Reactions of $RuClH(CO)(PPh_3)_3$ with Allylic Amines: Insertions and an Unusual Carbon–Nitrogen Bond Cleavage of Allylic Amines

Katsuma Hiraki* and Takahiro Matsunaga

Department of Applied Chemistry, Faculty of Engineering, Nagasaki University, Bunkyo-machi, Nagasaki 852, Japan

Hiroyuki Kawano

Graduate School of Marine Science and Engineering, Nagasaki University, Bunkyo-machi, Nagasaki 852, Japan

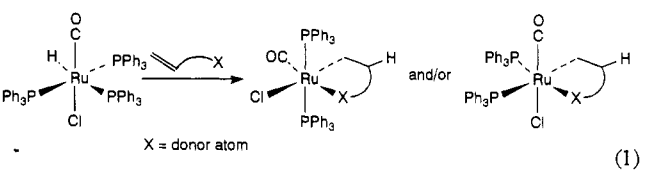
Received August 30, 1993®

Reactions between $RuClH(CO)(PPh_3)_3$ and primary or secondary allylamines give olefin-insertion products: $Ru(CH_2CH_2CH_2NHR)Cl(CO)(PPh_3)_2$ (R = H (**1**), CH_3 (**4**), and $CH_2CH{=}CH_2$ (**5**)). Analytical and spectroscopic studies on these products show they have an octahedral six-coordinate structure in which two triphenylphosphines are located mutually cis, and a phosphine-*trans* isomer is obtained only in the case of R = H. The insertion of the primary allylamine occurs after the initial ligand exchange of the allylamine with one PPh_3 of the starting complex. The variable-temperature NMR analyses reveal that the complexes derived from the secondary allylamines liberate one of the two PPh_3 ligands at high temperatures. When R = CH_3, an isolable dichloro-bridged dinuclear complex $[Ru(\mu\text{-}Cl)(CH_2CH_2CH_2NHCH_3)(CO)(PPh_3)]_2$ (**6**) is formed by the liberation of PPh_3. A carbon—nitrogen bond of some tertiary allylic amines is cleaved in the reaction with $RuClH(CO)(PPh_3)_3$ to give the (π-allyl)ruthenium(II) complex $Ru(\eta^3\text{-}C_3H_5)Cl(CO)(PPh_3)_2$ (**7**) and its analog. The direct interaction between the Ru—H bond and the allylic amine leads to the formation of the (π-allyl)ruthenium(II) complex and the corresponding secondary amine without an increase of the oxidation state. Catalytic isomerization of some allylic amines to the enamines is also recognized during the insertion and the carbon—nitrogen bond cleavage.

Introduction

Insertion of a multiple bond into a metal–hydride bond is regarded as an important step of metal-catalyzed hydrogenation and isomerization.[1,2] Few of the olefin-insertion products have been isolated and characterized because of the instability of a carbon–metal bond of an intermediary alkyl complexes derived from olefin substrates and hydride complexes.[3-7] Therefore, investigation of coordination behavior of olefins dealing with the isolable insertion products still has been attracting many chemists' interests.

In this field, we have continuously studied the insertion of olefin substrates such as vinyl compounds,[8,9] conjugated dienes,[9] dialkyl maleates,[10] and alkyl allylic sulfides[11] into the Ru–H bond of a hydridoruthenium(II) complex $RuClH(CO)(PPh_3)_3$. Some of these substrates produce isolable alkylruthenium(II) complexes, of which the substrate inserts to form a chelate ligand. The chelation of the potentially donating atom of the substrate stabilizes the Ru–C bond of these alkylruthenium complexes (eq 1).



(1)

Related reactions of $RuClH(CO)(PPh_3)_3$ with various types of unsaturated substrates have been reported. Heterocumulenes,[12] acetylenes,[13] and conjugated enynes[14] give the stable insertion products with some types of chelating ligands.

We studied the reactions of allylic amines with $RuClH(CO)(PPh_3)_3$. Allylic amines are potentially chelating substrates with an amino group as a donor. Therefore it is a matter of interest to deal with the reactions of RuClH-

® Abstract published in *Advance ACS Abstracts*, April 1, 1994.

(1) Tolman, C. A. In *Transition Metal Hydrides*; Muetterties, E. L., Ed.; Mercel Decker: New York, 1971; pp 271–312 (see also references cited therein).

(2) Jardine, F. H. *Prog. Inorg. Chem.* **1984**, *31*, 318 and references cited therein.

(3) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333.

(4) Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* **1973**, *95*, 7262.

(5) Thomas, K.; Osborn, J. A.; Powell, A. R.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 1801.

(6) Baddley, W. H.; Fraser, M. S. *J. Am. Chem. Soc.* **1969**, *91*, 3661.

(7) Clark, H. C.; Jablonski, C. R. *Inorg. Chem.* **1974**, *13*, 2213.

(8) Hiraki, K.; Ochi, N.; Kitamura, T.; Sasada, Y.; Shinoda, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2356.

(9) Hiraki, K.; Ochi, N.; Sasada, Y.; Hayashida, H.; Fuchita, Y.; Yamanaka, S. *J. Chem. Soc., Dalton Trans.* **1985**, 873.

(10) Hiraki, K.; Ochi, N.; Takaya, H.; Fuchita, Y.; Shimokawa, Y.; Hayashida, H.; *J. Chem. Soc., Dalton Trans.* **1990**, 1679.

(11) Hiraki, K.; Fuchita, Y.; Kawabata, H.; Iwamoto, K.; Yoshimura, T.; Kawano, K. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 3027.

(12) (a) Robinson, S. D.; Sahajpal, A. *Inorg. Chem.* **1977**, *16*, 2718, 2722. (b) Brown, L. D.; Robinson, S. D.; Sahajpal, A.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 2728. (c) Sahajpal, A.; Robinson, S. D. *Inorg. Chem.* **1979**, *18*, 3572.

(13) (a) Torres, M. R.; Vegas, A.; Santos, A.; Ross, J. *J. Organomet. Chem.* **1986**, *309*, 169. (b) Torres, M. R.; Vegas, A.; Santos, A.; Ros, J. *J. Organomet. Chem.* **1987**, *326*, 413. (c) Torres, M. R.; Santos, A.; Ros, J.; Solans, X. *Organometallics* **1987**, *6*, 1091.

(14) (a) Wakatsuki, Y.; Yamazaki, H.; Maruyama, Y.; Shimizu, I. *J. Chem. Soc., Chem. Commun.* **1991**, 261. (b) Wakatsuki, Y.; Yamazaki, H.; Maruyama, Y.; Shimizu, I. *J. Organomet. Chem.* **1992**, *430*, C60.

