Chemical and electrochemical oxidation of permethylmetallocenecarbaldehydes and the related μ-acyl Os_3-clusters

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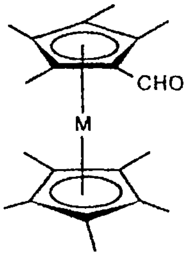
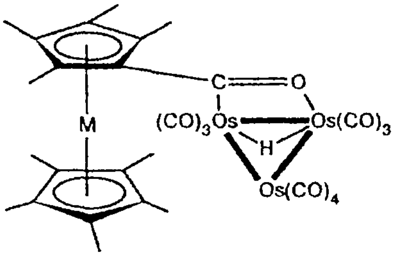
Oxidation of nonamethylmetallocenecarbaldehydes $C_5Me_5MC_5Me_4CHO$ (M = Ru or Os) and the related μ-acyl clusters $C_5Me_5MC_5Me_4COOs_3(CO)_{10}H$ with silver salts afforded η^6-metallonium cations, whose structures and compositions were confirmed by the data of elemental analysis and ^1H, ^{19}F, and ^{13}C NMR and IR spectroscopy. The results of studies by cyclic voltammetry demonstrated that oxidation of the compounds under study proceeded through 17-electron radical-cationic intermediates and that the μ-acyl Os_3-cluster fragment is a weaker electron-withdrawing group than the CHO group.

Key words: μ-acyl clusters, permethylmetallocenecarbaldehydes, ruthenium, osmium, IR spectroscopy, ^1H NMR spectroscopy, ^{19}F NMR spectroscopy, ^{13}C NMR spectroscopy, oxidation, cyclic voltammetry, η^6-metallonium cations.

As part of our continuing studies of cationic η^6-metallonium and η^5-carbocationic derivatives of metallocenes, it was of interest to investigate compounds containing electron-withdrawing groups. Chemical oxidation of nonamethylferrocenecarbaldehyde (**1a**) demonstrated[1] that, as in the case of $(C_5Me_5)_2Fe$, the use of silver salts afforded the corresponding ferrocenium salt $[C_5Me_5FeC_5Me_4CHO]^+X^-$. Therefore, the presence of one electron-withdrawing CHO group along with nine electron-donating methyl groups affects only slightly the chemical behavior of compound **1a**. At the same time, it is known that oxidation of ruthenium and osmium decamethylmetallocenes is not terminated in the stage of formation of metallocenium salts and affords η^6-metallonium salts.[2—5] The introduction of electron-withdrawing groups would be expected to retard deep oxidation.



1a—c



2a—c

M = Fe (**a**), Ru (**b**), Os (**c**)

To elucidate this question and to determine the electronic effect of the μ-acyl Os_3-cluster group, we carried out chemical and electrochemical oxidation of ruthenium and osmium nonamethylmetallocenecarbaldehydes (**1b,c**) and μ-acyl Os_3-clusters (**2b,c**), which have been prepared recently based on compounds **1b,c**.[6]

Results and Discussion

Chemical oxidation of **1b,c** and **2b,c** was performed in a 2.5 : 1 CH_2Cl_2—$MeNO_2$ mixture under the action of the complex of silver tetrafluoroborate with dioxane ($AgBF_4 \cdot 3C_4H_8O_2$). It was found that oxidation of **1b,c** was not terminated in the stage of metallocenium salts and proceeded further to form a mixture of cationic complexes containing the CH_2^+ fragment at the α-position with respect to the CHO group (1,2-isomer) or in the other ring (1,1′-isomer) (Scheme 1).

The ratio of the 1,2- and 1,1′-isomers was 9 : 1 and 8 : 2 in the case of M = Ru (**3b**) and M = Os (**3c**), respectively. The resulting salts are less stable than the permethylated salts $[C_5Me_5M^+C_5Me_4CH_2]X^-$ (M = Ru or Os; X = BF_4 or PF_6), which do not contain the CHO group and which we have prepared previously.[2] Attempts to grow crystals or separate a mixture of two isomers failed. The structures of salts **3b,c** were confirmed by elemental analysis of a mixture of isomeric salts and by IR and NMR spectroscopy.

