Oxidative Addition of Allylic Halides to Ruthenium(II) Compounds. Preparation, Reactions, and X-ray Crystallographic Structure of Ruthenium(IV)–Allyl Complexes

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The oxidative addition of allylic halides to $(C_5R_5)RuL_2X$ (R = H, Me; L = CO, PPh_3) gave new Ru(IV)–η^3-allyl complexes, $(C_5R_5)RuX_2(\eta^3\text{-allyl})$. An X-ray structure determination was carried out on $(C_5Me_5)RuBr_2(\eta^3\text{-}C_3H_5)$, indicating a pseudo-piano-stool structure having two Br atoms and two terminal carbons of the *endo*-η^3-allyl ligand located at the basal positions. There is a crystal mirror plane bisecting the pentamethylcyclopentadienyl and the π-allyl ligands. Crystal data: orthorhombic, space group $P2_12_12_1$, a = 11.738 (1) Å, b = 13.367 (7) Å, c = 9.383 (1) Å, Z = 4, data refined to R = 0.0695. Its ^1H and ^{13}C NMR spectra showed symmetric allyl signals, supporting that the above-described piano-stool structure is maintained even in solution. The oxidative addition of allylic halides to $(C_5R_5)Ru(CO)_2X$ is reversible, since the reductive elimination of allylic halides from the Ru(IV)–allyl complexes proceeded under a CO atmosphere to re-form the Ru(II)–carbonyl compounds. $(C_5H_5)RuCl_2(\eta^3\text{-}C_3H_5)$ reacted with DMSO to give the corresponding σ-allyl complex. This result indicates the involvement of σ–π interconversion in the reversible oxidative addition of allylic halides to the Ru(II) precursors. The extrusion of allylic halides from the Ru(IV)–allyl complexes also occurred in hot aromatic hydrocarbons to form cationic Ru(II) complexes, $[(C_5H_5)Ru(\text{arene})]^+X^-$.

A number of organometallic compounds of d^4 ruthenium(IV) complexes have been synthesized[1] since the discovery of stable bis(π-allyl)dichlororuthenium complexes derived from ruthenium trichloride and either 1,3-butadiene[1a] or isoprene.[1b] In our previous papers,[2] we reported that hetero- and homoleptic Ru(IV)–methyl–allyl complexes were easily prepared by methylation of $RuCl_2(1\text{-}3{:}6\text{-}7{:}10\text{-}12\text{-}\eta^8\text{-}C_{12}H_{18})$. Interestingly, the reactions of the heteroleptic methyl complex $Ru(CH_3)I(1\text{-}3{:}6\text{-}7{:}10\text{-}12\text{-}\eta^8\text{-}C_{12}H_{18})$ with CO, isonitriles, or phosphites resulted in the migration of the methyl group from the metal center to the π-allyl moiety.[2] Since reductive elimination is an important elementary step in transition-metal-catalyzed reactions, this facile coupling of the methyl and the allyl ligand on Ru(IV) is regarded as a clue for a new catalysis process of ruthenium complexes. Nonetheless, the butadiene trimer complexes showed spectra that were too complicated, which were not useful for further mechanistic studies on reductive elimination. In this context, the preparation of simple halo–Ru(IV)–allyl complexes suitable as precursors of various Ru(IV)–allyl–alkyl derivatives has been our important project.

The organometallic chemistry of transition-metal–π-allyl complexes has been extensively studied.[3] Especially, the oxidative addition of allylic halides to low-valent transition-metal species is a common process to obtain various halo–π-allyl complexes. In fact, various low-valent group 6 and 8–10 complexes having a d^6, d^8, or d^{10} electron configuration generally undergo oxidative addition. The reaction of $Ru_3(CO)_{12}$ (d^8) with allyl bromide led to the successful synthesis of $(\eta^3\text{-allyl})RuX(CO)_3$.[4] Our attention is focused on the unexplored oxidative addition of allylic halides to d^6 Ru(II) organometallic compounds to provide Ru(IV)–halo–π-allyl complexes (d^4). Although there has been no report of such reactions of organic halides with Ru(II) complexes, we were convinced that an appropriate choice of Ru(II) precursors could give Ru(IV)–π-allyl complexes by this method, because the isoelectronic Mo(0) complexes underwent oxidative addition of allylic halides.[5]

In this paper we describe the successful preparation of new Ru(IV)–π-allyl complexes having the general formula $(C_5R_5)RuX_2(\eta^3\text{-allyl})$ (R = H, Me; X = Cl, Br) by the oxidative addition of allylic halides to Ru(II) complexes, $(C_5R_5)Ru(L)_2X$ (R = H, Me; L = CO, PPh_3; X = Br, Cl). These new compounds were subjected to NMR analysis to determine the structure, which was confirmed by X-ray crystallographic analysis of a representative compound. During the course of this study, we found facile reductive elimination of allylic halides from the Ru(IV)–π-allyl complexes to form Ru(II)–carbonyl or Ru(II)–arene complexes, induced by contact with CO or aromatic solvents, respectively. This work was previously reported in preliminary form,[6,7] and full details on the preparation,

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Table I. Preparation of Ru(IV)–Allyl Complexes by Oxidative Addition of Allyl Halide[a]

precursor	method	X[b]	solvent[c]	temp, °C	time, h	product	yield, %
1	A	Cl (10)	D	140	20	5	10
		Cl (100)	D	140	10		90
		Cl (10)	X	140	20		0[d]
2	A	Br (10)	D	140	20	6	53
		Br (100)	D	140	12		92
		Br (10)	X	140	20		90
3	A	Cl (10)	D	140	20	7	44
		Cl (100)	D	140	12		90
		Cl (10)	X	140	20		14[d]
4	A	Br (10)	D	140	20	8	79
		Br (100)	D	140	9		96
		Br (10)	X	140	20		93
9	B	Cl (10)	D	120	2	5	73
10	C	Cl (2)	C	room temp	2	7	91
			C	40	1		94

[a] All reactions were carried out according to the procedures in the Experimental Section. [b] X is the halide in C_3H_5X; numbers in parentheses indicate the molar excess of the allyl halide relative to the Ru(II) precursor. [c] D = *n*-decane, X = *p*-xylene, C = CH_2Cl_2 containing aqueous ethanol. [d] Considerable amounts of [CpRu(*p*-xylene)]X were isolated.

structural analysis, and the reductive process are presented in this paper.

