1.62 (br, 1H, $RuCH^aH^b$), 1.82 (br, 1H, CH^cH^dO), 3.16 (br, 1H, CH^cH^dO), 7.05–7.34 (m, 30H, Ph). $^{31}P\{1H\}$-NMR ($CDCl_3$, −30°C): δ 34.8 (d, $J = 332.1$ Hz), 42.6 (d, $J = 332.1$ Hz).

3.2. Reaction of **1** with 2-methyl-2-propen-1-ol in the presence of water

A benzene solution (20 ml) involving **1** (477 mg, 0.50 mmol) and 2-methyl-2propen-1-ol (360 mg, 5.0 mmol) as purchased was refluxed for 48 h. The reaction mixture was concentrated under a reduced pressure and diluted with hexane to afford yellow precipitates, a mixture of the isomers of [RuCl{η^2-$(CH_3)_2CHCO_2$}(CO)$(PPh_3)_2$] (**3**) (320 mg, 67%). The precipitates were applied to silica-gel column chromatography. The first fraction was eluted with benzene to give the *P,P′-trans* isomer **3a**. Anal. Found: C, 63.39; H, 4.94. Calc. for $C_{41}H_{37}ClO_3P_2Ru$: C, 63.44; H, 4.80%. M.p. 252–255°C (dec.). IR (cm^{-1}): ν(C≡O) 1948vs. ^{1}H-NMR ($CDCl_3$): δ 0.07 (d, $J = 6.6$ Hz, 6H, CH_3), 1.05 (sep. $J = 6.6$ Hz, 1H, C*H*), 7.38 (t, $J = 7.3$ Hz, 12H, *m*-Ph), 7.42 (t, $J = 7.3$ Hz, 6H, *p*-Ph), 7.52 (q, $J = 7.3$ Hz, 12H, *o*-Ph). ^{13}C{^{1}H}-NMR ($CDC1_3$): δ 17.0 (s, CH_3), 35.4 (s, CH), 128.1 (br, *m*-Ph), 130.1 (s, *p*-Ph), 130.7 (t, $J = 25.3$ Hz, *ipso*-Ph), 134.8 (s, *o*-Ph), 191.8 (s, CO_2), 205.4 (t, $J = 14.6$ Hz, C≡O). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 33.9 (s).

The second fraction was eluted with chloroform to afford the *P,P′-cis*- form **3b**. Anal. Found: C, 57.81; H, 4.37. Calc. for $C_{41}H_{37}ClO_3P_2Ru{\cdot}CHCl_3$: C, 56.33; H, 4.27. Calc. for $C_{41}H_{37}ClO_3P_2Ru{\cdot}0.8CHCl_3$: C, 57.59; H, 4.37%. M.p. 248–251°C (dec.). IR (cm^{-1}): ν(C≡O) 1950vs. ^{1}H-NMR ($CDCl_3$): δ 0.63 (d, $J = 7.3$ Hz, 3H, CH_3), 0.75 (d, $J = 7.3$ Hz, 3H, CH_3), 1.79 (sep. $J = 7.3$ Hz, 1H, C*H*), 7.00 (t, $J = 7.7$ Hz, 6H, *p*-Ph), 7.12 (td, $J = 7.7$ and 2.2 Hz, 6H, *m*-Ph), 7.22 (td, $J = 7.7$ and 2.2 Hz, 6H, *m*-Ph), 7.33 (t, $J = 7.7$ Hz, 6H, *o*-Ph), 7.40 (t, $J = 7.7$ Hz, 6H, *o*-Ph). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 0.1 (s, CH_3), 1.1 (s, CH_3), 18.9 (s, C*H*), 128.0–134.9 (m, Ph), 191.8 (s, CO_2), 205.5 (t, $J = 12.7$ Hz, C≡O). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 45.3 (d, $J = 24.4$ Hz), 46.4 (d, $J = 24.4$ Hz).

