

## *p*-Cymene Ruthenium Halide Complexes with a Heterocyclic Carbene

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Received May 7, 2018

**Abstract**—The reaction of (*p*-cymene)Ru(Me<sub>2</sub>Im)Cl<sub>2</sub> with excess Me<sub>2</sub>ImCO<sub>2</sub> in acetonitrile in the presence of NH<sub>4</sub>PF<sub>6</sub> afforded the amino complex [(*p*-cymene)Ru(Me<sub>2</sub>Im)(NH<sub>3</sub>)Cl]PF<sub>6</sub>. The reaction of (*p*-cymene)Ru(Me<sub>2</sub>Im)Cl<sub>2</sub> with excess anhydrous SnCl<sub>2</sub> gave the complex (*p*-cymene)-Ru(Me<sub>2</sub>Im)Cl(SnCl<sub>3</sub>), whereas treatment of dimeric iodide complex [(*p*-cymene)RuI<sub>2</sub>]<sub>2</sub> with Me<sub>2</sub>ImCO<sub>2</sub> in acetonitrile gave the ionic compound [Me<sub>2</sub>ImH][(*p*-cymene)RuI<sub>3</sub>]. CIF files: CCDC nos. 1841649 (I), 1841650 (II), 1841648 (III).

**Keywords:** ruthenium, NHC, carbene, tin, X-ray diffraction, NMR

**DOI:** 10.1134/S1070328418120096

Ruthenium complexes with a coordinated N-heterocyclic carbene (NHC) are used as catalysts for some organic reactions. Ruthenium(II) complex containing a substituted allenylidene and N-heterocyclic carbene, which is bonded to the metal atom through additional η<sup>6</sup>-coordination of the N-aryl substituent, catalyzes ring closure reactions [1]. The catalytic hydrogenation of aqueous CO<sub>2</sub> to formic acid involves ruthenium(II) arene carbene chelates [2].

Ruthenium arene complexes with two different substituents are usually prepared by a two-stage procedure. First, the starting dimeric halide complexes react with the ligand to give monomeric complexes with a “three-legged piano stool” geometry; then one more equivalent of the ligand displaces the halogen atom to the outer sphere to give cationic complexes [3]. When two different ligands are used, a chiral center arises at the metal atom [4], which then undergoes racemization during catalytic transformations due to low transition barrier (<15 kcal/mol) via an intermediate with unsaturated “two-legged piano stool” geometry [5]. Therefore, compounds of this type do not influence the stereoselectivity of the catalyzed processes. However, the ionic nature of the complexes allows them to be successfully used as cytotoxic and anticancer agents [6].

### EXPERIMENTAL

All operations for product isolation were carried out under argon in anhydrous solvents. IR spectra

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were recorded on a Bruker Alpha with a Platinum ATR attachment. Chemical analysis was carried out using a EA3000 CHNS analyzer (EuroVector). The <sup>1</sup>H, <sup>13</sup>C, and <sup>119</sup>Sn NMR spectra were measured on a Bruker AV 300 spectrometer operating at 300.13, 75.4, and 111.95 MHz, respectively, with internal deuterium lock at 303 K. The <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are referred to TMS, while <sup>119</sup>Sn NMR chemical shifts are referred to Me<sub>4</sub>Sn. Deuterated solvents (CD<sub>3</sub>CN, CDCl<sub>3</sub>, CD<sub>2</sub>Cl<sub>2</sub>, and DMSO-d<sub>6</sub>) were dried over 4 Å molecular sieves. The complex [*p*-(cymene)RuCl<sub>2</sub>]<sub>2</sub> and dimethylimidazolium carboxylate were prepared according to published procedures [7] and [8], respectively.

**Synthesis of [(*p*-cymene)Ru(Me<sub>2</sub>Im)(NH<sub>3</sub>)Cl]PF<sub>6</sub> (I).** Powdered dimethylimidazolium carboxylate (Me<sub>2</sub>ImCO<sub>2</sub>) (0.186 g, 1.33 mmol) was added to an orange solution of [*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub> (0.203 g, 0.33 mmol) in 10 mL of MeCN, and the reaction mixture was refluxed for 3 h. NH<sub>4</sub>PF<sub>6</sub> (0.108 g, 0.66 mmol) was added over a period of 15 min to the magnetically stirred orange-red solution thus formed, and stirring was continued for another 15 min. Then the solution was filtered and concentrated to half volume, Et<sub>2</sub>O was added, and the mixture was kept at –26°C for 8 days. A green oil precipitated. The light orange solution above the oil was filtered, and the solvent was removed in vacuum. The light orange residue was recrystallized by diffusion through the gas phase in

the CH<sub>2</sub>Cl<sub>2</sub>–pentane system. The yield of orange crystals was 0.128 g (36%).

