Preparation and structure elucidation of novel organoruthenium amidinates bearing η⁴-diene ligands

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Abstract

A series of novel ruthenium amidinate complexes bearing η^4-cyclooctadiene (COD) or η^4-norbornadiene (NBD) ligand was prepared, and their structures were elucidated by spectroscopy and crystallography. A disilver amidinate, $Ag_2\{\mu_2,\eta$-Ph-NC(H)=NPh$\}_2$, was treated with either (η^4-COD)Ru(MeCN)$_2$Cl$_2$ or (η^4-NBD)Ru(pyridine)$_2$Cl$_2$ to form the corresponding bisamidinate complex, (η^4-COD)Ru$\{\eta^2$-PhNC(H)=NPh$\}_2$ (**5a**) or (η^4-NBD)Ru$\{\eta^2$-PhNC(H)=NPh$\}_2$ (**5a′**), respectively, in moderate to good yield. Alternatively, (η^4-COD)Ru$\{\eta^2$-^{i}PrNC(Me)=N^{i}Pr$\}_2$ (**5b**) or (η^4-NBD)Ru$\{\eta^2$-^{i}PrNC(Me)=N^{i}Pr$\}_2$ (**5b′**) was synthesized by reaction of [(η^4-COD)RuCl$_2$]$_n$ or (η^4-NBD)Ru(pyridine)$_2$Cl$_2$ with Li$\{^i$PrNC(Me)=N^{i}Pr$\}$. Careful treatment of (η^4-NBD)Ru(pyridine)$_2$Cl$_2$ with one equivalent of Li$\{^i$PrNC(Me)=N^{i}Pr$\}$ resulted in the formation of a monoamidinate complex, (η^4-NBD)Ru$\{\eta^2$-^{i}PrNC(Me)=N^{i}Pr$\}$(pyridine)Br (**6**) as a good precursor for a mixed amidinate complex, (η^4-NBD)Ru$\{\eta^2$-^{i}PrNC(Me)=N^{i}Pr$\}\{\eta^2$-PhNC(H)=NPh$\}$ (**5c′**), which was obtained by the reaction of **6** with Ag$_2\{\mu_2,\eta$-PhNC(H)=NPh$\}_2$. Crystal structures of these complexes revealed the octahedral arrangement of the ligands. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ruthenium; Amidinate; Diene ligand

1. Introduction

Allyl and pseudo-allyl moieties such as carboxylates, dithiocarbamates, and amidinates have been extensively studied as auxiliary ligands for a variety of transition metals [1]. In particular, amidinates are one of the well-investigated ligands [2], especially for early transition metals; for example, some of them have lately been investigated as a substitute of an η^5-cyclopentadienyl ligand for catalytically active metallocene compounds for polyolefin syntheses [3]. As reviewed by Kilner and Edelmann [2], amidinate ligands are in many cases bound to a metal through two metal–nitrogen bonds, donating four electrons to a cationic metal center [2]. Certain amidinates alternatively behave as bridging ligands for dinuclear complexes, in which each nitrogen

atom in the amidinate ligands bonds with a different metal center. In this case, amidinates also act as a 4-electron donor ligand to dimetal dication, M_2^{2+} [4].

Although a wide variety of transition metal amidinates has been reported, organoruthenium complexes having amidinate ligands are surprisingly rare [4f,5]. We have recently investigated the preparation and characterization of several organoruthenium complexes bearing amidinate ligands [6]. Half-sandwich ruthenium(II or IV) complexes bearing an amidinate and an η^5-C$_5$Me$_5$ ligand, **1–3**, were prepared and characterized [6a,b]. Interestingly, the formal valence electrons of **1** are 16, and thus **1** is highly reactive with various 2-electron donor ligands to form **2** and with allylic halides to form ruthenium(IV)–η^3-allyl complexes, **3**. An unusual bonding mode of the amidinate ligand was seen in the crystal structure of **1**, in which π-electrons on the amidinate ligand are likely to take part in stabilizing the coordinatively unsaturated ruthenium

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center; this π-donor character of the amidinate ligands was also suggested by the crystal structure of $(\eta^5\text{-}C_5Me_5)_2Ru_2\{\mu_2\text{-}^iPrNC(Me)=N^iPr\}Br$ [6c] and DFT calculations of $(\eta^5\text{-}C_5H_5)Ru\{\eta^2\text{-}HNC(H)=NH\}$ [6d]. Complexes bearing a η^6-arene (6-electron donor) ligand such as **4** were also studied [6e].

As an extension of these studies, we were interested in the synthesis of novel organoruthenium amidinates having a η^4-diene ligand (4-electron donor) shown as **5** and **6** in Fig. 1. These complexes are analogs of $(\eta^4\text{-diene})Ru(L')_2$ or $(\eta^4\text{-diene})Ru(L')(L)(X)$ (L = 2-electron donor ligand, L' = allyl or pseudo-allyl ligand, X = halogen atom). Although syntheses of several $(\eta^4\text{-diene})Ru(L')_2$ (L' = η^3-allyl [7], η^2-carboxylate [8], or η^2-dithiocarbamate [9]) are found in the literature, complete structure elucidation by crystallography and detailed NMR analyses have not been performed in many cases. The only example of $(\eta^4\text{-diene})Ru(L')(L)(X)$ reported was a dimeric complex having a bridging halogen ligand, $[(\eta^4\text{-COD})Ru(\eta^3\text{-allyl})X]_2$ (X = Cl or Br) [7a]. This prompts us to elaborate the preparation, spectroscopy, and crystallographic determination of novel organoruthenium amidinate complexes of types **5** and **6**, which are expected to contribute to better understanding of not only the chemistry of $(\eta^4\text{-diene})Ru(L')_2$ or $(\eta^4\text{-diene})Ru(L')(L)(X)$ but also that of organoruthenium amidinates. In this paper, we report the preparation and structure elucidation of $(\eta^4\text{-COD})Ru(\eta^2\text{-amidinate})_2$ (**5**) and $(\eta^4\text{-NBD})Ru(\eta^2\text{-amidinate})_2$ (**5'**) (COD = 1,5-cyclooctadiene, NBD = 2,5-norbornadiene); and syntheses of these novel organoruthenium amidinates by treatment of several dihalogenoruthenium(II) precursors with the corresponding lithium or silver amidinates. Interestingly, careful treatment of $(\eta^4\text{-NBD})Ru(pyridine)_2Cl_2$ with one equivalent of $Li\{^iPrNC(Me)=CN^iPr\}$ led to successful preparation of a monoamidinate complex, $(\eta^4\text{-NBD})Ru\{\eta^2\text{-}^iPrNC(Me)=CN^iPr\}(pyridine)Br$ (**6**). This complex is expected to be a good precursor for other

novel organoruthenium amidinates by replacement of the halide by other nucleophiles. As one example, synthesis of a 'mixed' amidinate complex **5c'** was achieved by treatment of **6** with $Ag_2\{\mu_2,\eta\text{-}PhNC(H)=NPh\}_2$.

