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Oxidation of Ruthenium(II) to Ruthenium(IV) η^4-Diene Complexes: Swing Mechanism and Diene−Allyl Conversion

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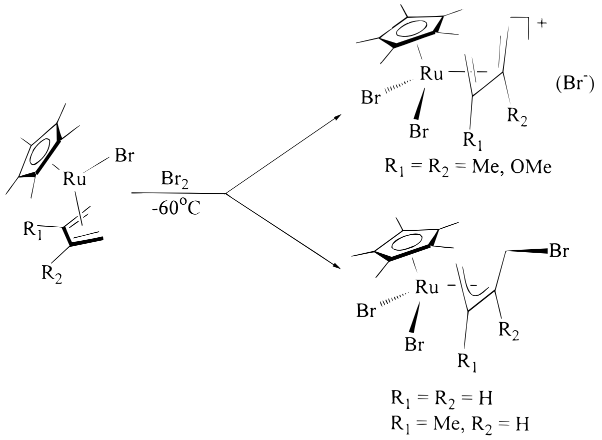
This paper reports on the synthesis and reactivity of Ru(IV) η^4-diene complexes of the type Ru(η^5-C_5Me_5)(η^4-diene)Br_2^+ obtained by oxidative bromine additions to Ru(II) η^4-diene complexes. Mechanistic details are derived from the reaction products varying with the oxidizing agent and the leaving ligand and are backed up by extended Hückel molecular orbital calculations. The diene fragment in Ru(IV) is prone to *gauche* deformation and is therefore extremely susceptible to nucleophilic attack of even weak anionic bases generating the corresponding Ru(IV) η^3-allyl complexes. Accordingly, Ru(IV) η^4-diene complexes are stabilized either by using 2,3-disubstituted diene ligands in which case *gauche* deformation is highly unfavorable or else by excluding nucleophilic agents. For the latter method, two convenient routes to affording Ru(IV) η^4-diene complexes are (i) the reaction of $Br^+CF_3SO_3^-$ with Ru(η^5-C_5Me_5)(η^4-diene)Br and (ii) the reaction of dibromine with labile Ru(η^5-C_5Me_5)(η^4-diene)(CF_3SO_3). The conversion of the Ru(II) η^4-diene to the Ru(IV) η^4-diene complex is suggested to proceed via a swing of the diene ligand by changing the dihedral angle between the C_5Me_5 and diene ligands from about +20 to about −70° concomitantly pushing the leaving ligand (Br^- or $CF_3SO_3^-$) out.

Introduction

Higher oxidation state η^4-diene complexes are interesting compounds in which the diene moiety is bound in a σ^2,π fashion approaching a metallacyclopentene limiting structure. Such complexes are often highly reactive species participating in a variety of stoichiometric and catalytic transformations of organic molecules.[1] Hitherto, however, restriction was largely to early transition metals. Previously we have reported on the first Ru(IV) η^4-diene complexes of the type [Ru(η^5-C_5Me_5)(η^4-diene)Br_2]$^+$ as obtained via oxidative addition of Br_2 to Ru(η^5-C_5Me_5)(η^4-diene)Br.[2,3] However, these transformations take place only in the case of 2,3-disubstituted dienes like 2,3-dimethyl- and 2,3-dimethoxy-1,3-butadiene. For all other dienes considered, Ru(IV) η^3-allyl complexes are obtained (Scheme 1). In the context of this scheme several challenging questions concerning the mechanistic details arise: (i) Are the two products formed competitively or consecutively; in other words, is the Ru(IV) η^3-allyl compound formed via intermediacy of the Ru(IV) η^4-diene complex and, if so, how is the diene complex transformed into the allyl complex? (ii) Why is the formation of the Ru(IV) η^4-diene complexes restricted to 2,3 disubstituted dienes? Is the addition of bromide to the diene a separate step of reaction, prohibited in the case of 2,3 disubstituted dienes?

Scheme 1



In the present contribution we will introduce two general synthetic strategies to obtaining Ru(IV) η^4-diene complexes. One utilizes, for the first time as it appears, the bromonium ion Br^+ as a strong electrophile reacting with Ru(η^5-C_5Me_5)(η^4-diene)Br. The other proceeds from the labile Ru(II) complexes Ru(η^5-C_5Me_5)(η^4-diene)(η^1-OSO_2CF_3) to be reacted with Br_2. Furthermore, we shall try to get an answer to the above questions by means of extended Hückel molecular orbital (EHMO) calculations.

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(1) (a) Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120. (b) Yasuda, H.; Tatsumi, K.; Okamoto, T.; Mashima, K.; Lee, K.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1995**, *107*, 2410. (c) Mashima, K.; Fujikawa, S.; Tanaka, Y.; Urata, H.; Oshiki, T.; Tanaka, E.; Nakamura, A. *Organometallics* **1995**, *14*, 2633. (d) Mashima, K.; Fujikawa, S.; Nakamura, A. *J. Am. Chem. Soc.* **1993**, *115*, 10990. (e) Wielstra, Y.; Gambarotta, S.; Spek, A. L. *Organometallics* **1990**, *9*, 572.

(2) Gemel, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1995**, *14*, 1405.

(3) Gemel, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 532.

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Experimental Section

General Information. Manipulation were performed under an inert atmosphere of purified argon by using Schlenk techniques. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures and dried over 4 Å molecular sieves.[4] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC-250 spectrometer operating at 250.13 and 62.86 MHz, respectively, and were referenced to $SiMe_4$. Microanalysis were done by Microanalytical Laboratories, University of Vienna.

