

An NMR Study on the Ruthenium Complex-Catalyzed C–H/Olefin Coupling Reaction

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A dihydridoruthenium(II) complex, $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$, reacts with styrene to give two species: a bis(styrene)-ruthenium(0) complex, $[\text{Ru}(\text{CO})(\text{CH}_2=\text{CHPh})_2(\text{PPh}_3)_2]$, and a cyclometallated hydridoruthenium(II) one, $[\text{Ru}(\text{C}_6\text{H}_4\text{PPh}_2)\text{H}(\text{CO})(\text{PPh}_3)_2]$. The complex $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ reacts with isoprene to give a piano-stool type ruthenium(0) complex $[\text{Ru}(\eta^4\text{-CH}_2=\text{CMeCH}=\text{CH}_2)(\text{CO})(\text{PPh}_3)_2]$. In reactions among $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$, styrene, and 3'-(trifluoromethyl)acetophenone, three cyclometallated hydridoruthenium(II) complexes: *P,P'*-*cis*-C,*H*-*cis*-, *P,P'*-*trans*-C,*H*-*trans*-, and *P,P'*-*trans*-C,*H*-*cis*- $[\text{Ru}\{\text{C}_6\text{H}_3(\text{CF}_3)\text{C}(=\text{O})\text{Me}\}\text{H}(\text{CO})(\text{PPh}_3)_2]$ are detected by NMR spectroscopy. The ^1H NMR spectra of the reaction mixture exhibit the catalytic formation of 2'-(2-phenylethyl)- and 2'-(1-phenylethyl)-5'-(trifluoromethyl)acetophenones. On the basis of these findings, a mechanism for the C–H/olefin coupling reaction is discussed. The first of the three complexes is assigned to an active intermediate in the catalytic coupling reaction, whereas the other two are assigned as quasi-stable ruthenium(II) complexes which are in equilibrium with active species.

Ruthenium complex-catalyzed C–H/olefin coupling reactions were found for reactions between terminal olefins and aromatic ketones by Murai et al.^{1–3} and have been developed not only for similar reactions between terminal olefins and α,β -unsaturated ketones,^{4,5} α,β -unsaturated carboxylates,⁵ aromatic imines,⁶ or electron-deficient aromatic carboxylates,⁷ but also for those between inner acetylenes and aromatic ketones.⁸ It was reported that parallel C–H/olefin coupling reactions of (2-pyridyl)arenes⁹ and -ethenes^{10,11} were catalyzed with rhodium complex. Furthermore, imidazole-derivatives brought about C–H/olefin coupling reactions by the catalytic action of $[\text{Ru}_3(\text{CO})_{12}]$.¹²

In the ruthenium complex-catalyzed C–H/olefin coupling reactions^{1–7} and their related reactions,⁸ generation of active ruthenium(0) species and successive activation of the C–H bond to form an intermediary cyclometallated hydridoruthenium(II) species have been considered as the key steps. In spite of the usefulness of these reactions, however, the real active species and the intermediary cyclometallated hydridoruthenium(II) complexes have not been characterized clearly so far, although Matsubara et al.¹³ have reported a theoretical study on the mechanism of the C–H/olefin coupling reaction. Here we report the results of NMR spectroscopic study on the catalytic C–H/olefin coupling reaction, providing new information about the active species and their closely-related complexes in the catalytic reactions.

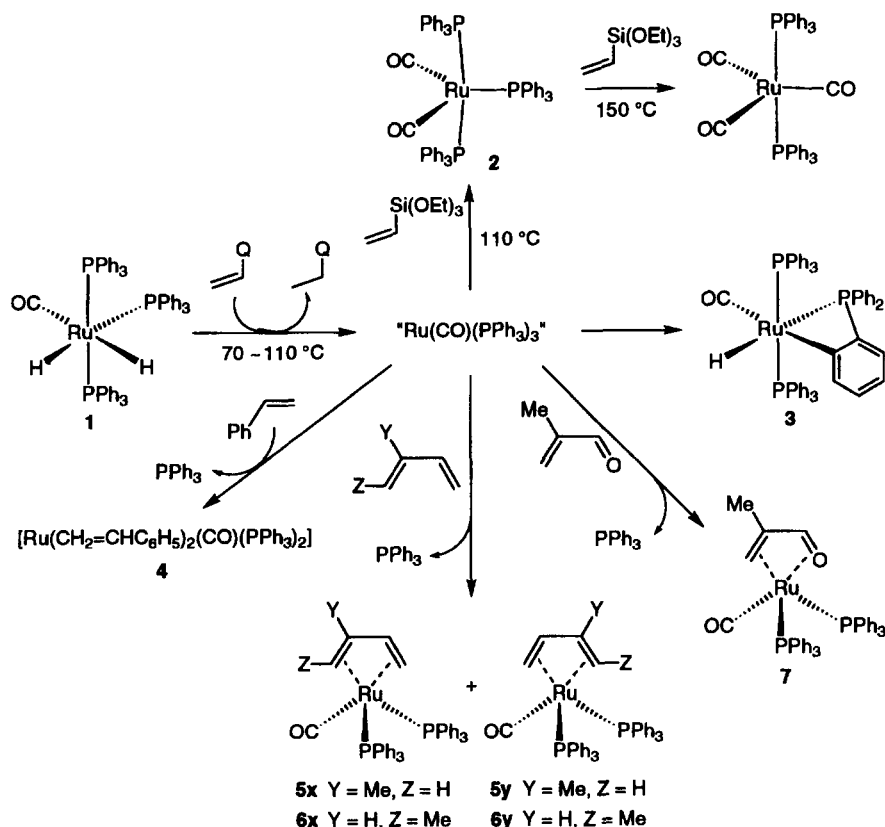
Results and Discussion

Reaction of $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ (**1**) with Triethoxyvinylsilane.

Triethoxyvinylsilane has been used as an effective olefin for the catalytic C–H/olefin coupling reactions.^{1–7,9,10} The vinylsilane plays two roles: as a good hydrogen acceptor to produce an active ruthenium(0) species from **1** and as a terminal olefin that gives a coupling product. However, we have reported that the use of the vinylsilane brings about the unfavorable formation of $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ (**2**) and $[\text{Ru}(\text{CO})_3(\text{PPh}_3)_2]$.¹⁴ The vinylsilane is a source of the second and the third carbonyl ligands of the less reactive di- and tricarbonylruthenium(0) complexes. Therefore, in order to reveal how the vinylsilane is converted into the carbonyl ligand under the catalytic conditions, we reinvestigated the reaction of **1** with triethoxyvinylsilane.

The reaction of **1** with a threefold amount of triethoxyvinylsilane was followed by measuring the NMR spectra. When the reaction was carried out at 110 °C for 5 min, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the resulting solution showed that about 50% of **1** was consumed, and the dicarbonylruthenium(0) complex **2**¹⁴ and a four-membered cyclometallated hydridoruthenium(II) one $[\text{Ru}(\text{C}_6\text{H}_4\text{PPh}_2)\text{H}(\text{CO})(\text{PPh}_3)_2]$ (**3**),¹⁴ appeared (Scheme 1). Moreover, four weak unidentified signals were also observed in the range of $\delta = 42.6\text{--}49.0$. The relative ratio of **2** and **3** was about 3 : 1, and the sum of the ^{31}P -areas of the unidentified signals was nearly equal to that of **3**. After 1 h, **2** was dominant in the mixture, and **1** decreased to about 1%, whereas **3** and the unidentified signals remained. These NMR data show that the second carbonyl ligand in **2** was derived from the CH_2O

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Scheme 1. Reactions of **1** with terminal olefins, 1,3-dienes, and 2-methyl-2-propenal. Q = Si(OEt)₃ for triethoxyvinylsilane and 2-methyl-2-propenal, Q = C₆H₅ for styrene, Q = CMe=CH₂ for isoprene, Q = CH=CHMe for (*E*)-1,3-pentadiene.

moiety of the ethoxy group in triethoxyvinylsilane. That is, the CH₃CH₂O–Si bond was activated and cleaved, and the CH₂O moiety was converted into the carbonyl ligand by the active ruthenium species under the catalytic C–H/olefin coupling conditions.