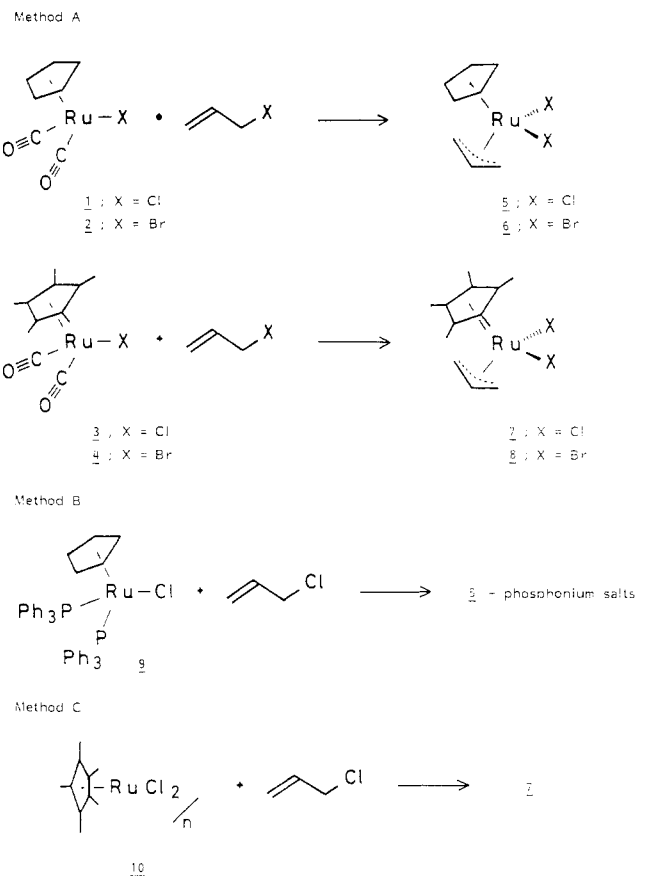
Preparation

Nowell and co-workers reported that the reaction of $[(\eta^5\text{-}C_5Me_4Et)Ru(CO)_2]_2$ with bromine gave $(\eta^5\text{-}C_5Me_4Et)RuBr_3(CO)$.[1c] Cleavage of the metal–metal bond by bromine was followed by the oxidative addition of bromine to $(\eta^5\text{-}C_5Me_4Et)Ru(CO)_2Br$. We found that allylic halides were also useful as the addenda of the oxidative addition to certain Ru(II)–carbonyl complexes. Thus, the Ru(II)–carbonyl precursors $(C_5R_5)Ru(CO)_2X$ (X = Cl, Br; **1–4**) reacted with allylic halides around 140 °C to generate new halo–Ru(IV)–π-allyl complexes, $(C_5R_5)RuX_2(\eta^3\text{-allyl})$ (**5–8**) (Scheme I, method A). The Ru(IV) complexes were precipitated from a refluxing decane or xylene solution of the Ru(II) precursor and allylic halides. Representative results are summarized in Table I.

Comparison of the yields of the Ru(IV) complexes in *n*-decane indicates that the pentamethylcyclopentadienyl–Ru(II)–carbonyl complexes reacted faster than the corresponding cyclopentadienyl complexes. The reactions with allyl bromide were faster than those with allyl chloride. In contrast to the successful oxidative addition in *n*-decane, those carried out in *p*-xylene showed somewhat indefinite behavior (Table I). In the reactions of **2** or **4** with allyl bromide, *p*-xylene accelerated the reaction to raise the conversion of the reactant, but no π-allyl complexes were obtained in the reactions of **1** or **3** with allyl chloride. Details of this strange solvent effect will be discussed later. Other polar solvents such as diglyme also gave the corresponding Ru(IV) complexes in 40–60% yields.

As described above, the Ru(IV) complexes **5–8** were generally obtained by oxidative addition of allylic halides to the Ru(II)–carbonyl precursors **1–4**. However, this process is not satisfactory because the starting carbonyl complexes **1–4** must be prepared by a several-step procedure from the commercially available hydrated $RuCl_3$. We have found alternative precursors for the Ru(IV) complexes. One is a process that uses $(C_5H_5)Ru(PPh_3)_2Cl$ (**9**),[8] which is readily available from cyclopentadiene, hydrated

Scheme I



$RuCl_3$, and PPh_3.[8] Thus, **9** reacted with allyl chloride in *n*-decane at around 120 °C to form **5** together with phosphonium salts (Scheme I, method B). Halogen exchange of **5** by aqueous HBr afforded **6** in quantitative yields. Singleton and co-workers[7] reported the oxidative addition of allyl chloride to $(C_5H_5)Ru(diene)Cl$ as an alternative pathway for **5**. The most convenient preparative process for the pentamethylcyclopentadienyl–Ru(IV)–π-allyl complexes involves the reaction of allylic compounds with a Ru(III) precursor, $[(C_5Me_5)RuCl_2]_n$ (**10**)[9] (Scheme I, method C). The reaction formally involves one-electron oxidation of Ru(III) species by allylic halides.[10] The

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Table II. Preparation of Ru(IV)–Allyl Complexes

halide	product	method[a]	time, h	yield, %
methallyl chloride	$CpRuCl_2(\eta^3\text{-}CH_2CMeCH_2)$ (11)	A (100)	3	94
methallyl bromide	$CpRuBr_2(\eta^3\text{-}CH_2CMeCH_2)$(12)	A (10)	10	82
methallyl chloride	$Cp^*RuCl_2(\eta^3\text{-}CH_2CMeCH_2)$ (13)	A (100)	3	90
		C (2)	3.5	86
3-bromo-2-phenylpropene	$Cp^*RuBr_2(\eta^3\text{-}CH_2CPhCH_2)$ (14)	A (10)	15	93
3-chloro-2-phenylpropene	$Cp^*RuCl_2(\eta^3\text{-}CH_2CPhCH_2)$ (15)	C (2)	6	91
2,3-dichloropropene	$Cp^*RuCl_2(\eta^3\text{-}CH_2CClCH_2)$ (16)	C (2)	7	91
crotyl chloride	$Cp^*RuCl_2(\eta^3\text{-}CH_2CHCHCH_3)$ (17)	C (2)	2	78
1,4-dichloro-2-butene	$Cp^*RuCl_2(\eta^3\text{-}CH_2CHCHCH_2Cl)$ (18)	C (2)	2	92

[a] Method A: Oxidative addition to carbonyl precursors 1–4 in *n*-decane at 140 °C. Method C: Oxidative allylation to 10 in CH_2Cl_2 at room temperture. Numbers in parentheses show the molar excess of the allylic halide relative to the Ru(II) or Ru(III) precursor.

Table III. Selected Bond Distances and Angles[a]

	Bond Distances (Å)		
Ru–CP	1.844 (1)	Ru–C16	2.164 (19)
Ru–Br2	2.553 (2)	C14–C15	1.461 (30)
Ru–Br3	2.561 (2)	C15–C16	1.439 (27)
Ru–C14	2.227 (18)	C4–C5	1.491 (23)
Ru–C15	2.175 (20)	C4–C9	1.505 (26)
	Bond Angles (deg)		
CP–Ru–Br2	115.24 (7)	C14–Ru–C15	66.6 (7)
Br2–Ru–Br3	84.15 (8)	C14–C15–C16	112.6 (17)

[a] CP = center of the Cp* ring calculated from the average of the coordinates of ring carbons. Detailed data are given in the supplementary material.

halogen exchange of 7 with aqueous HBr also gave the bromoallyl complex 8.

Several Ru(IV)–allyl complexes having different π-allyl moieties were also prepared by the reaction of allylic halides with Ru(II) or Ru(III) precursors as summarized in Table II.

Structure and Spectroscopy

The obtained Ru(IV)–π-allyl complexes are generally brown to red microcrystals. $(C_5Me_5)RuBr_2(\eta^3\text{-}C_3H_5)$ (8) was subjected to X-ray crystallography. The ORTEP drawing is shown in Figure 1, and selected bond distances and angles are listed in Table III. The complex 8 has a square-pyramidal structure, with two bromines and terminal carbons of the π-allyl ligand at the basal positions. There is a mirror plane through Ru, C9, C13, and the central carbon of the π-allyl ligand (C15), which bisects the pentamethylcyclopentdienyl and the π-allyl ligands. The average Ru–Br distance is 2.55 Å and Br–Ru–Br angle is 84.2°, while all Ru–C(allyl) bond distances are within 2.2 ± 0.1 Å. C–C distances in the π-allyl ligand are ca. 1.45 Å. These data are similar to those reported for two other Ru(IV)–allyl complexes, $Ru(1\text{–}3{:}6\text{–}7{:}10\text{–}12\text{-}\eta^8\text{-}C_{12}H_{18})$[1a] and $(C_5H_5)RuCl_2(\eta^3\text{-}C_4H_4OMe)$.[7] Interestingly, the π-allyl ligand in 8 or in these known Ru(IV) complexes have C–C distances significantly longer than those reported for the Ru(II)–allyl complexes $(\eta^3\text{-}C_3H_5)Ru(NO)(PPh_3)_2$,[11] $(\eta^3\text{-}C_3H_5)_2Ru(PPh_3)_2$,[12] and $(C_5H_5)Ru(CO)(\eta^3\text{-}CH_2CMeCH_2)$.[13]

