New one-step methods for the synthesis of the metallonium dication $[Ru(\eta^5\text{-}C_5Me_5)(\eta^5{:}\sigma{:}\sigma\text{-}C_5Me_3(CH_2)_2)]^{2+}$ and its heteroannular analog starting from decamethylruthenocene

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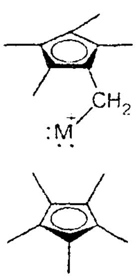
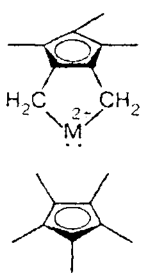
The reaction of decamethylruthenocene with oleum or with an oleum—acid (CF_3SO_3H or CF_3CO_2H) mixture as well as UV photolysis of a $Cp^*{}_2Ru$ solution in CF_3SO_3H in the presence of a small amount of oleum afforded two metallonium dications, *viz.*, $[Ru(\eta^5\text{-}C_5Me_5)(\eta^5{:}\sigma{:}\sigma\text{-}C_5Me_3(CH_2)_2)]^{2+}$ and $[Ru(H_2)(\eta^5{:}\sigma\text{-}C_5Me_4CH_2)_2]^{2+}$. The structures of these dications were confirmed by the results of their alkaline hydrolysis and NMR spectra.

Key words: decamethylruthenocene, protonation, UV photolysis, metallonium dications, hydrolysis, NMR spectra.

Previously,[1] we have demonstrated that the Ru- and Os-containing cations $[C_5Me_5MC_5Me_4CH_2]^+$ are metallonium compounds of type **A** rather than carbocations.



A



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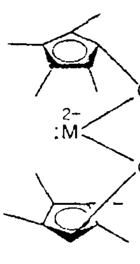

C

Analogously, metallonium dications of types **B** and **C** are formed when two α-CH_2 groups are present at positions 1,2- or 1,1′.[1,2] Of three lone electron pairs (d_{xy}, d_{z^2}, and $d_{x^2-y^2}$) of the metal atoms in these compounds, only two electron pairs efficiently interact with the α-carbocationic centers. Previously, we have prepared cations of types **A**—**C** (M = Ru or Os)[2,3] from decamethylmetallocenes according to multistage procedures through the corresponding carbinols. In this work, we developed two one-step procedures for the synthesis of metallonium dications based on decamethylruthenocene $Cp^*{}_2Ru$ ($Cp^* = C_5Me_5$).

Results and Discussion

Previously, we have demonstrated[4] that the protonation product $[Cp^*{}_2RuH]^+An^-$ (**2**) was formed from $Cp^*{}_2Ru$ (**1**) in the presence of strong acids (CF_3CO_2H or CF_3SO_3H). UV photolysis of this product afforded the salt of the onium monocation $[Ru(\eta^5\text{-}C_5Me_5)(\eta^5{:}\sigma\text{-}C_5Me_4CH_2)]^+$ (**3**). When developing a preparative procedure for the synthesis of monocation **3**, we found that the addition of a small amount of oleum resulted in the formation of 6—9% of cationic species. The present study demonstrated that these species are dications.

With the aim of preparing the dications as the major reaction products, we studied the reactions of ruthenocene **1** with oleum and with a mixture of oleum and acid (CF_3SO_3H or CF_3CO_2H) taken in a ratio of ~1 : 1. We also used broad-band UV photolysis for generating metallonium dications according to a procedure developed previously.[4]

