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# Chemistry of coordinatively unsaturated organoruthenium amidinates as entry to homogeneous catalysis

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## Contents

## Abstract

The chemistry of coordinatively unsaturated organoruthenium complexes is reviewed in this article. In particular, the subject is focused on neutral and cationic organoruthenium amidinates, which formally have 16 valence electrons and show signs of coordinative unsaturation. The ruthenium amidinates, ($\eta^5$-$C_5Me_5$)Ru($\eta$-amidinate) (**1**), and their isoelectronic analogues, [($\eta^6$-arene)Ru($\eta$-amidinate)]$^+$ (**2**), are synthesized and characterized; a possible stabilizing factor of the unsaturated metal center is weak coordination of $\pi$-electrons in the amidinates ligands. Reactions of various two-electron donor ligands with **1** or **2** reveal the strong $\pi$-donor property of **1** and Lewis acid nature of **2**. One or two-electron redox processes of **1** in the reactions with organic halides are studied by isolation of the corresponding Ru(III) and Ru(IV) products; the results lead to their catalysis for the Tsuji–Trost reaction and the intramolecular Kharasch reaction. The treatment of **2** with trimethylsilyldiazomethane results in the formation of cationic amidinato-carbene complexes, which involve unusual reversible metal-to-carbon silyl group migration.

*Keywords:* Coordinative unsaturation; Ruthenium amidinates; Redox processes; Catalysis; Carbenes; Silyl group migration

## 1. Introduction

Coordinatively unsaturated organometallic complexes as key intermediates in the catalytic cycle have received much attention from organic and organometallic chemists who work with homogeneous catalysis [1,2]. Since capture and characterization of the catalytic species in actual transition

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metal-catalyzed reactions are generally difficult, due to low concentration and high reactivity of the metal component, the coordinatively unsaturated nature of isolable metal complexes having fewer than 18 electrons has been investigated through studies of their molecular structures, solution dynamics, and reactions of various organic substrates [3]. Transition metals at the middle of the periodic table are generally faithful to the 18 electron rule, so that the synthesis and characterization of ruthenium complexes with 16 or fewer valence electrons have been actively researched [4–47].

An excellent review by Poli in 1996 has provided important insights of organometallic compounds that are stable with less than 18 valence electrons [3]. Although the subject of Poli's paper is a systematic review of theoretical and experimental results of "open-shell organometallics", studies on 14- and 16-electron ruthenium compounds, many of which are diamagnetic and easily characterized by spectroscopic tools, aid in understanding structures and reactivity of coordinatively unsaturated transition metal complexes. For instance, recent topics derived from these studies are consideration of spin states in the coordinatively unsaturated iron complexes in comparison with the ruthenium homologues; recent progress is reviewed by Sapunov et al. [47] and Sitzmann [48]. A series of coordinatively unsaturated ruthenium(0) [8–14] and ruthenium(II) complexes [15–28] were systematically synthesized and characterized by Caulton and coworkers, who proposed the importance of π-donor ligands for the effective stabilization of 14- and 16-electron ruthenium complexes. Coordination of two-electron donor ligands including molecular $N_2$ and activation of $H_2$ and $H\text{-}SiR_3$ by Caulton's ruthenium compounds were also investigated in relation to their potential involvement in homogeneous catalysis. Typical ruthenium catalysts having 16 valence electrons are the Grubbs's carbenes, $RuCl_2(=CHR)(PR_3)_2$, which are actually involved in the catalytic cycle of olefin methathesis [49–55].

When the subject is more focused on the half-sandwich ruthenium complexes, studies on the compounds shown in Fig. 1 reveal detailed factors for the effective stabilization of the coordinatively unsaturated Ru(II) complexes and their reactivity towards various substrates [4–6,25–47]. Although these compounds are generally sensitive to air and moisture, careful manipulation allowed us to learn a number of interesting aspects regarding the stabilizing factors of these unsaturated compounds: (1) blocking of the metal center by sterically hindered ligands, (2) π-stabilization of the adjacent functional group, and (3) the strong σ-donor. The Tilley's complex, $(\eta^5\text{-}C_5Me_5)RuCl(P^iPr_3)$, where the bulky $P^iPr_3$ group sterically protects the reactive metal center, is one of the first example of a 16 genuine valence electron half-sandwich Ru(II) complex [4] and the chemistry of its analogues has been actively investigated since then [5,6,25–31]. Extensive studies on $(\eta^5\text{-}C_5Me_5)RuX(PR_3)$ where X = Cl, Br, I, OR, $OSiR_3$, NHR, SR, and $C_2R$ by Caulton and coworkers showed the importance of "π-stabilization" by the ligand X [25–28], whereas the ruthenium thiolates and amides reported by Mashima and coworkers [34–37], and Burrell and Steedman [45] are also stabilized by the SR and NHR ligands. Diaminocarbene complexes were investigated by Nolan and coworkers [32,33]. The two legged piano-stool ruthenium complexes having phosphine [40,41] or chelate diamine ligands [42–44] were recently reported by Kirchner and Valerga; the factors of stabilization are discussed in terms of σ-donor character and through-space coupling concept [47]. A unique ligand, $^iPrN_2PPhNH^iPr$ (N-TAP), which behaves both as α- and π-donor to the ruthenium center, is reported [48].

Many of these coordinatively unsaturated Ru(II) complexes facilely react with a variety of two-electron donor ligands such as CO, phosphines, olefins, and acetylenes, and are even reactive towards molecular hydrogen, resulting in either its coordination or oxidative addition to the metal center. Such high reactivity has provided a clue to the mechanism of catalytic reactions. One of the clearest examples for the involvement of coordinatively unsaturated Ru(II) complexes in homogeneous catalysis was reported by Noyori and coworkers in 1997; the 16-electron complex, $(\eta^6\text{-}p\text{-cymene})Ru(NHCHPhCHPhNTs)$, and its

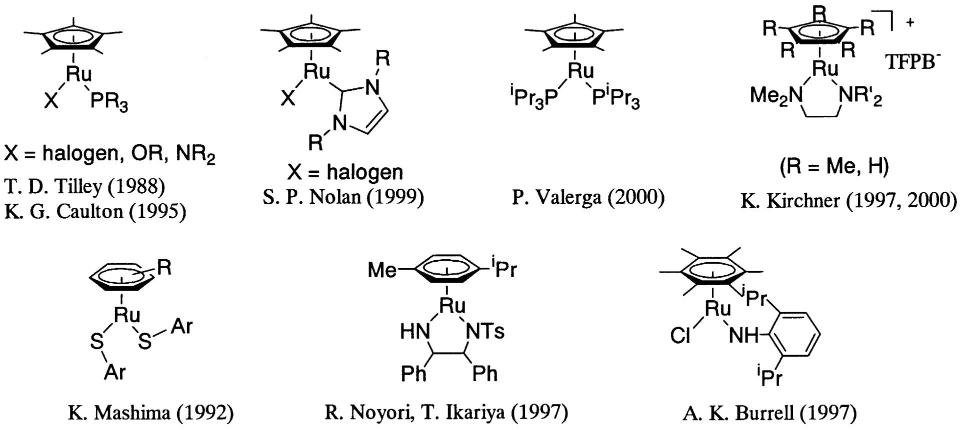


Fig. 1. Representative examples of coordinatively unsaturated half-sandwich ruthenium complexes.

analogues are good catalysts for asymmetric hydrogen transfer reactions between alcohols and ketones [38,39].