Synthesis. Ru(η^5-C_5Me_5)(η^4-$CH_2CHCHCH_2$)(η^1-OSO_2CF_3) (2). A solution of **1a** (410 mg, 1.11 mmol) in CH_2Cl_2 (5 mL) was treated with $AgCF_3SO_3$ (285 mg, 1.11 mmol) at room temperature and was stirred for 30 min. The mixture was filtered, and the volatile materials were removed under reduced pressure. The residue was redissolved in 0.5 mL of CH_2Cl_2. On addition of diethyl ether a yellow precipitate was formed which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 378 mg (77%). Anal. Calcd for $C_{15}H_{21}F_3O_3RuS$: C, 41.00; H, 4.82. Found: C, 40.86; H, 4.97. ^1H NMR (δ, $CDCl_3$, 20 °C): 4.70 (m, 2H), 3.86 (d, 2H, ^3J = 6.2 Hz), 2.32 (d, 2H, ^3J = 10.3 Hz), 1.59 (s, 15H). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 97.1 (C_5Me_5), 96.4 (internal C atoms), 56.6 (terminal C atoms), 9.9 (C_5Me_5).

Ru(η^5-C_5Me_5)(η^4-$CH_2CHCHCH_2$)(η^1-$OCOCF_3$) (3). This compound has been synthesized by an analogous route to **2** but using $AgCF_3COO$ instead of $AgCF_3SO_3$. Yield: 75%. Anal. Calcd for $C_{16}H_{21}F_3O_2Ru$: C, 47.52; H, 5.24. Found: C, 47.38; H, 5.12. ^1H NMR (δ, $CDCl_3$, 20 °C): 4.59 (m, 2H), 3.75 (dd, 2H, ^3J = 6.4 Hz, ^2J = 2.1 Hz), 1.63 (m, 2H), 1.60 (s, 15H).

[Ru(η^5-C_5Me_5)(η^4-$CH_2CHCHCH_2$)Br_2]CF_3SO_3 (4a). Method A. $Br^+CF_3SO^-$ has been prepared according to a literature procedure developed for the synthesis of $I^+CF_3COO^-$.[5] A Schlenk flask which was protected from light with aluminum foil was charged with a solution of Br_2 (20.8 μL, 0.405 mmol) in CH_2Cl_2, and $AgCF_3SO_3$ (104 mg, 0.405 mmol) was added. After 30 min of stirring at room temperature, the mixture was transferred via cannula to a solution of **1a** (150 mg, 0.405 mmol) in CH_2Cl_2 (3 mL). After 30 min of stirring at −60 °C, the reaction mixture was allowed to warm to −20 °C and the solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2, insoluble materials were removed by filtration, and addition of diethyl ether afforded an orange precipitate of analytically pure **4a**. Yield: 197 mg (87%). Anal. Calcd for $C_{15}H_{21}Br_2F_3O_3RuS$: C, 30.07; H, 3.53; Br, 26.67. Found: C, 29.92; H, 3.65; Br, 26.80. ^1H NMR (δ, CD_3NO_2, −20 °C): 7.27 (m, 2H), 3.97 (dd, 2H, J = 7.5 Hz, J = 1.2 Hz), 2.41 (dd, 2H, J = 7.8 Hz, J = 1.2 Hz), 2.15 (s, 15H). $^{13}C\{^1H\}$ NMR (δ, CD_3NO_2, −20 °C): 125.4, 118.5 (C_5Me_5), 72.1, 12.1 (C_5Me_3).

Method B. A solution of **2** (120 mg, 0.273 mmol) in CH_2Cl_2 (5 mL) was treated with Br_2 (7.9 μL, 0.273 mmol) at −60 °C. After being stirred for 30 min, the solution was allowed to warm to −20 °C and the solvent was removed under vacuum. The resulting orange solid was dissolved in CH_2Cl_2 at −20 °C, and insoluble materials were removed by filtration. On addition of diethyl ether, a dark red precipitate was formed which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 140 mg (86%).

[Ru(η^5-C_5Me)(η^4-$CH_2CHCMeCH_2$)Br_2]CF_3SO_3 (4b). This complex has been prepared analogously to **4a** (method A) with **1b** as starting material. Yield: 68%. Anal. Calcd for $C_{17}H_{23}Br_2F_3O_3RuS$: C, 31.34; H, 3.78; Br, 26.06. Found: C, 31.23; H, 3.92; Br, 26.38. ^1H NMR (δ, acetone-d_6, −20 °C): 6.89 (dd, 1H, ^3J = 7.5 Hz, ^3J = 10.0 Hz), 4.15 (d, 1H, ^3J = 7.5 Hz), 3.64 (s, 1H), 2.92 (s, 3H), 2.72 (d, 1H, ^3J = 10.0 Hz), 2.54 (s, 1H), 2.19 (s, 15H). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, −20 °C): 145.6, 123.4, 117.8 (C_5Me_5), 72.4, 68.5, 24.9 (Me), 12.6 (C_5Me_5).

Ru(η^5-C_5Me_5)(η^3-$CH_2CHCHCH_2OCOCF_3$)Br_2 (5a). Method A. A Schlenk flask which was protected from light with aluminum foil was charged with a solution of Br_2 (20.8 μL, 0.446 mmol) in CH_2Cl_2, and $AgCF_3COO$ (99 mg, 0.446 mmol) was added. After 30 min of stirring at room temperature, the mixture was transferred via cannula to a solution of **1a** (165 mg, 0.446 mmol) in CH_2Cl_2 (3 mL). After 30 min of stirring at −60 °C, the reaction mixture was allowed to warm to −20 °C, and the solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2, insoluble materials were removed by filtration, and addition of diethyl ether afforded a red precipitate of analytically pure **5a**. Yield: 206 mg (82%). Anal. Calcd for $C_{16}H_{21}Br_2F_3O_2Ru$: C, 34.12; H, 3.76; Br, 28.37. Found: C, 33.93; H, 3.54; Br, 27.78. ^1H NMR (δ, nitromethane-d_3, 20 °C): 5.60 (m, 1H), 5.23 (m, 1H), 4.19 (dd, 1H, J = 6.3 Hz, J = 1.6 Hz), 3.76 (dd, 1H, J = 8.7 Hz, J = 3.8 Hz), 3.15 (dd, 1H, J = 11.8 Hz, J = 8.7 Hz), 3.12 (dd, 1H, J = 10.4 Hz, J = 1.6 Hz), 1.76 (s, 15H).