Our experiments demonstrated (control by the ^1H NMR spectra) that the reaction of ruthenocene **1** with oleum (method 1) as well as UV photolysis of ruthenocene **1** in CF_3SO_3H with the addition of a small amount of oleum (method 2) afforded two dications (Table 1). One of them was identified as the homoannular 1,2-dication $[Ru(\eta^5\text{-}C_5Me_5)(\eta^5{:}\sigma{:}\sigma\text{-}C_5Me_3(CH_2)_2)]^{2+}$ (**4**) (the structure of type **B**, M = Ru) based on the fact that the ^1H and ^{13}C NMR spectra coincide with the published data on this cation.[2] The ^1H NMR spectrum of the second dication differs from the spectrum of the expected 1,1′-heteroannular dication $[Ru(\eta^5{:}\sigma\text{-}C_5Me_4CH_2)_2]^{2+}$ (**5**) with the structure of type **C** (M = Ru) reported previously.[3] Based on the ^1H and ^{13}C NMR spectra (Tables 2 and 3, respectively) as well as on the results of chemical conversions (alkaline hydrolysis), the $[Ru(H_2)(\eta^5{:}\sigma\text{-}C_5Me_4CH_2)_2]^{2+}$ structure (**6**) was tentatively assigned to this dication. Previously,[1] we have demonstrated that dications **4** and **5** are very

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Table 1. Effects of the concentration of oleum and the time of UV irradiation on the formation of the cationic complexes from Cp^*_2Ru (**1**)

Run	Medium[b]	Amount		τ[a] /h	Distribution of the complexes (%)			
		Acid /mmol	Oleum /g		**2**	**3**	**4**	**6**
1	I	—	0.71	—	—	—	50	50
2	II	4.02	0.45	—	—	—	49	51
3	III	2.95	0.38	—	—	—	43	57
4	II	2.75	0.06	—	58	35	4	3
5	II	2.75	0.06	5	9	86	3	2
6	II	2.75	0.06	10	—	92[c]	5	3
7	II	3.68	0.14	—	56	28	9	7
8	II	3.68	0.14	5	—	58[c]	23	19
9	II	3.68	0.14	10	—	33[c]	39	28
10	II	3.68	0.14	15	—	—	49	51

[a] τ is the time of irradiation.

[b] I, oleum, II, CF_3SO_3H—oleum; III, CF_3CO_2H—oleum.

[c] In the ^1H NMR spectrum, the signals of monocation **3** are broadened.

moisture-sensitive and we failed to isolate these compounds as free salts.

Dications **4** and **6** were immediately formed in approximately equal amounts in the reactions of ruthenocene **1** with oleum (Table 1, run 1) as well as with a mixture of acid (CF_3SO_3H or CF_3CO_2H) and oleum taken in a weight ratio of ~1 : 1 (Table 1, runs 2 and 3). When CF_3SO_3H and oleum were taken in a ratio of 5 : 1, the reaction substantially slowed down. We attempted to use UV photolysis to accelerate this reaction. In this case, the reaction proceeded more slowly compared to method 1; however, this allowed us to follow the stages of the conversion of ruthenocene **1** into dications **4** and **6**.

With the aim of searching for optimum conditions of generation of the dications with the use of UV photolysis, we studied the effect of the reagent ratio and the duration of irradiation (Table 1, runs 4—10). It appeared that the reaction can be directed toward the formation of monocation **3** or dications **4** and **6** by varying the CF_3SO_3H—oleum ratio. Thus monocation **3** was obtained in 86—92% yield with the use of the CF_3SO_3H—oleum weight ratio of 7 : 1 after irradiation for 5—10 h (Table 1, runs 4—6). In this case, the total content of dications **4** and **6** was 5—8%. An increase in the amount of oleum (the CF_3SO_3H—oleum ratio was 4 : 1) led to an increase in the yield of the dications. Thus irradiation for 5 h afforded monocation **3** and a mixture of the dications in almost equal amounts (58% and 42%, respectively; Table 1, runs 7 and 8). In this case, cationic hydride **2** completely disappeared. Further irradiation of the mixture (run 9) led to a decrease in the yield of monocation **3** (33%) and to an increase in the total yield of dications **4** and **6** (up to 67%). After irradiation for 15 h (Table 1, run 10), the reaction mixture contained only dications **4** and **6** in a ratio of 1 : 1. An analogous result was obtained under the action of oleum or a 1 : 1 CF_3SO_3H—oleum mixture on the monocation $[Ru(\eta^5\text{-}C_5Me_5)(\eta^5\text{:}\sigma\text{-}C_5Me_4CH_2)]^+PF_6^-$ (**3a**).