It was pointed out by several workers that the orientation of the π-allyl ligand in solution provided two isomeric structures of $(C_5H_5)Ru(L)(\eta^3\text{-allyl})$.[15,16] In the complexes

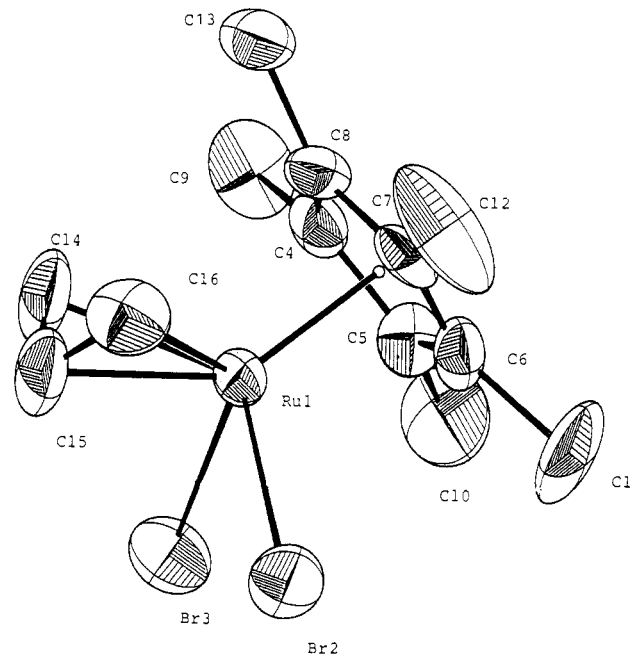

Figure 1.

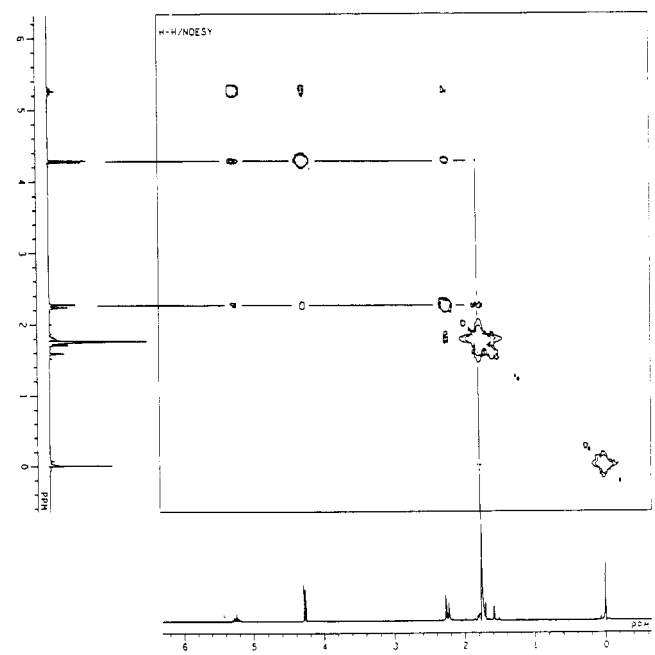

Figure 2. NOESY spectrum of 8 in $CDCl_3$.

where L = CO and PPh_3, the corresponding exo isomers are thermodynamically stable.[13–15] The interconversion between the two isomers was observed by ^1H NMR spectroscopy in these cases. Although similar exo–endo interconversion may occur in the Ru(IV)–allyl complexes

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5–8, variable-temperature NMR studies showed no stereoisomerism in solution (−60 °C to room temperature in $CDCl_3$ and room temperature to 100 °C in toluene-d_8). As described above, the orientation of the π-allyl ligand in 8 was determined as the endo isomer by X-ray analysis. The NOESY spectrum of 8 in $CDCl_3$ showed a strong correlation between the methyl protons of the pentamethylcyclopentadienyl ligand and the anti protons of the π-allyl ligand, despite the absence of correlation between the methyl protons and the proton on the central carbon of the π-allyl ligand (Figure 2). This result strongly indicates that the endo structure is maintained even in solution. NOE studies of 6–8 also showed similar results. Thus, these complexes are concluded to have the endo structure. This endo orientation of the Ru(IV)–allyl complexes is in sharp contrast to the thermodynamic stability of the exo isomer of the Ru(II) complexes $(C_5H_5)Ru(L)(\pi\text{-allyl})$.

^1H NMR spectra of **5** in DMSO-d_6 suggested that the π-allyl ligand reacted with DMSO-d_6 to provide a substantial change in the spectral patterns. At the initial stage, symmetric π-allyl signals of **5** appeared at 3.97 (d), 4.08 (d), and 4.66 (m) ppm, which were assigned to the anti, syn, and central protons, respectively (Figure 3a). However, these peaks slowly diminished at room temperature, and signals at lower field grew in intensity. After the solution was heated at 40 °C overnight, most of the π-allyl signals disappeared to give the spectrum shown in Figure 3b. One explanation for this change of the allylic signals involves the formation of cationic species such as $[(C_5H_5)RuCl(DMSO)(\pi\text{-allyl})]^+Cl^-$. However, the spectrum shown in Figure 3b should rather be assigned to two σ-allyl species, because the doublets at 3.9 and 4.2 ppm are assigned to two sets of allylic methylene protons and the multiplets from 4.8 to 6.1 ppm are ascribed to free olefinic patterns. Careful $^1H\{^1H\}$ decoupling experiments and simulation of the spectrum supported that these peaks resulted from two sets of σ-allyl patterns (Figure 3c,d). Thus, the coordination of DMSO would result in the interconversion of π-allyl to σ-allyl moieties. The two kinds of σ-allyl signals were attributed to the location of the coordinated DMSO, which produces two isomers having two chlorine atoms at mutually trans and cis positions. Attempted isolation of these σ-allyl complexes only resulted in a complex mixture including the π-allyl complex **5**, suggesting that this σ–π interconversion is in equilibrium. Such a σ–π interconversion in polar solvents or by contact with the neutral ligand[17] is a clue in understanding the facile reductive elimination of the coordinated π-allyl moieties by CO or arenes.

