Functionalization of one or two methyl groups in the $[Cp*_2RuBr]^+Br^-$ complex in the reaction with bromine

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The reaction of $[Cp*_2RuBr]^+Br^-$ with bromine in CH_2Cl_2 (CD_2Cl_2) in an inert atmosphere at room temperature produces the complexes $[Cp*Ru(Br)C_5Me_4CH_2Br]^+Br_3^-$ (*syn* conformer), $[Cp*Ru(Br)C_5Me_3(CH_2Br)_2]^+$ (*syn* and *anti* conformers), and $[Ru(Br)(C_5Me_4CH_2Br)_2]^+$ (*syn* conformer). All complexes were characterized by ^{1}H and ^{13}C NMR spectroscopy; the former complex, by elemental analysis. These complexes were also prepared by the reaction of $[Cp*RuC_5Me_4CH_2]^+BF_4^-$ with bromine in CH_2Cl_2.

Key words: decamethylruthenocene, bromination, singly charged cations, ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, quantum-chemical calculations.

Singly, doubly, and triply charged metallocenyl carbocations are of interest because of the ability of metal atoms (Fe, Ru, and Os) to stabilize the α-carbocationic centers through donor-acceptor interactions between one, two, or three lone pairs of the metal atom and unoccupied orbitals of the carbocationic center. Earlier, multistep and one-pot methods of oxidation of one, two, and three Me groups in decamethylmetallocenes $Cp*_2M$ ($Cp* = C_5Me_5$; M = Ru or Os) giving rise to singly, doubly, and triply charged carbocations have been documented.[1] The generation of the singly charged $[(\eta^5:\sigma\text{-}C_5Me_4CH_2)(\eta^5\text{-}Cp*)M]^+$ cations from neutral decamethylmetallocenes $Cp*_2M$ in acidic media (CF_3SO_3H or fuming sulfuric acid) affords cationic hydrides $[Cp*_2RuH]^+$ and $[Cp*_2OsH_2]^{2+}$ as intermediates.[1] Subsequent oxidation of the Me groups in the singly charged $[(\eta^5:\sigma\text{-}C_5Me_4CH_2)(\eta^5\text{-}Cp*)M]^+$ cations (M = Ru or Os) in fuming sulfuric acid occurs through protonation of the cations.[2] Protonation of the 18-electron complexes gives 17- and 19-electron paramagnetic cations,[3] in which the Me groups of the Cp* rings are readily oxidized to give the CH_2^+ groups. Oxidation of two Me groups of the Cp* ring in acidic media (fuming sulfuric acid or CF_3SO_3H/O_2) affords[1] the isomeric doubly charged homoannular and heteroannular cations, $[1,2\text{-}(\eta^5:\sigma:\sigma\text{-}(CH_2)_2C_5Me_3)(\eta^5\text{-}Cp*)M]^{2+}$ and $[1,1'\text{-}(\eta^5:\sigma\text{-}(C_5Me_4CH_2)_2M]^{2+}$ (M = Ru or Os), respectively.

In the present study, we investigated transformations of $Cp*_2Ru$ in the reactions with bromine in dichloromethane. The cationic complex $[Cp*_2RuBr]^+Br^-$ (**1**) was used as the starting decamethylruthenocene derivative. Earlier, it has been demonstrated[4] that bromine in a heterogeneous toluene—HBr—H_2O system can oxidize one Me group in the $Cp*_2Ru$ molecule to form the cationic hydroxyl-containing $[Cp*Ru(Br)C_5Me_4CH_2OH]^+Br_3^-$ complex along with the $[Cp*_2RuBr]^+[Ru(Br)_4C_5Me_4CH_2OH]^-$ complex. Under these conditions, activation of the C—H bonds in the Me group of the Cp* ring is accompanied by bromination of the Ru atom, functionalization of the CH_2 group, and oxidative cleavage of the Cp*—Ru bonds.[4]

Cationic complex **1** was synthesized in high yield (87%) by bromination of $Cp*_2Ru$ in CCl_4 according to a known procedure.[5] The reaction of complex **1** with bromine was carried out in an NMR tube in CD_2Cl_2 or in a flask with stirring in CH_2Cl_2 either at room temperature or with heating (40 °C). Bromination of the $[Cp*RuC_5Me_4CH_2]^+BF_4^-$ complex (**2**) (which was prepared according to a procedure described earlier[6]) was performed analogously. It appeared that the reaction of complex **1** with an excess of bromine (Table 1, entries *1—3*) at room temperature in CD_2Cl_2 occurs as bromination of the Me group of the Cp* ring giving rise to singly charged cationic complex *syn*-**3** (Scheme 1).

The reaction does not stop at the step of bromination of one Me group of complex **1**. A mixture of brominated complexes **4** and **5** containing the 1,2- or 1,1′-arranged $BrCH_2$ groups, respectively, (Fig. 1) can be obtained by increasing the reaction time (see Table 1, entries *1—4*) and the amount of bromine (entries *1* and *5*). The 1,2-arrangement of the bromomethyl groups was established by nuclear Overhauser effect (NOE) measurements in the low-temperature region (up to −50 °C). The ^{1}H and ^{13}C NMR spectroscopic data suggest that complex **4** is present in solution as two conformers, *anti*-**4** and *syn*-**4**, with the former substantially predominating (see Table 1).