These results demonstrate that the formation of dications **4** and **6** occurs in stages through cationic monohydride **2** followed by its conversion into monocation **3** (Scheme 1).

Special experiments demonstrated that the final products, *viz.*, cationic complexes **4** and **6**, are rather stable. Thus when this mixture of the dications in a CF_3SO_3H—oleum medium (taken in the ratio used in run 10, Table 1) was irradiated for 10 h or heated at 60 °C for 5 h, the ratio between these complexes remained unchanged and no new complexes were formed.

The structures of complexes **4** and **6** were confirmed by ^1H and ^{13}C NMR spectroscopy (Tables 2 and 3, respectively). The identity of dications **4**, which were prepared upon protonation of the corresponding dicarbinol[3] and upon protonation of ruthenocene **1** in a CF_3SO_3H—oleum medium, was established by the ^1H NMR spectra (Table 2, *cf.* spectra 5 and 2) and the ^{13}C NMR spectra (Table 3, *cf.* spectra 3 and 2). In the ^1H NMR spectrum (Table 2, spectrum 5; Fig. 1) recorded at room temperature, two doublets at δ 4.75 and δ 5.16 ($^2J_{HH}{}^{gem}$ = 1.8 Hz) for the H_A and H_B protons of two CH_2 groups ($\Delta\delta_{AB}$ = 0.42) were assigned to dication **4**. The singlet for the protons of the β-Me group (3 H) is observed at lower field than the singlet for the protons of two α-Me groups (6 H) in the $C_5Me_3(CH_2)_2$ ring, *i.e.*, $\delta_{\beta\text{-Me}} > \delta_{\alpha\text{-Me}}$.

Two broadened low-field singlets (2 H each) for the H_A and H_B protons of two CH_2 groups observed in this spectrum (Table 2, spectrum 5; Fig. 1) were assigned to

Scheme 1

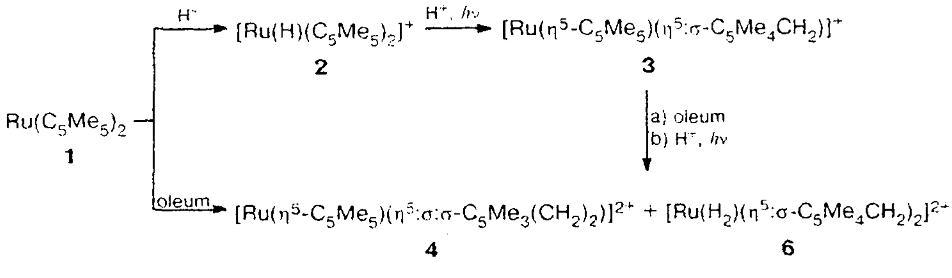


Table 2. ^{1}H NMR spectra of the ruthenium complexes in different media

Spectrum	Medium	Complex	Chemical shift of the protons (δ)				
			C_5Me_5	$C_5Me_{5-n}(CH_2)_n$, n = 1, 2			
				α,α′-Me	β,β′-Me	CH_AH_B	
1	CD_3CO_2D—oleum	**3**[a]	1.85[b]	1.61[b]	1.94[b]	4.48[b]	
2[3]	CF_3SO_3H—CD_3NO_2	**4**	2.07	1.96	2.28	4.70	5.12
3[2]	CF_3SO_3H—CD_2Cl_2—CD_3NO_2	**5**	—	1.79 1.82	2.20 2.22	4.88	4.99
4	CF_3CO_2H—oleum	**4**[c]	2.35	2.22	2.54	4.94	5.32
		6[c]	—	2.04 2.26	2.35 2.60	5.32	5.95
5	CF_3SO_3H—oleum	**4**[a]	2.22	2.09	2.42	4.75	5.16
		6[a]	—	1.92 2.14	2.22 2.47	5.16	5.77
6	CF_3SO_3H—oleum	**4**[c]	2.14	2.01	2.33	4.68	5.09
		6[c]	—	1.84 2.06	2.14 2.39	5.09	5.70
7[d]	CF_3SO_3H—oleum	**4**[c]	2.09	1.96	2.28	4.62	5.07
		6[c]	—	1.79 2.01	2.11 2.33	5.09	5.65
8	Oleum	**4**	2.00	1.86	2.19	4.49	4.90
		6	—	1.69 1.92	2.00 2.25	4.90	5.51

[a] Cations **3**, **4**, and **6** were prepared from **3a**.

