

Synthesis and structure of ruthenium(II)–diene complexes

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Abstract

The reaction of $\text{Ru}(\text{acac})_3$ in ethanol in the presence of dienes (diene = 2,5-dimethyl-2,4-hexadiene, isoprene, 1,2,4,5-tetramethyl-1,4-cyclohexadiene) with zinc as reducing agent affords $\text{Ru}(\text{acac})_2(\text{diene})$ complexes. For the acyclic diene ligands, the $\text{Ru}(\text{acac})_2$ unit exhibits a preference for the *trans*-diene coordination. The structures for the 2,5-dimethyl-1,3-hexadiene and 1,2,4,5-tetramethyl-1,4-cyclohexadiene derivatives have been determined crystallographically. The $\text{Ru}(\text{acac})_2(\text{hexadiene})$ complex crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.658(2)$ Å, $b = 12.075(3)$ Å, $c = 15.332(3)$ Å and $\beta = 108.07(5)^\circ$ for $Z = 4$. The cyclohexadiene complex crystallizes in a triclinic space group $P\bar{1}$, with $a = 8.495(4)$ Å, $b = 8.456(4)$ Å, $c = 14.364(6)$ Å, and $\alpha = 78.88(2)^\circ$, $\beta = 82.60(2)^\circ$, $\gamma = 78.04(2)^\circ$ for $Z = 2$. The solid-state structure for the dimethylhexadiene complex revealed an η^4 -*trans*-diene coordination, while for the cyclic diene it revealed isolated olefin interactions.

Keywords: Ruthenium; Diene complexes; *trans*-Diene coordination

1. Introduction

η^4 -*cis*-Diene (I) and enediyl (II) coordination modes are the most common bonding interactions of acyclic conjugated dienes to transition metals [1]. The latter coordination mode is frequently encountered in early transition metals whereas the η^4 -*cis*-diene bonding is characteristic of middle and late transition metals. It is interesting to note that in both coordination modes the diene has adopted the *cis* geometry despite the fact that the *trans* conformer is the predominant isomer for the free diene at ambient temperature.

The η^4 -*trans*-diene coordination (III) to mononuclear complexes was reported for the first time in 1980 with a $\text{ZrCp}_2(\text{butadiene})$ complex [2]. At the present time, there are not many reports concerning metal complexes containing this novel coordination mode [3,4]. These species are of current interest since they should display different bonding and reactivity patterns compared with metal complexes containing an η^4 -*cis*-diene or enediyl coordination mode [5].

Previous research on ruthenium–diene chemistry [3d] showed that the $\text{Ru}(\text{acac})_2$ unit has the ability to bind conjugated diene ligands in the *cis* or *trans* conformation, depending on the ligand geometry. We now wish to report new examples of *trans*-diene coordination of unsymmetrical and highly substituted acyclic diene ligands and the coordination pattern of an unconjugated cyclic diene ligand to $\text{Ru}(\text{acac})_2$. Their structures and bonding patterns are discussed.

2. Experimental

All procedures involving the handling of organometallic compounds were carried either in a glove box or in double manifold vacuum lines. Solvents and liquids were added by glass syringes with stainless steel needles. Hydrocarbon solvents were dried and degassed by distillation over Na/K-benzophenone under nitrogen. All NMR solvents were dried over potassium. Infrared spectra were taken in dried KBr pellets. The NMR spectra were obtained on 300 MHz General Electric and 200 MHz Varian spectrometers. Analytical data were obtained by Atlantic MicroLab Inc.

$\text{Ru}(\text{acac})_3$ was prepared by a published procedure [6]. Diene ligands were obtained commercially from Aldrich.

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2.1. Synthesis of bis(acetylacetonate)(η^4 -2,5-dimethyl-2,4-hexadiene)ruthenium(II), $Ru(C_5H_7O_2)_2(\eta^4$ -2,5- $C_8H_{14})$, **1**

To an ethanolic solution of 0.5 g (1.26 mmol) of $Ru(acac)_3$ was added 1.38 g (12.6 mmol) of 2,5-dimethyl-2,4-hexadiene and 1.0 g of zinc dust under nitrogen. The reaction mixture was refluxed for 6 h, developing an orange-green color. The solvent was removed in vacuo and the residue was extracted with three 15 ml portions of pentane and filtered through a coarse fritted funnel padded with celite. The resulting orange solution was concentrated to about 20 ml and cooled to $-23^\circ C$ for 12 h, precipitating first $Zn(acac)_2$ as a by-product. The supernatant was transferred to another flask, the volume reduced to about 7 ml and cooled to $-23^\circ C$ for 24 h affording a bright-orange, air-stable crystalline solid in 65% yield based on $Ru(acac)_3$.

Infrared data (KBr): 3078(w), 3000(w), 2976(sh), 2945(w), 2893(m), 1575(s), 1517(s), 1446(m), 1403(s), 1365(m), 1264(m), 1064(m), 1024(m), 935(m), 803(m) cm^{-1} . 1H NMR δ (benzene- d_6 , ambient) major isomer: 5.21 (s, 2H), 3.77 (s, 2H), 2.02 (s, 6H), 1.77 (s, 6H), 1.66 (s, 6H), 1.30 (s, 6H). ^{13}C NMR δ (benzene- d_6 , ambient): 186.95 (s, 2C), 184.59 (s, 2C), 98.43 (d, 2C, $J = 155$ Hz), 93.71 (d, 2C, $J = 165$ Hz), 90.60 (s, 2C), 28.03 (q, 2C, $J = 127$ Hz), 27.90 (q, 2C, $J = 127$ Hz), 26.22 (q, 2C, $J = 125$ Hz), 18.94 (q, 2C, $J = 127$ Hz). Anal. Found: C, 52.72; H, 6.88. $C_{18}H_{28}O_4Ru$. Calc.: C, 52.83; H, 6.89%.

