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Structure and redox behavior of Ru(II)-diene complexes

Enrique Meléndez [a,*], Vilmarí López [a], Thomas Concolino [b], Arnold L. Rheingold [b,1]

[a] Department of Chemistry, University of Puerto Rico, P.O. Box 9019, Mayaguez, PR 00681, USA
[b] Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA

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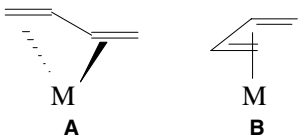
Abstract

A series of Ru(acac)$_2$(η^4-diene) complexes containing *cis*- and *trans*-diene coordination have been investigated by cyclic voltammetry to correlate structural bonding and conformation patterns of diene ligands with redox behaviors. The solid-state structure of Ru(acac)$_2$(2,3-dimethyl-1,3-butadiene) has been determined by single crystal X-ray diffraction methods. Ru(acac)$_2$(2,3-dimethyl-1,3-butadiene) crystallizes in the monoclinic space group $C2/c$ with $a = 12.368(2)$ Å, $b = 17.0600(2)$ Å, $c = 16.0110(2)$ Å, $\beta = 98.4405(10)°$ and $V = 3341.38(10)$ Å^3 for $Z = 8$. A structural comparison between several Ru-*trans*-η^4-diene complexes and Ru-η^4-1,3-cyclohexadiene revealed no difference in the Ru–C(diene) bond distances. However, through cyclic voltammetry experiments these species demonstrated different redox behavior, as function of the coordinated diene ligand.

Keywords: *trans*-η^4-Diene coordination; *cis*-η^4-Diene coordination Ru(II)-diene; Cyclic voltammetry; Solid-state structure

1. Introduction

Tris(acetylacetonato)ruthenium(III), Ru(acac)$_3$, has been a versatile precursor for many inorganic and organometallic complexes [1–5]. In the past, our research group has reported the solid-state structure of a series of Ru(acac)$_2$(diene) complexes in which for acyclic diene exhibited a rather unusual *trans*-η^4-diene coordination (A), while for the cyclic diene, the *cis*-η^4-diene coordination (B) is observed due to geometric constrains [1,2,6]. Particularly interesting for the η^4-*trans*-diene coordination is that two diastereisomers, I and II (Fig. 1), are observed depending on which enantiophase is coordinated by Ru(acac)$_2$ [1,2,6]. NMR studies on the Ru-acyclic diene complexes have shown that both Ru-η^4-*trans*-diene diastereisomers interconvert each other and have about the same thermodymanic stability in solution while the *cis*-diene coordination is only present in less than 10% at high temperature (85 °C) [2]. Thus, there is a thermodynamic preference for the *trans*-diene coordination over the *cis* when bound to Ru(acac)$_2$.



It is known that there exists a relationship between diene conformation and reactivity patterns when the diene is coordinated to metal centers. The remarkable differences between η^4-*cis*- and *trans*-η^4-diene coordina-

* Corresponding author. Tel.: +1-787-8324040x2524; fax: +1-787-2653849.
E-mail address: emelendez@uprm.edu (E. Meléndez).
[1] Present address: Department of Chemistry, University of California, San Diego, La Jolla, CA 92093, USA.

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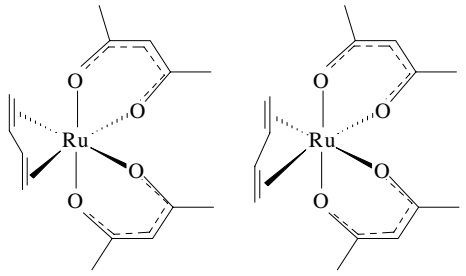

I II

Fig. 1. Two diastereoisomers of *trans*-diene coordination.

tion have been used for the synthesis and design of many non-trivial products [7–9]. In addition, the structural studies of metal complexes containing η^4-*cis*-diene coordination are extensive but the corresponding structural data on η^4-*trans*-diene coordination is more limited. As part of our research program aimed at the understanding of bonding properties of $Ru(acac)_2$ unit toward diene ligands, we have studied the solid-state structure of $Ru(acac)_2$(2,3-dimethyl-1,3-butadiene) and the cyclic voltammetry of a series of Ru(II)-diene complexes of known solid-state structures, to correlate structure and redox patterns. Herein we report our findings.