2. Results and discussion

2.1. Syntheses of bisamidinate complexes, $(\eta^4\text{-diene})Ru(\eta^2\text{-amidinate})_2$, **5a**, **5b**, **5a'** and **5b'**

It is known that Ru complexes, $[(\eta^4\text{-COD})RuCl_2]_n$ (**7**) and $[(\eta^4\text{-NBD})RuCl_2]_n$ (**8**), where COD = 1,5-cyclooctadiene and NBD = 2,5-norbornadiene, are useful precursors for a variety of Ru(II)–diene complexes. Treatment of these compounds with two equivalents of amidinate anions was expected to give the corresponding $(\eta^4\text{-diene})Ru(\eta^2\text{-amidinate})_2$, **5**. However, complexes **7** and **8** have polymeric structures and are hardly soluble in common organic solvents; this sometimes causes a serious decrease of the reactivity. In this context, soluble monomeric Ru(II) complexes, $(\eta^4\text{-COD})Ru(MeCN)_2Cl_2$ (**9**) and $(\eta^4\text{-NBD})Ru(pyridine)_2Cl_2$ (**10**), were also examined as precursors for **5**. As the amidinate anion, a lithium amidinate, $Li\{^iPrNC(Me)=N^iPr\}$ (**11**) was used [2]. A silver salt, $Ag_2\{\mu_2,\eta\text{-}PhNC(H)=NPh\}_2$ (**12**) [10], having a unique dinuclear structure was expected to be an effective source for introduction of the amidinate moiety to ruthenium.

Syntheses of **5a**, **5b**, **5a'**, and **5b'** by combination of ruthenium precursors and amidinate reagents are summarized in Scheme 1 and Table 1. In a typical example, treatment of the soluble ruthenium precursor **9** with an equimolar amount of the silver salt **12** in CH_2Cl_2 at room temperature for 6 h resulted in the formation of $(\eta^4\text{-COD})Ru\{\eta^2\text{-}PhNC(H)=NPh\}_2$ (**5a**) as a yellow solid in 65% yield. When the polymeric precursor **7** was used as the starting material, treatment with the silver salt **12** gave only a trace amount of **5a**. Assignment of **5a** was performed by ^1H- and ^{13}C-NMR, IR, mass spectra, and elemental analysis, and supported by crystallography as described later. No reaction took place in the attempted synthesis of $(\eta^4\text{-COD})Ru\{\eta^2\text{-}^iPrNC(Me)=N^iPr\}_2$ (**5b**) by reaction of **9** with the lithium salt **11**; this is attributed to poor solubility of **9** in ether and THF, which are suitable solvents for the reaction with **11**. Interestingly, the polymeric precursor **7** reacted with **11** to give **5b** in ∼20% yield. NMR spectra of the reaction mixture revealed that a number of byproducts were formed. Since uncoordinated COD was also detected, it is likely that extensive decomposition of the reaction intermediates occurred by the liberation of COD ligand. The yield of **5b** was somewhat improved when the reaction was carried out in the presence of COD (20 equivalents to **7**) as shown in
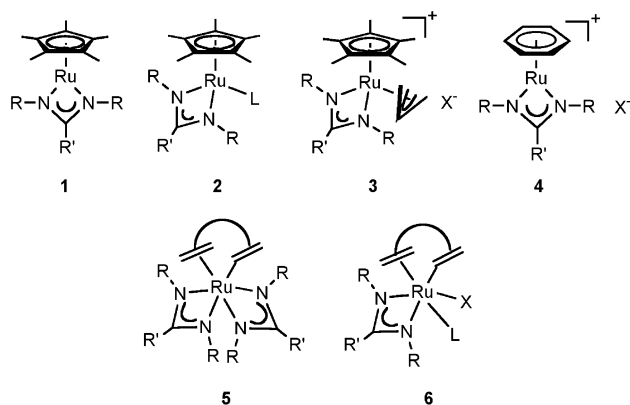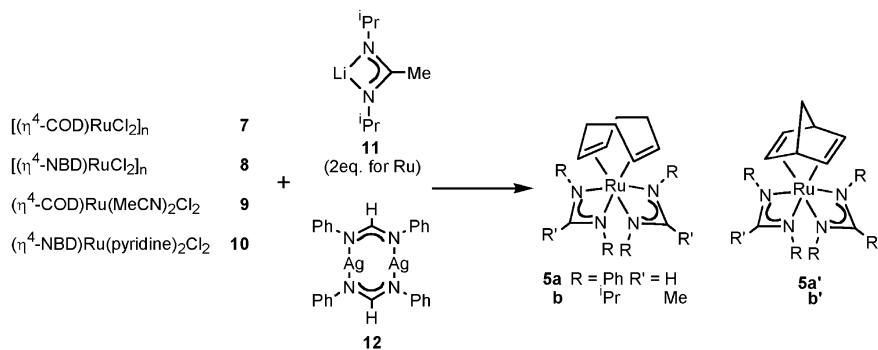

Fig. 1. Ruthenium amidinate complexes bearing η^5-C_5Me_5, η^6-arene, or η^4-diene ligands.

Scheme 1.

Table 1
Synthesis of $(\eta^4\text{-diene})\text{Ru}(\eta^2\text{-amidinate})_2$ (**5**)

Entry	Ru-precursor	Amidinate salt	Reaction conditions			Product	Yield (%)
			Solvent	Temperature	Time (h)		
1	**9**	**12**	CH$_2$Cl$_2$	Room temperature	6	**5a**	65
2	**9**	**11**	THF	Room temperature	12	–[a]	–
3	**7**	**12**	CH$_2$Cl$_2$	Room temperature	24	**5a**	Trace
4	**7**	**11**	THF	Room temperature	48	**5b**	21
5[b]	**7**	**11**	THF	Room temperature	24	**5b**	30
6[c]	**10**	**12**	CH$_2$Cl$_2$	60 °C	6	**5a′**	66
7	**10**	**11**	THF	Room temperature	24	**5b′**	71
8	**8**	**12**	CH$_2$Cl$_2$	Reflux	24	**5a′**	Trace
9	**8**	**11**	THF	Room temperature	12	**5b′**	20

[a] Trace amount of unknown complexes was obtained.
[b] 20 equivalents of COD were added.
[c] No reaction occurred at room temperature.