[b] $^2J_{HD}{}^{gem}$ = 2.00 Hz.

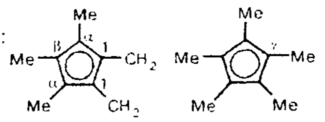
[c] Dications **4** and **6** were prepared from **1**; the acid—oleum ratio was ~1 : 1.

[d] The spectrum was recorded at −35 °C.

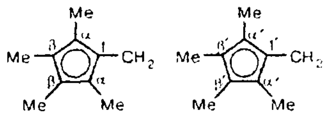
Table 3. ^{13}C NMR spectra of the ruthenium complexes*

Spectrum	Medium	Complex	δ ($^1J_{CH}$/Hz)							
			CH_2	α-Me	β-Me	γ-Me	Carbon atoms of the Cp* rings			
							C(1)	α-C, α′-C	β-C, β′-C	γ-C
1	H_2SO_4	**2**				8.91				95.86
2[2]	CF_3SO_3H—CH_3NO_2	**4**	88.38 t (171)	9.43 q (131)	10.10 q (131)	10.45 q (131)	138.23	126.64	111.32	112.80
3	CF_3SO_3H—oleum	**4**	87.25 t (171)	8.52 q (132)	9.18 q (132)	9.59 (131)	137.37	125.89	110.29	112.01
		6	88.99 t (171)	6.84 (131) 8.34 (131)	8.89 (130) 11.16 (132)	—	107.00	124.05	116.24	—
4	Oleum	**4**	87.21	8.63	9.27	9.76	137.15	125.47	110.12	111.18
		6	88.90	7.00 8.48	9.02 11.37	—	106.87	119.85 123.88	111.79 116.07	—

* The labeling schemes for the carbon atoms in ruthenium complexes **4** and **6** are as follows:



for complex **4**



for complex **6**

dication **6**. The difference $\Delta\delta_{AB}$ is 0.61 ppm. One of the signals (δ 5.16) of dication **6** coincides with the signal for the protons of the CH_2 group of dication **4**, which is manifested in an increase in the integral intensity of this signal. A better resolution is observed in the spectrum recorded at −35 °C (Table 2, spectrum 7). In the region characteristic of the protons of the methyl groups, four signals with equal intensities (6 H each) were assigned

