

Oxidative Addition of Allylic Substrates to Coordinatively Unsaturated Ruthenium Compounds, [Ru(η^5-C_5Me_5)(η-amidinate)]: Preparation, Structure Elucidation, and Catalysis of Novel Ruthenium (IV)-η^3-Allyl Complexes

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Oxidative addition reactions of allylic halides, acetates, and carbonates with [Ru(η^5-C_5Me_5)(η-amidinate)] [amidinate: ^{i}PrNC(Me)=N^{i}Pr (**1a**), ^{t}BuNC(Ph)=N^{t}Bu (**1b**)], which shows signs of coordinative unsaturation, gave novel cationic π-allyl ruthenium(IV) species. The compounds [Ru(η^3-allyl)(η^5-C_5Me_5)(η^2-amidinate)]$^+X^-$ were isolated by anion exchange of the products (X = PF_6, BF_4, BPh_4), and were characterized by spectroscopic analysis. The crystallography of two of the [Ru(η^3-allyl)(η^5-C_5Me_5)(η^2-amidinate)]$^+X^-$ revealed a four-legged piano stool structure in which two nitrogen atoms in the amidinate ligand and two carbon atoms in the η^3-allyl ligands occupy the positions of four legs; the orientation of the η^3-allyl ligand was endo. Although cyclic voltammograms of the precursor, [Ru(η^5-C_5Me_5)(η-amidinate)], indicated possible oxidative addition of organic halides other than allylic halides to [Ru(η^5-C_5Me_5)(η-amidinate)], only allylic halides gave the corresponding Ru(IV) products. The importance of prior coordination of the carbon-carbon double bond of allylic substrates was evidenced by NMR observation of the intermediate in the reaction of **1a** or **1b** with allyl acetate. Addition of nucleophiles such as PhLi, dimethyl methylsodiomalonate, and piperidine to the [Ru(η^3-allyl)(η^5-C_5Me_5)(η^2-amidinate)]$^+X^-$ gave rise to allylation of these nucleophiles and regeneration of [Ru(η^5-C_5Me_5)(η-amidinate)]. The reactions of allyl methyl carbonate with nucleophiles were also achieved by catalysis of either [Ru(η^5-C_5Me_5)(η-amidinate)] or [Ru(η^3-allyl)(η^5-C_5Me_5)(η^2-amidinate)]$^+X^-$.

Coordinatively unsaturated species[1] have attracted the attention of organometallic chemists in relation to possible intermediates in transition metal-catalyzed organic reactions.[2] In particular, the coordinatively unsaturated nature of certain ruthenium complexes has been actively investigated, because ruthenium complexes are generally faithful to the 18-electron rule, and preparation and characterization of rare examples of isolable ruthenium complexes bearing 16 valence electrons contributes to better understanding of factors to stabilize the reactive ruthenium center.[1a,c,3] Recent work has revealed the possible contribution of sterically hindered circumstances around the metal center[3a–m] and donation of π-[3a–l,n–s] and σ-electrons[3t–v] of the ligand to the vacant orbitals of the metal for the stabilization of 16 electron half sandwich ruthenium complexes.

We have recently discovered a novel type of ruthenium complexes formally bearing 16 valence electrons, in which amidinato ligands[4] play an important role in stabilizing the ruthenium center.[5] These novel ruthenium-amidinate complexes are assignable to [Ru(η^5-C_5Me_5)(η-amidinate)] on the basis of NMR analysis, and are considered to have 16 valence electrons, because the amidinato ligand generally acts as a 4 electron ligand to Ru^{2+}.[5a] Possible coordination of π-electrons in the amidinato ligand as an additional stabilizing factor was suggested by crystallographic analysis,[5a] and recently supported by DFT calculations of [Ru(η^5-C_5H_5)(η-HN=CH–NH)][6] and the molecular structure of [Ru_2(η^5-C_5Me_5)$_2$Br(μ_2:η-amidinate)].[5c] The coordinatively unsaturated nature of [Ru(η^5-C_5Me_5)(η-amidinate)] was evidenced by high reactivity of this complex with various two-electron donor ligands, leading to formation of [Ru(η^5-C_5Me_5)(η^2-amidinate)(L)].[5a] The strong π-donor property of [Ru(η^5-C_5Me_5)(η-amidinate)] is suggest-

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ed from formation of stable [Ru(η^5-C_5Me_5)(η^2-amidinate)(L)], where L is π-acceptor ligands such as CO and TCNE, and from the very low ν_{co} absorption of [Ru(η^5-C_5Me_5)(η^2-amidinate)(CO)] which has been observed.

Other typical reactions of coordinatively unsaturated complexes are oxidative addition reactions.[1a,3a–e,i,m,v] It is well known that the oxidative addition reactions are involved in various catalytic cycles,[2] and numerous studies on the oxidative addition of a wide variety of addenda have been undertaken. As reported earlier,[7a,b] we discovered oxidative addition of allylic halides to [Ru(η^5-C_5R_5)X(L)$_2$] (R = H, Me; L = PPh_3, CO) to afford [Ru(η^3-allyl)(η^5-C_5R_5)X$_2$], which is a rare example of a reaction involving change of the oxidation state of the complex from Ru(II) to Ru(IV). Other Ru(II) or Ru(III) precursors, [Ru(η^5-C_5H_5)Cl(COD)],[8a,c] [Ru(η^5-C_5Me_5)Cl(COD)],[8d] [Ru(η^5-C_5H_5)$(NCMe)_3]^+$,[8e] [Ru(η^5-C_5Me_5)$Cl_2]_n$,[7c] and [Ru(η^5-C_5Me_5)Cl]$_4$,[8b] were later proved to be active towards the oxidative addition of allylic substrates. In particular, a successful reaction of [Ru(η^5-C_5Me_5)Cl]$_4$, which might produce coordinatively unsaturated "Ru(η^5-C_5Me_5)Cl" species in solution,[8b,9] indicates that appropriate coordinatively unsaturated Ru(II) compounds could be useful as precursors to produce Ru(IV)-η^3-allyl complexes by the oxidative addition of allylic substrates.

In this paper, we describe the reaction of [Ru(η^5-C_5Me_5)(η-amidinate)] with allylic substrates, leading to synthesis of novel cationic Ru(IV) compounds: [Ru(η^3-allyl)(η^5-C_5Me_5)(η^2-amidinate)]$^+$. The formed Ru(IV) products were reactive towards nucleophiles, and catalytic nucleophilic substitution of allylic substrates with several nucleophiles was achieved by [Ru(η^5-C_5Me_5)(η-amidinate)] or [Ru(η^3-allyl)(η^5-C_5Me_5)(η^2-amidinate)]$^+$. A part of this paper appeared as a communication,[5b] and full details are given in this paper.

Results and Discussion

Oxidative Addition of Allylic Substrates to [Ru(η^5-C_5Me_5)(η-amidinate)]. Two ruthenium amidinates, [Ru(η^5-C_5Me_5)(η-^{i}PrNC(Me)=N^{i}Pr)] (**1a**) and [Ru(η^5-C_5Me_5)(η-^{t}BuNC(Ph)=N^{t}Bu)] (**1b**), were prepared according to the procedure reported earlier.[5a] These ruthenium amidinates are good π-donors and are expected to undergo facile oxidation (Table 1). In fact, cyclic voltammmograms of **1a** or **1b** in THF showed a quasi-reversible one-electron oxidation wave (**1a;** E_{pa} = −0.32 V, E_{pc} = −0.46 V, **1b;** E_{pa} = −0.24 V, E_{pc} = −0.43 V vs Ag/Ag^+ at the scan rate of 0.1 V/s) which is assignable to the Ru(II)/Ru(III) oxidation process.[10] Another irreversible oxidation wave was observed at E_{pa} = 0.53 V (**1a**) and 0.63 V (**1b**), corresponding to the Ru(III)/Ru(IV) process. A higher Ru(II)/Ru(III) oxidation potential has been reported for [Ru(η^5-C_5H_5)Cl(PPh_3)$_2$], [Ru(η^5-C_5Me_5)Cl(PPh_3)$_2$], [Ru(η^5-indenyl)Cl(PPh_3)$_2$], and [Ru(Tp)Cl(PPh_3)$_2$], in $ClCH_2CH_2Cl$ (E_{pa} = 0.53–0.83 V, E_{pc} = 0.40–0.71 V vs Ag/Ag^+ at the scan rate of 0.1 V/s) compared to that for **1a** or **1b**. In addition, no peak corresponding to the oxidation of Ru(III) to Ru(IV) was seen within the potential window in these cases.[11a] The reported examples for a Ru(III)/Ru(IV) process are few.[11b,c,d] On the other hand, in the case of the present complex, **1a** or **1b** , the Ru(IV) state will be attained by the reaction with appropriate oxidants. Organic halides are a possible candidate for the oxidative reaction of **1a** or **1b** to Ru(IV) products; however, attempted treatment of **1a** or **1b** with MeI or benzyl chloride only afforded green paramagnetic products, presumably a halogeno-Ru(III) compound, showing several broad ^{1}H resonances at −12 to 28 ppm. In sharp contrast, reaction of allyl halides with **1a** actually gave the corresponding diamagnetic Ru(IV) products.

Table 1. Reactions of [Ru(η^5-C_5Me_5)(η-amidinate)] with Allylic Halides

Amidinate Complex	Allylic Halide			Product (Yield, %)[a]	
	R_1	R_2	X		
1a	H	H	Cl	**2a** (98)	**7** (2)
1b	H	H	Cl	**2b** (95)	**7** (5)
1a	H	H	Br	**3a** (77)	**8** (15)
1a	H	Me	Cl	**4a** (98)	**9** (2)
1b	H	Me	Cl	**4b** (96)	**9** (4)
1a	Ph	H	Cl	**5b** (70)	**10** (20)

a) Determined by ^{1}H NMR.