entry 5. In contrast, the reaction of **7** with Li{*t*BuNC(Ph)=N*t*Bu} gave many products, each structure of which could not be assigned by the NMR spectra. This result indicates that the reaction is sensitive to the steric bulkiness of the amidinate ligand, which is supported by the molecular structures of **5a** and **5b** described later. Similar results were obtained for the synthesis of the NBD analogs. Treatment of the soluble precursor **10** with the silver salt **12** in CH$_2$Cl$_2$ at 60 °C gave $(\eta^4\text{-NBD})\text{Ru}\{\eta^2\text{-PhNC(H)=NPh}\}_2$ (**5a′**) in 66% yield. Since **10** is soluble in THF, the lithium salt **11** also reacted with **10** and afforded $(\eta^4\text{-NBD})\text{Ru}\{\eta^2\text{-}$*i*$\text{PrNC(Me)=N}$*i*$\text{Pr}\}_2$ (**5b′**) in 71% yield. Although the polymeric precursor **8** hardly reacted with the silver salt **12**, it was converted to **5b′** by treatment with the lithium salt **11** ($\sim$ 20%). All of these results suggest that successful preparation of $(\eta^4\text{-diene})\text{Ru}(\eta^2\text{-amidinate})_2$ can be achieved by treatment of the soluble Ru(II) precursors, **9** and **10**, with the silver salt of amidinate, **12**. Easily available polymeric precursors, **7** and **8**, can also be used as the starting material; in this case, the lithium amidinate **11** is useful for the introduction of the amidinate moiety.

2.2. Characterization of $(\eta^4\text{-diene})\text{Ru}(\eta^2\text{-amidinate})_2$

The $(\eta^4\text{-diene})\text{Ru}(\eta^2\text{-amidinate})_2$, **5a**, **5b**, **5a′**, and **5b′**, are stable in air and moisture. No decomposition occurred when these complexes was heated in C$_6$D$_6$ at 80 °C for 2–3 days. In NMR spectroscopy, these complexes showed typical signals due to the coordinated carbon=carbon double bonds. For example, in the NMR spectra of **5a** [1]H resonances seen as a doublet of triplets ($J = 4.4$ and 8.8 Hz) at δ 3.34 and 4.48 ppm and ^{13}C signals observed at δ 82.5 and 88.9 ppm are assignable to the HC=CH moiety in the COD ligand. Compared with $(\eta^4\text{-COD})\text{Ru}(\eta^2\text{-carboxylate})_2$ complexes showing ^{13}C resonances due to the HC=HC moiety in the COD ligand at δ 84.6 and 89.2 ppm [8a], the ^{13}C signals of **5a** or **5b** appeared at higher field; this is attributed to the strong electron-donating ability of the amidinate ligand. The ^{13}C signals tended to appear at higher field than those of other $(\eta^4\text{-COD})\text{Ru}(\eta^2\text{-chelate})_2$ complexes; for example, ^{13}C signals of olefinic carbons of $(\eta^4\text{-COD})\text{Ru}(\eta^2\text{-quinolin-8-olate})_2$ [11c] or $(\eta^4\text{-COD})\text{Ru}\{\eta^4\text{-}N,N'\text{-ethylenebis(2-pyrrolyl)iminato}\}$ [11d] are observed at δ 92.9 and 93.0 ppm or δ 81.9–93.3 ppm in CDCl$_3$, respectively. Slightly higher field

shift of these carbon signals of **5b** than those of **5a** may suggest stronger electron-donating character of the η^2-^{i}PrNC(Me)=N^{i}Pr ligand than that of η^2-PhNC(H)=NPh ligand. As described above, two independent resonances due to the CH=CH moiety appeared in both ^{1}H- and ^{13}C-NMR. Similarly, peaks due to two phenyl groups in the η^2-PhNC(H)=NPh ligand in **5a** appeared independently. These results suggest the C_2 symmetric structure of **5a** in the solution state, which is in good accord with the crystal structure of **5a** described below. Similar spectral features were also seen in **5b**, **5a′**, and **5b′**.

The molecular structures of **5a**, **5b** and **5a′** determined by crystallography are in accord with the spectral features described above. The ORTEP drawings are shown in Fig. 2, and selected bond distances and angles are summarized in Table 2. All of the complexes have distorted octahedral structures, in which each coordi-
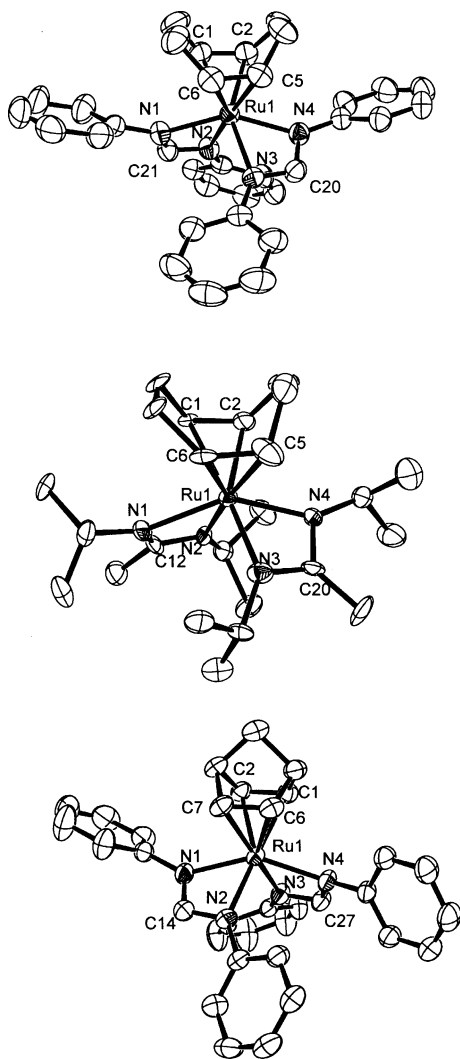

Fig. 2. ORTEP drawings of the complexes **5a** (top), **5b** (middle), and **5a′** (bottom) with thermal ellipsoids drawn at 50% probability level. All hydrogen atoms are omitted for clarity.