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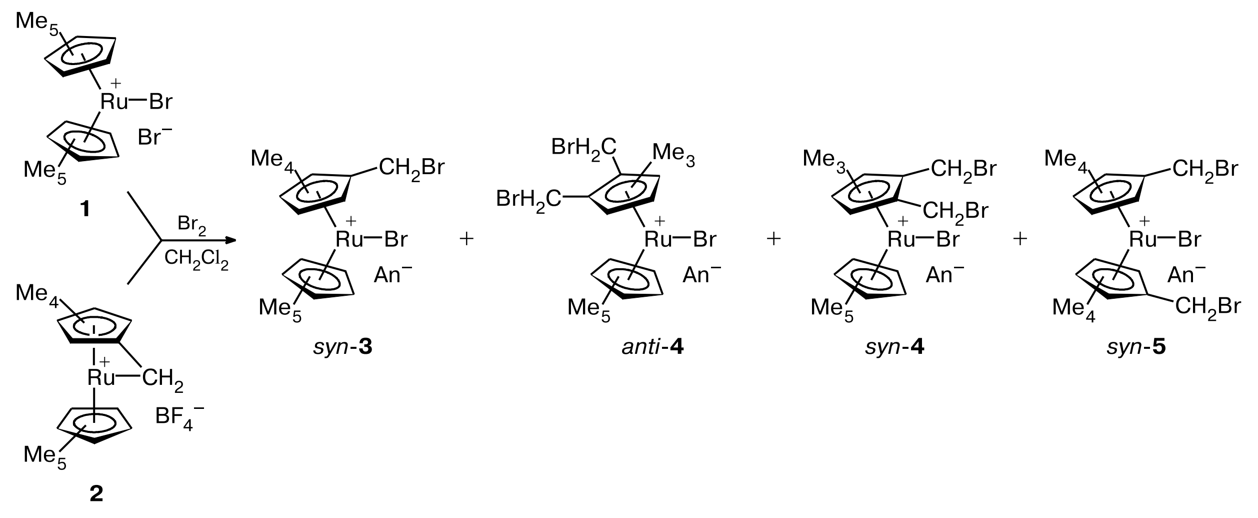
Scheme 1



An = Br_3, BF_4

Table 1. Influence of the conditions of the reaction performed at room temperature in CD_2Cl_2 on the composition of the reaction products

Starting complex	**A** : Br_2[a] (mol.)	Entry[b]	τ/h	Composition of the reaction mixture[c] (%)			
				syn-**3**	*anti*-**4**	*syn*-**4**	*syn*-**5**
1	1 : 2	*1*	24	100	0	0	0
		2	48	85	15	0	0
		3	72	51	35	8	6
		4	144	8	57	14	21
	1 : 5	*5*	24	59	29	3	9
	1 : 3	*6*[d]	24	69	22	3	6
		7[e]	0.5	62	27	3	8
		8[e]	3.5	29	52	5	14
		9[e]	6.5	11	66	6	17
	1 : 5	*10*[f]	24	38	28	10	24
2	1 : 2	*11*	24	51	34	8	7
		12	48	43	38	10	9
	1 : 7	*13*	24	7	53	20	20

[a] The ratio of the starting complex to Br_2.

[b] The complexes were oxidized with bromine in CD_2Cl_2 in argon-filled NMR tubes. A solution of complex **1** (~0.03 mmol) or complex **2** (~0.01 mmol), CD_2Cl_2 (0.28 g), and Br_2 (0.15—0.30 mmol) was placed into a tube, and the tube was sealed.