Reductive Elimination of Allylic Halides from Ru(IV)–π-Allyl Complexes

Carbonylation reactions of certain halo–metal–π-allyl complexes provide acyl halides.[17,18] The reactions involve the insertion of CO into the metal–carbon bond of these complexes and the subsequent reductive elimination of the resulting acyl and halo ligands from the metal center. For example, carbonylation of $[(\eta^3\text{-}C_3H_5)PdCl]_2$ gave 3-butenoyl chloride through the (3-butenoyl)chloropalladium intermediate.[18a] In alcoholic solvents, 3-butenoates were obtained instead of the chloride; addition of K_2CO_3 is reported to facilitate the formation of 3-butenoates.[19] We attempted the insertion of CO into the Ru–C bond of the Ru(IV)–π-allyl complexes **5–8**. However, butenoyl chloride was not formed at 100–140 °C under up to 50 atm of CO. Similarly, butenoates were not obtained in the attempted carbonylation of the Ru(IV)–allyl complexes in alcoholic solvents in either the presence or absence of K_2CO_3. In these reactions, the reductive elimination of allylic halides from **5–8** forms the Ru(II)–dicarbonyl compounds **1–4**. As shown in Table IV, the reductive elimination of allylic halides generally proceeded at 120–140 °C even under a CO atmosphere.

$$\underset{\textbf{5–8}}{(C_5R_5)RuX_2(\eta^3\text{-}C_3H_5)} + 2CO \rightarrow \underset{\textbf{1–4}}{(C_5R_5)Ru(CO)_2X} + C_3H_5X$$

1, **5**: R = H, X = Cl **2**, **6**: R = H, X = Br

3, **7**: R = Me, X = Cl **4**, **8**: R = Me, X = Br

The reductive elimination of allylic halides from the Ru(IV)–allyl complexes also took place in hot aromatic solvents, giving rise to the formation of cationic Ru(II)–arene complexes, $[(C_5H_5)Ru(arene)]^+X^-$. As shown in Table V, the cyclopentadienyl–Ru(IV)–allyl complexes **5** and **6** afforded the corresponding benzene or *p*-xylene complexes in high yields. In contrast, the yield of $[(C_5Me_5)Ru(p\text{-xylene})]^+Cl^-$ (**22**) from **7** was low, and a similar reaction of **8** did not afford any arene complexes.

$$\underset{\textbf{5–7}}{(C_5R_5)RuX_2(\eta^3\text{-}C_3H_5)} + \text{arene} \rightarrow \underset{\textbf{19–22}}{(C_5R_5)Ru^+(\eta^6\text{-arene})X^-} + C_3H_5X$$

5: R = H, X = Cl
6: R = H, X = Br
7: R = Me, X = Cl

19: R = H, X = Cl, arene = C_6H_6
20: R = H, X = Cl, arene = p-$Me_2C_6H_4$
21: R = H, X = Br, arene = p-$Me_2C_6H_4$
22: R = Me, X = Cl, arene = p-$Me_2C_6H_4$

As described above, Ru(II)–carbonyl complexes **1–4** react with allylic halides to form the Ru(IV)–allyl complexes **5–8**, whereas the carbonylation of the latter complexes re-forms the former by liberating the allylic halides. These results suggest that the oxidative addition of allylic halides to the Ru(II)–carbonyl compounds **1–4** is reversible. The reductive elimination of allylic halides is promoted not only

Table IV. Reductive Elimination of Allyl Halide from Ru(IV)–Allyl Complexes[a]

substrate	temp, °C	time, h	product	yield, %
5	140	2	**1**	92
6	140	2	**2**	48
	140	6		97
7	140	2	**3**	96
	120	2		16
8	140	2	**4**	96
	120	2		45

[a] All reactions were carried out under a CO atmosphere.

Table V. Preparation of Ru(II)–Arene Complexes[a]

substrate	arene	time, h	product	yield, %
5	benzene	30	**19**	56
	p-xylene	17	**20**	88
6	*p*-xylene	16	**21**	94
7	*p*-xylene	20	**22**	40

[a] The procedure is described in the Experimental Section; the temperature was 140 °C for all reactions.

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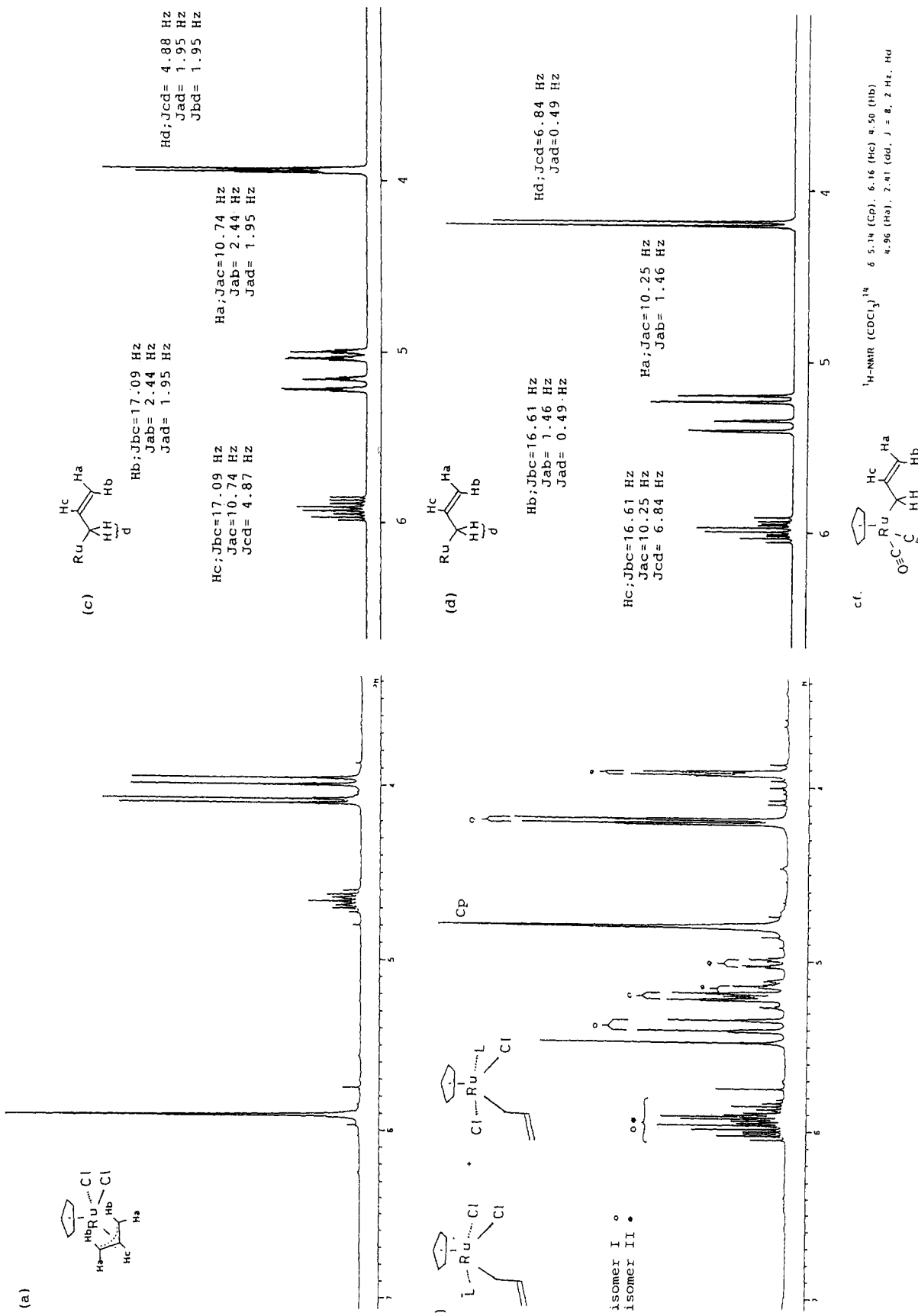
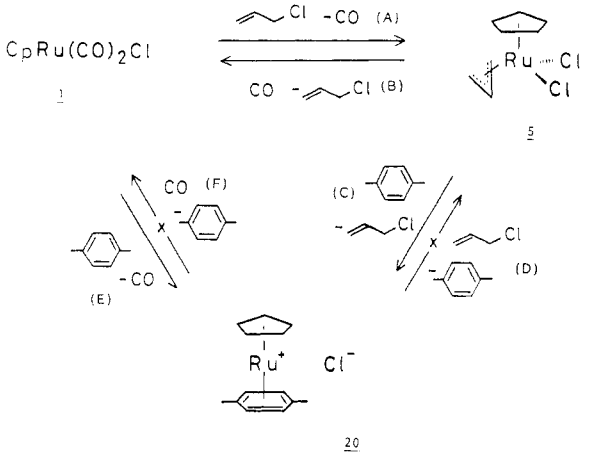


Figure 3. ^{1}H NMR spectra of **5** and its σ-allyl isomers in DMSO-d_6: (a) spectrum at room temperature; (b) spectrum after heating overnight at 40 °C; (c, d) computer-simulated spectra of the two σ isomers.