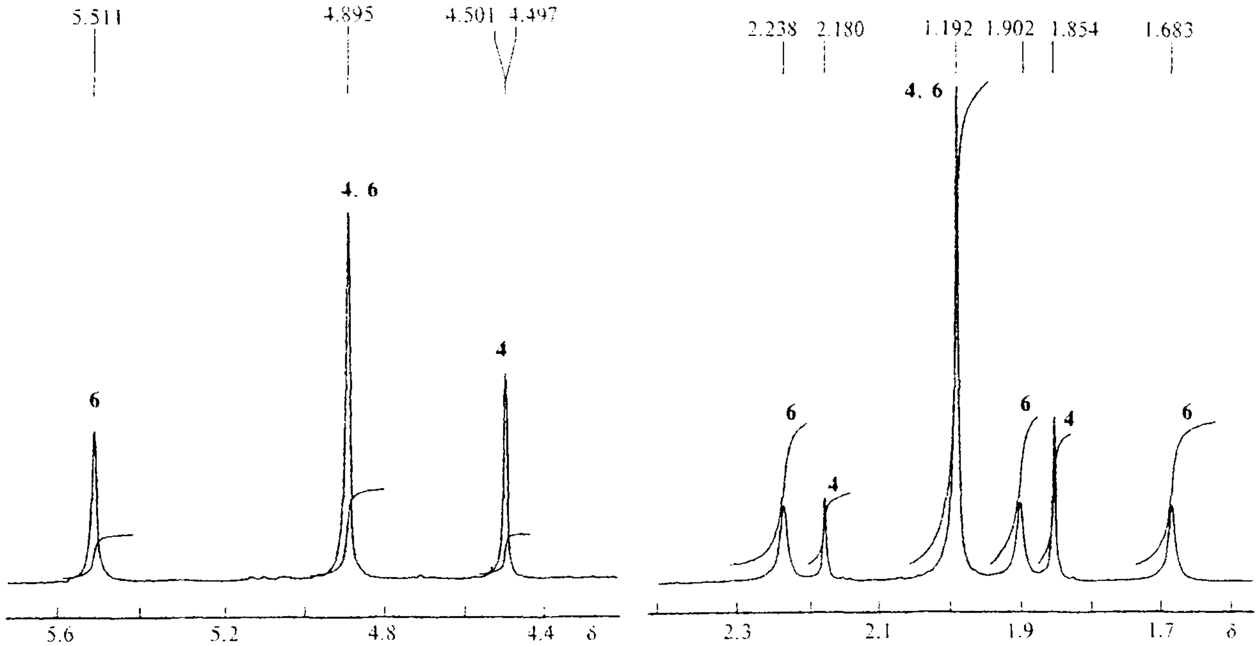


Fig. 1. ^{1}H NMR spectrum of dications **4** and **6** prepared by the reaction of monocation **3** with oleum.

to dication **6**, which is indicative of the presence of two $C_5Me_4CH_2$ rings in the molecule. An analogous pattern has been observed previously for dication **5**,[2] which adopts the *gauche* conformation. In the ^{1}H NMR spectrum of this dication, four singlets were assigned to the $\alpha,\beta,\alpha',\beta'$ methyl groups of two $C_5Me_4CH_2$ rings. Based on this fact, it can be suggested that dication **6**, apparently, also adopts the *gauche* conformation.

However, the spectra of dications **5** and **6** (Table 2, spectra 3 and 5) are substantially different. First, the signals of dication **6** are shifted downfield compared to the analogous signals of dication **5**. These shifts ($\Delta\delta$) of the protons of the Me groups are 0.05—0.24 ppm and those of the H_A and H_B protons of the CH_2 groups are 0.71 and 0.21 ppm, respectively. Second, the differences $\Delta\delta_{AB}$ for dications **5** and **6** are 0.11 and 0.61 ppm, respectively. In addition, the analysis of the spectrum of a mixture of dications **4** and **6** (Table 2, spectrum 6; Fig. 1) demonstrated that the signals of the latter are somewhat broadened. Thus the widths of the signals ($\Delta\nu_{1/2}$) of the Me group and of the signal of the protons of the CH_2 groups (δ 5.7) in dication **6** are 8.5—8.9 and 13.7 Hz, respectively, whereas the $\Delta\nu_{1/2}$ values for the corresponding signals of dication **4** are 6.6—7.1 and 10.4 Hz, respectively. When the temperature is decreased to −35 °C, the widths of the signals of dication **6** remain unchanged. The signals of dication **6** could be broadened due to the paramagnetism of this complex; however, the rather high stability of this complex and the absence of an unpaired electron (according to the ESR spectra) are contradictory to this suggestion.

In the ^{13}C NMR spectra of dication **6** (Table 3, spectrum 3), the signals for the carbon atoms are not broadened. The chemical shifts of the C atoms of the two CH_2 groups are identical (δ 88.99). In the spectrum without suppression of C—H coupling, these signals are observed as a triplet with $^1J_{CH}$ = 171 Hz, like in the spectrum of dication **4** (Table 3, spectrum 3), which coincides with the published data[2] (Table 3, spectrum 2). Since dication **6** and monocation **3** contain the same fragment, *viz.*, $C_5Me_4CH_2$, it is of interest to compare their ^{13}C NMR spectra. Thus the chemical shift of the C(1) atom in the spectrum of dication **6** (Table 3, spectrum 3) is close to the value found[3] for monocation **3** (δ 107.20). The methyl groups of dication **6** give four signals. Unlike the spectrum of monocation **3**, in which the signals for the carbon atoms of the Me groups are observed at δ 8.01—8.74,[3] the signals of two α-Me groups of dication **6** are substantially shifted upfield (δ 6.48) and the signals of two β-Me groups are shifted downfield (δ 11.16). In the case of dication **4**, the signals for the carbon atoms of the Me groups of the $C_5Me_3(CH_2)_2$ ring are observed at δ 8.52—9.18. As expected, the α-C, α′-C and β-C, β′-C atoms of two C_5Me_4 rings of dication **6** in an oleum solution (spectrum 4) give four signals, while these atoms in a CF_3SO_3H—oleum solution give only two signals (Table 3, spectrum 3).

