

# Preparation and Structural Elucidation of Unusually Thermally Stable Novel Alkylruthenium Complexes Bearing Amidinate Ligands, ( $\eta^6$ - C<sub>6</sub>H<sub>6</sub>)Ru( $\eta$ -amidinate)R (R=Me, Et, Bn)

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# Preparation and Structural Elucidation of Unusually Thermally Stable Novel Alkylruthenium Complexes Bearing Amidinate Ligands, $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\eta\text{-amidinate})\text{R}$ ( $\text{R} = \text{Me}, \text{Et}, \text{Bn}$ )

Taizo HAYASHIDA\* and Hideo NAGASHIMA

The first organoruthenium amidinates bearing a Ru-C  $\sigma$  bond were prepared, and their structures were elucidated by spectroscopy and crystallography. A halogenoruthenium amidinate precursor,  $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\eta\text{-}^t\text{BuNCPhN}^t\text{Bu})\text{Cl}]$ , was treated with Grignard reagents to form thermally and air stable alkyl ruthenium complexes,  $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\eta\text{-}^t\text{BuNCPhN}^t\text{Bu})\text{R}]$  ( $\text{R} = \text{Me}$  (**3a**), Et (**3b**), Bn (**3c**)).  $C_s$ -symmetric ‘piano stool’ structures of these complexes were suggested from NMR spectroscopic data. These were supported by crystallographic studies of **3b** and **3c**.

## Introduction

Organotransition metal compounds with metal-carbon  $\sigma$ -bonds, are involved in various homogeneous catalytic processes.<sup>1a)</sup> A number of metal alkyl complexes have been investigated in recent years, although transition metal alkyls remained very rare until the principles governing their stability were established in the 1960s and 1970s.<sup>1b)</sup> Homo- or heteroleptic transition metal alkyls, which have no auxiliary ligands to stabilize the complexes, are generally sensitive to air and moisture. Since isolable metal alkyls are limited to complexes bearing appropriate ligands such as phosphines, CO, and cyclopentadienyl,<sup>1b-d)</sup> a careful selection of the ligand is important for a successful synthesis of metal alkyl complexes. The first example of a stable ruthenium alkyl complex was  $[\text{Ru}(\text{dmpe})_2(\text{Me})(\text{Cl})]$  and was reported by Chatt and Hayter in 1959,<sup>2a)</sup> and since then many complexes have been studied in view of their preparation, their structural elucidation, as well as in view of their novel reactivity and physical properties.<sup>2)</sup> Experiments to isolate ethylruthenium complexes have been carried out,<sup>2b,2c,3)</sup> however, they are generally thermally unstable, and often decompose through facile  $\beta$ -hydrogen atom elimination to generate the corresponding hydride complexes and ethylene.<sup>3a,b,f,i)</sup> Because of their importance in the catalytic hydrogenation of ethylene, the mechanisms of the  $\beta$ -H elimination in alkylruthenium complexes and its reverse reaction, *i.e.* the insertion of ethylene in a Ru-H bond, have been actively investigated, and it is known that facile  $\beta$ -H elimination takes place in ethylruthenium complexes bearing phosphine ligands.<sup>3i)</sup> Thus,

ethylruthenium bearing phosphine ligands, such as  $[\text{CpRu}(\text{PPh}_3)_2\text{Et}]$ <sup>3b)</sup> and  $[\text{Ru}(\text{Cy}_3\text{P})_2(\text{Et})(\text{Cl})(\text{CO})]$ ,<sup>3i)</sup> are generally thermally unstable to give the corresponding hydride complexes.<sup>3)</sup> The only exception is  $[\text{Ru}(\text{dppe})(\text{Cl})(\text{Et})]$ ,<sup>2c)</sup> which is stable over 300 °C in its solid state. In contrast, a carbonyl complex,  $\text{CpRu}(\text{CO})_2\text{Et}$ , and a complex bearing a nitrogen ligand,  $[\text{Ru}(\text{Bu}_2\text{-bipy})_2(\text{Et})_2]$ , are rare examples of isolable ethylruthenium compounds not bearing phosphine ligands.<sup>2b,3c)</sup> They are reportedly “thermally stable”; however, no detailed studies on the thermal stability of these complexes have been reported.