All of these results on the reactive 16-electron Ru(II) complexes suggest that novel coordinatively unsaturated half-sandwich Ru(II) compounds, which are isolable yet highly reactive, can be synthesized by the judicious choice of the auxiliary ligands with appropriate steric bulkiness and good σ- and/or π-donor properties. Furthermore, Noyori's results showing that the coordinatively unsaturated Ru(II) species is actually involved in the catalytic cycle clearly demonstrate that studies on reactivity of such unsaturated complexes is a good entry to the development of catalytic reactions by appropriate planning of the catalytic cycle, in which the coordinatively unsaturated species are involved. In this context, we have been interested in the preparation of ruthenium complexes, $(\eta^5\text{-}C_5H_5)RuL$, where L are four electron donor ligands to $Ru^+$. These compounds have 16 valence electrons, and are isoelectronic with $(\eta^5\text{-}C_5H_5)_2Mo$, the fascinating reaction chemistry of which was extensively studied by Otsuka and coworker [56], and Green and coworkers [57] in the early 1970s. Our early studies aimed at synthesizing $(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-allyl})$ as one of the $(\eta^5\text{-}C_5H_5)RuL$ provided us with an opportunity to become familiar with the chemistry of new Ru(IV) complexes, $(\eta^5\text{-}C_5H_5)RuX_2(\eta^3\text{-allyl})$ and their $\eta^5\text{-}C_5Me_5$-homologues [58–62]; however, the attempted reduction of these Ru(IV)-allyl complexes did not give any isolable compounds which can be assigned as $(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-allyl})$. In our further investigation seeking for the other four electron donor ligands to $Ru^+$ which can effectively stabilize the coordinatively unsaturated Ru(II) center, we were interested in the use of heteroallyl ligands, in particular, the amidinates, $[RN{=}C(R')NR]^-$. Transition metal amidinates are a well investigated class of compounds as seen in the reviews by Kilner and coworker [63], and Edelmann [64] in 1994. Almost all of the mono- or dinuclear transition metal amidinates include the $\eta^2$ or $\mu_2$, $\eta^1$; $\eta^1$-bonding mode, in which two nitrogen atoms are bonded to the mono- or bimetallic center. Access to the amidinate complexes is in many cases easily accomplished by treatment of a Li or Ag salt of a amidinate with a transition metal halide precursor. Although a number of early transition metal amidinates have been synthesized, there are relatively few complexes of late transition metals in the literature [63,64]. In particular, the number of ruthenium amidinates was surprisingly low when we started this project (Fig. 2).

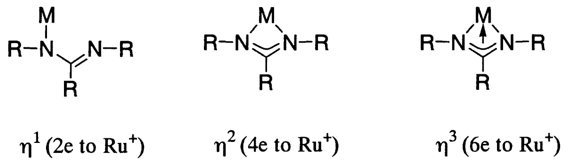


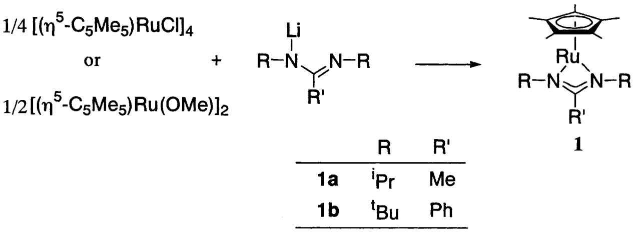
Fig. 2. Possible coordination modes of the amidinate ligands (M: transition metal).

In this paper, we wish to review our recent results of organoruthenium amidinate complexes which formally have 16 valence electrons and show a coordinatively unsaturated nature. As described above, the amidinate ligand actually realized "$(\eta^5\text{-}C_5Me_5)RuL$" as the isolable compounds, $(\eta^5\text{-}C_5Me_5)Ru(\eta\text{-amidinate})$ (**1**) [65]. We successfully prepared their isoelectronic complexes, $[(\eta^6\text{-arene})Ru(\eta\text{-amidinate})]^+$ (**2**) [66]. These complexes have characteristic features in spectroscopy and crystallography, exhibiting high reactivity towards a variety of two-electron donor ligands [65,66], organic halides [67–69], diazoalkanes [70], or metal fragments [71,72]. Studies on the crystal structures revealed the possible stabilizing factor of the amidinate ligands to be coordination of π-electrons of the amidinate ligand to the ruthenium center; this is supported by DFT calculations of the model compounds [73]. The reactions of the ruthenium amidinates contribute to understanding of the π-basic and Lewis acidic nature of **1** and **2**, respectively, opening up synthetic methods for a series of new mononuclear and dinuclear ruthenium amidinates, and providing a clue to catalysis by these complexes.

## 2. Results and discussion

### 2.1. Neutral 16-electron organoruthenium amidinates

A versatile synthetic route to transition metal amidinates is the treatment of lithium amidinates with transition metal halides as described above. In our synthetic planning of $(\eta^5\text{-}C_5Me_5)Ru(\eta\text{-amidinate})$ as one of the possible 16-electron complexes CpRuL, we were interested in $[(\eta^5\text{-}C_5Me_5)RuCl]_4$ or $[(\eta^5\text{-}C_5Me_5)Ru(OMe)]_2$ as the precursor [65]. These complexes were reported by Fagan et al. [74] and Koelle and coworkers [75,76] as useful precursors for a variety of ruthenium(II) complexes. In fact, the treatment of $[(\eta^5\text{-}C_5Me_5)Ru(OMe)]_2$ with a stoichiometric amount of lithium amidinate resulted in formation of the corresponding $(\eta^5\text{-}C_5Me_5)Ru(\eta\text{-amidinate})$ complexes, **1a** and **1b**, as air- and moisture sensitive but thermally stable solids with intense violet colors (Scheme 1). Since the amidinate ligands, $[R_1N{=}C(R_2)NR_1]^-$, generally behave as a four electron donor to $Ru^+$, the resulting new ruthenium amidinates, **1a** and **1b**, must have 16 valence electrons.



| | R | R' |
|---|---|---|
| **1a** | $^i$Pr | Me |
| **1b** | $^t$Bu | Ph |

Scheme 1. Preparation of typical neutral ruthenium amidinate complexes.

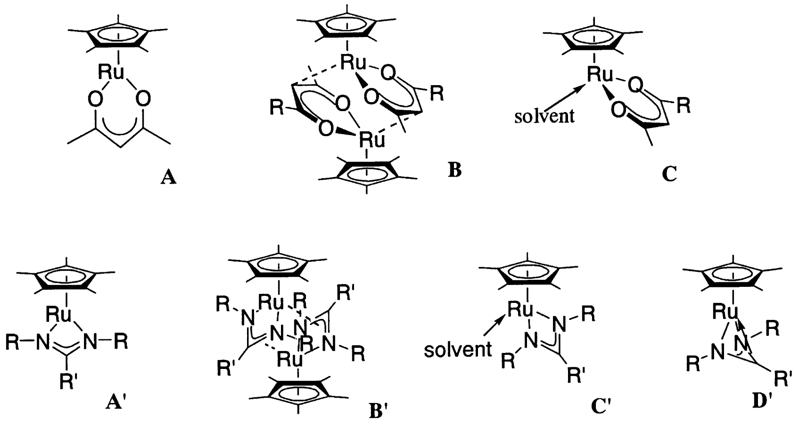


Fig. 3. Possible structures of ($\eta^5$-$C_5Me_5$)Ru($\eta$-acac) and ($\eta^5$-$C_5Me_5$)Ru($\eta$-amidinate).

Possible formation of 16 valence electron ruthenium complexes was discussed by Koelle et al. in their studies on ($\eta^5$-$C_5Me_5$)Ru($\eta$-acac) and related compounds; however, detailed studies revealed that ($\eta^5$-$C_5Me_5$)Ru($\eta$-acac) was a dimer in the solid states shown in Fig. 3 (structure B) [75]. Dynamic behavior in NMR spectroscopy, which may suggest the existence of a monomeric 16-electron species A in the solution could not exclude the possibility of C being effectively stabilized by the solvent. Similarly, the ruthenium amidinates have three possible structures A′, B′, and C′ as shown in the figure. NMR spectroscopy of the ruthenium amidinate **1a** bearing isopropyl substituents is a good method to differentiate the pseudo $C_{2v}$-symmetric A′ from B′ or C′ with the $C_s$ symmetry, in which only a single $^1$H resonance doublet due to methyl groups in the isopropyl moiety appeared even below −80 °C in a non-coordinating solvent, cyclohexane-$d_{14}$. This ruled out the possibility of dimer B′ and solvent stabilized species C′ in the solution, which would provide two independent doublets due to the magnetically inequivalent methyl groups.