0276-7333/94/2313-1878$04.50/0 © 1994 American Chemical Society

(CO)(PPh$_3$)$_3$ with the allylic amines. Here we will describe novel (3-aminopropyl-C^1,N)ruthenium(II) and (π-allyl)-ruthenium(II) complexes derived by the reactions of RuClH(CO)(PPh$_3$)$_3$ and some primary, secondary, and tertiary allylic amines. The structure, the behavior in the solution state, and the mechanism of the formation of these new complexes are discussed. Ruthenium complex-catalyzed isomerization of allylic amines to enamines is also mentioned.[15]

Results and Discussion

Insertion of Allylamine. When allylamine (a primary allylamine) was allowed to react with RuClH(CO)(PPh$_3$)$_3$ in refluxing tetrahydrofuran, insertion product Ru(CH$_2$-CH$_2$CH$_2$NH$_2$)Cl(CO)(PPh$_3$)$_2$ (**1**) was isolated in 65% yield as a yellow-white powdery product. The IR spectrum of **1** showed that the Ru—H stretching absorption (2010 cm^{-1}) of the starting complex disappeared and the C≡O stretching band was lowered from 1920 to 1914 cm^{-1}. The ^{31}P{^{1}H} NMR data at −30 °C revealed that **1** was a mixture of two isomers, one of which showed a singlet at δ 42.0 and the other showed a couple of doublets at δ 16.8 and 46.4 with ^2J(PP) = 14.7 Hz (Table 1). The former singlet corresponded to a P-trans isomer and the latter doublets to a P-cis one. Two apparent triplets with small C—P coupling constants at a carbonyl region in the ^{13}C{^{1}H} NMR spectrum supported the presence of the two isomers, indicating that the carbonyl ligand of each isomer was located cis to the two PPh$_3$ ligands. The trans/cis ratio of **1** fell within (0.8–1.2)/1 based on the peak areas of the ^{31}P signals. The most probable structure for the trans form of **1** is shown in Scheme 1 in consideration of the trans influence of the ligands as well as the NMR spectroscopic data. As for the cis isomer, the methylene carbon bound to the ruthenium resonated at δ 31.2 as a double doublet in the ^{13}C NMR, indicating unambiguously that the carbon was situated trans to one PPh$_3$ ligand and cis to another. The amino group is located trans to one of the two PPh$_3$ ligands in analogy with a *N*-methylallylamine-inserted complex (vide infra). Thus it is reasonable that the carbonyl and chloro ligands of the cis isomer are situated trans to each other in accord with our previous study on the related insertion to form a cis isomer.[9-11]

When RuClH(CO)(PPh$_3$)$_3$ was treated with allylamine at a room temperature for 1 day, the insertion did not proceed and an allylamine-coordinated hydridoruthenium(II) complex RuClH(CO)(NH$_2$CH$_2$CH=CH$_2$)(PPh$_3$)$_2$ was isolated. Its ^{1}H NMR spectrum exhibited a triplet assigned to the hydride (δ −14.50, ^2J(PH) = 19.1 Hz) and signals assigned to the olefin protons. The signal intensity of the aromatic protons corresponded to 30 H in total (two PPh$_3$ ligands). The ^{31}P{^{1}H} NMR spectrum showed only one singlet at δ 46.2, indicating that the two PPh$_3$ ligands were equivalent and located trans to each other in an octahedral six-coordinate structure.

In order to evaluate whether the amine function or the olefin function was bound to the ruthenium center of **2**, we examined the ligand exchange reaction between RuClH(CO)(PPh$_3$)$_3$ and propylamine, which has no olefin double bond. Grayish green powder, RuClH(CO)(NH$_2$-CH$_2$CH$_2$CH$_3$)(PPh$_3$)$_2$ (**3**), was obtained after the usual workup. In its ^{1}H NMR spectrum, a triplet of hydride was observed at δ −14.51 (^2J(PH) = 19.1 Hz), and in the ^{31}P{^{1}H} NMR, a singlet of δ 46.2. Virtually, these NMR data were similar to those of **2**. This result strongly implied that the amine function was bound to the ruthenium center of **2** or **3**. The PPh$_3$ ligand that was located trans to the hydrido ligand of RuClH(CO)(PPh$_3$)$_3$ was labilized to make a vacant coordination site because of the strong trans effect of the hydrido ligand. Therefore the amines were easily exchanged for the PPh$_3$. This explanation of the ligand exchange mechanism is supported by an X-ray structure of a closely related osmium complex OsBrH(CO)(PPh$_3$)$_3$.[16] The Os–P bond trans to H (2.56 Å) is longer than the two Os–P bonds that are trans to each other (2.34 Å). The lability of the PPh$_3$ trans to H of RuClH(CO)(PPh$_3$)$_3$ is completely compatible with the corresponding long and weak Os–P bond of OsBrH(CO)(PPh$_3$)$_3$.

Table 1. Selected NMR Data for the Complexes[a]

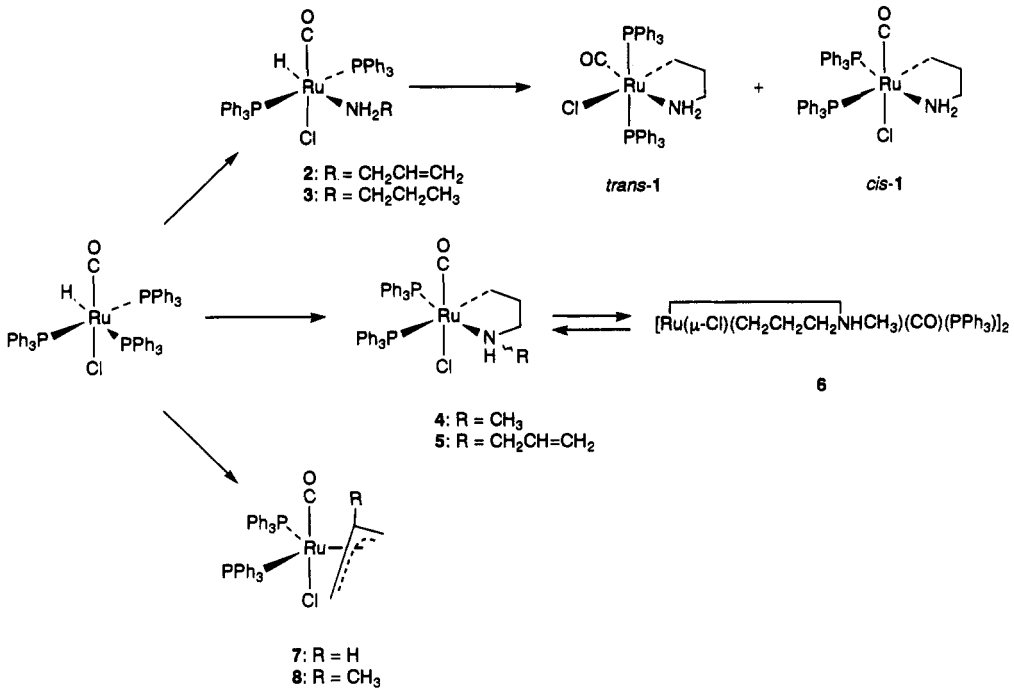
	^{1}H			^{31}P{^{1}H}	
complex	δ[b]	^3J(HH)/Hz	assgnt	δ[c]	^2J(PP)/Hz
trans-**1**[d]	1.14 (br)		RuCH_2	42.0 (s)	
	1.45 (br)		–CH_2–		
	1.84 (br)		CH_2NH$_2$		
cis-**1**[d]	1.60 (br)		RuCH_2	16.8 (d)	14.7
	1.75 (br)		RuCH_2	46.4 (d)	14.7
	2.13 (br)		–CH_2–		
	2.42 (br)		CH_2NH$_2$		
	2.49 (br)		–CH_2–		
	2.71 (br)		CH_2NH$_2$		
2	−14.50 (t)	19.1[e]	RuH	46.2 (s)	
	1.43 (br)		NH_2		
	2.22 (m)		CH_2NH$_2$		
	4.11 (dd)	16.5, 1.5[f]	CH=CH_2		
	4.46 (dd)	10.3, 1.5[f]	CH=CH_2		
	4.53 (ddt)	16.5, 10.3, 5.9	CH=CH$_2$		
3	−14.51 (t)	19.1[e]	RuH	46.2 (s)	
	0.33 (t)	7.3	CH_3		
	1.30 (br)		NH_2		
	1.61 (m)		–CH_2–		
	1.99 (br)		CH_2NH$_2$		
4[d]	1.27 (br)		RuCH_2	15.7 (d)	9.7
	1.73 (br)		–CH_2–	48.3 (d)	9.7
	1.81 (br)		–CH_2–		
	2.01 (br)		RuCH_2		
	2.18 (br)		CH_2NH		
	2.31 (dd)	6.5, 2.2[e]	CH_3		
	3.01 (br)		CH$_2$NH		
	3.15 (br)		CH_2NH		
5[d]	1.34 (br)		RuCH_2	16.2 (d)	9.8
	1.72 (br)		–CH_2–	48.7 (d)	9.8
	2.07 (br)		RuCH_2		
	2.36 (br)		CH_2NH		
	2.97 (br)		CH$_2$NH		
	3.04 (br)		CH_2NH		
	3.38 (m)		CH_2CH=CH$_2$		
	4.31 (m)		CH$_2$CH=CH$_2$		
	4.80 (d)	17.6	CH$_2$CH=CH_2		
	4.83 (d)	10.3	CH$_2$CH=CH_2		
6	0.67 (br)		RuCH_2	49.7 (s)	
	1.09 (br)		–CH_2–		
	1.58 (br)		CH_2NH		
	1.92 (br)		CH_2NH		
	2.19 (br)		CH$_2$NH		
	2.41 (dd)	5.9, 2.2[e]	CH_3		
7	2.58 (dd)	12.5, 5.1[e]	CH_2CHCH_2	33.3 (s)	
	2.98 (d)	7.3	CH_2CHCH_2		
	5.03 (tt)	12.5, 7.3	CH$_2$CHCH$_2$		
8	1.98 (s)		CH$_2$C(CH_3)CH$_2$	35.0 (s)	
	2.62 (d)	5.9[e]	CH_2C(CH$_3$)CH_2		
	2.83 (s)		CH_2C(CH$_3$)CH_2		