Treatment of a violet pentane solution of **1a** with allyl chloride at room temperature resulted in a dramatic color change of the solution to yellow, from which yellow solids were precipitated. NMR analysis revealed that the solids contained [Ru(η^3-CH_2CHCH_2)(η^5-C_5Me_5)(η^2-^{i}PrNC(Me)=N^{i}Pr)]$^+$Cl$^-$ (**2a**) and a small amount of [Ru(η^3-CH_2CHCH_2)(η^5-C_5Me_5)Cl_2] (**7**)[7b] (**2a**:**7** = 98:2). No paramagnetic by-product was observable in the product. ^{1}H NMR spectrum of **2a** showed three signals: two doublets (δ 2.32, J = 10.1 Hz, δ 4.03, J = 6.0 Hz) and a doublet of triplet (δ 4.94, J = 6.0, 10.1 Hz) in the integral ratio of 2:2:1, due to the typical symmetric η^3-allyl moiety. ^{1}H resonances derived from the amidinate ligand appeared as two doublets (δ 1.23 and 1.30, J = 7.0 Hz) due to the diastereotopic methyl groups and a septet (δ 3.22, J = 7.0 Hz) due to the methine proton of the isopropyl group. The methyl group on the central carbon of the amidinato ligand appeared as a singlet at δ 1.92. These ^{1}H NMR data suggest that **2a** has a C_s-symmetric structure, as shown in Scheme 1, which has a mirror plane containing the central carbon of the η^3-allyl ligand, the methyl carbon and the central carbon of the amidinate ligand, the ruthenium atom, and the center of the C_5Me_5 ligand. The C_s-symmetric structure was also supported by the appearance of nine ^{13}C resonances. The ^{13}C signal due to the Cp-ring carbon appeared at 104.9 ppm, which was significantly downfield (ca. 35 ppm) compared with that of **1a**, and the location was similar to that of a typical Ru(IV)-η^3-allyl complex, **7**.

The chloro complex **2a** was unstable in THF, acetone, or dichloromethane, and gradually decomposed to intractable products. This instability, which is presumably triggered by nucleophilic attack of the chloride counter anion to the η^3-allyl or amidinate moiety, made separation of **2a** from **7** difficult. Exchange of the chloride anion of **2a** by weakly coordinating PF_6 anion resulted in formation of [Ru(η^3-CH_2CHCH_2)(η^5-C_5Me_5)(η^2-^{i}PrNC(Me)=N^{i}Pr)]$^+PF_6^-$ (**2a-PF$_6$**). Structure of **2a-PF$_6$** was evidenced by similar spectral features of **2a-PF$_6$** to **2a**, which was supported by crystallographic determination of its homologues, **2b-PF$_6$** and **5a-PF$_6$** (vide infra). The ORTEP drawings of **2b-PF$_6$** and **5a-PF$_6$** are shown in Fig. 1, and se-

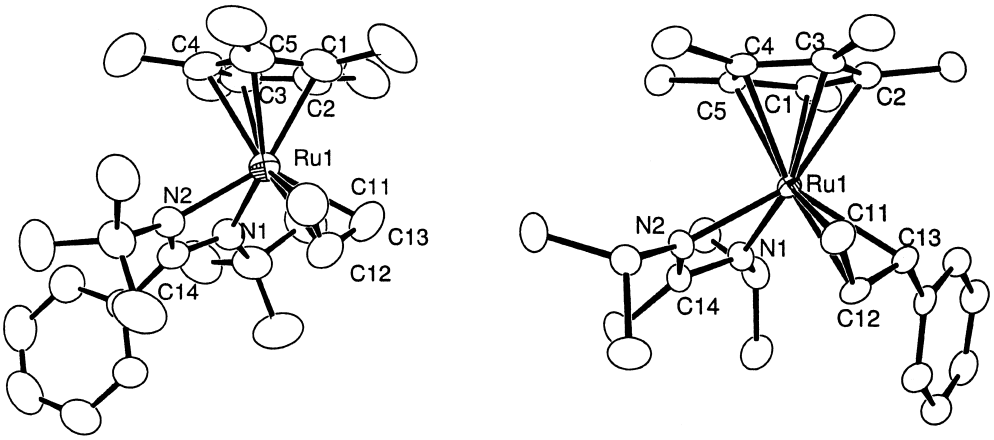
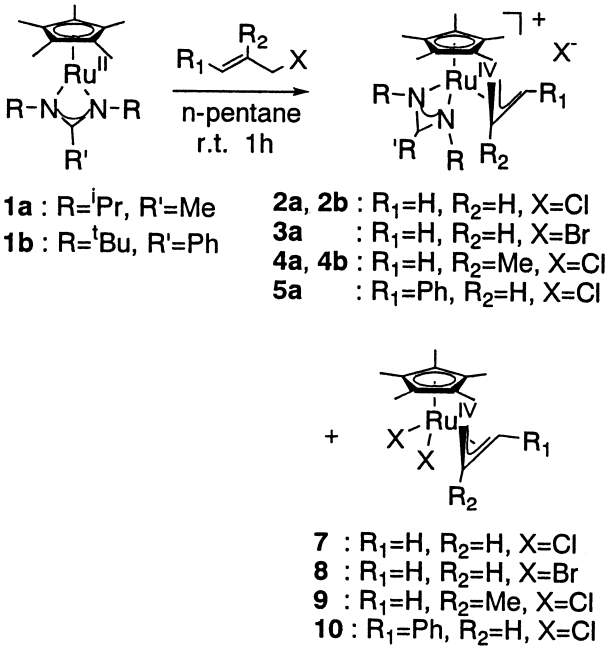


Fig. 1. The ORTEP drawings of **2b-PF$_6$** (left) and **5a-PF$_6$** (right) with thermal ellipsoids drawn at the 50% probability level. PF_6 anions are omitted for clarity.



Scheme 1.

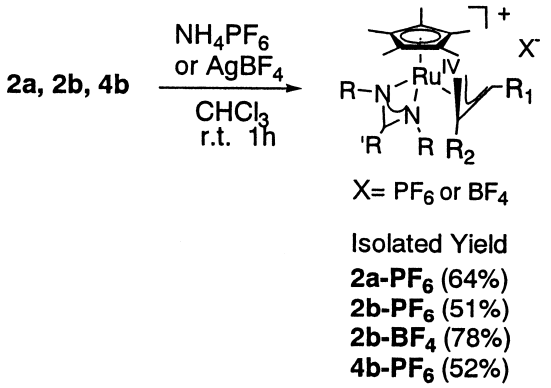
lected bond distances and angles are summarized in Table 2.

Complex **2b-PF$_6$** has a square-pyramidal structure with two nitrogen atoms of the amidinato ligand and terminal carbons of the η^3-allyl ligand at the basal positions. The Ru–N [2.128(3) and 2.125(3) Å] and average Ru–C(Cp) [2.263(4) Å] bonds of **2b-PF$_6$** are longer than those of **1b** [**1b:** Ru–N 2.073(3) Å, Ru–$C(Cp)_{av}$ 2.158(4) Å],[5a] and these bond distances are similar to those of a CO adduct of **1b**, [Ru(η^5-C_5Me_5) (η^2-amidinate)(CO)] [Ru–N 2.133(5) Å, Ru–C_{av} 2.240(7) Å].[5a] As reported earlier, a plane consisting of the Ru atom and two nitrogen atoms in **1b** makes an angle of 48.9(4)° with a plane of the amidinate N–C–N moiety; this contributes to better interaction of π-electrons of the amidinato ligand with the ruthenium center to mitigate the coordinatively unsaturated nature.[5a] In sharp contrast, the corresponding angle of 2.6(4)° in **2b-PF$_6$** shows that four atoms, N1, Ru1, N2, and C14 are almost in a plane.

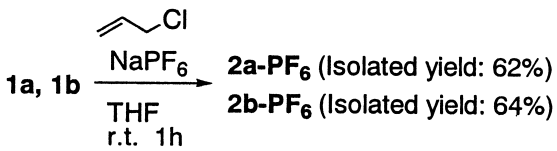
Table 2. Selected Bond Distances (Å) and Angles (°) for **2b-PF$_6$** and **5a-PF$_6$**

	2b-PF$_6$	**5a-PF$_6$**
Ru1–av.C_{1-5}	2.263 (4)	2.251 (4)
Ru1–C11	2.193 (5)	2.179 (4)
Ru1–C12	2.132 (4)	2.172 (4)
Ru1–C13	2.206 (5)	2.301 (4)
Ru1–N1	2.128 (3)	2.104 (4)
Ru1–N2	2.125 (3)	2.083 (3)
N1–C14	1.345 (5)	1.334 (6)
N2–C14	1.333 (5)	1.318 (5)
C11–C12	1.385 (8)	1.421 (6)
C12–C13	1.379 (8)	1.391 (6)
N1–Ru1–N2	62.0 (1)	61.6 (1)
Ru1–N1–C14	93.2 (2)	94.6 (3)
Ru1–N2–C14	94.4 (2)	96.0 (3)
N1–C14–N2	109.7 (3)	107.8 (4)
C11–Ru1–C12	37.3 (2)	38.1 (2)
C11–Ru1–C13	64.1 (2)	64.1 (2)
C12–Ru1–C13	37.0 (2)	36.1 (2)

This is generally seen in coordinatively saturated ruthenium amidinates such as [Ru(η^5-C_5Me_5) (η^2-amidinate)(CO)] (the corresponding angle = 3.9(4)°). The average Ru–C (terminal carbons of the allyl group) bond distances of **2b-PF$_6$** [2.200(5) Å] are similar to those reported for a Ru(IV)-allyl complex, [Ru(η^3-CH_2CHCH_2)(η^5-C_5Me_5)Br_2][7b] or its analogues (2.20–2.24 Å),[8a,c,d] while the average C–C distance of the π-allyl ligand in **2b-PF$_6$** (1.38 Å) is significantly shorter than that of [Ru(η^3-CH_2CHCH_2)(η^5-C_5Me_5)Br_2][7b] or its analogues (1.41–1.48 Å).[8a,c,d] These bond distances of **2b-PF$_6$** are similar to those seen in the two isomers of a half sandwich Ru(II)-allyl complex, [Ru(η^3-CH_2CMeCH_2)(η^5-C_5H_5)(CO)];[12] the Ru–C(terminal of allyl) and C–C(allyl)$_{av}$ distances are 2.20 and 1.40 Å, respectively.[12a] Orientation of the allyl group of **2b-PF$_6$** is endo, and variable temperature NMR studies showed that there was no equilibrium with the corresponding exo-isomer. This endo orientation is generally seen in half-sandwich Ru(IV)–allyl complexes. We also determined the crystal struc-



Scheme 2.



