

## Study of *cis*-Tetraammineruthenium(II) Chemistry with Linear Dienes

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### Introduction

We recently have done a series of studies to examine the coordination chemistry of *cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>. The complex of *cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>(acetone)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (**1**)<sup>1</sup> is a versatile precursor for tetraammineruthenium(II) complexes and this moiety is a good  $\pi$ -donor metal center toward a  $\pi$ -acceptor ligand. Dienes are also good  $\pi$ -acceptor ligands, and their complexes are of great general interest to the subject of structure in relation to reactivity. For numerous acyclic conjugated dienes, it has been demonstrated that the dienes when  $\eta^4$ -bound to a transition-metal center favor the *s-cis* arrangement over *s-trans* geometry.<sup>2</sup> However, for *cis*-[Ru(acac)<sub>2</sub>(2,3-dimethyl-1,3-butadiene)], the *s-trans*-diene coordination was observed.<sup>3</sup> We were interested in learning which isomer, *s-trans* or *s-cis*, is more stable in bonding *cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>. Furthermore, the chelating ligands, 1,4-pentadiene and 1,5-hexadiene, can reveal significant variation in the way they ligate.<sup>4</sup>

Here we report the preparations and the structures for *cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>(diene)<sub>2</sub>]<sup>2+</sup> (diene = 1,3-butadiene, 1,4-pentadiene, and 1,5-hexadiene).

### Experimental Section

**General Preparation of *cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>(diene)](PF<sub>6</sub>)<sub>2</sub>.** In a typical preparation, 50 mg of **1** was dissolved in 0.5 mL of acetone. About a 10-fold excess of the desired ligand was added, and the solution was stirred for 30 min. The solution was filtered, and the filtrate was treated with 3 mL of CH<sub>2</sub>Cl<sub>2</sub>. The resulting precipitate was filtered off. The solid was redissolved with acetone, and then the solution was treated with CH<sub>2</sub>Cl<sub>2</sub>. The precipitate was filtered off and washed with CH<sub>2</sub>Cl<sub>2</sub> and ether.

***cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>(1,3-butadiene)](PF<sub>6</sub>)<sub>2</sub>.** (**2**) In this preparation, the ligand was bubbled for 30 min. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>):  $\delta$  4.43 (br, 6H, 2NH<sub>3</sub>), 4.32 (d, *J* = 5.6, 2H), 4.15–4.02 (m, 2H), 4.08 (d, *J* = 7.3, 2H), 2.26 (br, 6H, 2NH<sub>3</sub>). <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>): 97.8, 66.6. Anal. Calcd for C<sub>4</sub>H<sub>18</sub>N<sub>4</sub>RuP<sub>2</sub>F<sub>12</sub>·<sup>1/2</sup>acetone: C, 12.18; H, 3.90; N, 10.33. Found: C, 12.37; H, 3.73; N, 10.24.

***cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>(1,3-butadiene)](ClO<sub>4</sub>)<sub>2</sub>.** (**2'**) A 38 mg sample of **2** was added to 1.4 mL of 1 M HClO<sub>4</sub> aqueous solution. The resulting suspension was warmed until the solid dissolved. Then saturated NaClO<sub>4</sub> aqueous solution (0.5 mL) was added to the hot solution. The solution was set aside to crystallize for one night. Anal. Calcd for C<sub>4</sub>H<sub>18</sub>N<sub>4</sub>RuCl<sub>2</sub>O<sub>8</sub>: C, 11.38; H, 4.30; N, 13.27. Found: C, 11.34; H, 4.26; N, 13.23.

**Caution!** Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

***cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>(1,4-pentadiene)](PF<sub>6</sub>)<sub>2</sub>.** (**3**) <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>): 4.17 (d, *J* = 12.5, 2H), 3.69 (d, *J* = 7.6, 2H), 3.67 (br, 6H, 2NH<sub>3</sub>), 3.20–3.11 (m, 2H), 3.08–3.01 (q, 2H), 2.92 (br, 6H, 2NH<sub>3</sub>). <sup>13</sup>C NMR

