Reactions of Dihydridotetrakis(triphenylphosphine)ruthenium(II) with Olefins and Isolation of New Ruthenium-Olefin Complexes

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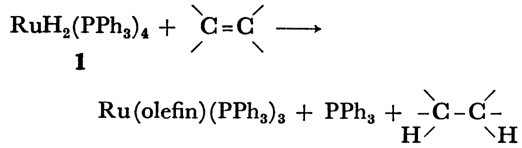
Dihydridotetrakis(triphenylphosphine)ruthenium(II), $RuH_2(PPh_3)_4$, reacts with olefins (ethylene, propylene, styrene and butadiene) to give olefin-coordinated complexes of the type, $Ru(olefin)(PPh_3)_3$ and equimolar amounts of their hydrogenation products per mol of the dihydride complex. The olefin coordinated with ruthenium can be exchanged with other olefins. Olefin-coordinated complexes easily react with molecular hydrogen to afford tetrahydridotris(triphenylphosphine)ruthenium, $RuH_4(PPh_3)_3$, releasing alkane at room temperature. Under hydrogen atmosphere, catalytic hydrogenation of the olefins smoothly takes place with $RuH_2(PPh_3)_4$. (Ethylene)tris(triphenylphosphine)ruthenium(0) reacts with methyl iodide to give propylene and a trace of butadiene along with methane, ethylene, and small amounts of ethane and butenes. The formation of propylene suggests that oxidative addition involving cleavage of the C–H bond of ethylene to ruthenium giving a hydrido-vinyl complex may be taking place. Reactions of $Ru(C_2H_4)(PPh_3)_3$ with methyl-d_3 iodide and ethyl iodide, and of $Ru(C_3H_6)(PPh_3)_3$ with methyl iodide were examined to test the generality of this type of reaction. The reaction of $Ru(C_2H_4)(PPh_3)_3$ with CD_3I released CD_4 and CD_2H_2 together with CD_3H suggesting the involvement of α-hydrogen abstraction.

Recent progress in organo-transition metal chemistry has contributed to better understanding of the reaction mechanisms in various olefin catalysis with transition metals and their compounds. Study of properties of transition metal dihydride complexes[1] or transition metal complexes, which form dihydride complexes on reaction with molecular hydrogen,[2] has shed light on the detailed mechanism how an olefin coordinates to the transition metal hydride and is inserted between the metal-to-hydrogen bond. Dihydridotetrakis(triphenylphosphine)ruthenium(II),[3] **1**, has been found to serve as a particularly illustrative model compound of olefin catalyses, since it is itself catalytically active in hydrogenation, isomerization,[4] polymerization[5] and isotopic hydrogen exchange[6] of olefins, and on the other hand it gives many olefin-coordinated complexes on reactions with various olefins. We describe here characterization and properties of these olefin-coordinated complexes (ethylene, propylene, styrene and butadiene complexes) and the mechanism of formation of the olefin complexes from **1**. We have previously found that a seemingly simple olefin-coordinated complex with an apparent composition of Ru(alkyl methacrylate)$(PPh_3)_3$ was in fact a hydrido–propenyl type complex $RuH\{CH=C(CH_3)C(O)OR\}(PPh_3)_3$ which was formed by oxidative addition involving cleavage of C–H bond adjacent to the double bond.[7] Examination of the properties of the present olefin-complexes also revealed some features which may be best accounted for by assuming the contribution of a hydrido-vinyl type structure.

Results and Discussion

Reactions of $RuH_2(PPh_3)_4$ 1 with Olefins. The dihydridoruthenium complex **1** reacts with very electronegative olefins such as tetracyanoethylene and maleic anhydride to give stable olefin complexes[3] and initiates the polymerization of less electronegative vinyl compounds such as acrylonitrile, methacrylonitrile, acrylaldehyde and methyl acrylate.[5] Olefins such as ethylene, propylene, styrene and butadiene, on the other hand, react with **1** to give their hydrogenated products and ruthenium complexes containing these olefins.



2, olefin = ethylene
3, olefin = propylene
4, olefin = styrene
5, olefin = butadiene

These olefin-complexes **2**—**5** are thermally labile than complexes containing very electronegative olefins but can be isolated under appropriate conditions. Table 1 summarizes the analytical data, yields, NMR data and physical properties of the isolated complexes.

The reactions of ethylene, propylene and styrene with **1** proceed smoothly at room temperature to form quantitatively 1 equiv. of ethane, propane and ethylbenzene, respectively. The hydrogenation product of butadiene with **1** consisted of 1-butene and small amounts of *cis*- and *trans*-2-butene, the latters may be formed by isomerization of 1-butene catalyzed by **1**.[4] The molar ratio of the sum of the *cis*- and *trans*-2-butene to 1-butene decreased with increase in the amount of butadiene used in the reaction. The result also suggests that the isomerization of 1-butene was catalyzed by the remaining dihydride complex **1** and not by the butadiene-complex.

In the presence of a large excess of butadiene, **1** afforded an extremely soluble complex which could not be completely characterized but appears to contain two butadiene molecules coordinated with ruthenium.