nated C=C bond in the diene ligand is located at the *trans* position of one nitrogen atom in each amidinate ligand. The ruthenium atom and the N–C–N moiety in the amidinate ligand are in a plane, and two $\overline{\text{Ru–N–C=N}}$ planes make an angle of 93–94°. There is a C_2 axis in the molecules; for example, in the case of **5a**, the C_2 axis contains the ruthenium atom, the middle point of C1 and C5 and that of N1 and N4. Two of the Ph or ^{i}Pr groups are close to the COD or NBD ligands. If the introduction of bulky substituents such as a ^{t}Bu moiety in place of the ^{i}Pr group is considered, significant steric hindrance between the amidinate ligand and the diene moiety is expected, which may prevent the reaction of ^{t}Bu-substituted amidinates as described above. The C=C bond distances of the COD ligand in **5a** and **5b** are 1.39–1.44 Å, which are significantly longer than those of (η^4-COD)Ru(η^2-chelate)$_2$ (e.g. (η^4-COD)Ru(η^2-maltolato)$_2$ [11b]; 1.34 and 1.46 Å, (η^4-COD)Ru(η^2-quinolin-8-olate)$_2$ [11c]; 1.37 and 1.39 Å). Average of C=C bond distances of the NBD ligand in **5a′** is 1.39 Å, which is almost the same as (η^4-NBD)Ru(η^2-S$_2$CNEt$_2$)$_2$ (1.39 Å) [9], but slightly longer than that of Δ-[(η^4-NBD)Ru(η^2-L-phenylalanine)$_2$] (1.38 Å) [11a]. The longer C=C distances are attributed to strong back donation from the ruthenium amidinate moiety.

2.3. Preparation of a monoamidinate complex, (η^4-NBD)Ru{η^2-^{i}PrNC(Me)=N^{i}Pr}(pyridine)Br (6)

As described above, (η^4-diene)Ru(η^2-amidinate)$_2$, **5a**, **5b**, **5a′** and **5b′** were prepared by replacement of two chlorine atoms of the Ru(II) precursors, **7**–**10**, by the amidinate ligands. Although the reactions should be stepwise, there was only a small rate difference between the first and second substitution reactions in many cases, and an intermediate having only one amidinate ligand was rarely obtained. One successful example accomplished to date is preparation of (η^4-NBD)Ru{η^2-^{i}PrNC(Me)=N^{i}Pr}(pyridine)Br (**6**), which was obtained by careful treatment of monomeric precursor **10** with the lithium salt **11** in THF at room temperature for 1 h as shown in Scheme 2. The initial product of this reaction was (η^4-NBD)Ru{η^2-^{i}PrNC(Me)=N^{i}Pr}(pyridine)Cl. Since the lithium salt **11** is synthesized in situ from ^{i}PrN=C=^{i}Pr with MeLi containing a substantial amount of LiBr, replacement of the chlorine atom by bromine atom took place smoothly to give **6** as a single product.

This monoamidinate complex **6** was isolated in 64% yield as an orange solid, which was less stable to air or moisture than the bisamidinate complexes. In fact, **6** gradually decomposed in solution even under an inert gas atmosphere. ^{1}H- and ^{13}C-NMR spectra of **6** indicated no symmetry of the molecule. These spectroscopic data are consistent with the molecular structure of **6**

Table 2
Selected bond lengths (Å) and bond angles (°) for **5a**, **5b** and **5a′**

	5a		5b		5a′
Bond lengths					
Ru1–N1	2.138(2)		2.197(11)		2.122(3)
Ru1–N2	2.163(2)		2.179(9)		2.149
Ru1–N3	2.156(2)		2.089(10)		2.151(3)
Ru1–N4	2.141(3)		2.092(11)		2.150(3)
Ru1–C1	2.182(3)		2.184(11)	Ru–C1	2.160(3)
Ru1–C2	2.172(3)		2.194(8)	Ru–C2	2.156(3)
Ru1–C5	2.181(3)		2.156(9)	Ru–C6	2.162(3)
Ru1–C6	2.169(3)		2.155(11)	Ru–C7	2.162(3)
C1–C2	1.404(4)		1.416(15)	C1–C2	1.387(5)
C5–C6	1.388(5)		1.440(16)	C6–C7	1.400(5)
Bond angles					
N1–Ru1–N4	147.93(10)		143.68(10)		147.11(11)
N2–Ru1–N3	92.48(9)		95.03(12)		94.05(11)
N1–Ru1–N2	61.33(9)		60.9(4)		61.37(10)
N3–Ru1–N4	60.9799)		61.7(4)		61.51(10)
N1–C21–N2	112.8(2)	N1–C12–N12	117.0(10)	N1–C14–N2	111.8(3)
N3–C34–N4	112.6(3)	N3–C20–N4	104.8(9)	N3–C27–N4	113.1(3)

determined by crystallography. The ORTEP drawing is illustrated in Fig. 3, and selected bond distances and angles are listed in the figure caption. Two C=C moieties, two nitrogen atoms in the amidinate ligand, a bromine atom, and a nitrogen atom in the pyridine ligand are arranged octahedrally with Ru–N and Ru–C distances of ca. 2.10 and 2.16 Å, respectively.

The monoamidinate complex **6** has a Ru–Br bond, which is replaceable by other nucleophiles; this suggests that **6** could be a unique starting complex for other organoruthenium amidinates. In fact, treatment of **6** with the lithium amidinate **11** gave **5b′** in 71% yield as shown in Scheme 2. This suggests that **6** is an intermediate of the reaction from **10** to **5b′**, and that the reaction from **6** to **5b′** is slower than the substitution reaction of **10** to **6**. A further interesting application of this stepwise substitution is the successful preparation of a mixed amidinate complex, $(\eta^4\text{-NBD})Ru\{\eta^2\text{-}^iPrNC(Me)=N^iPr\}\{\eta^2\text{-PhNC(H)=NPh}\}$ (**5c′**) by reaction of **6** with the silver amidinate **12** as shown in Scheme 3.