[a] These NMR data were measured in $CDCl_3$ solution at 30 °C unless otherwise stated. The resonances due to the PPh$_3$ ligands are omitted. [b] In ppm downfield from TMS. [c] In ppm downfield from external 85% H_3PO_4. [d] Measured at −30 °C. [e] J(HP) value in Hz. [f] ^2J(HH) value in Hz.

(15) (a) Inoue, S.; Takaya, H.; Tani, K.; Otsuka, S.; Sato, T.; Noyori, R. *J. Am. Chem. Soc.* **1990**, *112*, 4897. (b) Schmid, R.; Hansen, H.-J. *Helv. Chim. Acta* **1990**, *73*, 1258.

(16) Orioli, P. L.; Vaska, L. *Proc. Chem. Soc.* **1962**, 333.

Scheme 1



Heating of **2** in refluxing tetrahydrofuran converted it into the olefin-inserted complex **1**, confirming that **2** was an intermediate of the insertion of allylamine. It is worth noting that the resulting **1** thus obtained consisted of not only the trans isomer but also the cis isomer as well as that obtained directly from $RuClH(CO)(PPh_3)_3$ and allylamine. The experiment in an NMR tube revealed that the conversion of **2** into **1** was retarded by the presence of free PPh_3. The starting **2** disappeared completely within 0.5 h in the absence of PPh_3, whereas the conversion spent several hours to be completed in the presence of additional PPh_3. The conversion of **2** into **1** can be rationalized as follows: The deceleration may suggest that the liberation of one PPh_3 is important for the insertion of the double bond of the coordinating allylamine. As a result of the liberation, there appears a vacant coordination site, on which the olefin function coordinates prior to the insertion into the Ru–H bond. Then a five-coordinated 3-aminopropyl-C^1,*N* chelate species was generated as an intermediate. Formation of *cis*-**1** is explained by the recombination of PPh_3 with the intermediate. As for *trans*-**1**, the turnstilelike rotation around the ruthenium center occurs prior to the recombination (Scheme 2).

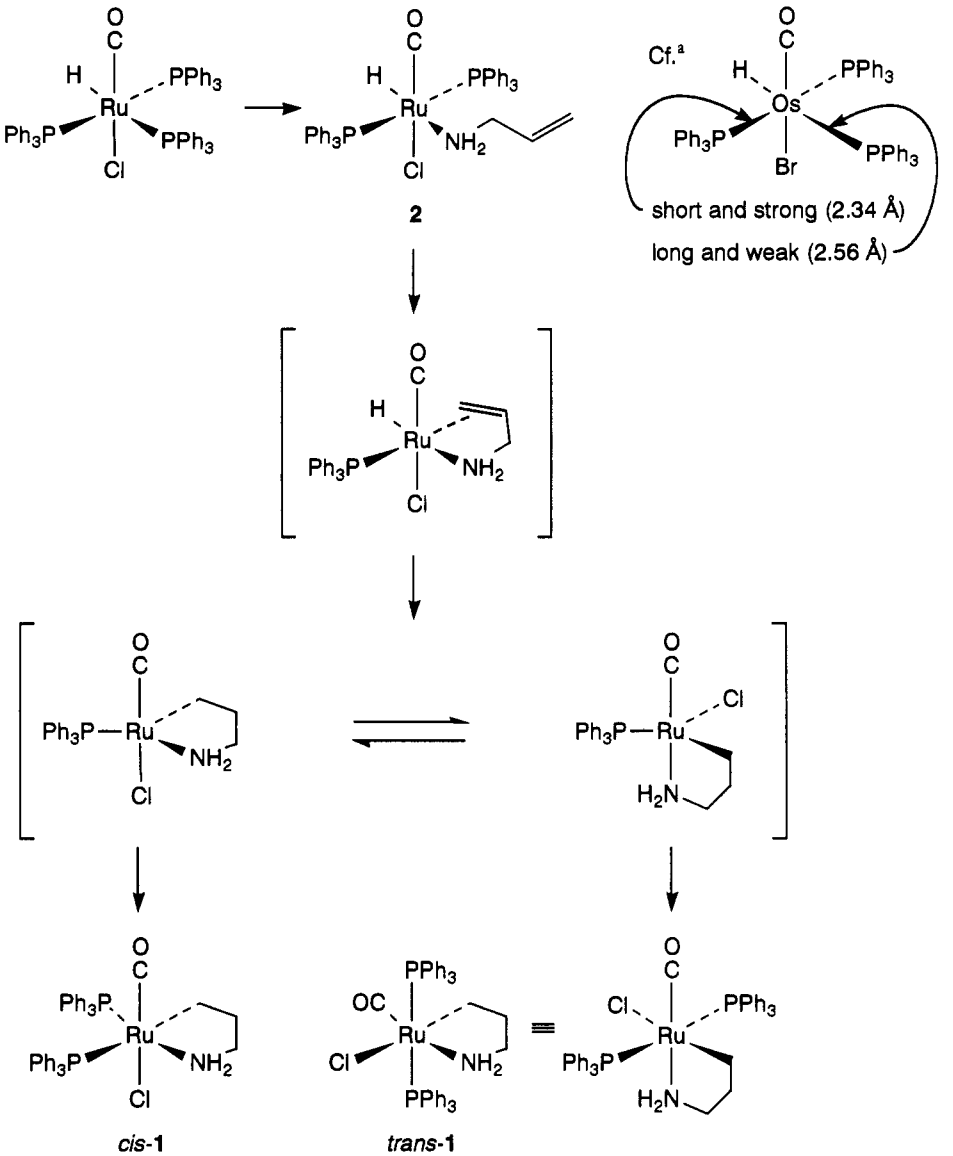
As shown above, the primary allylamine was inserted into the Ru–H bond of $RuClH(CO)(PPh_3)_3$ to form the five-membered 3-aminopropyl-C^1,*N* chelate ring. Such an insertion of the olefin function was the same class as the reaction between the vinyl compounds and $RuClH(CO)(PPh_3)_3$ that we had reported so far.[9,10] The resulting alkyl complex was stabilized by the chelation through the second coordination of the nitrogen atom in the molecule. The primary allylamine played the roll of an ordinary olefin accompanied by a potentially coordinating atom to give the chelate ligand.