Method B. To a solution of **3** (131 mg, 0.324 mmol) in CH_2Cl_2 (3 mL) at −60 °C was added Br_2 (6.3 μL, 0.324 mmol), and the mixture was stirred for 30 min. The volatile materials were removed under vacuum, and the residue was redissolved in CH_2Cl_2. On addition of diethyl ether, a red precipitate was formed which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 126 mg (69%).

Ru(η^5-C_5Me_5)(η^3-$CH_2CMeCHCH_2OCOCF_3$)Br_2 (5b). This complex was synthesized analogously to **5a** (method A) but with **1b** as starting material. Yield: 79%. Calcd for $C_{17}H_{23}Br_2F_3O_2Ru$: C, 35.37; H, 4.02; Br, 27.69. Found: C, 35.23; H, 4.17; Br, 27.92. ^1H NMR (δ, $CDCl_3$, 20 °C): 4.47 (dd, 1H, J = 11.0 Hz, J = 11.7 Hz), 4.03 (s, 1H), 3.46 (dd, 1H, J = 3.5 Hz, J = 11.7 Hz), 2.64 (dd, 1H, J = 3.5 Hz, J = 11.0 Hz), 2.39 (s, 3H), 2.22 (s, 1H), 1.71 (s, 15H). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 108.4, 104.7 (C_5Me_5), 77.9, 71.4, 63.9 (CH_2O), 34.4 (Me), 10.8 (C_5Me_5).

Reaction of 4a with NEt_4X ($X = Cl^-$, Br^-) and $NaCF_3COO$. A 5 mm NMR tube was charged with **4a** (30 mg, 0.081 mmol), and NEt_4Cl (27 mg, 0.162 mmol) and CD_3NO_2 (0.5 mL) was added via syringe. The sample was transferred to a NMR probe. A ^1H NMR spectra was immediately recorded showing the quantitative formation of Ru(η^5-C_5Me_5)(η^3-$CH_2CHCHCH_2Cl$)Br_2 **(6)**. ^1H NMR (δ, CD_3NO_2, 20 °C): 5.27 (m, 1H), 5.09 (m, 1H), 4.06 (dd, 1H, J = 6.1 Hz, J = 1.4 Hz), 3.65 (dd, 1H, J = 9.9 Hz, J = 4.5 Hz), 3.00 (m, 2H), 1.63 (s, 15H).

The same reaction performed with both NEt_4Br (2 equiv) and $NaCF_3COO$ (2 equiv) revealed the quantitative formation of Ru(η^5-C_5Me_5)(η^3-$CH_2CHCHCH_2$-Br)Br_2 **(7)** and **5a**. The ^1H NMR spectrum of **7** is in agreement with literature-reported values.[2,3]

X-ray Structure Determination for 2, 3, and 7. Crystal data and experimental details are given in Table 1. X-ray data were collected on a Philips PW 1100 four-circle diffractometer using graphite-monochromated Mo Kα (λ = 0.710 69 Å) radiation and the θ-2θ scan technique. Three representative reference reflections were measured every 120 min and used to correct for crystal decay and system instability. Corrections for Lorentz and polarization effects and for absorption were applied. The structures were solved by direct methods.[6] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in idealized positions.[7] The structures were refined against F^2.

EHMO Calculations. The extended Hückel molecular orbital calculations were conducted by using the original

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(4) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: New York, 1988.

(5) Liebeskind, L. S.; Bombrun, A. *J. Am. Chem. Soc.* **1991**, *113*, 8736.

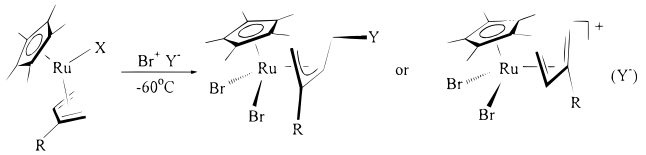
(6) Sheldrick, G. M. SHELX86: Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1986.

(7) Sheldrick, G. M. SHELX86: Program for Crystal Structure Refinement, University of Göttingen, Germany, 1993.

Table 1. Crystallographic Data

	2	3	7
formula	$C_{15}H_{21}F_3O_3RuS$	$C_{16}H_{21}F_3O_2Ru$	$C_{14}H_{21}Br_3Ru$
fw	439.45	403.40	530.11
cryst size, mm	0.25 × 0.28 × 0.50	0.28 × 0.33 × 0.72	0.16 × 0.20 × 0.35
space group	*Pbca* (No. 61)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	9.029(2)	7.248(2)	7.349(2)
b, Å	14.396(5)	14.750(4)	13.758(4)
c, Å	27.132(6)	15.889(5)	16.841(5)
β, deg		94.12(1)	96.42(1)
V, Å^3	3527(2)	1694.3(8)	1692.1(8)
$F(000)$	1776	816	1016
Z	8	4	4
ρ_{calc}, g cm^{-3}	1.655	1.581	2.081
T, K	296	300	293
μ, mm^{-1} (Mo Kα)	1.046	0.958	7.994
abs corr	none	empirical	empirical
transm factors, min/max		0.91/1.09	0.91/1.09
θ_{max}, deg	25	25	24.1
index ranges	$0 \le h \le 10$ $0 \le k \le 17$ $0 \le l \le 32$	$-8 \le h \le 8$ $0 \le k \le 17$ $0 \le l \le 18$	$0 \le h \le 8$ $0 \le k \le 15$ $-19 \le l \le 19$
no. of rflns measd	3480	3362	3022
no. of unique rflns	3103	2989	2669
no. of rflns $F > 4\sigma(F)$	1750	2564	1992
no. of params	214	232	171
no. of restraints	35	11	
$R(F)(R > 4\sigma(F))$	0.051	0.024	0.041
$R(F)$(all data)	0.123	0.033	0.065
$wR(F^2)$(all data)	0.113	0.061	0.082
min/max diff Fourier peaks, e Å^{-3}	−0.36/0.43	−0.32/0.28	−0.76/0.74