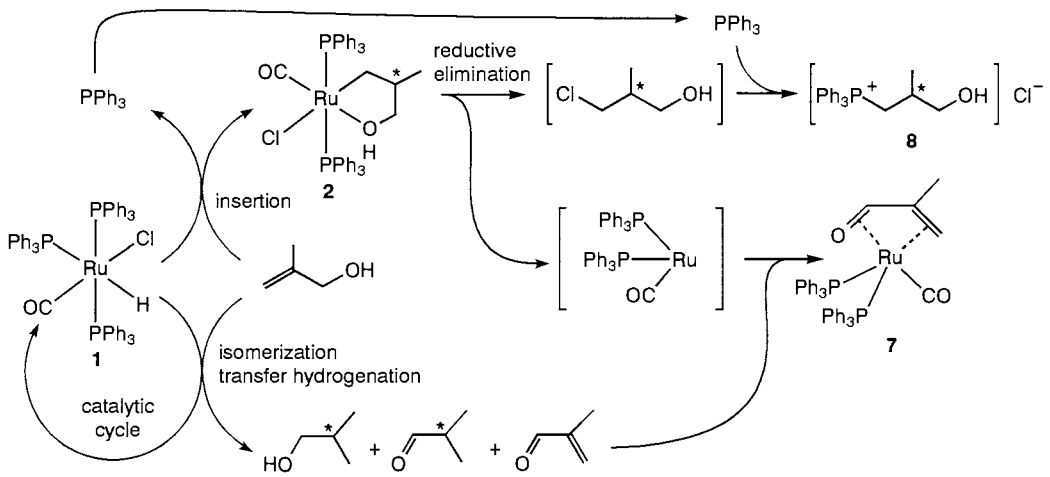
3.3. Reaction of **1** with aldehydes in the presence of water

A benzene solution (20 ml) involving **1** (190 mg, 0.20 mmol) and 2-methylpropanal (as purchased, 144 mg, 2.0 mmol) was refluxed for 48 h. The reaction mixture was treated with a similar work-up as the case of 2-methyl-2-propen-1-ol to precipitate a yellow powdery mixture of **3a** and **3b** in a ratio of 6:1 (140 mg, 92%).

A mixture of **1** (160 mg, 0.17 mmol) and cyclohexanecarbaldehyde (as purchased, 44 mg, 0.40 mmol) in benzene (6 ml) was sealed in a glass reaction tube and heated at 80°C. After heating for 48 h, the reaction mixture was concentrated under a reduced pressure and applied to NMR analysis. The ^{31}P{^{1}H}-NMR spectra of the reaction mixture revealed the formation of the isomers of the carboxylato complex, [RuCl(η^2-$C_6H_{11}CO_2$)(CO)$(PPh_3)_2$] (**4**) (38% yield based on ^{31}P-NMR). ^{31}P{^{1}H}-NMR ($CDCl_3$) for **4a** (*trans*-form): δ 33.9 (s), 4b (*cis*-form): δ 45.4 (d, $J = 24.4$ Hz), 46.1 (d, $J = 24.4$ Hz). The GLPC analysis of the reaction mixture revealed the formation of cyclohexylmethanol.

In a similar manner, a mixture of **1** (94 mg, 0.10 mmol) and benzaldehyde (as purchased, 24 mg, 0.22 mmol) in benzene (6.5 ml) was allowed to react in a sealed tube. The NMR analysis showed that [RuCl(η^2-$C_6H_5CO_2$)(CO)$(PPh_3)_2$] (**5**) was produced (12% yield based on ^{31}P-NMR). ^{31}P{^{1}H}-NMR ($CDCl_3$) for **5a** (*trans*-form): δ 34.3 (s), **5b** (*cis*-form): δ 45.0 (d, $J_{PP} =$ 24.4 Hz), 46.9 (d, $J = 24.4$ Hz).