3. Conclusions

We have described preparation of three types of novel ruthenium amidinate complexes which have one η^4-diene ligand and either one or two amidinate ligands. These complexes are a rare example of well-characterized $(\eta^4\text{-diene})Ru(L')_2$ or $(\eta^4\text{-diene})Ru(L')(L)(X)$ (L = 2-electron donor ligand, L′ = allyl or pseudo-allyl ligand, X = halogen atom). This study contributes to a better understanding of the chemistry of $(\eta^4\text{-diene})Ru(\text{pseudo-allyl})_2$ complexes and that of organoruthenium amidinates. Furthermore, as shown
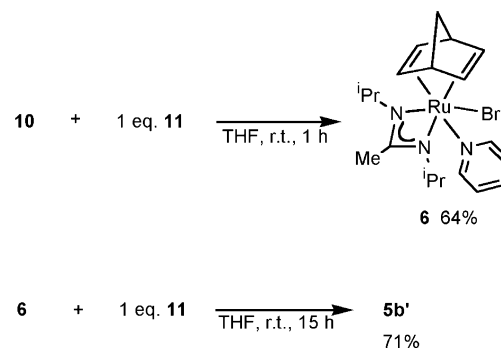
Scheme 2.
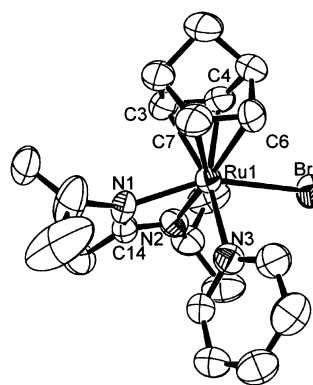
Fig. 3. Molecular structure of **6**. Anisotropic displacement parameters are drawn at 50% probability level. All hydrogen atoms are omitted for clarity. Representative bond distances (Å) and angles (°) are as follows: Ru1–N1 = 2.093(7), Ru1–N2 = 2.114(7), Ru1–N3 = 2.176(7), Ru–Br = 2.5803(12), Ru–C3 = 2.151(9), Ru–C4 = 2.172(10), Ru–C6 = 2.158(10), Ru–C7 = 2.170(10), C3–C4 = 1.400(15), C6–C7 = 1.383(16), N1–Ru1–N2 = 61.5(3), N1–C14–N2 = 109.2(7).
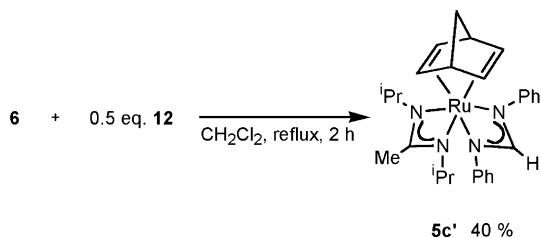
Scheme 3.

in the synthesis of mixed amidinate complex, **5c′**, the fact that $(\eta^4\text{-diene})Ru(\eta^2\text{-amidinate})(L)Br$ (**6**) is an interesting precursor for novel organoruthenium amidinates by nucleophilic substitution of the bromide suggests that this complex is an interesting starting point for further organoruthenium chemistry. We are currently concentrating on a search for new reactions of these novel amidinate complexes.

4. Experimental

4.1. General procedure

Manipulation of air- and moisture-sensitive organometallic compounds was carried out under a dry argon atmosphere using standard Schlenk tube techniques associated with a high-vacuum line. All solvents were distilled over appropriate drying reagents prior to use (THF, toluene, hexane; Ph_2CO/Na, CH_2Cl_2; CaH_2). $RuCl_3$ hydrate purchased from Furuya Metal Co. Ltd. or Nacalai Tesque Inc. was used as received. A lithium reagent, MeLi in Et_2O (containing LiBr) was purchased from Kanto Chemical Co. Inc. and titrated prior to use. Other reagents employed in this research were used without further purification. $(\eta^4\text{-COD})Ru(CH_3CN)_2Cl_2$ [12], $[(\eta^4\text{-COD})RuCl_2]_n$ [12], $(\eta^4\text{-NBD})Ru(pyridine)_2Cl_2$ [13], $[(\eta^4\text{-NBD})RuCl_2]_n$ [14], $Ag_2\{\mu_2,\eta\text{-PhNCHNPh}\}_2$ [10], and $Li\{^iPrNC(Me)=N^iPr\}$ [6a] were prepared as described in the literature. Column chromatography and thin layer chromatography were carried out using Al_2O_3 (Merck aluminum oxide 90 standardized, and Merck TLC aluminum sheets aluminum oxide 150 F_{254} neutral (type T), respectively).

^1H and ^{13}C spectra were recorded on JEOL Lambda 600 and Lambda 400 spectrometers at ambient temperature. ^1H- and ^{13}C-NMR chemical shifts (δ values) are given in ppm relative to solvent resonances. All coupling constants were reported in Hertz. IR spectra were recorded on a JASCO FT/IR-550 spectrometer. Melting points were measured on a Yanaco micro melting point apparatus. EIMS and HRMS spectra were recorded on a JEOL Mstation JMS-70 apparatus. Elemental analyses were performed at the Elemental Analysis Center, Faculty of Science, Kyushu University.

4.2. Preparation of $(\eta^4\text{-COD})Ru\{\eta^2\text{-PhNC(H)=NPh}\}_2$ (**5a**)

In a Schlenk tube, $(\eta^4\text{-COD})Ru(CH_3CN)_2Cl_2$ (380 mg, 1.05 mmol) and $Ag_2\{\mu_2,\eta\text{-PhNC(H)=NPh}\}_2$ (636 mg, 1.05 mmol) were dissolved in CH_2Cl_2 (20 ml) at room temperature (r.t.), and the reaction mixture was stirred for 6 h. After the precipitated silver salts were removed by filtration through celite, the resulting solution was concentrated in the presence of celite (500 mg). The crude products adsorbed to celite were placed on the head of an alumina column (ϕ 17 × 80 mm), and eluted with a mixture of hexane and Et_2O (10:1). The desired product (**5a**) was obtained as an orange solid (409 mg, 0.68 mmol, 65% yield). M.p.: 138 °C (dec.). TLC: $R_f = 0.40$ (hexane:Et_2O = 10:1, Al_2O_3). ^1H-NMR (400 MHz, $CDCl_3$): δ 1.77–1.87 (m, 4H, CH_2 of COD), 1.93–2.02 (m, 4H, CH_2 of COD), 3.34 (dt, $J = 4.4, 8.8$ Hz, 2H, olefinic protons of COD), 4.48 (dt, $J = 4.4, 8.8$ Hz, 2H, olefinic protons of COD), 6.92–6.97, 6.99–7.04, 7.09–7.18, 7.25–7.34 (m each, 20H in total, integral ratio = 2:4:10:4, C_6H_5 of amidinates), 8.34 (s, 2H, CH of amidinates). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ 29.56, 29.58 (CH_2 of COD), 82.57, 89.23 (olefinic carbons of COD), 120.75, 122.36, 122.58, 123.10, 128.79, 129.16, 147.92, 149.80 (C_6H_5 of amidinates), 157.50 (NCN of amidinates). EIMS: $[M^+] = 600$. Anal. Calc. for $C_{34}H_{34}N_4Ru$: C, 68.09; H, 5.71; N, 9.34. Found: C, 68.12; H, 5.74; N, 9.33%.