2. Experimental

2.1. Methods and materials

All procedures involving handling of organometallic compounds were carried out under an atmosphere of prepurified nitrogen either in a glove box or in double manifold vacuum lines. Solvents and solutions were added by glass syringes with stainless steel needles. Solvents were distilled over K and a nitrogen atmosphere. ^1H spectra were recorded on a 500 MHz Avance Bruker spectrometer under controlled temperature. TMS was used as internal reference.

Electrochemical characterization was carried out on a BAS CV-50W voltammetric analyzer. $Ru(acac)_2$(diene) solutions were prepared at a 1 mM concentration in previously dried (over K) THF, using $[NBu^n4][ClO_4]$ as supporting electrolyte in a concentration of 100 mM. The CV analyses were performed using the following parameters: the initial potential was 0 mV and the maximum potential was 1100 mV, the scan rates were of 30 and 100 mV/s and, each sample was purged with nitrogen gas ultrapure (UHP 99.999%) for 120 s to remove oxygen from the solution. The three electrodes used were Pt as the working electrode, an Ag/AgCl as a reference electrode, and a Pt wire as an auxiliary electrode. The working electrode was polished with 0.05 μm alumina slurry for 1–2 min, and then rinsed with deionized water and THF. Blank CV experiments were carried out in fresh THF solutions containing 1 mM of the diene ligands and $[NBu^n4][ClO_4]$ as supporting electrolyte in a concentration of 100 mM and demonstrated to be electrochemically inactive between 0 and 1100 mV.

2.2. General synthesis and NMR spectroscopic data

To an ethanolic solution of 0.25 g (63 mmol) of $Ru(acac)_3$ was added 630 mmol of the corresponding diene and 1 g of activated zinc under nitrogen. The reaction mixture was refluxed for 6 h yielding an orange-green solution. The solvent was removed in vacuo and the product was extracted with two 15 mL portions of fresh destilled pentane and filtered through a coarse fritted funnel padded with Celite. The filtrate was concentrated to about 5 mL and cooled for several days at 0 °C, obtaining a light orange (for acyclic ligands) or brown (for cyclic ligand) crystals in 65–70% yield. NMR data were acquired in a Bruker 500 MHz NMR spectrometer and

Table 1
Crystal data and structure refinement for $Ru(acac)_2$(2,3-dimethyl-1,3-butadiene)

Empirical formula	$C_{16}H_{24}O_2Ru$
Formula weight	349.42
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions	$a = 12.3668(2)$ Å, $\alpha = 90°$ $b = 17.0600(2)$ Å, $\beta = 98.4405(10)°$ $c = 16.0110(2)$ Å, $\gamma = 90°$
Volume	3341.38(10) Å^3
Z	8
Density (calculated)	1.389 Mg/m^3
Absorption coefficient	0.935 mm^{-1}
F(000)	1440
Crystal size	$0.20 \times 0.10 \times 0.10$ mm^3
θ Range for data collection	2.05–28.34
Index ranges	$-16 \leqslant h \leqslant 16$, $0 \leqslant k \leqslant 21$, $0 \leqslant l \leqslant 21$
Reflections collected	7065
Independent reflections	3618 [$R_{int} = 0.0476$]
Completeness to theta = 28.34	86.7%
Absorption correction	Empirical from DIFABS
Max. and min. transmission	1.000 and 0.611
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3618/0/191
Goodness-of-fit on F^2	1.428
Final *R* indices[a] [$I > 2\sigma(I)$]	$R_1 = 0.0587$, $wR_2 = 0.1716$
R indices[a] (all data)	$R_1 = 0.0698$, $wR_2 = 0.1867$
Largest difference peak and hole	1.302 and −0.910 e Å^{-3}

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \{\sum[\omega(F_o^2 - F_c^2)^2] / \sum[\omega(F_o^2)^2]\}^{1/2}$; $\omega = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \max(F_o, 0)]/3$.

showed to be identical to the previous published data [1,2,6], see Supplementary Materials.

2.3. Crystallographic studies

Suitable crystals for single X-ray diffraction studies were obtained by cooling to 0–5 °C a concentrated hexane solution of $Ru(acac)_2$(2,3-diemthyl-1,3-butadiene) for 3 days. Diffraction intensity data were collected with a Bruker P4/CCD diffractometer at 173 K. Crystal data, details of data collection and refinement parameters are given in Table 1. The space group was suggested from systematic absences in the diffraction data and the distribution of normalized *E*-values. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full matrix least-squares procedures on F^2. DIFABS absorption corrections were applied ($T_{min}/T_{max} = 0.61$). All non-hydrogen atoms were refined with anisotropic displacement coefficients. Positions of the H atoms were calculated. All software and sources of scattering factors are contained in the SHELXTL (5.10) program package (G. Sheldrick, Bruker XRD, Madison, WI).