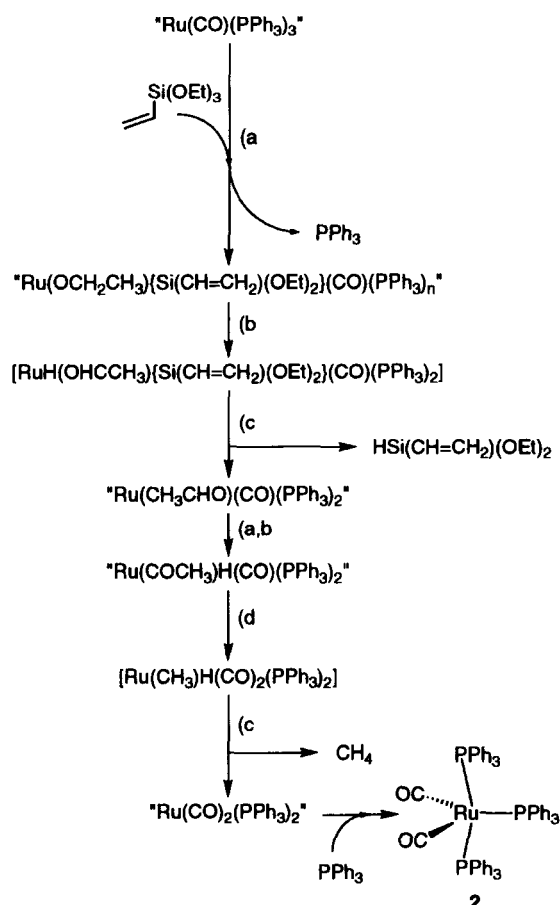
After a mesitylene suspension containing **1** and a threefold amount of triethoxyvinylsilane was treated at 110 °C in nitrogen atmosphere for 1.0 h, the gas phase was analyzed by GC–MS to involve methane in 63% yield based on **1** together with a small amount of ethane. This fact indicates that methane was caused by the methyl moiety of the ethoxy group in triethoxyvinylsilane, suggesting that the CH₃–CH₂O bond was also cleaved. Komiya et al.¹⁵ reported that [RuH₂(PPh₃)₄] reacted with 2- and 1-alkenyloxytrimethylsilanes to give alkenes, alkanes, and the carbonylruthenium complex **1**, and they proposed mechanisms for the reactions involving the cleavage of C–O, Si–O, and OC–CH_n bonds as key steps.

On the basis of these facts, a mechanism for the formation of **2** and methane from the reaction between **1** and triethoxyvinylsilane is shown in Scheme 2. At first, **1** reacted with the vinyl moiety of triethoxyvinylsilane to afford triethoxyethylsilane and a four-coordinate ruthenium(0) species “Ru(CO)(PPh₃)₃”. Since this ruthenium(0) species is coordinatively-unsaturated and highly reactive, a part of this species abstracts one *ortho*-hydrogen from the phenyl group in the three coordinated PPh₃ ligands to give **3**. The other part reacts with triethoxyvinylsilane to form “Ru(OCH₂CH₃)₂{Si-

(CH=CH₂)(OEt)₂}(CO)(PPh₃)_n” (*n* = probably 2) by oxidative addition, accompanying the Si–OCH₂ bond cleavage. The ruthenium center abstracts β-hydrogen of the ethoxy ligand to form an (acetaldehyde)hydridoruthenium(II) species, [RuH{Si(CH=CH₂)(OEt)₂}(CO)(CH₃CH=O)(PPh₃)₂]. Reductive elimination of this species takes place to afford diethoxyvinylsilane and a coordinatively-unsaturated ruthenium(0) species “Ru(CO)(CH₃CH=O)(PPh₃)₂”. Furthermore, it is well known that aldehyde (RCHO) reacts with ruthenium(0) species to afford the corresponding hydrocarbon (RH) and carbonylruthenium(0) species.¹⁵ Then, it is reasonable that “Ru(CO)(CH₃CH=O)(PPh₃)₂” is converted into methane and a coordinatively-unsaturated ruthenium(0) species, “Ru(CO)₂(PPh₃)₂”. At the last stage, this ruthenium(0) species traps one triphenylphosphine molecule instantaneously to afford **2**. Colombo et al.¹⁶ have reported that laser-flash photolysis of **1** in benzene yields transient [Ru(CO)(PPh₃)₃], which reacts with H₂ to reform **1** with a rate constant of *k*₂ = (8.4 ± 0.4) × 10⁷ dm³ mol^{−1} s^{−1}. At higher temperature, **2** changes to [Ru(CO)₃(PPh₃)₂]¹⁴ in a similar mechanism.

If the reaction between **1** and triethoxyvinylsilane proceeds according to the mechanism shown in Scheme 2, the formation of diethoxyvinylsilane is expected, but attempts to detect it failed. The diethoxyvinylsilane formed might be consumed in hydrosilylation of triethoxyvinylsilane, since silanes containing Si–H bond are known to be reactive for hydrosilylation of olefines.¹⁷

Generation and Detection of the Ruthenium(0) Species.



Scheme 2. The proposed mechanism for the formation of **2** and methane by the reaction between **1** and triethoxyvinylsilane. (a; oxidative addition, (b; β -hydrogen abstraction, (c; reductive elimination, (d; alkyl migration.

Since styrene gives almost no catalytically less active species, we tried to detect active species or their closely-related complexes in the reaction between **1** and styrene. Complex **1** reacted with an excess amount of styrene at 110 °C, and was converted mainly into two species within 1 h. At 30 °C, the major species showed a broad $^{31}\text{P}\{^1\text{H}\}$ NMR signal around $\delta = 55$ –57, overlapping with the doublet of **1** at $\delta = 56.4$. When the reaction mixture was cooled at -50 °C, the broad signal turned into a pair of doublets at $\delta = 55.7$ and 57.0 ($^2J_{\text{PP}} = 9.8$ Hz), separating from the signal of **1**. The ^1H NMR spectrum at 30 °C showed a double triplet at $\delta = -0.96$ ($^3J_{\text{HH}} = 8.5$ Hz, $^3J_{\text{HP}} = 6$ Hz) and a very broad signal near $\delta = 1.85$, which changed to a slightly broad multiplet at $\delta = 1.74$ at -50 °C. The small $^2J_{\text{PP}}$ value and the higher field shifts of the olefinic protons strongly suggest the presence of a bis(styrene)ruthenium(0) species $[\text{Ru}(\text{CO})(\text{CH}_2=\text{CHPh})_2(\text{PPh}_3)_2]$ (**4**) (Scheme 1). The temperature-dependent NMR spectra imply that a partial fluxional motion takes place in **4** above room temperature. A similar bis(styrene)ruthenium(0) complex without a carbonyl ligand, $[\text{Ru}(\text{CH}_2=\text{CHPh})_2(\text{PPh}_3)_2]$, was synthesized and characterized crystallographically by Chaudret et al.¹⁸

The minor species was the four-membered cyclometallated hydridoruthenium(II) complex **3**.¹⁴