Table 2. Reaction of Ru(η^5-C_5Me_5)(η^4-diene)X with Br^+Y^- in CH_2Cl_2 at −60 °C



I II III

	reactants		products			
entry	I	Br^+Y^-	II	yield, %	III	yield, %
1	**1a**, R = H, X = Br	Y = Br	Y = Br	92		
2	**1b**, R = Me, X = Br	Y = Br	Y = Br	96		
3	**2**, R = H, X = CF_3SO_3	Y = Br			**4a**, Y = CF_3SO_3	86
4	**3**, R = H, X = CF_3COO	Y = Br	**5a**, Y = CF_3COO	69		
5	**1a**, R = H, X = Br	Y = CF_3SO_3			**4a**, Y = CF_3SO_3	87
6	**1b**, R = Me, X = Br	Y = CF_3SO_3			**4b**, Y = CF_3SO_3	68
7	**1a**, R = H, X = Br	Y = CF_3COO	**5a**, Y = CF_3COO	82		
8	**1b**, R = Me, X = Br	Y = CF_3COO	**5b**, Y = CF_3COO	79		

program developed by Hoffmann and Lipscomb[8] and modified by Mealli and Proserpio.[9] The atomic parameters used in this study were taken from the CACAO program.

Results

Reaction of Ru(η^5-C_5Me_5)(η^4-diene)Br Complexes with $Br^+CF_3SO_3^-$. Treatment of Ru(η^5-C_5Me_5)(η^4-$CH_2CHCHCH_2$)Br **(1a)** or Ru(η^5-C_5Me_5)(η^4-$CH_2CHCMeCH_2$)Br **(1b)** with 1 equiv of $Br^+CF_3SO_3^-$ ($Br^+CF_3SO_3^-$ has been prepared *in situ* by the reaction of Br_2 with 1 equiv of $AgCF_3SO_3$ in CH_2Cl_2) at −60 °C in CH_2Cl_2 affords the cationic Ru(IV) η^4-diene complexes [Ru(η^5-C_5Me_5)(η^4-$CH_2CHCHCH_2$)Br_2]CF_3SO_3 **(4a)** and [Ru(η^5-C_5Me_5)(η^4-$CH_2CHCMeCH_2$)Br_2]CF_3SO_3 **(4b)** in 87 and 68 % yield, respectively (Table 2). These complexes are stable to air in the solid state but decompose in solution at elevated temperatures. Characterization of these complexes was by elemental analysis and particularly by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy carried out at −20 °C in CD_3NO_2 or acetone-d_6 as the solvents.

The ^1H NMR spectrum of **4a** displays the characteristic resonances of the diene ligand. The *syn* and *anti* protons (H_a, H_b) give rise to two doublets of doublets centered at 3.97 (2H, $^3J_{ac} = 7.5$ Hz, $^2J_{ab} = 1.2$ Hz) and 2.41 ppm (2H, $^3J_{bc} = 7.8$ Hz, $^2J_{ab} = 1.2$ Hz), respectively, while the signal of the internal protons (H_c) of the butadiene ligand is extremely downfield shifted resonating at 7.27 ppm (2H). The signal for the C_5Me_5 ligand appears at 2.15 ppm (15H) (*cf*, the respective Ru(II) η^4-diene complex **1a** exhibits resonances at 4.36 (m, 2H, H_c), 3.14 (dd, $^3J_{ac} = 8.3$ Hz, $^2J_{ab} = 1.6$ Hz, H_a), 1.69 (15H), and 1.61 ppm (dd, $^3J_{bc} = 9.9$ Hz, $^2J_{ab} = 1.6$ Hz, H_b). In complex **4a** the vicinal *trans* and *cis* coupling constants are very similar, while in **4b**, as expected for η^4-diene complexes, the vicinal *trans* coupling constant is larger (10.0 Hz) than the vicinal *cis* coupling constant

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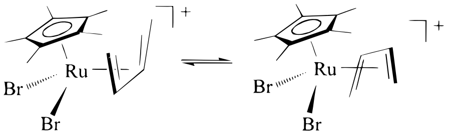
[8] (a) Hoffman, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179. (b) Hoffman, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 3489. (c) Hoffman, R. *J. Chem. Phys.* **1963**, *39*, 1397.

[9] Mealli, C.; Proserpio, D. M. *J. Chem. Educ.* **1990**, *67*, 399.

(7.5 Hz). The $^{13}C\{^1H\}$ NMR spectrum of **4a** shows singlets at 125.4 (internal C atoms), 118.5 (C_5Me_5), 72.1 (terminal C atoms), and 12.1 ppm (C_5Me_5). The marked downfield shifts are indicative of the high oxidation state of the ruthenium center (*cf.* in **1a** the respective resonances are found at 95.4 (internal C atoms), 91.4 (C_5Me_5), 52.4 (terminal C atoms), and 10.4 ppm (C_5Me_5)). The ^1H and $^{13}C\{^1H\}$ NMR spectra of **4b** are very similar to those of **4a** and are not discussed here.

Both ^1H and $^{13}C\{^1H\}$ NMR spectra of complexes **4** indicate the existence of only one isomer in solution without observation of a possible conformational equilibrium between *endo* **(I)** and *exo* **(II)** isomers:



I (endo) **II** (exo)

In order to establish what kind of diene orientation is being adopted we performed NOE enhancement experiments on **4a**. Irradiation of the C_5Me_5 ligand singlet showed a strong interaction between the C_5Me_5 protons and the H_a protons of the diene moiety (16%) suggesting that the *endo* isomer **I** is the predominant conformer in solution, at least at low temperature. The solid-state structures of complexes **4** could not be determined since no X-ray-quality crystals could be obtained. However, we have previously shown that the *endo* conformation is adopted in the crystalline state for the 2,3-dimethyl-1,3-butadiene and 2,3-dimethoxy-1,3-butadiene analogues.[2,3] Therefore it is likely that in complexes **4** the diene ligand is *endo* oriented also in the solid state.