3. Results

The reaction of $Ru(acac)_3$ in the presence of a 10-fold excess of diene, 95% ethanol and zinc as reducing agent affords the corresponding Ru(II)-diene complex in about 65–70% yield,

$$Ru(acac)_3 + \text{xs diene} \xrightarrow[EtOH]{Zn} Ru(acac)_2(\text{diene}) \qquad (1)$$

diene = 2,3-dimethyl-1,3-butadiene, 2,5-dimethyl-2,4-hexadiene, 2,4-hexadiene, 2,4-dimethyl-1,3-pentadiene, 1,3-cyclohexadiene.

This reaction scheme has been used in the past for the synthesis of Ru-diene complexes [6]. The substitution of anhydrous ethanol for 95% ethanol increased the yield by 15% and afforded the product as pure crystalline product without any contamination from $zinc(acac)_2$, as previously reported [6]. As reported previously, $Ru(acac)_2$ fragment has thermodymanic preference for η^4-*trans*-diene coordination in contrast to the common η^4-*cis*-diene coordination [1,2,6]. While spectroscopic data demonstrated that the isolated crystals contain one predominant Ru(η^4-*trans*-diene) diastereoisomer (as result of lower degree of solubility), in solution interconversion between diastereoisomers I and II (Fig. 1) takes place reaching to an isomeric ratio of 1:1 in about 30–60 min at room temperature. This suggests that both diastereisomers have very similar, if not identical, thermodymanic stability but different degree of solubility. The chemical nature of the $Ru(acac)_2$(2,3-dimethyl-1,3-butadiene) complex was investigated by X-ray crystallographic methods. In addition, we have analyzed by cyclic voltammetry a series of Ru-diene complexes to elucidate trends between the redox behaviors and structural patterns.

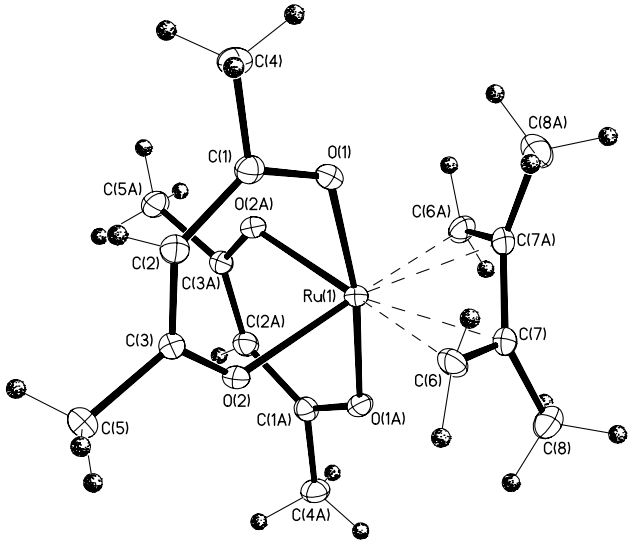

Fig. 2. Solid-state structure of $Ru(acac)_2$(2,3-diemethyl-1,3-butadiene) drawn with 30% thermal ellipsoids.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Ru(acac)_2$(2,3-dimethyl-1,3-butadiene)

	x	*y*	*z*	*U*(eq)
Ru(1)	0	4621(1)	2500	20(1)
Ru(1′)	0	−919(1)	2500	21(1)
O(1′)	−1088(3)	−1819(2)	2157(2)	26(1)
O(1)	−1066(3)	4709(2)	1392(2)	24(1)
O(2)	959(3)	5526(2)	2165(2)	26(1)
O(2′)	639(3)	−1001(2)	1390(2)	28(1)
C(1)	−1005(4)	5238(3)	847(3)	24(1)
C(1′)	−1205(4)	−2145(3)	1433(3)	25(1)
C(2)	−164(4)	5784(3)	846(3)	26(1)
C(2′)	−605(4)	−1992(3)	787(4)	31(1)
C(3)	728(4)	5909(3)	1480(3)	26(1)
C(3′)	295(4)	−1478(3)	796(3)	29(1)
C(4′)	−2087(4)	−2763(3)	1312(4)	33(1)
C(4)	−1928(4)	5245(3)	131(3)	30(1)
C(5)	1549(4)	6541(3)	1349(4)	31(1)
C(5′)	926(5)	−1492(3)	76(4)	38(1)
C(6′)	−1181(4)	−108(3)	1779(4)	31(1)
C(6)	938(4)	3808(3)	1806(4)	31(1)
C(7′)	−587(4)	259(3)	2491(4)	27(1)
C(7)	581(4)	3438(3)	2494(4)	28(1)
C(8)	1390(5)	3133(3)	3223(4)	39(1)
C(8′)	−1139(4)	577(4)	3202(4)	39(1)