Scheme 3.

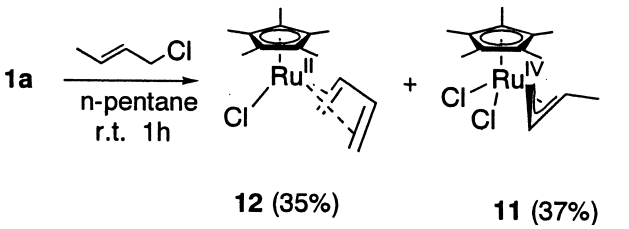
ture of **5a-PF$_6$**, in which a phenyl group is bonded with a terminus of the η^3-allyl group. The phenyl group is located at the syn-position of the allyl fragment similar to [Ru(η^3-$CH_2CHCHPh$)(η^5-C_5Me_5)Cl_2].[8d] Other structural features of **5a-PF$_6$** are analogous to those of **2b-PF$_6$**.

Other allylic halides summarized in Table 1 also reacted with **1a** or **1b** to give the corresponding [Ru(η^3-allyl)(η^5-C_5Me_5)(η^2-amidinate)]$^+X^-$ (X = Cl or Br) in good yields. In all cases, some amounts of [Ru(η^3-allyl)(η^5-C_5Me_5)X_2][7b,8d] were formed as the by-product. As shown in Schemes 2 and 3 as representative examples, treatment of [Ru(η^3-allyl)(η^5-C_5Me_5)(η^2-amidinate)]$^+Cl^-$ with NH_4PF_6 in $CHCl_3$ resulted in successful anion exchange reactions to give the corresponding PF_6 salt. A BF_4 analogue was also obtained using $AgBF_4$ instead of NH_4PF_6. The PF_6 salts were alternatively obtainable by treatment of **1a** or **1b** with allylic chlorides in THF in the presence of $NaPF_6$. The PF_6 or BPh_4 salts were available in higher yields by the reactions with allylic acetates or allylic carbonates, as shown in Table 3.

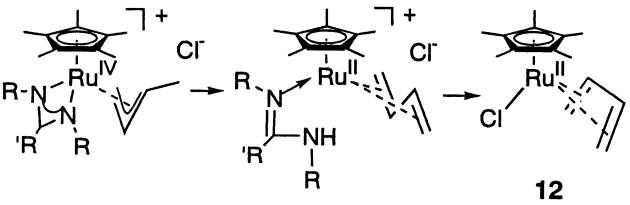
The following interesting observations were available from the experiments which changed the structure of allylic sub-

Table 3. Reactions of [Ru(η^5-C_5Me_5)(η-amidinate)] with Allylic Acetates or Carbonates in the Presence of $NaPF_6$ or $NaBPh_4$

Amidinate Complex	Allylic Compound X	R_1	R_2	Product (Isolated Yield/%)
1a	OAc	H	H	**2a-PF$_6$** (90)
1b	OAc	H	H	**2b-PF$_6$** (97)
1a	OCO_2Me	H	H	**2a-PF$_6$** (90)
1b	OCO_2Me	H	H	**2b-PF$_6$** (97)
1a	OCO_2Me	H	Me	**4a-PF$_6$** (90)
1b	OCO_2Me	H	Me	**4b-PF$_6$** (98)
1a	OCO_2Me	Ph	H	**5a-PF$_6$** (96)
1a	OAc	H	CH_2SiMe_3	**6a-PF$_6$** (99)
1a	OAc	H	CH_2SiMe_3	**6a-BPh$_4$** (69)

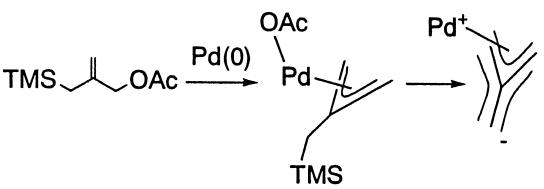


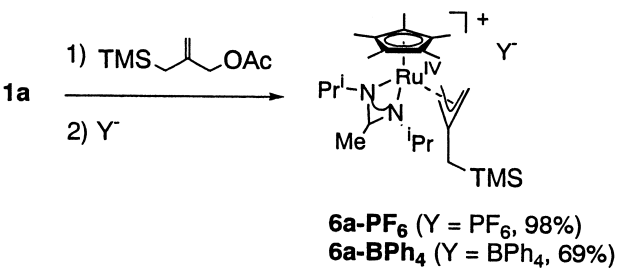
Scheme 4.



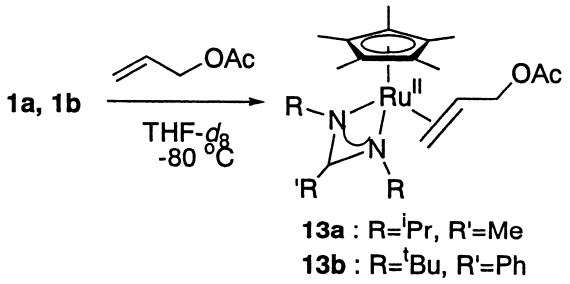
Scheme 5.

strates: the reaction of **1a** with crotyl chloride gave a mixture of [Ru(η^5-C_5Me_5)Cl(η^4-butadiene)] (**12**)[13] and [Ru(η^3-$MeCHCH_2CH_2$)(η^5-C_5Me_5)Cl_2] (**11**)[7b] in 35 and 37% yields, as shown in Scheme 4. Formation of **12** can be attributed to rapid β-hydrogen elimination, which is one of the general features of organoruthenium(II) compounds.[14] A possible reaction mechanism is shown in Scheme 5. Similarly, treatment of 1-acetoxy-2-butene or 3-acetoxy-1-butene with **1b** in THF at room temperature for 1 h gave a mixture of compounds. The ^{1}H NMR spectrum of this mixture showed that they contained products similar to **12**; signals due to the η^4-butadiene were seen at δ 1.61 (overlapping with the C_5Me_5 signal), 3.52 (dd, J = 1.6, 8.3 Hz, 2H), and 4.57 (m, 2H). It was proposed that activation of 2-(trimethylsilylmethyl)-2-propenyl acetate by Pd(0) species resulted in formation of a η^3-allylpalladium intermediate, followed by attack of the resulting acetate anion to the trimethylsilyl group to furnish a trimethylenemethane palladium species, as shown in Scheme 6.[15] Although similar tri-





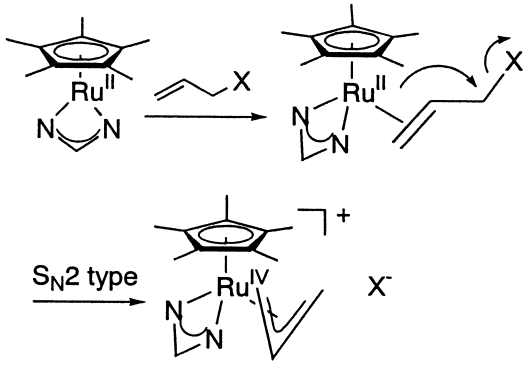
Scheme 6.



Scheme 7.

methylenemethane formation may occur in the reaction of **1a** with 2-(trimethylsilylmethyl)-2-propenyl acetate, stable η^3-allyl complexes **6a-PF$_6$** and **6a-BPh$_4$** were formed in 98% and 69% yields, respectively (Scheme 6).