2.2. Synthesis of bis(acetylacetonate)(η^4 -2-methyl-1,3-butadiene)ruthenium(II), $Ru(C_5H_7O_2)_2(\eta^4$ -3- $C_5H_8)$, **2**

This yellow air-stable product was prepared in an analogous manner as described for $Ru(\eta^4$ -2,5- $C_8H_{14})(C_5H_7O_2)_2$. The final product is purified by sublimation at $60^\circ C$ and reduced pressure (10^{-2} Torr).

Infrared data (KBr): 3077(w), 2993(w), 2981(w), 2907(w), 1577(s), 1515(s), 1458(m), 1438(m), 1394(s), 1378(s), 1265(m), 1201(m), 1092(w), 1025(m), 936(m), 803(m) cm^{-1} . 1H NMR δ (benzene- d_6 , ambient), iso-

mer I: 5.36 (s, 1H), 5.34 (s, 1H), 3.94 (d, 1H, $J = 7$ Hz), 3.79 (s, 1H), 3.71 (dd, 1H, $J = 7$; 12 Hz), 3.58 (d, 1H, $J = 12$ Hz), 3.21 (s, 1H), 2.00 (s, 3H), 1.99 (s, 3H), 1.73 (s, 3H), 1.70 (s, 3H), 1.33 (s, 3H). ^{13}C NMR δ (benzene- d_6 , ambient): 187.58 (s, 1C), 187.03 (s, 1C), 185.93 (s, 1C), 185.38 (s, 1C), 109.26 (s, 1C), 99.60 (d, 1C, $J = 156$ Hz), 99.36 (d, 1C, $J = 156$ Hz), 97.72 (d, 1C, $J = 166$ Hz), 69.80 (t, 1C, $J = 161$ Hz), 65.39 (t, 1C, $J = 162$ Hz), 27.99 (q, 1C, $J = 125$ Hz), 27.94 (q, 1C, $J = 125$ Hz), 27.71 (q, 1C, $J = 125$ Hz), 27.48 (q, 1C, $J = 127$ Hz), 14.72 (q, 1C, $J = 125$ Hz). 1H NMR δ (benzene- d_6 , ambient), isomer II: 5.49 (s), 5.24(s), 5.08 (s), 4.99 (s), 4.40 (d, $J = 12$ Hz), 4.14(s), 4.11 (s), 3.86 (s), 1.97(s), 1.95(s), 1.88 (broad s), 1.60 (s), 1.59 (s), 1.08 (s). $^{13}C\{^1H\}$ NMR δ 108.7, 98.79, 98.67, 96.41, 69.80, 66.28, 15.37. Other resonances apparently obscured by the major isomer. Anal. Found: C, 48.86; H, 5.99. $C_{15}H_{22}O_4Ru$. Calc.: C, 49.03; H, 6.03%.

2.3. Synthesis of bis(acetylacetonate)(η^4 -1,2,4,5-tetramethyl-1,4-cyclohexadiene)ruthenium(II), $Ru(C_5H_7O_2)_2(\eta^4$ -1,2,4,5- $C_{10}H_{16})$, **3**

To a solution of 0.5 g (1.26 mmol) of $Ru(acac)_3$ in 20 ml of ethanol under nitrogen was added 0.52 g (3.78 mmol) of 1,2,4,5-tetramethyl-1,4-cyclohexadiene and 1.5 g of zinc dust. The reaction mixture was refluxed overnight, resulting in a brown solution. The solvent was removed in vacuo, the unreacted diene sublimed and the crude product extracted with two 15 ml portions of pentane. The brown solution was concentrated to about 10 ml and cooled to $-23^\circ C$, yielding a brick-red air-stable crystalline product (55% yield based on $Ru(acac)_3$).

Infrared data (KBr): 2961(m), 2897(w), 2799(m), 1585(s), 1516(s), 1401(s), 1368(m), 1263(m), 1196(w), 1097(s), 1023(s), 935(w), 802(s) cm^{-1} . 1H NMR δ (benzene- d_6 , ambient): 5.22 (s, 2H), 3.70 (d, 2H, $J = 12$ Hz), 3.23 (d, 2H, $J = 12$ Hz), 2.13 (s, 6H), 1.70 (s, 6H), 1.67 (s, 6H), 1.19 (s, 6H). $^{13}C\{^1H\}$ NMR δ (benzene- d_6 , ambient): 186.38, 185.96, 98.52, 77.65, 76.85, 46.10, 28.60, 26.92, 18.30, 17.67. Anal. Found: C, 54.92; H, 6.88. $C_{20}H_{30}O_4Ru$. Calc.: C, 55.14; H, 6.94%.

2.4. Crystallographic studies

Crystal, data collection, and refinement parameters are given in Table 1. Suitable crystals for single-crystal X-ray diffraction were sectioned and mounted with epoxy cement on thin glass fibers. The unit-cell parameters were obtained by the least squares refinement of the angular settings of 24 reflections ($20 \leq 2\theta \leq 25^\circ$).