For C<sub>15</sub>H<sub>25</sub>N<sub>3</sub>F<sub>6</sub>PClRu (*M* = 529)

Anal. calcd., %	C, 34.06	H, 4.76	N, 7.95
Found, %	C, 34.39	H, 4.81	N, 8.02

IR (KBr;  $\nu$ , cm<sup>-1</sup>): 3367 vw, 3320 vw, 3254 vw, 3218 vw, 3176 w, 2976 vw, br, 1615 vw, 1577 vw, 1474 vw, 1455 w, br, 1397 vw, 1380 vw, 1363 vw, 1341 vw, 1322 vw, 1266 w, 1219 w, 1143 vw, 1120 vw, 1094 vw, 1081 vw, 1051 vw, 1031 vw, 1009 vw, 907 vw, 877 vw, 825 vs, br, 737 s, 685 w, 671 m, 632 vw, 607 vw, 554 vs, 492 vw, 467 vw, 443 w, 427 w.br. <sup>1</sup>H NMR (CD<sub>3</sub>CN;  $\delta$ , ppm): 1.15 (d, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, (CH<sub>3</sub>)<sub>2</sub>CH), 1.24 (d, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, (CH<sub>3</sub>)<sub>2</sub>CH), 1.94 (s, CH<sub>3</sub>), 2.76 (s, br, NH<sub>3</sub>), 2.78 (sept., <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, (CH<sub>3</sub>)<sub>2</sub>CH), 3.61 (s, br, NCH<sub>3</sub>), 3.86 (s, br, NCH<sub>3</sub>), 5.34, 5.40, 5.53, 5.72 (m, C<sub>6</sub>H<sub>4</sub>), 7.22 (s, br, CHCH). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN;  $\delta$ , ppm): 18.58, 21.22, 23.74, 31.7, 38.4 br, 39.5 br, 81.93, 84.32, 85.41, 85.97, 101.36, 111.93, 125.38 br, 173.58.

#### Synthesis of (*p*-cymene)Ru(Me<sub>2</sub>Im)Cl(SnCl<sub>3</sub>) (II).

Powdered (Me<sub>2</sub>ImCO<sub>2</sub>) (0.138 g, 0.99 mmol) was added to a magnetically stirred solution of [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub> (0.301 g, 0.49 mmol) in 15 mL of MeCN, and the reaction mixture was refluxed for 3 h. The solvent was removed in vacuum. The orange oily residue was dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> and stirred with SnCl<sub>2</sub> (0.272 g, 1.4 mmol) for 30 min. The resulting bright orange solution above the precipitate was filtered, and the residue was washed with CH<sub>2</sub>Cl<sub>2</sub> (3 × 10 mL). The combined orange CH<sub>2</sub>Cl<sub>2</sub> solution was concentrated to 2/3 of the volume and kept at -50°C. The yield of orange crystals was 0.331 g (57%).

For C<sub>15</sub>H<sub>22</sub>N<sub>2</sub>Cl<sub>4</sub>SnRu (*M* = 592)

Anal. calcd., %	C, 30.44	H, 3.75	N, 4.73
Found, %	C, 29.98	H, 3.69	N, 4.86

IR (KBr;  $\nu$ , cm<sup>-1</sup>): 3165 w, 3125 m, 3113 w, 2960 m, br, 2868 w, 1684 w, 1576 w, 1536 w, 1493 w, 1450 s, br, 1420 m, 1389 m, 1370 m, br, 1355 m, 1315 m, 1276 m, 1221 vs, 1158 w, 1117 m, 1078 m, 1054 s, 1034 m, 1004 m, 955 w, 927 w, 908 m, 883 w, 862 m, 801 m, 741 vs, 691 m, 678 vs, 609 m, 574 m, 507 w, 476 w, 467 w, 449 m, 427 w.