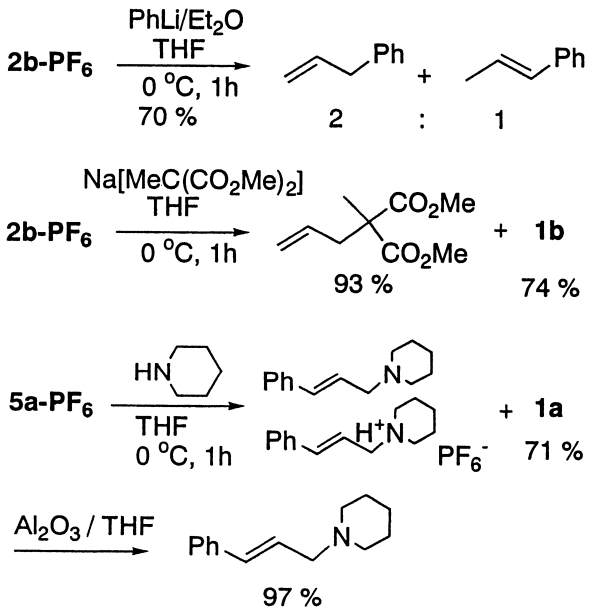
As noted earlier, the reaction of **1a** or **1b** with MeI or benzyl chloride did not afford the corresponding diamagnetic Ru(IV) alkyl complex. This suggests that involvement of coordination of a carbon–carbon double bond in the allylic substrates may play a crucial role in the oxidative addition reaction. Coordination of a carbon–carbon double bond of allyl acetate to **1a** or **1b** as the intermediates for the oxidative addition was evidenced by variable temperature ^{1}H NMR, as shown in Scheme 7. In the spectra of a 1:1 mixture of **1a** or **1b** with allyl acetate in THF-d_8 at -80 °C, ^{1}H and ^{13}C resonances due to the H_2C=CH moiety appeared at the significantly more upfield region ($\Delta\delta_H = 3$ ppm, $\Delta\delta_c = 70$ ppm), due to coordination to the ruthenium center, than those derived from the uncoordinated allyl acetate. The chemical shifts were similar to those observed in the spectra of [Ru(η^5-C_5Me_5)(η^2-amidinate)(η^2-CH_2=CH_2)].[5a] As described earlier, two methyl groups in the isopropyl group in **1a** appeared as a single doublet due to the C_{2v} symmetry of the molecule. Upon coordination of ethylene, they were observed as two doublets because of the C_s symmetry. The lack of symmetry in the compound formed by coordination of allyl acetate to **1a** made all of the methyl signals unequal; thus they appear as four doublets. These data are consistent with the structure **13a**. It is likely that the coordination of the carbon–carbon double bond of allyl acetate facilitates the carbon-oxygen bond cleavage, as shown in Scheme 8. In fact, the cationic η^3-allyl complex **2a-PF$_6$** or **2b-PF$_6$** was formed quantitatively via the displacement of the OAc group by **PF$_6$** upon warming the solution of **13a** or **13b** to room temperature in the presence of $NaPF_6$.



Scheme 8.

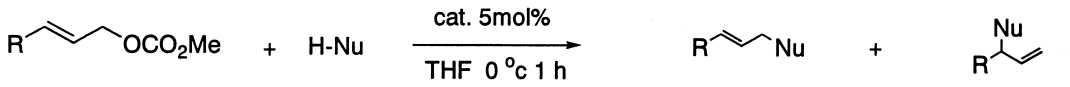
Stoichiometric and Catalytic Transformation of Allylic Substrates by [Ru(η^5-C_5Me_5)(η-amidinate)]. Reactions of η^3-allyl complexes with nucleophiles are a well investigated issue in organometallic chemistry.[2,15–17] In particular, extensive studies on η^3-allyl palladium species revealed that stoichiometric as well as catalytic transformation of allylic substrates was easily accomplished by a wide variety of nucleophiles.[15–18] Mitsudo and co-workers reported analogous stoichiometric reactions of nucleophiles with η^3-allyl ruthenium compounds as well as ruthenium-catalyzed reactions of allylic carbonates with nucleophiles.[8d,19] Although the ruthenium-mediated reactions are less versatile for application to various allylic substrates or nucleophiles than the reactions using palladium complexes, in some cases there exist interesting differences in catalytic activity and product selectivity.[8d,19] The η^3-allyl complexes presented in this paper are cationic, and are expected to undergo facile reactions with nucleophiles. In fact, addition of one equivalent of PhLi in ether to a THF solution of **2b-PF$_6$** at room temperature for 1 h afforded a mixture of 1-phenyl-2-propene and 3-phenyl-1-propene in a ratio of 2:1 in 70% yield, whereas attempted reactions of **2b-PF$_6$** with ethylene (1 atm) or benzaldehyde resulted in complete recovery of **2b-PF$_6$**. Similar reaction of **2b-PF$_6$** with an equimolar amount of dimethyl methylsodiomalonate in THF at 0 °C for 1 h furnished the formation of dimethyl allylmethylmalonate in 93% yield. Regeneration of **1b** (74% yield) was confirmed from the NMR spectrum of the reaction mixture. Treatment of **5a-PF$_6$** with an equimolar amount of piperidine at 0 °C for 1 h gave a mixture of 1-phenyl-3-piperidino-1-propene and its HPF_6 salt, and recovery of **1a** was also observed (71%). By passing this mixture through a short pad of Al_2O_3, 1-phenyl-3-piperidino-1-propene was obtained in 97% yield (Scheme 9). The corresponding regio-isomer, 3-phenyl-3-piperidino-1-propene, was not formed.

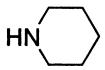
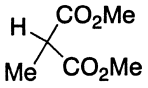
Similar to [Ru(η^5-C_5Me_5)(OMe)]$_2$[20] and other half-sand-



Scheme 9.

Table 4. Catalytic Allylations of Piperidine or Dimethyl Methylmalonate with Allylic Methyl Carbonates



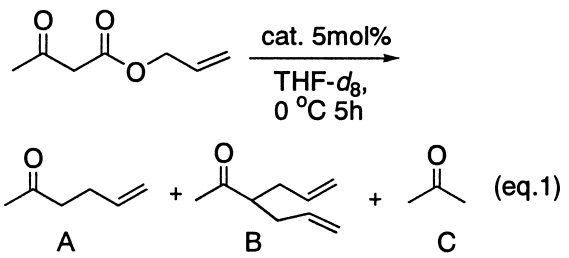
Entry	H-Nu	R	Cat	overall yield/%[a]	R–Nu	:	Nu / R [a]
1		Ph	**1a**	> 99	23	:	77
2		Ph	**1b**	> 99	13		87
3		Ph	**5a-PF$_6$**	> 99	100	:	0
4		Ph	**Ru^{II}**[b]	> 99	15	:	85
				(> 99	17	:	83)[c]
5		Me	**1a**	90	21	:	79
6		H	**1a**	40		—	
7		H	**1b**	51 (100)[d]		—	
8		H	**2b-PF$_6$**	no reaction		—	
9		H	**Ru^{II}**[b]	no reaction		—	
10		Ph	**1b**	2 (18)[e]	100	:	0
11		Me	**1b**	12 (37)[e]	100	:	0

a) Determined by ^{1}H NMR. b) Ru^{II} = [Ru(η^5-C_5Me_5)(OMe)]$_2$ (0.5 eq.). c) Reported by T. Mitsudo et al., see Ref. 8d. d) Reaction condition: room temperature, 4h. e) Reaction condition: 45 °C, 6 h.

wich Ru(II) complexes reported by Mitsudo,[8d,19] the amidinatoruthenium(II) complexes, **1a** and **1b**, act as the catalysts for the allylation of various nucleophiles. As selected examples, reactions of allyl methyl carbonates with piperidine and dimethyl methylmalonate were examined. As summarized in Table 4, the reactions of cinnamyl methyl carbonate or crotyl methyl carbonate with piperidine in the presence of 5 mol% of **1a** or **1b** at 0 °C proceeded in good yields within 1 h. Catalytic activity was similar to that of [Ru(η^5-C_5Me_5)(OMe)]$_2$. Piperidine moiety was generally introduced favorably at the more substituted position between two possible reaction points of the allyl moiety by catalysis of either **1a**, **1b**, or [Ru(η^5-C_5Me_5)(OMe)]$_2$. Interestingly, **5a-PF$_6$** also catalyzed the reaction of cinnamyl methyl carbonate with piperidine to give N-cinnamylpiperidine as the single product. This regioselectivity is similar to that obtained by the stoichiometric reaction described above, but is apparently different from those available by catalysis of **1a**, **1b**, or [Ru(η^5-C_5Me_5)(OMe)]$_2$.

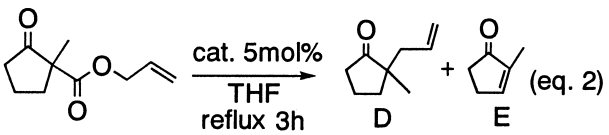
A significant difference in reactivity of **1a** or **1b** from that of [Ru(η^5-C_5Me_5)(OMe)]$_2$ was seen in the reaction of allyl methyl carbonate with dimethyl methylmalonate; **1a** or **1b** gave the corresponding product in moderate yields, whereas no reaction took place with [Ru(η^5-C_5Me_5)(OMe)]$_2$. The reaction was sensitive towards substituents of the allyl carbonates; the reactions of crotyl methyl carbonate or cinnamyl methyl carbonate were slower.

Ruthenium-catalyzed Carrole reactions shown in Scheme 10 were also achieved using **1a**, **1b**, or [Ru(η^5-C_5Me_5)(OMe)]$_2$ as the catalyst. Three products **A**–**C** were obtained by treatment of allyl acetoacetate with the ruthenium catalyst (Eq. 1) at 0 °C , while the reaction shown in Eq. 2 proceeded at 70 °C, giving the desired product **D** and a small amount of enone **E**. In these cases, little difference in rate and selectivity was seen between **1a**, or **1b**, or [Ru(η^5-C_5Me_5)(OMe)]$_2$ as the catalyst. Similar reactions catalyzed by palladium were well investigated by Tsuji and co-workers.[18]



cat.	overall yield (%)[a]	A : B : C[a]
2a	>99	61 : 20 : 20
2b	>99	63 : 18 : 18
Ru^{II} [b]	>99	70 : 15 : 15

a) Determined by ^{1}H NMR. b) ***Ru^{II}*** = [Ru(η^5-C_5Me_5)(OMe)]$_2$ (0.5 eq.).