In order to confirm the formation of **4**, we tried to isolate an (η^4 -conjugated diene)ruthenium(0) complex. A twentyfold amount of isoprene was allowed to react with **1** at 70 °C for 6 h. Reddish-brown powdery product $[\text{Ru}(\eta^4\text{-(CH}_2=\text{CMeCH=CH}_2)(\text{CO})(\text{PPh}_3)_2]$ (**5**) was isolated in 82% yield. Similarly, (*E*)-1,3-pentadiene also reacted with **1** to afford $\{\eta^4\text{-(E)-1,3-pentadiene}\}$ ruthenium(0) complex, $[\text{Ru}(\text{CO})\{\eta^4\text{-(E)-CH}_2=\text{CHCH=CHMe}\}(\text{PPh}_3)_2]$ (**6**). The product **5** consisted of two isomers, **5a** and **5b**, in a ratio of 93 : 7. Both isomers **5a** and **5b** showed two broad signals near $\delta = 45$ and 57, with small coupling constants in its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The olefinic protons were shifted up to $\delta = -1.41$ –5.08, and those of the major isomer **5a** were observed as multiplets coupled with each other and two ^{31}P nuclei, although the coupling of the olefinic protons in **5b** could not be detected clearly. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5a** supported the coordination of isoprene and a carbonyl ligand. It is certain that **5a** and **5b** have the piano-stool type structures **5x** and **5y** shown in Scheme 1. At the present time, however, whether the major isomer **5a** has the structure **5x** or **5y** is ambiguous. This is also the case with two isomers of **6**, **6a** and **6b**. Furthermore, 2-methyl-2-propenal reacted with **1** in the presence of triethoxyvinylsilane to give (η^4 -2-methyl-2-propenal)ruthenium(0) complex $[\text{Ru}(\text{CO})(\eta^4\text{-CH}_2=\text{CMeCH=O})(\text{PPh}_3)_2]$ (**7**)¹⁹ in a fairly good yield. As stated above, the $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR features of **4** are common to those of **5**, **6**, previously-reported (conjugated diene)ruthenium(0) complexes,^{20,21} and **7**, supporting strongly the formation of the bis(styrene)ruthenium(0) complex **4**. Isoprene certainly did react with **1** in the presence of 2'-methylacetophenone, but the formation of the fairly stable and catalytically inactive (η^4 -isoprene)ruthenium(0) complex, **5** is the reason why isoprene did not couple with the aromatic ketone in the presence of **1**.²

The formations of the olefin-, conjugated diene-, and 2-methyl-2-propenal-monocarbonylruthenium(0) complexes such as **4**–**7** indicate unambiguously that **1** reacted with styrene to give the highly reactive ruthenium(0) species, " $\text{Ru}(\text{CO})(\text{PPh}_3)_3$ ", in a similar fashion to the case of triethoxyvinylsilane (vide ante), liberating ethylbenzene. Furthermore, a major part of the highly reactive ruthenium(0) species trapped two styrene molecules, liberating one phosphine ligand, to afford bis(styrene)ruthenium(0) complex **4**. Thus, the reaction of **1** with terminal olefin in the presence of an adequate ligand provides a good method to prepare "carbonylbis(triphenylphosphine)ruthenium(0) complexes".

Reactions among **1, Styrene, and 3'-(Trifluoromethyl)acetophenone.** The C–H/olefin coupling reaction between styrene and acetophenone was already reported by Murai et al.^{1–3} In order to stabilize the ruthenium-phenyl bond which is expected to form in the active species and their closely-related ones in the catalytic C–H/olefin coupling reaction, 3'-(trifluoromethyl)acetophenone was used in place of acetophenone. Sonoda et al.³ reported that 3'-(trifluoromethyl)acetophenone and triethoxyvinylsilane were coupled catalytically.

ically by **1** to afford a single product, in contrast with acetophenone giving 2'-mono- and 2',6'-disubstituted products.^{1,2}

When the complex **1** was heated at 70 °C with an excess amount of styrene and 3'-(trifluoromethyl)acetophenone for only 5 min, the first species emerged. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture showed two doublets at $\delta = 33.5$ and 36.9 ($^2J_{\text{PP}} = 19.5$ Hz), indicating that two phosphine ligands were located *cis* to each other [Fig. 1(a)]. Furthermore, in the ^1H NMR spectrum, a double doublet at $\delta = -6.07$ ($^2J_{\text{HP}} = 91$ and 26 Hz) was ascribed to a hydrido proton. The former large coupling constant implies that the hydrido is situated *trans* to one of the two phosphine ligands. On the basis of these spectroscopic data, the first species was assigned to a cyclometallated hydridoruthenium(II) complex, *P,P'*-*cis*-*C,H-cis*-[Ru{C₆H₃(CF₃)C(=O)Me}H(CO)(PPh₃)₂] (**8**) (Scheme 3). In consideration of *trans*-influences and electron-withdrawing or -donating characters of the carbonyl ligand and the ketone-oxygen, these two ligands are assumed to be coordinated *trans* to each other.

After 10 min, the second species appeared, showing a singlet at $\delta = 52.3$ in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum and triplet at $\delta = -3.10$ ($^2J_{\text{HP}} = 21.3$ Hz) in the ^1H NMR [Fig. 1(b)]. The features and the chemical shifts of the $^{31}\text{P}\{^1\text{H}\}$ singlet and the triplet in the hydrido region are closely similar to those of reported cyclometallated hydridoruthenium(II) complexes, *P,P'*-*trans*-*C,H-trans*-[Ru(C₆H₄CH=NC₆H₅)H(CO)-(PPh₃)₂] and -[Ru(C₆H₄C₅H₄N)H(CO)(PPh₃)₂] (C₅H₄N = 2-pyridyl) (Fig. 2).²² Especially, the hydrido signal in the relatively lower field indicates *trans*-coordination to the

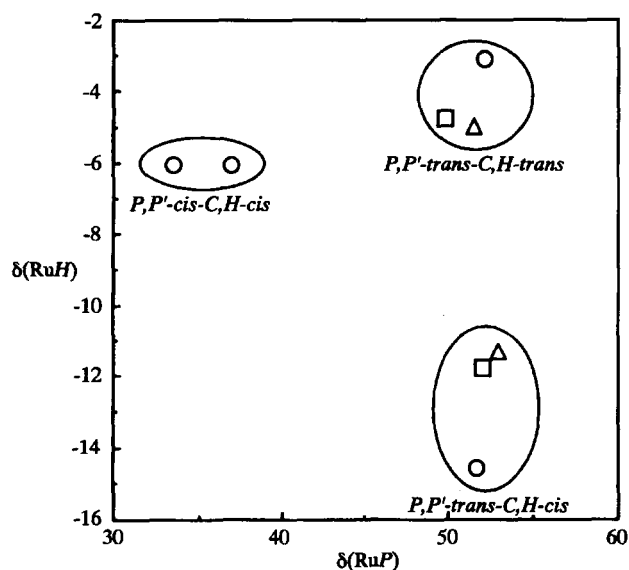


Fig. 2. $^{31}\text{P}\{^1\text{H}\}$ - ^1H Correlation between $\delta(\text{RuP})$ and $\delta(\text{RuH})$ for the cyclometallated hydridoruthenium(II) complexes, ○: [Ru{C₆H₃(CF₃)C(=O)Me}H(CO)(PPh₃)₂]; □: [Ru(C₆H₄CH=NC₆H₅)H(CO)(PPh₃)₂];²² and △: [Ru(C₆H₄C₅H₄N)H(CO)(PPh₃)₂].²²

phenyl group. Therefore, the second species is assigned to a cyclometallated complex with a similar structure, *P,P'*-*trans*-*C,H-trans*-[Ru{C₆H₃(CF₃)C(=O)Me}H(CO)(PPh₃)₂] (**9**).