The X-ray structure determination of **1b** revealed that the ruthenium amidinate existed as a monomer as shown in Fig. 4; no coordinating solvent was observed. However, its molecular structure is $C_s$-symmetric as shown. Of particular interest in this structure is the short distance between the ruthenium atom and the central carbon of the amidinate ligand, which leads to a “folded structure” as illustrated in D′ in Fig. 3. The folded structure provided $^1$H NMR spectra in which peaks due to the two methyl groups in the isopropyl moiety in **1a** or those derived from five protons in the phenyl group in **1b** appeared independently. However, such signals suggesting $C_s$-symmetric structures were not observed in variable temperature $^1$H NMR of either **1a** or **1b**. A reasonable interpretation of these spectroscopic and crystallographic results is that the most stable geometry of the ruthenium amidinate is the folded structure D′ but that this species is converted to other forms, A′ and E′, with a low energy barrier, so that we can only detect average signals close to A′ in NMR spectroscopy (Fig. 5). In fact, DFT calculations of the model compound, ($\eta^5$-$C_5H_5$)Ru($\eta$-HN=C(H)NH), showed that the optimized structure has a “folded structure” close to the one observed in crystallography, inversion of the metal center occurs between two folded structures through the $C_{2v}$-symmetric transition states with a few kcal/mol of activation energy, and the energy barrier of the geometrical change from D′ to E′ is also small [73].

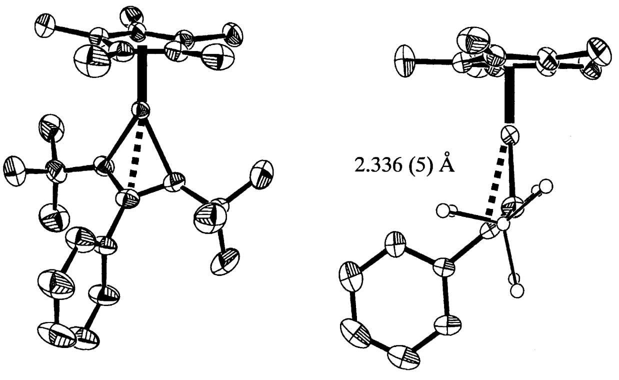


Fig. 4. The ORTEP drawings of **1b**; front view (left) and side view (right).

The folded structure observed in the crystallographic structure of **1b** is unusual in the transition metal amidinates [63,64]. The amidinate ligand in almost all of the transition metal amidinates in the literature is bonded to the metal center through two nitrogen–metal bonds, and the metal center; two nitrogen atoms, and the central carbon of the amidinate ligand are in a plane. There is only one example in the literature which has the folded structure, and this is titanium amidinate reported by Sita and coworkers [77]. These authors concluded, however, that this unusually short Ti–C bond was ascribable to crystal packing. Although the effect of the crystal packing should also not be excluded in our ruthenium amidinates, we believe that the origin of the folded structure in these amidinates, which provides the short distance between the ruthenium atom and the central carbon of the amidinate ligand, could be derived

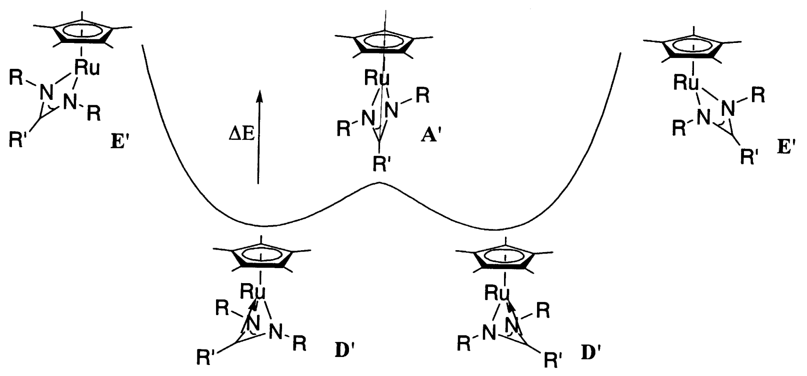
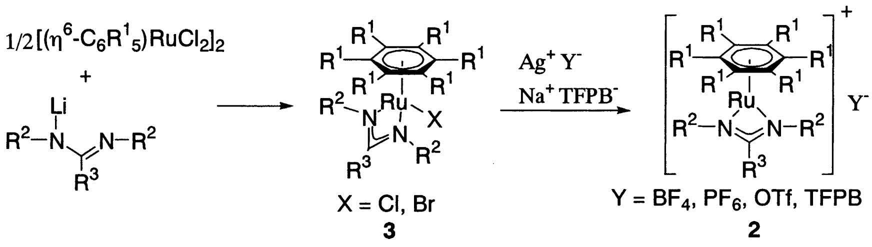


Fig. 5. Dynamic behavior of the ruthenium amidinates.

from coordination of the π-electrons in the amidinate ligand to the ruthenium center; the DFT calculation supported this. In contrast to the $d^0$-titanium complex reported by Sita and coworkers [77], the metal center in the ruthenium amidinates has d-electrons which were able to interact with both π- and π*-orbitals in the amidinate ligand. The possible π-coordination of the amidinate ligand may resemble the "π-stabilized coordinative unsaturation" as proposed by Caulton and coworkers, who reported many examples of the π-stabilized coordinatively unsaturated ruthenium alkoxides and amides [7]. There is a brief mention in their articles suggesting that the π-electrons in the acetylide were able to stabilize the unsaturated metal center, which may be analogous to the π-stabilization of the amidinate ligand in the ruthenium amidinates. The strong σ-donation of the nitrogen atom and the TSC concept proposed by Kirchner and coworkers in their $[(\eta^5\text{-}C_5R_5)Ru(\eta^2\text{-TMEDA})]^+$ [42–44,47] may be an alternative explanation for the stabilizing factor in the ruthenium amidinates; however, the contribution of the σ-donor ability should be small, because conjugation of the amidinate ligand reduces the σ-donor ability of the nitrogen atoms compared with those in TMEDA.

### 2.2. Cationic 16-electron organoruthenium amidinates

The above results confirmed that the amidinate ligands effectively stabilize the coordinatively unsaturated ruthenium species, with the weak coordination ability of the π-electrons in the amidinate ligand being a possible stabilizing factor. This observation prompted us to synthesize cationic ruthenium amidinates, $[(\eta^6\text{-arene})Ru(\eta\text{-amidinate})]^+$, as the isoelectronic compounds of $(\eta^5\text{-}C_5Me_5)Ru(\eta\text{-amidinate})$ [66]. The cationic ruthenium amidinates were synthesized by exchange of the halogen atom in $(\eta^6\text{-arene})RuX(\eta\text{-amidinate})$ with weakly coordinating anions as shown in Scheme 2. Thus, several $(\eta^6\text{-arene})RuX(\eta\text{-amidinate})$ complexes **3** were prepared from the reaction of $[(\eta^6\text{-arene})RuX_2]_2$ with lithium amidinates. Treatment of $(\eta^6\text{-}C_6H_6)RuBr(^iPrN{=}C(Me)N^iPr)$ (**3a**-Br) with AgOTf (OTf: trifluoromethanesulfonate) gave the corresponding triflate complex **2a**-OTf in good yield; however, the triflate ligand was relatively tightly bonded to the ruthenium center in **2a**, as was confirmed by both NMR and crystallography. When the counter anion exchange of **3a** was carried out by $Na^+(TFPB)^-$ (TFPB: [tetrakis{3,5-bis(trifluoromethyl)phenylborate}]), the corresponding TFPB complex, **2a**-TFPB,



| | $R^1$ | $R^2$ | $R^3$ | X |
|---|---|---|---|---|
| **3a-Cl** | H | $^i$Pr | Me | Cl |
| **3b-Cl** | Me | $^i$Pr | Me | Cl |
| **3a-Br** | H | $^i$Pr | Me | Br |
| **3b-Br** | Me | $^i$Pr | Me | Br |

| | $R^1$ | $R^2$ | $R^3$ | Y |
|---|---|---|---|---|
| **2a-OTf** | H | $^i$Pr | Me | OTf |
| **2a-TFPB** | H | $^i$Pr | Me | TFPB |
| **2b-PF$_6$** | Me | $^i$Pr | Me | $PF_6$ |
| **2b-OTf** | Me | $^i$Pr | Me | OTf |
| **2b-TFPB** | Me | $^i$Pr | Me | TFPB |

Scheme 2. Preparation of typical cationic ruthenium amidinate complexes.