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>;  $\delta$  ppm): 1.17 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, (CH<sub>3</sub>)<sub>2</sub>CH), 1.26 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, (CH<sub>3</sub>)<sub>2</sub>CH), 2.04 (s, CH<sub>3</sub>), 2.78 (sept., <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, (CH<sub>3</sub>)<sub>2</sub>CH), 3.75 (s, br, NCH<sub>3</sub>), 4.05 (s, br, NCH<sub>3</sub>), 5.28, 5.52, 5.75, 5.88 (m, C<sub>6</sub>H<sub>4</sub>), 7.12 (s, br, CHCH), 7.16 (s, br, CHCH). <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>SO;  $\delta$ , ppm): 1.08 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, (CH<sub>3</sub>)<sub>2</sub>CH), 1.21 (d,

<sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, (CH<sub>3</sub>)<sub>2</sub>CH), 2.04 (s, CH<sub>3</sub>), 2.72 (sept., <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, (CH<sub>3</sub>)<sub>2</sub>CH), 3.84 (s, NCH<sub>3</sub>), 3.87 (s, NCH<sub>3</sub>), 6.00, 6.03, 6.18, 6.28 (m, C<sub>6</sub>H<sub>4</sub>), 7.58 (d, <sup>3</sup>J<sub>H-H</sub> = 1.9 Hz, CHCH), 7.62 (d, <sup>3</sup>J<sub>H-H</sub> = 1.9 Hz, CHCH). <sup>13</sup>C{<sup>1</sup>H} NMR ((CD<sub>3</sub>)<sub>2</sub>SO;  $\delta$ , ppm): 17.45, 21.03, 22.70, 30.45, 38.34, 78.25, 88.54, 91.54, 92.02, 103.72, 116.30, 125.19, 126.44, 164.64. <sup>119</sup>Sn{<sup>1</sup>H} NMR ((CD<sub>3</sub>)<sub>2</sub>SO;  $\delta$ , ppm) -134 s, br.

#### Synthesis of [Me<sub>2</sub>ImH][(p-cymene)RuI<sub>3</sub>] (III).

Method 1. [(*p*-Cymene)RuCl<sub>2</sub>]<sub>2</sub> (0.140 g, 0.23 mmol) was stirred with KI (0.927 g, 5.6 mmol) in 10 mL of acetone for 30 min. The solvent was removed in vacuum, and the residue was dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>. [Me<sub>2</sub>ImH]I (0.103 g, 0.46 mol) was added to the reaction mixture and the mixture was stirred for 1 h. The resulting dark red solution was concentrated to half volume, the product was crystallized by benzene layering on a CH<sub>2</sub>Cl<sub>2</sub> solution. The yield of red-brown crystals was 0.278 g (85%).

For C<sub>15</sub>H<sub>23</sub>N<sub>2</sub>I<sub>3</sub>Ru (*M* = 713)

Anal. calcd., %	C, 25.26	H, 3.25	N, 3.93
Found, %	C, 25.29	H, 3.28	N, 4.29

IR (KBr;  $\nu$ , cm<sup>-1</sup>): 3523 w, br, 3139 s, 3087 vs, br, 2956 vs, br, 2867 m, 2508 vw, br, 1862 vw, 1733 w, 1627 w, 1566 vs, 1531 m, 1494 m, 1467 s, br, 1447 s, 1385 s, 1363 s, br, 1342 m, 1325 w, 1276 w, 1198 w, 1165 vs, 1105 m, 1085 m, 1055 m, 1017 m, 1002 w, 955 w, 933 w, 883 w, 853 m, 823 m, 801 m, 759 m, br, 734 m, 663 w, 616 vs, 565 vw, 436 w, 410 w.

<sup>1</sup>H NMR for [Me<sub>2</sub>ImH][(p-cymene)RuI<sub>3</sub>]. (CDCl<sub>3</sub>;  $\delta$ , ppm): 1.24 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 2.89H, (CH<sub>3</sub>)<sub>2</sub>CH), 1.31 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 3.2H, (CH<sub>3</sub>)<sub>2</sub>CH), 2.35 (s, 1.43H, CH<sub>3</sub>), 2.54 (s, 1.56H CH<sub>3</sub>), 3.00 (sept., <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 0.49 H, (CH<sub>3</sub>)<sub>2</sub>CH), 3.37 (sept., <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 0.53 H, (CH<sub>3</sub>)<sub>2</sub>CH), 4.07 (s, 6.18 H, NCH<sub>3</sub>), 5.27 (d, <sup>3</sup>J<sub>H-H</sub> = 5.9 Hz, 1.03 H, C<sub>6</sub>H<sub>4</sub>), 5.42 (d, <sup>3</sup>J<sub>H-H</sub> = 6.0 Hz, 0.96 H, C<sub>6</sub>H<sub>4</sub>), 5.50 (d, <sup>3</sup>J<sub>H-H</sub> = 5.9 Hz, C<sub>6</sub>H<sub>4</sub>), 5.52 (d, <sup>3</sup>J<sub>H-H</sub> = 5.9 Hz, C<sub>6</sub>H<sub>4</sub>), 7.24 (d, <sup>4</sup>J<sub>H-H</sub> = 1.6 Hz, 1.94 H, C<sub>2</sub>H<sub>2</sub>), 9.83 (s, br, 1 H, CH). <sup>1</sup>H NMR of [(p-cymene)RuI<sub>2</sub>]<sub>2</sub> (CDCl<sub>3</sub>;  $\delta$ , ppm): 1.25 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, (CH<sub>3</sub>)<sub>2</sub>CH), 2.36 (s, CH<sub>3</sub>), 3.02 (sept., <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, (CH<sub>3</sub>)<sub>2</sub>CH), 5.43 (d, <sup>3</sup>J<sub>H-H</sub> = 6.0 Hz, C<sub>6</sub>H<sub>4</sub>), 5.53 (d, <sup>3</sup>J<sub>H-H</sub> = 6.0 Hz, C<sub>6</sub>H<sub>4</sub>).