**Table 1.** Crystallographic Data for **2'**

C <sub>4</sub> H <sub>18</sub> N <sub>4</sub> O <sub>8</sub> Cl <sub>2</sub> Ru	space group: <i>Pb2<sub>1</sub>a</i> (No. 29)
fw = 422.2	T = 150 K
<i>a</i> = 16.887(4) Å	$\lambda$ (Mo K $\alpha$ ) = 0.710 73 Å
<i>b</i> = 16.934(5) Å	<i>d</i> (calc) = 1.82 g cm <sup>-3</sup>
<i>c</i> = 10.805(3) Å	$\mu$ = 13.8 cm <sup>-1</sup>
<i>V</i> = 3090 Å <sup>3</sup>	<i>R</i> <sup>a</sup> = 0.050
<i>Z</i> = 8	<i>R</i> <sub>w</sub> <sup>b</sup> = 0.076
$\theta$ range for data collen:	no. of unique reflns: 2824
3° < 2 $\theta$ < 55°	
abs treatment: $\psi$ scan	no. of data with <i>I</i> > 3 $\sigma$ ( <i>I</i> ): 2419
tot. no. of reflns: 3189	goodness of fit: 1.56

$$^a R = \sum(|F_o| - |F_c|)/\sum|F_o|. \quad ^b R_w = [\sum(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}.$$

(acetone-*d*<sub>6</sub>): for a main isomer, 73.8, 61.6, 30.3 (for a subproduct, 72.3, 62.0, 30.6). Anal. Calcd for C<sub>5</sub>H<sub>20</sub>N<sub>4</sub>RuP<sub>2</sub>F<sub>12</sub>: C, 11.39; H, 3.82; N, 10.63. Found: C, 11.87; H, 3.90; N, 10.74.

***cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>(1,5-hexadiene)](PF<sub>6</sub>)<sub>2</sub>.** (**4**) <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>): (a) 4.58–4.46 (m, 2H), 4.09 (br, 3H, NH<sub>3</sub>), 3.81 (br, 3H, NH<sub>3</sub>), 3.32 (d, *J* = 8.6, 2H), 3.07 (d, *J* = 12.9, 2H), 3.15 (br, 6H, 2NH<sub>3</sub>), 2.62–2.49 (m, 2H), 2.1 (m, 2H). (b) 4.19–4.10 (m, 2H), 3.96 (d, *J* = 13.2, 2H), 3.62 (d, *J* = 8.6, 2H). <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>): a) 94.2, 70.2, 32.6. b) 95.4, 70.4, 27.2. Anal. Calcd for C<sub>6</sub>H<sub>22</sub>N<sub>4</sub>RuP<sub>2</sub>F<sub>12</sub>: C, 13.31; H, 4.10; N, 10.35. Found: C, 13.74; H, 4.09; N, 9.82.

**X-ray Structural Determination.** A pale yellow crystal (0.3 × 0.3 × 0.3 mm<sup>3</sup>) of **2'** was affixed in a glass tube using silicone grease and transferred to the goniostat, where it was cooled to 150 K for characterization and data collection. X-ray data were collected on an MAC Science MXC-18 diffractometer using a graphite-monochromator and Mo K $\alpha$  radiation ( $\lambda$  = 0.710 73 Å). Cell constants were determined by a least-squares fit to the setting parameters of 24 independent reflections in the range 30° ≤ 2 $\theta$  ≤ 35°. Intensities of three standard reflections measured every 100 reflections showed no significant changes, therefore no decay correction was applied. An empirical absorption correction ( $\psi$ -scans) was applied. A summary of the experimental and structure solution procedure is given in Table 1. The structure was solved by a direct method and subsequent Fourier techniques by using a program package CRYSTAN-GM (the direct method program is SIR).<sup>5</sup> The space group *Pb2<sub>1</sub>a* (No. 29) was chosen on the basis of intensity statistics and the fact that the structure could be solved and refined successfully only in this space group.<sup>6</sup> Non-hydrogen atoms except one nitrogen<sup>7</sup> were refined anisotropically by a full-matrix least-squares method. Hydrogen atoms were omitted from the calculation. Some of the oxygen atoms and the carbon atoms showed somewhat higher than usual thermal parameters, indicating possible disorder. Refinements with partial occupancies for the central two carbon atoms of the butadienes were not successful. Final agreement indices of *R* = 0.050 and *R*<sub>w</sub> = 0.076. Weights were estimated from counter statistics. The final atomic coordinates are presented in the Supporting Information. Selected bond distances and angles are presented in Table 2.