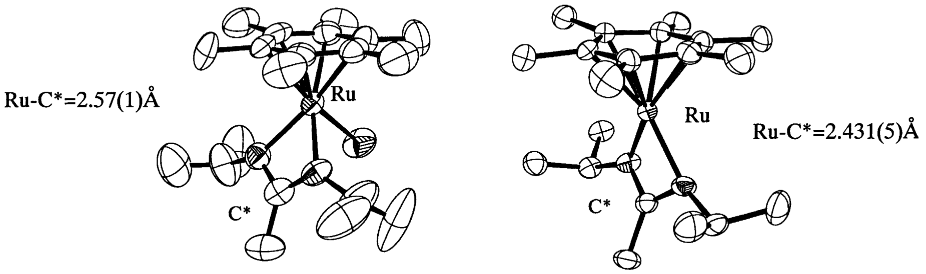


Fig. 6. The ORTEP drawings of **3a**-Br (left) and **2b**-$PF_6$ (right).

was prepared. No interaction of the counter anion with the metal center was observed by $^1H$ or $^{19}F$ NMR spectroscopy of **2a**-TFPB. Although crystallographic analysis of **2a**-TFPB was unsuccessful because of the difficulty in preparing a single crystal suitable for the X-ray structure determination, analysis of an analogue of **2a**-TFPB, $[(\eta^6\text{-}C_6Me_6)Ru(^iPrN{=}C(Me)N^iPr)]^+PF_6^-$ (**2b**-$PF_6$), gave the molecular structure shown in Fig. 6 (right). In contrast to the crystal structures of **3a**-Br (Fig. 6 (left)) which have a typical three-legged piano-stool geometry, **2b**-$PF_6$ has a "folded structure" similar to that seen in the molecular structure of **1b**. The folded structure has resulted from the relatively short bond distance between the ruthenium atom and the central carbon of the amidinate ligand in **2b**-$PF_6$ [2.43(5) Å], suggesting stabilization of the unsaturated metal center by weak coordination of the π-electrons in the amidinate ligand to the ruthenium atom. Results of DFT calculations of a model compound, $[(\eta^6\text{-benzene})Ru(\eta\text{-}HN{=}CHNH)]^+$, are similar to those of $(\eta^5\text{-}C_5H_5)Ru(\eta\text{-}HN{=}C(H)NH)$, suggesting the weak π-coordination of the amidinate ligand.

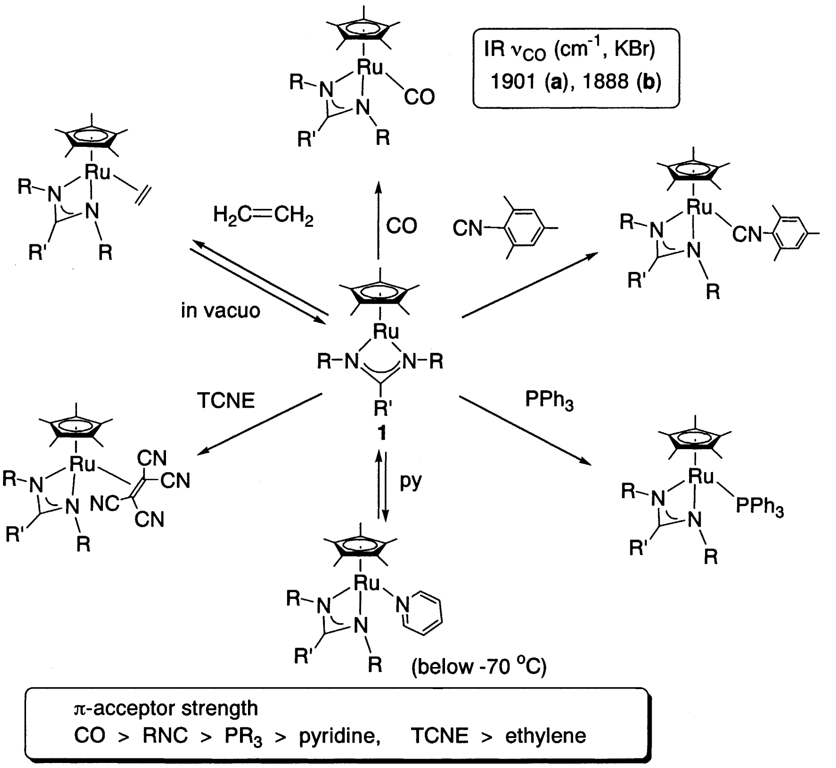
Variable temperature NMR spectroscopy of **3a**-Br, **2a**-OTf, and **2a**-TFPB showed the order of strength of the metal–anion interaction. In $CD_2Cl_2$, two doublets due to two magnetically inequivalent methyl moieties of the isopropyl group in the amidinate ligand appeared at −90 °C in the $^1H$ NMR of **2a**-OTf, but they were broadened by warming the NMR sample. The signals coalesced at −30 °C, and appeared as a single sharp doublet at 25 °C. This dynamic behavior is interpreted as dissociation and re-coordination of the triflate anion including inversion of the ruthenium center, and the energy of the inversion was estimated as approximately 11.4 kcal/mol. In sharp contrast, $^1H$ NMR spectra of **3a** showed two doublets at the same temperature range in the same solvent, whereas only a single doublet was seen in the spectra of **2a**-TFPB. The results indicate no cleavage of the Ru–Br bond of **2a** under the conditions used, whereas there was no interaction of the TFPB anion with the metal center in **2a**-TFPB in solution. It is known that the triflate anion is not a weakly coordinating counter anion in organoruthenium chemistry, whereas $BF_4$, $PF_6$, $SbF_6$, and fluorinated borates do not have strong interactions with transition metal species [42–44]. Appropriate choice of the weakly coordinated counter anion is important to synthesize coordinatively unsaturated cationic ruthenium amidinates, $[(\eta^6\text{-arene})Ru(\eta\text{-amidinate})]^+$.

### 2.3. *Reaction chemistry and catalysis*

#### 2.3.1. *Reactions of ruthenium amidinates with two-electron donor ligands*

Reactions of 16-electron complexes with a series of two-electron donors producing stable compounds bearing 18 valence electrons are an interesting entry to understanding the nature of the coordinatively unsaturated metal center [65,66]. Treatment of the ruthenium amidinates **1a** and **2a**-TFPB with CO, $^tBuNC$, $PPh_3$, pyridine, and olefins gave the corresponding adducts, $(\eta^5\text{-}C_5Me_5)Ru(L)(\eta^2\text{-amidinate})$ (**4**) [65] and $[(\eta^6\text{-benzene})Ru(L)(\eta^2\text{-amidinate})]^+TFPB^-$ (**5**-TFPB) [66] instantly. The results are summarized in Schemes 3 and 4. The neutral ruthenium amidinate easily reacted with the π-acceptor ligands, CO, $^tBuNC$, and TCNE. The $\nu_{CO}$ absorption is one of the lowest in the analogous compounds, suggesting that the $(\eta^5\text{-}C_5Me_5)Ru(\eta^2\text{-amidinate})$ fragment is a strong π-donor. In contrast to the fact that the reaction of **1a** with TCNE afforded the stable π-adduct, $(\eta^5\text{-}C_5Me_5)Ru(\eta^2\text{-amidinate})(\eta\text{-TCNE})$, the adduct of less π-basic ethylene was detected by spectroscopy under an ethylene atmosphere, but was easily regenerated as **1a** by dissociation of ethylene when the solution was concentrated in vacuo. Reaction of **1a** with pyridine was also reversible, and did not afford the corresponding stable adduct. In sharp contrast to the π-donor property of the neutral ruthenium amidinate, the cationic ruthenium amidinate **2a**-TFPB is Lewis acidic. The $\nu_{CO}$ absorption of the CO adduct is 2202 $cm^{-1}$, suggesting the electron withdrawing nature of the ruthenium center in the $[(\eta^6\text{-benzene})Ru(\eta^2\text{-amidinate})]^+$ fragment. Pyridine and ethylene easily reacted with **2a**-TFPB to give the corresponding stable adducts.