Although the coordination of one carbonyl ligand was not evidenced directly for **4**, **8**, **9**, and **12** (vide post) ow-

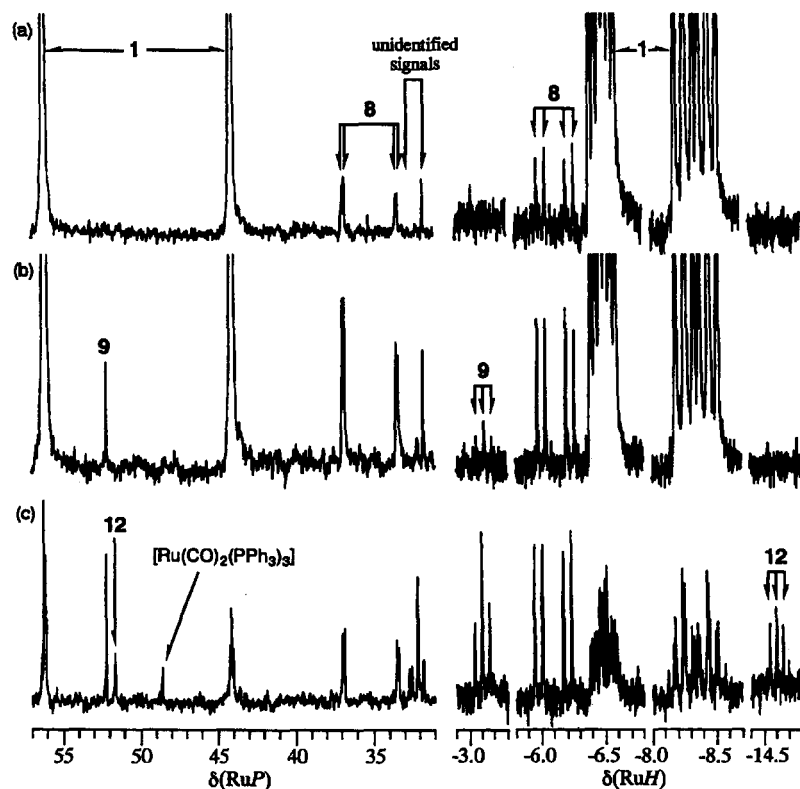
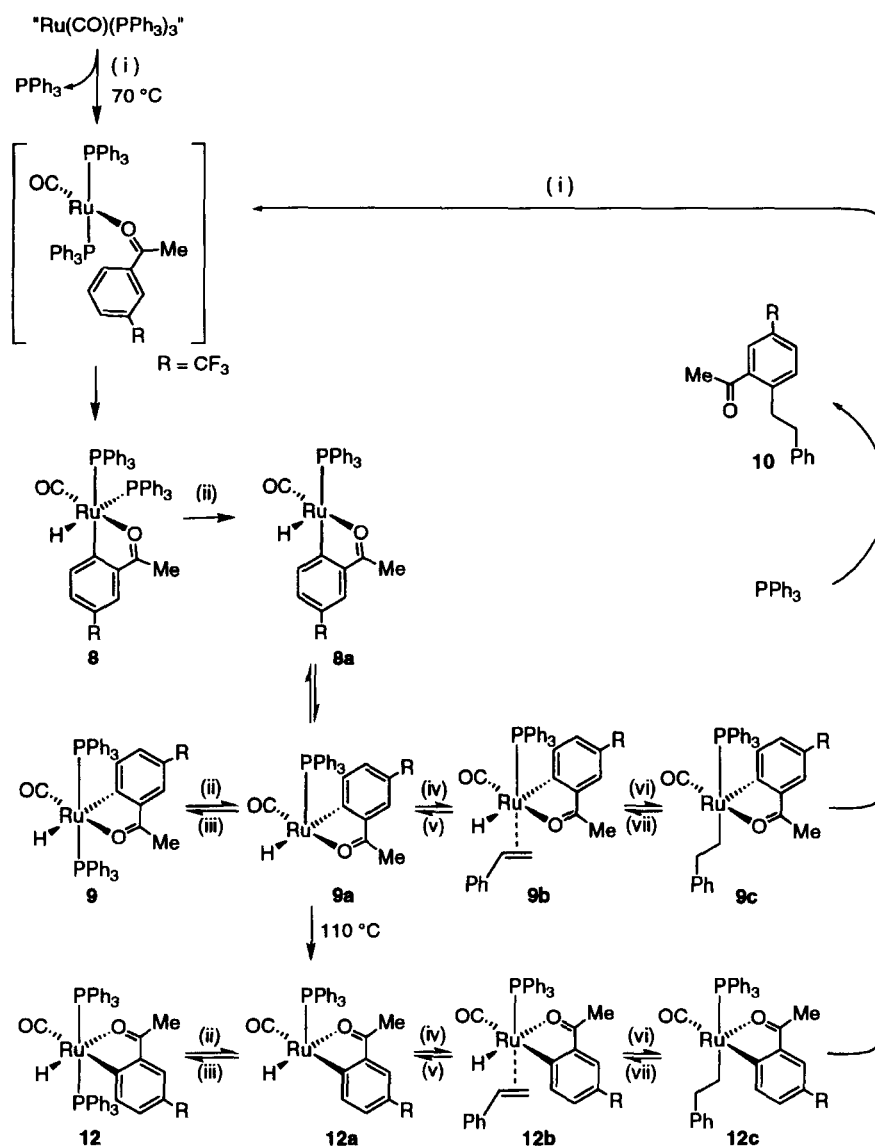


Fig. 1. The $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra of the reaction mixture among **1**, styrene, and 3'-(trifluoromethyl)acetophenone. (a) After 5 min at 70 °C. (b) After 10 min at 70 °C. (c) After 30 min at 110 °C.



Scheme 3. The proposed mechanism for the C-H/olefin coupling reaction between styrene and 3'-(trifluoromethyl)acetophenone. For clarity, the active species containing the 1-phenylethyl group and **11** are deleted. (i) +3'-(trifluoromethyl)acetophenone; (ii) $-\text{PPh}_3$; (iii) $+\text{PPh}_3$; (iv) +styrene; (v) $-\text{styrene}$; (vi) hydride shift; (vii) β -hydrogen abstraction.

ing to difficulty of detection by means of $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, it is reasonable from the following points of views: i) A carbonyl ligand has a strong π -electron-withdrawing character, whereas triphenylphosphine is electron-donating. Accordingly, these ligands are bonded rigidly together to ruthenium(0) and -(II) centers with delocalization of electron through push-pull effect. This stabilizes the " $\text{Ru(CO)(PPh}_3)_2$ " core in both Ru(0) and Ru(II) species and forces it not to dissociate the carbonyl ligand from the ruthenium center; ii) Especially, it is well known that the carbonyl group plays a role as a good stabilizing ligand for the low-valent metal center such as Ru(0); iii) Almost all ruthenium(0) and -(II) species isolated from the reactions of **1** in the presence of terminal olefin, such as **2**, **5**, **7**, and P,P' -*trans*-C,H-*trans*- and P,P' -*trans*-C,H-*cis*- $[\text{Ru}(\text{C}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_5)\text{H(CO)(PPh}_3)_2]$ and $[\text{Ru}(\text{C}_6\text{H}_4\text{C}_5\text{H}_4\text{N})\text{H(CO)(PPh}_3)_2]$,²² have at least one carbonyl ligand; iv)

The mono(carbonyl)dihydridoruthenium(II) complex **1** has higher catalytic activity for the C-H/olefin coupling reaction between α -tetralone and triethoxyvinylsilane than a non-carbonyl dihydridoruthenium(II) one, $[\text{RuH}_2(\text{PPh}_3)_4]$.² This suggests that the active species for the catalytic coupling reaction has at least one carbonyl ligand.

After 20 min, the ^1H NMR spectrum of the reaction mixture showed two sets of signals due to two coupling products, 2'-(2-phenylethyl)- and 2'-(1-phenylethyl)-5'-(trifluoromethyl)acetophenones (**10** and **11**, respectively), besides signals due to the hydrogenated product, ethylbenzene and unreacted 3'-(trifluoromethyl)acetophenone and styrene. The molar ratio of the sum of **10** and **11** to the amount of ethylbenzene was about 1.7. These data indicate that the catalytic C-H/olefin coupling reaction between 3'-(trifluoromethyl)acetophenone and styrene took place slowly at this temperature. The relative ratio of **10** to **11** was about 1 : 1.1.

When the reaction among **1**, styrene, and 3'-(trifluoromethyl)acetophenone was carried out at 110 °C, **8** and **9** were formed within 10 min and decreased gradually along with reaction time. After 30 min, there appeared a third species having a singlet at $\delta = 51.7$ in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum and a triplet at $\delta = -14.6$ ($^2J_{\text{HP}} = 21.3$ Hz) in the ^1H NMR one, and this increased slowly [Fig. 1(c)]. The spectroscopic feature of the third species are very similar to those of *P,P'*-*trans*-*C,H-cis*-[Ru(C₆H₄CH=NC₆H₅)H(CO)(PPh₃)₂] and [Ru(C₆H₄C₅H₄N)H(CO)(PPh₃)₂] (Fig. 2).²² Analogously to the case of **9**, the third species is assigned to a cyclometallated hydridoruthenium(II) complex, *P,P'*-*trans*-*C,H-cis*-[Ru{C₆H₃(CF₃)C(=O)Me}H(CO)(PPh₃)₂] (**12**), an isomer of **8** and **9**.