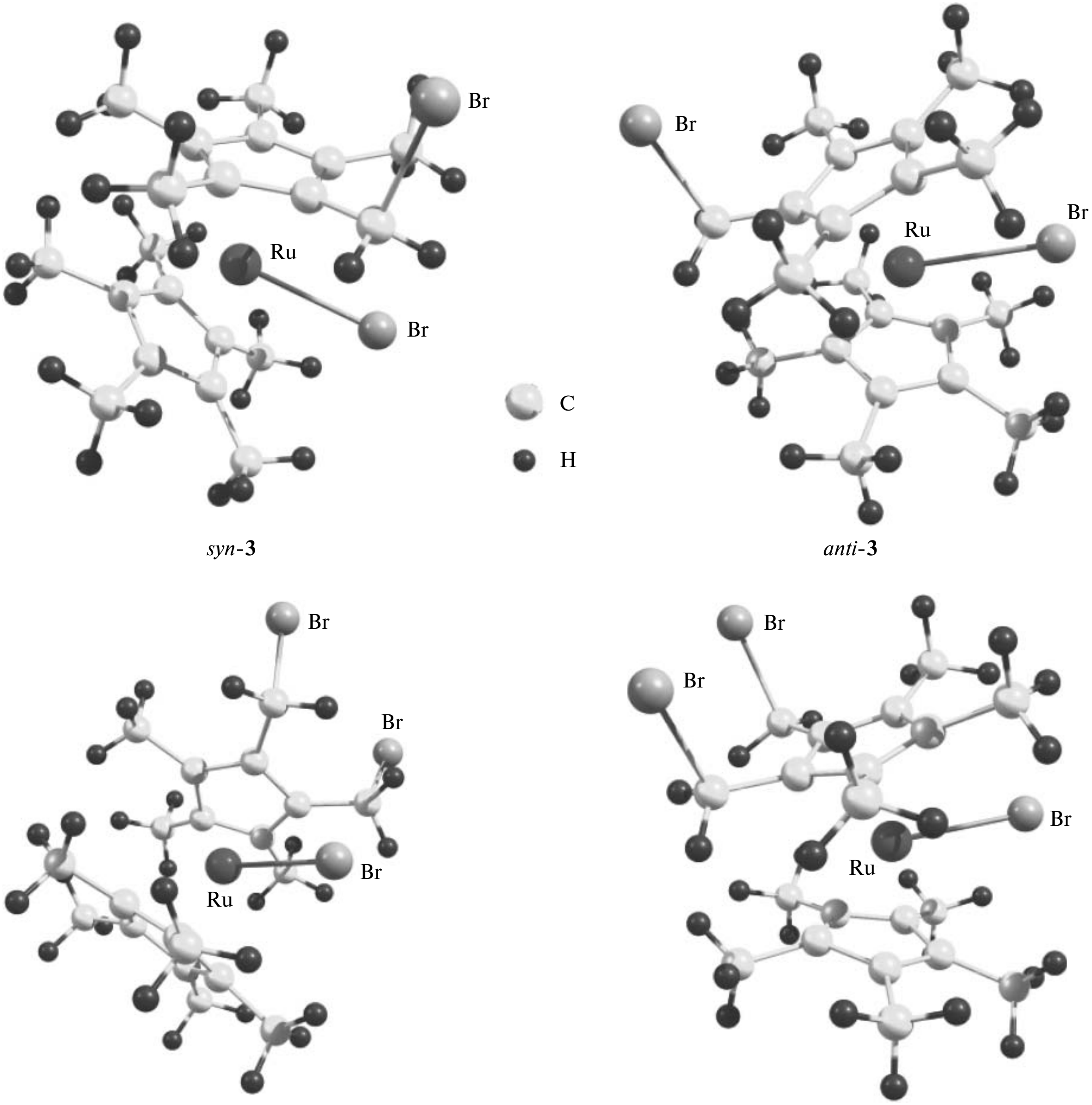
[c] The percentage of the complexes was calculated from the ^1H NMR spectra.

[d] The *anti*-**4**/*syn*-**4** ratios were as follows: *6*, ~7.3; *7*, 9.0; *8*, 10.4; *9*, 11.0.

[e] The reaction was carried out at 40 °C.

[f] The experiment was performed in CF_3CO_2H.

In experiments performed at high temperature (see Table 1, entries *7—9*), a decrease in the amount of complex *syn*-**3** is accompanied by an increase in the amount of complexes **4** and **5** in the mixture (^1H NMR spectroscopic data), the *anti*-**4**/*syn*-**4** ratio being increased from ~7 to 11 (see Table 1). The percentage of complex **5** (*syn* conformer) containing the 1,1´-arranged $BrCH_2$ groups in the mixture was at most 20%. Bromination of the Me group in complex **2** occurs somewhat faster (see Table 1, *cf.* entries *1* and *11*) to give the same products **3—5** (see Table 1, entries *11—13*). Note that the ^1H NMR spectra of the reaction mixtures showed a signal for the acidic proton of the HBr molecule at δ 7.37—8.40. In the first step of the reaction giving rise to complex **3** as the major product (from complex **1**), the integrated intensity ratio of the signals for the protons of the HBr molecule and the $BrCH_2$ group in the ^1H NMR spectra is 1 : 2. This is consistent with the fact that the formation of complex **3** is accompanied by elimination of the HBr molecule. Bromination of complex **1** in CF_3CO_2H for 24 h afforded the same products **3—5** (see Table 1, entry *10*). In these reaction, products derived through Ru—Cp* bond cleavage were not detected.[4] High solubility of reaction products **3—5** in CH_2Cl_2 and poor solubility in diethyl ether may be indicative of the ionic character of these complexes. Bromination of complex **1** in CH_2Cl_2 on a preparative scale (see the Experimental section) afforded a mixture of complexes *syn*-**3**, *syn*- and *anti*-**4**, and *syn*-**5** in a ratio of 59 : 32 : 9. Precipitation with diethyl ether gave complex **3** (47%). Elemental analysis of the latter demonstrated that it contains Br_3^- as the anion. The formation of the tribromide anion has been observed earlier.[4,7] Bromination of complex **2** in CH_2Cl_2 at room temperature produced complex **3** (An = BF_4) (87%), which was characterized by ^1H and ^{13}C NMR spectra (Tables 2 and 3), as well as by ^{11}B and ^{19}F NMR spectra (see the Experimen-



syn-**3** *anti*-**3**

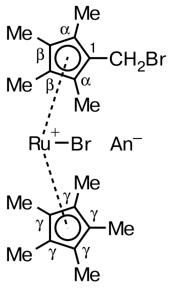
syn-**4** *anti*-**4**

Fig. 1. Molecular structures of the *syn* and *anti* conformers of brominated complexes **3** and **4**.