Method 2. Powdered Me<sub>2</sub>ImCO<sub>2</sub> (0.07 g, 0.50 mmol) was added to a magnetically stirred solution of [(p-cymene)RuCl<sub>2</sub>]<sub>2</sub> (0.151 g, 0.25 mmol) in 7 mL of MeCN. The reaction mixture was refluxed for 3 h and then the solvent was removed in vacuum. The residue was dissolved in 10 mL of acetone in the presence of KI (0.324 g, 0.99 mmol). After stirring for 30 min, the solution turned red. The solvent was

**Table 1.** Crystallographic data and structure refinement parameters

Parameter	Value		
	I	II	III
Molecular formula	C <sub>15</sub> H <sub>25</sub> F <sub>6</sub> N <sub>3</sub> PClRu	C <sub>15</sub> H <sub>22</sub> N <sub>2</sub> Cl <sub>4</sub> RuSn	C <sub>15</sub> H <sub>23</sub> N <sub>2</sub> I <sub>3</sub> Ru
<i>M</i>	528.87	591.90	713.12
Radiation ( $\lambda$ , Å)	MoK $\alpha$ ( $\lambda$ = 0.71073)		
Temperature of measurements, K	150(2)	150(2)	120(2)
System	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
<i>a</i> , Å	9.1998(6)	15.739(2)	8.5788(3)
<i>b</i> , Å	11.2732(7)	15.331(2)	10.1713(4)
<i>c</i> , Å	11.8242(8)	26.525(3)	12.2280(4)
$\alpha$ , deg	103.1381(9)	90	88.3290(5)
$\beta$ , deg	105.2152(9)	104.772(1)	73.9643(4)
$\gamma$ , deg	113.1511(8)	90	76.5446(4)
<i>V</i> , Å <sup>3</sup>	1009.73(11)	6189(1)	996.62(6)
<i>Z</i>	2	12	2
$\rho$ (calcd.), g/cm <sup>-3</sup>	1.739	1.906	2.376
$\mu$ , mm <sup>-1</sup>	1.047	2.460	5.430
<i>F</i> (000)	532.0	3456.0	660.0
Scanning range of $\theta$ , deg	4.234–61.116	2.676–54.000	5.082–60.894
Scan mode	$\omega$		
Number of unique reflections ( <i>N</i> <sub>1</sub> )	6130 ( <i>R</i> <sub>int</sub> = 0.0208)	13491 ( <i>R</i> <sub>int</sub> = 0.0364)	5959 ( <i>R</i> <sub>int</sub> = 0.0190)
Number of reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> ) ( <i>N</i> <sub>2</sub> )	5534	10100	5782
Number of refined parameters	261	385	196
GOOF ( <i>F</i> <sup>2</sup> )	1.036	1.103	1.197
<i>R</i> <sub>1</sub> for <i>N</i> <sub>2</sub>	0.0262	0.0526	0.0232
<i>wR</i> <sub>2</sub> for <i>N</i> <sub>1</sub>	0.0608	0.1301	0.0552
$\Delta\rho_{\max}/\Delta\rho_{\min}$ , e Å <sup>-3</sup>	1.20/–0.61	3.59/–1.67	1.18/–1.55

removed in vacuum and the residue was crystallized by benzene layering on a CH<sub>2</sub>Cl<sub>2</sub> solution. The yield of red-brown crystals of **III** was 0.115 g (32%).