The change in relative ratio among **8**, **9**, and **12** indicates the sequential isomerization of these complexes in the reaction mixture (Fig. 3). It is reasonable to consider that the *P,P'*-*cis*-*C,H-cis*-**8** is formed directly via usual *cis*-oxidative addition of 3'-(trifluoromethyl)acetophenone onto the active species "Ru(CO)(PPh₃)₃", liberating one phosphine ligand. Steric repulsion between the two *cis*-coordinated triphenylphosphine ligands causes **8** to isomerize to *P,P'*-*trans*-*C,H-trans*-**9**. Above 110 °C, **9** is successively converted into *P,P'*-*trans*-*C,H-cis*-**12**. We have already reported the isomerization of *P,P'*-*trans*-*C,H-trans*-type complexes to the corresponding *P,P'*-*trans*-*C,H-cis*-ones in the series of [Ru(C₆H₄CH=NC₆H₅)H(CO)(PPh₃)₂] and [Ru(C₆H₄C₅H₄N)H(CO)(PPh₃)₂].²² In the literature we have also predicted that the *P,P'*-*trans*-*C,H-trans*-type complexes should be produced via quick replacement from another *C,H-cis*-species formed with the ordinary oxidative addition of the C-H bond.

At 110 °C, styrene was consumed completely within 1 h,

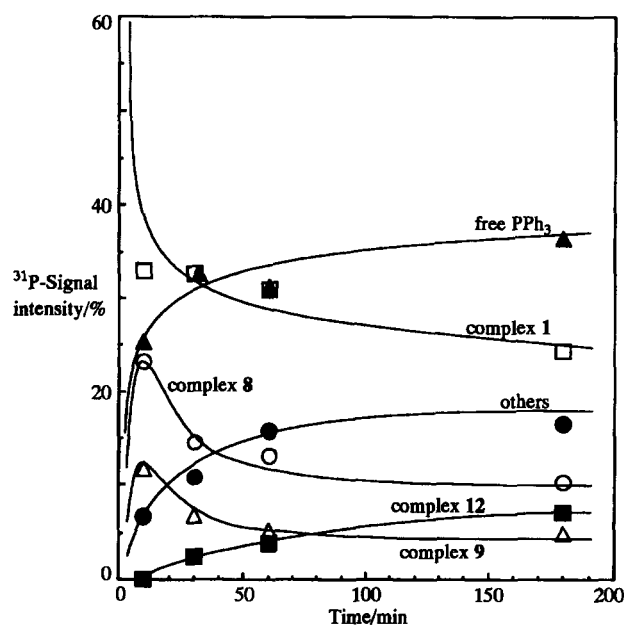


Fig. 3. Time vs. phosphorus content curves in the reaction among **1**, styrene, and 3'-(trifluoromethyl)acetophenone at 110 °C. The sum of the ^{31}P -areas of the unidentified signals is shown as "others".

and the coupling reaction was terminated; the excess ketone remained unreacted in the reaction mixture. The ^1H NMR spectrum of the reaction mixture showed that the coupling products **10** and **11** were produced in a ratio of about 1 : 0.33, respectively, implying that the terminal carbon of styrene was easily bonded to the aromatic ring to give **10** dominantly at 110 °C. Kakiuchi et al.² reported that acetophenone coupled with styrene to give two isomeric products in a similar manner to 3'-(trifluoromethyl)acetophenone. Moreover, in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, four new unidentified singlets appeared at $\delta = 32.1$, 32.3, 32.7, and 32.9, while the singlet at $\delta = 31.8$ decreased. The sum of the phosphorus contents of these five unidentified singlets reached about 17% of total phosphorous content after 1 h.

Mechanisms for the Sequential Isomerization and the C-H/Olefin Coupling Reaction. Since the ruthenium(II) center in **8**, **9**, and **12** has a $4d^6$ electronic configuration, these complexes have nearly octahedral six-coordinate structure and are electronically stable. However, the steric repulsion between the two *cis*-coordinated triphenylphosphine ligands in **8** causes one of the two phosphines to dissociate above 70 °C, affording a five-coordinated active species **8a**, as shown in Scheme 3. The phenyl group in **8a** shifts to the vacant site to convert **8a** into a new five-coordinate species, **9a**, in which the phenyl group and the hydrido ligand are situated *trans* to each other. Triphenylphosphine molecule adds to the vacant site of **9a** to give **9**, the isomer of **8**. Equilibrium exists probably between the active species **9a** and the active species-related quasi-stable complex **9** through addition-dissociation of triphenylphosphine molecule.

Above 110 °C, the phenyl group and the ketone-oxygen in **9a** exchange their coordination sites to form a new five-coordinate species, **12a**, where the phenyl group and the hydrido are located *cis* to each other. Addition of triphenylphosphine molecule to the vacant site of **12a** produces **12**. Similarly, there is possibly equilibrium between **12a** and **12**.

In the sequential isomerization course, the three active five-coordinate species, **8a**, **9a**, and **12a**, have been proposed. Styrene is coordinated to the vacant site of **12a** to afford a hydrido (η^2 -styrene)ruthenium(II) species, **12b** (Scheme 3). The hydrido ligand shifts instantly to α -carbon of the coordinated styrene to form a [2-acetyl-4-(trifluoromethyl)phenyl- $\kappa\text{C}^1, \kappa\text{O}$](2-phenylethyl)ruthenium(II) species, **12c**. The liberated triphenylphosphine molecule attacks the vacant site of **12c**, combining the 2-phenylethyl group and the 2-acetylphenyl one in **12c**. Thus, this reductive elimination process proceeds to give the coupling product, **10**, liberating a zerovalent ruthenium species "Ru(CO)(PPh₃)₂". This highly coordinatively-unsaturated species is very reactive and traps the remaining 3'-(trifluoromethyl)acetophenone instantaneously to return to **8**. Thus the catalytic cycle of the C-H/olefin coupling reaction is completed. Parallel with the above process, the hydrido ligand in **12b** shifts to β -carbon of the coordinated styrene to produce an [2-acetyl-4-(trifluoromethyl)phenyl- $\kappa\text{C}^1, \kappa\text{O}$](1-phenylethyl)ruthenium(II) species. Similar reductive elimination of this species takes place to afford the coupling product, **11**. Since the

hydrido-shift to the α -carbon occurs more easily than that to the β -carbon at 110 °C, **10** is produced in a larger ratio than **11**. This mechanism is quite consistent with the simple catalytic cycle proposed by Murai et al.^{1,2} and reinforces it strongly.

Since there is equilibrium between **12a** and **12c** via **12b**, a part of **12c** returns to **12a** and styrene by abstracting β -hydrogen of the 2-phenylethyl group in itself. This is quite consistent with the fact that treatment of acetophenone-*d*₅ [CH₃C(=O)C₆D₅] and triethoxyvinylsilane in the presence of **1** at 135 °C resulted in complete H–D-scrambling of recovered triethoxy(vinyl-*d*_{1.21})silane.²

As stated above, small amounts of the coupling products **10** and **11** were detected even at 70 °C, where the active species **12a** was not formed. This indicates that **9a** also traps styrene directly to form a hydrido (η^2 -styrene)ruthenium(II) species **9b**, which affords the coupling products slowly via processes similar to those via **12b** and **12c**.