The IR spectra of compounds **1b,c** have C=O stretching vibration bands of the aldehyde group in addition to absorption bands typical of $(C_5Me_5)_2M$.[7] The former bands are retained in the spectra of compounds **3b,c** (**1b**,

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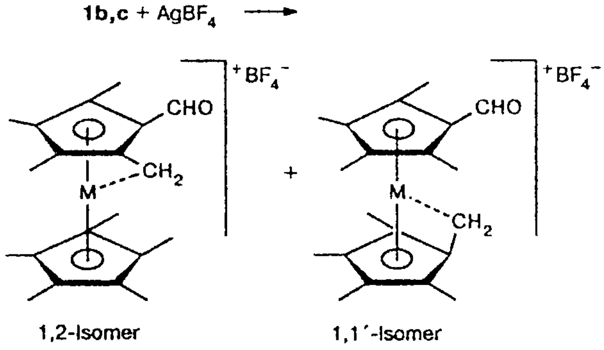
Scheme 1



M = Ru (**3b**) or Os (**3c**)

1663 cm^{-1}; **3b**, 1666 cm^{-1}; **1c**, 1667 cm^{-1}; and **3c**, 1675 cm^{-1}). The formation of the salts is confirmed by the appearance of broad intense absorption bands of the anion BF_4 (**3b**, 1084 and 1035 cm^{-1}; **3c**, 1080 and 1059 cm^{-1}) in the spectra of **3b,c** and by the absence of deformation vibration bands of the C_5Me_5—M—C_5Me_5 fragment in the region of 190 cm^{-1}, which are typical of neutral metallocenes (including aldehydes). The intense band at 188 cm^{-1} observed in the spectrum of **1b** is absent in the spectrum of **3b**. Changes in the region of 520 cm^{-1} are also observed. The intensities of the other bands associated with metal—ring vibrations decrease substantially.

The ^{1}H NMR spectra appeared to be the most informative for establishing the structures of the 1,2- and 1,1′-isomers of **3b,c**.

The ^{1}H NMR spectrum contains two sets of signals characterizing each isomer (Table 1). Thus, the chemical shifts for the signals of the aldehyde groups (**3b**, δ_{CHO} = 9.53 (1,2-isomer) and 9.79 (1,1′-isomer); and **3c**, δ_{CHO} = 9.61 and 9.81, respectively) are observed in the same region as those for the protons of the CHO groups of the initial compounds **1b,c**. The protons of the CH_2 group of the 1,2- and 1,1′-isomers are manifested as two resonance signals and one signal, respectively, in the region of 4.6—4.8 ppm typical of η^6-metallonium salts $[C_5Me_5M^+C_5Me_4CH_2]BF_4^-$ (M = Ru or Os) (**4b,c**). The assignment of the signals for the methyl protons was based on comparison of the integral intensities. The methyl protons of the C_5Me_5 rings are manifested as one signal with an intensity corresponding to 15 protons. The substituted ring in the 1,2-isomers gives three signals for the nonequivalent Me groups. The substituted ring in the 1,1′-isomers gives two signals for two pairs of equivalent Me groups. The proposed structures of salts **3b,c** agree also with the data of ^{19}F NMR spectroscopy. The structure of the 1,2-isomer of salt **3b** formed in a ninefold excess with respect to the 1,1′-isomer is confirmed by the data of ^{13}C NMR spectroscopy (see the Experimental section).

The same procedure was used for oxydizing μ-acyl clusters **2b,c** with $AgBF_4 \cdot 3C_4H_8O_2$. The reaction was also not terminated in the stage of formation of 17-electron metallocenium salts and gave salts **5b,c**. However, the structural specificity of μ-acyl clusters **2b,c** plays a significant role in this process. As we have mentioned previously,[6] the bulky asymmetrical μ-acyl Os_3-cluster fragment is responsible for the nonequivalence of the methyl groups at positions 2 and 5 (or at α and α′), which hinder free rotation of this fragment. Therefore, oxidation of compounds **2b,c** would be expected to yield two isomers containing CH_2 groups at positions 2 and 5 with respect to the μ-acyl fragment (1,2- and 1,5-isomers) and one isomer containing the CH_2 group in the other ring (1,1′-isomer). Actually, oxidation gave all three isomers (Scheme 2).