4.3. Preparation of $(\eta^4\text{-COD})Ru\{\eta^2\text{-}^iPrNC(Me)=N^iPr\}_2$ (**5b**)

In a Schlenk tube, $[(\eta^4\text{-COD})RuCl_2]_n$ (170 mg, 0.61 mmol) and $Li\{^iPrNC(Me)=N^iPr\}$ (179 mg, 1.21 mmol) were dissolved in THF (10 ml) at r.t., and the reaction mixture was stirred for 48 h. After the solvent was removed in vacuo, the residue was dissolved in hexane (30 ml). The insoluble materials were filtered off through celite, and the resulting solution was concentrated to two-thirds of its original volume. Brown crystals were grown by cooling the solution at − 30 °C (62 mg, 0.13 mmol, 21% yield). M.p.: 151 °C (dec.). ^1H-NMR (400 MHz, $CDCl_3$): δ 0.99 (d, $J = 6.6$ Hz, 6H, CH(CH_3)$_2$ of amidinates), 1.04 (d, $J = 6.6$ Hz, 6H, CH(CH_3)$_2$ of amidinates), 1.40 (d, $J = 6.8$ Hz, 6H, CH(CH_3)$_2$ of amidinates), 1.46 (d, $J = 7.1$ Hz, 6H, CH(CH_3)$_2$ of amidinates), 1.85 (s, 6H; CCH_3 of amidinates), 1.80–1.91 (m, 2H, CH_2 of COD), 2.15–2.29 (m, 4H, CH_2 of COD), 2.32–2.46 (m, 2H, CH_2 of COD), 2.63–2.74 (m, 2H, olefinic protons of COD), 3.59 (sep, $J = 6.6$ Hz, 2H, CH(CH$_3$)$_2$ of amidinates), 3.51–3.65 (m, 2H, olefinic protons of COD), 3.78 (sep, $J = 6.8$ Hz, 2H, CH(CH$_3$)$_2$ of amidinates). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ 17.44 (CCH_3 of amidinates), 24.51, 24.63, 24.77, 25.23 (CH(CH_3)$_2$ of amidinates), 29.84,

32.85 (CH$_2$ of COD), 47.80, 49.26 (CH(CH$_3$)$_2$ of amidinates), 81.18, 82.88 (olefinic carbons of COD), 166.24 (NCN of amidinates). EIMS: [M$^+$] = 492. Anal. Calc. for C$_{24}$H$_{46}$N$_4$Ru: C, 58.62; H, 9.43; N, 11.39. Found: C, 58.67; H, 9.36; N, 11.21%.

4.4. Preparation of (η^4-NBD)Ru{η^2-PhNC(H)=NPh}$_2$ (5a′)

In a Schlenk tube, a mixture of (η^4-NBD)Ru(pyridine)$_2$Cl$_2$ (101 mg, 0.24 mmol) and Ag$_2${μ_2,η-PhNC(H)=NPh}$_2$ (140 mg, 0.231 mmol) dissolved in CH$_2$Cl$_2$ (10 ml) was heated under reflux for 6 h. After removal of the silver salts formed by filtration through celite, the solution was concentrated. Chromatographic purification (Al$_2$O$_3$, ϕ 17 × 40 mm, eluents; hexane:Et$_2$O = 10:1) of the residue adsorbed to celite (200 mg) afforded 5a′ as a yellow solid (91 mg, 0.16 mmol, 66% yield). Recrystallization from CH$_2$Cl$_2$–hexane gave a red crystal of 5a′. M.p.: 181 °C (dec.). TLC: R_f = 0.30 (hexane:Et$_2$O = 10:1, Al$_2$O$_3$). ^{1}H-NMR (400 MHz, CDCl$_3$): δ 1.23 (t, J = 1.3 Hz, 2H, CH$_2$ of NBD), 3.36–3.41 (m, 2H, CH of NBD), 3.69–3.75 (m, 2H, olefinic protons of NBD), 4.43–4.48 (m, 2H, olefinic protons of NBD), 6.89 (tt, J = 1.0, 7.5 Hz, 2H, C$_6$H$_5$ of amidinates), 6.97 (dd, J = 7.5, 8.3 Hz, 4H, C$_6$H$_5$ of amidinates), 7.09 (dd, J = 1.0, 8.3 Hz, 4H, C$_6$H$_5$ of amidinates), 7.18 (tt, J = 7.5, 8.4 Hz, 2H, C$_6$H$_5$ of amidinates), 7.26 (dd, J = 7.5, 8.4 Hz, 4H, C$_6$H$_5$ of amidinates), 7.38 (dd, J = 1.0, 8.5 Hz, 4H, C$_6$H$_5$ of amidinates), 8.41 (s, 2H, CH of amidinates). ^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$): δ 49.09 (CH of NBD), 56.49 (CH$_2$ of NBD) 64.28, 65.18 (olefinic carbons of NBD) 118.22, 120.96, 121.34, 122.0, 127.73, 128.23, 146.35, 149.05 (C$_6$H$_5$ of amidinates), 154.46 (NCN of amidinates). EIMS: [M$^+$] = 584. Anal. Calc. for C$_{33}$H$_{30}$N$_4$Ru: C, 67.91; H, 5.18; N, 9.60. Found: C, 68.03; H, 5.22; N, 9.57%.

4.5. Preparation of (η^4-NBD)Ru{η^2-^{i}PrNC(Me)=N^{i}Pr}$_2$ (5b′)

In a Schlenk tube, (η^4-NBD)Ru(pyridine)$_2$Cl$_2$ (180 mg, 0.43 mmol) was treated with Li{^{i}PrNC(Me)=N^{i}Pr} (201 mg, 0.86 mmol) in THF (10 ml) at r.t. for 24 h. The solvent was removed in vacuo and the residue was adsorbed to celite (350 mg). This adsorbed material was moved to the head of an alumina column (ϕ 17 × 40 mm) and eluted with a mixture of hexane and Et$_2$O (10:1). The desired product (145 mg, 0.30 mmol) was obtained in 71% yield as a yellow solid. M.p.: 95 °C (dec.). TLC: R_f = 0.35 (hexane:Et$_2$O = 10:1 Al$_2$O$_3$). ^{1}H-NMR (400 MHz, CDCl$_3$): δ 0.73 (d, J = 6.5 Hz, 6H, CH(CH$_3$)$_2$ of amidinates), 0.99 (d, J = 6.5 Hz, 6H, CH(CH$_3$)$_2$ of amidinates), 1.23 (t, J = 1.6 Hz, 2H, CH$_2$ of NBD), 1.48 (d, J = 6.8 Hz, 6H, CH(CH$_3$)$_2$ of amidi-

nates), 1.52 (d, J = 6.8 Hz, 6H, CH(CH$_3$)$_2$ of amidinates), 1.82 (s, 6H, CCH$_3$ of amidinates), 3.10–3.17 (m, 2H, olefinic protons of NBD), 3.51 (sep, J = 6.5 Hz, 2H, CH(CH$_3$)$_2$ of amidinates), 3.52–3.58 (m, 2H, CH of NBD), 3.75–3.82 (m, 2H, olefinic protons of NBD), 3.93 (sep, J = 6.8 Hz, 2H, CH(CH$_3$)$_2$ of amidinates). ^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$): δ 15.33 (CCH$_3$ of amidinates), 23.80, 24.48, 25.10, 25.57 (CH(CH$_3$)$_2$ of amidinates), 47.70, 50.96 (CH(CH$_3$)$_2$ of amidinates), 50.37 (CH of NBD), 56.41 (CH$_2$ of NBD), 60.22, 60.32 (olefinic carbons of NBD), 164.33 (NCN of amidinates). EIMS: [M$^+$] = 476. HRMS: Anal. Calc. for C$_{23}$H$_{42}$N$_4$Ru: 476.2453. Found: 476.2456.