Kakiuchi et al.² have reported that acetophenone-*d*₅ is treated with triethoxyvinylsilane in the presence of **1** at 50 °C to result in the recovery of partially-H–D-scrambled triethoxy(vinyl-*d*_{0.82})silane, whereas the coupling products are not formed at all. These facts indicate that there is a path in which the partial H–D-scrambling takes place between acetophenone-*d*₅ and triethoxyvinylsilane, but the coupling products are not produced at 50 °C. Our Scheme 3 explains well similar H^{Ar}–H^{Vinyl}-scrambling between 3'-(trifluoromethyl)acetophenone and styrene, though it is not evidenced experimentally. Parallel to the step from **8** to **8a**, another five-coordinate ruthenium(II) species, "Ru{C₆H₃(CF₃)C(=O)Me}H(CO)(PPh₃)" (**8b**) may be formed from **8** by liberating the triphenylphosphine ligand situated *trans* to the phenyl group. This species traps one styrene molecule to produce a (2-phenylethyl)ruthenium(II) species "C, C' – *trans* – Ru{C₆H₃(CF₃)C(=O)Me}(CH₂CH₂C₆H₅)(CO)(PPh₃)" (**8d**) via an η^2 -styrene-coordinated ruthenium(II) species (**8c**). However, the 2-phenylethyl group and the 2-acetylphenyl one in **8d** are situated *trans* to each other, and can not couple mutually. There is equilibrium between **8** and **8d** via **8b** and **8c**, and the metal center in **8d** abstracts β -hydrogen of the 2-phenylethyl group to return to **8**, accompanying the H^{Ar}–H^{Vinyl}-scrambling between 3'-(trifluoromethyl)acetophenone and styrene. However, this course is not shown in Scheme 3, since it has not been confirmed directly by our spectroscopic method. This is also the case with the other path via the (1-phenylethyl)ruthenium(II) species. In our case, small amounts of the coupling products were formed at 70 °C, as stated above, whereas the temperature, the olefin, and the aromatic ketone were different from the ones used by Kakiuchi's group.

It has been reported that the C–H/olefin coupling reaction between 2'-methylacetophenone and triethoxyvinylsilane proceeds very smoothly in vigorously-refluxing toluene to give the coupling product in 93% yield after 2 h, whereas the same reaction proceeds very slowly in refluxing benzene to afford the product in 55% yield after 24 h.² These facts are well explained by our mechanism, in which the active species

such as **12a**–**12c** are formed only at an adequately high temperature like 110–135 °C. At a lower temperature near 70 °C, however, the coupling reaction is controlled by the catalytically-less active intermediates (**9b** and **9c**), while there are the active intermediates (**8**, **8a**, and **9a**) besides the less active species and the catalytically-inactive ones (**8b**–**8d**, and **9**) in the reaction mixture. At 140–160 °C, the yield of the same reaction was about 7–10% even after 24 h.² At the very high temperature, **1** reacts with triethoxyvinylsilane to change to the less active species **2** and probably to an inactive one, [Ru(CO)₃(PPh₃)₂].¹⁴

Comparison with the Theoretical Study. Matsubara et al.¹³ reported theoretical calculations for a model catalytic cycle of the C–H/olefin coupling reaction using DFT method. They used ethylene and benzaldehyde as models of olefin and aromatic ketone, respectively, and PH₃ as the phosphine ligand instead of PPh₃. Furthermore, they assumed the three-coordinate *trans*-[Ru(CO)(PH₃)₂] as an active species derived from [RuH₂(CO)(PH₃)₃], recognizing the four-coordinate [Ru(CO)(PH₃)₃] as another candidate. Their theoretical calculation elucidated that *P, P'*-*cis*-C, *H*-*cis*- and *P, P'*-*trans*-C, *H*-*cis*-[Ru(C₆H₄CH=O)H(CO)(PH₃)₂] (**8t** and **12t**, respectively) were quasi-stable intermediates, and that the reaction course via **8t** was more favorable than that via **12t**, since **8t** was formed with a smaller activation energy than **12t**. The theoretical intermediates **8t** and **12t** correspond well to the detected complexes **8** and **12**, respectively, from the viewpoint of structure. Moreover, these theoretical results and our spectroscopic ones are common in the conclusions that the *P, P'*-*cis*-C, *H*-*cis*-type complexes, **8t** and **8** are the first-formed intermediates. In the theoretical study, however, **12t** was formed directly from the highly coordinatively-unsaturated species with a relatively high activation energy, and the *P, P'*-*trans*-C, *H*-*trans*-type intermediate, such as **9**, was not recognized. These are different from the results of our spectroscopic study.

As for the latter part of the catalytic reaction,^{13b} **8t** dissociates the phosphine *trans* to the phenyl group and traps ethylene. The coordinated ethylene couples with the hydrido (not with the hydrido-shift to the coordinated ethylene) upon ruthenium, followed by recombination of the dissociated phosphine to give a quasi-stable intermediate, *P, P'*-*cis*-C, C' – *cis*-[Ru(C₆H₄CH=O)(CH₂CH₃)(CO)(PH₃)₂]. In our mechanism, however, **8** can not produce the coupling products **10** and **11**, when **8** dissociates the PPh₃ ligand *trans* to the phenyl group, as discussed above. Matsubara et al.^{13b} suggested that the *P, P'*-*trans*-C, *H*-*cis*-type **12t** exchanged also the coordinated phosphine with ethylene, accompanied by the similar steps to those from **8t** to afford the coupling product. This reaction course seems to be analogous to our route via **12a**–**12c**. At the present stage, we have confirmed neither *P, P'*-*cis*-C, C' – *cis*-type complex, nor *P, P'*-*trans*-C, C' – *cis*-type one, corresponding to *P, P'*-*cis*-C, C' – *cis*- and *P, P'*-*trans*-C, C' – *cis*-[Ru(C₆H₄CHO)(C₂H₅)(CO)(PH₃)₂] derived from **8t** and **12t**, respectively.

Comments on a Proposal of Trost's Group. Trost et al.⁵ reported that **1** catalyzed the C–H/olefin coupling

reaction between (*E*)-3-methyl-3-penten-2-one or methyl 1-cyclopentenecarboxylate and terminal olefin in refluxing toluene. On the basis of the fact that the catalytic reactions were strongly inhibited in the presence of a CO atmosphere, they proposed that a highly coordinatively unsaturated ruthenium bearing only the three phosphine ligands, stabilized by solvent serving as a weakly coordinating ligand, might be the active species. We can appreciate the former part of this proposal in which the highly coordinatively-unsaturated ruthenium may be the active species. However, the latter part of the proposal of Trost's group is not at all consistent with our results. It is well known that ruthenium(0) species is converted into the less active $[\text{Ru}(\text{CO})_3(\text{PPh}_3)_2]$ ¹⁴ in the presence of CO and PPh_3 . As discussed above, the fact that **1** acted more actively than $[\text{RuH}_2(\text{PPh}_3)_4]$ as the catalyst for the C–H/olefin coupling reaction² suggests strongly that the active species holds at least one carbonyl ligand, in contradiction to the proposal of Trost's group.⁵ In addition, the “ $\text{Ru}(\text{CO})(\text{PPh}_3)_2$ ” moiety is very rigid, owing to the push-pull effect of electron between the PPh_3 and CO ligands, and does not dissociate the carbonyl ligand so easily, as Trost et al.⁵ proposed.

Experimental

The experimental procedures and the solvents have been described in the previous paper.¹⁴ All reagents except **1** were purchased and used without further purification. Infrared spectra were recorded on a JASCO A-202 spectrometer using KBr disks prepared under inert atmosphere. ^1H , ^{13}C , ^{31}P , and ^1H - ^{31}P HMBC NMR spectra were measured on a JEOL GX-400 spectrometer. GLC was recorded on a Hitachi GC-3BT (for H_2 ; a Molecular Sieve 5A column), and GC-MS on a Nichiden-Anelva TE-600 equipped with a 5 mm $\phi \times 3$ m column of Unibeads 1S.