**Kinetic and Thermodynamic Experiments.** Formation ratios of the isomers of **4** were determined with HPLC. HPLC was carried out on a Shimadzu liquid chromatograph LC-6A system. YMC-PACK R-ODS-5 (Yamamura Chemical, 5  $\mu$ m, 4.6 × 250 mm) columns were used. A solvent system containing 10% CH<sub>3</sub>OH/90% H<sub>2</sub>O and 0.25% CF<sub>3</sub>COOH (pH 2.5 adjusted with NaOH) was used for the elution of the complexes.

Acetone solutions of **4** in vials were stored for 24 h in a thermostatic bath (20, 30, 40, and 50 °C). Then the solution was poured in a vessel at liquid N<sub>2</sub> temperature and was quickly frozen. The solid remelted, and then it was injected to the column at 0 °C. Formation ratios of the isomers of **4** were determined at each temperature.

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- (1) Sugaya, T.; Sano, M. *Inorg. Chem.* **1993**, *32*, 5878.
- (2) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley and Sons, Inc.: New York, 1988; p 1152.
- (3) Ernst, R. D.; Melendez, E.; Stahl, L.; Ziegler, M. L. *Organometallics* **1991**, *10*, 3635.
- (4) Nickel, T.; Porschke, K.; Goddard, R.; Kruger, C. *Inorg. Chem.* **1992**, *31*, 4428.

- (5) SIR: Altomare, A.; Casciaro, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435. The least-squares program: Mallinson, P. R.; Muir, K. W. *J. Appl. Crystallogr.* **1985**, *18*, 51.
- (6) Any tetragonal space groups tetragonal are omitted by the reflection data and the extinction rule.
- (7) An anisotropic refinement for all non-hydrogen atoms gives very low thermal parameters for the N(1) atom, indicating possible disorder.

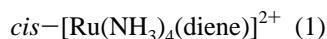
**Table 2.** Selected Bond Distances (Å) and Angles (deg) for **2'**

Ru(1)–N(1)	2.14(1)	Ru(1)–N(2)	2.19(2)
Ru(1)–N(3)	2.15(1)	Ru(1)–N(4)	2.17(2)
Ru(1)–C(1)	2.27(2)	Ru(1)–C(2)	2.15(3)
Ru(1)–C(3)	2.10(3)	Ru(1)–C(4)	2.23(4)
C(1)–C(2)	1.24(4)	C(2)–C(3)	1.32(4)
C(3)–C(4)	1.29(4)		
Ru(2)–N(5)	2.27(2)	Ru(2)–N(6)	2.15(2)
Ru(2)–N(7)	2.09(3)	Ru(2)–N(8)	2.14(2)
Ru(2)–C(5)	2.27(2)	Ru(2)–C(6)	2.09(3)
Ru(2)–C(7)	2.09(3)	Ru(2)–C(8)	2.28(3)
C(5)–C(6)	1.31(4)	C(6)–C(7)	1.17(4)
C(7)–C(8)	1.36(4)		
N(1)–Ru(1)–N(2)	88.1(6)	N(1)–Ru(1)–N(3)	87.3(5)
N(1)–Ru(1)–N(4)	171.7(5)	N(1)–Ru(1)–C(1)	97.4(7)
N(1)–Ru(1)–C(2)	87.9(8)	N(1)–Ru(1)–C(3)	97.2(9)
N(1)–Ru(1)–C(4)	92.6(9)	N(2)–Ru(1)–N(3)	87.7(6)
C(1)–C(2)–C(3)	135.2(26)	C(2)–C(3)–C(4)	146.2(28)
N(5)–Ru(2)–N(6)	87.1(6)	N(5)–Ru(2)–N(7)	88.2(5)
N(5)–Ru(2)–N(8)	170.3(6)	N(5)–Ru(2)–C(5)	95.3(7)
N(5)–Ru(2)–C(6)	89.8(9)	N(5)–Ru(2)–C(7)	95.0(10)
N(5)–Ru(2)–C(8)	93.9(9)	N(6)–Ru(2)–N(7)	83.8(5)
C(5)–C(6)–C(7)	147.8(29)	C(6)–C(7)–C(8)	152.1(31)

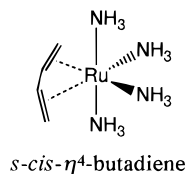
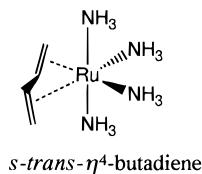
Kinetic experiments have been done as follows. A main fraction of an isomer of **4** was obtained with HPLC. The solution in a vial was stored at 20 °C and was analyzed every 10 min for 3 h. The formation ratio of the isomers in the solution was determined at each time.