Characterization of the Olefin-coordinated Complexes. The isolated complexes were characterized by means of elemental analysis, IR and NMR spectroscopy and chemical reactions.

None of the isolated olefin-complexes showed an IR

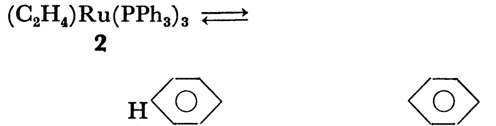
TABLE 1. ANALYTICAL AND NMR DATA AND PHYSICAL PROPERTIES OF OLEFIN COMPLEXES

	Complex[a]	Analysis (Found) C %	Analysis (Found) H %	Color Dec. pt. (°C)	Yield	^{1}H-NMR[b]	^{31}P-NMR[f]
2	$Ru(E)(PPh_3)_3$	73.8	5.5	White	49%	1.5—2.5 (br, $C_2\underline{H}_4$)[c]	
		(73.4)	(5.4)	150—155			
3	$Ru(P)(PPh_3)_3$	74.9	5.1	White	—		
		(73.6)	(5.5)	170			
4	$Ru(St)(PPh_3)_3$	76.0	5.4	Red purple	—	7.51 (br, $=C\underline{H}_2$)[d]	
		(75.1)	(5.4)	—		5.79 (br, $=C\underline{H}-$)	
5	$Ru(BD)(PPh_3)_3$	74.4	6.2	Greenish yellow	37%	−0.05 (br, H_a)[c,e]	58.7 (t, P_1)[g]
		(74.0)	(5.4)	185		1.49 (br, H_b)[c,e]	50.5 (d, P_2)[g]
						4.91 (br, H_c)[c,e]	

a) Abbreviation: E, ethylene; P, Propylene; St, styrene; BD, butadiene. b) δ Value in ppm downfield from TMS positive; t, triplet; d, doublet; br, broad unresolvable signal. c) Solvent: benzene-d_6. d) Solvent: styrene. e) See text for the designation. f) Chemical shifts in ppm downfield positive from external PPh_3 g) $J_{P_1-P_2}=12$ Hz, see text for designation of P_1 and P_2.

band ascribable to ν(Ru–H). Unambiguous assignment of the ν(C=C) band of the coordinated olefin was not feasible because the shift of the weak ν(C=C) band to lower frequency on coordination of the olefin to ruthenium makes it overlap with other strong bands due to triphenylphosphine.

a) Ethylene- and Propylene-coordinated Complexes: On iodolysis in benzene solution at room temperature complex **2** released one equiv. of ethylene, whereas thermolysis and acidolysis of **2** liberated ethane in addition to ethylene. The reaction product of **2** with acetic acid gave the known hydrido acetate complex $RuH(OAc)(PPh_3)_3$.[8] The formation of ethane in the acidolysis and thermolysis may be caused by intervention of an ethylruthenium complex formed by *ortho*-metallation of one of the triphenylphosphine ligands in **2** by presence of equilibria such as:



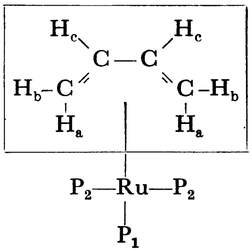
A low activity of the ethylene complex **2** in comparison to the high activity of the dihydride complex **1** for polymerization of vinyl compounds may be also due to the presence of the above equilibria. In contrast with **2**, the propylene-coordinated complex **3** released only small amounts of propylene on iodolysis, thermolysis and acidolysis.

The NMR spectrum of **2** in benzene showed a broad band at δ 1.5—2.5 which may be due to the coordinated ethylene. In the presence of added ethylene both peaks of the coordinated and uncoordinated ethylene were observed and they showed broadening on raising the temperature suggesting an exchange reaction taking place between the coordinated and uncoordinated ethylene. Further support for the exchange was obtained by studying the exchange reaction of C_2D_4 with **2**.[4,6]

b) Styrene-coordinated Complex 4: The styrene-coordinated complex **4** can be obtained as a purple solid which can be crystallized from toluene containing styrene. In the absence of free styrene, complex **4** is unstable and readily decomposed in many solvents. Addition of a large excess of toluene to **4** caused the separation of a yellow precipitate which was identified as $RuH_2(PPh_3)_4$ on the basis of its elemental analysis and IR spectrum showing a ν(Ru–H) band at 2080 cm^{-1}. The decomposition of **4** in toluene released ethylbenzene and strene in a molar ratio of *ca.* 3: 1. The combined molar amount of ethylbenzene and styrene was equivalent to **4**. When **4** was decomposed in tetrachloroethylene, which carries no hydrogen to be abstracted, the molar ratio of ethylbenzene to styrene sharply decreased to 1: 9. The fact indicates that the solvent was the major hydrogen source in decomposition of **4** in toluene. The generation of the small amount of ethylbenzene in the decomposition of **4** in tetrachloroethylene may be ascribed to hydrogen abstraction from the triphenylphosphine ligands. The decomposition product in tetrachloroethylene had a composition close to $Ru(C_2Cl_4)(PPh_3)_3$. The molar ratio of ethylbenzene to styrene generated in the decomposition of **4** in various solvents depended on the solvents used; *e,g.*, in pyridine the ratio was 1:3. No gas was released on iodolysis of **4**.