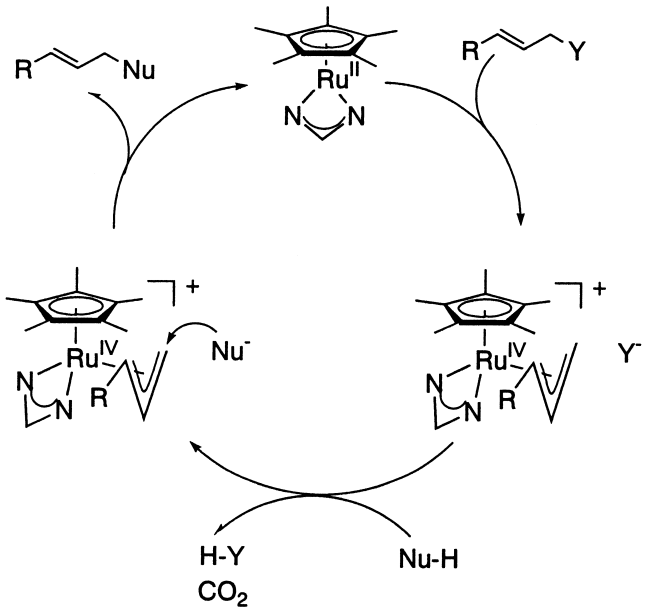


cat.	overall yield (%)[a]	D : E[a]
2b	>99	92 : 8
Ru^{II} [b]	90	90 : 10

a) Determined by ^{1}H NMR. b) ***Ru^{II}*** = [Ru(η^5-C_5Me_5)(OMe)]$_2$ (0.5 eq.).

Scheme 10.

As described above, we found that the reaction of **1a** or **1b**



Scheme 11.

with allylic carbonate afforded the oxidative adducts [Ru(η^3-allyl)(η^5-C_5Me_5)(η^2-amidinate)]$^+$ in good yield. Stoichiometric reactions of [Ru(η^3-allyl)(η^5-C_5Me_5)(η^2-amidinate)]$^+$ with nucleophiles gave rise to allylation of these nucleophiles and regeneration of [Ru(η^5-C_5Me_5)(η-amidinate)]. Thus, a possible catalytic cycle can be illustrated as Scheme 11, in which the oxidative adducts [Ru(η^3-allyl)(η^5-C_5Me_5)(η^2-amidinate)]$^+$ are involved as key intermediates.[23]

Conclusion

Although several coordinatively unsaturated organoruthenium(II) complexes bearing 16 valence electrons have successfully been isolated and there reactivity has been subjected to study, none of them was referred to oxidative addition of allylic substrates. We discovered the oxidative addition of allylic substrates to the isolable coordinatively unsaturated organoruthenium(II) complex **1a** or **1b**, which offers a new cationic organoruthenium(IV) complex stabilized by a nitrogen-donor ligand, [Ru(η^3-allyl)(η^5-C_5Me_5)(η^2-amidinate)]$^+$. The strong donor property of the ruthenium center of **1a** or **1b** derived from the C_5Me_5 and amidinato ligands contributes to facile oxidative addition of allylic substrates. In contrast, the formed [Ru(η^3-allyl)(η^5-C_5Me_5)(η^2-amidinate)]$^+$ is an acceptor, and facilely reacted with nucleophiles. There are several examples of organoruthenium(IV) compounds; however, only a few examples of the complexes bearing nitrogen donor ligand have been reported to our knowledge.[3v,21] Reaction of halogens with certain Ru(II) precursors bearing nitrogen donor ligands reportedly resulted in formation of halogeno-Ru(III) products.[3t,22] As described earlier, the reaction of organic halides with **1a** or **1b** also gave rise to formation of halogeno-Ru(III) species. Since the complexes of late transition metals in higher oxidation states are one of the unexplored fields in organometallic chemistry, we believe that these findings contribute to the progress of this field.

Stoichiometric and catalytic transformations of allylic substrates mediated by **1a**, **1b**, or [Ru(η^3-allyl)(η^5-C_5Me_5)(η^2-amidinate)]$^+$ were achieved. Involvement of the oxidative addition of allylic substrates to **1a** or **1b** affording [Ru(η^3-allyl)(η^5-C_5Me_5)(η^2-amidinate)]$^+$ and the subsequent reaction with nucleophiles supports the reaction mechanism shown in Scheme 11. The interesting effect of PF_6 anion described in the text requires further investigation.

Experimental

General Methods. All manipulations were carried out under a dry argon atmosphere using the standard Schlenk tube technique associated with a high-vacuum line and a glove box under a purified N_2 atmosphere. All solvents were distilled over appropriate drying reagents prior to use (Et_2O, THF, pentane; Ph_2CO/Na, CH_2Cl_2, $CHCl_3$; CaH_2). An ether solution of PhLi was prepared from PhBr and Li wire, and was titrated prior to use. Allylic compounds and piperidine were distilled before use. [Ru(η^5-C_5Me_5)(η-amidinate)] was synthesized from [Ru(η^5-C_5Me_5)(OMe)]$_2$ and lithium amidinate according to the procedure reported previously.[5a] Column chromatography was performed with Merck, neutral aluminum oxide 90 (70–230 mesh ASTM). ^{1}H and ^{13}C NMR spectra were recorded on JEOL Lambda 600 and Lambda 400 spectrometers at ambient temperature unless otherwise noted. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to solvent resonances. All coupling constants (J) are reported in Hz. IR spectra were recorded on a JASCO FT/IR-550 spectrometer. Elemental analyses were performed at the Analysis Center in the Faculty of Science of Kyushu University.

Reactions of Allylic Halides with [Ru(η^5-C_5Me_5)(η-amidinate)] (1a,1b). I. Preparation of Chloro-Ru(IV)-η^3-allyl Complexes. In a typical example, **1a** (70 mg, 0.185 mmol) was dissolved in dry pentane (ca. 10 mL) in a Schlenk tube. To the resulting clear purple solution, allyl chloride (15 μL, 0.184 mmol) was added at room temperature. The color of the solution immediately changed to yellow, from which yellow precipitates were formed. After 1 h, the solvent was removed under a reduced pressure to give a yellow solid (84 mg) containing **2a** and **7**. Assignment of **7** was performed according to the literature.[7b] Yields of **2a** and **7** were determined by ^{1}H NMR spectrometry on the basis of the integrated intensity of internal standard (mesitylene). (**2a**: 98%, **7**:2%). By a similar procedure, products described in Table 1 and Scheme 4, **2b**, **3a**, **4a**, **4b**, **5a**, **8**,[7b] **9**,[7b] **10**,[8d] **11**,[7b] and **12**,[13] were obtained. These new halo-Ru(IV)-π-allyl complexes, **2a**, **2b**, **3a**, **4a**, **4b**, and **5a**, are unstable at room temperature, and attempts to remove a small amount of **7**, **8**, **9**, and **10** by chromatography and fractional crystallization failed. Therefore, assignment of the products was carried out by NMR spectroscopy, and full characterization was made using PF_6 or BF_4 analogue obtained by the following anion exchange reaction or by direct preparation from **2a** or **2b**.

II. Preparation of PF_6 and BF_4 Salts from Chloro-Ru(IV)-η^3-allyl Complexes. In a typical example, the mixture (65 mg) of **2a** (0.140 mmol) and **7** was treated with NH_4PF_6 (23 mg, 0.141 mmol) in $CHCl_3$ (ca. 10 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred at this temperature for 1 h. After removal of the solvent in vacuo, purification of the residue by column chromatography [alumina (0.5 cmΦ × 1.5 cm); CH_2Cl_2] was followed by recrystallization from CH_2Cl_2–Et_2O to form **2a-PF$_6$** (56 mg, 0.089 mmol, 64% yield; yellow crystals). By a similar procedure, **2b-PF$_6$**, **2b-BF$_4$**, and **4b-PF$_6$** were obtained from **2b** and **4b**.

2a: yellow microcrystals. ^{1}H NMR ($CDCl_3$) δ 1.23 (d, J = 7.0 Hz, 6H, CH(CH_3)$_2$), 1.30 (d, J = 7.0 Hz, 6H, CH(CH_3)$_2$), 1.79 (s, 15H, C_5(CH_3)$_5$), 1.92 (s, 3H, CCH_3), 2.32 (d, J = 10.1 Hz,, 2H, anti-CH of the allyl group), 3.22 (sep, J = 7.0 Hz, 2H, CH(CH$_3$)$_2$), 4.03 (d, J = 6.0 Hz, 2H, syn-CH of the allyl group), 4.94 (dt, J = 6.0 Hz, 10.1, 1H, central-CH of the allyl group). ^{13}C{^{1}H}NMR ($CDCl_3$) δ 10.3 (C_5(CH$_3$)$_5$), 22.5 (CCH$_3$), 25.7, 26.1 (CH(CH$_3$)$_2$), 51.1 (CH(CH$_3$)$_2$), 60.8 (CH$_2$ of the allyl group), 98.6 (CH of the allyl group), 104.9 (C_5(CH$_3$)$_5$), 174.3 (NCN).

2a-PF$_6$: Orange crystals. Anal. Calcd for $C_{21}H_{37}F_6N_2PRu$: C, 44.76; H, 6.62; N, 4.97%. Found: C, 44.75; H, 6.58; N, 4.90%. ^{1}H NMR (in $CDCl_3$) δ 1.22 (d, J = 7.0 Hz, 6H, CH(CH_3)$_2$), 1.29 (d, J = 7.0 Hz, 6H, CH(CH_3)$_2$), 1.71 (s, 15H, C_5(CH$_3$)$_5$), 1.90 (s, 3H, CCH$_3$), 2.09 (d, J = 10.3 Hz,, 2H, anti-CH of the allyl group), 3.20 (sep, J = 7.0 Hz, 2H, CH(CH$_3$)$_2$), 4.00 (d, J = 6.1 Hz,, 2H, syn-CH of the allyl group), 4.93 (dt, J = 6.1 Hz,, 10.3, 1H, central-CH of the allyl group). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 9.8 (C_5(CH$_3$)$_5$), 22.4 (CCH$_3$), 25.6 (CH(CH$_3$)$_2$), 25.9 (CH(CH$_3$)$_2$), 51.0 (CH(CH$_3$)$_2$), 60.2 (CH$_2$ of the allyl group), 98.3 (CH of the allyl group), 104.9 (C_5(CH$_3$)$_5$), 174.3 (NCN). IR (KBr,) 3422, 2979, 2932, 1520, 1485, 1457, 1214, 1140, 839cm^{-1}. mp: 138 °C (dec.).