Insertion of Secondary Allylamines. Secondary amines, *N*-methylallylamine and diallylamine, also reacted smoothly with $RuClH(CO)(PPh_3)_3$ under the same conditions as above to give the insertion products $Ru(CH_2CH_2CH_2NHR)Cl(CO)(PPh_3)_2$ (**4**, R = CH_3; **5**, R = $CH_2CH{=}CH_2$). The products **4** and **5** gave satisfactory IR spectroscopic and elementary analysis data for the formulas. So far as the formulas of **4** and **5** were concerned, the insertion of the secondary allylamines was seemingly similar to that of the primary allylamine. The isolated insertion products **4** and **5**, however, differed from **1** in some aspects owing to the N substituents.

The $^{31}P\{^1H\}$ NMR spectrum of **4** at −30 °C showed mainly a set of two doublets at δ 48.3 and 15.7 with reasonable $^2J(PP)$ values (9.7 Hz for P-cis). A characteristic double doublet appeared at δ 2.31 in the ^1H NMR spectrum, indicating the *N*-methyl protons were coupled with the N-bound proton and one phosphorus nucleus, which indicated that the secondary amino group was located trans to one of the PPh_3 ligands. Neither olefin protons nor the hydride proton was observed in the spectrum. This spectroscopic information showed that **4** was a P-cis species with the *N*-methylallylamine moiety inserted. A smaller set of doublets was also recognized at δ 41.1 and 7.6 with $^1/_{17}$th of the intensities of the main doublets in the ^{31}P spectrum. However, none of the ^1H signals corresponding to the smaller ^{31}P doublets was distinguished because of the weakness of the signals compared to those of the main species. Therefore, the minor species could not be identified. When the primary allylamine was inserted, not only the cis isomer but also the trans isomer were formed in the reaction mixture. In the case of *N*-methylallylamine, no trans isomer was recognized in the NMR data for **4**. This was one of the different aspects from the insertion of the primary allylamine.

The ^{31}P doublet of **4** at δ 48.3 observed at −30 °C turned into a singlet (δ 48.2) at 20 °C. The other doublet at δ 15.7 was broadened above 20 °C. Simultaneously with these changes, a broad signal of free PPh_3 appeared at δ *ca.* −6, implying that a part of the PPh_3 ligands of **4** was liberated at 20 °C. Since the P–P coupling was lost in the lower-field resonance, the spectrum suggested the evolution of a five-coordination ruthenium(II) species that was coor-

Scheme 2



[a] See ref 16.

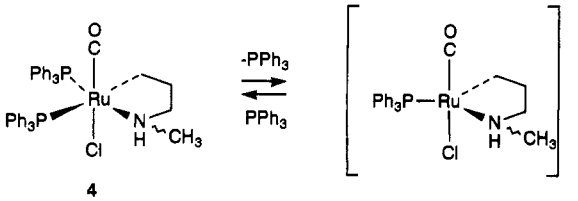
dinated by only one PPh_3. Complex **4** and the five-coordinate species seemed to be in rapid equilibrium at 20 °C.

Meanwhile, an additional ^{31}P singlet emerged at δ 50.1 at 20 °C. This singlet at the lowest field was attributed to a dichloro-bridged dinuclear complex $[Ru(\mu\text{-}Cl)(CH_2CH_2CH_2NHCH_3)(CO)(PPh_3)]_2$ (**6**) due to the following reasons. Addition of hexane to the dichloromethane solution of **4** precipitated **6** as an olive-yellow complex, which showed the one and only singlet that was identical to the signal at the lowest field in the ^{31}P spectrum of **4**. The elemental analysis data for **6** indicated a loss of one PPh_3 ligand from **4** in composition. The dichloro-bridged dinuclear structure was determined by the distribution of the observed m/z value of the parent peaks in the FAB-MS data.[17]

Treatment of **6** with an equimolar amount of PPh_3 in solution caused the formation of **4** to give a mixture of **4** and **6**. The conversion of **6** into **4** indicated that **6** was dissociated to the five-coordinate species followed by the coordination of the free PPh_3 to form the six-coordinate **4**. In other words, the complexes **4** and **6** were in equilibrium presumably through the five-coordinate species. When a $CDCl_3$ solution of **4** was warmed up in an NMR tube from −30 to +50 °C, the $^{31}P\{^1H\}$ signals exhibited that the ratio of **4** to **6** decreased from 40:1 to 1:2. The equilibrium between **4** and **6** goes left at low temperatures and goes right at high temperatures, as shown in eq 2.

The diallylamine derivative **5** showed elementary analysis data that were very consistent with the formula representing the six-coordinated mononuclear structure $Ru(CH_2CH_2CH_2NHCH_2CH{=}CH_2)Cl(CO)(PPh_3)_2$. The $^{31}P\{^1H\}$ NMR spectroscopic features of **5** were very similar to those of **4**. The NMR spectrum at −30 °C mainly exhibited a set of two doublets at δ 48.7 and 16.2. Each ^{31}P doublet of **5** turned into a singlet at 30 °C, and the resonance at the higher fields broadened at about δ 16. A small broad signal of free PPh_3 appeared at 30 °C,

(17) The parent peaks of **6** in the FAB-MS was distrbuted in the range from m/z 988 to 1008. The observed distribution of the parent peaks is very consistent with that of the calculated peaks for the dinuclear formula in consideration with the isotopes included. The molecular weight of **6** measured in benzene fell within the range from 800 to 1000. The molecular weight measurement includes an error of about 200 because of poor solubility of **6**. However, the value of the molecular weight is large enough to confirm the dinuclear structure of **6** in the solution state.



4

representing the release of PPh_3 from **5**. No additional singlet, however, was observed at fields lower than δ 50 at any temperatures, in contrast to the case of **4**. These NMR data indicated that complex **5** had the P-cis configuration and liberated one PPh_3 to some extent, like the *N*-methyl analog **4**. Despite the liberation of PPh_3 from **5**, no diallylamine-inserted dinuclear species was found by ^{31}P NMR spectroscopy. The *N*-allyl substituent of the five-coordinate species likely prevented formation of the dinuclear complex because of its steric factors. Attempts to isolate the dinuclear species or the five-coordinate species from the solution resulted only in the recrystallization of **5**.

Reaction of $RuClH(CO)(PPh_3)_3$ with Tertiary Allylamines. When a large excess amount of *N,N*-dimethylallylamine was allowed to react with $RuClH(CO)(PPh_3)_3$, no ordinary insertion product, 3-(dimethylamino)propyl-C^1,*N* chelating complex was formed. The only metal-containing product was characterized as an unexpected π-allyl complex, $Ru(\eta^3\text{-}C_3H_5)Cl(CO)(PPh_3)_2$ (**7**), by following analytic and spectroscopic data. The elemental analysis of the product indicated the absence of nitrogen, implying neither the amine-inserted complex nor the amine-coordinated one was produced. A singlet at δ 33.3 in the $^{31}P\{^1H\}$ NMR data showed the presence of the two equivalent phosphine ligands and one carbonyl ligand. The $^2J(CP)$ value of the triplet (15.7 Hz) expressed that the two phosphines and the carbonyl ligand were positioned mutually cis. Three proton signals at 5.03, 2.98, and 2.58 with the intensity ratio 1:2:2 showed a coupling pattern typical of a π-allyl moiety. These NMR data were consistent with those of the substituted (π-allyl)ruthenium(II) complexes for which we have reported the preparation from some conjugated dienes and $RuClH(CO)(PPh_3)_3$.[9] Although two isomeric structures were possible for **7**, only one π-allyl species was recognized and isolated. An octahedral-like structure of **7** with a plane of symmetry is depicted in Scheme 1.