We failed to separate the mixture of the salts obtained. Their structures agree with the data of elemental analysis of the mixture of isomers and with the results of

Table 1. ^{1}H NMR spectral data for compounds **1b,c**, **3b,c**, and **4b,c** (CD_2Cl_2)

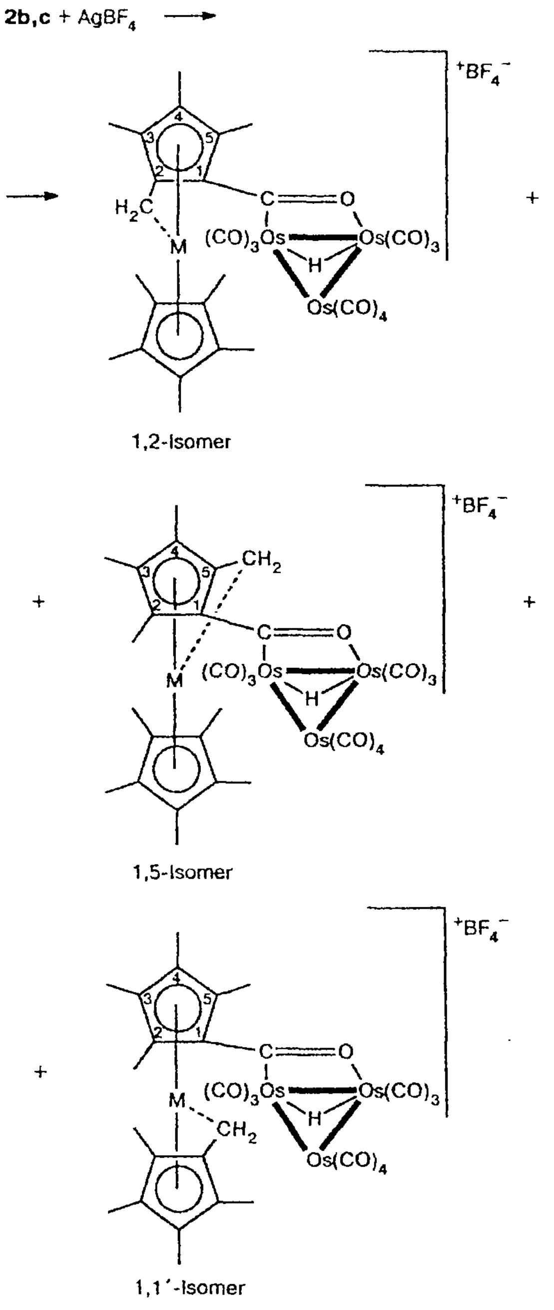
Compound	δ				
	CHO (1 H)	$^+CH_2$ (2 H)	C_5Me_5 (15 H)	C_5Me_4 (12 H)	C_5Me_3 (9 H)
1b[a]	9.61		1.63	1.89 (6 H); 1.70 (6 H)	
3b, 1,2-isomer	9.53	4.77 (1 H); 4.72 (1 H)	1.82		2.19 (3 H); 1.96 (3 H); 1.66 (3 H)
3b, 1,1′-isomer	9.79	4.69		1.88 (6 H); 1.80 (6 H); 2.18 (6 H); 1.60 (6 H)	
1c[b]	9.69		1.73	1.97 (6 H); 1.74 (6 H)	
3c, 1,2-isomer	9.61	4.81 (1 H); 4.72 (1 H)	1.97		1.93 (3 H); 1.72 (3 H); 1.70 (3 H)
3c, 1,1′-isomer	9.81	4.63		2.35 (6 H); 1.68 (6 H); 2.17 (3 H); 1.87 (3 H); 1.86 (3 H); 1.66 (3 H)	
4b[a,b]		4.75	1.86	1.96 (6 H); 1.63 (6 H)	
4c[a,b]		4.40	1.86	1.85 (6 H); 1.59 (6 H)	

[a] Lit. data.[10] [b] Lit. data.[11]

IR and ^1H NMR spectroscopy. The IR spectra demonstrated that the mixture of salts **5b,c**, like the initial **2b,c**, contained the μ_3-acyl cluster group (absorption in the region of 1970—2105 cm^{-1}). As in the case of **3b,c**, the ^1H NMR spectra appeared to be the most informative for confirming the structures of **5b,c**.