Reaction of $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-diene})Br$ Complexes with $Br^+CF_3COO^-$. In contrast to the reactions described above, addition of $Br^+CF_3COO^-$ ($Br^+CF_3COO^-$ has been prepared *in situ* by the reaction of Br_2 with 1 equiv of $AgCF_3COO$ in CH_2Cl_2) to **1a** or **1b** does not yield the cationic complexes **4a,b** with CF_3COO^- remaining as the counterion but results in the formation of the trifluoroacetato-substituted Ru(IV) η^3-allyl complexes **5a,b** (Table 2). This reaction involves regioselective addition of the CF_3COO^- anion at the terminal carbon atom and apparently on the face of the cisoid η^4-diene moiety opposite to the metal center. In case of **5b**, addition occurs such that the methyl substituent ends up on the central allyl carbon atom. Under these conditions, the addition is kinetically controlled resulting in the sole formation of *anti* η^3-allyl isomers (as drawn). Confirmation of the regioselectivity of this process is readily apparent from the spectroscopic characterization of the products in comparison with literature analogs.[2,3,10] The ^1H NMR spectra of **5a,b** show the expected singlet resonances of the C_5Me_5 rings at 1.76 and 1.71 ppm, respectively, while characteristic multiplet resonances assignable to the allyl ligands are observed in the usual ranges. The signal of the CH_2OCOCF_3 moiety gives rise to multiplets in the range 2.6−3.7 ppm. The instability of **5a** in solution precluded the recording of a $^{13}C\{^1H\}$ NMR spectrum. The $^{13}C\{^1H\}$ NMR spectra of **5b** contains no surprising features with the resonance of the sp^3 carbon atom bearing the trifluoracetato substituent observed at 63.9 ppm. The signals of the CF_3COO group were not detected.

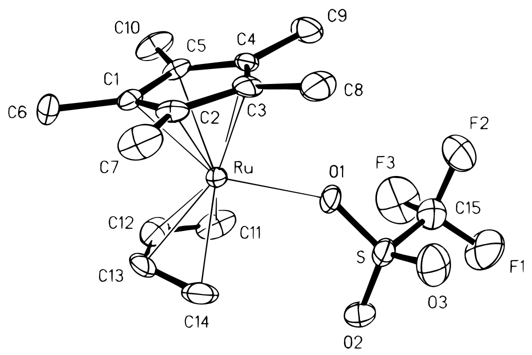
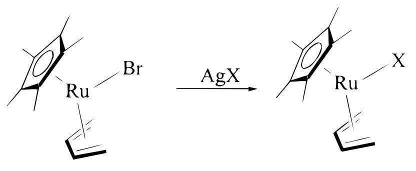


Figure 1. Structural view of $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}CH_2CHCHCH_2)(\eta^1\text{-}OSO_2CF_3)$ **(2)**. Selected bond lengths (Å) and angles (deg): Ru−C(1-5)$_{av}$ 2.205(5), Ru−C(11) 2.206(8), Ru−C(12) 2.129(7), Ru−C(13) 2.139(7), Ru−C(14) 2.211(8), Ru−O(1) 2.177(4), Ru−O(1)−S 146.4(3).

Scheme 2



1a

2 X = $CF_3SO_3^-$
3 X = CF_3COO^-

Reaction of $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-diene})X$ Complexes with Br_2 ($X = CF_3SO_3^-$, CF_3COO^-). Chloride abstraction from **1a** using $AgCF_3SO_3$ in CH_2Cl_2 as the solvent gives quantitatively AgCl and a new species **2**, which could be isolated as yellow crystals in good yield (Scheme 2). Since the ^1H and $^{13}C\{^1H\}$ solution NMR data for **2** are very similar to those of neutral **1a** and not consistent with an ionic $[Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}CH_2CHCHCH_2)]^+CF_3SO_3^-$ composition, a single-crystal X-ray structure determination of **2** has been undertaken. This study shows **2** to be the neutral complex $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}CH_2CHCHCH_2)(\eta^1\text{-}OSO_2CF_3)$. A structural view of **2** is depicted in Figure 1 with important bond distances and angles reported in the caption. The diene ligand is *exo* oriented with respect to the $CF_3SO_3^-$ ligand; i.e., the terminal CH_2 groups of the diene are directed toward the $CF_3SO_3^-$ ligand. The dihedral angle between the C_5Me_5 and butadiene planes is 20.2° (*cf.* in $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}CH_2CHCHCH_2)I$ this angle is 33.2°).[11] The diene C−C bonds exhibit a short−long−short pattern (1.364(9) vs 1.401(4) Å). The average Ru−C(C_5Me_5) distance is 2.205(5) Å. The bond distances between Ru and the diene are long for C(11) and C(14), 2.206(8) and 2.211(8) Å, respectively, and short for C(12) and C(13), 2.129(7) and 2.137(7) Å, respectively, a feature that is characteristic of transition metal complexes where the diene is predominantly π-bound. The Ru−O(1) distance and the Ru−O(1)−C(15) angle are 2.177(4) Å and 146.4(3)°, respectively. It is worth noting that only few ruthenium complexes with the $\eta^1\text{-}OSO_2CF_3$ ligand are known and structurally characterized.[12−14]

Following the procedure above, halide abstraction from **1a** with $AgCF_3COO$ in CH_2Cl_2 gave complex $Ru(\eta^5$-

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[10] Masuda, K.; Saitoh, M.; Aoki, K.; Itoh, K. *J. Organomet. Chem.* **1994**, *473*, 285.