Furthermore, **1** (160 mg, 0.17 mmol) reacted similarly with 3-phenylpropanal (as purchased, 50 mg, 0.37 mmol) in benzene (6 ml) to give [RuCl(η^2-$C_6H_5CH_2CH_2CO_2$)(CO)$(PPh_3)_2$] (**6**) (42% yield based on ^{31}P-NMR). ^{31}P{^{1}H}-NMR ($CDCl_3$) for **6a** (*trans*-form): δ 34.8 (s), **6b** (*cis*-form): δ 45.4 (d, $J = 24.4$ Hz), 46.2 (d, $J = 24.4$ Hz).



Scheme 3. A plausible mechanism for the formation of **7** and **8**.

3.4. Reaction of **1** with 2-methyl-2-propen-1-ol at high temperature

A mixture of **1** (602 mg, 0.63 mmol) and dried 2-methyl-2-propen-1-ol (10 ml) was heated at 80°C for 48 h. The reaction mixture was concentrated under a reduced pressure and applied to silica-gel column chromatography. The first fraction was eluted with hexane–diethyl ether (1:2) to afford pale yellow solids of $[Ru\{CH_2{=}C(CH_3)CH{=}O\}(CO)(PPh_3)_2]$ (**7**) (312 mg, 68%). Anal. Found: C, 67.66; H, 5.13. Calc. for $C_{41}H_{36}O_2P_2Ru$: C, 68.04; H, 5.01%. M.p. 191–193°C (dec.). IR (cm^{-1}): ν(C≡O) 1915vs. ^{1}H-NMR ($CDCl_3$): δ 1.18 (m, 1H, CH^aH^b), 1.50 (m, 1H, CH^aH^b), 1.99 (d, $J = 2.9$ Hz, 3H, CH_3), 5.81 (d, $J = 4.4$ Hz, 1H, CH). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 17.4 (s, CH_3), 39.7 (d, $J = 31.3$ Hz, CH_2), 99.6 (s, CCH_3), 123.8 (s, CHO), 207.6 (t, $J = 11.7$ Hz, C≡O). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 31.0 (d, $J = 2.1$ Hz), 40.7 (d, $J = 2.1$ Hz).

The second fraction was eluted with chloroform–methanol (4:1) to give $[Ph_3PCH_2CH(CH_3)CH_2OH]Cl$ (**8**) (112 mg, 48%). Anal. Found: C, 70.53; H, 6.46. Calc. for $C_{22}H_{24}ClOP$: C, 71.25; H, 6.52%. M.p. 233–235°C. IR (cm^{-1}): ν(OH) 3275br, ν(P–C) 1462vs, $\nu(C_6H_5)$ 1440s, ν(C–OH) 1113s. ^{1}H-NMR ($CDCl_3$): δ 0.52 (d, $J = 6.6$ Hz, 3H, CH_3), 2.17 (m, 1H, CH), 2.66 (ddd, $J = 16.0$, 9.5 and 12.0 Hz, 1H, PCH^aH^b), 3.66 (dt, $J = 11.4$ and 4.6 Hz, 1H, CH^cH^dO), 3.59 (dd, $J = 11.4$ and 9.0Hz, 1H, CH^cH^dO),4.94(t, $J = 16.0$ Hz, 1H, PCH^aH^b). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 17.6 (s, CH_3), 26.1 (d, $J = 50.9$ Hz, PCH_2), 32.0 (s, CH), 66.8 (d, $J = 11.8$ Hz, CH_2O), 119.3 (d, $J = 86.1$ Hz, *ipso*-Ph), 130.5 (d, $J = 11.8$ Hz, *m*-Ph), 133.7 (d, $J = 11.8$ Hz, *o*-Ph), 135.0 (s, *p*-Ph). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 21.2 (s).