**X-ray diffraction** study of compounds **I–III** was performed on a Bruker APEX II CCD diffractometer. The absorption corrections were applied by multiple

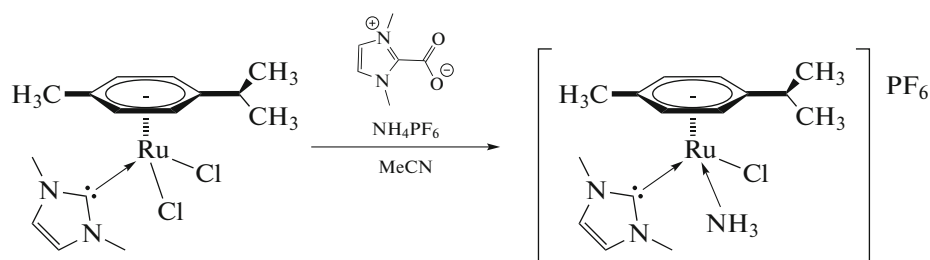
measurement of equivalent reflections using the SADABS program [9]. The structures of **I–III** were solved by direct methods and refined by least squares calculations on *F*<sup>2</sup> in the anisotropic approximation for non-hydrogen atoms (SHELX-2014 [10] and OLEX2 [11] program packages). The positions of the

H atoms of coordinated  $\text{NH}_3$  in **II** were determined from electron density map and refined in the isotropic approximation. The positions of other H atoms were calculated geometrically. The crystal unit cell of **II** contains three independent molecules related by pseudo-translation operations close to  $(1/3, 0, 1/3)$  and  $(2/3, 0, 2/3)$ . The structure was refined with the same geometry restraint (SAME) for independent molecules and equal thermal parameters between the atoms related by pseudo-translations in independent molecules, except for Ru and Sn atoms. The crystallographic data and structure refinement parameters for **I–III** are summarized in Table 1. Selected bond lengths and bond angles of **I–III** are given in figure captions.

The atom coordinates and other structure parameters are deposited with the Cambridge Crystallographic Data Centre (nos. 1841649 (**I**), 1841650 (**II**), 1841648 (**III**); [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)).

## RESULTS AND DISCUSSION

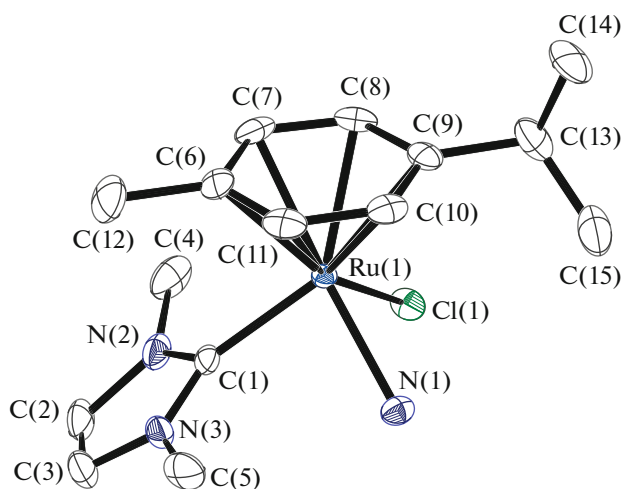
The reaction of  $(p\text{-cymene})\text{Ru}(\text{Me}_2\text{Im})\text{Cl}_2$  with excess  $\text{Me}_2\text{ImCO}_2$  in acetonitrile in the presence of  $\text{NH}_4\text{PF}_6$  unexpectedly gives amino complex **I** (Scheme 1). A similar formation of ruthenium amino complexes in the presence of  $\text{NH}_4\text{PF}_6$  has been observed previously on treatment of the  $[(p\text{-cymene})\text{RuCl}_2]_2$  dimer with  $N,N$ -dimethylbenzylamine [12] or 1-(2-hydroxyethyl)piperazine [13].



(I)

Scheme 1.