Systematic absences in the diffraction data for **1** are uniquely consistent for space group $P2_1/n$. No evidence of symmetry higher than triclinic was observed in either the photographic or diffraction data for **3**. The

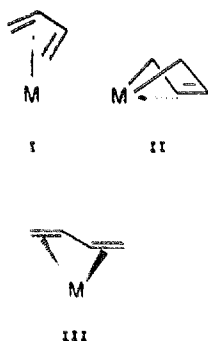


Table 1
Crystallographic data for **1** and **3**

	1	3
<i>Crystal parameters</i>		
Formula	C ₁₈ H ₂₈ O ₄ Ru	C ₂₀ H ₃₀ O ₄ Ru
Formula weight	409.5	435.5
Crystal system	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	10.658(2)	8.495(4)
<i>b</i> (Å)	12.075(3)	8.456(4)
<i>c</i> (Å)	15.332(3)	14.364(6)
α (deg)	–	78.88(2)
β (deg)	108.07(5)	82.60(2)
γ (deg)	–	78.04(2)
<i>V</i> (Å ³)	1876(1)	1010(3)
<i>Z</i>	4	2
Crystal dimensions (mm ³)	0.2 × 0.3 × 0.4	0.2 × 0.2 × 0.3
Crystal color	yellow	orange
<i>D</i> (calc) (g cm ⁻³)	1.450	1.433
μ (MoK α) (cm ⁻¹)	8.52	7.96
Temperature (K)	298	298
<i>T</i> (max)/ <i>T</i> (min)	0.427/0.359	0.532/0.459
<i>Data collection</i>		
Diffractometer	Siemens P4	
Monochromator	graphite	
Radiation	MoK α	
	($\lambda = 0.71073$ Å)	
2 θ scan range (deg)	4.0–47.0	4.0–60.0
Data collected (<i>h, k, l</i>)	± 11, + 13, + 17	± 11, ± 11, + 20
Reflections collected	2834	6099
Independent reflections	2720	5883
Independent observed reflections	2209 (<i>n</i> = 4)	4790 (<i>n</i> = 5)
$F_o \geq nr(F_o)$		
Std./rfln	3/197	3/197
Var. in stds. (%)	< 1	< 1
<i>Refinement</i> ^a		
<i>R</i> (<i>F</i>) (%)	3.03	3.07
<i>R</i> (<i>wF</i>) (%)	4.10	3.77
Δ/σ (max)	0.000	0.002
$\Delta/(e \text{ \AA}^{-3})$	0.39	0.42
<i>N</i> _o / <i>N</i> _v	10.6	21.1
GOF	1.05	1.20

^a Quantity minimized = $\sum w\Delta^2$; $R = \sum \Delta / \sum (F_o)$; $R(w) = \sum \Delta w^{1/2} / \sum (F_o w^{1/2})$; $\Delta = |F_o - F_c|$.

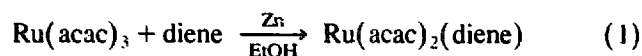
structures were solved by direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least squares procedures. Semi-empirical ellipsoid absorption corrections were applied to the data.

All software and sources of the scattering factors are contained in either the SHELXTL (5.1) or the SHELXTL PLUS (4.2) program libraries (Sheldrick, Siemens XRD, Madison, WI).

3. Results and discussion

Ru(acac)₃ has proved to be a versatile precursor for a variety of organometallic complexes [3d,7]. Thus, the

reaction of Ru(acac)₃ with excess of diene and Zn as reducing agent affords pseudo-octahedral Ru(acac)₂(diene) complexes, in yield greater than 50%. (Eq. (1)).



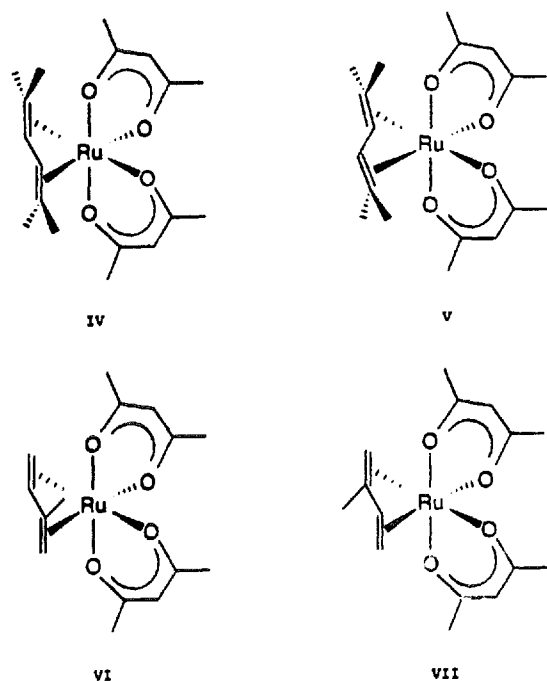
diene = 2,5-dimethyl-2,4-hexadiene, **1**; 2-methyl-1,3-butadiene, **2**; 1,2,4,5-tetramethyl-1,4-cyclohexadiene, **3**.

For the acyclic ligands, the complexes exhibit a η^4 -*trans*-diene coordination mode, as verified by NMR spectroscopy and X-ray diffraction studies (vide infra). All the Ru(acac)₂(diene) complexes show IR bands in the region of 1600–1500 cm⁻¹ corresponding to the C–O functional group of the acac ligands.

The ¹H NMR spectrum of Ru(acac)₂(2,5-dimethyl-2,4-hexadiene), **1**, displays a six-line pattern, indicating the presence of a two-fold rotation axis (*C*₂) as a result of an η^4 -*trans*-diene coordination. An η^4 -*cis*-diene coordination in a pseudo-octahedral environment would lower the symmetry and the two-fold rotation axis will be nonexistent, rendering in a more complex 12-line ¹H NMR pattern. The spectrum of **1** shows four signals at 1.29–2.0 ppm corresponding to the methyl groups of the acac and diene ligands. Only one signal is observed for the Hs attached to the central carbon atoms of the diene ligand (3.77 ppm); also, only one resonance is displayed for the methyne protons of the acac ligands (5.21 ppm).