3.4.1. The NMR analysis of the time-programmed experiment

A mixture of **1** (308 mg) and dried 2-methyl-2-propen-1-ol (10 ml) was allowed to react in a Schlenk tube sealed with a rubber septum. After being kept at room temperature for 72 h, a small part of the reaction mixture was sampled through the septum with a syringe. Before the sample was applied to the NMR measurement, it was concentrated under a reduced pressure and successively diluted with $CDCl_3$. The rest of the reaction mixture was allowed to react for additional 48 h at 50°C before the second sampling. The last sample was taken after extra 70 h at 65°C.

3.5. Single crystal X-ray structure analysis

Crystal data and details of the measurement for **7** and **8** are summarized in Table 4. The final atomic coordinates with the equivalent isotropic thermal parameters for **7** and **8** are reported in Tables 5 and 6, respectively. Tables of hydrogen atom coordinates, anisotropic displacement parameters and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. The intensity data were collected at 20°C on a Rigaku AFC7S automatic four-circle diffractometer with graphite-monochromated Mo–K_α radiation. Cell constants were obtained from the least-squares refinement of the setting angles of the carefully centered reflections (16 reflections in the range $35.87° \leq 2\theta \leq 39.42°$ for **7**, and 25 in the range $22.69° \leq 2\theta \leq 36.04°$ for **8**). Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects. During the data collection, the intensities of three representative reflections were measured after every 150 reflections; no variation was observed.

Table 4
Crystal data for **7** and **8**

	7	**8**
Formula	$C_{41}H_{36}O_2P_2Ru$	$C_{22}H_{24}ClOP$
Formula weight (M)	723.75	370.86
Color and habit	Pale yellow prism	Colorless prism
Crystal size (mm)	$0.40 \times 0.20 \times 0.50$	$0.40 \times 0.20 \times 0.50$
Crystal system	Monoclinic	Monoclinic
Space group	Cc (No.9)	$P2_1/c$ (No.14)
a (Å)	19.080(2)	11.564(3)
b (Å)	10.396(2)	10.032(7)
c (Å)	18.994(2)	17.586(2)
β (°)	10.442(8)	106.61(1)
V (Å^3)	3530.3(8)	1954(1)
Z	4	4
D_{calc} (g cm^{-3})	1.362	1.260
F(000)	1488.00	784.00
μ(Mo–K_α) (cm^{-1})	5.69	2.84
R, R_w	0.31, 0.028	0.050, 0.036
Goodness-of-Fit	1.59	1.59

As for **7**, of the 4406 reflections which were collected, 4277 were unique. The structure was solved by heavy-atom Patterson methods [28] and expanded using Fourier techniques [29]. The non-hydrogen atoms were refined anisotropically; the hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 3572 observed reflections $\{I > 3\sigma(I)\}$ and 423 variable parameters; the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(F_o) + [(0.010/2)F_o]^2$.

As for **8**, of the 4966 reflections which were collected, 4740 were unique. The structure was solved by direct methods [30] and expanded using Fourier techniques [29]. Thc non-hydrogen atoms were refined anisotropically; the hydrogen atom coordinates were refined but their isotropic thermal parameters were held fixed. The final cycle of full-matrix least-squares refinement was based on 1730 observed reflections $\{I > 3\sigma(I)\}$ and 299

variable parameters; the function minimized was $\Sigma w(|F_o|-|F_c|)^2$, where $w^{-1}=\sigma^2(F_o)+[(0.010/2)F_o]^2$.

Neutral atom scattering factors, corrected for anomalous dispersion, were taken from a literature [31]. All calculations were performed on a Rigaku RASA-7 automatic structure analysis system using the teXsan crystallographic software package [32].