Hence, the above-mentioned differences in the ^{1}H NMR spectra of dications **5** and **6** as well as the peculiarities of the ^{13}C NMR spectrum of the latter suggest the presence of the ligand at the ruthenium atom.

With the aim of elucidating the reason for these spectral differences and of establishing the structures of dications **4** and **6**, we performed their hydrolysis to the

Scheme 2

$$[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_5Me_5})(\eta^5{:}\sigma{:}\sigma\text{-}\mathrm{C_5Me_3(CH_2)_2})]^{2+} + [\mathrm{Ru}(\mathrm{H_2})(\eta^5{:}\sigma\text{-}\mathrm{C_5Me_4CH_2})_2]^{2+} \xrightarrow[\mathrm{H_2O}]{\mathrm{KOH}}$$

4 **6**

$$\longrightarrow \mathrm{Ru(C_5Me_5)[C_5Me_3(CH_2OH)_2]} + \mathrm{Ru(C_5Me_5)(C_5Me_4CH_2OH)}$$

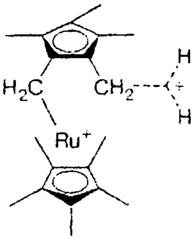
7 **8**

corresponding carbinols. A mixture of dications **4** and **6**, which was prepared analogously to run 2 (Table 1), was subjected to alkaline hydrolysis. It is significant that monocation **3** was absent in this mixture (according to the ^{1}H NMR spectral data). 1,2-Dicarbinol **7** (49%) and, quite unexpectedly, monocarbinol **8** (51%) (according to the ^{1}H NMR spectral data) were isolated from an ethereal extract of the alkaline solution. The total yield of the carbinols was 87% (Scheme 2).

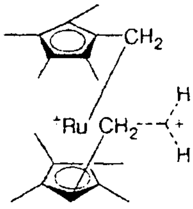
Hence, as expected, dication **4** undergoes hydrolysis to form 1,2-dicarbinol **7**, whereas one of the CH_2 groups in dication **6** is, apparently, reduced to the CH_3 group to form monocarbinol **8**. This suggests that the ruthenium atom in complex **6** is coordinated by molecular hydrogen. This is not surprising because the formation of dications **4** and **6** from ruthenocene **1** should be accompanied by liberation of molecular hydrogen. The hydrogen involved in the complex can participate in reduction to form monocarbinol **8**. The reducing ability of organometallic complexes with molecular hydrogen in an alkaline medium has been reported previously.[5] The structures of carbinols **7** and **8** were confirmed by the ^{1}H NMR spectra (*cf.* the data reported previously[1,4]) and the mass spectra (see the Experimental section).

Therefore, the results obtained in the case of alkaline hydrolysis made it possible to attribute the peculiarities observed in the ^{1}H and ^{13}C NMR spectra of dication **6** to the fact that the ruthenium atom is coordinated by the H_2 molecule. However, the ^{1}H NMR spectrum of a mixture of dications **4** and **6** measured in an acidic medium does not contain a signal of the complex-bound H_2 molecule due, apparently, to the participation of this ligand in the dynamic exchange processes with the protons of a CF_3SO_3H—oleum mixture or of oleum. It is also known[5] that the signal of the η^2-H_2 ligand in ^{1}H NMR spectra of σ-complexes with molecular hydrogen is broadened ($\Delta\nu_{1/2}$ 15—140 Hz) even in neutral solvents, which was explained by exchange processes and/or by dipole-dipole interactions in the $M(H_2)$ group. Apparently, this broadening increases in a strongly protic medium. The detailed structure of complex **6** and the mechanism of its formation are presently being refined.