[11] Fagan, P. J.; Mahoney, W. S.; Calabrese, J. C.; Williams, I. D. *Organometallics* **1990**, *9*, 1843.

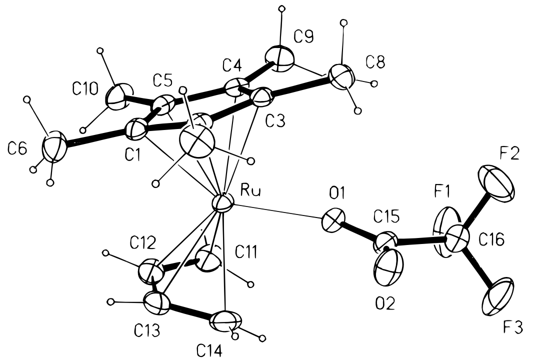


Figure 2. Structural view of Ru(η^5-C_5Me_5)(η^4-$CH_2CHCHCH_2$)(η^1-$OCOCF_3$) **(3)**. Selected bond lengths (Å) and angles (deg): Ru−C(1-5)$_{av}$ 2.204(3), Ru−C(11) 2.193(3), Ru−C(12) 2.158(3), Ru−C(13) 2.178(3), Ru−C(14) 2.238(3), Ru−O(1) 2.146(2), Ru−O(1)−C(15) 126.2(2).

C_5Me_5)(η^4-$CH_2CHCHCH_2$)(η^1-$OCOCF_3$) **(3)** in 75% yield (Scheme 2). Both ^1H and $^{13}C\{^1H\}$ NMR spectra of **3** are similar to those of **1** and **2** and are not discussed here. The structure of **3**, as depicted in Figure 2, has been determined by X-ray crystallography. Important bond distances and angles are given in the caption. The overall structure of **3** is very similar to that of **2** showing that the diene ligand is also *exo* oriented. The dihedral angle between the C_5Me_5 and butadiene planes is 19.7°. The diene character of the 1,3-butadiene ligand is still apparent as indicated by the long−short−long pattern of C−C distances (1.388(5) vs 1.411(6) Å). The Ru−C distances are slightly shorter by about 0.04 Å for C(12) and C(13) than for C(11) and C(14). The CF_3COO^- molecule is coordinated to the metal center as an η^1-oxygen donor ligand (Ru−O(1) = 2.146(2) Å). The Ru−O(1)−C(15) angle is 126.2(2)°.

The weakly coordinating nature of the $CF_3SO_3^-$ and CF_3COO^- ligands in complexes **2** and **3** should enable these complexes to react as the formally 16e fragment [Ru(η^5-C_5Me_5)(η^4-$CH_2CHCHCH_2$)]$^+$. Oxidative addition, which involves ligand displacement in octahedral d^6 systems, would thus be expected to be a facile process. This has indeed been demonstrated by adding a stoichiometric amount of Br_2 to **2** in CH_2Cl_2 at −60 °C yielding **4a** in essentially quantitative yield. While the reaction of **3** with Br_2 also proceeds smoothly to a single product, not **4a** but the Ru(IV) η^3-allyl complex **5a** was obtained (Table 2). The latter reaction, likewise, appears to proceed via the intermediacy of a Ru(IV) η^4-diene complex, but in contrast to $CF_3SO_3^-$, CF_3COO^- is already nucleophilic enough to attack the activated diene ligand.

Therefore, in sharp contrast to Ru(IV) η^4-diene complexes with diene = 2,3-disubstituted 1,3-butadienes reported previously, **4a** might be quite reactive toward nucleophiles. This has been tested by reacting **4a** with NEt_4Cl, NEt_4Br, and $NaCF_3COO$.

Reaction of 4a with NEt_4X (X = Cl^-, Br^-) and $NaCF_3COO$. Addition of 2 equiv of NEt_4X and $NaCF_3COO$ to **4a** affords quantitatively the Ru(IV) η^3-allyl complexes Ru(C_5Me_5)(η^3-$CH_2CHCHCH_2Cl$)Br_2 **(6)**, Ru(C_5Me_5)(η^3-$CH_2CHCHCH_2Br$)Br_2 **(7)**, and **5a**, respectively, as monitored by ^1H NMR spectroscopy (Scheme 3). A structural view of complex **7** (Figure 3), as determined by X-ray crystallography, demonstrates that Br^- addition on the diene has occurred at a terminal carbon atom and *anti* to the coordinated ruthenium. Selected bond distances and angles are given in the captions. The allyl function of the $CH_2CHCHCH_2Br$ ligand is bonded asymmetrically to the metal center with the Ru−C bond to the central allyl carbon atom C(12) (2.123(7) Å) shorter than those of the outer carbon atoms C(11) and C(13) and 2.271(9) Å, respectively). This bonding pattern is similar to that found for many asymmetrically substituted Ru(IV) η^3-allyl complexes.[2,3,10,15] The Ru−Br(1) and Ru−Br(2) distances are very similar, being 2.553(1) and 2.544(1) Å, respectively.

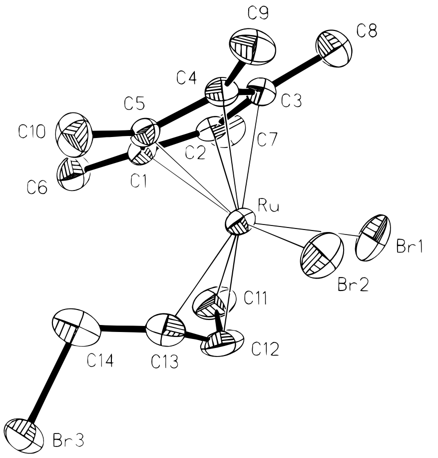
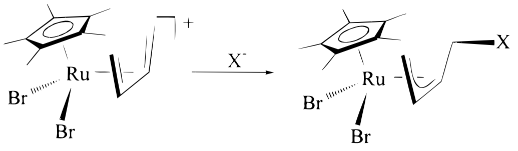


Figure 3. Structural view of Ru(η^5-C_5Me_5)(η^3-$CH_2CHCHCH_2Br$)Br_2 **(7)**. Selected bond lengths (Å) and angles (deg): Ru−C(1-5)$_{av}$ 2.242(6), Ru−C(11) 2.188(7), Ru−C(12) 2.123(7), Ru−C(13) 2.271(9), Ru−Br(1) 2.553(1), Ru−Br(2) 2.544(1), C(11)−C(12)−C(13) 119.1(8).