Because of the instability of **4** in solvents other than styrene itself, the NMR spectrum of **1** was observed in styrene. In addition to the signals of ethylbenzene, two broad peaks at δ 7.51 and 5.79 were observed in a ratio of 1: 2. By comparison of the peak intensities of these peaks with the resonances of ethylbenzene, 1 equiv. of which was confirmed to be formed by an independent method using gas chromatography, these broad peaks are assigned to vinyl protons of styrene coordinated to ruthenium in a 1: 1 molar ratio.

c) Butadiene-coordinated Complex 5: The ^{1}H-NMR spectrum of **5** in benzene shows three peaks of an equal intensity at δ −0.05, 1.49, and 4.91 ppm. These signals may be due to protons H_a, H_b, and H_c of butadiene coordinated with ruthenium as illustrated by a model below to represent one of the possible structures for this complex:



5　$P_1=P_2=PPh_3$

Keim reported the preparation of a butadiene-coordinated rhodium complex having a composition of $Rh(C_4H_6)(PPh_3)(Ph_2PC_6H_4)$ which shows three peaks of equal intensity at δ 0.4, 2.3, and 4.9 ppm and assigned these peaks in a similar manner to the present case.[9]

The proton decoupled ^{31}P-NMR spectrum of **5** shows an AX_2 type spectrum at 58.7 (triplet) and 50.5 ppm (doublet) downfield from reference PPh_3 in a ratio of 1 : 2. The spectrum is consistent with the above structure having two equivalent and one non-equivalent triphenylphosphine ligands.

Reactions of the Olefin-complexes with Hydrogen. Contact of a benzene solution of $Ru(olefin)(PPh_3)_3$ with molecular hydrogen at room temperature converts the coordinated olefin into its hydrogenated product and gives the known tetrahydridotris(triphenylphosphine)-ruthenium.[10] The reaction probably proceeds through an unstable intermediate $RuH_2(olefin)(PPh_3)_3$ from which alkane may be produced.

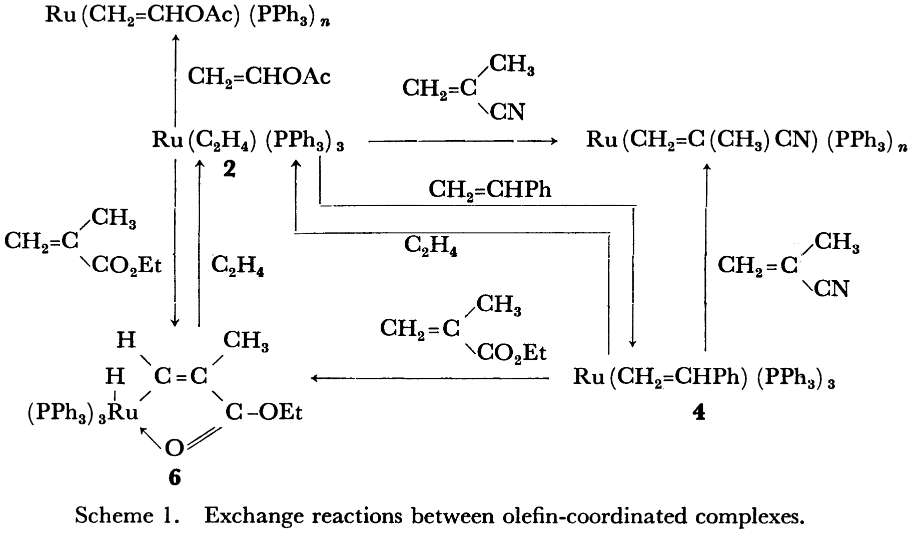
$$\begin{tikzcd} Ru(olefin)(PPh_3)_3 + H_2 \arrow[r] & RuH_2(olefin)(PPh_3)_3 \arrow[d] \\ & Ru(PPh_3)_3 + alkane \arrow[d, "+2H_2"] \\ & RuH_4(PPh_3)_3 \end{tikzcd}$$

Olefin Exchange Reactions. The olefin coordinated with ruthenium in the isolated complexes **2**—**5** can be readily displaced by another olefin. Scheme 1 summarizes the typical exchange reactions. Ethylene in **2** may be readily displaced by styrene with liberation of ethylene and ethane, and styrene in **4** by ethylene with release of styrene and ethylbenzene. Methacrylonitrile displaces ethylene in **2** and styrene in **4** to give a methacrylonitrile-coordinated complex with a ν(C≡N) band at 2180 cm^{-1} which is shifted to lower frequency by *ca.* 40 cm^{-1} from the ν(C≡N) band of free methacrylonitrile, the shift indicating a coordination through the olefinic double bond to ruthenium.[11] The ^1H-NMR spectrum of the methacrylonitrile-complex having broad peaks of the vinylic protons of the coordinated methacrylonitrile at δ 5.3 and 4.9 ppm, which are shifted to higher field than the resonances of free methacrylonitrile, also suggests the π-type coordination. Purification of the complex by recrystallization has failed.