All of these results revealed the coordinatively unsaturated nature of the neutral and cationic ruthenium amidinates. Of particular importance are the characteristic π-donor property of the $(\eta^5\text{-}C_5Me_5)Ru(\eta\text{-amidinate})$ and the Lewis acidic nature of $[(\eta^6\text{-arene})Ru(\eta\text{-amidinate})]^+$ complexes. In other words, use of these characteristics in activation of organic molecules could lead to the discovery of new aspects in reaction chemistry of ruthenium

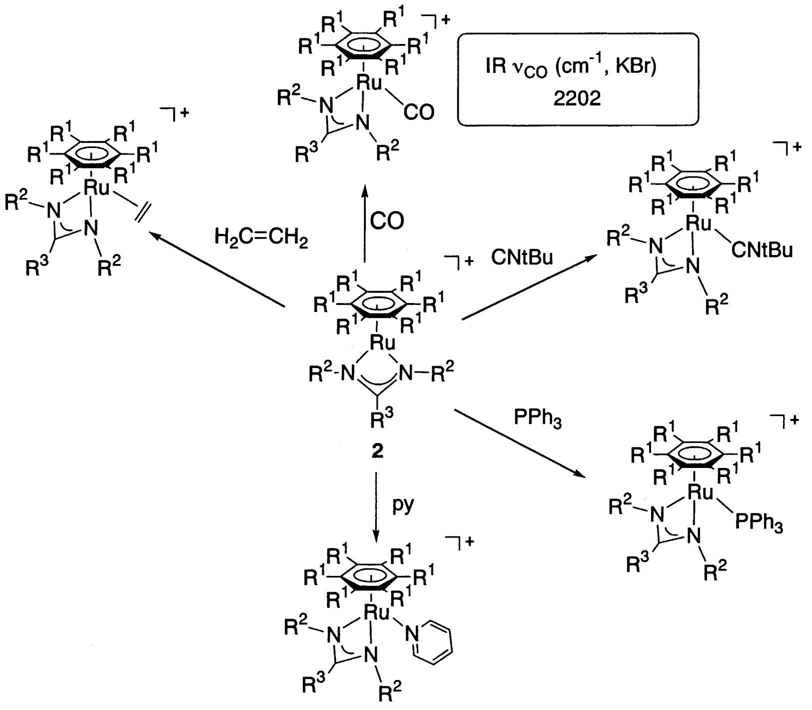


Scheme 3. Reactions of ($\eta^5$-$C_5Me_5$)Ru($\eta$-amidinate) with various two-electron donor ligands.

amidinates, including their catalysis. In this context, we next carried out the oxidative addition reaction and formation of carbene complexes starting from the ruthenium amidinates.

### 2.3.2. One and two-electron redox pathways of ($\eta^5$-$C_5Me_5$)Ru($\eta$-amidinate) by organic substrates

The neutral ruthenium amidinates show a strong π-donor property in their reactions with electron-withdrawing



Scheme 4. Reactions of [($\eta^6$-benzene)Ru($\eta$-amidinate)]$^+$ with various two-electron donor ligands.

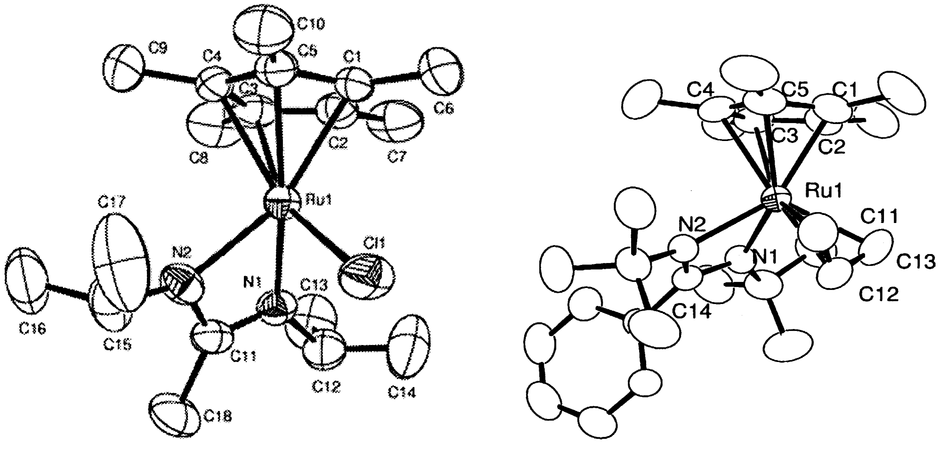
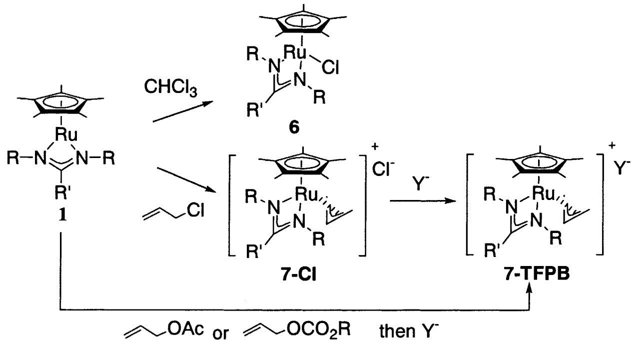


Fig. 7. The ORTEP drawings of **6a** (left) and **7b** (right).

ligands as described above. The existence of the electron-rich metal center in the neutral ruthenium amidinates is also indicated by facile oxidation of ($\eta^5$-$C_5Me_5$)Ru($\eta$-amidinate) [67–69]. The cyclic voltammogram of **1a** revealed one quasi-reversible and one irreversible oxidation peak [$E_{pa} = -0.32$, $E_{pc} = -0.46$ V; $E_{pa} = +0.53$ V versus Ag/Ag$^+$ at the scan rate of 0.1 V/s in THF], which could be assigned as the electrochemical oxidation of Ru(II) species to Ru(III) and the resulting Ru(III) species to Ru(IV), respectively. This indicates that **1a** can be oxidized by appropriate organic oxidants. Organic halides are a good candidate for the oxidant, and in fact, treatment of **1a** with chloroform afforded the chloro-Ru(III) compound, **6a** [69], whereas reaction of **1a** with allyl chloride resulted in formation of a cationic Ru(IV)-$\eta^3$-allyl complex **7a** [67] (Scheme 5). The cationic Ru(IV)-$\eta^3$-allyl complexes were alternatively prepared by treatment of **1a** with allylic acetates or methyl allyl carbonates followed by counter anion exchange to $PF_6^-$, $BF_4^-$, or $Ph_4B^-$. We also examined the reactions of chloroform or allylic halides with cationic ruthenium amidinates, **7a**-TFPB, but no oxidation or oxidative addition reaction was observed.