Preparation of $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ (1**).** The starting complex $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ was prepared by a modified manner of the reported method.²³ In a four-necked round-bottomed flask equipped with three dropping funnels and a reflux condenser was placed a solution of triphenylphosphine (6.31 g, 24 mmol) in ethanol (280 cm^3). The three dropping funnels were filled with a suspension of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (1.08 g, 4.01 mmol) in ethanol (40 cm^3), a solution of potassium hydroxide (1.50 g, 27 mmol) in ethanol (40 cm^3), and aqueous formaldehyde (40 cm^3). Into the vigorously refluxing solution of triphenylphosphine, the suspension of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and the solutions of potassium hydroxide and formaldehyde were added from the funnels simultaneously. The reaction mixture precipitated crude product gradually and turned into a light-brown suspension. Refluxing for one day was essential to complete the formation of **1** and to reduce the amount of by-products. The reaction mixture was cooled to room temperature and then passed through a glass filter. The grayish solids on the filter were dissolved in benzene (100 cm^3) and filtered. The resulting solution was concentrated to one-fourth of the original volume under the reduced pressure. Precipitation of **1** was completed by standing overnight after the addition of hexane (150 cm^3) to the concentrated solution. The resulting grayish powder was collected on a glass filter, washed with hexane three times, and dried under reduced pressure to give $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ (**1**). Yield 2.27 g (60%).

Reaction of **1 with Triethoxyvinylsilane.** A toluene- d_8 suspension (0.6 cm^3) of **1** (40 mg, 0.04 mmol) containing triethoxyvinylsilane (23 mg, 0.12 mmol) in an NMR tube was degassed with

freeze-thaw cycles and sealed under vacuum. After the mixture was heated at 110 °C for 5 min, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the resulting solution showed two singlets at $\delta = 48.7$ and 48.9, a pair of one doublet at $\delta = 50.3$ ($^2J_{\text{PP}} = 15$ Hz) and one triplet at $\delta = -36.9$ and three slightly broad signals at $\delta = 46.1$, 45.3, and 42.6, besides the signals due to **1** and free PPh_3 . The singlet at $\delta = 48.7$ was assigned to **2**,¹⁴ whereas the pair of the doublet and the triplet was ascribed to **3**.¹⁴ The four small singlets at $\delta = 48.9$, 46.1, 45.3, and 42.6, have not been identified so far.

Analyses of the Gas Phase. A mixture of **1** (80 mg, 0.087 mmol) and triethoxyvinylsilane (120 mg, 0.63 mmol) in 20 cm^3 of mesitylene was placed in a glass tube sealed with a rubber septum. The mixture was degassed with the freeze-thaw cycles before dry nitrogen was introduced into the glass tube. The glass tube was heated at 110 °C for 1 h. The gas phase of the glass tube was analyzed on a GC-MS instrument. Methane was detected in 63% yield based on **1**.

Reaction of **1 with Styrene.** An NMR tube involving **1** (20 mg, 0.02 mmol), styrene (7 mg, 0.07 mmol), and 0.50 cm^3 of toluene- d_8 was sealed and heated at 110 °C. After 30 min, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 30 °C showed a broad signal near $\delta = 55$ –57, overlapping with a doublet at $\delta = 56.4$ ($^2J_{\text{PP}} = 17$ Hz) due to **1**, together with a triplet at $\delta = 44.3$ caused by **1** and the signals ascribed to **3** and PPh_3 . On cooling at -50 °C, the broad signal near $\delta = 55$ –57 changed to two doublets at $\delta = 55.7$ ($^2J_{\text{PP}} = 9.8$ Hz) and 57.0 ($^2J_{\text{PP}} = 9.8$ Hz), ascribed to the major species, $[\text{Ru}(\text{CO})(\text{CH}_2=\text{CHPh})_2(\text{PPh}_3)_2]$ (**4**). **4**: ^1H NMR (toluene- d_8 , 30 °C) $\delta = -0.96$ (dt, $^3J_{\text{HH}} = 8.5$ Hz, $^3J_{\text{HP}} = 6$ Hz, 2H, $\text{HC}=\text{C}$), 1.85 (br, 2H, $\text{HC}=\text{C}$), 5.34 (m, 2H, $\text{PhHC}=\text{C}$). The very broad signal near $\delta = 1.85$ changed to a slightly broad multiplet at $\delta = 1.74$ at -50 °C.

Reaction of **1 with Isoprene.** A reaction tube containing **1** (0.20 mmol), isoprene (270 mg, 4.0 mmol), and 10 cm^3 of benzene was degassed and sealed. After the reaction tube was heated at 70 °C for 6 h, the reaction mixture was diluted with hexane to give reddish-brown powders, $[\text{Ru}(\text{CO})(\eta^4\text{-CH}_2=\text{CMeCH}=\text{CH}_2)(\text{PPh}_3)_2]$ (**5**). Yield 82%. Found: C, 69.47; H, 5.57%. Calcd for $\text{C}_{42}\text{H}_{38}\text{OP}_2\text{Ru}$: C, 69.89; H, 5.31%. IR $\nu(\text{C}=\text{O})$ 1900 (vs) cm^{-1} . This complex **5** was confirmed to be composed of two isomers, **5a** and **5b**, in a ratio of about 93 : 7 by means of NMR data. ^1H NMR (CDCl_3) **5a**: $\delta = -1.41$ (qua, $^3J_{\text{HP}} \approx ^3J_{\text{HH}} = 7$ Hz, 0.93H, $\text{H}_{\text{anti-C}^{\text{term}}}$), -1.07 (t, $^3J_{\text{HP}} = 6$ Hz, 0.93H, $\text{H}_{\text{anti-C}^{\text{term}}}$), 0.78 (t, $^3J_{\text{HP}} = 5$ Hz, 0.93H, $\text{H}_{\text{syn-C}^{\text{term}}}$), 1.78 (br, 0.93H, $\text{H}_{\text{syn-C}^{\text{term}}}$), 2.28 (d, $J = 2$ Hz, 2.79H, CH_3), 4.64 (br, 0.93H, $\text{H}-\text{C}^3$), 7.08–7.29 (30H, phenyl-H's of **5a** and **5b**). **5b**: $\delta = -1.30$ (br, 0.07H, $\text{H}_{\text{anti-C}^{\text{term}}}$), -0.81 (br, 0.07H, $\text{H}_{\text{anti-C}^{\text{term}}}$), 0.99 (br, 0.07H, $\text{H}_{\text{syn-C}^{\text{term}}}$), 2.25 (br, 0.21H, CH_3), 5.08 (br, 0.07H, $\text{H}-\text{C}^3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) **5a**: $\delta = 47.4$ (slightly br s, 0.93P), 57.5 (slightly br s, 0.93P). **5b**: $\delta = 44.0$ (br, 0.07P), 56.4 (br, 0.07P). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) **5a**: $\delta = 22.2$ (s, CH_3), 40.3 (s, C^{term}), 40.3 (d, $^2J_{\text{CP}} = 26$ Hz, C^{term}), 88.4 (s, C^2), 97.2 (s, C^3), 127.2 (d, $^3J_{\text{CP}} = 7$ Hz, *m*-C of PPh_3), 127.6 (d, $^3J_{\text{CP}} = 7$ Hz, *m*-C), 128.2 (s, *p*-C of PPh_3), 128.7 (s, *p*-C), 133.4 (d, $^2J_{\text{CP}} = 14$ Hz, *o*-C of PPh_3), 133.8 (d, $^2J_{\text{CP}} = 14$ Hz, *o*-C), 138.4 (d, $^1J_{\text{CP}} = 24$ Hz, *ipso*-C of PPh_3), 138.8 (d, $^1J_{\text{CP}} = 24$ Hz, *ipso*-C), 207.3 (d, $^2J_{\text{CP}} = 7$ Hz, $\text{C}=\text{O}$). No $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum due to **5b** was observed because there was less available than there was of major isomer **5a**.