In recent years, we have investigated the preparation and characterization of a series of organoruthenium complexes bearing amidinate ligands.<sup>4,5)</sup> These coordinatively unsaturated half-sandwich Ru(II) complexes with one amidinate unit,  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\eta\text{-amidinate})]$  (**1**)<sup>5a)</sup> and  $[(\eta^6\text{-arene})\text{Ru}(\eta\text{-amidinate})]^+$  (**2**),<sup>5c)</sup> where the amidinate unit acts as a 4-electron  $\sigma$ -donor ligand forming two strong Ru-N bonds, were prepared and characterized. They are quite reactive to air, moisture, and various organic molecules. In particular, facile reactions with two electron donor ligands and with organic halides have led to unique reaction chemistry of these organoruthenium amidinates, which included the discovery of a catalytic transformation of allylic substrates.<sup>5b)</sup> In an extension of these studies, we were interested in the synthesis and the thermal stability of alkylruthenium amidinates, in particular, of ethylruthenium amidinate complexes. In this paper, we report the successful preparation and structural elucidation of novel alkylruthenium amidinates,  $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\eta\text{-amidinate})\text{R}]$  ( $\text{R} = \text{Me}, \text{Et}, \text{Bn}$ ) (**3**),

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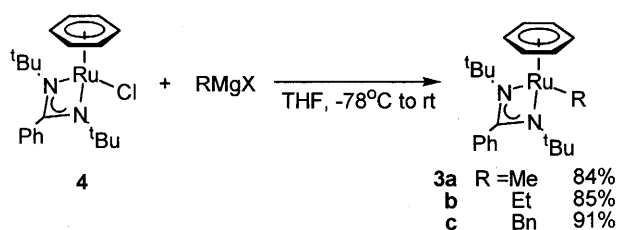
Dedicated to Professor Yukio Nishimura on the occasion of his retirement.

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which are obtainable by the reaction of  $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\eta\text{-amidinate})\text{Cl}]$  (**4**) with Grignard reagents. To our surprise, even the ethyl derivative could be isolated as a thermally stable and air- and moisture-insensitive solid, though facile  $\beta$ -hydrogen atom elimination had been expected to occur.

### Results and Discussion

As shown in Scheme 1, treatment of a halogenoruthenium amidinate complex,  $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\eta\text{-}^t\text{BuNCPhN}^t\text{Bu})\text{Cl}]$  (**4**) with a Grignard reagent,  $\text{RMgX}$  ( $\text{R} = \text{Me}$ ,  $\text{Et}$ , or  $\text{Bn}$ ), in THF at  $-78^\circ\text{C}$  with warming to room temperature gave the corresponding alkylruthenium amidinates,  $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\eta\text{-}^t\text{BuNCPhN}^t\text{Bu})\text{R}]$  (**3a–c**), as yellow solids in good yields. Reaction of **4** with one equivalent of  $\text{MeMgBr}$  or  $\text{PhCH}_2\text{MgBr}$  was complete within 1 h. In contrast, the ethylation of **4** required two equivalents of  $\text{EtMgBr}$  and a prolonged reaction time (about 1 day). The reason why ethylation needs larger amounts of the Grignard reagent and prolonged reaction time is not clear at present. Alkylruthenium amidinates **3** were also obtained by the reaction of **4** with alkyl lithium reagents in moderate yields, but here unknown by-products were also formed.