Table 5
Atomic coordinates and equivalent isotropic thermal parameters (Å^2) for **7**

Atom	x	y	z	B_{eq}
Ru(1)	0.0025	0.10481(3)	−0.0010	2.797(7)
P(1)	0.02717(7)	0.2167(1)	0.11340(7)	2.87(3)
P(2)	−0.10441(8)	0.2082(1)	−0.08456(8)	3.02(3)
O(1)	0.1183(3)	0.2555(4)	0.0373(3)	6.6(1)
O(2)	−0.0386(2)	0.0607(4)	0.0422(2)	4.0(1)
C(1)	0.0718(3)	0.2018(5)	−0.0238(3)	4.0(1)
C(2)	0.0334(4)	−0.0785(5)	0.0553(3)	3.7(1)
C(3)	0.0583(3)	−0.0790(5)	−0.0067(4)	3.9(1)
C(4)	0.024(4)	−0.0531(6)	−0.0775(4)	4.3(2)
C(5)	0.1409(3)	−0.0895(6)	0.0077(4)	5.7(2)
C(10)	−0.0523(3)	0.2453(5)	0.1437(3)	3.4(1)
C(11)	−0.0600(3)	0.3596(6)	0.1790(3)	4.9(2)
C(12)	−0.1236(4)	0.3785(7)	0.1976(4)	6.6(2)
C(13)	−0.1786(4)	0.2862(7)	0.1813(5)	7.0(2)
C(14)	−0.1708(4)	0.1755(6)	0.1467(5)	6.6(2)
C(15)	−0.1078(3)	0.1544(5)	0.1280(4)	4.6(1)
C(20)	0.0731(3)	0.3744(4)	0.1279(3)	3.1(1)
C(21)	0.1187(3)	0.4158(5)	0.1983(3)	4.4(1)
C(22)	0.1462(3)	0.5415(6)	0.2089(4)	5.7(2)
C(23)	0.1305(3)	0.6216(6)	0.1485(5)	5.9(2)
C(24)	0.0877(5)	0.5832(7)	0.0800(5)	5.6(2)
C(25)	0.0570(3)	0.4585(5)	0.0670(4)	4.4(1)
C(30)	0.0914(3)	0.1231(4)	0.1910(3)	3.0(1)
C(31)	0.1655(3)	0.1110(5)	0.1937(3)	3.8(1)
C(32)	0.2156(3)	0.0320(6)	0.2467(3)	4.6(1)
C(33)	0.1921(4)	−0.0385(6)	0.2947(4)	5.5(2)
C(34)	0.1197(4)	−0.0297(6)	0.2927(3)	5.3(2)
C(35)	0.0692(3)	0.0525(5)	0.2404(3)	4.2(1)
C(40)	−0.1117(3)	0.2015(5)	−0.1834(3)	3.6(1)
C(41)	−0.1774(4)	0.1720(6)	−0.2419(3)	5.0(2)
C(42)	−0.1806(4)	0.1688(7)	−0.3143(4)	6.3(2)
C(43)	−0.1192(5)	0.1966(7)	−0.3331(4)	6.6(2)
C(44)	−0.0545(4)	0.2266(8)	−0.2773(5)	6.9(2)
C(45)	−0.0502(3)	0.2274(7)	−0.2043(4)	5.4(2)
C(50)	−0.1936(3)	0.1407(4)	−0.0859(3)	3.3(1)
C(51)	−0.2594(3)	0.2113(5)	−0.1082(3)	3.8(1)
C(52)	−0.3258(3)	0.1564(6)	−0.1081(4)	4.9(2)
C(53)	−0.3268(4)	0.0324(7)	−0.0861(4)	6.0(2)
C(54)	−0.2619(4)	−0.0413(6)	−0.0652(4)	6.4(2)
C(55)	−0.1961(3)	0.0143(5)	−0.0651(4)	5.0(1)
C(60)	−0.1159(3)	0.3811(4)	−0.0706(3)	3.4(1)
C(61)	−0.1424(3)	0.4206(5)	−0.0151(3)	4.1(1)
C(62)	−0.1440(4)	0.5500(6)	0.0020(4)	5.3(2)
C(63)	−0.1188(4)	0.6415(5)	−0.0368(4)	6.2(2)
C(64)	−0.0921(5)	0.6037(6)	−0.0904(5)	5.9(2)
C(65)	−0.0912(4)	0.4739(5)	−0.1095(4)	4.6(1)