In contrast to the reaction of vinyl acetate with **1** which causes the C–O bond cleavage of vinyl acetate to give ethylene and $RuH(OAc)(PPh_3)_3$[12] the reaction of vinyl acetate with **2** gave a vinyl acetate–ruthenium complex with a ν(C=O) band at 1736 cm^{-1}. The structure of the complex has not been fully characterized.

As reported separately, the reaction of ethyl methacrylate with **2** or **4** gave a new oxidative addition product **6**, which has a five-membered ring as shown in Scheme 1.[7] Reaction of ethylene with **6** partially converted **6** to **2**.

Evidence for Oxidative Addition of Olefins to Ruthenium Affording Hydrido-vinylic Complexes. The bonding between an olefin and a transition metal in an olefin-coordinated complex is generally elucidated in terms of Dewar-Chatt-Duncanson model[13] and there are ample examples[14] in which the side-on type π-coordination of the olefin to the metal has been established by X-ray structural determination.[15] However, we recently encountered a case that a seemingly simple olefin complex between between alkyl methacrylate and ruthenium turned out to have a σ-vinylic-hydrido structure, $RuH(CH=C(CH_3)COOR)(PPh_3)_3$, **6**. This complex appeared first as a simple olefin complex on the basis of characterization technique we routinely employ. For example, thermolysis, iodolysis and acidolysis of the complex liberated the alkyl methacrylate. However the treatment with methyl iodide released the methyl substituted product of the alkyl methacrylate at the β-position, *i.e.*, $CH_3CH=C(CH_3)(COOR)$. This result



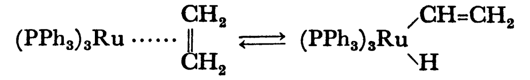
Scheme 1. Exchange reactions between olefin-coordinated complexes.

TABLE 2. REACTIONS OF OLEFIN COMPLEXES WITH ALKYL HALIDES

Olefin complex	RX	Temp (°C)	Compositions of gases evolved[b)]									
			CH_4[a)]	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_6	Δ^1-C_4H_8	Δ^2-C_4H_8 *cis*	2-C_4H_8 *trans*	C_4H_{10}
$Ru(C_2H_4)(PPh_3)_3$ **2**	MeI	−30		100	0	t	0	0	tt	0	0	0
	MeI	rt	86	82	7	9	0	tt	tt	2	tt	0
	MeI	65	79	81	7	12	0	t	t	t	tt	0
	EtI	rt	0	80	t	0	0	tt	10	tt	tt	10
$Ru(C_3H_6)(PPh_3)_3$ **3**	MeI	65		t	t	58	6	11	21	1	3	0

a) Percentage of gas evolved per mol of olefin complex. b) Compositions of the gases other than methane in percentage. The symbols t and tt mean that very small amounts of the gases were detected; t, <0.5%; tt, 0.05%.

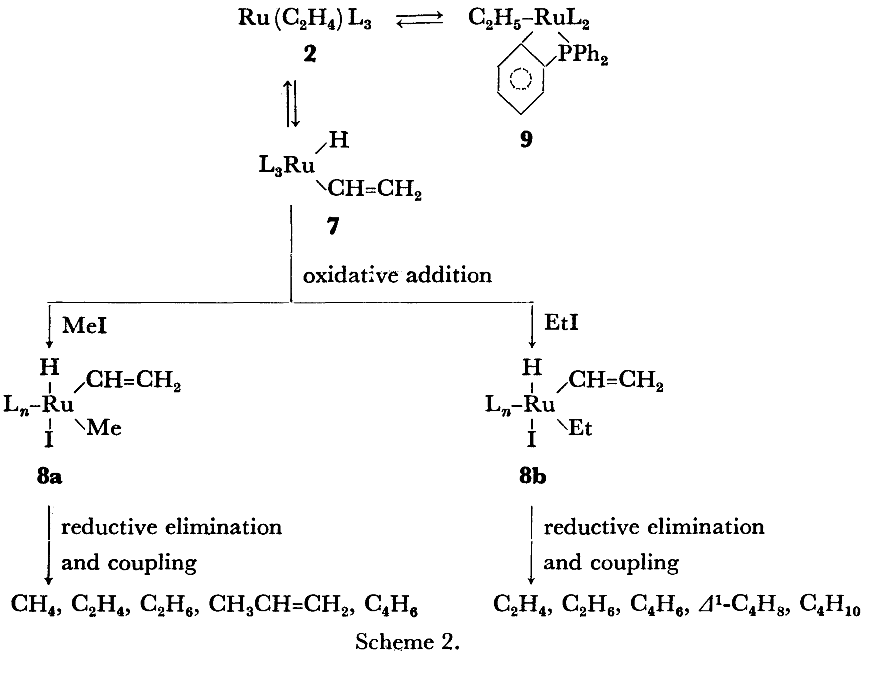
together with the IR and NMR spectral analysis led us to the conclusion that the methacrylate-coordinated complex has the hydrido-vinylic structure, which has prompted us to reexamine the olefin-coordinated complexes reported here to see if the seemingly olefin-coordinated complexes actually have hydrido-σ-vinyl structures or if a tautomeric equilibrium such as shown below may exist:



$$(PPh_3)_3Ru\cdots\cdots\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} \rightleftarrows (PPh_3)_3Ru\begin{matrix}/CH{=}CH_2\\ \backslash H\end{matrix}$$