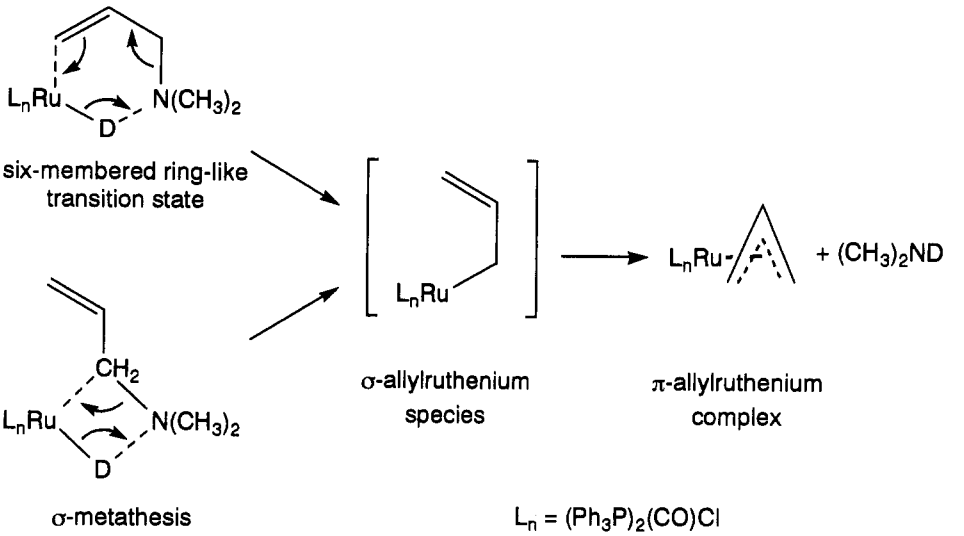
The other tertiary allylamines, *N,N*-diethylallylamine and triallylamine, also reacted with $RuClH(CO)(PPh_3)_3$ to give the same isomer of **7**. The reaction, however, proceeded rather slowly and required 1–3 days to be completed, probably due to the bulkier nature of their N substituents. The steric hindrance of the N substituents prevents initial access of the amino group to the active site on the ruthenium, therefore the allyl–nitrogen bond cleavage of the bulky tertiary allylamines proceeds more slowly than that of *N,N*-dimethylallylamine. Additionally, *N,N*-diethylmethallylamine reacted very slowly with the hydrido complex to give the analogous η^3-methallyl complex (**8**). Only one of the two possible isomers of **8** was recognized in its ^1H and ^{31}P NMR spectra as well as in the case of **7**. It is noteworthy that the C–N bond cleavage and the formation of the η^3-allyl complexes were achieved only in the cases of tertiary allylic amines. Even when primary and secondary allylamines were reacted with $RuClH(CO)(PPh_3)_3$ under severe reaction conditions (at a higher temperature and for a longer reaction period), the ^{31}P NMR spectra of the products showed no signal attributable to **7**.

The formation of the (π-allyl)ruthenium(II) complex is one of the few examples of the ruthenium-promoted activation of carbon–heteroatom bonds.[18] The transition metal-promoted activation of an allyl–heteroatom bond is well-known and formation of (π-allyl)platinum(II) complexes from allylamines has been reported so far.[19] However, allyl–nitrogen bond cleavage followed by (π-allyl)ruthenium(II) complex formation has rarely been reported. Ito and collaborators[20] have reported such a formation of a (π-allyl)ruthenium(IV) complex, $(C_5(CH_3)_5)RuCl_2(\eta^3\text{-}C_3H_5)$ from a pentamethylcyclopentadienylruthenium(III) complex, $[(C_5(CH_3)_5)RuCl_2]_n$ and allylamine. In their report, the formation of the (π-allyl)ruthenium(IV) complex is accompanied with an increase in the oxidation number of the ruthenium metal. They conclude that the formation of the (π-allyl)ruthenium(IV) complex proceeds with one-electron oxidation of the ruthenium center via a radical intermediate. On the contrary, the formation of the (π-allyl)ruthenium(II) complex **7** or **8** causes no oxidation of the ruthenium. This fact implies the C–N bond is cleaved by the hydridoruthenium(II) complex without a radical intermediate.

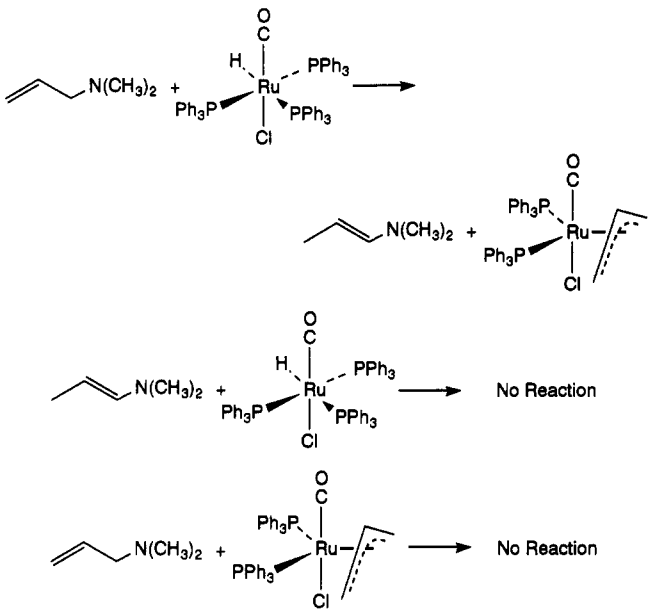
Formation of dimethylamine was ascertained by analyzing the reaction mixture of $RuClH(CO)(PPh_3)_3$ and *N,N*-dimethylallylamine using a GC method. Dimethylamine was a key byproduct to postulate the mechanism of the π-allyl complex formation. A definitive clue to the reaction mechanism was obtained by an experiment with a deuterated starting complex $RuClD(CO)(PPh_3)_3$ (approximately 60% deuterated).[21] Deuterium was not incorporated into the π-allyl moiety by the reaction of *N,N*-dimethylallylamine and $RuClD(CO)(PPh_3)_3$ in an NMR tube. The ^2D NMR spectrum of the reaction mixture in benzene-d_6 showed no signals in the π-allyl region. Only a slightly broadened singlet at δ 1.34 was observed except for the signals in the arylic region (C_6D_6 and *o*-D of PPh_3). The singlet was assigned to $(CH_3)_2ND$ because a new *N*-methyl signal emerged in addition to those of the tertiary allylamine and of the enamine (see the next section) in both ^1H and ^{13}C NMR spectra. This fact shows that the deuterium bound to the ruthenium was transferred directly to the nitrogen of the tertiary allylamine without scrambling. Two speculative pathways to form the π-allyl complex was postulated in Scheme 3. One is the bond migration via a six-membered ringlike transition state. In this route, the ruthenium attacks the terminal carbon of the allyl group and the deuteride is transferred to the nitrogen to give $(CH_3)_2ND$ and a (σ-allyl)ruthenium species, which is consequently converted

(18) Hayashi, Y.; Komiya, S.; Yamamoto, T.; Yamamoto, A. *Chem. Lett.* **1984**, 977.
(19) Kurosawa, H. *Inorg. Chem.* **1976**, *15*, 120.
(20) Nagashima, H.; Mukai, K.; Shiota, Y.; Ara, K.; Ito, K.; Suzuki, H.; Oshima, N.; Moro-oka, Y. *Organometallics* **1985**, *4*, 1314.
(21) The deuteridoruthenium complex was prepared by the treatment of the hydrido complex $RuClH(CO)(PPh_3)_3$ with ethanol-d_1. The extent of the deuteration was evaluated by measuring the NMR and IR spectra. During the deuteration, deuterium substituted for not only the hydride but also the *ortho* hydrogens of the triphenylphosphines because of the ruthenium-promoted activation of the *ortho* C–H bonds. Vaska, L.; DiLuzio, J. W. *J. Am. Chem. Soc.* **1961**, *83*, 1262.