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table 3
Selected bond lengths (Å) and angles (°) for $Ru(acac)_2$(2,3-dimethyl-1,3-butadiene)

Bond lengths			
Ru(1)–O(1)#1	2.054(3)	Ru(1′)–O(2′)#1	2.054(4)
Ru(1)–O(1)	2.055(3)	Ru(1′)–O(2′)	2.054(4)
Ru(1)–O(2)#1	2.065(3)	Ru(1′)–O(1′)	2.063(3)
Ru(1)–O(2)	2.065(3)	Ru(1′)–O(1′)	2.063(3)
Ru(1)–C(7)	2.141(5)	Ru(1′)–C(7′)	2.136(5)
Ru(1)–C(7)#1	2.141(5)	Ru(1′)–C(7′)#1	2.136(5)
Ru(1)–C(6)	2.210(5)	Ru(1′)–C(6′)	2.209(4)
Ru(1)–C(6)#1	2.210(5)	Ru(1′)–C(6′)#1	2.209(4)
Bond angles			
O(1)#1–Ru(1)–O(1)	171.57(18)	O(1)#1–Ru(1)–O(2)#1	92.35(13)
O(1)–Ru(1)–O(2)#1	81.32(13)	O(1)#1–Ru(1)–O(2)	81.32(13)
O(1)-Ru(1)–O(2)	92.35(13)	O(2)#1–Ru(1)–O(2)	83.2(2)
O(2′)#1–Ru(1′)–O(2′)	172.17(19)	O(2′)#1–Ru(1′)–O(1′)	82.02(14)
O(2′)–Ru(1′)–O(1′)	92.13(14)	O(2′)#1–Ru(1′)–O(1′)#1	92.13(14)
O(2′)–Ru(1′)–O(1′)#1	82.02(14)	O(1′)–Ru(1′)–O(1′)#1	83.73(19)

3.1. Solid-state structure of $Ru(acac)_2$(2,3-dimethyl-1,3-butadiene)

The solid-state structure of $Ru(acac)_2$(2,3-dimethyl-1,3-butadiene) complex is shown in Fig. 2 and the positional (atomic coordinates) and selected bonding parameters are provided in Tables 2 and 3. The unit cell has two crystallographically independent but chemically identical half molecules. The discussion of geometrical features will be addressed on one molecule since both have almost identical bonding patterns. X-ray analysis of $Ru(acac)_2$(2,3-dimethyl-1,3-butadiene) complex revealed that the diene is bound to Ru(II) in a less common η^4-*trans* coordination. The complex has a pseudo octahedral coordination environment occupied by four oxygens from acac and two olefinic units from the diene ligand. The intraligand (*cis*) Ru-acac angles [O(1)–Ru–O(2) and O(1)#1–Ru–O(2)#1 92.35(13)°] are within the expected octahedral values, while the interligand *cis* [O(1)–Ru–O(2)#1 81.32(13)° and O(2)#1–Ru–O(2) 83.2(2)°] and *trans* [O(1)#1–Ru–O(1) 171.57(18)°] angles showed contractions from the ideal octahedral angles apparently to make room for the diene coordination.

The Ru–C bond distances in the diene interaction revealed a pattern of Ru–C(internal) < Ru–C(terminal) (2.141(5) vs. 2.210(5) Å), as previously observed for other $Ru(acac)_2$diene complexes [1,2,6]. These patterns indicate that the *trans*-η^4-diene coordination has no contribution from the enediyl bonding character, analogous to the *cis*-η^4-diene coordination. In fact, there are no remarkable differences in terms of Ru–C bond distances between a diene coordinated in *cis* or *trans* conformation, see Table 4. The C–C bond distances within the butadiene skeleton also showed a typical short-long-short pattern for conjugated diene ligand.