Scheme II



by CO but also by aromatic solvents. In Scheme II is shown a correlation diagram of the redox reactions between Ru(II) and Ru(IV) oxidation states by way of the oxidative addition and the reductive elimination of allylic halides. Interconversion between **1** and **5** occurred by association and dissociation of either allylic halides or CO (route A or B). Although the reductive elimination of allylic halides from the Ru(IV)–allyl complex **5** took place in *p*-xylene (route C), the reverse reaction from the *p*-xylene complex **20** to **5** by the oxidative addition of allylic chloride did not occur (route D). Since allyl bromide is a better addend than allyl chloride, allyl bromide reacted with **21** gave the Ru(IV)–allyl complex **6**, but in low yields. Furthermore, the ligand exchange between **20** and **1** revealed that the reaction of **1** with *p*-xylene gave **20** (route E), whereas that of **20** with CO did not form **1** (route F). These results showed a variety of redox reactions between Ru(II) and Ru(IV) oxidation states being induced with CO, allylic halides, or arenes.

Halogen Exchange Reactions

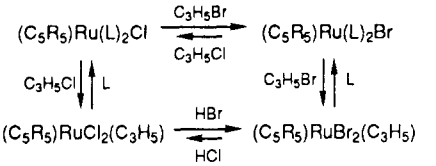
Treatment of the chloro–Ru(IV)–allyl complexes **5** and **7** with HBr provided an excellent preparative route to the corresponding dibromide complexes **6** and **8**, respectively, as noted previously. The corresponding diiodide complexes **23** and **24** were formed in high yields with HI. The results are summarized in Table VI.

$$(C_5R_5)RuCl_2(\eta^3\text{-}C_3H_5) \xrightarrow{HX(aq)} (C_5R_5)RuX_2(\eta^3\text{-}C_3H_5)$$

5: R = H; **7**: R = Me

6: R = H, X = Br; **23**: R = H, X = I; **8**: R = Me, X = Br; **24**: R = Me, X = I

The halogen exchange of the chloro complex to the bromo complex also occurred in the oxidative addition of allyl *bromide* to the *chloro*–Ru(II)–carbonyl complexes and that of allyl *chloride* to the *bromo*–Ru(II)–carbonyl complexes. The former resulted in the selective formation of the allyl–dibromo–Ru(IV) complex, while the latter yielded a mixture of compounds including those containing $Ru^{IV}Br_2$ and $Ru^{IV}Cl_2$ moieties. An unsymmetric π-allyl complex, presumably containing the Ru(IV)BrCl moiety, was also observed spectroscopically in the latter case. In these cases, the halogen exchange of Ru(II) precursors took place prior to the oxidative addition. In fact, the halogen-exchanged Ru(II) carbonyl compounds were recovered at the early stages of the reaction. Control experiments revealed that either the reaction from **1** to **2** or that from **3** to **4** took place even at 40 °C in quantitative yields. In contrast, the bromo–Ru(II)–carbonyl complexes **2** and **4** were hardly converted to the corresponding chloro complexes **1** and **3** by allyl chloride. Thus, the halogen exchange is an equilibrium that favors the formation of the Ru–Br bond rather than the Ru–Cl bond. Similar halogen exchange was also observed in the reaction of allyl bromide with $CpRu(PPh_3)_2Cl$ (**9**).



Mechanistic Considerations

The oxidative addition of allylic halides to the Ru(II)–carbonyl complexes is composed of several elementary steps. Precedence of the facile halogen exchange to the oxidative addition suggests the dissociation of one CO ligand and the coordination of the allylic halide to the metal center. The subsequent oxidative addition of the allylic halide to the Ru moiety forms the σ-allyl intermediate, which then is converted to the π-allyl complex by liberation of the remaining coordinated CO. Since these reactions are essentially in equilibrium, the suppression of the reductive elimination of allylic halides from the resulting Ru(IV)–allyl complexes is crucially important for the efficient isolation of the Ru(IV)–allyl complexes. Thus, the addition of an excess of the allylic halide is necessary for the favorable equilibration to Ru(IV) in the oxidative addition of allylic halides to the Ru(II)–carbonyl precursors. The reaction of allyl chloride with $(C_5H_5)Ru(PPh_3)_2Cl$ (**9**) proceeded under relatively mild conditions, because the dissociated PPh_3 was removed from the reaction mixture by the formation of allylphosphonium salts. Singleton and co-workers reported that $(C_5H_5)Ru(COD)Cl$ underwent oxidative addition of allylic chloride in refluxing ethanol.[7] We found that COD did not promote the reductive elimination of allylic halides from the Ru(IV)–allyl complexes, and hence, this procedure is irreversible.

We have mentioned the strange solvent effect by *p*-xylene in the oxidative addition of allylic halides to Ru(II)–carbonyl complexes. The bromo complexes **2** and **4** reacted faster in *p*-xylene than in *n*-decane. In sharp contrast, the chloro complexes **1** and **3** did not afford the corresponding Ru(IV)–allyl complexes but the Ru(II)–*p*-xylene complexes **20** and **22**, respectively, were formed instead. In the oxidative addition of **1** or **3** with allyl chloride in *p*-xylene, reactions of either the starting Ru(II)–carbonyl precursors or the formed Ru(IV)–allyl complexes with *p*-xylene compete with the formation of Ru(IV)–allyl complexes. Since these competitive reactions are fast and the oxidative addition of allyl chloride to the Ru(II)–arene complexes does not occur, the reactions of **1** or **3** in *p*-xylene only result in the formation of $[(C_5H_5)Ru(arene)]^+X^-$. In contrast, either the bromo–Ru(II)–carbonyl precursors **2** and **4** or the Ru(IV)–bromo–allyl complexes **6** and **8** reacted with *p*-xylene slowly. Thus, the reactions with *p*-xylene do not impede the formation of the Ru(IV)–allyl complexes in these cases.

An interesting feature of the effect of *p*-xylene is that the reactions of **2** or **4** with allyl bromide are somewhat faster than those in *n*-decane. This rate difference is due to the coordination of *p*-xylene to the Ru(II) precursors, accelerating the formation of the Ru(IV)–allyl complexes. The interaction of **2** or **4** with *p*-xylene may promote the ligand exchange of the coordinating CO ligands to η^2- or η^4-*p*-xylene. These η^2- or η^4-bound *p*-xylene compounds would be more reactive toward ligand exchange by allyl

bromide than η^6-*p*-xylene complexes, undergoing facile oxidative addition by allyl bromide.