The Ru(III) amidinate **6a** is paramagnetic and has a three-legged piano-stool structure with the two nitrogen atoms of the amidinate ligand and the chlorine atom as the three legs as shown in Fig. 7 (left). In contrast, the Ru(IV)-$\eta^3$-allyl complex **7b** is diamagnetic and has a four-legged piano-stool structure with two nitrogen atoms of the amidinate group and two terminal carbon atoms of the $\eta^3$-allyl moiety as the four legs as shown in Fig. 7 (right).



Scheme 5. Oxidative addition of organic substrates to neutral ruthenium amidinates.

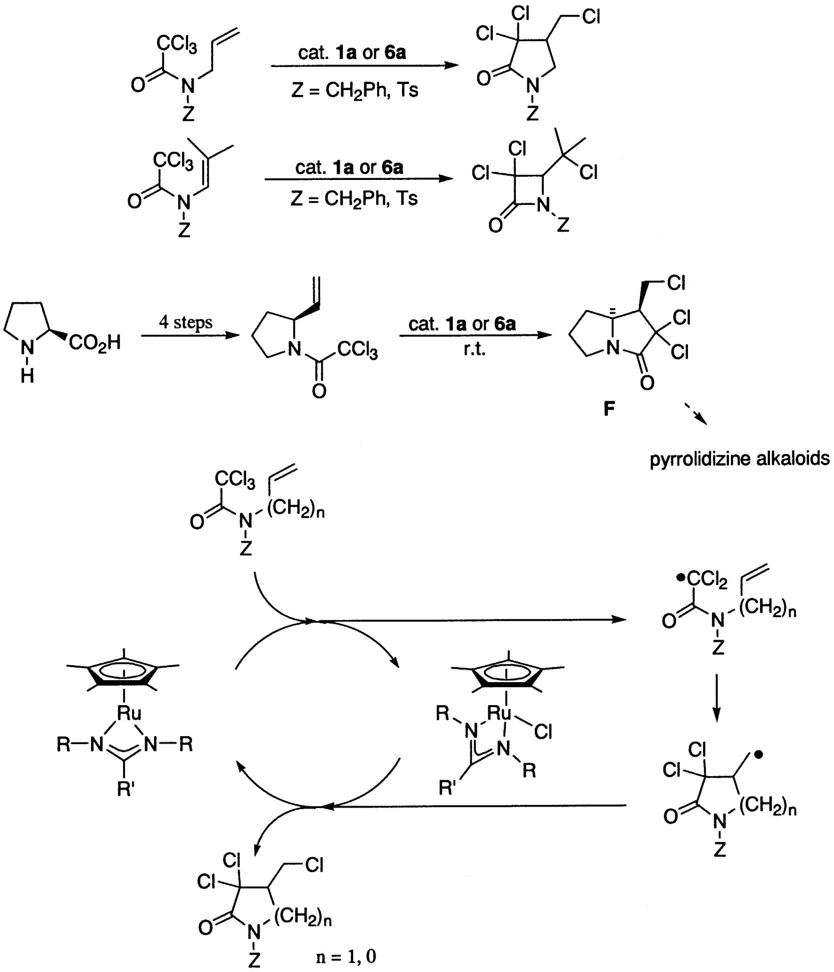
Certain Ru(II) complexes are known to be reactive with polychloroalkanes and to result in chlorine atom abstraction to form the corresponding Ru(III) complexes [78]. Oxidation of **1a** with chloroform is one of these; however, it is of interest that the reaction of **1a** with chloroform quickly proceeds even at room temperature. Although further oxidation of **6a** to ($\eta^5$-$C_5H_5$)Ru$X_2$($\eta$-amidinate) can possibly be deduced from the cyclic voltammogram of **1a**, no evidence of the formation of Ru(IV) complexes was obtained in the further reaction of **6a** with chloroform. In sharp contrast, in the reaction of allylic halides with **1a**, the product formed is not the Ru(III) complex but the Ru(IV) compound. Oxidative addition of allylic halides to Ru(II) precursors was first reported by us in 1984 [58]; ($\eta^5$-$C_5H_5$)Ru(L)$_2$X (L = CO, $PPh_3$) and ($\eta^5$-$C_5Me_5$)Ru(CO)$_2$X react with allylic halides at high temperature to form *neutral* dihalogeno Ru(IV)-$\eta^3$-allyl complexes, ($\eta^5$-$C_5R_5$)Ru$X_2$($\eta^3$-allyl) (R = H, Me). Compared with this reaction, the formation of **7a** from **1a** occurs at room temperature to give *cationic* Ru(IV)-$\eta^3$-allyl complexes as a single product. Allylic substrates other than allyl halides can also be used as the oxidant. When the reaction of allylic acetate with **1a** was monitored at low temperature, coordination of the olefinic part of the allylic acetate was first observed, and the resulting alkene complex was converted to the Ru(IV)-$\eta^3$-allyl product when the solution was heated. Thus, it is likely that the formation of the Ru(IV)-$\eta^3$-allyl product involves displacement of the leaving group (halogen, acetate, or carbonate) at the allylic position by Ru(II) species in the Ru(II)-($\eta^2$-$CH_2$=$CHCH_2OAc$) intermediate.

### *2.3.3. Catalytic intramolecular Kharasch reactions involving Ru(II) and Ru(III) amidinates*

The formation of ($\eta^5$-$C_5Me_5$)RuCl($\eta^2$-amidinate) is accomplished by chlorine abstraction from $CHCl_3$ with

($\eta^5$-$C_5Me_5$)Ru($\eta$-amidinate). This type of oxidation reaction is widely seen in transition metal salts and complexes [78], and its application to catalysis provided the Kharasch reaction; the addition of polyhaloalkanes to olefins by metal catalysts [79–82]. The inter- and intramolecular metal-catalyzed Kharasch reactions are not only useful for the preparation of various synthetically useful polyhalogenated compounds including natural product skeletons [79,80], but are also applicable to polymer synthesis [81,82], and numerous studies have been undertaken. A typical intramolecular Kharasch reaction is the preparation of trichlorinated $\gamma$-lactams reported by our group, of which the possible catalytic cycle is illustrated in Scheme 6 [83–85]. The most widely used catalysts in the $\gamma$-lactam formation is CuCl(bipy) and its analogues, which catalyzed the cyclization of N-protected *N*-allyl trichloroacetamides at room temperature [83].

Since the redox between Cu(I) and Cu(II) promotes the catalytic reaction, similar redox property between Ru(II) and Ru(III) or Ru(III) and Ru(IV) of the amidinate complexes may provide catalytic activity towards the intramolecular Kharasch reaction [69]. We carried out the cyclization in the presence of catalytic amounts of Ru(II) or Ru(III) amidinates, **1a** and **6a**, and found that both complexes showed the catalytic activity towards the cyclization of N-protected *N*-allyl and *N*-vinyltrichloracetamides, in particular, the reaction of the *N*-benzyl derivatives as shown in Scheme 6. A striking feature of the catalysis of **1a** and **6a** is seen in the preparation of a precursor of pyrolizidine alkaloid, F, which was accomplished by Seijas et al. using a stoichiometric amount of CuCl in acetonitrile [86]. A serious problem of this cyclization is the requirement of a high reaction temperature (160 °C) and a stoichiometric amount of the copper salt. We reexamined this cyclization using CuCl(bipy) as the catalyst, and successfully reduced the reaction temperature in the presence of 10–30 mol% of the catalyst, but the reaction still needed heating at 80 °C. Use of the ruthenium catalysts, **1a** or **6a**, dramatically reduced the reaction temperature, and the desired bicyclic lactam was obtained in good yield even at room temperature. The results clearly demonstrate that the neutral ruthenium amidinates are good catalysts for the intramolecular Kharasch reaction with catalytic activity comparable to the CuCl(bipy) catalyst in the cyclization of simple *N*-benzyl, *N*-vinyl or *N*-allyl trichloroacetamides; it