Neither NMR nor IR spectra of **2** showed any sign of the hydridovinyl structure and chemical reactions of **2**, such as thermolysis, iodolysis, and acidolysis provide no information to support the presence of the hydrido-vinyl species. However, experimental results in favor of the involvement of the hydrido-vinylic species were obtained from the analysis of the reaction products of **2** and **3** with alkyl halides. Table 2 shows the compositions of gases evolved on reactions of **2** and **3** with methyl and ethyl iodides. The composition of the evolved gas on treatment of **2** with methyl iodide varied depending on the reaction temperature. At −30° the gas evolved consisted predominantly of ethylene and traces of propylene and 1-butene. Upon raising the reaction temperature the content of propylene in the evolved gas significantly increased. The similar reaction of **2** with ethyl iodide produced a considerable amount of 1-butene. Noteworthy here is the formation of butadiene although in a minute amount. Scheme 2 shows the reaction paths and olefins expected to be produced, provided that the oxidative addition of methyl iodide to the suspected vinyl-hydrido species should take place.

Formation of methane and ethane in the reaction of methyl iodide with **2** may be accounted for by assuming reductive elimination of the methyl and hydrido ligands and intermolecular coupling of the methyl ligands in the assumed reaction intermediate **8a** which may be formed by oxidative addition of methyl iodide to the hydrido-vinylic intermediate **7** in Scheme 2. Ethylene may arise directly by liberation of the coordinated ethylene from **2** and/or by reductive elimination of the ethyl and hydrido ligands in **8a**. The formation of propylene may be accounted for by reductive elimination of the methyl and vinyl ligands in **8a**. Butadiene may also arise by intermolecular coupling of the two vinyl groups in **8a**. If the assumption of the presence of the vinyl-hydrido species **7** should be valid, the fact that the amount of propylene increases at the

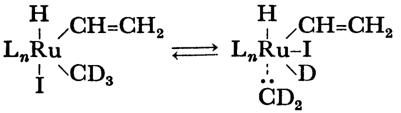


Scheme 2.

expense of ethylene as temperature rises may indicate the shift of the equilibrium between **2** and **7** to the side of **7**. The reaction path **2**→**7**→**8a**, on the other hand, does not account for the formation of butenes in the reaction of **2** with methyl iodide, and it seems necessary to invoke the intervention of the previously discussed ethylruthenium species *(vide supra)* which might produce butene by cross-coupling with the vinyl complex **8a**. The presence of the ethylruthenium species such as **9** in Scheme 2 has previously been suggested on the basis of experiments using deuterated compounds.[6,16]

Similar arguments may be advanced to account for the reaction products of **2** with ethyl bromide by assuming an intermediate **8b** in Scheme 2. 1-Butene formed in the reaction of **2** with ethyl iodide may be produced by reductive elimination of the ethyl and vinyl groups and butane by an intermolecular coupling of the ethyl groups in **8b**.

In order to obtain further information on the reaction of the olefin complex with alkyl halide, the reaction products of **2** with methyl-d_3 iodide were examined. The gas evolved on reaction of **2** with CD_3I at 65 °C was fractionated by GLC and analyzed by mass spectrometry. The result of the product analysis revealed another unexpected aspect of the reaction as shown in experimental section. The formation of CD_4 may be explained by deuterium abstraction from CD_3I or by α-elimination process. The former possibility does not reconcile with the formation of polydeuterated butenes C_4D_8, C_4D_7H and others. Therefore we propose that α-elimination is involved here as shown below.

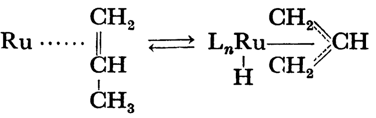


8a　**10**

We have previously presented evidence for such α-elimination reaction in the decomposition of a methyl–iron complex.[17] Formation of CD_3H, C_2H_4, C_2H_3D, C_2D_6, and $C_3H_3D_3$ can be elucidated by assuming the species **8a** and **10** shown above The formation of polydeuterated butenes may be accounted for by H–D exchange in the ethyl group in species **9** and in the vinyl group in species **10** and cross-coupling of the ethyl and vinyl groups.

In order to examine the generality of this type of reaction the reaction products of other ethylene-complexes, $Fe(C_2H_4)(diphos)_2$[18] and $Pd(C_2H_4)(PPh_3)_2$,[19] with methyl iodide were examined. Ethylene and methane were the main products and only traces of propylene and butenes were detected.

Table 2 also includes the reaction products of $Ru(C_3H_6)(PPh_3)_3$ **3** with methyl iodide at 65 °C. In addition to propylene and propane considerable amounts of butadiene and butenes accompanied by traces of ethylene and ethane were produced. The pattern of the product distribution is noticeably different from that of the reaction of **2** and alkyl halide, and it is required to invoke another type of a reaction intermediate as shown below.