3a: Yellow microcrystals. ^{1}H NMR ($CDCl_3$) δ 1.21 (d, J = 7.0 Hz, 6H, CH(CH_3)$_2$), 1.28 (d, J = 7.0 Hz, 6H, CH(CH_3)$_2$), 1.76 (s, 15H, C_5(CH_3)$_5$), 1.81 (s, 3H, CCH_3), 2.25 (d, J = 10.1 Hz,, 2H, anti-CH of the allyl group), 3.20 (sep, J = 7.0 Hz, 2H, CH(CH$_3$)$_2$), 4.01 (d, J = 6.0 Hz,, 2H, syn-CH of the allyl group), 4.92 (dt, J = 6.0 Hz,, 10.1, 1H, central-CH of the allyl group). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 10.2 (C_5(CH$_3$)$_5$), 22.4 (CCH$_3$), 25.6 (CH(CH$_3$)$_2$), 25.9 (CH(CH$_3$)$_2$), 51.0 (CH(CH$_3$)$_2$), 60.6 (CH$_2$ of the allyl group), 98.4 (CH of the allyl group), 104.8 (C_5(CH$_3$)$_5$), 174.2 (NCN).

2b: Yellow microcrystals. ^{1}H NMR ($CDCl_3$) δ 0.95 (s, 18H, C(CH$_3$)$_3$), 1.90 (s, 15H, C_5(CH$_3$)$_5$), 2.51 (d, J = 10.4 Hz, 2H, anti-CH of the allyl group), 4.59 (d, J = 6.3 Hz, 2H, syn-CH of the allyl group), 5.36 (dt, J = 6.3 Hz, 10.4, 1H, central-CH of the allyl group), 7.14 (m, 1H, C_6H_5), 7.24 (m, 1H, C_6H_5), 7.31 (m, 1H, C_6H_5), 7.36 (m, 1H, C_6H_5), 7.44 (m, 1H, C_6H_5). ^{13}C{^{1}H} NMR (in $CDCl_3$) δ 11.4 (C_5(CH$_3$)$_5$), 35.5 (C(CH$_3$)$_3$), 58.0 (C(CH$_3$)$_3$), 60.4 (CH$_2$ of the allyl group), 97.4 (CH of the allyl group), 106.5 (C_5(CH$_3$)$_5$), 127.5, 127.6, 127.8, 130.0, 132.6, 138.6 (C_6H$_5$), 179.2 (NCN).

2b-PF$_6$: Orange crystals. Anal. Calcd for $C_{28}H_{43}F_6N_2PRu$: C, 51.45; H, 6.63; N, 4.29%. Found: C, 51.22; H, 6.62; N, 4.34%. ^{1}H NMR ($CDCl_3$) δ 0.95 (s, 18H, C(CH$_3$)$_3$), 1.81 (s, 15H, C_5(CH$_3$)$_5$)), 2.22 (d, J = 10.2 Hz,, 2H, anti-CH of the allyl group), 4.53 (d, J = 6.1 Hz,, 2H, syn-CH of the allyl group), 5.36 (dt, J = 6.1 Hz,, 10.2, 1H, central-CH of the allyl group), 7.16 (m, 1H, C_6H_5), 7.24 (m, 1H, C_6H_5), 7.32 (m, 1H, C_6H_5), 7.35 (m, 1H, C_6H_5), 7.44 (m, 1H, C_6H_5). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 10.9 (C_5(CH$_3$)$_5$), 35.5 (C(CH$_3$)$_3$), 58.0 (C(CH$_3$)$_3$), 59.7 (CH$_2$ of the allyl group), 97.2 (CH of the allyl group), 106.6 (C_5(CH$_3$)$_5$), 127.4, 127.6, 127.8, 129.9, 132.8, 138.6 (C_6H$_5$), 178.9 (NCN). IR (KBr) 3437, 2966, 1442, 1208, 1183, 840 cm^{-1}. mp: 164 °C (dec.).

2b-BF$_4$: Orange crystals. Anal. Calcd for $C_{28}H_{43}BF_4N_2Ru$: C, 56.47; H, 7.28; N, 4.70%. Found: C, 56.00; H, 7.24; N, 4.70%. ^{1}H NMR ($CDCl_3$) δ 0.94 (s, 18H, C(CH$_3$)$_3$), 1.82 (s, 15H, C_5(CH$_3$)$_5$), 2.42 (d, J = 10.4 Hz, 2H, anti-CH of the allyl group), 4.54 (d, J = 6.1, 2H, syn-CH of the allyl group), 5.36 (dt, J = 6.1, 10.4 Hz, 1H, central-CH of the allyl group), 7.15 (m, 1H, C_6H_5), 7.25 (m, 1H, C_6H_5), 7.31 (m, 1H, C_6H_5), 7.35 (m, 1H, C_6H_5), 7.43 (m, 1H, C_6H_5). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 11.0 (C_5(CH$_3$)$_5$), 35.5 (C(CH$_3$)$_3$), 58.0 (C(CH$_3$)$_3$), 59.7 (CH$_2$ of the allyl group), 97.2 (CH of the allyl group), 106.7 (C_5(CH$_3$)$_5$), 127.5, 127.6, 127.9, 129.9, 132.7, 138.6 (C_6H$_5$), 178.9 (NCN). IR (KBr) 3421, 3005, 2965, 1437, 1395, 1360, 1289, 2207, 1182, 1048, 954, 880, 802, 751, 718 cm^{-1}. mp: 160 °C (dec.).

4a: Yellow microcrystals. ^{1}H NMR ($CDCl_3$) δ 1.20 (d, J = 7.0 Hz, 6H, CH(CH_3)$_2$), 1.24 (d, J = 7.0 Hz, 6H, CH(CH_3)$_2$), 1.71 (s, 15H, C_5(CH_3)$_5$), 1.90 (s, 3H, CCH_3), 2.07 (s, 3H, CH$_3$ of the methallyl group), 2.18 (s, 2H, anti-CH of the methallyl group), 3.13 (sep, J = 7.0 Hz, 2H, CH(CH$_3$)$_2$), 3.58 (s, 2H, syn-CH of the methallyl group). ^{13}C{^{1}H} NMR (in $CDCl_3$) δ 10.2 (C_5(CH$_3$)$_5$), 17.6 (CH$_3$ of the methallyl group), 22.8 (CCH$_3$), 24.6 (CH(CH$_3$)$_2$), 26.0 (CH(CH$_3$)$_2$), 50.3 (CH(CH$_3$)$_2$), 58.3 (CH$_2$ of the allyl group), 104.6 (C_5(CH$_3$)$_5$), 113.1 (CH of the allyl group), 172.2 (NCN).

4a-PF$_6$: Yellow microcrystals. Anal. Calcd for $C_{22}H_{39}F_6N_2PRu$: C, 45.75; H, 6.81; N, 4.85%. Found: C, 45.84; H, 6.76; N, 4.82%. ^{1}H NMR ($CDCl_3$) δ 1.23 (d, J = 7.0 Hz, 6H, CH(CH_3)$_2$), 1.27 (d, J = 7.0 Hz, 6H, CH(CH_3)$_2$), 1.68 (s, 15H, C_5(CH_3)$_5$), 1.92 (s, 3H, CCH_3), 2.05 (s, 2H, anti-CH of the methallyl group), 2.10 (s, 3H, CH$_3$ of the methallyl group), 3.16 (sep, J = 7.0 Hz, 2H, CH(CH$_3$)$_2$), 3.60 (s, 2H, syn-CH of the methallyl group). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 9.8 (C_5(CH$_3$)$_5$), 17.5 (CH$_3$ of the methallyl group), 22.8 (CCH$_3$), 24.6 (CH(CH$_3$)$_2$), 26.0 (CH(CH$_3$)$_2$), 50.3 (CH(CH$_3$)$_2$), 58.0 (CH$_2$ of the allyl group), 104.6 (C_5(CH$_3$)$_5$), 113.0 (CH of the allyl group), 172.3 (NCN). IR (KBr) 2981, 1519, 1489, 1384, 1337, 1213, 1138, 843, 557 cm^{-1}. mp: 184 °C (dec.).

4b: Yellow microcrystals. ^{1}H NMR ($CDCl_3$) δ 0.91 (s, 18H, C(CH$_3$)$_3$), 1.82 (s, 15H, C_5(CH$_3$)$_5$), 2.40 (s, 2H, anti-CH of the methallyl group), 2.41 (s, 3H, CH$_3$ of the methallyl group), 4.06 (s, 2H, syn-CH of the methallyl group), 7.15–7.40 (m, 5H, C_6H_5). ^{13}C{^{1}H} NMR (in $CDCl_3$) δ 11.3 (C_5(CH$_3$)$_5$), 18.2 (CH$_3$ of the methallyl group), 35.6 (C_5(CH$_3$)$_5$), 57.0 (C(CH$_3$)$_3$), 58.5 (CH$_2$ of the methallyl group), 106.1 (C_5(CH$_3$)$_5$), 112.8 (central-C of the methallyl group), 127.0, 127.3, 128.2, 129.8, 133.1, 137.9 (C_6H$_5$), 177.2 (NCN).