Table 4
Ruthenium–carbon bond distances of a series of $Ru(acac)_2$(diene) complexes

Complex	Ru–C(t) (Å)	Ru–C(i) (Å)	Reference
$Ru(acac)_2$ (1,3-cyclohexadiene)	2.236(3)	2.120(3)	[2]
$Ru(acac)_2$ (2,4-dimethyl-1,3-pentadiene)	2.291(3) 2.196(3)	2.107(3) 2.146(3)	[2]
$Ru(acac)_2$ (2,5-dimethyl-2,4-hexadiene)	2.255(4) 2.278(5)	2.091(4) 2.089(4)	[1]
$Ru(acac)_2$ (2,4-hexadiene)	2.226(5) 2.242(5)	2.104(5) 2.104(5)	[6]
$Ru(acac)_2$ (2,3-diemethyl-1,3-butadiene)	2.210(5) 2.209(4)	2.141(5) 2.136(5)	This work

The diene ligand is nonplanar with a torsion [C(6)C(7)–C(7)AC(6)A] angle of 120°, equivalent to a tilt of the C(6)–C(7) and C(7)A–C(6)A bonds of 30° toward the Ru atom. In comparison with other reported η^4-*trans*-diene-Ru complexes with torsion angles of 122–127°, this butadiene complex shows a larger tilt angle, indicating closer proximity of the olefinic units to the metal center. This is a result of less steric interaction present in 2,3-dimethyl-1,3-butadiene vs. 2,4-hexadiene, 2,5-diemethyl-2,4-hexadiene and 2,4-dimethyl-1,3-pentadiene ligands which contain methyl substituents in the terminal carbons. Two sets of Ru–O bond distances are evident, *cis* and *trans* to the diene ligand. The Ru–O(*trans*), 2.065(3) Å, is longer than Ru–O(*cis*), 2.054(3) Å, which reflects a *trans* effect from the diene ligand.

3.2. Cyclic voltammetry studies

A series of ru(acac)$_2$(diene) complexes (diene = 2,5-diemethyl-2,4-hexadiene, 2,3-dimethyl-1,3-butadiene, 2,4-dimethyl-1,3-pentadiene, 1,3-cyclohexadiene, 2,4-hexadiene) have been analyzed by cyclic voltammetry to study the effect of ligand substitution and conformation on the redox behavior. As a baseline, solution 1 mM of the diene ligands were in THF and [NBu^{n}4][ClO$_4$] were also analyzed by cyclic voltammetry. The diene ligands were inactive in the potential range (0–1100 mV) through which the complexes were studied.

Table 5
Redox potentials (mV) and currents (μA) for 1 mM solution of Ru-diene complexes in THF (100 mM [NBu^{n}4][ClO$_4$]), at a platinum electrode and Ag/AgCl as reference electrode at room temperature

Complex	E_{pc} (mV)	E_{pa} (mV)	i_c (μA)	i_a (μA)
Ru(acac)$_2$ (1,3-cyclohexadiene)		412[a]		−3.03
		455[b]		−5.11
		787[b,sh]		−0.29
Ru(acac)$_2$ (2,4-dimethyl-1,3-pentadiene)	–	770[a]		−3.12
		962[b]		−3.81
Ru(acac)$_2$ (2,5-dimethyl-2,4-hexadiene)	–	777[a]		−3.53
		911[b]		−4.89
Ru(acac)$_2$ (2,4-hexadiene)	758[a]	950[a]	1.34	−3.32
	745[b]	1034[b]	1.93	−6.15
Ru(acac)$_2$ (2,3-dimethyl-1,3-butadiene)	876[a]	976[a]	4.25	−6.54
	855[b]	1060[b]	3.37	−8.45

sh = shoulder.
[a] Scan rate of 30 mV/s.
[b] Scan rate of 100 mV/s.