When discussing a possible scheme of the conversions of monocation **3** into dications **4** and **6**, two directions of the attack of the proton should be considered. As mentioned previously,[6] the conversion of the cationic dihydride $[\mathrm{Re}(\eta^5\text{-}\mathrm{C_5Me_5})_2\mathrm{H_2}]^+$ upon UV photolysis in CD_3CN proceeded through formation of the cationic monohydride $[\mathrm{Re}(\eta^5\text{-}\mathrm{C_5Me_5})(\eta^6\text{-}\mathrm{C_5Me_4CH_2})\mathrm{H}]^+$ (**9**) to yield a cation containing two CH_2 groups, *viz.*, $[\mathrm{Re}(\eta^5\text{-}\mathrm{C_5Me_5})(\eta^7\text{-}\mathrm{C_5Me_3(CH_2)_2})]^+$ (**10**). In the case of permethylmetallocenes containing several proton-acceptor centers, either the metal atom or the Cp* ring (of the π type) can be subjected to protonation. In superacids, protonation can also occur at the methyl group. It is known[7—10] that activation of saturated hydrocarbons under the action of protic superacids proceeds through the hypervalent C atom, *i.e.*, through the carbonium ion. The question arises as to whether the CH_3 group in monocation **3**, in which a positive charge is located on the metal atom, can be subjected to protonation. For this purpose, we attempted to introduce deuterium into the molecule of the salt of monocation **3a** in the reaction with oleum in a CD_3CO_2D medium. It appeared that the H/D exchange proceeded only in the presence of oleum (the CD_3CO_2D—oleum ratio was ≈ 5 : 1). In the ^{1}H NMR spectrum, all four signals of monocation **3** (the α-, β-, and γ-Me and CH_2 groups) are observed as multiplets (see Table 2, spectrum 1). In the absence of oleum, this exchange was not observed. Consequently, protonation of the Me group of monocation **3** to form α-permethylmetallocenylcarbonium ions of types **D** and **E** occurs only in oleum. The presence of the deuterium atom in the CHD group can be also indicative of the attack of D^+ on the metal atom.



D



E

At the same time, it should be remembered that the three-center bond in carbonium ions of types **D** and **E** is readily cleaved to form a thermodynamically more stable van der Waals complex formed by the carbenium ion $>C^+$ and molecular hydrogen. This was demonstrated by *ab initio* [(MP2-full)/6-31G**] calculations[8] using isobutonium cations and the corresponding van der Waals complexes as examples. This suggests that carbonium ions **D** and **E** can be readily converted into the complexes of the metallonium ion with dihydrogen coordinated to the metal atom, *viz.*, into $[Ru(H_2)(\eta^5{:}\sigma{-}C_5Me_4CH_2)_2]^{2+}$ and $[Ru(H_2)(\eta^5{-}C_5Me_5)(\eta^5{:}\sigma{:}\sigma{-}C_5Me_3(CH_2)_2)]^{2+}$, respectively.

However, only one complex with molecular hydrogen that formed from an intermediate protonated complex of type **E** was detected in our case. In the case of a complex of type **D**, H_2 is apparently readily eliminated due to smaller steric hindrances resulting in the formation of dication **4**.

According to the published data,[6] an increase in the time of irradiation from 1 to 20 h is large enough for the stepwise conversion of rhenium cationic monohydride **9** into the cation containing two CH_2 groups (**10**) to occur. Our experiments demonstrated that UV photolysis of ruthenium cationic complex **3** in CF_3SO_3H did not afford dications **4** and **6** even upon irradiation over a long period. It is necessary to use oleum for obtaining these dications.