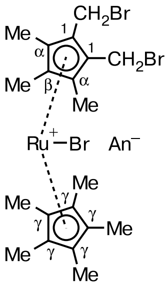
tal section). Unfortunately, we failed to isolate complexes **4** and **5** because of their high susceptibility to hydrolysis.

The existence of the *syn* conformer of complex **3** and the *syn* and *anti* conformers of complex **4** in solution is evidence for the absence of free rotation of the C_5 ligands. This can be attributed to a steric interaction between the organometallic cation and the Br_3^- anion. It should be noted that the predominant formation of the *syn* configuration of the allyl complex $Cp^*Ru(Br)_2(CHR^1CHCHCHR^2Br)$ was accounted[**8**] for by the presence of a weak three-center four-electron C—Br...Ru interaction. For the complexes under consideration, the existence of an CH_2Br...Ru interaction of this type without violation of the molecular symmetry is also probable, but only for complex *anti*-**4**. It should be noted that the signals for the protons of the $BrCH_2$ groups in the ^1H NMR spectrum of complex *anti*-**4** are slightly broadened ($\nu_{1/2}$ = 3.2—3.5 Hz) compared to the signals for the protons of the Me groups ($\nu_{1/2}$ = 2.6—3.2 Hz), whereas the widths of the signals for the protons of both the Me groups and the $BrCH_2$ group in the spectrum of complex *syn*-**3** are at most 2.3—2.8 Hz. In particular, this can be attributed to hindered rotation about the C_c—CH_2Br bonds (C_c is the C atom of the ring) in complex *anti*-**4** at room temperature. Complexes **3**—**5** were

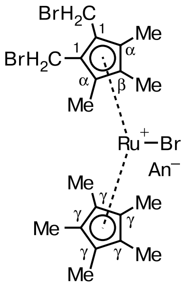
Table 2. ^{1}H NMR spectroscopic data for the cationic ruthenium complexes in CD_2Cl_2



syn-**3**



syn-**4**



anti-**4**

Complex	An	δ (*J*/Hz)			
		γ-Me (s, 15 H)	α,α′-Me (s)	β,β′-Me (s)	CH_2^{AB}
2[a]	PF_6	1.86	1.63 (6 H)	1.96 (6 H)	4.75 (s, 2 H)
2[b]	Br	1.79	1.57 (6 H)	1.87 (6 H)	4.48 (s, 2 H)
	BF_4	1.77	1.54 (6 H)	1.85 (6 H)	4.41 (s, 2 H)
syn-**3**	Br_3	1.97	1.90 (6 H)	2.09 (6 H)	3.93 (s, 2 H)
	BF_4	1.94	1.88 (6 H)	2.08 (6 H)	3.94 (s, 2 H)
syn-**4**	Br_3	2.00	1.97 (6 H)	1.98 (3 H)	4.00, 4.14 (dd, 4 H, *J* = 11.5)
	BF_4	1.97	1.95 (6 H)	1.96 (3 H)	4.02, 4.15 (dd, 4 H, *J* = 11.5)
anti-**4**	Br_3	2.02	2.06 (6 H)	2.39 (3 H)	3.79, 3.96 (dd, 4 H, *J* = 11.3)
	BF_4	1.99	2.04 (6 H)	2.37 (3 H)	3.82, 3.97 (dd, 4 H, *J* = 11.2)
syn-**5**	Br_3	—	1.95 (12 H)	2.13 (12 H)	3.94 (s, 4 H)
	BF_4	—	1.93 (12 H)	2.12 (12 H)	3.96 (s, 4 H)

[a] Lit. data.[9]

[b] Complex **2** was prepared by UV irradiation of complex **1** in CD_2Cl_2.[10]

characterized by ^{1}H and ^{13}C NMR spectroscopy (see Tables 2 and 3, respectively).