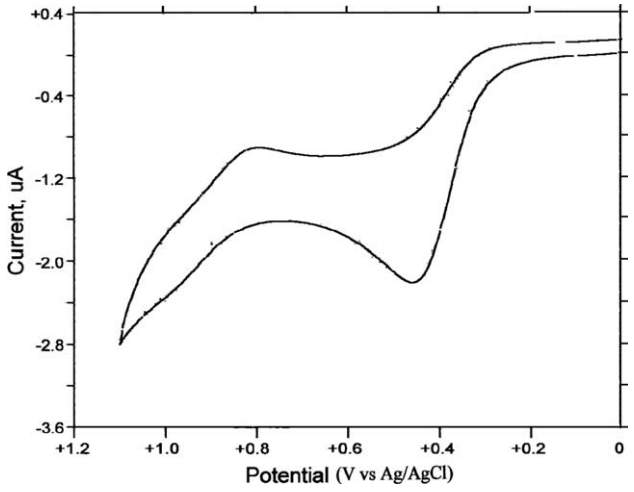

Fig. 3. Cyclic voltammogram of a 1 mM solution of Ru(acac)$_2$(1,3-cyclohexadiene) in THF at a platinum electrode (0.1 M [NBu^{n}4][ClO$_4$]; scan rate 30 mV/s).

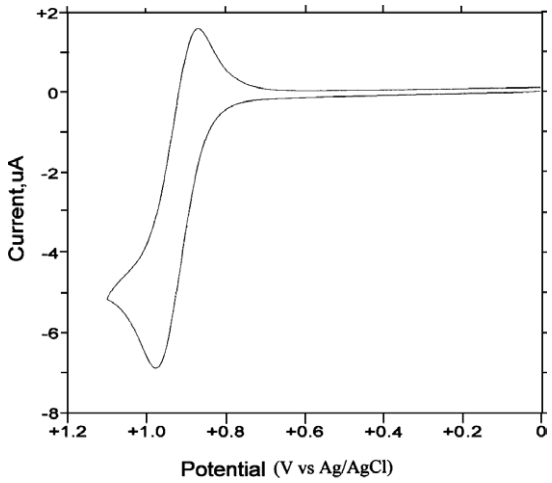

Fig. 4. Cyclic voltammogram of a 1 mM solution of Ru(acac)$_2$(2,3-dimethyl-1,3-butadiene) in THF at a platinum electrode (0.1 M [NBu^{n}4][ClO$_4$]; scan rate 30 mV/s).

Table 5 summarizes the CV results for each complex. Figs. 3 and 4 show representative cyclic voltammograms for Ru(acac)$_2$(1,3-cyclohexadiene) and Ru(acac)$_2$(2,3-dimethyl-1,3-butadiene) complexes. All the Ru-η^4-*trans*-diene complexes showed a major oxidation peak (E_{pa}) from 770 to 976 mV at a scan rate of 30 mV/s, but the reversibility character varies according to the diene ligand. On the other hand, Ru(acac)$_2$(1,3-cyclohexadiene) exhibited different redox behavior.

The Ru(acac)$_2$(1,3-cyclohexadiene) showed an irreversible oxidation potential, E_{pa}, at 412 mV suggesting that the cyclic nature of the diene facilitates the oxidation of the complex as compared to the acyclic diene ligands. Particularly important, the Ru–C bond distances for the 1,3-cyclohexadiene complex are about the same as the acyclic *trans*-diene ligands. Thus, this electrochemical data suggests that cyclohexadiene is a better electrodonating ligand than the acyclic ligands, making the oxidation process more feasible. Notably, this irreversible oxidation potential for Ru(acac)$_2$(1,3-cyclohexadiene) at 412 mV is substantially lower than the remaining Ru-diene complexes, which exhibited oxidation potentials from 770 to 976 mV which is more typical for Ru(II)/Ru(III) couple [10,11].

In terms of the acyclic ligands, the 2,4-hexadiene and 2,3-dimethyl-1,3-butadiene complexes showed similar oxidation potentials as well as quasi-reversible (for 2,4-hexadiene, E_{pa} 950 mV) and reversible (for butadiene, E_{pa} 976 mV) redox behaviors, while the 2,4-dimethyl-1,3-pentadiene and 2,5-dimethyl-2,4-hexadiene complexes demonstrated completely irreversible oxidation processes at much lower potentials, 770 and 777 mV, respectively. The latter two complexes apparently

decompose in THF solution when oxidized from Ru(II) to Ru(III), forming non-electroactive species.