4b-PF$_6$: Orange crystals. Anal. Calcd for $C_{29}H_{45}F_6N_2PRu$: C, 52.16; H, 6.79; N, 4.20%. Found: C, 52.31; H, 6.80; N, 4.26%. ^{1}H NMR ($CDCl_3$) δ 0.96 (s, 18H, C(CH$_3$)$_3$), 1.79 (s, 15H, C_5(CH$_3$)$_5$), 2.28 (s, 2H, anti-CH of the methallyl group), 2.46 (s, 3H, CH$_3$ of the methallyl group), 4.06 (s, 2H, syn-CH of the methallyl group), 7.21 (m, 1H, C_6H_5), 7.25 (m, 1H, C_6H_5), 7.32 (m, 1H, C_6H_5), 7.34 (m, 1H, C_6H_5), 7.43 (m, 1H, C_6H_5). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 11.0 (C_5(CH$_3$)$_5$), 18.3 (CH$_3$ of the methallyl group), 35.7 (C_5(CH$_3$)$_5$), 57.1 (C(CH$_3$)$_3$), 58.1 (CH$_2$ of the methallyl group), 106.6 (C_5(CH$_3$)$_5$), 112.5 (central-C of the methallyl group), 127.2, 127.3, 128.4, 129.9, 133.4, 138.2 (C_6H$_5$), 177.1 (NCN). IR (KBr) 3437, 3001, 2966, 1439, 1207, 1183, 842 cm^{-1}. mp: 184 °C (dec.).

5a: Yellow microcrystals. ^{1}H NMR ($CDCl_3$) δ 0.47 (d, J = 7.0 Hz, 3H, CH(CH_3)$_2$), 0.98 (d, J = 7.0 Hz, 3H, CH(CH_3)$_2$), 1.32 (d, J = 7.0 Hz, 3H, CH(CH_3)$_2$), 1.33 (d, J = 7.0 Hz, 3H, CH(CH_3)$_2$), 1.83 (s, 3H, CCH_3), 1.84 (s, 15H, C_5(CH_3)$_5$), 2.27 (sep, J = 7.0 Hz, 1H, CH(CH$_3$)$_2$), 2.52 (d, J = 9.8 Hz, 1H, CHH (anti)), 3.18 (sep, J = 7.0 Hz, 1H, CH(CH$_3$)$_2$), 4.16 (d, J = 6.1 Hz, 1H, CHH (syn)), 4.28 (d, J = 10.8 Hz, 1H, CHPh), 5.62 (ddd, J = 6.1, 9.8, 10.8 Hz, 1H, CH$_2$CH), 7.29–7.42 (m, 5H, Ph). ^{13}C{^{1}H} NMR (in $CDCl_3$) δ 10.4 (C_5(CH$_3$)$_5$), 23.6 (CCH$_3$), 24.8, 25.7, 26.2, 26.7 (CH(CH$_3$)$_2$), 47.7, 50.4 (CH(CH$_3$)$_2$), 60.0 (CH$_2$ of the cinnamyl group), 86.0 (CHPh of the cinnamyl group), 95.6 (CH$_2$$C$H of the cinnamyl group), 104.6 (C_5(CH$_3$)$_5$), 128.6, 129.3, 129.6, 136.9 (Ph), 173.8 (NCN).

5a-PF$_6$: Yellow microcrystals. Anal. Calcd for

$C_{27}H_{41}F_6N_2PRu$: C, 50.70; H, 6.46; N, 4.38%. Found: C, 50.21; H, 6.40; N, 4.26%. ^{1}H NMR ($CDCl_3$) δ 0.45 (d, J = 7.0 Hz, 3H, $CH(CH_3)_2$), 0.95 (d, J = 7.0 Hz, 3H, $CH(CH_3)_2$), 1.28 (d, J = 7.0 Hz, 3H, $CH(CH_3)_2$), 1.30 (d, J = 7.0 Hz, 3H, $CH(CH_3)_2$), 1.73 (s, 15H, $C_5(CH_3)_5$), 1.81 (s, 3H, CCH_3), 2.23 (sep, J = 7.0 Hz, 1H, $CH(CH_3)_2$), 2.24 (d, J = 9.1 Hz, 1H, CH*H* (anti)), 3.13 (sep, J = 7.0 Hz, 1H, $CH(CH_3)_2$), 4.05 (d, J = 10.8 Hz, 1H, C*H*Ph), 4.10 (d, J = 6.1 Hz, 1H, C*H*H (syn)), 5.61 (ddd, J = 6.1, 9.1, 10.8 Hz, 1H, CH_2CH), 7.31–7.40 (m, 5H, Ph). ^{13}C{^{1}H} NMR (in $CDCl_3$) δ 9.9 ($C_5(CH_3)_5$), 23.4 (CCH_3), 24.7, 25.5, 26.0, 26.6 ($CH(CH_3)_2$), 47.7, 50.3 ($CH(CH_3)_2$), 59.5 (CH_2 of the cinnamyl group), 85.2 (*C*HPh of the cinnamyl group), 95.4 (CH_2CH of the cinnamyl group), 104.6 ($C_5(CH_3)_5$), 128.6, 129.3, 129.3, 137.0 (Ph), 173.9 (N*C*N). IR (KBr) 2968, 2933, 1522, 1487, 1463, 1437, 1380, 1360, 1338, 1210, 1138, 839, 700 cm^{-1}. mp: 142 °C (dec.).

Direct Preparation of PF_6 and BPh_4 Salts from 2a or 2b. A mixture of **1a** (42 mg, 0.111 mmol), allyl chloride (11 µL, 0.135 mmol) and $NaPF_6$ (19 mg, 0.113 mmol) in THF (5 mL) was stirred at room temperature for 1 h. After removal of the solvent in vacuo, the residue was purified by column chromatography [alumina (0.5 cmΦ ×1.0 cm); CH_2Cl_2]. Recrystallization of the product from CH_2Cl_2–Et_2O gave **2a-PF$_6$** in 62% yield (39 mg; yellow crystal). Alternatively, **1a** (70 mg, 0.185 mmol) was treated with allyl acetate (20 µL, 0.185 mmol) in the presence of $NaPF_6$ (31 mg, 0.185 mmol) in THF (10 mL) at room temperature. The mixture was stirred at room temperature for 1 h. After removal of the solvent in vacuo, the residue was extracted with several portions of CH_2Cl_2 (10 mL) and the combined extracts were filtered through Celite to remove insoluble materials. After removal of the solvent in vacuo, analytically pure **2a-PF$_6$** was obtained without further purification (90% yield, 94 mg). By a similar procedure, products described in Table 3 were isolated.

6a-PF$_6$: Yellow microcrystals. ^{1}H NMR ($CDCl_3$) δ 0.18 (s, 9H, $Si(CH_3)_3$) 1.23 (d, J = 7.0 Hz, 6H, $CH(CH_3)_2$), 1.25 (d, J = 7.0 Hz, 6H, $CH(CH_3)_2$), 1.66 (s, 2H, CH_2SiMe_3), 1.68 (s, 15H, $C_5(CH_3)_5$), 1.93 (s, 2H, CH*H* (anti)), 1.91 (s, 3H, CCH_3), 3.17 (sep, J = 7.0 Hz, 2H, $CH(CH_3)_2$), 3.42 (s, 2H, C*H*H (syn)). ^{13}C{^{1}H} NMR ($CDCl_3$) δ −1.7 ($Si(CH_3)_3$), 9.8 ($C_5(CH_3)_5$), 22.4 (CH_2SiMe_3), 22.8 (CCH_3), 25.0, 26.0 ($CH(CH_3)_2$), 50.2 ($CH(CH_3)_2$), 54.8 ($C(CH_2)_2$), 104.4 ($C_5(CH_3)_5$), 118.6 ($CH_2C(CH_2)_2$), 172.2 (s, N*C*N). ^{29}Si{^{1}H} NMR ($CDCl_3$) δ 5.1 (s, $SiMe_3$). IR (KBr) 2977, 1511, 1487, 1465, 1383, 1343, 1330, 1251, 1212, 1139, 841 cm^{-1}. mp: 170 °C (dec.). **6a-PF$_6$** is unstable in the air, and elementary analysis of **6a-PF$_6$** has not been accomplished. Therefore, full characterization was carried out using the BPh_4 analogue.

6a-BPh$_4$: Yellow microcrystals. Anal. Calcd for $C_{49}H_{67}BN_2RuSi$: C, 71.42; H, 8.19; N, 3.40%. Found: C, 70.77; H, 8.18; N, 3.37%. ^{1}H NMR ($CDCl_3$) δ 0.21 (s, 9H, $Si(CH_3)_3$), 1.20 (d, J = 7.0 Hz, 12H, $CH(CH_3)_2$), 1.45 (s, 15H, $C_5(CH_3)_5$), 1.63 (s, 2H, CH_2SiMe_3), 1.78 (s, 2H, CH*H* (anti)), 1.84 (s, 3H, CCH_3), 3.06 (sep, J = 7.0 Hz, 2H, $CH(CH_3)_2$), 3.31 (s, 2H, C*H*H (syn)), 6.89 (m, 4H, $B(C_6H_5)_4$), 7.04 (m, 8H, $B(C_6H_5)_4$), 7.42 (m, 8H, $B(C_6H_5)_4$). ^{13}C{^{1}H} NMR ($CDCl_3$) δ −1.6 ($Si(CH_3)_3$, 9.9 ($C_5(CH_3)_5$), 22.5 (CH_2SiMe_3), 22.7 (CCH_3), 25.0, 26.0 ($CH(CH_3)_2$), 50.2 ($CH(CH_3)_2$), 54.8 ($C(CH_2)_2$), 104.3 ($C_5(CH_3)_5$), 118.7 ($CH_2C(CH_2)_2$), 121.5 (*p*-CH of $B(C_6H_5)_4$), 125.4 (q, $^2J_{BC}$ = 2.6 Hz, *o*-CH of $B(C_6H_5)_4$), 136.3 (*m*-CH of $B(C_6H_5)_4$), 164.2 (q, $^1J_{BC}$ = 49.3 Hz, *ipso*-C of $B(C_6H_5)_4$), 172.3 (s, N*C*N). ^{29}Si{^{1}H} NMR ($CDCl_3$) δ 6.0 (s, $SiMe_3$). IR (KBr) 3419, 3054, 3033, 2983, 1579, 1525, 1481, 1428, 1379, 1360, 1335, 1260, 1249, 1212, 1135, 853, 749, 732, 703, 610 cm^{-1}. mp: 178 °C (dec.).