## Results and Discussion

The starting material for the synthesis of the diene complexes was compound **1**. The reaction of **1** with various dienes leads to *cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>(diene)]<sup>2+</sup> complex (eq 1) within 10 min. The product as a solid (light yellow) shows resistance to air oxidation but is more sensitive in solution.



**Structure of *cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>(1,3-butadiene)]<sup>2+</sup>.** We determined the structure by X-ray crystal analysis for **2'** at 150 K because a proper single crystal of **2** was not obtained for structure analysis. A picture of the two independent molecules in the unit cell showing the atomic labeling scheme is shown in Figure 1. Although the data were collected at 150 K, the crystal structure is somewhat obscured by relatively high thermal motion of the oxygens of the ClO<sub>4</sub> ions and the central two carbon atoms of the diene ligand, where C–C distances are artificially shortened. It can be attributed to disorder of the crystal. The conformation of the ligand, however, appears to be *s-trans*- $\eta^4$ -butadiene. The distances obtained between the end C and end C atoms for the butadiene in the complex are 3.5 Å, which is a reasonable value for the coordinated *s-trans* butadiene and is too long for *s-cis*- $\eta^4$ -butadiene.<sup>8</sup> We conclude that the conformation of the ligand is *s-trans*- $\eta^4$ -butadiene.



In order to confirm formation of any isomers of **2** in acetone solution, we measured <sup>1</sup>H NMR spectra. Two NH<sub>3</sub> signals are found at 4.43 and 2.26 ppm with a 3:3 intensity ratio and three signals are also found at 4.32, 4.15–4.02, and 4.08 ppm from 1,3-butadiene. The complex of *s-trans*- $\eta^4$ -butadiene is C<sub>2</sub>-symmetrical, in which two NH<sub>3</sub> signals are observed with the

same intensity ratio. On the other hand, the *s-cis*- $\eta^4$ -butadiene complex can be C<sub>s</sub>-symmetrical, which would give three NH<sub>3</sub> signals with a 2:1:1 intensity ratio. Since we could not observe any other signals for byproducts, formation ratio of the *s-trans* to the *s-cis* can be 50 or more.

In earlier transition-metal complexes,<sup>9,10</sup> the *trans*- $\eta^4$ -diene coordination is a relatively rare bonding mode. On the other hand, Ernst et al.<sup>3</sup> also reported (*s-trans*- $\eta^4$ -2,3-dimethyl-1,3-butadiene)bis(acetylacetonato)ruthenium(II) and then the *s-trans* isomer has been found to be higher in thermodynamic stability than the corresponding *s-cis* form. It seems that the characteristic bonding features favor coordination of the *s-trans* over the *s-cis* conjugated-diene complex for Ru(II) complexes.

**Structures and Isomers of *cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>(1,5-hexadiene)]<sup>2+</sup>.** Because of the variety of coordination modes encountered for 1,5-hexadiene bound to metal,<sup>4</sup> we were interested in discovering whether Ru(II) would also form a complex with a chelating 1,5-hexadiene ligand. There are three possibilities in formation of 1,5-hexadiene complex, *R,R*-(C<sub>2</sub>-symmetrical), *S,S*-(C<sub>2</sub>-symmetrical), and *R,S*-(C<sub>s</sub>-symmetrical)  $\eta^2, \eta^2$ -bonded 1,5-hexadiene.