Conclusion

Metal–alkyl complexes of group VIII transition metals in high oxidation states have not received much attention for a long time. In fact, research on these compounds has not been active except for the study of several Pt(IV) compounds.[21] Recently, excellent work even including catalysis has been emerged from the group of Maitlis on the chemistry of Rh(V)[22] and Ir(V),[23] which are isoelectronic with Ru(IV). In the present paper, we reported the preparation and structure determination of new Ru(IV) complexes. The simple structure of these compounds facilitates exploration of the organometallic chemistry of the Ru(IV) oxidation state. We have found facile redox reactions involving oxidative addition and reductive elimination of allylic halides that result from the dissociation and association of CO or aromatic solvents. Although organometallic research on Ru(IV) compounds has been undertaken in recent years, to our knowledge catalytic reactions unequivocally involving Ru(IV) intermediates have not been reported. Discovery of the facile redox pathway between Ru(II) and Ru(IV) is very important in this context. Intrigued by the results presented in this paper, we have reported the reductive allyl–alkyl coupling on seveal Ru(IV)–allyl–alkyl complexes to form Ru(II) compounds[24] and its application to the catalytic oligomerization of dienes. This is the first catalytic carbon–carbon bond-forming reaction unambiguously involving the redox process between Ru(II) and Ru(IV).[25] Thus, the findings described in this paper have led to new homogeneous catalytic chemistry of ruthenium.

Experimental Section

Materials, Instrumentation, and General Information. The precursor compounds $(C_5H_5)Ru(CO)_2Cl$ (**1**),[26] $(C_5H_5)Ru(CO)_2Br$ (**2**),[27] $(C_5H_5)Ru(PPh_3)_2Cl$ (**9**),[28] and $[Cp^*RuCl_2]_n$ (**10**)[9] were prepared by reported methods. NMR spectra were taken on a JEOL FX-90Q or JEOL GX-270 spectrometer, and the chemical shifts were recorded in ppm from TMS. IR spectra were recorded on a JASCO IR-A3 spectrometer and recorded in cm^{-1}. Elemental analyses were carried out by the Elemental Analysis Center at Kyoto University or by a Yanaco CHN meter. Melting points were measured in a sealed tube under a nitrogen atmosphere. All manipulation was carried out by standard Schlenk techniques under an inert-gas atmosphere. All solvents were distilled in the presence of drying reagents before use.

Table VI. Halogen Exchange of Ru(IV)–Allyl Complexes[a]

substrate	HX	time, h	product	yield, %
5	HBr	2	**6**	90
	HI	1	**23**	91
7	HBr	1.5	**8**	90
	HI	1	**24**	94

[a] The procedure is described in the Experimental Section; the temperture was 40 °C for all reactions.

Preparation of $(C_5Me_5)Ru(CO)_2Cl$ (3) and $(C_5Me_5)Ru(CO)_2Br$ (4). These compounds were synthesized according to the procedure used to prepare the corresponding cyclopentadienyl analogues. $(C_5Me_5)Ru(CO)_2Cl$ (**3**) was prepared from the carbonyl dimer $[(C_5Me_5)Ru(CO)_2]_2$ by the oxidative cleavage of its Ru–Ru bond by HCl and O_2. Typically, the dimer (179 mg, 0.3 mmol) was dissolved in $CHCl_3$ (3 mL). EtOH (1 mL) and 2 N aqueous HCl (1 mL) were added to the solution to make a two-layer mixture. Then, concentrated HCl (0.1 mL) was added and air was bubbled through the mixture for 4 h. Periodic additions of $CHCl_3$ were made to maintain the volume of the organic layer. The organic layer was separated, and the aqueous layer was extracted with $CHCl_3$. The combined $CHCl_3$ solution was concentrated, and the residue was passed through alumina with ether as eluent. The yellow $(C_5Me_5)Ru(CO)_2Cl$ (**3**) was obtained as microcrystals in 85% yield (170 mg, 0.52 mmol). ^1H NMR ($CDCl_3$): 1.90 (s) ppm. IR (CH_2Cl_2): 2025, 1975 cm^{-1}. Anal. Calcd for $C_{12}H_{15}O_2ClRu$: C, 43.97; H, 4.61. Found: C, 43.78; H, 4.60. For the preparation of $(C_5Me_5)Ru(CO)_2Br$, bromine was used as the oxidant. To a solution of $[(C_5Me_5)Ru(CO)_2]_2$[28] (500 mg, 0.82 mmol) in dichloromethane (30 mL) was added dropwise an equimolar amount of bromine (42 μL, 0.82 mmol) dissolved in dichloromethane (3 mL) at room temperature. After it was stirred for 30 min, the reaction mixture was concentrated in vacuo. Chromatographic purification of the residue (alumina, elution with ether) gave $Cp^*Ru(CO)_2Br$ (**4**)[29] as orange crystals in 84% yield (600 mg, 1.38 mmol). ^1H NMR ($CDCl_3$): 1.93 (s) ppm. IR (CH_2Cl_2): 2028, 1976 cm^{-1}. Anal. Calcd for $C_{12}H_{15}O_2BrRu$: C, 38.72; H, 4.06. Found: C, 38.76; H, 3.99.

General Procedure for Preparation of $(C_5R_5)RuX_2(\eta^3$-allyl) from Ru(II) Carbonyls. As noted in the text, the reaction time and amounts of allyl halide were dependent on the starting Ru(II) compounds. A 10-mL round-bottomed flask containing $(C_5H_5)Ru(CO)_2Cl$ (50 mg, 0.194 mmol) was fitted with an efficient reflux condenser, and the atmosphere was replaced by argon. Allyl chloride (0.158 mL, 1.94 mmol) and *n*-decane (3 mL) were added, and the mixture was heated at 140 °C under an inert-gas atmosphere. The Ru(II) compound was dissolved at elevated temperatures to give a yellow solution, from which red microcrystals precipitated. The reaction mixture was cooled and passed through a short silica-gel column, with hexane as eluent, in order to remove decane. Unreacted $CpRu(CO)_2Cl$ was recovered as a yellow band with ether as the eluent. An orange band obtained with dichloromethane–methanol as the eluent was concentrated to afford the desired Ru(IV)–allyl compound in 30–60% yields. Since the reaction is essentially reversible, *efficient cooling so as not to release allyl chloride from the reaction vessel is crucially important.* In order to raise the yields, addition of excess allyl chloride (1 mL, 100 equiv relative to **1**) is recommended. When the reaction mixture was heated for 3 h, the yields were increased over 95%.

Reactions for other Ru(II) compounds were carried out with smaller amounts of allylic halides and shorter reaction times as listed in Table II. Typically, $(C_5Me_5)Ru(CO)_2Br$ (372 mg, 1 mmol) and allyl bromide (0.17 mL, 2 mmol) were heated in *n*-decane (10 mL) at 140 °C for 10 h to afford the Ru(IV)–allyl complex in 96% yield. In our previous communication, we reported over 90%

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(27) Haines, R. J.; du Preez, A. L. *J. Chem. Soc., Dalton Trans.* **1972**, 944.

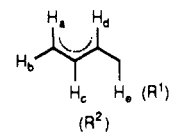
(28) King, R. B.; Iqbal, M. Z.; King, A. D., Jr. *J. Organomet. Chem.* **1979**, *171*, 53.

(29) See also: Weber, L.; Reizig, K.; Boese, R. *Organometallics* **1985**, *4*, 2097.