The ^1H NMR spectrum of the mixture of salts **5b,c** had three resonance signals for the hydride protons of the μ_3-Os_3H-acyl fragment in the region of −13.5 ppm (**5b**) and the corresponding three signals in the region of −10.4 ppm (**5c**), which indicated that the mixture contained three isomers. This agrees also with the fact that salts **5b,c** each give five resonance signals for the three isomers in the region of 4.5—4.7 ppm typical of CH_2 groups, namely, two signals for the 1,2-isomer, two signals for the 1,5-isomer (α and α′), and one signal for the 1,1′-isomer. The assignment of these signals to particular isomers was based on comparison of the integral intensities of the signals for the hydride protons and for the protons of the CH_2 groups (Table 2). The ratio of the 1,2-, 1,5-, and 1,1′-isomers was 5 : 2 : 1 and 5 : 1 : 1.6 for **5b** and **5c**, respectively. The protons of the Me groups in the mixture of the isomers gave a complex pattern, namely, 14 resonance signals in the region of 1.6—2.2 ppm, of which signals for the C_5Me_5 ring only of the predominant 1,2-isomer can be unambiguously assigned. It should be emphasized that the resonance signals for the protons of the CH_2 groups at positions 2 and 5 with respect to the μ-acyl fragment in compounds **5b,c** can be readily assigned because these protons are nonequivalent and their chemical shifts are different, while their integral intensities are equal. Previously, we have observed an analogous pattern in the ^1H NMR spectra of the dications $[C_5Me_5MC_5Me_3(CH_2)_2\text{-}1,2]^{2+}$ (M = Ru or Os).[8,9] As can be seen from Table 2, which gives the data of ^1H NMR spectroscopy of **5b,c**, and Table 1, which lists analogous data for $(C_5Me_5MC_5Me_4CH_2)^+$ (**4b,c**, M = Ru or Os) studied previously,[10,11] the fact that the chemical shifts for the protons of the CH_2 groups of **3b,c**, **4b,c**, and **5b,c** and the values[10] of δ of the CH_2 groups in the ^{13}C NMR spectra of **3b** (74.75 ppm) and **4b** (74.74 ppm) have similar values makes it possible to assign compounds **3b,c** and **5b,c** to η^6-metallonium cations containing the M—CH_2 σ-bond, where M is the metal atom of the metallocenyl fragment.

Scheme 2



M = Ru (**5b**) or Os (**5c**)

The results of electrochemical studies by cyclic voltammetry on a Pt electrode in a THF medium confirm that oxidation of **1a—c** and **2a—c** proceeds through 17-electron intermediates. The determined values of oxidation and reduction potentials of the complexes under study are given in Table 3. It was found that the cyclic voltammograms of complexes **1a—c** and **2a—c**, like those of $(C_5Me_5)_2M$ studied by us previously,[3—5] have a reversible one-electron anodic peak corresponding to oxidation of the metal atom (Fe, Ru, or Os) of the metallocenyl fragment to form substituted metallonium cations. In the case of compounds **2a—c**, this process is additionally confirmed by the fact that under these conditions an oxidation peak of $Os_3(CO)_{12}$ is absent at potentials lower than +1.8 V. A comparison of the determined oxidation potentials of **1a—c** and **2a—c** with those of $(C_5Me_5)_2M$ demonstrated that the μ-acyl group, as well as the aldehyde fragment, possesses electron-withdrawing properties. This is manifested in the shifts of the oxidation

Table 2. ^{1}H NMR spectral data for compounds **5b,c**[a] (CD_2Cl_2)

Compound	δ		
	Os_3H (1 H)	$^+CH_2$ (2 H)	C_5Me_5 (15 H), C_5Me_4 (12 H), C_5Me_3 (9 H)
5b, 1,2-isomer	−13.65	4.56 (1 H); 4.51 (1 H)	2.01; 1.94; 1.91; 1.85; 1.81; 1.79; 1.76;
5b, 1,5-isomer	−13.96	4.87 (1 H); 4.42 (1 H)	1.75; 1.72; 1.67; 1.65; 1.62; 1.58; 1.53
5b, 1,1′-isomer	−13.75	4.48	
5c, 1,2-isomer	−10.42	4.82 (1 H); 4.56 (1 H)	1.60; 1.66; 1.88; 1.94
5c, 1,5-isomer	−10.46	4.75 (1 H); 4.68 (1 H)	2.15; 1.08; 1.63; 1.91
5c, 1,1′-isomer	−10.43	4.64	1.84; 2.08; 1.98; 1.82; 1.75; 1.69