As can be seen from Table 2, the signals for the protons of the CH_2 groups in the ^{1}H NMR spectra of cationic complexes **2** with different anions are observed at δ 4.41—4.75, whereas the signals for the protons of the $BrCH_2$ groups of products **3**—**5** appear in a rather narrow range (Δδ 0.36) at δ 3.79—4.15. This fact may be evidence that complexes **3**—**5** have the same charge. The assignment of the signals for the protons of the α- and β-Me groups of the $C_5Me_4CH_2Br$ ring in complex *syn*-**3** was made taking into account the data for complexes **4** (*syn* and *anti*). The latter are characterized by different integrated intensity ratios of the signals for the protons of the α-Me (6 H) and β-Me (3 H) groups. It should be noted that $\delta_{\alpha\text{-Me}} < \delta_{\beta\text{-Me}}$ regardless of the conformation. Analysis of the spectra of monocationic complexes **2** and **3** (An = Br_3) shows that the introduction of two Br atoms into the molecule (CH_2Br and Ru—Br) leads to downfield shifts of the signals for the protons of the Me groups in the α, β, and γ positions by 0.33, 0.22, and 0.18 ppm, respectively. As can be seen from a comparison of the spectra of monocationic complexes *anti*-**4** and *syn*-**3**, the second CH_2Br group causes downfield shifts of all signals for the protons of the Me groups by 0.16 (α), 0.30 (β), and 0.05 ppm (γ). The largest shifts are observed for the signals for the protons of the α-Me-groups of complex *syn*-**3** and of the β-Me group of complex *anti*-**4**. These shifts cannot be attributed merely to the negative inductive effect (−*I*) of the bromine-containing substituent. Apparently, the downfield shift is associated with anisotropy of the nearby bulky Br atom at the Ru atom. Hence, the complex presumably has a *syn* and *anti* conformation in the former and latter cases, respectively. The fact that the signal for the protons of the CH_2Br group of complex *syn*-**3** is observed at lower field (δ 3.93) compared to the signal of the analogous groups of complex *anti*-**4** (dd, the center at δ 3.88) is also consistent with the proposed assignment of the conformations. In complexes *anti*-**4** and *syn*-**4**, the protons of the CH_2Br groups appear as an AB system (see Table 2), its center for complex *syn*-**4** (δ 4.07) being shifted downfield compared to that for *anti*-**4** (see above). Evidently, this difference is also associated with the influence of anisotropy of the nearby bulky Br atom at the Ru atom in complex *syn*-**4**. The analogous influence of the Cl atoms bound to the Ru atom on the *syn*- and *anti*-CH_2Cl groups in the Cp*Ru[1-(*syn*-CH_2Cl)All]Cl_2 and Cp*Ru[1-(*anti*-CH_2Cl)All]Cl_2 complexes has been observed[11] in the ^{1}H and ^{13}C NMR spectra. The proton signals of the *syn*-CH_2Cl group appear at lower field compared to those of the analogous group in the *anti* isomer. Complex *syn*-**5** has a symmetric structure and is characterized by three singlets in the ^{1}H NMR spectrum at δ 1.95, 2.13, and 3.94 having an integrated intensity ratio of 12 : 12 : 4. The absence of nonequivalent Me groups and the similar chemical shifts of the protons of the $BrCH_2$ groups for complexes *syn*-**5** and *syn*-**3** (δ 3.94 and 3.93, respectively) are consistent with the above assignment of the conformations.

The ^{13}C NMR spectroscopic data (see Table 3) confirm the proposed structures of the complexes. The signals for the C atoms of the $BrCH_2$ groups are in a rather narrow range δ 21.8—23.8, the most downfield signal corresponding to complex *syn*-**3**, which is also consistent with the *syn* arrangement of the C(1)—CH_2Br and Ru—Br bonds. An analogous arrangement of these bonds is also possible for complex *syn*-**5**, for which the signal of the CH_2Br group is observed at δ 23.11. For complex *anti*-**4**, the signals for the C atoms of the $BrCH_2$ groups and for

Table 3. ^{13}C NMR spectroscopic data for the cationic ruthenium complexes in CD_2Cl_2

Complex	An	δ							
		α,α′-Me	β,β′-Me	γ-Me	CH_2	C atoms of Cp* rings			
						C(1)	α,α′-C	β,β′-C	γ-C
1	Br	—	—	11.38	—	—	—	—	105.80
2	PF_6*	8.01	8.74	9.51	74.67	105.36	97.22	107.20	96.92
	Br	8.43	9.10	9.88	75.11	105.41	97.22	107.17	96.95
syn-**3**	Br_3	10.17	11.59	11.45	23.82	98.49	109.98	103.81	107.30
	BF_4	10.09	11.59	11.35	23.67	98.17	110.13	103.60	107.18
syn-**4**	Br_3	9.94	10.21	11.50	22.92	103.31	107.76	104.02	108.28
	BF_4	9.72	9.89	11.13	23.01	102.90	106.42	104.11	108.22
anti-**4**	Br_3	10.04	13.87	11.73	21.79	96.13	105.76	111.55	108.28
	BF_4	9.78	13.68	11.35	21.89	96.02	105.76	111.53	108.22
syn-**5**	Br_3	10.41	11.85	—	23.11	99.56	108.53	104.94	—
	BF_4	10.07	11.62	—	23.16	99.13	108.46	104.96	—

* Lit. data.[9]

C(1) appear at higher field (δ 21.79 and 96.13) compared to those for *syn*-**4** (δ 22.92 and 103.31, respectively). An analogous dependence of the chemical shifts of the C atoms of the CH_2Cl group on the mutual arrangement of the $RuCl_2$ and CH_2Cl groups has also been observed[11] in the ^{13}C NMR spectra of the above-mentioned isomeric complexes: $\delta_{syn\text{-}CH_2Cl} > \delta_{anti\text{-}CH_2Cl}$. The assignment of the signals of the C atoms of the α- and β-Me groups and the C atoms of the cyclopentadienyl rings of complexes **4** (*syn* and *anti*) was made taking into account their integrated intensities. For example, the signals for both the C atoms of the β-Me groups and the C_β atoms of the cyclopentadienyl ring $\underline{C}_5Me_3(CH_2Br)_2$ in the ^{13}C NMR spectrum of complex *anti*-**4** appear at higher field than the analogous signals for the C atoms in the α position. Complex *syn*-**4**, like complex *anti*-**4**, is characterized by $\delta_{\alpha\text{-Me}} < \delta_{\beta\text{-Me}}$. The reverse situation is observed for the C_α and C_β atoms of the $\underline{C}_5Me_3(CH_2Br)_2$ ring of complex *syn*-**4**. Taking into account these data, the assignment of the signals for the C atoms of complex *syn*-**3** was made. Due to the presence of two equivalent $C_5Me_4CH_2Br$ rings in complex *syn*-**5**, its ^{13}C NMR spectrum shows two equal-intensity signals (4 C each) of the α- and β-Me groups and two signals with an intensity of 4 C in the region of signals for the ring carbon atoms. The additive contributions[12] of the Br atom upon the replacement of one or two Me-groups with the CH_2Br groups (α, β, and γ effects of the substituent) can be estimated by comparing the chemical shifts of the C atoms of complexes **3**—**5** with those of the analogous C atoms of the starting complex **1**. These differences are given in Table 4. It can be seen that the CH_2Br group in complexes **3**—**5** has the most substantial shielding effect on the C(1) atoms. The monotonicity of the series, which characterizes the α effect of the CH_2Br group in going from complex *syn*-**3** containing one CH_2Br group to complex *syn*-**5** containing two CH_2Br groups in the 1,1′ position and to complex *syn*-**4** containing two CH_2Br groups in the 1,2 position, and the fact the α effect for complex *anti*-**4** containing two CH_2Br groups in the 1,2 position is inconsistent with this series confirm the validity of the above assignment of the conformations. The β effect of the CH_2Br groups changes in parallel with the α effect.