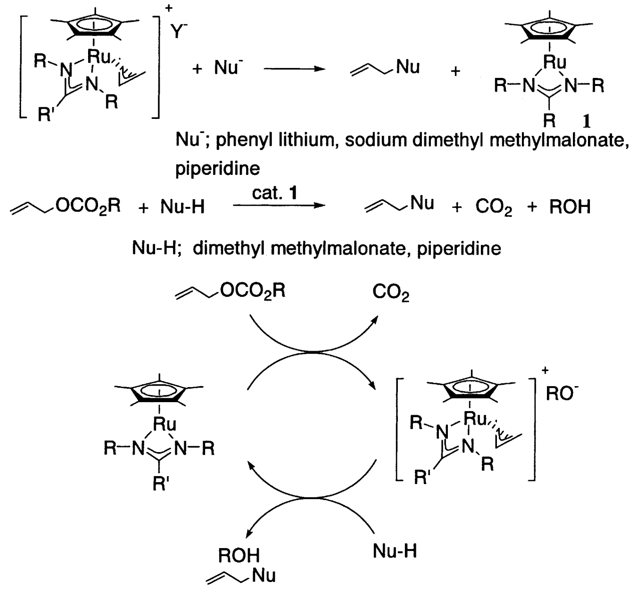


Scheme 6. Catalytic intramolecular Kharasch reactions by ruthenium amidinates.

is even better in the reaction of a certain substrate which cannot be achieved with conventional copper catalysts. As described above, the Kharasch reaction involves the one electron redox process of the metal species in the catalytic cycle. Since both the Ru(II) and Ru(III) amidinates exhibit catalytic activity, two redox processes, Ru(II)/Ru(III) and Ru(III)/Ru(IV), are possibly involved in the catalytic cycle, which makes it difficult to specify the net catalytically active redox process [87–89]. However, the fact that the typical violet color of Ru(II) amidinates instantly turned to green indicates the rapid formation of Ru(III) in the catalytic reaction using Ru(II); we thus believe that the redox process between ($\eta^5$-$C_5Me_5$)$Ru^{III}Cl$ ($\eta^2$-amidinate) and unstable ($\eta^5$-$C_5Me_5$)$Ru^{IV}Cl_2$($\eta^2$-amidinate) would promote the catalytic reaction.

### 2.3.4. Catalytic Tsuji–Trost reactions involving Ru(II) and Ru(IV) amidinates

Oxidative addition of allylic substrates to the Ru(II) amidinates provides the cationic Ru(IV)-$\eta^3$-allyl complexes [67,68] described above. The chemistry of $\eta^3$-allyl complexes has been thoroughly explored in organotransition metal chemistry, particularly, with palladium compounds [90–92]. Palladium-catalyzed nucleophilic substitution of allylic substrates has been investigated by Tsuji [90], and Trost and van Vranken [91], and its ruthenium version was reported by Mitsudo and coworkers [93–95]. The reaction proceeds through the oxidative addition of allylic substrates to the metal center followed by attack of a nucleophile to the resulting $\eta^3$-allyl intermediate to result in formation of the organic product and regeneration of the catalytically active metal species as shown in Scheme 7. We found that the cationic Ru(IV)-$\eta^3$-allyl complex **7a** reacted with malonate anion or piperidine to form the corresponding allyl malonate or *N*-allylpiperidine. Complete regeneration of the Ru(II) amidinate, **1a**, was confirmed by spectroscopic methods. The results clearly suggest that **1a** could be a good catalyst for the Tsuji–Trost reaction, and in fact, reaction of allyl carbonates with dimethyl methylmalonate or piperidine was efficiently catalyzed by **1a** as shown in Scheme 7. In the reaction with piperidine, the cationic Ru(IV)-amidinate, **6a**, also showed catalytic activity. Interestingly, selectivity between the two isomers of the product is significantly different between the two catalysts in the reaction of methyl cinnamyl carbonate with piperidine. The reason for this selectivity is not clear at present.

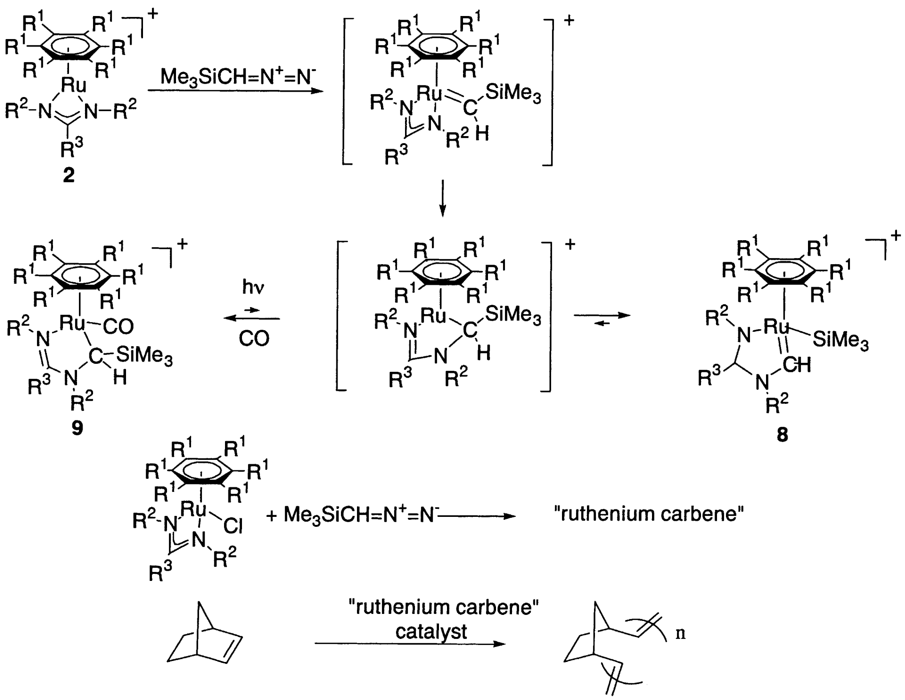


Scheme 7. Stoichiometric and catalytic transformation of allylic substrates with neutral ruthenium amidinates.

### 2.3.5. Reactions of [($\eta^6$-arene)Ru($\eta$-amidinate)]$^+$ with silyldiazomethane: Unusual trimethylsilyl group migration and catalysis [70]

One interesting examination to check for the reactivity of the coordinatively unsaturated complexes is the reaction with diazo compounds, which may produce the corresponding metal carbenes [96,97]. For example, a recent report from Caulton and Kirchner described the reaction of ($\eta^5$-$C_5H_5$)$Ru^+$(tmeda), a 16-electron complex stabilized by strong $\sigma$-donor ligand, with trimethylsilyldiazomethane to form the corresponding carbene complex, ($\eta^5$-$C_5H_5$)$Ru^+\{=C(H)SiMe_3\}$(tmeda) [44]. Attempted reaction of the neutral ruthenium amidinate **1a** with trimethylsilyldiazomethane gave no detectable carbene compound. However, similar reaction of the cationic ruthenium amidinate **2** occurred smoothly at room temperature to form novel Ru(II) compounds having a trimethyl silyl group and amidinato-carbene moiety bonded to the ruthenium center [70]. A single crystal suitable for the X-ray structure determination was obtained in one of the carbene complexes, **8b**, and its ORTEP drawing is illustrated in Fig. 7. The Ru–C (carbene) bond distance is 1.903(5) Å, suggesting the Ru=C character of this moiety. A possible mechanism for the formation of this amidinato-carbene complex is shown in Scheme 8, in which the silylcarbene intermediate is initially formed and undergoes insertion of the carbene moiety to the Ru–N bond in the amidinate ligand followed by regeneration of the carbene group by migration of the trimethyl silyl group from the carbon to the ruthenium atom. Although the silylcarbene intermediate was not detected by spectroscopic methods, supporting evidence of carbon to ruthenium silyl group migration was available from the following experiments: treatment of CO with **8** induced the ruthenium to carbon silyl group migration to form **9**, whereas the reverse reaction took place by photo-irradiation of **9**. This is the first unequivocal experimental evidence of the reversible carbon to metal silyl group migration (Fig. 8).