Scheme 1

The characterization of **3a–3c** was carried out by spectroscopic methods and elemental analyses. These were supported by X-ray single crystal structural determination of **3b** and **3c** as described below. In the

$^1\text{H}$  NMR spectra of **3a–3c** in  $\text{C}_6\text{D}_6$ , two magnetically equivalent  $^t\text{Bu}$  groups ( $\delta$  1.0 ~ 1.5 ppm) of the amidinate ligand could be observed.  $^1\text{H}$  resonance due to the benzene ring was seen as a sharp singlet at around  $\delta$  5.0 ppm. This suggests that these complexes have  $C_s$  symmetric structures, similar to the halogenoruthenium precursor **4**. The proton signal of the  $\alpha$ -position of the alkyl group is observed at  $\delta$  1.5 ppm as a singlet for **3a**, at  $\delta$  2.05–2.11 ppm as multiplets for **3b**, and at  $\delta$  3.15 ppm as a singlet for **3c**. The  $^{13}\text{C}$  resonance of the  $\alpha$ -carbon of the alkyl group in **3a**, **3b**, or **3c** is seen at  $\delta$  3.4, 21.4, and 30.0 ppm ( $\text{C}_6\text{D}_6$ ), respectively. Compared with other half metallocene methylruthenium complexes, the chemical shift of the methyl protons of **3a** is similar to that of  $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{PPh}_3)\text{ClMe}]$  ( $\delta$  1.24 ppm in  $\text{CDCl}_3$ ),<sup>2d</sup> but is at lower field than in  $[\text{CpRu}(\text{PPh}_3)(\text{CO})\text{Me}]$  ( $\delta$  0.07 ppm in  $\text{CDCl}_3$ ),<sup>2f</sup> in  $[\text{CpRu}(\text{CO})_2\text{Me}]$  ( $\delta$  0.34 ppm in  $\text{CDCl}_3$ ),<sup>2f</sup> or in  $[\text{CpRu}(\text{PPh}_3)_2\text{Me}]$  ( $\delta$  0.40 ppm in  $\text{CDCl}_3$ ).<sup>2f</sup> This shift towards lower field of the methyl group in the arene complexes might be attributed to a lower electron donor capacity of the neutral arene ligand as compared to the anionic Cp ligand, which should lead to a lower electron density around the ruthenium center.

The molecular structures of **3b** and **3c** as determined by crystallography are in accord with the spectral features described above. The ORTEP drawings are shown in Figure 1, and selected bond distances and angles are summarized in Table 1. The molecular structures of **3b** and **3c** reveal that these complexes have three-legged ‘piano stool’ structures, and that there is little difference in bond lengths or angles in **3b** and **3c**. The bond distances between the ruthenium atom and the  $\alpha$ -carbon of the alkyl group in **3b** and **3c** is 2.156(5) Å and 2.152(2) Å, respectively. The Ru–C bond length of **3b** is within the range of that of known ethyl ruthenium complexes (2.10 ~ 2.23 Å).<sup>3</sup> In **3b** and **3c**, the Ru–N(amidinate) bond distances are 2.11 ~ 2.14 Å, whereas the distances between the ruthenium

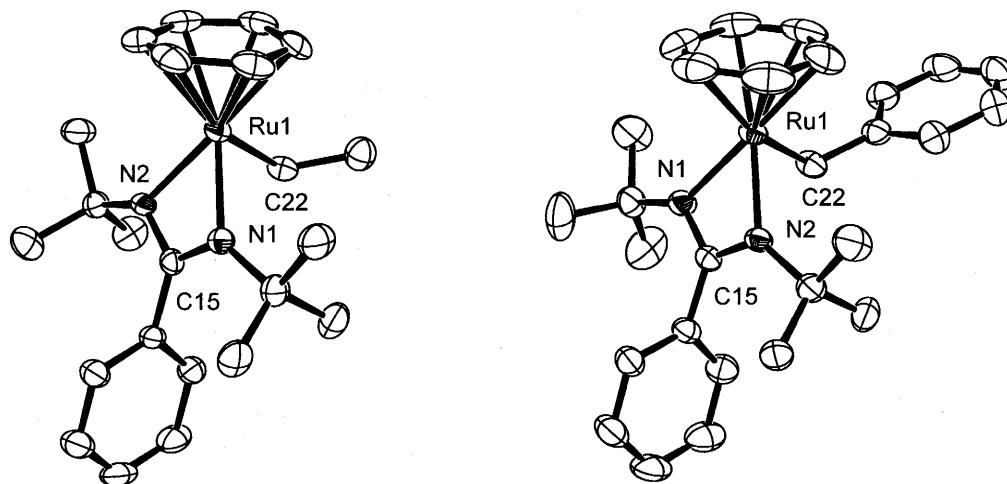


Figure 1. ORTEP drawings of the complexes, **3b** (left) and **3c** (right) with thermal ellipsoids drawn at the 50% provability level. All hydrogen atoms are omitted for clarity.