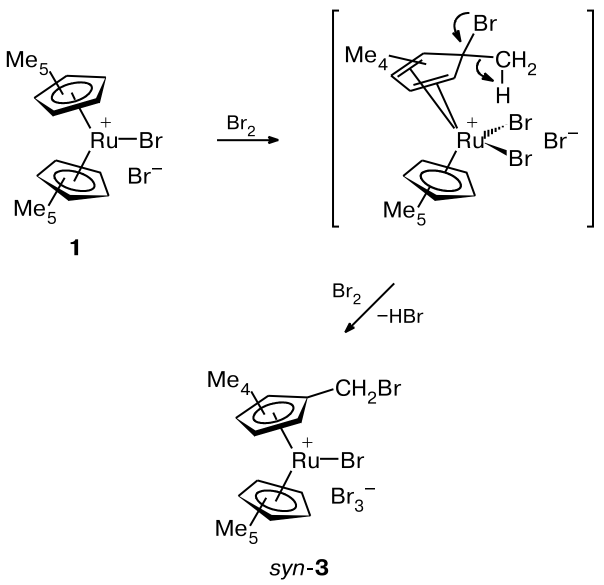
Table 4. Differences between the chemical shifts (Δδ) of the C atoms in the ^{13}C NMR spectra of complexes **3**—**5** and **1** (the α, β, and γ effects of the $BrCH_2$ substituent)

Complex	Δδ		
	α Effect (for C(1))	β Effect (for C_α)	γ Effect (for C_β)
syn-**3**	−7.31	+4.18	−1.99
syn-**4**	−2.49	+1.96	−1.78
anti-**4**	−9.67	−0.04	+5.75
syn-**5**	−6.24	+2.73	−0.86

Turning our attention to the discussion of the possible scheme of transformations of complex **1**, let us consider the direction of attack of the Br atom in oxidative addition to metallocenes. It is known[13,14] that bromination of the $Ru(\eta^5\text{-}Cp)(\eta^4\text{-}C_5H_4O)Br$ or $Ru(\eta^5\text{-}Cp^*)(\eta^4\text{-}DE)Br$ complexes (DE is diene) occurs at the metal atom and one of the rings, for which the addition of bromine leads to a change in the bonding mode with the metal atom $\eta^4 \to \eta^3$.

In the case under consideration, the initial addition of bromine to the Ru atom and the C atom of the Cp* ring accompanied by a change in the bonding mode $\eta^5 \to \eta^4$ cannot be ruled out as well (Scheme 2). Subsequent elimination of HBr affords complex **3**. Oxidation of the second Me group occurs apparently according to an analogous scheme.

Scheme 2



Therefore, bromine in a neutral medium (CH_2Cl_2) can oxidize one or even two Me groups of the Cp* ring followed by bromination of the CH_2 groups. Upon oxidation of the second Me group of the Cp* ring in complex **3**, the amount of the 1,2-isomer in the mixture became much larger than that of the 1,1´-isomer. Under the conditions used in the present study, no products formed through the Ru—Cp* bond cleavage (analogous to those observed earlier[4]) were detected.