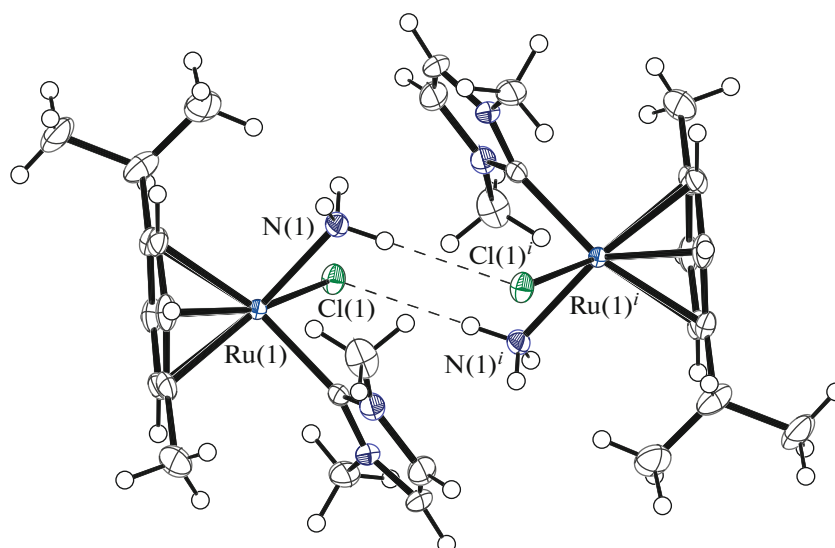
According to X-ray diffraction data (Fig. 1), the Ru–N bond length in complex **I** is 2.1407(16) Å, which corresponds to the sum of covalent radii



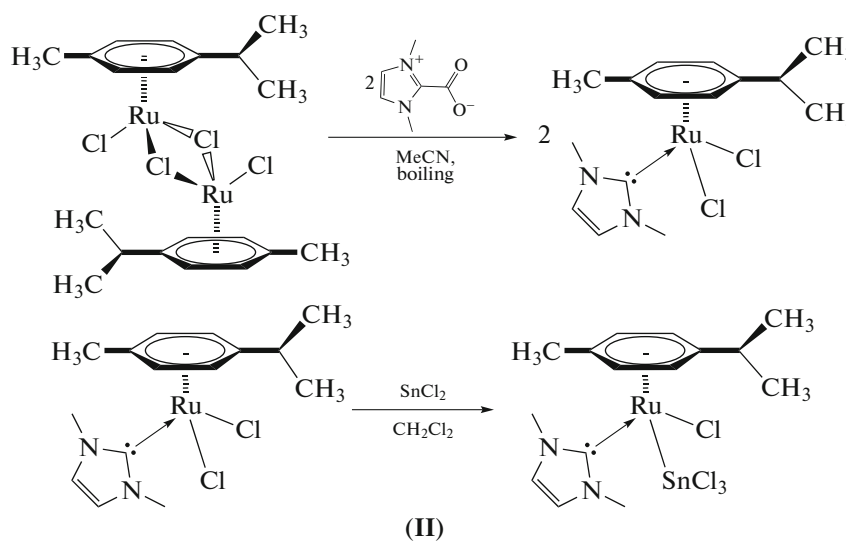
**Fig. 1.** Molecular structure of complex **I**. Hydrogen atoms are omitted. Selected bond lengths: Ru(1)–Cl(1), 2.4170(5); Ru(1)–N(1), 2.1407(16); Ru(1)–C(1), 2.077(2) Å.

(SCR) of the ruthenium and nitrogen atoms ( $r_{\text{Ru}} + r_{\text{N}} = 2.17$  Å) [14]. The Ru–C bond with the carbene carbon atom (2.077(2) Å) is shortened with respect to the ruthenium and carbon SCR ( $r_{\text{Ru}} + r_{\text{C}(\text{sp}^2)} = 2.19$  Å) [14]. Two  $\text{Cl}\cdots\text{H}\cdots\text{N}$  hydrogen bonds in the crystal connect molecules **I** into dimers (Fig. 2). In the  $^1\text{H}$  NMR spectrum of complex **I**, the signals of the diastereotopic aromatic protons and methyl groups in the coordinated cymene are split, which indicates retention of the Ru optical center in solution on the NMR time scale. The carbene ligand gives rise to a broad proton signal for the heterocycle and two broadened signals for the methyl groups, which is indicative of their non-equivalence and slow exchange caused by the hindered rotation of the ligand around the partially multiple Ru–carbene bond.

The reaction of the carbene complex  $(p\text{-cymene})\text{Ru}(\text{Me}_2\text{Im})\text{Cl}_2$  with excess anhydrous  $\text{SnCl}_2$  involves tin chloride insertion into the Ru–Cl bond to give the heterometallic complex  $(p\text{-cymene})\text{Ru}(\text{Me}_2\text{Im})\text{Cl}(\text{SnCl}_3)$  (**II**) (Scheme 2).