[a] In the case of compounds **5b,c** (particularly, **5b**), it is difficult to unambiguously assign the signals for the protons of the Me groups to the 1,2-, 1,5-, and 1,1′-isomers.

potentials of **1a—c** and **2a—c** to higher positive values compared to the oxidation potentials of $(C_5Me_5)_2M$, the accepting properties of the μ-group being less pronounced than those of the aldehyde fragment.

The cyclic voltammograms of compounds **2a—c** also have irreversible two-electron reduction peaks whose potentials are close to the reduction potential of $Os_3(CO)_{12}$, which indicates that reduction of compounds **2a—c** proceeds predominantly with the involvement of the μ-acyl Os_3-cluster fragment of the molecule. This is also confirmed by the absence of reduction peaks of **1a—c** at potentials lower than −2.8 V. A comparison of the reduction potentials of compounds **2a—c** and $Os_3(CO)_{12}$ demonstrated that the μ-acyl fragment is weakly sensitive to the electronic effect of the metallocenyl group. Analogous redox properties are typical of nonmethylated Fe-containing analog **2a**.[12] Therefore, both protonation of **2b,c** (as was demonstrated previously[6]) and the attack of the CH_2^+ group of the carbocation occur at the metal atom of the metallocenyl fragment, while the μ-acyl Os_3-cluster group is not involved in these processes.

Table 3. Oxidation (I) and reduction (II) potentials for compounds **1a—c** and **2a—c**

Compound	Number of electrons		Potential, *E*/V	
	I	II	I	II
1a	1	—	0.60	—[a]
2a	1	2	0.56	1.49
$(C_5Me_5)_2Fe$	1	—	0.12[b]	—[a]
1b	1	—	1.30	—[a]
2b	1	2	1.11	1.46
$(C_5Me_5)_2Ru$	1	—	0.73[b]	—[a]
1c	1	—	1.04	—[a]
2c	1	2	0.96	1.47
$(C_5Me_5)_2Os$	1	—	0.58[b]	—[a]
$Os_3(CO)_{12}$	1.43	2	—[c]	1.43

Note. Experimental conditions: a Pt electrode, THF, 0.1 *M* Bu_4NBF_4, relative to a saturated calomel electrode.

[a] The reduction peak was not observed at potentials lower than −2.8 V.

[b] Lit. data.[3]

[c] The oxidation peak was not observed at potentials lower than +1.8 V.

Experimental

The NMR spectra were recorded on a Bruker AMX-400 spectrometer (^{1}H, 400.26 MHz; ^{13}C, 100.62 MHz; Me_4Si as the internal standard; ^{19}F, 376.62 MHz; CF_3COOH as the external standard; CD_2Cl_2 as the solvent). The IR spectra were measured on a Nicolet 75 Magna Fourier spectrometer in the region of 4000—50 cm^{-1}. The samples of the aldehydes and salts were prepared as KBr pellets and as Nujol mulls. All syntheses were performed under an argon atmosphere in anhydrous solvents distilled immediately before use. Nonamethylmetallocenecarbaldehydes **1b,c** were synthesized according to known procedures.[10,11]

Oxidation of 1b. Aldehyde **1b** (0.09 g, 0.23 mmol) dissolved in CH_2Cl_2 (25 mL) was placed in a flask filled with argon and equipped with a reflux condenser and a magnetic stirrer. A solution of the $AgBF_4 \cdot 3C_4H_8O_2$ salt (0.11 g, 0.23 mmol) in $MeNO_2$ (10 mL) was added to the reaction mixture. The mixture was stirred at −20 °C for 8 h and kept without stirring for 10 h until silver salts completely precipitated. The solution was decanted and the residue of the reaction mixture was washed with CH_2Cl_2 (20 mL). The resulting fractions were combined and filtered through a folded paper filter. Then Et_2O (10 mL) was added to the solution and the mixture was kept for 2 h until the precipitate formed. The solvents were decanted and the precipitate was washed with Et_2O (30 mL) and dried *in vacuo*. The yield of the 1,2- and 1,1′-isomers of salt **3b** was 0.10 g (93%). Found (%): C, 50.84; H, 5.95; F, 15.68. $C_{20}H_{27}BF_4ORu$. Calculated (%): C, 50.96; H, 5.77; F, 16.13.