Table VII. ^{1}H NMR Spectra of Cp- or Cp*-Substituted Ru(IV)-Allyl Complexes[a,b]

compd	C_5R_5[c]	H_a, H_e (R^1)	H_b, H_d	H_c (R^2)
5	5.69	4.45 (d, $J_{ac} = J_{ce} = 6.08$)	3.72 (d, $J_{bc} = J_{cd} = 10.06$)	4.7–5.1 (m)
6	5.67	4.58 (d, $J_{ac} = J_{ce} = 6.08$)	3.53 (d, $J_{bc} = J_{cd} = 10.06$)	4.8–5.2 (m)
7	1.64	4.09 (d, $J_{ac} = J_{ce} = 5.86$)	2.43 (d, $J_{bc} = J_{cd} = 9.91$)	5.0–5.4 (m)
8	1.74	4.25 (d, $J_{ac} = J_{ce} = 5.86$)	2.25 (d, $J_{bc} = J_{cd} = 9.91$)	5.0–5.4 (m)
11	5.67	4.04 (s)	3.71 (s)	R^2 = Me: 2.26 (s)
12	5.75	4.77 (s)	3.64 (s)	R^2 = Ph: 7.2–7.4 (m), 7.6–7.8 (m)
13	1.65	3.60 (s)	2.30 (s)	R^2 = Me: 2.25 (s)
14	1.76	4.39 (s)	2.22 (s)	R^2 = Ph: 7.2–7.4 (m), 7.6–7.8 (m)
15	1.63	4.24 (s)	2.35 (s)	R^2 = Ph: 7.2–7.4 (m), 7.6–7.75 (m)
16	1.65	4.03 (s)	2.65 (s)	R^2 = Cl
17	1.57	H_a: 4.08 (d, $J_{ac} = 6.08$) R^1 = Me: 1.48 (d, $J = 6.08$)	H_b: 2.27 (d, $J_{bc} = 9.46$) H_d: 2.8–3.2 (m)	4.85–5.15 (m)
18	1.57	H_a: 4.00 (d, $J_{ac} = 6.08$) R^1 = CH_2Cl: 3.5–4.4 (m, 2 H)[d]	H_b: 2.33 (d, $J_{bc} = 9.46$) H_d: 2.81 (dt, $J_{cd} = 10.02$, $J_{R^1e} = 2.85$)	4.95–5.3 (m)
23	5.67	4.78 (d, $J_{ac} = J_{ce} = 5.40$)	3.23 (d, $J_{bc} = J_{cd} = 10.20$)	4.93 (m)
24	1.97	4.52 (d, $J_{ac} = J_{ce} = 6.10$)	1.90 (d, $J_{bc} = J_{cd} = 10.0$)	5.15 (m)

[a] All spectra were taken in $CDCl_3$ at room temperature. Chemical shifts are recorded in ppm. H_a–H_e, R^1, R^2 are defined as



The J_{cd} values in **17** and **18** were 9–10 Hz, indicating that these compounds have *syn*-π-allyl ligands. [b] Values in parentheses are coupling constants (Hz). [c] All peaks are sharp singlets. [d] The peaks corresponding to R^1 and H_d are split in an ABX pattern.

yields with a 2-mol excess of allyl bromide for this reaction. Efficient cooling was necessary to keep allyl bromide in the reaction medium; otherwise the yields were not reproducible. A procedure with a 10-mol excess of allyl bromide is recommended to obtain high yields of the Ru(IV)–allyl complexes. In a large-scale experiment in which all Ru(II) carbonyl precursors were consumed, Ru(IV)–allyl complexes were obtained simply by filtration and recrystallization from boiling dichloromethane. ^{1}H NMR data are summarized in Table VII. **5**: mp 170–173 °C dec. Anal. Calcd for $C_8H_{10}Cl_2Ru$: C, 34.55; H, 3.50. Found: C, 34.30; H, 3.50. **6**: mp 220–224 °C dec. Anal. Calcd for $C_8H_{10}Br_2Ru$: C, 26.18; H, 2.74. Found: C, 26.26; H, 2.55. **7**: mp 173–175 °C dec. Anal. Calcd for $C_{13}H_{20}Cl_2Ru$: C, 44.83; H, 5.79. Found: C, 44.69; H, 5.70. **8**: mp 200–205 °C dec. Anal. Calcd for $C_{13}H_{20}Br_2Ru$: C, 35.72; H, 4.61. Found: C, 35.53; H, 4.56. ^{13}C NMR ($CDCl_3$, 22.5 MHz): 103.7 (s, ring carbon), 96.2 (d, central carbon of π-allyl), 64.8 (t, terminal carbon of π-allyl), 9.6 (q, Me) ppm. **11**: mp 177–178 °C dec. Anal. Calcd for $C_9H_{12}Cl_2Ru$: C, 37.00; H, 4.14. Found: C, 36.94; H, 4.08. **12**: mp 228–230 °C dec. Anal. Calcd for $C_{14}H_{14}Br_2Ru$: C, 37.94; H, 3.18. Found: C, 37.15; H, 3.00. **13**: mp 170–172 °C dec. Anal. Calcd for $C_{14}H_{22}Cl_2Ru$: C, 46.41; H, 6.12. Found: C, 46.13; H, 6.15. **14**: mp 200–205 °C dec. Anal. Calcd for $C_{19}H_{24}Br_2Ru$: C, 44.46; H, 4.71. Found: C, 44.36; H, 4.82. **15**: mp 218–219 °C dec. Anal. Calcd for $C_{19}H_{24}Cl_2Ru$: C, 53.78; H, 5.70. Found: C, 53.44; H, 5.66. **16**: mp 197–198 °C dec. Anal. Calcd for $C_{13}H_{19}Cl_3Ru$: C, 40.80; H, 5.00. Found: C, 40.65; H, 5.08. **17**: mp 123–124 °C dec. Anal. Calcd for $C_{14}H_{22}Cl_2Ru$: C, 46.41;; H, 6.12. Found: C, 46.24; H, 6.20. **18**: mp 136–137 °C dec. Anal. Calcd for $C_{14}H_{21}Cl_3Ru$: C, 42.38; H, 5.37. Found: C, 42.06; H, 5.34.

Oxidative Addition of Allyl Chloride to (C_5H_5)Ru$(PPh_3)_2$Cl. In a round-bottomed flask fitted with an efficient reflux condenser was placed $(C_5H_5)Ru(PPh_3)_2Cl$ (**9**; 2.2 g, 3 mmol),[8] and the atmosphere was replaced by argon. Allyl chloride (3.4 mL, 30 mmol) and *n*-decane (3 mL) were added, and the mixture was heated at 120 °C for 2 h. The initially yellow solution gradually faded, and red-purple solids precipitated. The mixture was cooled and placed on the top of a long silica gel column (4 cm × 40 cm). Decane was removed by eluting with hexane. Trace amounts of unreacted **9** were isolated with ether as the eluent. The desired Ru(IV)–allyl complex was obtained from red dichloromethane–methanol (50:1) eluates (60–90% yields). The upper three-fourths of the silica gel column turned black, and the product band was obtained by bypassing the black section of the column. Careful elution is crucially important to separate **5** from dark brown byproducts.

Preparation of $(C_5Me_5)RuCl_2(\eta^3$-allyl) from $[(C_5Me_5)RuCl_2]_n$. $[(C_5Me_5)RuCl_2]_n$ (**10**;[9] 422 mg, 1.37 mmol) was dissolved in dichloromethane (20 mL) containing a mixture of ethanol and water (95:1, 0.4 mL) under a nitrogen atmosphere. Allyl chloride (0.24 mL, 2.74 mmol) was added to the solution, and the resulting dark brown solution was stirred at 40 °C for 2 h to afford a clear brown solution containing $(C_5Me_5)RuCl_2(\eta^3$-allyl) (**7**). The mixture was concentrated, and the residue was purified on a silica gel column with ethyl acetate as the eluent (90–95% yields). Contamination by oxygen of the reaction mixture or use of absolute ethanol produced a byproduct, in which a methyl group on the pentamethylcyclopentadienyl ring was chlorinated.[30] Its formation caused a decrease of the yields.