Reaction of **1 with (*E*)-1,3-Pentadiene.** A reaction tube involving **1** (0.20 mmol), (*E*)-1,3-pentadiene (4.0 mmol), and benzene (10 cm^3) was heated at 70 °C for 12 h. Addition of hexane to the reaction mixture gave no precipitate. Then, evaporation of the solvents afforded a reddish-brown oily product. The

$^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra indicate that the major component was $[\text{Ru}(\text{CO})\{\eta^4\text{-(E)-CH}_2\text{=CHCH=CHMe}\}(\text{PPh}_3)_2]$ (**6a**), and it was contaminated with about 19% of PPh_3 , 1% of O=PPh_3 , and a slight amount of the other isomer, (**6b**). **6a**; ^1H NMR (CDCl_3) δ = -1.01 (quar, $^3J_{\text{HP}} \equiv ^3J_{\text{HH}} = 7$ Hz, $\text{H}_{\text{anti-C}}^{\text{term}}$), -0.56 (quin, $^3J_{\text{HP}} \equiv ^3J_{\text{HH}} = 6$ Hz, $\text{H}_{\text{anti-C}}^{\text{term}}$), 1.16 (t, $^3J_{\text{HP}} = 4$ Hz, $\text{H}_{\text{syn-C}}^{\text{term}}$), 1.34 (t, $^3J_{\text{HH}} \equiv ^4J_{\text{HP}} = 5$ Hz, 3H, CH_3), 4.74 (d, $^3J_{\text{HP}} = 3$ Hz, H-C^3), 5.00 (s, H-C^2) 7.02–7.34 (30H, phenyl-H's of PPh_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) **6a**; δ = 44.6 (d, $^2J_{\text{PP}} = 3.1$ Hz), 56.6 (d, $^2J_{\text{PP}} = 3.1$ Hz). **6b**; δ = 44.2 (d, $^2J_{\text{PP}} = 17$ Hz), 56.2 (d, $^2J_{\text{PP}} = 17$ Hz).

Reaction of 1 with 2-Methyl-2-propenal. A reaction tube containing **1** (0.20 mmol), triethoxyvinylsilane (80 mg; 0.40 mmol), 2-methyl-2-propenal (42 mg, 0.60 mmol), and toluene (10 cm^3) was sealed and heated at 110 $^\circ\text{C}$ for 1 h. The reaction mixture was diluted with hexane to give yellow solids, $[\text{Ru}(\text{CO})(\eta^4\text{-CH}_2\text{=CMeCH=O})(\text{PPh}_3)_2]$ (**7**). Yield 69%. Found: C, 67.56; H, 5.16%. Calcd for $\text{C}_{41}\text{H}_{36}\text{O}_2\text{P}_2\text{Ru}$; C, 68.04; H, 5.01%. The spectroscopic data were identical with those of the authentic sample.¹⁹

Reaction among 1, Styrene, and 3'-(Trifluoromethyl)acetophenone at 70 $^\circ\text{C}$. An NMR tube involving **1** (40 mg, 0.04 mmol), styrene (21 mg; 0.20 mmol), 3'-(trifluoromethyl)acetophenone (70 mg, 0.37 mmol), and benzene- d_6 (0.50 cm^3) was sealed and heated at 70 $^\circ\text{C}$. The $^{31}\text{P}\{^1\text{H}\}$ - and ^1H NMR spectra were measured at adequate intervals. After 5 min, the first species P,P' -*cis*- C,H -*cis*- $[\text{Ru}\{\text{C}_6\text{H}_3(\text{CF}_3)\text{C(=O)Me}\}\text{H}(\text{CO})(\text{PPh}_3)_2]$ (**8**) appeared. **8**; $^{31}\text{P}\{^1\text{H}\}$ NMR δ = 33.5 (d, $^2J_{\text{PP}} = 19.5$ Hz) and 36.9 (d, $^2J_{\text{PP}} = 19.5$ Hz). ^1H NMR δ = -6.07 (dt, $^2J_{\text{HP}} = 91$ Hz and $^2J_{\text{HP}} = 26$ Hz). Furthermore, in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, three small unidentified singlets were also detected at δ = 24.1, 31.8, and 35.8.

The signals of **8** increased gradually with reaction time; meanwhile, the signals due to **1** decreased slowly. After 10 min, the second species P,P' -*trans*- C,H -*trans*- $[\text{Ru}\{\text{C}_6\text{H}_3(\text{CF}_3)\text{C(=O)Me}\}\text{H}(\text{CO})(\text{PPh}_3)_2]$ (**9**) emerged. **9**; $^{31}\text{P}\{^1\text{H}\}$ NMR δ = 52.3 (s). ^1H NMR δ = -3.10 (t, $^2J_{\text{HP}} = 21.3$ Hz, HRu).

After 20 min, one of the unidentified signal at δ = 35.8 disappeared. Then, the ratios of phosphorus contents of **1**, **8**, **9**, free PPh_3 , and the remaining unidentified singlets at δ = 24.1 and 31.8 were 79.6 : 8.3 : 1.8 : 8.8 : 0.5 : 1.0, respectively, corresponding to the approximate molar ratio of 82.1 : 12.8 : 2.7 : 27.1 (free PPh_3) : 0.8 : 1.5 (ruthenium species = 100) on the assumption that the unidentified singlets were caused by bis(triphenylphosphine)ruthenium species.

At the same time, the ^1H NMR spectrum of the reaction mixture showed two sets of signals due to the coupling products, besides signals of ethylbenzene, the hydrogenated product, and unreacted styrene and 3'-(trifluoromethyl)acetophenone. ^1H NMR; One coupling product, 2'-(2-phenylethyl)-5'-(trifluoromethyl)acetophenone (**10**) δ = 1.91 (s, 3H, CH_3), 2.77 (t, $^3J_{\text{HH}} = 7$ Hz, 2H, CH_2Ph), 3.05 (t, $^3J_{\text{HH}} = 7$ Hz, 2H, CH_2). The other product, 2'-(1-phenylethyl)-5'-(trifluoromethyl)acetophenone (**11**) δ = 1.38 (d, $^3J_{\text{HH}} = 7$ Hz, 3H, CH_3), 1.82 (s, 3H, $\text{CH}_3\text{C=O}$), 4.92 (quar, $^3J_{\text{HH}} = 7$ Hz, 1H, CH). The relative ratio of **10** : **11** was about 1 : 1.1.

Reactions among 1, Styrene, and 3'-(Trifluoromethyl)acetophenone at 110 $^\circ\text{C}$. An NMR tube containing **1** (0.04 mmol), styrene (27 mg; 0.26 mmol), 3'-(trifluoromethyl)acetophenone (71 mg; 0.38 mmol), and benzene- d_6 (0.50 cm^3) was sealed and heated at 110 $^\circ\text{C}$. The species **8** and **9** grew rapidly within 10 min, and decreased gradually along with reaction time. After 30 min, there appeared the third species, P,P' -*trans*- C,H -*cis*- $[\text{Ru}\{\text{C}_6\text{H}_3(\text{CF}_3)\text{C(=O)Me}\}\text{H}(\text{CO})(\text{PPh}_3)_2]$ (**12**). $^{31}\text{P}\{^1\text{H}\}$ NMR δ = 51.7 (s). ^1H NMR δ = -14.6 (t, $^2J_{\text{HP}} = 21.3$ Hz, HRu). The ^1H NMR spectrum indicated

that the two coupling products **10** and **11** were produced in a ratio of about 1 : 0.33. Moreover, five small unidentified singlets at 23.6, 31.8, 32.2, 32.6, and 32.8 were observed.

When the reaction was continued for an additional 30 min, styrene was consumed completely, and the coupling reaction was terminated. A slight amount of **2** was also formed. Then, the relative ratios of the phosphorus contents of **1**, **2**, **8**, **9**, **12**, free PPh_3 , and the unidentified singlets at δ = 23.6, 31.8, 32.2, 32.6, and 32.8 were 30.9 : 1.7 : 13.1 : 5.3 : 3.8 : 31.2 : 2.0 : 2.9 : 5.9 : 1.7 : 1.5, respectively, corresponding to the approximate molar ratio of 35.6 : 2.0 : 22.6 : 9.1 : 6.6 : 107.7 (free PPh_3) : 3.5 : 5.0 : 10.1 : 2.9 : 2.6 (ruthenium species = 100), on the assumption that the unidentified signals were due to bis(triphenylphosphine)ruthenium species. The sum of the intensities of the bis(triphenylphosphine)ruthenium species does not coincide well with that of the free PPh_3 , probably because of the errors of the calculated intensities for the $^{31}\text{P}\{^1\text{H}\}$ NMR signals and the possible presence of mono(triphenylphosphine)ruthenium species in the reaction mixture.

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