Another set of resonances (in less than 5% abundance) with a similar splitting pattern can be identified, suggesting the presence of another isomeric species with an η^4 -*trans*-diene coordination. The difference in solubility between these two isomers might explain the small percentage of the second diastereoisomer present in the NMR spectra. In fact, variable-temperature ¹H NMR studies of the 2,5-dimethyl-1,4-hexadiene complex (Supplementary material) showed that at 35 °C initially one species is observed. After 15 min at 35 °C, the second isomeric species with a six-line pattern appears. A ratio of 1:1 is reached after 45 min at 35 °C, which remained unchanged after 5 h. Based on these results, both species should have similar, if not identical, thermodynamic stability [3d].

The ¹³C NMR data for **1** further support the η^4 -*trans*-diene coordination with a very symmetric nine-line pattern. That is, two different sets of methyl groups, one set of C–H and quaternary carbons are displayed for the diene ligand. Furthermore, two different ketonic, C–H and CH₃, groups are clearly evident and belong to the acac ligands. The lack of symmetry brought by the η^4 -*cis*-diene conformation would make all the carbon atoms in the complex unequivalent, yielding an 18-line pattern in the ¹³C NMR spectrum. Two structures can be proposed for this complex in which the Ru(acac)₂ unit has distinguished between the two *trans*-diene enantiofaces, IV and V. However, the exact isomeric



species (IV or V) responsible for the ^1H NMR spectrum splitting pattern cannot be assigned with certainty, though it is clear that in the solid state the diene is bound in the trans conformation, as verified by X-ray diffraction studies.

The structure of $\text{Ru}(\eta^4\text{-}2,5\text{-dimethyl-}2,4\text{-hexadiene})$ is shown in Fig. 1 and pertinent positional and bonding parameters are provided in Tables 2 and 3. A structural study for **1** revealed an $\eta^4\text{-trans}$ -diene coordination for the hexadiene ligand in a pseudo-octahedral coordination environment. The compound pos-

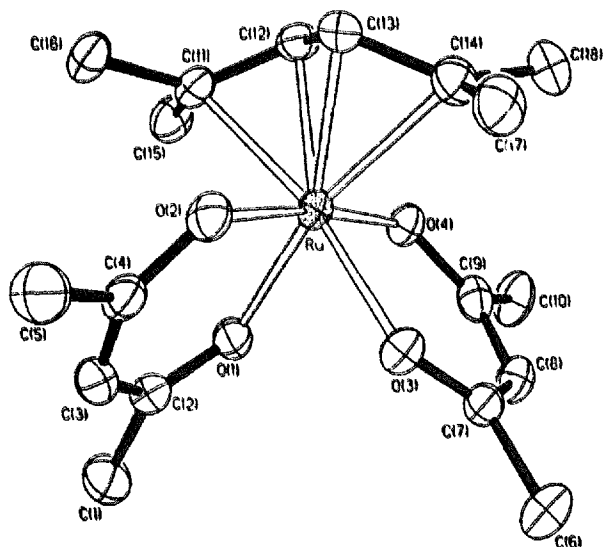


Fig. 1. Solid-state structure of $\text{Ru}(\eta^4\text{-}2,5\text{-C}_8\text{H}_{14})\text{X}(\text{C}_3\text{H}_7\text{O}_2)_2$ drawn with 35% thermal ellipsoids.

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for $\text{Ru}(\text{acac})_2(2,5\text{-dimethyl-}2,4\text{-hexadiene})$, **1**

	x	y	z	U_{eq}^a
Ru	160.6(3)	2009.6(3)	2341.0(2)	34(1)
O(1)	1009(3)	718(2)	3185(2)	42(1)
O(2)	-108(3)	2895(2)	3404(2)	44(1)
O(3)	2024(3)	2661(2)	2842(2)	41(1)
O(4)	653(3)	1052(2)	1405(2)	40(1)
C(1)	1830(5)	-300(4)	4537(4)	66(2)
C(2)	1192(4)	734(4)	4045(3)	46(2)
C(3)	872(4)	1572(4)	4539(3)	50(2)
C(5)	5(5)	3353(5)	4897(3)	67(2)
C(6)	4198(4)	3016(4)	2945(4)	57(2)
C(7)	2934(4)	2404(3)	2516(3)	41(2)
C(8)	2878(4)	1636(4)	1841(3)	45(2)
C(9)	1818(4)	1007(4)	1356(3)	44(2)
C(10)	2010(5)	169(4)	686(3)	62(2)
C(11)	-1827(4)	1210(3)	2118(3)	42(2)
C(12)	-1726(4)	1862(3)	1395(3)	44(2)
C(13)	-1399(4)	2999(4)	1571(3)	43(2)
C(14)	-349(4)	3428(4)	1312(3)	48(2)
C(15)	-1845(4)	-24(3)	2001(3)	56(2)
C(16)	-2496(4)	1578(4)	2796(3)	54(2)
C(17)	236(5)	4509(4)	1717(3)	59(2)
C(18)	-122(5)	3138(4)	420(3)	57(2)
C(4)	278(4)	2564(4)	4225(3)	45(2)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_i tensor.