Table 6
Atomic coordinates and equivalent isotropic thermal parameters (Å^2) for **8**

Atom	x	y	z	B_{eq}
Cl(1)	0.8838(2)	0.1457(2)	0.8363(1)	5.16(4)
P(1)	0.2706(1)	0.1836(1)	0.03744(8)	2.96(3)
O(1)	0.2688(3)	−0.2395(3)	0.0565(2)	5.1(1)
C(1)	0.1824(4)	0.0366(5)	0.0026(3)	3.1(1)
C(2)	0.2296(5)	−0.0656(5)	−0.0471(3)	3.5(1)
C(3)	0.2060(5)	−0.2064(6)	−0.0236(4)	4.9(2)
C(4)	0.1705(6)	−0.0437(7)	−0.1349(4)	5.2(2)
C(10)	0.1849(4)	0.2904(5)	0.0823(3)	2.8(1)
C(11)	0.1700(5)	0.4244(6)	0.0659(3)	4.0(2)
C(12)	0.1053(5)	0.5022(6)	0.1047(4)	4.6(2)
C(13)	0.0591(5)	0.4478(6)	0.1610(4)	4.5(2)
C(14)	0.0733(5)	0.3145(6)	0.1789(3)	4.5(2)
C(15)	0.1356(5)	0.2355(5)	0.1385(3)	3.9(1)
C(20)	0.3070(4)	0.2699(5)	−0.0417(3)	3.0(1)
C(21)	0.2151(4)	0.3239(6)	−0.1034(3)	4.3(1)
C(22)	0.2408(5)	0.3940(6)	−0.1634(3)	4.6(2)
C(23)	0.3580(6)	0.4071(6)	−0.1644(3)	4.8(2)
C(24)	0.4501(5)	0.3537(6)	−0.1047(4)	4.8(2)
C(25)	0.4254(4)	0.2850(5)	−0.0436(3)	4.0(1)
C(30)	0.4079(4)	0.1455(5)	0.1134(3)	3.0(1)
C(31)	0.4753(5)	0.2501(6)	0.1548(4)	4.6(2)
C(32)	0.5795(5)	0.2207(6)	0.2151(4)	4.8(2)
C(33)	0.6162(5)	0.0985(7)	0.2344(3)	4.3(2)
C(34)	0.5516(5)	−0.0057(6)	0.1940(3)	4.1(2)
C(35)	0.4458(4)	0.0160(6)	0.1330(3)	3.7(1)

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References

[1] K. Yamamoto, T. Hayashi, M. Kumada, J. Organomet. Chem. 54 (1973) 54.
[2] Y. Sasson, G.L. Rempel, Tetrahedron Lett. (1974) 4133.
[3] (a) M. Dedien, Y.-L. Pascal, J. Mol. Catal. 9 (1980) 71. (b) Y. Watanabe, T. Tsuji, Y. Ohsugi, Tetrahedron Lett. (1981) 2667.
[4] B.M. Trost, R.J. Kulawiec, J. Am. Chem. Soc. 115 (1993) 2027.
[5] P. Golborn, F. Scheinmann, J. Chem. Soc., Perkin Trans. I (1973) 2870.
[6] R.G. Salomon, J.M. Reuter, J. Am. Chem. Soc. 99 (1977) 4372.
[7] (a) H. Suzuki, Y. Koyama, Y. Moro-oka, T. Ikawa, Tetrahedron Lett. (1979) 1415. (b) H. Suzuki, H. Yashima, T. Hirose, M. Takahashi, Y. Moro-oka, T. Ikawa, Tetrahedron Lett. (1980) 4927. (c) K. Hirai, H. Suzuki, H. Kashiwagi, Chem. Lett. (1982) 23.
[8] J.M. Reuter, R.G. Salomon, J. Org. Chem. 42 (1977) 3360.
[9] C.-J. Li, D. Wang, D.-L. Chen, J. Am. Chem. Soc. 117 (1995) 12867.
[10] (a) B.M. Trost, R.J. Kulawiec, J. Am. Chem. Soc. 114 (1992) 5579. (b) B.M. Trost, J.A. Martinez, R.J. Kulawiec, A.F. Indolese, J. Am. Chem. Soc. 115 (1993) 10 402.