Scheme 3



Scheme 4



into the π-allyl form **7**. The other is the direct interaction between the Ru–D bond and the C–N bond, which activates these bonds to cause the metathesis between these two σ bonds.[22] The ruthenium-promoted σ-metathesis first brings about the (σ-allyl)ruthenium(II) intermediate.

Catalytic Isomerization of N-Substituted Allylamines to the Enamines. When a 10-fold amount of *N,N*-dimethylallylamine was allowed to react with RuClH(CO)(PPh$_3$)$_3$, a considerable amount of the enamine (*E*)-1-(dimethylamino)-1-propene was evolved in the reaction mixture. Neither the treatment of the starting complex with the enamine nor the treatment of **7** with *N,N*-dimethylallylamine caused any reaction (Scheme 4). When an amount of *N,N*-dimethylallylamine was cut down to 1.7 times as much as the starting hydridoruthenium(II) complex, the catalytic olefin isomerization was revealed to occur more rapidly than the C–N bond activation. The tertiary allylamine had been consumed completely to give the enamine until only 34% of the starting complex was converted into **7**. For these data, the catalytic isomerization of *N,N*-dimethylallylamine and the formation of the π-allyl complex **7** were proved to be independent and competitive with each other.

The isomerization of the tertiary allylamine catalyzed by RuClH(CO)(PPh$_3$)$_3$ has not been reported so far. To our knowledge, RuClH(PPh$_3$)$_3$-catalyzed isomerization of *N*-allylamides to enamides reported by Stille and Becker[23] is the only similar reaction found in the literature. As for the mechanism of the isomerization of olefin function, Wells and collaborators[24] have reported that the isomerization of 1-pentene to 2-pentene is catalyzed by RuClH(CO)(PPh$_3$)$_3$ via insertion/β-elimination. Two other mechanisms have been proposed for the catalytic intramolecular 1,3-hydrogen shift of the tertiary allylamine to the enamine by a transition metal complex. One is the 1,3-hydrogen shift via a π-allyl intermediate, which is common to transition metal-catalyzed isomerization of olefins.[25] The other is a mechanism via a nitrogen-anchored metallacycle intermediate, which is recognized in the Rh-catalyzed isomerization of tertiary allylamine to the corresponding enamine (Scheme 5).[15,26] If these mechanisms are applied to the isomerization of the allylamine catalyzed by RuClH(CO)(PPh$_3$)$_3$, the latter two mechanisms have to include Ru(IV) species as the key intermediates. In contrast, the insertion/β-elimination mechanism comprises the Ru(II) species all through the pathway. The d^4-Ru(IV) species are formed with difficulty from the d^6-Ru(II) hydride with stabilizing ligands such as carbonyl and triphenylphosphine. Although we have not obtained indeed the definitive clue to determine which of these mechanisms the isomerization of the allylamine follows, it is considered to follow the insertion/β-elimination as a general mechanism for the olefin isomerization catalyzed by RuClH(CO)(PPh$_3$)$_3$.

Catalytic isomerization to the enamine was also observed in the reaction of the secondary allylamine and RuClH-

(22) (a) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (b) Rappé, A. K. *Organometallics* **1990**, *9*, 466.

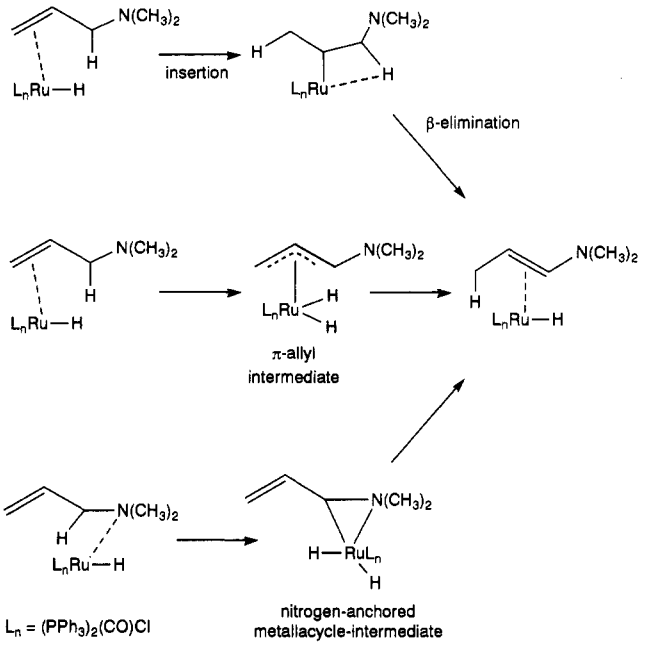
(23) Stille, J. K.; Becker, Y. *J. Org. Chem.* **1980**, *45*, 2139.

(24) (a) Bingham, D.; Webster, D. E.; Wells, P. B. *J. Chem. Soc., Dalton Trans.* **1974**, 1519. (b) Hendrix, W. T.; von Rosenberg, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 4850. (c) Tolman, C. A. *J. Am. Chem. Soc.* **1972**, *94*, 2994.

(25) (a) Bingham, D.; Hudson, B.; Webster, D. E.; Wells, P. B. *J. Chem. Soc., Dalton Trans.* **1974**, 1521. (b) Casey, C. P.; Cry, C. R. *J. Am. Chem. Soc.* **1973**, *95*, 2248.

(26) Yamakawa, M.; Noyori, R. *Organometallics* **1992**, *11*, 3167.

Scheme 5



$(CO)(PPh_3)_3$. The reaction of *N*-methylallylamine (amine: complex = 5.4:1) caused the formation of 1-(methylamino)-1-propene. After 24 h of reaction, about 10% of the secondary allylamine was revealed to be converted into the secondary enamine based on the ^1H NMR spectrum. All of the hydride complex was consumed to become **4** (and **6**), and the rest of the secondary allylamine remained unreacted. It was a very rare case that the presence of the secondary enamine was observed spectroscopically. Secondary enamines are generally very unstable and rapidly isomerized to the tautomer (imine form) as in the case of an enol and its keto form. However, it has been recently reported that an enol produced by catalytic isomerization of an allylic alcohol is exceptionally stable and observable in aprotic conditions.[27] This phenomenon can be applicable to the catalytic isomerizaion of the secondary allylamine to the corresponding enamine. The secondary enamine generated by our procedure was stable enough to be observed by NMR analysis in benzene-d_6.

The insertion of *N*-methylallylamine was proved to precede the isomerization to the enamine since a considerable amount of *N*-methylallylamine still remained in the reaction mixture. This behavior of the reaction was interpreted by the stability of the five-membered 3-aminopropyl chelate ring of **4**. The ruthenium prefers to attack the terminal carbon of the allylamine forming the 3-aminopropyl-C^1,*N* chelate ring because the five-membered chelate is favored over the four-membered chelate for its stability. The unstable intermediate with the four-membered chelate only affords the secondary enamine. In contrast, once the five-membered chelate complexes (**4** and **6**) have been formed, they resist the β-elimination to regenerate the starting allylamine.

Conclusion.