The reaction for 6 to 5b′: In a Schlenk tube, 6 (140 mg, 0.28 mmol) was treated with Li{^{i}PrNC(Me)=N^{i}Pr} (141 mg, 0.60 mmol) in THF (10 ml) at r.t. for 15 h. The solvent was removed in vacuo and the residue was adsorbed to celite (150 mg). This adsorbed material was moved to the head of an alumina column (ϕ 17 × 40 mm) and eluted with a mixture of hexane and Et$_2$O (10:1). The desired product (94 mg, 0.20 mmol) was obtained in 71% yield as a yellow solid.

4.6. Preparation of (η^4-NBD)Ru{η^2-^{i}PrNC(Me)=N^{i}Pr}(pyridine)Br (6)

In a Schlenk tube, (η^4-NBD)Ru(pyridine)$_2$Cl$_2$ (213 mg, 0.50 mmol) was treated with Li{^{i}PrNC(Me)=N^{i}Pr} (118 mg, 0.50 mmol) in THF (10 ml) at r.t. for 1 h. After the removal of the solvent, the residue was adsorbed to celite (300 mg). The adsorbed material was moved to the head of an alumina column (ϕ 17 × 40 mm) and eluted with a mixture of hexane and Et$_2$O (1:2). An orange band available was concentrated in vacuo to give 6 in 64% yield (158 mg, 0.32 mmol). Brown crystals were obtained by recrystallization of 6 from a mixture of toluene and hexane at −30 °C. M.p.: 85 °C (dec.). TLC: R_f = 0.38 (hexane:Et$_2$O = 1:2, Al$_2$O$_3$). ^{1}H-NMR (600 MHz, CDCl$_3$): δ 0.92 (d, J = 6.8 Hz, 3H, CH(CH$_3$)$_2$ of amidinate), 0.96 (d, J = 6.8 Hz, 3H, CH(CH$_3$)$_2$ of amidinate), 1.02 (d, J = 6.8 Hz, 3H, CH(CH$_3$)$_2$ of amidinate), 1.32 (d, J = 6.8 Hz, 3H, CH(CH$_3$)$_2$ of amidinate), 1.43 (dt, J = 1.6, 8.2 Hz, 1H, a proton due to the CH$_2$ group of NBD), 1.46 (dt, J = 1.6, 8.2 Hz, 1H, a proton due to the CH$_2$ group of NBD), 1.90 (s, 3H, CCH$_3$ of amidinate), 3.54 (sep, J = 6.8 Hz, 1H, CH(CH$_3$)$_2$), 3.57–3.66 (m, 2H, CH(CH$_3$)$_2$ of amidinate and an olefinic proton of NBD), 3.74 (t, J = 3.9 Hz, 1H, an olefinic proton of NBD), 3.78–3.83 (m, 1H, CH of NBD), 3.87–3.91 (m, 1H, CH of NBD), 4.08 (t, J = 3.9 Hz, 1H, an olefinic proton of NBD), 4.78 (t, J = 3.9 Hz, 1H, an olefinic proton of NBD), 7.22 (ddd, J = 1.6, 6.6, 7.5 Hz, 2H, C$_5$H$_5$N), 7.65 (tt, J = 1.6, 7.5 Hz, 1H, C$_5$H$_5$N), 8.21 (dd, J = 1.6, 6.6 Hz, 2H, C$_5$H$_5$N). ^{13}C{^{1}H}-NMR (150 MHz, CDCl$_3$): δ 15.47 (CCH$_3$ of amidinate), 24.20,

Table 3
Crystal data and structure refinement parameters for **5a**, **5b**, **5a′**, and **6**

	5a	5b	5a′	6
Empirical formula	$C_{34}H_{34}N_4Ru$	$C_{24}H_{46}N_4Ru$	$C_{33}H_{30}N_4Ru$	$C_{20}H_{30}BrN_3Ru$
Formula weight	599.74	491.72	583.68	493.45
Temperature (K)	293(2)	273(2)	293(2)	293(2)
Crystal habits, color	Prismatic, brown	Prismatic, yellow	Prismatic, brown	Prismatic, brown
Space group	$P2_1/n$	Cc	$P\bar{1}$	$P2_12_12_1$
Unit cell dimensions				
a (Å)	1.6209(11)	12.426(3)	10.6353(4)	106353(4)
b (Å)	14.7695(13)	15.357(19)	12.5532(9)	9.5779(12)
c (Å)	16.8303(11)	12.823(3)	10.4641(5)	22.936(3)
α (°)			96.1670(10)	
β (°)	101.720(4)	93.177(19)	99.770(2)	
γ (°)			79.361(2)	
V (Å^3)	2828.4(4)	2443(9)	1348.92(13)	2076.7(5)
Z	4	4	2	4
D_{calc} (g cm^{-3})	1.404	1.326	1.437	1.578
Absorption coefficient (mm^{-1})	0.584	0.658	0.610	2.686
$F(000)$	1232	1032	600	1000
Crystal size (mm)	$0.20 \times 0.20 \times 0.50$	$0.15 \times 0.20 \times 0.30$	$0.20 \times 0.30 \times 0.30$	$0.20 \times 0.30 \times 0.30$
θ range for data collection (°)	2.37–27.48	2.59–27.50	1.66–27.48	1.78–27.48
Index ranges	$0 \leq h \leq 15$, $0 \leq k \leq 19$, $-21 \leq l \leq 21$	$0 \leq h \leq 16$, $0 \leq k \leq 19$, $-16 \leq l \leq 16$	$0 \leq h \leq 13$, $-15 \leq k \leq 16$, $-13 \leq l \leq 13$	$0 \leq h \leq 12$, $0 \leq k \leq 12$, $0 \leq l \leq 29$
Reflection collected	6265	2929	6129	2681
Reflections observed ($>2\sigma$)	4866	2706	5291	2284
Independent reflections	6265 [$R_{int} = 0.0000$]	2928 [$R_{int} = 0.8602$]	6129 [$R_{int} = 0.0000$]	2681 [$R_{int} = 0.0000$]
Data/restraints/parameters	6265/0/352	2928/2/262	6129/0/343	2681/0/226
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0507$, $wR_2 = 0.1349$	$R_1 = 0.0224$, $wR_2 = 0.0626$	$R_1 = 0.0385$, $wR_2 = 0.1120$	$R_1 = 0.0552$, $wR_2 = 0.1547$
R indices (all data)	$R_1 = 0.0630$, $wR_2 = 0.1473$	$R_1 = 0.0272$, $wR_2 = 0.0646$	$R_1 = 0.0506$, $wR_2 = 0.1264$	$R_1 = 0.0650$, $wR_2 = 0.1642$
Goodness-of-fit on F^2	1.048	1.105	1.012	1.212
Largest difference peak and hole (e Å^{-3})	0.542 and -1.703	0.661 and -1.480	0.488 and -1.145	0.743 and -1.049