**Fig. 2.** Dimerization of molecule **I** in the crystal via two Cl⋯H–N hydrogen bonds.

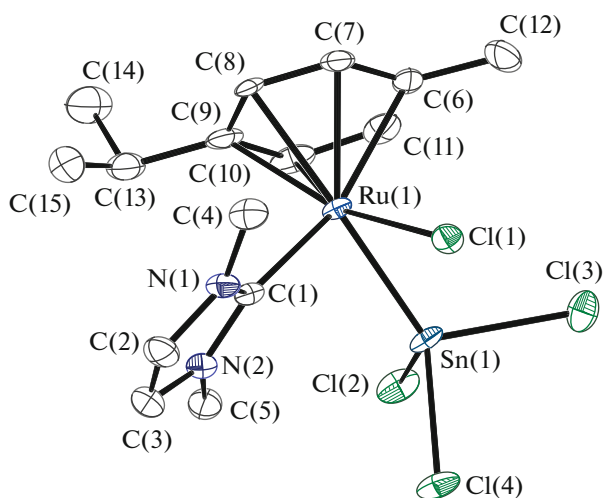


**Scheme 2.**

According to X-ray diffraction data (Fig. 3), the Ru–Sn bond length in **II** is 2.5605(7) Å, which is shorter than the SCR of the ruthenium and tin atoms ( $r_{\text{Ru}} + r_{\text{Sn}} = 2.85$  Å). The length of the Ru–C bond with the carbene carbon atom (2.075(6) Å) is shorter than the SCR ( $r_{\text{Ru}} + r_{\text{C}(\text{sp}^2)} = 2.19$  Å) [14].

The  $^1\text{H}$  NMR spectra of complex **II** do not show any signs of  $^1\text{H}$ – $^{119}\text{Sn}$  spin-spin coupling in either DMSO- $d_6$  or  $\text{CD}_2\text{Cl}_2$  solution, apparently, due to low values of the corresponding spin-spin coupling constants, because Ru–Sn bond dissociation in  $\text{CD}_2\text{Cl}_2$  is

unlikely. In addition, it is known for for [(*p*-cymene)Ru(PyTz)(SnCl<sub>3</sub>)]Cl (PyTz = 2-(pyridin-2-yl)thiazole) that the Ru–Sn bond is retained in the DMSO- $d_6$  solution [15]. Similarly to complex **I**, the presence of an optical center in **II** results in the appearance of separate signals for the diastereotopic aromatic protons and methyl groups in coordinated cymene. The methyl groups and protons in the heterocycle of the carbene ligand are also non-equivalent, indicating the lack of rotation around the Ru–carbene bond on the NMR time scale. The methyl groups, as well as protons in the carbene heterocycle proved to be