Table 3

Pertinent bond lengths (\AA) and bond angles (deg) for $\text{Ru}(\text{acac})_2(2,5\text{-dimethyl-}2,4\text{-hexadiene})$, **1**

Bond lengths			
Ru–O(1)	2.049(3)	Ru–O(2)	2.043(3)
Ru–O(3)	2.050(3)	Ru–O(4)	2.034(3)
Ru–C(11)	2.255(4)	Ru–C(12)	2.091(4)
Ru–C(13)	2.089(4)	Ru–C(14)	2.278(5)
O(1)–C(2)	1.271(5)	O(2)–C(4)	1.261(5)
O(3)–C(7)	1.260(6)	O(4)–C(9)	1.268(6)
C(1)–C(2)	1.507(7)	C(2)–C(3)	1.369(7)
C(3)–C(4)	1.371(7)	C(5)–C(4)	1.497(8)
C(6)–C(7)	1.498(6)	C(7)–C(8)	1.378(6)
C(8)–C(9)	1.373(6)	C(9)–C(10)	1.501(7)
C(11)–C(12)	1.391(7)	C(11)–C(15)	1.501(6)
C(11)–C(16)	1.498(7)	C(12)–C(13)	1.421(6)
C(13)–C(14)	1.399(7)	C(14)–C(17)	1.495(6)
C(14)–C(18)	1.502(8)		
Bond angles			
O(1)–Ru–O(2)	92.2(1)	O(1)–Ru–O(3)	82.5(1)
O(2)–Ru–O(3)	81.9(1)	O(1)–Ru–O(4)	81.5(1)
O(2)–Ru–O(4)	172.4(1)	O(3)–Ru–O(4)	92.9(1)
Ru–O(1)–C(1)	122.6(3)	Ru–O(2)–C(4)	123.2(3)
Ru–O(3)–C(7)	122.2(2)	Ru–O(4)–C(9)	122.5(2)
O(1)–C(2)–C(3)	126.9(4)	C(2)–C(3)–C(4)	128.2(4)
O(1)–C(2)–C(1)	114.0(4)	O(3)–C(7)–C(8)	127.2(4)
C(1)–C(2)–C(3)	119.1(4)	C(7)–C(8)–C(9)	128.0(5)
O(3)–C(7)–C(6)	113.8(4)	O(4)–C(9)–C(10)	114.5(4)
C(6)–C(7)–C(8)	119.0(4)	C(12)–C(11)–C(15)	117.9(4)
O(4)–C(9)–C(10)	126.9(4)	C(12)–C(11)–C(16)	123.8(4)
C(8)–C(9)–C(10)	118.6(4)	C(11)–C(12)–C(13)	118.0(4)
C(12)–C(13)–C(14)	118.3(4)	C(13)–C(14)–C(17)	118.2(5)
O(2)–C(4)–C(5)	114.4(4)	O(2)–C(4)–C(3)	126.8(5)
O(3)–C(7)–C(8)	122.8(4)	C(3)–C(4)–C(5)	118.8(4)

esses a pseudo C_2 symmetry as deduced by NMR spectroscopic data. The Ru–C bond distances for the terminal carbon atoms (2.255(4) and 2.278(5) Å) are considerably longer than the Ru–C(internal) bonds (2.091(4) and 2.089(4) Å). The diene skeleton exhibits a carbon–carbon bond pattern of short (C(11)–C(12), 1.391(7) Å), long (C(12)–C(13), 1.421(6) Å), short (C(13)–C(14), 1.399(7) Å), characteristic of a neutral free diene. Although the diene is attached in the trans conformation, the Ru–C bonding patterns (Ru–C(terminal) > Ru–C(internal)) are similar to those of the η^4 -*cis*-diene coordination in the previously reported $Ru(acac)_2$ (cyclohexadiene) complex [3d]. The Ru–O bond distances range from 2.034(3) to 2.050(3) Å. Notably, Ru–O(4) is shorter than the rest of the Ru–O bonds. This shortening results in a lengthening of the Ru–C(14) bond apparently due to steric crowding. The O–Ru–O angles within the chelates(acac) average 92.6(1)° while the interligand (*cis*) O–Ru–O angles range from 81.5(1) to 82.5(1)°. The trans O–Ru–O angle is 172.4(1)°.

The diene fragment is nonplanar with a torsion angle of 122°, equivalent to a tilt of the C(11)–C(12) and C(13)–C(14) bonds of 29° toward the Ru atom. For comparison, similar patterns have been observed in $Ru(acac)_2(\eta^4$ -*trans*-2,4-dimethyl-1,3-pentadiene) with a torsion angle of 123° and a tilt of the olefinic units of 28° [3d].

The use of an unsymmetric diene leads to the formation of more isomeric species, complicating the structure assignment by NMR spectroscopy, as is the case of $Ru(acac)_2$ (isoprene) complex. Four diastereoisomers can exist, two involving the *cis* coordination and two with the *trans* diene coordination, as shown in VI and VII.

Furthermore, the nature of the ligand increases the number of resonances in the NMR spectra even if the diene attains the *trans* conformation, due to its unsymmetrical substitution. We have characterized this complex using 2D COSY and 2D NOE spectral data (see Supplementary material) and by comparing its 1H NMR spectrum to that of $Ru(benzene)(\eta^4$ -*cis*-isoprene) complex [8] and of the closely related $Ru(acac)_2(\eta^4$ -*trans*-2,3-dimethyl-1,3-butadiene) [3d]. The COSY spectrum of the $Ru(acac)_2$ (isoprene) complex contains one major isomeric species with a 12-line pattern and another isomeric species in less than 10% abundance, partially obscured by the major isomer. The olefinic region from 3–4.5 ppm is perhaps the most important region which exhibits resonances corresponding to the isoprene ligand. Two singlets at 3.21 and 3.80 ppm and two doublets at 3.57 and 3.96 ppm can be readily identified and correspond to the protons attached to the terminal carbon atoms of the diene ligand. The multiplet at 3.70 ppm can be attributed to the hydrogen attached to the unmethylated internal carbon atom of the isoprene, which exhibits coupling to the terminal protons located

at 3.57 and 3.96 ppm. The isoprene ligand is believed to be bound in the *trans* conformation based on the following arguments. The NOESY spectrum, in the olefinic region of the diene, revealed a strong correlation between the hydrogens attached to the same terminal carbon atom. However, no correlation is observed between the two endo protons (3.21 and 3.58 ppm) of the two terminal carbon atoms of the isoprene ligand, which supports the presence of the diene in the *trans* conformation. Otherwise, a correlation between the two endo protons of the terminal carbons would have been observed. The *cis*-diene conformer typically exhibits a larger chemical shift difference between endo(*anti*) and exo(*syn*) protons of the diene ligand [5,8,9]. The rather small chemical shift difference between the *syn* and *anti* protons (*exo* and *endo*), as well as its resonance pattern, strongly support our proposed structures. Also, the geminal protons of the diene show no measurable coupling between them, suggesting the diene has adopted the *trans* conformation.