The predominant formation of 1-butene and its isomerization products may be accounted for by postulating the involvement of the π-allyl-hydrido species. The formation of butadiene requests α-elimination of the methyl group to produce a hydrido-carbene species, which may combine with the π-allyl group. The formation of π-allyl-hydrido species from a π-propylene complex has a precedent in a nickel complex prepared by Bönneman *et al.*,[20] and we have also observed hydrogen abstraction from the methyl group in the alkyl methacrylate complex **6**.[7]

The formation of propylene and butenes from **2** and methyl and ethyl iodides may be alternatively explained by postulating the insertion of ethylene into the $Ru-CH_3$ or $Ru-C_2H_5$ bond formed by oxidative addition of the alkyl halides to **2**, followed by β-elimination to produce propylene and butenes leaving a ruthenium hydride. However, the bulk of evidence presented here is difficult to explain without assuming the hydrogen abstraction from the coordinated olefins.

The results we reported here indicates the quite complicated nature of the olefin complexes when they are subjected to various reactions. The behavior of the olefin complexes has implications in the mechanisms of ethylene polymerization by Phillips process using chromium oxide,[21] and palladium-promoted substitution reactions of olefins.[22]

Experimental

General. All the reactions were carried out under nitrogen atmosphere or in a vacuum. Solvents and olefins were purified by usual methods and stored under nitrogen before use. Liquid olefins were introduced by trap-to-trap distillation in a vacuum into the reaction vessel containing the dihydrido-ruthenium complex, **1**. Gaseous olefins were bubbled into or brought in contact with the solution of the dihydrido complex.

Analysis of gases was carried out by mass spectrometry and gas chromatography. Non-condensable gas at liquid nitrogen temperature was collected using a Toepler pump, by which the volume of the gas was measured. Analysis of the hydrogenated products in the reaction of olefins with the ruthenium complexes were carried out by gas chromatography using Shimadzu-3BT Gas Chromatograph after collecting the liquid by trap-to-trap method. IR and NMR spectra were measured with a Hitachi-EPI-G3 spectrometer and a JEOL-100 MHz spectrometer. Complex **1** was prepared by the method reported previously.[3]

(Ethylene)tris(triphenylphosphine)ruthenium, **2**. Complex **1** (798 mg, 0.693 mmol) in benzene was brought in contact with ethylene (3.73 mmol) for a day at room temperature. The color of the solution changed from yellow to red brown accompanied by evolution of ethane which was 110% per mol of complex **1**. By concentration of or on addition of hexane to the solution, white crystals were obtained which were washed several times with hexane and dried in a vacuum. Bubbling ethylene into the 20 ml toluene suspension of complex **1** (4.0 g, 3.5 mmol) at room temperature turned the color of the solution to red in an hour and off-white crystals precipi-

tated in a few hours. (Yield: 49%).

*Reaction of **2** with Iodine.* Complex **2** (0.1569 g, 0.171 mmol) in benzene readily reacted with excess iodine liberating only ethylene (3.96 ml, 0.177 mmol) which was 103% of the calculated value, at room temperature.

*Thermal Decomposition, Acidolysis and Oxidation of Complex **2**.* By thermal decomposition of complex **2** up to 200 °C ethylene and ethane (the molar ratio was 1: 0.6 and total amount was 56% for complex **2**) were evolved. By the reaction of complex **2** (0.16 mmol) with sulfuric acid (10 ml), ethylene and ethane (the molar ratio was 1: 1 and total amount was 0.058 mmol, 36%) were evolved. Oxidation of **2** by dry oxygen liberated ethylene.

*Reaction of **2** with Methyl Iodide.* Methyl iodide (1 ml) was introduced to complex **2** (245 mg, 0.267 mmol) by trap-to-trap distillation. The colorless mixture turned rapidly to black accompanied by evolution of a gas mixture at room temperature. The contents of C_1, C_2, C_3, C_4 olefins and alkanes evolved at −30 °C, room temperature and 65 °C are listed in Table 2.

*Reaction of **2** with Methyl-d$_3$ Iodide.* Methyl-d_3 iodide (0.5 ml) reacted with complex **2** to liberate various gases at 65 °C. The content of the isotopic mixture of the gaseous hydrocarbons formed was analyzed by mass spectrometry after separating the components by gas chromatography. The product consisted of the following compositions.

Methane: CD_4, 65%; CD_3H, 35%, the other, trace. Ethylene: C_2H_4, 79%, C_2H_3D, 21%; the other, trace. Ethane: C_2D_6, main; the other, trace. Propylene: $C_3H_3D_3$, main; the other, trace. Butene: the whole range of butenes from C_4D_8 to C_4H_8 were detected.

*Reaction of Complex **2** with Ethyl Iodide.* Excess ethyl iodide was introduced to complex **2** to release ethylene, butane and 1-butene, and small amounts of ethane, and *cis*- and *trans*-2-butene at room temperature. (see Table 2).