To further investigate the electrochemical (reversibility) behavior of these complexes, CV experiments were run on at a higher scan rate, 100 mV/s. Our experiments revealed that all complexes, including the Ru(cylohexadiene), experience shifts to higher oxidation potentials (cathodic shifts). Now the oxidation potentials for all the acyclic diene complexes fall in a range 911–1060 mV but the reversibility character on the redox behavior decreases. In particular, the redox behavior of Ru-$(acac)_2$(2,3-dimethyl-1,3-butadiene) becomes quasi-reversible at scan rate of 100 mV/s. Notably at a scan rate of 100 mV/s, $Ru(acac)_2$(1,3-cyclohexadiene) starts to show a second oxidation process at 787 mV suggesting a secondary species, perhaps proceeding from the ruthenium-cyclohexadiene oxidation, undergoes further oxidation but in a minor extent. The fact that increasing the scan rate led to make the redox processes more irreversible suggests that the scan rate of 30 mV/s is the optimum to characterize these complexes. Finally, we have investigated the redox behavior in solutions containing 1 mM in both, ru complex and diene ligand. Our experiments showed that none of the complexes changed their electrochemical behavior (reversibility and potentials) in the presence of the diene ligands. This suggests that the Ru(III) species formed from Ru-cyclohexadiene, -2,5-dimethyl-2,4-hexadiene and -2,4-dimethyl-1,3-pentadiene complexes upon oxidation may not contain the the diene ligand and form very robust and stable inorganic complexes, perhaps coordinated by THF.

4. Discussion

Our study reveals the following points. First, while the reactivity of coordinated *cis*- and *trans*-η^4-diene are different, structurally their Ru–C distances are very similar that no major differences are observed. On the other hand, the redox potential can be used as a tool to pinpoint these minor differences and has been used very often in organometallic/inorganic chemistry as a characterization technique [12–16]. As can be seen, in general the *trans*-diene coordination appears to be more robust to oxidation than the *cis* one. The 1,3-cyclohexadiene complex exhibited the lowest oxidation potential while the *trans*-diene complexes showed much higher stability to oxidation. Also, among the *trans*-diene coordination, the dienes with less substituents in the terminal carbons seem to be more stable than those with two substituents on the terminal carbons. Lastly, this study suggests that the *cis*-η^4-diene ligand can be a better electron donor to Ru(II) center than *trans*-η^4-diene but, the *trans*-η^4-diene coordination can attain better Ru → diene back-bonding interactions providing more stability to their complexes and less likely to undergo oxidation.

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Appendix A. Supplementary material

NMR data (chemical shifts and coupling constants) available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2004.06.058.

References

[1] E. Meléndez, R. Ilarraza, G.P.A. Yap, A.L. Rheingold, J. Organomet. Chem. 522 (1996) 1.
[2] R.D. Ernst, E. Meléndez, L. Stahl, M.L. Ziegler, Organometallics 10 (1991) 3635.
[3] P. Powell, J. Organomet. Chem. 65 (1974) 89.
[4] C. Potvin, J.M. Manoli, A. Dereigne, G. Panetier, J. Less-Common Met. 25 (1971) 373.
[5] C. Potvin, G. Panetier, J. Less-Common Met. 22 (1970) 91.
[6] E. Meléndez, R. Ilarraza, G.P.A. Yap, A.L. Rheingold, Acta Crystallogr., Sect. C 54 (1998) 449.
[7] H. Yasuda, A. Nakamura, Angew. Chem., Int. Ed. Engl. 26 (1987) 723.
[8] A. Nakamura, H. Yasuda, K. Tatsumi, K. Mashima, M. Akita, K. Nagasuna, Organometallic compounds: synthesis, in: B.L. Shapiro (Ed.), Structure and Theory, vol. 1, Texas A & M University Press, Austin, 1983, pp. 29–45.
[9] G. Erker, C. Krüger, G. Müller, Adv. Organomet. Chem. 24 (1985) 1–39.
[10] R.Y. Lai, M. Chiba, N. Kitamura, A.J. Bard, Anal. Chem. 74 (2002) 551.
[11] D. Pomeranc, V. Heitz, J.-C. Chambron, J.-P. Sauvage, J. Am. Chem. Soc. 123 (2001) 12215.
[12] A.J. Downard, N.J. Goodwin, W. Henderson, J. Organometal. Chem. 676 (2003) 62.
[13] P. de Wolf, S.L. Heath, J.A. Thomas, Inorg. Chim. Acta 355 (2003) 280.
[14] R.L. Williams, H.N. Toft, B. Winkel, K.J. Brewer, Inorg. Chem. 42 (2003) 4394.
[15] J.A. Lewis, D.T. Puerta, S.M. Chen, Inorg. Chem. 42 (2003) 7455.
[16] S.M. Morehouse, H. Suliman, J. Haff, D. Nguyen, Inorg. Chim. Acta 297 (2000) 411.