Our examination to synthesize carbene complexes of ruthenium amidinates provided the unprecedented formation of the amidinato-carbene complexes, as the first experimental evidence of reversible carbon-to-metal silyl group migration. Although the amidinato-carbene complexes are



Scheme 8. Formation of amidinato-carbene complexes via carbene intermediates.

not the products we expected, they contain a Ru=C moiety in the molecule. Does the Ru=C moiety exhibit the characteristic nature of ruthenium carbene complexes? We tried to figure out the nature of the amidinato-carbene complexes by examining their catalytic activity towards ring opening methathesis polymerization (ROMP) of norbornene [49–51]. As seen in the typical example in the Grubbs's catalysts [52–55,98], carbene ruthenium complexes exhibit excellent catalytic activity towards ROMP of norbornene. Attempted reaction of norbornene with a catalytic amount of the amidinato-carbene complexes, **8a** and **8b**, provided low ROMP activity. The catalytic activity is somewhat higher in the reactions using the catalyst generated by ($\eta^6$-arene)RuX($\eta^2$-amidinate) and trimethylsilyldiazomethane, which could produce ruthenium carbene species in situ. The highest activity was available when ($\eta^6$-benzene)RuBr[$\eta^2$-$^i$PrN=C(Me)NiPr] (**3a**-Br) was used as the catalyst precursor; this gave the corresponding polynorbornadiene ($M_n = 1.3 \times 10^6$, $M_w/M_n = 1.9$) within minutes at room temperature. Combination of several arene-Ru(II) complexes with diazoalkanes as a catalyst for ROMP has been extensively studied by Noels and coworkers [99,100], and the present results suggest that the ruthenium amidinates associated with trimethylsilyldiazomethane are also useful as catalysts for ROMP [101].

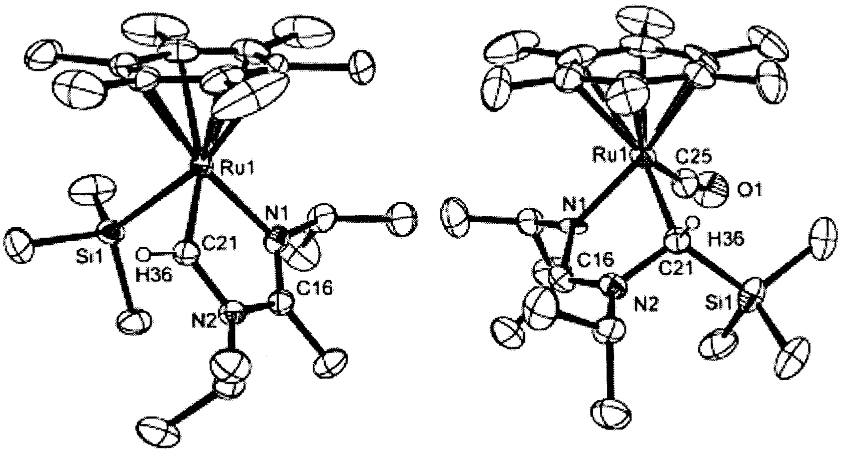


Fig. 8. The ORTEP drawings of **8** (left) and **9** (right).

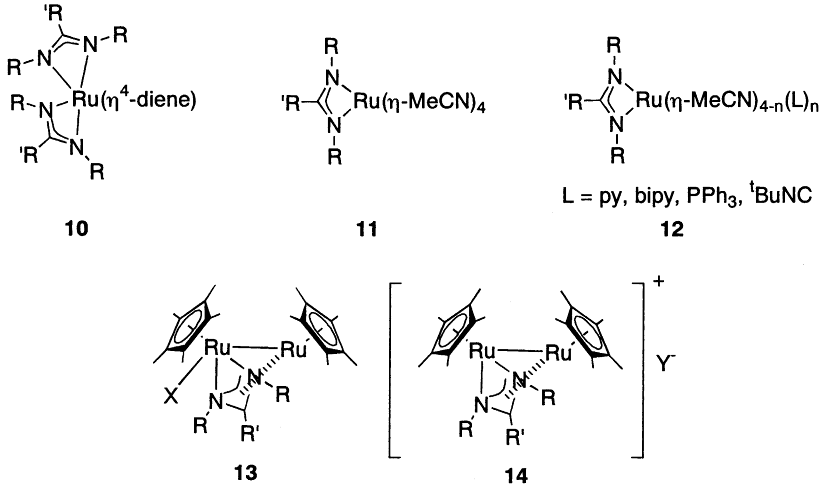


Fig. 9. Other organoruthenium amidinates for new chemistry.

## 3. Conclusion and further perspective

Coordinatively unsaturated transition metal complexes are generally unstable and difficult to be isolated and characterized. Are the studies to synthesize these just a challenge in organometalic chemistry to treat such unstable compounds? The present results apparently show that this is beyond that; appropriate planning of the coordinatively unsaturated complexes, which show high reactivity towards various organic and inorganic substrates, actually leads to development of new catalysts for organic synthesis.

The amidinate ligand usually behaves as a four-electron donor ligand in coordination chemistry. However, studies on the preparation, spectroscopy, and crystallography of neutral as well as cationic ruthenium amidinate described above clearly demonstrate that interaction of π-electrons on the amidinates ligand contribute to stabilizing the coordinatively unsaturated ruthenium center. As described in Section 1, π-stabilization of the neighboring functional groups to mitigate the coordinatively unsaturated nature of the ruthenium center was proposed by Caulton [7], who showed that the alkoxy, amino, and acetylide ligands were effective for the neighboring group. Thus, the amidinate group in this study may add a new page in the chemistry of coordinatively unsaturated complexes as a novel ligand which effectively stabilize the metal center by π-interaction. Interestingly, the interaction is weak and easily replaced by other ligands such as CO, phosphines, and others. Such high reactivity could expose a clue to the development of catalysis of ruthenium amidinates, and we have actually achieved efficient intramolecular Kharasch reactions, the Tsuji–Trost reaction, and ROMP of norbornene as introductory examples of the catalytic reactions by these new amidinate complexes. The results suggest that similar chemistry could be possible in other ruthenium amidinates, and we have recently reported three new ruthenium amidinates, ($\eta^4$-diene)Ru($\eta^2$-amidinate)$_2$ (**10**) [102], ($\eta^2$-amidinate)Ru$^+$(MeCN)$_4$ (**11**) [103], and ($\eta^2$-amidinate)Ru$^+$(MeCN)$_{4-n}$(L)$_n$ (L = pyridines, phosphines, isonitriles) (**12**) [103] as candidates.

The chemistry of the coordinatively unsaturated ruthenium amidinates is now expanding to bimetallic chemistry. As reported elsewhere, the neutral ruthenium amidinate **1a** is allowed to react with [($\eta^5$-C$_5$Me$_5$)RuX]$_4$ to form a novel diruthenium complex, [($\eta^5$-C$_5$Me$_5$)Ru($\mu_2$-amidinate)Ru(X) ($\eta^5$-C$_5$Me$_5$)] (**13**) [71]. This complex contains a bridging amidinate ligand located perpendicular to the Ru–Ru axis. The coordination mode is unusual in well-known dinuclear transition metal amidinate chemistry: one ruthenium atom is bonded to two nitrogen atoms, whereas the other ruthenium center is bound to the face of the amidinate ligand. This is clear evidence that the π-electrons on the amidinate ligand have actually coordinated to the metal center. Of interest in this new dinuclear amidinates is that the bridging amidinates can tightly bind the two ruthenium centers in the reactions with several organic and inorganic substrates [71]. In particular, treatment of **13** with weakly coordinating counter anions resulted in coordinatively unsaturated diruthenium amidinates **14** showing high reactivity towards two-electron donor ligands and molecular hydrogen [72]. Investigation of the reactions and catalysis of **14** and its analogues is now producing a number of fruitful results; however, detailed chemistry of the diruthenium amidinates is beyond the scope of this review (Fig. 9).

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