Scheme 3



4a

6 X = Cl
7 X = Br
5a X = CF_3COO

Discussion

As depicted in Table 2, when Br_2 is reacted with Ru(η^5-C_5Me_5)(η^4-diene)Br where diene is 1,3-butadiene or 2-methyl-1,3-butadiene (entries 1 and 2), dibromoruthenium(IV) η^3-allyl compounds are formed. Bromine attack occurred selectively at one of the termini of the diene ligand and from the face opposite to the metal center (see Figure 3). This reaction can be envisioned as occurring by an electrophilic attach of Br_2 with either Br−Br or Ru−Br bond cleavage leaving a Br^- anion behind which than nucleophilically attacks the activated diene moiety. Whether this process proceeds in a

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(12) Sutter, J.-P.; James, S. L.; Steenwinkel, P.; Karlen, T.; Grove, D. M.; Veldman, N.; Smeets, W. J. J.; Speck, A. L.; van Koten, G. *Organometallics* **1996**, *15*, 941.

(13) Kraakman, M. J. A.; Klerk-Engels, B. d.; de Lange, P. P. M.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1992**, *11*, 3774.

(14) Plosser, P. W.; Gallucci, J. C.; Wojcicki, A. *Inorg. Chem.* **1992**, *31*, 2376.

(15) Kondo, T.; Ono, H.; Satake, N.; Mitsudo, T.; Watanabe, Y. *Organometallics* **1995**, *14*, 1945.

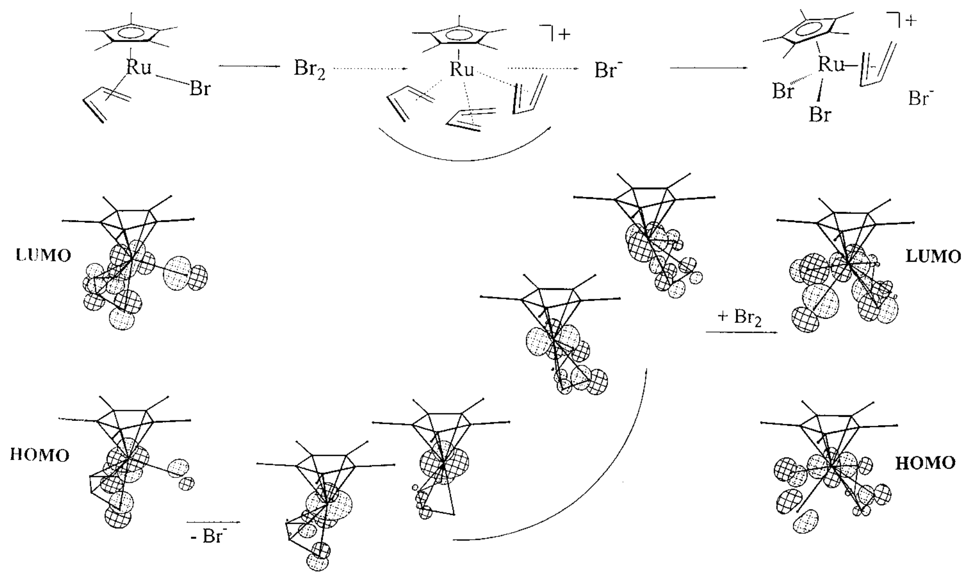

Figure 4. Oxidative addition of Br_2 to Ru(η^5-C_5Me_5)(η^4-diene)Br complexes. CACAO drawing for the LUMO and HOMO of reactant and product (C_5Me_5 AOs omitted for clarity) and the symmetry change of the LUMO during this reaction (swing of the diene fragment).

concerted or stepwise manner will be discussed in the following paragraph.

In order to establish whether the bromide substituent on the allyl moiety stems from the internal source (from Ru−Br bond cleavage) or an external source (from Br−Br bond cleavage), we used complexes Ru(η^5-C_5Me_5)(η^4-$CH_2CHCHCH_2$)(η^1-OSO_2CF_3) **(2)** and Ru(η^5-C_5Me_5)(η^4-$CH_2CHCHCH_2$)(η^1-$OCOCF_3$) **(3)** bearing the weakly coordinating $CF_3SO_3^-$ and CF_3COO^- anions as the leaving ligands (entries 3 and 4). Reaction of Br_2 with **2** gave exclusively the Ru(IV) η^4-diene complex **4a**, whereas with the somewhat more nucleophilic CF_3COO^- anion (entry 4), solely the Ru(IV) η^3-allyl complex **5a** is obtained. When **1a,b** are reacted with $Br^+CF_3SO_3^-$ as the oxidant instead of Br_2 (entries 5 and 6), no allyl formation occurs. On the other hand, with $Br^+CF_3COO^-$ as the oxidant (entries 7 and 8) Ru(IV) η^3-allyl complexes **5a,b** are obtained exclusively. These findings strongly suggest that the dibromoruthenium(IV) η^3-allyl complexes are generated in a stepwise fashion. First, a cationic Ru(IV) η^4-diene complex is formed which, in the absence of potential nucleophiles, can even be isolated. The Ru(IV) η^4-diene intermediates are extremely susceptible toward nucleophilic attack of even weak nucleophiles such as Cl^-, Br^-, and CF_3COO^- to furnish quantitatively the corresponding Ru(IV) η^3-allyl complexes (Scheme 3).