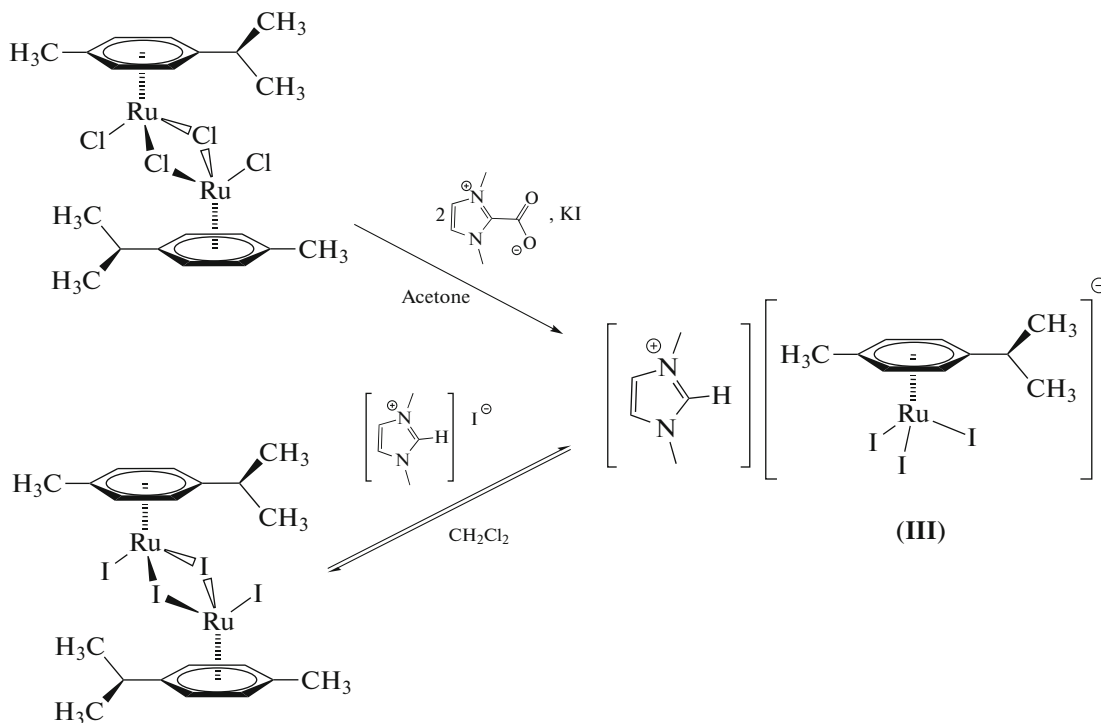


**Fig. 3.** Molecular structure of complex **II**. Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (deg): Sn(1)–Ru(1), 2.5605(7); Sn(1)–Cl(2), 2.397(2); Sn(1)–Cl(3), 2.382(2); Sn(1)–Cl(4), 2.387(2); Ru(1)–Cl(1), 2.431(2); Ru(1)–C(1), 2.075(6) Å; and Cl(2)Sn(1)Ru(1), 19.93(5)°; Cl(3)Sn(1)Ru(1), 14.90(5)°; Cl(3)Sn(1)Cl(2), 5.97(7)°; Cl(3)Sn(1)Cl(4), 7.97(7)°; and Cl(4)Sn(1)–Ru(1), 24.71(5)°.

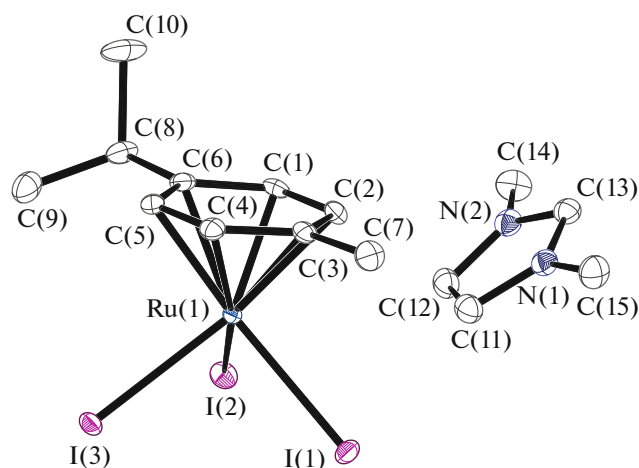
non-equivalent, but their signals are considerably broadened (the signal width at half-height is ~12 Hz). This is indicative of the internal hindered rotation of

the carbene around the Ru–C bond with increased multiplicity at 303 K.

Treatment of the dimer [(*p*-cymene)RuI<sub>2</sub>]<sub>2</sub> with two equivalents of dimethylimidazolium iodide gives ionic compound **III**, in which the anion containing three coordinated iodine atoms at ruthenium is accompanied by dimethylimidazolium cation. According to X-ray diffraction data, the Ru–I bond lengths are 2.7257(3)–2.7535(3) Å (Fig. 4), which is less than the sum of the ruthenium and iodine covalent radii ( $r_{\text{Ru}} + r_{\text{I}} = 2.85$  Å) [14]. The anion is devoid of the plane of symmetry passing through the ruthenium atom and the cymene substituent. This ionic complex can also be obtained by the reaction of the [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub> dimer with two equivalents of dimethylimidazolium carboxylate (Me<sub>2</sub>ImCO<sub>2</sub>). This yields the monomeric ruthenium complex with the coordinated N-heterocyclic carbene (NHC), (*p*-cymene)Ru(NHC)Cl<sub>2</sub> [8]. However, further treatment with KI in acetone gives rise to **III** (Scheme 3). The <sup>1</sup>H NMR spectrum of a solution of complex **III** in CDCl<sub>3</sub> exhibits signals for the dimethylimidazolium cation and two sets of signals for the coordinated cymene in a nearly 1 : 1 ratio, one of which is virtually identical to the signals of [(*p*-cymene)RuI<sub>2</sub>]<sub>2</sub>, and the overall cymene : imidazolium ratio corresponds to complex **III**. Thus, the reverse reaction occurs in solution to an equilibrium reached at 1 : 1 ratio.



**Scheme 3.**



**Fig. 4.** Molecular structure of complex **III**. Hydrogen atoms are omitted. Selected bond lengths: Ru(1)–I(1), 2.7430(3); Ru(1)–I(3), 2.7535(3); and Ru(1)–I(2), 2.7257(3) Å.

#### ACKNOWLEDGMENTS

The study was carried out using the equipment of the Center for Collective Use of the Institute of General and Inorganic Chemistry, Russian Academy of Sciences.

This work was supported by the Russian Science Foundation (project no. 17-73-10503).

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Translated by Z. Svitanko