Halogen Exchange of Ru(IV)–Allyl Complexes. The general procedure is given below. $(C_5Me_5)RuCl_2(\eta^3$-allyl) (**7**; 574 mg, 1.65 mmol) was dissolved in dichloromethane (20 mL), and an aqueous soluion of HBr (47%, 5.7 mL) was added to the solution. The mixture was heated at 40 °C for 2 h. Then, water (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with dichloromethane. The combined organic layer was washed with brine and dried over $MgSO_4$. After concentration, purification of the residue by passing through a short silica gel column with ethyl acetate as eluent afforded the desired bromide in 93% yield (670 mg, 1.53 mmol). NMR data are shown in Table VII. **23**: mp 268–270 °C dec. Anal. Calcd for $C_{13}H_{20}I_2Ru$: C, 20.84; H, 2.19. Found: C, 20.61; H, 2.23. **24**: mp 255–260 °C dec. Anal. Calcd for $C_8H_{10}I_2Ru$: C, 29.39; H, 3.79. Found: C, 29.15; H, 3.88.

Reductive Elimination of Allylic Halides from the Ru(IV)–Allyl Complexes by CO. A typical example is given below. In a 10-mL round-bottomed flask fitted with a reflux condenser was placed $(C_5H_5)RuCl_2(\eta^3$-$C_3H_5)$ (**5**; 50 mg, 0.18 mmol) and the atmosphere was replaced by CO. *n*-Decane (3 mL) was then added, and the suspension was heated at 140 °C for 2 h. The red-brown crystals gradually dissolved, and finally a yellow solution was obtained. The cooled solution was passed through a silica gel column with hexane as the eluent in order to remove decane. $(C_5H_5)Ru(CO)_2Cl$ (**1**) was obtained from a yellow band by elution with ether (43 mg, 93%).

Reductive Elimination of Allylic Halides from the Ru(IV)–Allyl Complexes by Arenes. A typical example is given below. $(C_5H_5)RuCl_2(\eta^3$-$C_3H_5)$ (**5**; 30 mg, 0.018 mmol) and benzene (3 mL) were heated in a sealed tube at 140 °C for 30 h. The initially red solids gradually turned white. The cooled mixture was concentrated, and the residue was purified on a silica gel column. Unreacted starting material was recovered as a red band by elution with dichloromethane–methanol (50:1) (10 mg, 32%).

(30) Nagashima, H.; Mukai, K.; Itoh, K. Unpublished results.

Table VIII. Final Positional Parameters of 8

	x/a	x/b	x/c
Ru1	0.9810 (1)	0.5080 (1)	0.3664 (1)
Br2	0.8316 (1)	0.3685 (1)	0.3735 (2)
Br3	1.0326 (2)	0.4327 (1)	0.1247 (2)
C4	1.1536 (14)	0.5598 (12)	0.4320 (17)
C5	1.1554 (14)	0.4483 (12)	0.4367 (16)
C6	1.0747 (14)	0.4196 (11)	0.5367 (19)
C7	1.0209 (11)	0.5039 (12)	0.5959 (13)
C8	1.0733 (14)	0.5938 (11)	0.5306 (18)
C9	1.2351 (15)	0.6218 (17)	0.3452 (22)
C10	1.2384 (18)	0.3843 (17)	0.3537 (27)
C11	1.0561 (18)	0.3110 (12)	0.5890 (25)
C12	0.9390 (17)	0.5054 (23)	0.7158 (19)
C13	1.0597 (18)	0.7016 (12)	0.5790 (21)
C14	0.9732 (17)	0.6463 (12)	0.2344 (21)
C15	0.8596 (19)	0.6055 (13)	0.2597 (20)
C16	0.8323 (16)	0.5988 (14)	0.4090 (19)

Elution with methanol gave a colorless solution containing (C_5H_5)RuCl(benzene), spectral data of which were identical with those reported by Zelonka and Baird.[20] The reactions with other arenes were carried out in a 10-mL round-bottomed flask fitted with a reflux condenser under a nitrogen atmosphere. **19**: mp 161 °C dec (lit.[20] mp 161 °C). ^{1}H NMR ($CDCl_3$, 90 MHz): 5.48 (Cp), 6.36 (benzene) ppm (lit.[20] NMR 5.35, 6.12 ppm). **20**: An analytically pure sample was not obtained. ^{1}H NMR ($CDCl_3$, 90 MHz): 2.36 (Me), 5.36 (Cp), 6.28 (aromatic) ppm. The halogen exchange of **20** with KPF_6 in wet acetone at room temperature afforded the corresponding PF_6 complex, which provided an analytically pure sample after recrystallization from dichloromethane–ether. ^{1}H NMR ($CDCl_3$, 270 MHz): 2.33 (Me), 5.30 (Cp), 6.10 (Me) ppm. ^{13}C NMR (acetone-d_6, 67.8 MHz): 20.11 (Me), 49.89 (ipso of xylene), 81.65 (Cp), 87.48 (CH of xylene) ppm. IR (KBr): 832 (P–F) cm^{-1}. Anal. Calcd for $C_{13}H_{15}F_6PRu \cdot {}^1/_2H_2O$: C, 36.63; H, 3.78. Found: C, 36.88; H, 3.59. **21**: mp 180–190 °C dec. Anal. Calcd for $C_{13}H_{15}BrRu$: C, 44.66; H, 4.42. Found: C, 44.33; H, 4.29. ^{1}H NMR ($CDCl_3$, 90 MHz): 2.38 (Me), 5.38 (Cp), 6.25 (aromatic) ppm. **22**: An analytically pure sample was not obtained. ^{1}H NMR ($CDCl_3$, 90 MHz): 1.96 (Cp*), 2.20 (Me), 5.85 (aromatic) ppm.

X-ray Crystallographic Analysis. Crystals of 8 grown from dichloromethane and hexane solutions were found suitable for an X-ray crystal structure determination. A single crystal of dimensions 0.2 × 0.2 × 0.6 mm was sealed on a glass fiber and mounted on a Rigaku AFC-5 automated four-circle diffractometer for data collection. The orthorhombic $P2_12_12_1$ unit cell dimensions were determined and refined by a least-squares fit of 20 independent reflections with $25° < 2\theta < 30°$ (crystal data: a = 11.738 (1) Å, b = 13.367 (7) Å, c = 9.383 (1) Å, $\alpha = \beta = \gamma = 90°$, Z = 4). Intensity data were measured by the ω–2θ scan technique (scan range: $2° < 2\theta < 60°$, scan speed 6 deg/min) with Mo Kα radiation (λ = 0.71068 Å) from a graphite monochromator. If $\sigma(F)/F$ was more than 0.1, a scan was repeated up to three scans and the results were added to the first scan. Three standard reflections were monitored every 100 measurements. All data processing was performed on a FACOM A-70 computer by using the R-CRYSTAN structure-solving program obtained from the Rigaku Corp. Neutral scattering factors were obtained from ref 31. In the reduction data Lorentz and polarization corrections were made and no adsorption correction was made. Full-matrix least-squares refinements minimized the function $[\sum w(|F_o| - |F_c|)^2/w|F_o|^2]^{1/2}$, where $w = 1/[\sigma(F_o)^2 + p(F_o)^2]$, the parameter p being automatically optimized. The positions of the Ru and Br atoms were revealed by the inspection of a Patterson map. Subsequent difference Fourier maps revealed the positions of all other non-hydrogen atoms. The final cycle of block-diagonal least-squares refinement of the structure, including the anisotropic thermal parameters for the non-hydrogen atoms, converged at R = 0.0695 for 2647 unique data ($F > 3\sigma(F)$) from 4696 total collected data. In Table VIII are listed final positional parameters and their standard deviations for all non-hydrogen atoms.

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Supplementary Material Available: Tables of positional parameters and Cartesian coordinates, bond distances and bond angles, and temperature factors (3 pages); an F_o–F_c table (10 pages). Ordering information is given on any current masthead page.

(31) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.