The hydridoruthenium(II) complex $RuClH(CO)(PPh_3)_3$ reacts with various allylamines to give the novel ruthenium(II) complexes and the corresponding enamines. The reactions with the primary and secondary allylamines bring about the insertion of the allylic function into the Ru–H bond to yield the five-membered aminopropyl chelate complexes. The tertiary allylic amines react with the hydrido complex to give the corresponding (π-allyl)ruthenium(II) complexes. The allyl–nitrogen bond of the tertiary allylic amine is activated directly by the Ru–H bond of the hydrido complex.

Experimental Section

General Information. All manipulations of the complexes were carried out by means of ordinary Schlenk-tube techniques under a nitrogen atmosphere. Melting points were measured on a Yanaco micro melting point apparatus and not corrected. Molecular weight measurement by vapor pressure osmometry was carried out using a CORONA type 114 molecular weight apparatus. Infrared spectra were recorded on a JASCO A-100 spectrophotometer with KBr disks. Elemental analyses, FAB-MS measurement, and ^1H (400-MHz), ^2D (61-MHz), ^{13}C (101-MHz), and ^{31}P (162-MHz) NMR measurements were carried out at the Center for Instrumental Analysis, Nagasaki University, with a Yanaco MT-3 CHN Corder, a JEOL JMS-DX303 mass spectrometer, and a JEOL GX-400 spectrometer, respectively.

$RuClH(CO)(PPh_3)_3$[28] and $RuClD(CO)(PPh_3)_3$[21] were prepared according to the literature. All the allylic amines and the other reagents were purchased and used without further purification. All the solvents were dried and distilled under nitrogen before use.

$Ru(CH_2CH_2CH_2NH_2)Cl(CO)(PPh_3)_2$ (1). In a Schlenk tube, a mixture of $RuClH(CO)(PPh_3)_3$ (190 mg, 0.20 mmol) and allylamine (114 mg, 2.00 mmol) in THF (20 mL) was refluxed. The starting creamy white suspension turned to the homogeneous olive-yellow solution within 2 h. The solution was concentrated under reduced pressure until one-fourth to one-fifth its original volume. Addition of hexane to the concentrated solution precipitated a slightly yellowish white powder, which was washed with hexane to give **1** (124 mg, 65%). Mp: 156–163 °C dec. IR (KBr): 1914 (s), 1482 (s), 1432 (s), 1092 (m) cm^{-1}. $^{13}C\{^1H\}$ NMR (30 °C, $CDCl_3$) for *trans*-**1**: δ 16.9 (t, $^2J(CP)$ = 5.8 Hz), 36.3 (s), 43.5 (s), 127–136 (m), 207.2 (t, $^2J(CP)$ = 17.6 Hz). $^{13}C\{^1H\}$ NMR (30 °C, $CDCl_3$) for *cis*-**1**: δ 31.2 (dd, $^2J(CP)$ = 7.8 and 56.7 Hz), 34.1 (s), 48.7 (s), 127–136 (m), 202.1 (t, $^2J(CP)$ = 15.7 Hz). Anal. Calcd for $C_{40}H_{38}ClNOP_2Ru$: C, 64.30; H, 5.13; N, 1.87. Found: C, 64.56; H, 5.48; N, 1.91.

$RuClH(CO)(NH_2CH_2CH{=}CH_2)(PPh_3)_2$ (2) and $RuClH(CO)(NH_2CH_2CH_2CH_3)(PPh_3)_2$ (3). A mixture of $RuClH(CO)(PPh_3)_3$ (382 mg, 0.40 mmol) and allylamine (229 mg, 4.01 mmol) in 20 mL of THF was stirred at room temperature. The creamy-colored suspension turned to a yellow solution after 24 h. The solvent was removed under reduced pressure. Hexane was added to the concentrated solution, and then the light gray powder formed was collected by filtration and washed with hexane. The yield of the product **2** after drying *in vacuo* was 228 mg (60%). Mp: 146–148 °C dec. IR (KBr): 2020 (m), 1918 (s), 1482 (s), 1482 (s), 1435 (s), 1095 (m) cm^{-1}. Anal. Calcd for $C_{40}H_{38}ClNOP_2Ru$: C, 64.30; H, 5.13; N, 1.87. Found: C, 64.40; H, 5.45; N, 2.02.

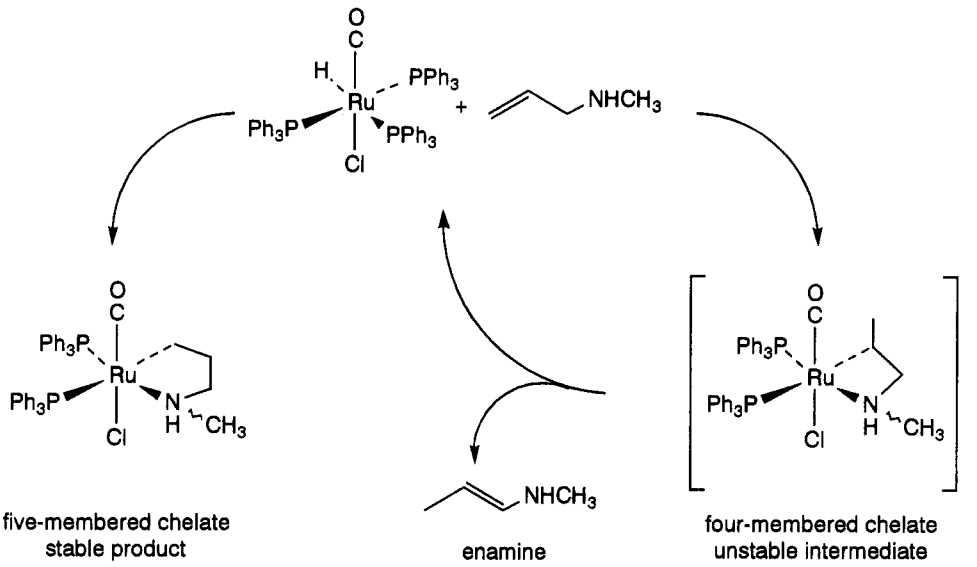
When propylamine (59.1 mg, 1.00 mmol) was reacted with $RuClH(CO)(PPh_3)_3$ (95.3 mg, 0.10 mmol) in place of allylamine, a grayish green powdery product **3** was obtained (60 mg, 63%). Mp: 135–142 °C dec. IR (KBr): 2000 (m), 1910 (s), 1478 (s), 1428 (s), 1089 (m) cm^{-1}. Anal. Calcd for $C_{40}H_{40}ClNOP_2Ru$: C, 64.13; H, 5.38; N, 1.87. Found: C, 63.75; H, 5.40; N, 1.91.

$Ru(CH_2CH_2CH_2NHCH_3)Cl(CO)(PPh_3)_2$ (4) and $[Ru(\mu\text{-}Cl)(CH_2CH_2CH_2NHCH_3)(CO)(PPh_3)]_2$ (6). To a suspension containing $RuClH(CO)(PPh_3)_3$ (518 mg, 0.54 mmol) in 20 mL of THF, *N*-methylallylamine (0.42 g, 5.9 mmol) was added. After the reaction under refluxing for 24 h, the solvent and the amine were removed under reduced pressure. The residue was dissolved in a small amount of CH_2Cl_2 (4 mL) followed by the addition of

(27) (a) Bergens, S. H.; Bosnich, B. *J. Am. Chem. Soc.* **1991**, *113*, 958. (b) Chin, C. S.; Lee, B.; Kim, S.; Chun, J. *J. Chem. Soc., Dalton Trans.* **1991**, 443.

(28) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 45.

Scheme 6



hexane to the solution to give yellow-white powdery product **4**. The powder was collected, washed with hexane, and dried *in vacuo*; the yield of **4** was 290 mg (70%). Mp: 169–171 °C dec. IR (KBr): 1900 (s), 1480 (s), 1430 (s), 1100 (m) cm^{-1}. Anal. Calcd for $C_{41}H_{40}ClNOP_2Ru$: C, 64.69; H, 5.30; N, 1.84. Found: C, 64.48; H, 5.43; N, 1.91.