The preference of the $Ru(acac)_2$ unit to bind conjugated dienes in the *trans* conformation is clearly evident, at least for acyclic diene ligands. However, the $Ru(acac)_2$ unit is also able to bind conjugated dienes in the *cis* conformation, as is the case for the $Ru(acac)_2$ (1,3-cyclohexadiene) complex [3d]. As a result, it was of interest to explore the coordination properties of a nonconjugated cyclic diene to the $Ru(acac)_2$ unit. Indeed, the coordination of a more rigid but symmetric cyclic diene, 1,2,4,5-tetramethyl-1,4-cyclohexadiene, can be attained by $Ru(acac)_2$ unit.

The 1H and ^{13}C NMR spectral data for $Ru(acac)_2$ (1,2,4,5-tetramethyl-1,4-cyclohexadiene) show a very symmetric environment, suggesting the presence of a two-fold rotation axis in the complex, as a result of the diene being symmetrically coordinated to the metal center, at least in solution. Despite the simplicity of the NMR spectral data, we pursued the determination of the solid-state structure for this complex. The solid-state structure of **3** is depicted in Fig. 2 and related structural data are presented in Tables 4 and 5.

The solid-state structure of **3** revealed the diene is coordinated in a pseudo-octahedral environment. The diene did not undergo isomerization from 1,4- to a more conjugated 1,3-diene. Ru–O bonds are almost identical (2.068(2), 2.072(2), 2.068(2) and 2.066(2) Å) but considerably longer than Ru–O bonds for the 2,5-dimethyl-2,4-hexadiene complex, **1**.

The intraligand O–Ru–O angles for acac are 89.3(1)°, the *cis* O–Ru–O angles range from 80.7(1) to 87.4(1)° and the *trans* O–Ru–O angle is 166.3(1)°. When compared with the *trans*-hexadiene complex, **1**, we observe a contraction of the *trans* and intraligand O–Ru–O angles as we change from an acyclic to a cyclic diene. It seems that the cyclic diene is sterically more demanding than the acyclic diene. This increase in steric demands

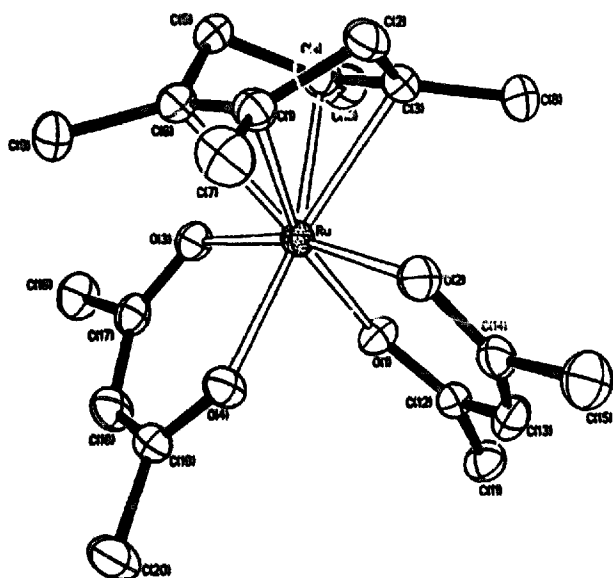


Fig. 2. Solid-state structure of $\text{Ru}(\eta^4\text{-}1,2,4,5\text{-C}_{10}\text{H}_{16})(\text{C}_5\text{H}_7\text{O}_2)_2$ drawn with 35% thermal ellipsoids.

by the cyclic diene is reflected in longer Ru–O bond distances (vide infra) compared with the hexadiene complex. Similar patterns have been observed in $\text{Ru}(\text{acac})_2(1,3\text{-cyclohexadiene})$ vs. $\text{Ru}(\text{acac})_2(2,4\text{-dimethyl-}1,3\text{-pentadiene})$ [3d].

Table 4

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for $\text{Ru}(\text{aca})_2(1,2,4,5\text{-tetramethyl-}1,4\text{-cyclohexadiene})$, 3

	x	y	z	U_{eq}^a
Ru	2497(2)	2414(2)	7477.6(1)	30(1)
O(1)	4636(2)	761(2)	7452(1)	38(1)
O(2)	2964(2)	3192(2)	6030(1)	40(1)
O(3)	2608(2)	1642(2)	8927(1)	38(1)
O(4)	3862(2)	4105(2)	7533(1)	39(1)
C(1)	206(3)	4003(3)	7083(2)	43(1)
C(2)	-181(3)	2871(3)	6496(2)	46(1)
C(3)	855(3)	1276(3)	6863(2)	41(1)
C(4)	725(3)	789(3)	7837(2)	40(1)
C(5)	-435(3)	1909(3)	8413(2)	45(1)
C(6)	67(3)	3516(3)	8058(2)	42(1)
C(7)	295(4)	5692(3)	6594(3)	60(1)
C(8)	1598(3)	179(3)	6163(2)	53(1)
C(9)	-19(3)	4602(4)	8770(2)	55(1)
C(10)	1312(4)	-891(3)	8324(2)	54(1)
C(11)	7224(3)	-525(3)	6950(2)	49(1)
C(12)	5712(3)	698(3)	6760(2)	36(1)
C(13)	5608(3)	1632(3)	5864(2)	46(1)
C(14)	4281(3)	2759(3)	5545(2)	41(1)
C(15)	4342(4)	3522(4)	4515(2)	61(1)
C(16)	3368(4)	1317(4)	10464(2)	56(1)
C(17)	3462(3)	2112(3)	9431(2)	40(1)
C(18)	4405(3)	3282(3)	9144(2)	47(1)
C(19)	4537(3)	4218(3)	8249(2)	38(1)
C(20)	5550(4)	5494(4)	8076(2)	58(1)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 5