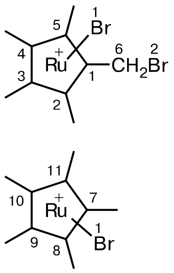
To confirm the structures of brominated cations **3** and **4** (*syn* and *anti* conformations), we performed quantum-chemical calculations by density functional theory (DFT). The geometric parameters of the molecules in the gas phase (bond lengths and bond angles) are given in Table 5. The influence of the Br(1) atom at the Ru atom is manifested not only in the deviation from the planar arrangement of the five-membered rings in all complexes but also in elongation of one of the C—C bonds in both Cp rings (elongation of the C(5)—C(1) and C(7)—C(8) bonds in complex *syn*-**3**, the C(3)—C(4) and C(7)—C(8) bonds in complex *anti*-**3**, the C(1)—C(2) and C(8)—C(9) bonds in complex *syn*-**4**, and the C(3)—C(4) and C(8)—C(9) bonds in complex *anti*-**4**). The bond between the Ru atom and two Cp rings is of the classical η^5 type. In four complexes, *syn*-**3**, *anti*-**3**, *syn*-**4**, and *anti*-**4**, the Ru—C bond lengths in the unsubstituted Cp ring are only slightly different. The difference between the longest and shortest Ru—C bonds in complexes *syn*-**3**, *anti*-**3**, *syn*-**4**, and *anti*-**4** are 0.085, 0.077, 0.095, and 0.057 Å, respectively. In the substituted Cp ring of *syn*-complexes **3** and **4**, the difference between the longest and shortest Ru—C bonds are 0.076 and 0.068 Å, respectively; in the *anti* conformers, 0.126 and 0.114 Å. The smaller difference in the bond lengths and, consequently, the smaller angle of deviation from the planar arrangement of the rings are, apparently, attributed to the fact that the Ru—CCH_2Br bond is the shortest one in all the complexes under consideration: 2.306 Å for *syn*-**3**, 2.278 Å for *anti*-**3**, 2.302 Å for *syn*-**4** (Ru—C(2)), and 2.284 Å for *anti*-**4** (Ru—C(1)). An analogous decrease in the Ru—C(1) bond length compared to the other Ru—C bond lengths was observed[15] also for the $[Cp^*RuC_5Me_4CH_2]^+$ cation (2.156 (DFT) and 2.066 Å (X-ray diffraction data); 2.430 (DFT) and 2.273 Å (X-ray diffraction data), respectively). According to the results of calculations by DFT,[15] the Ru—C(1) and Ru—C(2) bonds in the doubly charged $[Cp^*RuC_5Me_3(CH_2)_2]^{2+}$ cation (2.200 and 2.192 Å, respectively) are also shortened compared to the other Ru—C bonds (2.634—2.901 Å). The interatomic Ru—C(6) distances in complexes *syn*- and *anti*-**3** (3.474 and 3.519 Å, respectively) and the Ru—C(6) and Ru—C(7) distances in complexes *syn*- and *anti*-**4** (3.537 and 3.449 Å, 3.505 and 3.444 Å, respectively) are indicative of the absence of bonding between the Ru atom and the CH_2Br groups. Therefore, the smaller Ru—C(1) bond lengths estimated by quantum-chemical calculations (DFT) account for the upfield shifts of the signals for the C(1) atoms in the ^{13}C NMR spectra of complexes **3**—**5**. For complexes *syn*-**3** and *anti*-**4**, quantum-chemical calculations showed that both the Ru—Br (2.776 and 2.770 Å, respectively) and C—Br bonds (2.115 and 2.110 Å, respectively) are longer than those in the brominated Ru complexes (2.547 and 1.879 Å, respectively).[16]

Experimental

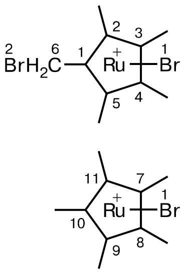
The ^1H and ^{13}C NMR spectra of solutions of the complexes were recorded on a Bruker AMX-400 spectrometer (400.13 and 100.61 MHz, respectively) in CD_2Cl_2. The chemical shifts of the signals in the ^1H and ^{13}C NMR spectra were measured relative to $CHDCl_2$ (δ_H 5.32) and CD_2Cl_2 (δ_C 53.61), respectively. The ^{11}B and ^{19}F NMR spectra were recorded on Bruker WP-200 SY (64.2 MHz) and Bruker Avance-300 (282.4 MHz) spectrometers, respectively, with the use of $BF_3 \cdot Et_2O$ and $CFCl_3$ as the external standard. Quantum-chemical calculations were carried out by the DFT method using the Becke—Lee—Yang—Parr functional (BLYP/LanL2DZ) with full geometry optimization on a dual processor SC760-D minisupercomputer (A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences) with the use of the GAUSSIAN-98 program package.[17] Complex **2** was synthesized from $Cp^*RuC_5Me_4CH_2OH$ and $HBF_4 \cdot OEt_2$ according to a procedure described earlier.[6]

Bromo[(decamethyl)bis(cyclopentadienyl)]ruthenium bromide, $[Cp^*_2RuBr]^+Br^-$ (1) was prepared according to a known procedure.[5] A solution of Br_2 (0.1043 g, 0.652 mmol) in CCl_4 (3 mL) was added dropwise with stirring to a solution of Cp^*_2Ru (0.2027 g, 0.546 mmol) in CCl_4 (10 mL) at 20 °C for 10 min. The reaction mixture was stirred for 2 h, the solvent was removed *in vacuo*, and dark-green crystals of compound **1** were obtained in a yield of 87% (0.2513 g, 0.473 mmol). The spectro-

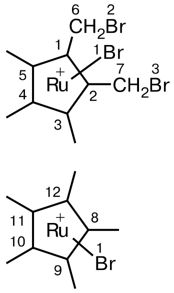
Table 5. Optimized geometric parameters of singly charged cations **3** and **4** in the *syn* and *anti* conformations*