An insight into a possible mechanism of the reaction under consideration is provided by extended Hückel molecular orbital calculations using bond parameters established by X-ray crystallography.[2,3,11] As can be seen in Figure 4, the HOMO of the Ru(II) η^4-diene complex, which, as shown by the calculations, is relevant for electrophilic attack of either Br_2 or Br^+, is a metal-centered hybrid orbital predominantly derived from d_{z^2} and is essentially nonbonding in character. A minor contribution stems from the p_z orbitals of the terminal carbon atoms of the diene. In the ground state, however, electrophilic attack resulting in the formal oxidation from d^6 to d^4 is not possible without prior change of the orbital symmetry at the metal center as well as a reorientation of the diene moiety from an *exo* to an *endo* conformation with respect to the bromide ligands. What would be required is a metal-centered orbital of the $d_{x^2-y^2}$ type (see LUMO of the Ru(IV) η^4-diene complex in Figure 4). The LUMO reflects basically the $\sigma-\sigma$ interaction between the two bromide ligands and the Ru $d_{x^2-y^2}$ orbital, with the latter also interacting with the π_2 of the diene. All these interactions are antibonding in character.

In order to establish a reasonable mechanism for the above reactions the required changes in orbital symmetry and ligand orientations have been examined by performing EHMO calculations. We investigated the effect of positional changes of the individual ligands on both overall orbital symmetries and energies by means of computer simulations using a Walsh analysis. Slipping barriers for both the C_5Me_5 and the diene ligand, resulting in a change in hapticity, are low[16] but have only small effects on the orbital symmetries. On the other hand, rotation of the diene around the metal ligand axis would produce the desired symmetry change but is unfavorable by about 1 eV, the more so in the presence of bulky substituents (up to 5 eV). Finally, dissociation of bromide affects solely the orbital energies but not their symmetries. Therefore, it is reasonable to suggest that the symmetry change and ligand orientation is affected by a “swing” of the diene ligand by changing the dihedral angle between the C_5Me_5 and diene ligand from about +20 (see X-ray structures of Ru(II) η^4-diene complexes[11]) to about −70° (see X-ray structures of Ru(IV) η^4-diene complexes[2,3]) (Figure 4) concomitantly pushing the bromide ligand out. In fact, an optimization analysis on the Ru(η^5-C_5Me_5)(η^4-diene) fragment points to an energy minimum for a dihedral angle between 30 and 40° in line with experiment[11] and a second slightly less favorable one at about −40°. Isomerization through the planar sandwich structure has small activation barriers of ca. 0.2−0.5 eV depending on the diene. The intermediate Ru(II) η^4-diene complex so brought about has the appropriate symmetry for both Br^+ and Br_2 attack to be feasible. Since Br^+

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(16) Sapunov, V. N.; Mereiter, K.; Schmid, R.; Kirchner, K. *J. Organomet. Chem.* **1996**, in press.

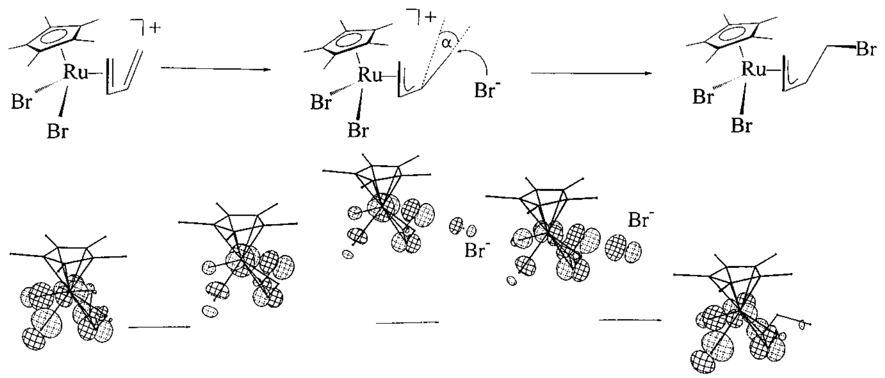

Figure 5. Addition of Br$^-$ to [Ru(η^5-C_5Me_5)(η^4-diene)Br_2]$^+$ complexes. CACAO drawing for the LUMO (C_5Me_5 AOs omitted for clarity) of the reactant and product as well as the *gauche* deformation of the diene in the course of conversion.

withdraws two electrons essentially from the metal-centered high-lying $d_{x^2-y^2}$ orbital, another vacant site emerges for attachment of the remaining Br$^-$ anion. Our former suggestion that Br_2 attacks the Ru(II) η^4-diene without prior reorganization is thus revised.[3]

The next question concerns the mechanism of the diene allyl conversion. As shown in Figure 5 the LUMO of the ground state of the Ru(IV) η^4-diene complex, since not containing the p_z AO of the terminal diene carbons, has not the necessary symmetry for nucleophilic attack to take place. An appealing possibility to overcome this problem is a *gauche* deformation of the diene ligand in the activated complex. As shown in Figure 5, such a deformation shifts the p_z AO from the inner to the terminal carbon atoms induced nucleophilic attack. Furthermore, this mechanism rationalizes in a straightforward way the inability to form Ru(IV) η^3-allyl complexes from 2,3-disubstituted diene compounds, as in this case a *gauche* deformation is prohibited due to the repulsion between one of the substituents of the diene and one of the two bromide coligands. In fact, according to pertinent computer simulations, the activation barrier of such a processs would be as high as about 4 eV in the case of the 2,3-disubstituted dienes but is otherwise very small, only ca. 0.2 eV.

Acknowledgment. Financial support by the "Jubiläumsfond der österreichischen Nationalbank" is gratefully acknowledged (Project 5305).

Supporting Information Available: Listings of atomic coordinates and *U* values, anisotropic temperature factors, complete bond lengths and angles, and least-squares planes for complexes **2**, **3**, and **7** (30 pages). Ordering information is given on any current masthead page.

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