**Table 1.** Selected bond length (Å) and angles (°) for **3b** and **3c**.

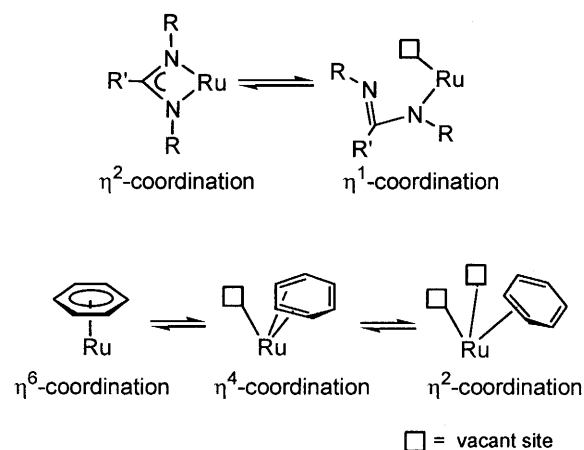
	<b>3b</b>	<b>3c</b>
Ru1-N1	2.135(3)	2.114(2)
Ru1-N2	2.118(3)	2.136(2)
Ru1-CEN <sup>a)</sup>	1.718	1.712
Ru1-C22	2.156(5)	2.152(2)
N1-C15	1.320(5)	1.325(3)
N2-C15	1.340(5)	1.335(3)
N1-Ru1-N2	62.5(1)	61.48(8)
N1-C15-N2	109.6(4)	109.5(2)
N1-Ru1-C22	83.8(2)	82.11(9)
N2-Ru1-C22	84.2(2)	85.80(9)

a) CEN = the centroid of the aromatic ring carbons

atom and the centre of the benzene ligand (CEN) is 1.71 Å. These are slightly longer compared with those of the halogen complex **4** (Ru-N; 2.10 ~ 2.13 Å, Ru-CEN; 1.69 Å), and this indicates that the introduction of an alkyl group in place of the chloride makes the ruthenium center more electronically negative.

All of the alkyl complexes **3** described here are stable towards air and moisture in their solid state, and the color of these solids did not change when the substances were exposed to air for a week. In solution and under aerobic conditions, these complexes are less stable, and slow decomposition of the complexes occurs in C<sub>6</sub>D<sub>6</sub> to give insoluble black solids within a few days. In the absence of air and moisture, the thermal stability of these alkyl complexes is high. In fact, heating of a C<sub>6</sub>D<sub>6</sub> solution of the methyl complex **3a** at 80°C *in vacuo* did not result in any decomposition of the complexes even after a week. Although the ethyl complex **3b** has a possibility of generating the hydride complex, [(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)Ru(η-amidinate)H] through β-H elimination from the ethyl group, such reaction did not occur, even when the substance was heated in C<sub>6</sub>D<sub>6</sub> at 80°C for two weeks. Thermolysis of **3b** occurs at over 150°C in C<sub>6</sub>D<sub>6</sub> to give unknown products with liberation of the benzene ligand. Ethylene was not observed. As described above, ethylruthenium complexes, in particular those bearing phosphine ligands, such as [CpRu(PPh<sub>3</sub>)<sub>2</sub>(Et)]<sup>3a)</sup> and [Ru(PCy<sub>3</sub>)<sub>2</sub>(Et)(Cl)(CO)]<sup>3i)</sup> readily undergo β-H elimination. The high thermal stability of **3b** makes **3b** one of the rare examples of stable ethylruthenium complexes [for other examples refer to lit. ref. 2b,2c,3c].