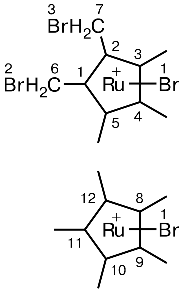
syn-**3**



anti-**3**



syn-**4**



anti-**4**

Parameter	*syn*-**3**	*anti*-**3**	*syn*-**4**	*anti*-**4**
Bond		d/Å		
Ru—Br(1)	2.776	2.762	2.782	2.770
C(1)—C(6)	1.510	1.513	1.514	1.515
C(2)—C(7)	—	—	1,516	1.512
C(6)—Br(2)	2.115	2.112	2.110	2.110
C(7)—Br(3)	—	—	2.107	2.111
C(1)—C(2)	1.440	1.479	**1.507**	1.480
C(2)—C(3)	1.475	1.431	1.440	1.437
C(3)—C(4)	1.471	**1.508**	1.474	**1.506**
C(4)—C(5)	1.436	1.432	1.470	1.434
C(5)—C(1)	**1.506**	1.478	1.438	1.476
C(7)—C(8)	**1.507**	**1.508**	—	—
C(8)—C(9)	1.437	1.435	**1.508**	**1.507**
C(9)—C(10)	1.473	1.475	1.437	1.438
C(10)—C(11)	1.479	1.477	1.473	1.473
C(11)—C(7)	1.434	1.435	—	—
C(11)—C(12)	—	—	1.479	1.475
C(12)—C(8)	—	—	1.435	1.439
Ru—C(1)	**2.306**	**2.278**	2.346	**2.284**
Ru—C(2)	2.336	2.365	**2.302**	2.333
Ru—C(3)	2.319	2.404	2.350	2.392

Parameter	*syn*-**3**	*anti*-**3**	*syn*-**4**	*anti*-**4**
Bond		d/Å		
Ru—C(4)	2.369	2.397	2.339	2.398
Ru—C(5)	2.482	2.357	2.368	2.365
Ru—C(6)	3.474	3.519	3.537	3.505
Ru—C(7)	2.359	2.376	3.449	3.444
Ru—C(8)	2.387	2.387	2.360	2.342
Ru—C(9)	2.363	2.358	2.390	2.372
Ru—C(10)	2.302	2.310	2.333	2.350
Ru—C(11)	2.345	2.368	2.295	2.315
Ru—C(12)			2.353	2.347
Angle		ω/deg		
Ru—C(1)—C(6)	129.98	135.32	131.42	133.54
Ru—C(2)—C(7)	—	—	128.17	125.85
Ru—C(3)—Me	136.29	133.29	—	—
Ru—(C5)—Me	134.52	130.16	—	—
Ru—C(8)—Me	134.84	133.97	—	—
Ru—C(10)—Me	135.89	135.85	—	—
Ru—C(4)—Me	—	—	136.45	133.10
Ru—C(9)—Me	—	—	134.61	133.54
Ru—C(11)—Me	—	—	135.03	136.60

* The structural formulas show the projections of the Ru—Br(1) bond onto the substituted and unsubstituted Cp* rings.

scopic characteristics of complex **1** are consistent with the published data.[5]

Bromo(bromomethyltetramethylcyclopentadienyl)(pentamethylcyclopentadienyl)ruthenium tribromide, [Cp*Ru(Br)C$_5$Me$_4$CH$_2$Br]$^+$Br$_3$$^-$ (3, An = Br$_3$). A solution of Br$_2$ (0.2211 g, 1.38 mmol) in CH$_2$Cl$_2$ (3 mL) was added dropwise with stirring to a solution of complex **1** (0.1470 g, 0.277 mmol) in CH$_2$Cl$_2$ (10.54 g) at 20 °C under argon for 0.5 h. After one day, the ^{1}H NMR spectroscopic analysis showed that the mixture contained complexes *syn*-**3** (59%), *anti*-**4** (29%), *syn*-**4** (3%), and *syn*-**5** (9%). The solution was concentrated *in vacuo*, and diethyl ether was added until a precipitate was obtained. Complex **3** was obtained in 47% yield (0.0784 g, 0.129 mmol). Found (%): C, 30.80; H, 3.64; Br, 51.58. C$_{20}$H$_{29}$Br$_5$Ru. Calculated (%): C, 31.19; H, 3.80; Br, 51.89. The ^{1}H and ^{13}C NMR spectroscopic data are given in Tables 2 and 3, respectively.

Bromo(bromomethyltetramethylcyclopentadienyl)(pentamethylcyclopentadienyl)ruthenium tetrafluoroborate, [Cp*Ru(Br)C$_5$Me$_4$CH$_2$Br]$^+$BF$_4$$^-$ (3, An = BF$_4$). Complex **3** (An = BF$_4$) was prepared analogously in a yield of 87% (0.0715 g, 0.116 mmol) by the reaction of complex **2** (0.0613 g, 0.134 mmol), Br$_2$ (0.1006 g, 0.629 mmol), and CH$_2$Cl$_2$ (13 mL) at ~20 °C for 3.5 h. The ^{1}H and ^{13}C NMR spectroscopic data are given in Tables 2 and 3, respectively. ^{11}B NMR, δ: −1.35. ^{19}F NMR, δ: −74.79 (sept, 0.2 F, $J_{\mathrm{F,B}}$ = 0.3 Hz); −74.84 (q (1 : 1 : 1 : 1), 0.8 F, $J_{\mathrm{F,B}}$ = 1.0 Hz).

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