24.69, 24.70, 25.3 (CH(CH$_3$)$_2$ of amidinate), 49.86 (CH of NBD), 50.17, 50.36 (CH(CH$_3$)$_2$ of amidinate), 51.80 (CH of NBD), 58.27 (CH$_2$ of NBD), 60.66, 64.59, 66.98, 68.47 (olefinic carbons of NBD), 124.03, 136.59, 150.86 (C$_5$H$_5$N) 167.05 (NCN of amidinate). EIMS: [M$^+$] = 493. Anal. Calc. for C$_{20}$H$_{30}$N$_3$BrRu: C, 48.68; H, 6.13; N, 8.52. Found: C, 48.82; H, 5.81; N, 8.43%.

4.7. Preparation of (η^4-NBD)Ru{η^2-PhNC(H)=NPh}-{η^2-N^{i}PrC(Me)=N^{i}Pr} (5c′)

In a Schlenk tube, a mixture of **6** (75 mg, 0.15 mmol) and Ag$_2${μ$_2$,η-PhNC(H)=NPh}$_2$ (46 mg, 0.075 mmol) was dissolved in CH$_2$Cl$_2$ (10 ml) at r.t., and the reaction mixture was heated under reflux for 2 h. After removal of the formed silver salts by filtration through celite, the residue was adsorbed to celite (170 mg) and the adsorbed material was moved to the head of an alumina column (φ 17 × 40 mm). By eluting with a mixture of hexane and Et$_2$O (10:1), a yellow band was available, the concentration of which gave **5c′** as a yellow solid (32 mg, 0.06 mmol, 40% yield). M.p.: 145 °C (dec.). TLC: $R_f = 0.30$ (hexane:Et$_2$O = 10:1, Al$_2$O$_3$). ^{1}H-NMR (400 MHz, CDCl$_3$): δ 0.84 (d, $J = 6.4$ Hz, 3H, CH(CH$_3$)$_2$ of amidinate), 0.96 (d, $J = 6.4$ Hz, 3H, CH(CH$_3$)$_2$ of amidinate), 1.22 (dt, $J = 1.5$, 8.2 Hz, 1H, a proton due to the CH$_2$ of NBD), 1.31 (dt, $J = 1.5$, 8.2 Hz, 1H, a proton due to the CH$_2$ of NBD), 1.40 (d, $J = 6.8$ Hz, 3H, CH(CH$_3$)$_2$ of amidinate), 1.44 (d, $J = 6.8$ Hz, 3H, CH(CH$_3$)$_2$ of amidinate), 1.84 (s, 3H, CCH$_3$ of amidinate), 3.27–3.31 (m, 1H, CH of NBD), 3.33 (t, $J = 3.9$ Hz, 1H, an olefinic proton of NBD), 3.53 (t, $J = 3.9$ Hz, 1H, an olefinic proton of NBD), 3.53 (sep, $J = 6.4$ Hz, 1H, CH(CH$_3$)$_2$ of amidinate), 3.88–3.93 (m, 1H, CH of NBD), 4.02 (sep, $J = 6.8$ Hz, 1H, CH(CH$_3$)$_2$ of amidinate), 4.18 (t, $J = 3.9$ Hz, 1H, an olefinic proton of NBD), 4.20 (t, $J = 3.9$ Hz, 1H, an olefinic proton of NBD), 6.90–6.99, 7.04–7.11, 7.15–7.22, 7.30–7.40 (m each, 10H in total, integral ratio = 3:1:2:4; C$_6$H$_5$ of amidinate), 8.29 (s, 1H, CH of amidinate). ^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$): δ 14.69 (CCH$_3$ of amidinate), 24.76, 24.81, 24.82, 25.72 (CH(CH$_3$)$_2$ of amidinate), 48.06 (CH(CH$_3$)$_2$ of amidinate), 50.31 (CH of NBD), 50.74 (CH(CH$_3$)$_2$ of amidinate), 51.15 (CH of NBD), 57.14 (CH$_2$ of NBD), 59.03, 61.87, 63.80, 68.42 (olefinic carbons of NBD), 120.69,

121.28, 121.60, 121.78, 128.39, 129.03, 148.71, 151.27 (C_6H_5 of amidinate), 154.72 (NC(H)N of amidinate), 166.84 (NC(CH$_3$)N of amidinate). EIMS: [M^+] = 530. HRMS: Anal. Calc. for $C_{28}H_{36}N_4Ru$: 530.1983. Found: 530.1988.

4.8. X-ray determination of 5a, 5b, 5a' and 6

Crystallographic details are listed in Table 3. Single crystals for X-ray diffraction were grown from a hot CH_3CN solution at r.t. for **5a**, from a solution of toluene–n-hexane at -30 °C for **5b**, from a concentrated CH_2Cl_2 solution at r.t. for **5a'**, and from a solution of toluene–n-hexane at r.t. for **6**. Diffraction data for **5a**, **5a'**, and **6** were collected on a Rigaku R-AXIS RAPID IP diffractometer (Mo–K$_\alpha$, $\lambda =$ 0.71069 Å) and then processed with TEXSAN [15]; for **5b** they were collected on a Rigaku AFC-7R four-circle diffractometer (Mo–K$_\alpha$, $\lambda = 0.71069$ Å) using ω–2θ scan technique. Structure solutions were performed by direct methods (**5b**, **5a'** and **6**) with the program SIR-92 [16] and the Patterson method (**5a**) with the program DIRDIF-94-PATTY [17]. Refinements were carried out by full-matrix least-squares on F^2 with all non-hydrogen atoms refined anisotropically using the program SHELXL-97-2 PC version [18]. The positions of all hydrogen atoms were calculated assuming idealized geometries.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 164059, 164057, 164058 and 164060 for compounds **5a**, **5b**, **5a'** and **6**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: $+$44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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