This unusually high stability of the ethyl complex provides a fresh insight in the coordinative flexibility of the amidinate and arene ligands. As shown in Figure 2, the amidinate ligand potentially induces a η<sup>2</sup> ↔ η<sup>1</sup> hapticity change similar to cases found for allyl or pseudo-allyl ligands.<sup>4)</sup> Multiple hapticity changes leading to ring slippage of the benzene ligand (η<sup>6</sup> ↔ η<sup>4</sup> ↔ η<sup>2</sup> hapticity change) are known in the chemistry of arene transition metal complexes.<sup>6)</sup> The hapticity change opens vacant coordination sites of the metal. Generally, it is considered that β-hydrogen atom



**Figure 2.** Hapticity change of the amidinate and arene ligands

elimination is rapid and occurs as soon as vacant coordination sites are available. High thermal stability of the ethyl complex **3b** suggests that the hapticity change of either the amidinate or the arene ligand does not readily take place to give vacant coordination sites required for the β-H elimination.

## Conclusions

We have achieved the successful preparation and complete structural elucidation of novel alkylruthenium amidinates, **3**, by the reaction of halogen complex, **4**, with Grignard reagents. These alkyl complexes are thermally stable and insensitive to air and moisture. The ethyl complex **3b** shows unusual thermal stability in comparison to other ethylruthenium compounds; the great stability indicates that the hapticity change of the amidinate or arene ligand, which would contribute to inducing facile β-hydrogen atom elimination, does not proceed with ease.

## Experimental Sections

### 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, pentane; Ph<sub>2</sub>CO/Na). RuCl<sub>3</sub> hydrate, purchased from Nakarai Tesque Co., Ltd., was used as received. [(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)Ru(η<sup>1</sup>-BuNCPhN<sup>t</sup>Bu)Cl] (**4**) was prepared as described in the literature.<sup>5c)</sup> MeMgBr in THF was purchased from Kanto Chemical Co. Inc., and EtMgBr and BnMgBr were prepared by appropriate methods. These Grignard reagents were titrated prior to use.

<sup>1</sup>H and <sup>13</sup>C spectra were recorded on JEOL Lambda 600 and Lambda 400 spectrometers at ambient temperature unless otherwise noted. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts (δ values) are given in ppm relative to solvent resonances. All coupling constants are reported in Hz. IR spectra were recorded on a JASCO

FT/IR-550 spectrometer. Melting points were measured on a Yanaco micro melting point apparatus. EI Mass spectra were recorded on a JEOL MSStation JMS-70 apparatus. Elemental analyses were performed by the Elemental Analysis Center, Faculty of Science, Kyushu University.

### Preparation of Alkyl complexes, 3

**3a:** In a Schlenk tube, **4** (46 mg, 0.10 mmol), dissolved in THF (ca. 5 mL), was treated with a solution of MeMgBr in THF (0.94 M, 150  $\mu$ l, 0.141 mmol) at  $-78^{\circ}\text{C}$ . The reaction mixture was allowed to warm to room temperature under stirring (1h). After removal of the solvent, the residual products were dissolved in hexane and insoluble materials were removed by filtration. The filtrate was concentrated and dried *in vacuo* to give **3a** (37 mg, 0.087 mmol, 84 %) as a yellow solid. EI Mass:  $[M^+] = 426$ . HRMS Calcd. for  $\text{C}_{22}\text{H}_{32}\text{N}_2\text{Ru}$ : 426.1609. Found: 426.1615. m.p.  $160^{\circ}\text{C}$  (dec.).  $^1\text{H}$  NMR (600 Hz,  $\text{C}_6\text{D}_6$ ):  $\delta$  1.02 (s, 18H;  $\text{C}(\text{CH}_3)_3$ ), 1.54 (s, 3H; Ru-CH<sub>3</sub>), 4.86 (s, 6H;  $\text{C}_6\text{H}_6$ ), 6.88 (dt,  $J = 7.5$ , 1.8 Hz, 1H;  $\text{C}_6\text{H}_5$ ), 6.92 ~ 7.00 (m, 2H;  $\text{C}_6\text{H}_5$ ), 7.13 (dt,  $J = 7.5$ , 1.3 Hz, 1H;  $\text{C}_6\text{H}_5$ ), 7.31 (dt,  $J = 7.5$ , 1.6 Hz, 1H;  $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  3.47 (Ru-CH<sub>3</sub>), 33.95 ( $\text{C}(\text{CH}_3)_3$ ), 54.35 ( $\text{C}(\text{CH}_3)_3$ ), 81.69 ( $\text{C}_6\text{H}_6$ ), 126.89, 127.31, 127.95, 130.43, 131.47, 141.00 ( $\text{C}_6\text{H}_5$ ), 166.51 (NCN).