*Reaction of Complex **2** with Ethyl Methacrylate.* Ethyl methacrylate (2 ml) was introduced to complex **2** (106 mg, 0.108 mmol) by trap-to-trap distillation. Ethylene (20 ml) was evolved and yellow crystals were obtained after the reaction mixture was stirred for a day at room temperature. The yellow complex was identified as $RuH(CH{=}C(CH_3)COOEt)(PPh_3)_3$ on the basis of its IR spectrum; ν(Ru–H), 1960 cm^{-1}; ν(C=O), 1580 cm^{-1}. In the case of the reaction of **2** with *cis*-β-ethyl methacrylate-d_1 (isotopic purity, 72%), deuterated ethylene (C_2H_4, 52%; C_2H_3D, 39%; $C_2H_2D_2$, 9%) was evolved but the resulted complex was scarcely deuterated. Deuteriums in ethyl methacrylate recovered after the reaction were found to be distributed in vinyl and methyl positions (isotopic purity, 9%).

*Reaction of Complex **2** with Styrene.* Styrene (2 ml) was introduced to complex **2** (155 mg, 0.192 mmol) by trap-to-trap distillation. The initial partly heterogeneous solution gradually changed to a reddish purple homogeneous solution liberating ethylene (4.23 ml, 0.189 mmol) in a day at room temperature. Although the resultant complex was not purified sufficiently because of its instability toward solvents, it is considered to be a styrene-coordinated complex $Ru(St)(PPh_3)_3$ by comparison of its color and stability with the styrene complex prepared from **1** and styrene.

*Reaction of **2** with Acetic Acid.* Acetic acid (0.5 ml) in benzene (2.5 ml) was introduced to complex **2** (191 mg, 0.209 mmol) by trap-to-trap distillation. The colorless heterogeneous mixture thus formed changed to a yellow homogeneous solution liberating ethylene and ethane in a molar ratio of 2: 1 (total amount of the gas was 0.167 mmol) at room temperature in a few hours. The yellow precipitate was obtained by concentrating the homogeneous solution and was identified as $RuH(OAc)(PPh_3)_3$ by comparison of its IR spectrum with that of an authentic sample. ($\nu(OCO)_{asym}$, 1530 cm^{-1}; $\nu(OCO)_{sym}$, 1450 cm^{-1}).

*Reaction of **2** with Methacrylonitrile.* Methacrylonitrile (2.0 ml) was introduced to complex **2** (482 mg, 0.527 mmol) by trap-to-trap distillation. A yellow homogeneous solution was obtained accompanied by evolution of ethylene (0.392 mmol) in a day at room temperature. Excess methacrylonitrile was evaporated completely to give a yellow oily product. From its extract with hexane a yellow solid was obtained. The IR spectrum of the yellow solid showed a ν(C≡N) band at 2180 cm^{-1} and its NMR spectrum in C_6D_6 showed signals attributable to coordinated methacrylonitrile through the double bond. (δ C=CH$_2$, 5.3 and 4.9 ppm; CH$_3$, 1.3 ppm) and some other unidentified small peaks in a range 1—3 ppm. The resultant complex is tentatively assigned as Ru(methacrylonitrile)-$(PPh_3)_3$.

*(Propylene)tris(triphenylphosphine)ruthenium, **3**.* Propylene (147 ml) was brought in contact with complex **1** (533 mg, 0.463 mmol) in toluene (15 ml) in a sealed system for 2 days at room temperature. Propane (11.4 ml, 110% per complex **1**) was liberated. By adding hexane to the toluene solution a pale brown precipitate was obtained which was washed with hexane and dried in a vacuum. Thermolysis at *ca.* 170 °C and acidolysis by sulfuric acid liberated a small amount of propylene. (5%).

*Reaction of **3** with Methyl Iodide.* Excess methyl iodide (2 ml) was introduced to complex **3** (*ca.* 100 mg) by trap-to-trap distillation at room temperature and methane, propylene and 1-butene were liberated. Small amounts of *cis*- and *trans*-2-butene, butadiene and propane were also detected.

*(Styrene)tris(triphenylphosphine)ruthenium, **4**.* Styrene (3.12 g) was introduced to complex **1** (1.20 mmol) to give a homogeneous purple solution at room temperature in a day. No polymer was obtained from the solution. The solution was evaporated in a vacuum line and ethylbenzene (1.13 mmol) which corresponds to 94% equivalent of complex **1** was detected in the volatile matter. Red crystals were obtained on crystallization from the mixture of styrene and toluene. When complex **4** was dissolved in excess toluene, styrene and ethylbenzene in a molar ratio of 67: 33 were released. From the solution yellow crystals of $RuH_2(PPh_3)_4$ were recovered. (Found: C, 74.9; H, 5.2%. Calcd for $C_{72}H_{62}P_4Ru$: C, 75.1; H, 5.4%.) ν(Ru–H), 2080 cm^{-1} (KBr disk). Complex **4** decomposed also in pyridine to produce a yellow precipitate, apparently $RuH_2(PPh_3)_4$. In pyridine, styrene and ethylbenzene in a molar ratio of 26: 74 were evolved. Complex **4** reacted with tetrachloroethylene to afford a brown complex $Ru(C_2Cl_4)(PPh_3)_3$ releasing styrene and ethylbenzene in a molar ratio of 89: 11. The brown complex was washed several times with hexane and dried in a vacuum. (Found: C, 63.8; H, 4.5%. Calcd for $C_{56}H_{45}Cl_4Ru$: C, 63.7; H, 4.3%.)