*R,R* (or *S,S*) -(C<sub>2</sub>-symmetrical)    *R,S*-(C<sub>s</sub>-symmetrical)

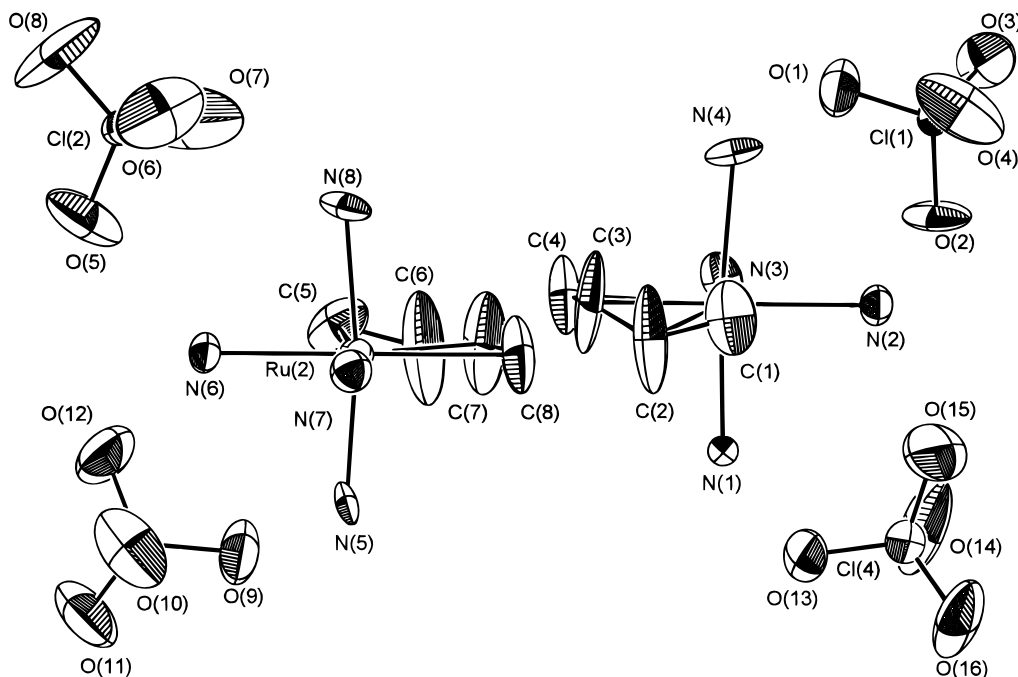
The *R,R*- and *S,S*-1,5-hexadiene complexes are in fact identical, having C<sub>2</sub> symmetry and leading to the same intensity for the two NH<sub>3</sub> signals observed. On the other hand, the *R,S*-complex shows C<sub>s</sub> symmetry, which gives three NH<sub>3</sub> signals with 2:1:1 intensity ratio. The <sup>1</sup>H NMR spectrum of **4** in acetone-*d*<sub>6</sub> shows three NH<sub>3</sub> signals with a 3:3:6 intensity ratio at 4.09, 3.81 and 3.15 ppm and five signals with same intensities at 4.58–4.46, 3.32, 3.07, 2.62–2.49, and 2.17 ppm from 1,5-hexadiene for a main product. Furthermore, small signals have been observed for a side product. In the <sup>13</sup>C NMR spectrum, we observed three main carbon signals with the other three carbon signals being lower in intensity by a factor of 4. We conclude that the main product is the *R,S* complex and the subproduct is the *R,R* and/or *S,S* complex.

In order to measure accurate formation ratios of the isomers, we separated the isomers by HPLC. The retention times for the main fraction of the *R,S* complex and for the subfraction are 6.5 and 6.0 min, respectively. We measured equilibrium constants, 0.245 ± 0.01, 0.28 ± 0.01, 0.29 ± 0.01, and 0.30 ± 0.01, for the isomers of the *R,S* complex and the *R,R* (and/or the *S,S*) complex in acetone solution at 20, 30, 40, and 50 °C,

(8) The distance of the end C–end C bond in *s-trans*-butadiene is calculated to be 3.62 Å for *cis*-Ru(acac)<sub>2</sub>(2,4-dimethyl-1,3-pentadiene).<sup>3</sup> In the case of *s-cis*-butadiene with the same bond lengths and bond angles as *cis*-Ru(acac)<sub>2</sub>(2,4-dimethyl-1,3-pentadiene), the end C–end C distance can be 2.98 Å. Our unpublished structural data for *cis*-Ru(acac)<sub>2</sub>(1,3-butadiene) shows the *s-trans*-butadiene with 3.45 Å for the end C–end C distance.