**3b:** In a Schlenk tube, **4** (39 mg, 0.087 mmol), dissolved in THF (ca. 5 mL), was treated with a solution of EtMgBr in THF (0.71 M, 250  $\mu$ l, 0.18 mmol) at  $-78^{\circ}\text{C}$ . The reaction mixture was allowed to warm to room temperature under stirring for 24 h. After removal of the solvent, the residual products were dissolved in hexane and insoluble materials were removed by filtration. The filtrate was concentrated and dried *in vacuo* to give **3b** (32 mg, 0.072 mmol, 82 %) as a yellow solid. EI Mass:  $[M^+] = 440$ . m.p.  $131^{\circ}\text{C}$ . Anal. Calcd. for  $\text{C}_{23}\text{H}_{35}\text{N}_2\text{Ru}$ : C, 62.84; H, 7.80; N, 6.37. Found: C, 62.38; H, 7.73; N, 6.29.  $^1\text{H}$  NMR (600 Hz,  $\text{C}_6\text{D}_6$ ):  $\delta$  1.00 (s, 18H;  $\text{C}(\text{CH}_3)_3$ ), 2.04 ~ 2.19 (m, 5H; Ru-C<sub>2</sub>H<sub>5</sub>), 4.84 (s, 6H;  $\text{C}_6\text{H}_6$ ), 6.86 ~ 6.91 (m, 1H;  $\text{C}_6\text{H}_5$ ), 6.96 ~ 7.00 (m, 2H;  $\text{C}_6\text{H}_5$ ), 7.07 ~ 7.11 (m, 1H;  $\text{C}_6\text{H}_5$ ), 7.30 ~ 7.34 (m, 1H;  $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  21.67, 24.95 (Ru-C<sub>2</sub>H<sub>5</sub>), 34.21 ( $\text{C}(\text{CH}_3)_3$ ), 54.22 ( $\text{C}(\text{CH}_3)_3$ ), 81.70 ( $\text{C}_6\text{H}_6$ ), 127.10, 127.40, 128.12, 130.82, 132.06, 141.25 ( $\text{C}_6\text{H}_5$ ), 166.93 (NCN).

**3c:** **3c** was prepared from **4** (42 mg, 1.06 mmol) and an ethereal solution of BnMgBr (0.070 M, 150 ml, 0.105 mmol) in the same manner as described for the preparation of **3a** (43 mg, 0.086 mmol, 91 %). EI Mass:  $[M^+] = 538$ . m.p.  $116^{\circ}\text{C}$ . Anal. Calcd. for  $\text{C}_{28}\text{H}_{36}\text{N}_2\text{Ru}$ : C, 67.04; H, 7.23; N, 5.58. Found: C, 67.14; H, 7.34; N, 5.43.  $^1\text{H}$  NMR (400 Hz,  $\text{C}_6\text{D}_6$ ):  $\delta$