When hexane was added to the solution of mononuclear **4** in CH_2Cl_2, olive-yellow dinuclear **6** was crystallized slowly. Mp: 207–211 °C dec. IR (KBr): 1900 (s), 1480 (s), 1430 (s), 1100 (m) cm^{-1}. Anal. Calcd for $C_{46}H_{50}Cl_2N_2O_2P_2Ru_2$: C, 55.37; H, 5.05; N, 2.81. MS (simulated relative intensities of M$^+$): *m/z* 1008 (0.2), 1007 (0.7), 1006 (2.3), 1005 (5.8), 1004 (15), 1003 (23), 1002 (50), 1001 (54), 1000 (92), 999 (87), 998 (100), 997 (93), 996 (72), 995 (59), 994 (43), 993 (24), 992 (22), 991 (11), 990 (6.2), 989 (4.2), 988 (1.2). Found: C, 55.08; H, 5.07; N, 2.75. MS (FAB, CH_2Cl_2, relative intensities of M$^+$): *m/z* 1008 (4), 1007 (5), 1006 (5), 1005 (6), 1004 (16), 1003 (22), 1002 (47), 1001 (53), 1000 (92), 999 (86), 998 (89), 997 (100), 996 (75), 995 (60), 994 (47), 993 (32), 992 (26), 991 (19), 990 (13), 989 (4), 988 (2).

Ru(CH$_2$CH$_2$CH$_2$NHCH$_2$CH=CH$_2$)Cl(CO)(PPh$_3$)$_2$ (5). Diallylamine (38.9 mg, 0.40 mmol) and RuClH(CO)(PPh$_3$)$_3$ (190 mg, 0.20 mmol) were allowed to react for 0.5 h in refluxing THF (20 mL). The resulting yellow solution was concentrated under reduced pressure. Addition of hexane formed a slightly yellow powdery product **5** (110 mg, 58%). Mp: 157–160 °C. IR (KBr): 1900 (s), 1480 (s), 1432 (s), 1088 (m) cm^{-1}. Anal. Calcd for $C_{43}H_{42}ClNOP_2Ru$: C, 65.60; H, 5.38; N, 1.78. Found: C, 65.72; H, 5.74; N, 1.77.

Recrystallization of **5** from CH_2Cl_2–hexane solution yielded olive-yellow microcrystals containing one CH_2Cl_2 per two molecules of the complex. Mp: 139–142 °C dec. Anal. Calcd for $C_{43}H_{42}ClNOP_2Ru \cdot {}^1/_2CH_2Cl_2$: C, 62.96; H, 5.22; N, 1.69. Found: C, 62.38; H, 5.23; N, 1.70.

Ru(η^3-C$_3$H$_5$)Cl(CO)(PPh$_3$)$_2$ (7) and Ru(η^3-CH$_2$C(CH$_3$)CH$_2$)Cl(CO)(PPh$_3$)$_2$ (8). A beige-colored suspension of RuClH(CO)(PPh$_3$)$_3$ (381 mg, 0.40 mmol) and *N,N*-dimethylallylamine (681 mg, 4.00 mmol) in THF (30 mL) was refluxed for 0.5 h until it turned to a clear orange solution. Olive-yellow powder was precipitated by addition of hexane to the concentrated reaction mixture. The powdery product **7** was collected, washed with hexane, and dried *in vacuo* (205 mg, 54%). Recrystallization from CH_2Cl_2–hexane gave olive-green crystals of **7**. Mp: 183–186 °C dec. IR (KBr): 1935 (s), 1482 (s), 1435 (s), 1095 (m) cm^{-1}. $^{13}C\{^1H\}$ NMR (30 °C, $CDCl_3$): δ 62.0 (d, ^2J(CP) = 23.5 Hz), 101.5 (s), 127–136 (m), 202.1 (t, ^2J(CP) = 15.7 Hz). Anal. Calcd for $C_{40}H_{35}ClOP_2Ru$: C, 65.80, H, 4.83; N, 0.00. Found: C, 65.36; H, 4.87; N, 0.00.

The same π-allyl complex **7** was obtained after a similar procedure by using *N,N*-diethylallylamine and triallylamine in place of *N,N*-dimethylallylamine. When we used *N,N*-diethylmethallylamine, the η^3-methallyl complex Ru(η^3-CH$_2$C(CH$_3$)CH$_2$)Cl(CO)(PPh$_3$)$_2$ (**8**) was formed. Complex **8** was characterized spectroscopically because **8** could not be isolated from the mixture with some unidentified metal-containing byproducts.

Experiments on the Reaction of the Allylamines and the Ruthenium(II) Complexes in NMR Tubes. Some experiments were carried out in NMR tubes with benzene-d_6 when it was not necessary to isolate the resulting products. The following procedure for the reaction of RuClH(CO)(PPh$_3$)$_3$ with *N*-methylallylamine is typical. In an NMR tube, *N*-methylallylamine (7.8 mg, 109 μmol) and RuClH(CO)(PPh$_3$)$_3$ (19.3 mg, 20.2 μmol) were placed with benzene-d_6. The mixture was degassed three times with the freeze–thaw cycle, then the tube was sealed under vacuum. The sealed tube was heated at 60 °C, and the NMR spectra were observed at appropriate intervals.

For the NMR-tube reaction of RuClH(CO)(PPh$_3$)$_3$ and 1-(dimethylamino)-1-propene (enamine), the following procedure was carried out. Treatment of *N,N*-dimethylallylamine (201 mg, 2.36 mmol) with a catalytic amount of RuClH(CO)(PPh$_3$)$_3$ (204 mg, 0.21 mmol) in refluxing benzene (30 mL) converted the allylamine to the corresponding enamine. After the isomerization was complete, the reaction mixture was distilled carefully to give the enamine solution in benzene. The concentration of the enamine was determined to be 0.032 M by its ^{1}H NMR spectrum on the basis of the integrated peak area. The enamine solution in benzene (0.5 mL, 16 μmol) and RuClH(CO)(PPh$_3$)$_3$ (9.9 mg, 10 μmol) were placed in an NMR tube with benzene-d_6 (0.1 mL) for the internal ^{2}D lock. The mixture was degassed with the freeze–thaw method and sealed under vacuum. The mixture was heated at 60 °C, and the NMR spectra were observed at 30 °C.

The evolution of enamines was ascertained by measuring the NMR spectra of the isomerization mixture. The ^{1}H NMR (30 °C, C_6D_6) data for the enamines are as follows: (*E*)-1-(dimethylamino)-1-propene δ 1.71 (dd, 3H, ^3J(HH) = 6.6 Hz, ^4J(HH) = 1.5 Hz), 2.29 (s, 6H), 4.22 (dq, 1H, ^3J(HH) = 6.6, 13.2 Hz), 5.84 (dd, 1H, ^3J(HH) = 13.2 Hz, ^4J(HH) = 1.5 Hz); (*E*)-1-(methylamino)-1-propene δ 1.73 (dd, 3H, ^3J(HH) = 7.3 Hz, ^4J(HH) = 1.5 Hz), 2.35 (s, 3H), 4.26 (dq, 1H, ^3J(HH) = 7.3, 11.0 Hz), 5.88 (dd, 1H, ^3J(HH) = 11.0 Hz, ^4J(HH) = 1.5 Hz).

Acknowledgment. The present work was supported by a Grant-in-Aid for Scientific Research No. 04650778 from the Ministry of Education, Science, and Culture, Japan.

OM9306077