Pertinent bonding lengths (\AA) and bond angles (deg) for $\text{Ru}(\text{acac})_2(1,2,4,5\text{-tetramethyl-}1,4\text{-cyclohexadiene})$, 3

Bond lengths			
Ru–O(1)	2.068(2)	Ru–O(2)	2.072(2)
Ru–O(3)	2.068(2)	Ru–O(4)	2.066(2)
Ru–C(1)	2.208(3)	Ru–C(3)	2.218(3)
Ru–C(4)	2.216(3)	Ru–C(6)	2.217(3)
O(1)–C(12)	1.263(3)	O(2)–C(14)	1.266(3)
O(3)–C(17)	1.260(4)	O(4)–C(19)	1.269(3)
C(1)–C(2)	1.517(5)	C(1)–C(6)	1.381(4)
C(1)–C(7)	1.507(4)	C(2)–C(3)	1.514(3)
C(3)–C(4)	1.379(4)	C(3)–C(8)	1.506(4)
C(4)–C(5)	1.516(4)	C(4)–C(10)	1.499(3)
C(5)–C(6)	1.514(4)	C(6)–C(9)	1.502(5)
C(11)–C(12)	1.503(3)	C(12)–C(13)	1.384(3)
C(13)–C(14)	1.393(4)	C(14)–C(15)	1.498(4)
C(16)–C(17)	1.509(4)	C(17)–C(18)	1.389(4)
C(18)–C(19)	1.386(4)	C(19)–C(20)	1.501(4)
Bond angles			
O(1)–Ru–O(2)	89.3(1)	O(1)–Ru–O(3)	80.7(1)
O(2)–Ru–O(3)	166.3(1)	O(1)–Ru–O(4)	87.4(1)
O(2)–Ru–O(4)	80.9(1)	O(3)–Ru–O(4)	89.3(1)
C(3)–Ru–C(4)	36.2(1)	C(1)–Ru–C(6)	36.4(1)
C(3)–Ru–C(6)	76.9(1)	Ru–O(2)–C(14)	124.6(2)
Ru–O(1)–C(12)	125.7(1)	Ru–O(4)–C(19)	126.0(2)
Ru–O(3)–C(17)	124.8(2)	C(3)–C(4)–C(5)	116.3(2)
C(1)–C(6)–C(5)	116.1(3)	C(5)–C(6)–C(9)	117.8(2)
O(1)–C(12)–C(11)	115.4(2)	O(1)–C(12)–C(13)	126.0(2)
O(2)–C(14)–C(13)	126.8(2)	O(2)–C(14)–C(15)	114.7(2)
O(3)–C(17)–C(18)	127.2(2)	O(4)–C(19)–C(20)	115.0(2)
C(17)–C(18)–C(19)	126.5(3)	O(3)–C(17)–C(16)	114.2(2)
C(12)–C(13)–C(14)	126.7(2)	O(4)–C(19)–C(18)	125.6(3)

The Ru–C bonds are all very similar (2.208(3)–2.218(3) \AA) and in general are slightly shorter than for the hexadiene complex. In contrast to the hexadiene complex, a pattern of Ru–C(terminal) bonds longer than Ru–C(internal) bonds is not observed for the 1,2,4,5-tetramethyl-1,4-cyclohexadiene complex, owing to the nonconjugated nature of the diene ligand. Furthermore, as a free diene, all four olefinic carbon atoms of the 1,2,4,5-tetramethyl-1,4-cyclohexadiene are equivalent, but upon coordination, owing to the C_2 symmetry of the $\text{Ru}(\text{acac})_2$ unit, C(3) and C(6) are not necessarily equivalent to C(1) and C(4). Nevertheless, upon examination of the Ru–C bond distances, it seems that these differences are marginal and no major distortion of the olefinic units are detected in the structure. Thus, the complex can be considered as a ruthenium–bis(olefin) variant.

In general, 1 and 3 are structurally similar pseudo-octahedral complexes but with some differences in the Ru–C and Ru–O bond distances. Their similarity can be extended to $\text{Ru}(\text{acac})_2(1,3\text{-cyclohexadiene})$ and $\text{Ru}(\text{acac})_2(\textit{trans}\text{-}2,4\text{-dimethyl-}1,3\text{-pentadiene})$ complexes. That is, cyclic diene complexes exhibit shorter Ru–C bond distances than acyclic diene complexes. The opposite trend is observed in the Ru–O bond distances, the acyclic diene complexes exhibiting shorter

Ru–O bonds. This behavior is supported by previous molecular orbital calculations for other *trans*-diene complexes. Legzdins and co-workers [10] have suggested that *trans*-diene coordination occurs when the ligand to metal bond interaction (ligand donation) is more important than metal to ligand (π -backbonding) interaction, at least for molybdenum species.