**Table 2.** Crystal data and structure refinement for **3b** and **3c**

	<b>3b</b>	<b>3c</b>
Empirical formula	C <sub>23</sub> H <sub>34</sub> N <sub>2</sub> Ru	C <sub>28</sub> H <sub>36</sub> N <sub>2</sub> Ru
Formula weight	463.61	501.66
Crystal habits, color	platelet, yellow	prismatic, yellow
Crystal size, mm	0.10 x 0.30 x 0.60	0.15 x 0.20 x 0.30
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> -1
Unit cell dimensions		
<i>a</i> / Å	10.2975(9)	10.0332(9)
<i>b</i> / Å	12.1900(12)	14.260(1)
<i>c</i> / Å	16.6236(19)	9.9808(9)
$\alpha$ / deg		98.290(4)
$\beta$ / deg	91.754(4)	117.499(3)
$\gamma$ / deg		74.362(2)
Volume / Å <sup>3</sup>	2085.7(4)	1.219.4(2)
<i>Z</i>	4	2
Density (calculated) / Mg/m <sup>3</sup>	1.476	1.366
Absorption coefficient / mm <sup>-1</sup>	0.765	0.660
<i>F</i> (000)	968	524
Temperature / K	293(2)	293(2)
<i>Q</i> range for data collection / deg	2.07 to 27.48	2.30 to 27.48
Index ranges	0 $\leq$ <i>h</i> $\leq$ 13 0 $\leq$ <i>k</i> $\leq$ 15 -21 $\leq$ <i>l</i> $\leq$ 21	0 $\leq$ <i>h</i> $\leq$ 12 -17 $\leq$ <i>k</i> $\leq$ 18 -12 $\leq$ <i>l</i> $\leq$ 11
Reflection collected	4467	5508
Independent reflections	4467 [ <i>R</i> (int) = 0.0000]	5508 [ <i>R</i> (int) = 0.0000]
Reflections observed (>2 $\sigma$ )	3636	5244
Data/ restraints / parameters	4467 / 0 / 235	5508 / 0 / 280
<i>R</i> indices ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	<i>R</i> 1 = 0.0528 <i>wR</i> 2 = 0.1627	<i>R</i> 1 = 0.0391 <i>wR</i> 2 = 0.1287
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0653 <i>wR</i> 2 = 0.1728	<i>R</i> 1 = 0.0410 <i>wR</i> 2 = 0.1321
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.277	251
Largest diff. peak and hole / e. Å <sup>3</sup>	0.752 and -1.564	0.601 and -1.338

1.50 (s, 18H; C(CH<sub>3</sub>)<sub>3</sub>), 3.68 (s, 2H; Ru-CH<sub>2</sub>), 5.11 (s, 6H; C<sub>6</sub>H<sub>6</sub>), 7.35 ~ 7.40 (m, 1H; C<sub>6</sub>H<sub>5</sub>), 7.44 ~ 7.53 (m, 3H; C<sub>6</sub>H<sub>5</sub>), 7.57 (t, *J* = 7.3 Hz, 1H; C<sub>6</sub>H<sub>5</sub>), 7.71 ~ 7.75 (m, 1H; C<sub>6</sub>H<sub>5</sub>), 7.83 (t, *J* = 7.6 Hz, 2H; C<sub>6</sub>H<sub>5</sub>), 8.03 (d, *J* = 6.8 Hz, 2H; C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, C<sub>6</sub>D<sub>6</sub>): δ 30.04 (Ru-CH<sub>2</sub>), 34.10 (C(CH<sub>3</sub>)<sub>3</sub>), 54.02 (C(CH<sub>3</sub>)<sub>3</sub>), 81.87 (C<sub>6</sub>H<sub>6</sub>), 121.83, 127.01, 127.13, 128.08, 128.12, 128.53, 130.04, 132.18, 140.75, 159.40 (C<sub>6</sub>H<sub>5</sub> of amidinate or benzyl), 167.37 (NCN).

#### X-ray determination of 3c and 3b

Crystallographic details are listed in Table 2. Single crystals for X-ray diffraction were grown in a concentrated hexane solution at -30°C. Diffraction data were collected on Rigaku R-Axis RAPID IP diffractometer (Mo-Kα, λ = 0.71069 Å) and then processed with teXsan. Structure solutions were performed by direct methods with the program SIR 92. The refinement was carried out by full-matrix-block least squares on *F*<sup>2</sup> on with all non hydrogen atoms refined anisotropically using the program SHELEXL-97-2 PC version. The positions of all hydrogen atoms were calculated assuming idealized geometries.

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