*Reaction of Complex **4** with Ethylene.* Ethylene (300 ml) was brought in contact with complex **4** (*ca.* 300 mg) which was frozen in benzene (5 ml) at −196 °C. Temperature of the reaction mixture was raised up to room temperature immediately. A brown homogeneous solution was obtained in 1 h. In the solution styrene and ethylbenzene were detected in a molar ratio of 1: 1. The benzene solution was evaporated to dryness by freeze-drying method to give a pale yellow solid which was tentatively assigned to $Ru(C_2H_4)(PPh_3)_3$ based on the result of thermolysis giving ethylene and ethane in a molar ratio of 2: 1 and no styrene.

*Reaction of Complex **4** with Ethyl Methacrylate.* Ethyl methacrylate (2 ml) was introduced to complex **4** (*ca.* 300 mg) by trap-to-trap distillation. The color of the solution changed to yellow in an hour and yellow crystals were obtained with release of styrene. The yellow crystals were identified as $RuH(CH{=}C(CH_3)COOEt)(PPh_3)_3$ by IR spectroscopy. ν(Ru–H), 1960 cm^{-1}; ν(C=O) 1580 cm^{-1}.

Reaction of Complex 4 with Dry Deuterium Chloride. Dry deuterium chloride was introduced to complex **4** (*ca.* 300 mg) in C_6D_6 by trap-to-trap distillation. After 1 day a red purple precipitate was obtained. All the volatile matter was collected and examined by NMR spectroscopy. Deuterated styrene in which vinyl protons were deuterated by 20% were detected.

Reaction of Complex 4 with Methacrylonitrile. Excess methacrylonitrile reacted with complex **4** at room temperature giving the same compound as the complex obtained from the reaction of complex **2** with methacrylonitrile.

Reaction of Complex 4 with Acrylonitrile. Acrylonitrile (5.0 ml) was introduced to complex **4** (*ca.* 100 mg) by trap-to-trap distillation. Slow polymerization of acrylonitrile took place at room temperature. Yield 1.26 g (31%).

Reaction of Complex 4 with Carbon Dioxide. Carbon dioxide was bubbled into a mixture of toluene and styrene containing the styrene complex for a day at room temperature to give a brown solution. By adding hexane to the brown solution, a brown precipitate was obtained and was washed several times with hexane and dried in a vacuum. The IR spectrum of the brown precipitate shows new bands at 1932 (w), 1660 (m), 1635 (s), 1505 (m), and 600 (s) cm^{-1}. Thermolysis of the brown precipitate (82 mg) liberated carbon dioxide (1.47 ml, 0.0656 mmol). dec 120 °C.

Reaction of Complex 4 with Hydrogen. Hydrogen was bubbled into the styrene solution of complex **4** for a week at room temperature to give a yellow precipitate. Styrene was found to be completely converted to ethylbenzene and $RuH_2(PPh_3)_4$ was obtained. ν(Ru–H), 2080 cm^{-1}.

(Butadiene)tris(triphenylphosphine)ruthenium, 5. Butadiene (2.22 mmol) was brought in contact with complex **1** (1.30 g, 1.13 mmol) in benzene (10 ml) in a sealed system for a day at room temperature to give greenish yellow crystals releasing butenes. In the gas phase 1-butene, *trans*-2-butene and *cis*-2-butene (the molar ratio of 75: 18: 7) were formed and no butadiene was detected. Greenish yellow crystals were recrystallized from benzene or toluene as yellowish green needles which were washed several times with hexane and dried in a vacuum. Thermolysis of the resulted crystals gave *ca.* 5% of 1-butene and acidolysis gave no gas.

A large excess of butadiene (9.59 mmol) reacted with complex **1** (1.86 g, 1.62 mmol) to give an oily product and 1-butene with a small amount of *trans*- and *cis*-2-butene. The oily product could not be characterized because of the difficulty of purification, but the NMR spectrum of the oily product showed signals attributable to the coordinated butadiene (−0.75, 2.00, and 4.54 ppm down field from TMS) and triphenylphosphine. As the amount of butadiene absorbed in the reaction was *ca.* 2.7—3.8 mmol, two butadiene molecules appear to be coordinated to ruthenium.

Reaction of Complex 2 and 5 with Hydrogen. Hydrogen (300 ml) was brought in contact with a benzene suspension (*ca.* 5 ml) of **2** (*ca.* 200 mg) giving a yellow brown homogeneous solution at room temperature. Only ethane was detected in the gas phase. After 1 day white needles were formed, which were identified as $RuH_4(PPh_3)_3$ on the basis of IR analysis and its reaction with PPh_3 affording hydrogen and $RuH_2(PPh_3)_4$. Complex **5** in benzene also reacted with hydrogen at room temperature similarly giving $RuH_4(PPh_3)_3$ and butane. ν(Ru–H), 1940 cm^{-1}.

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