A mixture of the 1,2- and 1,1′-isomers of salt 3b. IR (KBr, Nujol mulls), ν/cm^{-1}: 2964, 2948, 2913, and 2855 m (C—H); 1666 s (C=O); 1472 and 1452 m (Me, CH_2); 1415 s (C—C, C—Me); 1380 v.s (Me); 1084 and 1035 v.s (BF_4); 345 m and 330 w (Ru—C_5Me_5). ^{19}F NMR (CD_2Cl_2), δ: 74.85 and 74.90 in a ratio of 1 : 4. The relative yields of the 1,2- and 1,1′-isomers of salt **3b** were 87 and 13%, respectively (the ^{1}H NMR spectral data, see Table 1). ^{13}C NMR of the 1,2-isomer (CD_2Cl_2), δ: 187.87 ($\underline{C}HO$); 112.83, 110.97, 105.57, 103.95, 77.99 ($\underline{C}_5Me_3$); 8.93, 8.83, 8.42 ($C_5\underline{Me}_3$); 77.71 ($^+\underline{C}H_2$); 99.72 ($\underline{C}_5Me_5$); 10.19 ($C_5\underline{Me}_5$).

Oxidation of 1c was carried out analogously to **1b** starting from aldehyde **1c** (0.09 g, 0.20 mmol) and the $AgBF_4 \cdot 3C_4H_8O_2$ salt (0.09 g, 0.20 mmol). The yield of the 1,2- and 1,1′-isomers of salt **3c** was 0.10 g (90%). Found (%): C, 42.98; H, 4.40; F, 15.76; Os, 34.33. $C_{20}H_{27}BF_4OOs$. Calculated (%): C, 42.86; H, 4.86; F, 13.56; Os, 33.94.

A mixture of the 1,2- and 1,1′-isomers of salt 3c. IR (KBr, Nujol mulls), ν/cm^{-1}: 2961, 2918, 2913, and 2850 m (C—H);

1675 s (C=O); 1473 and 1456 m (Me, CH_2); 1406 s (C—C, C—Me); 1380 v.s (Me); 1080 and 1059 v.s (BF_4); 338 m and 314 w (Ru—C_5Me_5). ^{19}F NMR (CD_2Cl_2), δ: 73.79 and 73.82 in a ratio of 1 : 4. The final yields of the 1,2- and 1,1′-isomers of salt **3c** were 80 and 20%, respectively (the ^1H NMR spectral data are given in Table 1).

Oxidation of 2b was carried out analogously to **1b** starting from cluster **2b** (0.13 g, 0.098 mmol) and the salt $AgBF_4 \cdot 3C_4H_8O_2$ (0.05 g, 0.101 mmol). The yield of the 1,2-, 1,5-, and 1,1′-isomers of salt **5b** was 0.093 g (72%). Found (%): C, 27.04; H, 2.16; F, 6.32; Os, 39.53. $C_{30}H_{28}BF_4O_{11}Os_3Ru$. Calculated (%): C, 27.26; H, 2.06; F, 5.75; Os, 43.64.

Oxidation of 2c was carried out analogously to **1b** starting from cluster **2c** (0.14 g, 0.099 mmol) and the salt $AgBF_4 \cdot 3C_4H_8O_2$ (0.05 g, 0.101 mmol). The yield of the 1,2-, 1,5-, and 1,1′-isomers of salt **5c** was 0.098 g (70%). Found (%): C, 25.14; H, 2.04; F, 5.28; Os, 53.50. $C_{30}H_{28}BF_4O_{11}Os_4$. Calculated (%): C, 25.53; H, 1.93; F, 5.39; Os, 53.91.

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