Experimental

The ^1H NMR spectra were recorded on Bruker WP-200 SY (200.13 MHz) and Bruker AMX-400 (400.13 MHz) spectrometers in $CDCl_3$ solutions (Me_4Si). For acidic solutions, C_6D_6 (98% of D) (δ C_6D_5H 7.25) was used as the external standard. The ^{13}C NMR spectra were measured on a Bruker AMX-400 spectrometer (100.61 MHz) with C_6D_6 as the external standard (δ 127.96). The mass spectra (EI) were obtained on an MS-890 instrument (70 eV, 150 °C, direct introduction of the sample) in a $CDCl_3$ solution.

Protonation and photolysis were carried out in NMR tubes filled with argon. Weighed samples of ruthenocene **1** (~0.1 mmol) or monocation **3a** (~0.05 mmol), acid (3—5 mmol), and oleum were placed into tubes, and the tubes were sealed. UV photolysis was carried out with the use of an OKN-11 Hg lamp (850 W). The ratios of the reaction products were calculated from the ratios of the integral intensities of the signals in the ^1H NMR spectra of the reaction mixtures.

The reactions were performed with the use of 60% oleum.

Preparation of the dication (η^5-pentamethylcyclopentadienyl)($\eta^5{:}\sigma{:}\sigma$-trimethyl-1,2-dimethylenecyclopentadienyl)ruthenium (4) and the dication bis($\eta^5{:}\sigma$-tetramethylmethylenecyclopentadienyl)(dihydrogen)ruthenium (6) and their hydrolysis to form (η^5-pentamethylcyclopentadienyl)(η^5-trimethyl-1,2-dihydroxymethylcyclopentadienyl)ruthenium (7) and (η^5-pentamethylcyclopentadienyl)(η^5-tetramethylhydroxymethylcyclopentadienyl)ruthenium (8). Ruthenocene **1** (0.07 g, 0.19 mmol) was placed into a two-neck flask and the flask was filled with argon. Then CF_3SO_3H (0.8 g, 5.3 mmol) and oleum (0.6 g) were added with stirring using a magnetic stirrer. The reaction mixture was stirred at ~20 °C for 2 h (control by the ^1H NMR spectra). An aqueous solution of KOH was added with stirring and cooling until the reaction mixture became weakly alkaline. The reaction mixture was stirred at ~20 °C for 2 h and extracted with ether and then with dichloromethane. The ethereal extract was dried over $MgSO_4$ and concentrated. A light powder was obtained in a yield of 0.0646 g. According to the ^1H NMR spectral data, this powder contained 49% of dicarbinol **7** and 51% of monocarbinol **8**. The CH_2Cl_2 extract was concentrated and the solid reside was obtained in a yield of 0.0015 g. Compounds **7** and **8** were obtained in yields of 0.032 g (0.079 mmol; 42%) and 0.033 g (0.085 mmol; 45%), respectively. ^1H NMR ($CDCl_3$), δ, **7**: 1.61 (15 H); 1.71 (3 H); 1.76 (6 H); 3.82 and 4.02 (both dd, 4 H) (*cf.* Ref. 1); **8**: 1.59 (6 H); 1.64 (21 H); 3.88 (2 H); 4.01 (1 H) (*cf.* Ref. 4). MS, m/z (I_{rel} (%)): **7**, 404 $[M]^+$ (7), 387 $[M - OH]^+$ (26), 373 $[M - CH_2OH]^+$ (56), 370 $[M - 2\ OH]^+$ (77), 342 $[M - (CH_2OH)_2]^+$; **8**, 388 $[M]^+$ (33), 371 $[M - OH]^+$ (100), 357 $[M - CH_2OH]^+$ (75) (30).

H/D exchange. *A.* A mixture of compound **3a** (0.0127 g, 0.025 mmol) and CD_3CO_2D (0.2598 g, 3.95 mmol) was studied by ^1H NMR spectroscopy: 2.24 (6 H); 2.48 (15 H); 2.57 (6 H); 5.23 (2 H); 2.70 (CH_3CO); 12.25 (COOH).

B. A mixture of compound **3a** (0.006 g, 0.012 mmol), CD_3CO_2D (0.2741 g, 4.28 mmol), and oleum (0.0602 g) was studied by ^1H NMR spectroscopy (see Table 2, spectrum 1) (δ_{MeCO} 2.66 and δ_{COOH} 13.42).

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