In our case, for Ru–*trans*-diene complexes, this rationale could be invoked, since better ligand to metal donation will make the metal center more electron rich, yielding shorter and presumably stronger Ru–O bonds. This is the trend observed in Ru(acac)₂(2,5-dimethyl-2,4-hexadiene) and Ru(acac)₂(2,4-dimethyl-1,3-pentadiene) [3d] complexes. Besides the electronic factors, steric effects can also be present in the acyclic conjugated diene complexes but to a lesser extent. Although it is clear that the η^4 -*cis*-diene coordination of 2,5-dimethyl-2,4-hexadiene would experience unfavorable steric interactions brought by the two endo methyl groups, for isoprene or 2,3-dimethyl-1,3-butadiene [3d] ligands, such interactions are not present and the η^4 -*trans*-diene coordination still prevails.

The Ru(acac)₂ unit has demonstrated the capability to coordinate a wide variety of diene ligands, both cyclic and acyclic, containing conjugated and unconjugated double bonds. It also shows a thermodynamic preference for η^4 -*trans*-diene coordination and the ability to distinguish between diene enantiofaces. The above properties are of interest for the selective preparation of nontrivial natural products of biological importance. At the present time, we have activated 1-methoxy-3-(trimethyl-siloxy)-1,3-butadiene with an Ru(acac)₂ unit [11], a precursor for the synthesis of a natural product [12]. The use of this complex in the synthesis of natural products will be investigated.

4. Supplementary material

Tables of anisotropic thermal parameters, hydrogen atoms parameters (4 pages) and structure factors (21 pages). ¹H NMR of **1** and NOESY and COSY spectra of **2** are available. Ordering information may be found on any current masthead page.

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References and notes

- [1] J.R. Collman, L.S. Hege, J.R. Norton and R.G. Finke, (Eds.), *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987.
- [2] G. Erker, J. Wicher, K. Engel, F. Rosenfelt, W. Dietrich and C. Kruger, *J. Am. Chem. Soc.*, **102** (1980) 6344.
- [3] (a) Y. Kai, N. Kanehisa, K. Miki, N. Kasai, K. Mashima, K. Nagasuna, H. Yasuda and A. Nakamura, *J. Chem. Soc. Chem. Commun.* (1982) 191. (b) A.D. Hunter, P. Legzdins, C.R. Nurse, F.W.B. Einstein and A.C. Willis, *J. Am. Chem. Soc.*, **107** (1985) 1791. (c) E. Meléndez, A.M. Arif, A.L. Rheingold and R.D. Ernst, *J. Am. Chem. Soc.*, **110** (1988) 8703. (d) R.D. Ernst, E. Meléndez, L. Stahl and M.L. Ziegler, *Organometallics*, **10** (1991) 3635.
- [4] (a) Other complexes have been reported containing η^4 -*trans*-diene coordination but their structure have been elucidated using NMR spectroscopic data and not on X-ray diffraction studies [4b–e]. (b) T. Okamoto, H. Yasuda, A. Nakamura, Y. Kai, N. Kanehisa and N. Kasai, *J. Am. Chem. Soc.*, **110** (1988) 5008. (c) S.A. Benyunes, J.P. Day, M. Green, A.W. Al-Saadoon and T.L. Waring, *Angew. Chem. Int. Ed. Engl.*, **29** (1990) 1416. (d) S.A. Benyunes, M. Green and M.J. Grimshire, *Organometallics*, **8** (1989) 2268. (e) P.J. Fagan, W.S. Mahoney, J.C. Calabrese and T.D. Williams, *Organometallics*, **9** (1990) 1843.
- [5] (a) G. Erker, C. Krüger and G. Müller, *Adv. Organomet. Chem.*, **24** (1985) 1. (b) H. Yasuda, A. Nakamura, *Angew. Chem. Int. Ed. Engl.*, **26** (1987) 723.
- [6] A. Johnson and G.W. Everett, Jr., *J. Am. Chem. Soc.*, **94** (1972) 1419.
- [7] (a) C. Potvin and G. Pannetier, *J. Less-Common Met.*, **22** (1970) 91. (b) C. Potvin, J.M. Manoli, A. Dereigne, G. Pannetier, *J. Less-Common Met.*, **25** (1971) 373. (c) P. Powell, *J. Organomet. Chem.*, **65** (1974) 89.
- [8] J. Müller, K. Qiao, M. Siewing and B. Westphal, *J. Organomet. Chem.*, **458** (1993) 219.
- [9] For coordinated acyclic diene ligands in the *cis* conformation, the endo protons experience more shielding by the metal than the exo protons, resulting in a large chemical shift difference between them, as is the case for CpMo(CO)₂(diene) [4d] and Cp⁺Ru(η^4 -2,3-dimethyl-1,3-butadiene)Cl [4e] species.
- [10] A.D. Hunter, P. Legzdins, F.W.B. Einstein, A.C. Willis, B.E. Burten and M.G. Gatter, *J. Am. Chem. Soc.*, **108** (1986) 3843.
- [11] Initial characterization of Ru(acac)₂(1-methoxy-3-(trimethyl-siloxy)-1,3-butadiene) has been pursued. ¹H NMR δ (benzene-d₆, ambient): 6.51 (d, 1H, *J* = 9 Hz), 5.39 (s, 1H), 5.38 (s, 1H), 3.61 (s, 1H), 3.47 (d, 1H, *J* = 9 Hz), 3.26 (s, 3H), 2.89 (s, 1H), 2.00 (s, 3H), 1.98 (s, 3H), 1.74 (s, 3H), 1.71 (s, 3H), 0.16 (s, 9H).
- [12] (a) S. Danishefsky, N. Kato, D. Askin and J.F. Kerwin, Jr., *J. Am. Chem. Soc.*, **104** (1982) 358. (b) S. Danishefsky, M. Hiram, K. Gombatz, T. Harayama, E. Berman and P. Schuda, *J. Am. Chem. Soc.*, **100** (1978) 6536. (c) R. Boeckman, Jr., T.M. Dolak and K.O. Culos, *J. Am. Chem. Soc.*, **100** (1978) 7098.