[11] K. Hiraki, Y. Fuchita, H. Kawabata, K. Iwamoto, T. Yoshimura, H. Kawano, Bull. Chem. Soc. Jpn. 65 (1992) 3027.
[12] K. Hiraki, T. Matsunaga, H. Kawano, Organometallics 13 (1994) 1878.
[13] S.D. Robinson, M.F. Uttley, J. Chem. Soc., Dalton Trans. (1973) 1912.
[14] B.M. Trost, R.J. Kulawiec, J. Am. Chem. Soc. 115 (1993) 2027.
[15] C.G. Swain, A.L. Powell, W.A. Sheppard, C.R. Morgan, J. Am. Chem. Soc. 101 (1979) 3576.
[16] J. Cook, J.E. Hamlin, A. Nutton, P.M. Maitlis, J. Chem. Soc., Chem. Commun. (1980) 144.
[17] T. Ito, H. Horino, Y. Komiya, A. Yamamoto, Bull. Chem. Soc. Jpn. 55 (1982) 504.
[18] A. Marcuzzi, A. Linden, W. von Philipsborn, Helv. Chim. Acta 76 (1993) 976.
[19] (a) B. Chamberlain, R.J. Mawby, J. Chem. Soc., Dalton Trans. (1991) 2067. (b) M.P. Waugh, R.J. Mawby, J. Chem. Soc., Dalton Trans. (1997) 21.
[20] (a) F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc., Perkin Trans. II (1987) S1. (b) A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson, R. Taylor, J. Chem. Soc., Dalton Trans. (1989) S1.
[21] (a) D.J. Darensbourg, F. Joó, Á. Kathó, J.N.W. Stafford, A. Bényei, J.H. Reibenspies, Inorg. Chem. 33 (1994) 175. (b) S.W. Lee, W.C. Trogler, J. Org. Chem. 55 (1990) 2644.
[22] J.E. Lyons, J. Chem. Soc., Chem. Commun. (1975) 418.
[23] H. Kawano, T. Ishimoto, K. Hiraki, unpublished results, 1997.
[24] K. Hiraki, M. Koizumi, S. Kira, H. Kawano, Chem. Lett. (1998) 47.
[25] A.M. Castaño, A.M. Echavarren, J. López, A. Santos, J. Organomet. Chem. 379 (1989) 171.
[26] (a) K. Hiraki, N. Ochi, H. Takaya, Y. Fuchita, Y. Shimokawa, H. Hayashida, J. Chem. Soc., Dalton Trans. (1990) 1679. (b) Y. Maruyama, K. Yamamura, I. Nakayama, K. Yoshiuchi, F. Ozawa, J. Am. Chem. Soc. 120 (1998) 1421. (e) B. Marciniec, C. Pietraszuk, Organometallies 16 (1997) 4320. (d) G.R. Clark, K.R. Flower, W.R. Roper, L.J. Wright, Organometallics 12 (1993) 259.
[27] G.W. Parshall, Inorg. Synth. 15 (1973) 46.
[28] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. Garcia-Granda, R.O. Gould, J.M.M. Smits, C. Smykalla, PATTY, The DIRDIF Program System, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992.
[29] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. Garcia-Granda, R.O. Gould, J.M.M. Smits, C. Smykalla, DIRDIF92, The DIRDIF Program System, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992.
[30] H.-F. Fan, SAPI91, Structure Analysis Programs with Intelligent Control, Rigaku Corporation, Tokyo, Japan, 1991.
[31] International Tables for X-Ray Crystallography, vol. IV, Kynoch Press, Birmingham, UK, 1974.
[32] teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation, 1985 and 1992.