NMR Observation of 13a and 13b. **1a** (20 mg, 0.053 mmol) was dissolved in THF-d_8 (0.5 mL) in a 5 mm o.d. NMR tube. To the resulting purple solution, allyl acetate (5.7 µL, 0.053 mmol) was added at −78 °C. The color of solution changed to yellow immediately. ^{1}H, ^{13}C{^{1}H} and HMQC NMR spectra of **13a** were recorded at −80 °C. Using a similar procedure, **13b** was detected.

13a: ^{1}H NMR (THF-d_8, −80 °C) δ 0.76 (d, J = 6.3 Hz, 3H, $CH(CH_3)_2$), 0.90 (d, J = 6.3 Hz, 3H, $CH(CH_3)_2$), 1.27 (d, J = 6.3 Hz, 3H, $CH(CH_3)_2$), 1.30 (d, J = 6.3 Hz, 3H, $CH(CH_3)_2$), 1.60 (s, 15H, $C_5(CH_3)_5$), 1.71 (s, 3H, CCH_3 or CH_3CO_2), 1.99 (s, 3H, CCH_3 or CH_3CO_2), 2.45 (d, J=7.1 Hz, 1H, CH=CH_2), 2.58 (m, 1H, C*H*=CH_2), 2.91 (d, J = 9.9 Hz, 1H, CH=CH_2), 3.22 (sep, J = 6.3 Hz, 1H, $CH(CH_3)_2$), 3.52 (sep, J = 6.3 Hz, 1H, $CH(CH_3)_2$), 3.80 (dd, J = 10.8, 10.8 Hz, 1H, CH_2OAc), 4.75(dd, J = 2.6, 10.8 Hz, 1H, CH_2OAc). ^{13}C{^{1}H} NMR (in THF-d_8, −80 °C) δ 11.1 ($C_5(CH_3)_5$), 17.6 (CCH_3 or CH_3CO_2), 21.2 (CCH_3 or CH_3CO_2), 24.9, 25.6, 26.6, 26.6 ($CH(CH_3)_2$), 47.8 ($CH(CH_3)_2$), 47.9 (CH=CH_2), 51.4 ($CH(CH_3)_2$), 59.1 (*C*H=CH_2), 70.8 (CH_2OAc), 89.8 ($C_5(CH_3)_5$), 167.1 (NCN or CH_3CO_2), 170.9 (NCN or CH_3CO_2).

13b: ^{1}H NMR (in THF-d_8, −80 °C) δ 0.82 (s, 9H, $C(CH_3)_3$), 1.04 (s, 9H, $C(CH_3)_3$), 1.65 (s, 15H, $C_5(CH_3)_5$), 2.03 (s, 3H, CH_3CO_2), 2.60 (d, J = 7.5 Hz, 1H, CH=CH_2), 3.03 (d, J = 9.8 Hz, 1H, CH=CH_2), 3.13 (m, 1H, C*H*=CH_2), 3.84 (t, J = 11.0 Hz, 1H, CH_2OAc), 4.99 (dd, J = 3.7, 11.0 Hz, 1H, CH_2OAc), 7.23–7.36 (m, 5H, C_6H_5). ^{13}C{^{1}H} NMR (THF-d_8, −80 °C) δ 10.7 ($C_5(CH_3)_5$), 21.2 (CH_3CO_2), 35.4, 36.0 ($C(CH_3)_3$), 48.4 (CH=CH_2), 53.8, 55.4 ($C(CH_3)_3$), 56.7 (*C*H=CH_2), 70.9 (CH_2OAc), 91.0 ($C_5(CH_3)_5$), 127.4, 127.5, 128.9, 130.8, 134.6, 141.3 (C_6H_5), 170.4 (NCN or CH_3CO_2), 170.8 (NCN or CH_3CO_2).

Reactions of 2b-PF$_6$ and 5a-PF$_6$ with Nucleophiles. In a typical example, an ether solution of PhLi (0.27 mL, 0.54 M) was added to the THF yellow solution (10 mL) of **2b-PF$_6$** (70 mg, 0.15 mmol) at 0 °C, and the mixture was stirred at this temperature for 1 h. Color of the reaction mixture changed from yellow to black. After removal of the solvent in vacuo, an oily residue was obtained (103 mg). This residue contained 3-phenyl-1-propene and 1-phenyl-1-propene in a ratio of 2:1 in 70% yield. The yield and ratio were determined by ^{1}H NMR spectrometry on the basis of the integrated intensity of internal standard (mesitylene). The spectral data were in accord with those of commercially available authentic samples. Using a similar procedure, reaction of **2b-PF$_6$** with a THF solution of $Na[MeC(CO_2Me)_2]$ (0.63 M), which was prepared from $MeHC(CO_2Me)_2$ and NaH before use, was carried out, and afforded a mixture of dimethyl allylmethylmalonate and **1b** in 93% and 74% yields, respectively. The reaction of **5a-PF$_6$** with piperidine gave a mixture of 1-phenyl-3-piperidino-1-propene, its HPF_6 salt, and **1a** (71%), which were determined by ^{1}H NMR spectrometry. The spectral data of the HPF_6 salt was in accord with those of the sample prepared by reaction with 1-phenyl-3-piperidino-1-propene and aqueous HPF_6. When the sample was passed through a short pad of Al_2O_3 by elution with THF, 1-phenyl-3-piperidino-1-propene was obtained in 97% yield.

General Procedure for the Catalytic Allylation of Piperidine and $MeHC(CO_2Me)_2$ and Decarboxylative Allylation. In a typical procedure, a THF solution (0.5 mL) of **1a** (9.5 mg, 0.025 mmol) was added to a mixture of cinnamyl carbonate (80 µL, 0.5 mmol), piperidine (50 µL, 0.5 mmol), and THF (0.5 mL) at 0 °C, and the mixture was stirred at this temperature. After 1 h, the resulting yellow mixture was transferred to the head of a short pad of silica gel to remove metal species. Eluents available by Et_2O (80 mL) were concentrated in vacuo to give a mixture of 1-phenyl-

3-piperidino-1-propene and 3-phenyl-3-piperidino-1-propene (100 mg).[8d] Yields of these products were determined by ^{1}H NMR spectrometry on the basis of the integrated intensity of internal standard (mesitylene). By a similar procedure, the products[18,24] in Table 4 and Scheme 10 were obtained.

X-ray Data Collection, Solution, and Refinement of Structure. Single crystals of **2b-PF$_6$** and **5a-PF$_6$** were grown from a mixture of CH_2Cl_2 and ether. Each X-ray crystallography measurement was performed on a Rigaku AFC-7R four circle axis diffraction meter in the case of **2b-PF$_6$**, and on a Rigaku RAXIS RAPID imaging plate diffraction meter in the case of **5a-PF$_6$** with graphite monochromated Mo $K\alpha$ radiation (λ = 0.71070 Å). The data were collected at 293(2) K (**2b-PF$_6$**) and 153(2) K (**5a-PF$_6$**). The structures were solved by direct method (SIR92)[25] in the case of **2b-PF$_6$** and by Patterson method (DIRDIF99 PATTY)[26] in the case of **5a-PF$_6$**. Atomic coordinates and the anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least squares on F^2 (SHELXL97-2).[27] The positions of all hydrogen atoms were calculated assuming idealized geometry. Several cycles of a full-matrix least-squares refinement with anisotropic temperature factors for non-hydrogen atoms led to final R_1 and wR_2 values ($I > 2\sigma(I)$). All calculations were performed on a Pentium computer. Crystallographic data are summarized in Table 5.

Table 5. Crystallographic Date for **2b-PF$_6$** and **5a-PF$_6$**

Complex	**2b-PF$_6$**	**5a-PF$_6$**
Formula	$C_{28}H_{43}F_6N_2PRu$	$C_{27}H_{41}F_6N_2PRu$
Formula weight	653.68	639.66
Temp/K	293(2)	153(2)
Habit	Orange prism	Orange Prism
Crystal size/mm	0.34×0.25× 0.18	0.50×0.50× 0.25
Crystal system	Orthorhombic	Monoclinic
Space group	*P*bca	$P2_1$/c
a/Å	31.771(6)	12.5817(12)
b/Å	14.034(4)	9.2301(9)
c/Å	13.366(5)	24.013(2)
β/deg		90.762(3)
V/Å^3	5961(3)	2788.4(5)
Z	8	4
D_{calcd}/gc m^{-3}	1.457	1.524
Diffractometer	AFC-7R (Rigaku)	RAXIS Rapid (Rigaku)
Radiation(λ/Å)	Mo $K\alpha$ (0.71070)	Mo $K\alpha$ (0.71070)
Monochromator	graphite	graphite
μ_{calcd}/cm^{-1}	0.637	0.679
F(000)	2704	1320
Scan type	$\omega-2\theta$	
θ range/deg	$2.56 < \theta < 27.50$	$1.70 < \theta < 27.48$
No. of date collected	6849	5347
No. of used date ($F_o > 2\sigma(F_o)$)	4403	4441
No. of variables	343	334
GOF	1.037	1.091
$R_1(I > 2\sigma(I))$	0.0492	0.0525
w$R_2(I > 2\sigma(I))$	0.1418	0.1212
R_1(all data)	0.0917	0.0660
wR_2(all data)	0.1620	0.1304
$\Delta\rho$ max/e Å^{-3}	0.833	0.571

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quating the publication citation and deposition numbers CCDC 146850 and 164869. The data are also deposited as Document No. 74048 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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