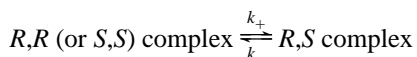
(9) (a) Erker, G.; Kruger, C.; Muller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1. (b) Yasuda, H.; Nakamura, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723. (c) Hunter, A. D.; Legzdins, P.; Einstein, F. W. B.; Willis, A. C.; Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1986**, *108*, 3843. (d) Melendez, E.; Arif, A. M.; Rheingold, A. L.; Ernst, R. D. *J. Amer. Chem. Soc.* **1988**, *110*, 8703.

(10) Other ruthenium(II) *trans*-diene compounds have been reported. (a) Fagan, P. J.; Mahoney, W. A.; Calabrese, J. C.; Williams, I. D. *Organometallics* **1990**, *9*, 1843. (b) Benyunes, S. A.; Green, M.; Grimshire, M. J. *Organometallics* **1989**, *8*, 2268. (c) Benyunes, S. A.; Day, J. P.; Green, M.; Al-Saadoon, A. W.; Waring, T. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1416.



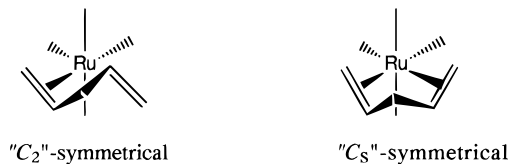
**Figure 1.** ORTEP plot (50% of probability) of complex **2'** with the atom-labeling scheme.

respectively, and then obtained the values of  $5 \pm 1 \text{ kJ mol}^{-1}$  and  $6 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$  for  $\Delta H^\circ$  and  $\Delta S^\circ$  between the isomers. We also measured the isomerization rate from the *R,S* complex to the *R,R* or *S,S* complex at 20.0 °C in aqueous methanol solution. We analyzed the data obtained by a first-order equation in the reversible equilibrium as follows:



The values for  $k_+$  and the  $k_-$  are  $(30 \pm 2) \times 10^{-5} \text{ s}^{-1}$  and  $(7 \pm 1) \times 10^{-5} \text{ s}^{-1}$ , respectively, at 20.0 °C. These values of the rates are close to those of conversion rates for isomerizations of *cis*-[Ru(acac)<sub>2</sub>(1,3-butadiene)].<sup>11</sup> Then the *R,R* (or *S,S*) to *R,S* interconversions must necessarily involve a change from  $\eta^4$  to  $\eta^2$  diene coordination in the transition state.

**Structures and Isomers of *cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>(1,4-pentadiene)]<sup>2+</sup>.** The following isomers are possibilities in formation of 1,4-pentadiene complex, "*C*<sub>2</sub>"-symmetrical  $\eta^2, \eta^2$ -bonded 1,4-pentadiene and "*C*<sub>s</sub>"-symmetrical  $\eta^2, \eta^2$ -bonded 1,4-pentadiene.<sup>12</sup>



Carbon-13 NMR of **3** in acetone-*d*<sub>6</sub> spectra gave main three carbon signals with the other three carbon signals with about 7:1 intensity ratios. Proton NMR of the main product of **3** gives two NH<sub>3</sub> signals with the same intensity ratio at 3.67 and 2.92 ppm and four signals with same intensities at 4.17, 3.69, 3.20–3.11, and 3.08–3.01 ppm from 1,4-pentadiene. Thus the main product has the "*C*<sub>2</sub>" symmetry and the byproduct may have "*C*<sub>s</sub>" symmetry. Since the geminal methylene protons –CH<sub>a</sub>H<sub>b</sub>– for the ligand are different, the 1,4-pentadiene statically bounds the metal. However, we could not separate any isomers by HPLC.

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**Supporting Information Available:** A complete set of tables, giving crystallographic data, atomic coordinates, anisotropic thermal parameters, bond distances, bond angles, and torsion angles (10 pages). Ordering information is given on any current masthead page.

IC950427K

(11) Takemoto, M.; Tomita, A.; Sano, M. To be published.

(12) Considering the RuN<sub>4</sub>C<sub>5</sub> unit neglecting hydrogen atoms, the *C*<sub>2</sub> and *C*<sub>s</sub> symmetries are defined.