Protonation and acylation of the heterometallic complexes $(\mu\text{-H})Os_3(\mu\text{-}O_2CC_5H_4FeCp)(CO)_{10}$ and $Fe\{(\mu\text{-}O_2CC_5H_4)(\mu\text{-H})Os_3(CO)_{10}\}_2$

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The reactions of the heterometallic complexes $(\mu\text{-H})Os_3(\mu\text{-}O_2CC_5H_4FeCp)(CO)_{10}$ (**1**) and $Fe\{(\mu\text{-}O_2CC_5H_4)(\mu\text{-H})Os_3(CO)_{10}\}_2$ (**2**) with CF_3COOH, CF_3SO_3H, and AcCl were studied. The reaction of **1** with CF_3COOH involves interaction with the Cp ligands, protonation of the O atom of the bridging carboxylate group, and oxidative degradation of the complex. At low concentrations, CF_3SO_3H protonates the O atom of the bridging carboxylate group, while at high concentrations, degradation of the complex takes place. The reaction of complex **2** with either CF_3COOH or low concentrations of CF_3SO_3H results in successive elimination of two $[(\mu\text{-H})Os_3(CO)_{10}]$ cluster fragments due to protonation of the O atoms of the carboxylate groups. In the case of high CF_3SO_3H concentrations, the Os—Os bonds of both cluster fragments of **2** are also protonated to give the $[Fe\{(\mu\text{-}O_2CC_5H_4)(\mu\text{-H})_2Os_3(CO)_{10}\}_2]^{2+}$ dication. The Friedel—Crafts acylation of **1** takes place only when a large excess of AcCl and $AlCl_3$ is used to give two new complexes, $(\mu\text{-H})Os_3(\mu\text{-}O_2CC_5H_4FeC_5H_4C(O)CH_3)(CO)_{10}$ and $(\mu\text{-H})Os_3(\mu\text{-}O_2CC_5H_3C(O)CH_3FeCp)(CO)_{10}$ in a 2 : 1 ratio.

Key words: osmium and iron heterometallic complexes, protonation, acylation, ^{1}H NMR spectroscopy.

A large number of studies published in recent years have been devoted to the synthesis of heterometallic complexes in which either a cluster fragment and a mononuclear fragment or several cluster fragments are linked by polyfunctional ligands.[1—4] For many compounds of this type, chemical properties of the constituent metal complexes have been studied fairly comprehensively. It appears pertinent and important to study the influence of metal fragments in these complexes on their reactivities.

Previously, we have prepared several heterometallic complexes containing anilinechromiumtricarbonyl,[5] cymantrenecarboxylic,[6] ferrocenecarboxylic, and ferrocenedicarboxylic acids[7] as ligands in triosmium carbonyl clusters. The last-mentioned case was represented by three complexes in which the ferrocenyl fragment is linked to either one ($(\mu\text{-H})Os_3(\mu\text{-}O_2CC_5H_4FeCp)(CO)_{10}$ (**1**) and $(\mu\text{-H})Os_3(\mu\text{-}O_2CC_5H_4FeC_5H_4COOH)(CO)_{10}$) or two ($Fe\{(\mu\text{-}O_2CC_5H_4)(\mu\text{-H})Os_3(CO)_{10}\}_2$ (**2**)) triosmium clusters. Later, more detailed procedures for the synthesis of complexes **1** and **2** have been published and the electrochemical properties of these complexes have been studied.[8] Here we describe the behavior of complexes **1** and **2** in reactions with electrophilic reagents, namely, protonation and Friedel—Crafts acylation.

Compounds **1** and **2** can be protonated at the Fe atom, the Os_3 ring, or the Cp ligands. The protonation of the O atoms of the bridging carboxylate groups also cannot be ruled out, although their basicities are expected to decrease upon the coordination to the cluster. The protonation site in ferrocene and its derivatives depends on the strength of the acid used and the nature of substituents in the Cp ligands. Weak and medium-strength acids react with cyclopentadienyl ligands[9,10] and strong acids protonate the Fe atom.[11] When oxygen-containing functional groups (aldehyde,[12] acyl,[13] or hydroxy[14] groups) are introduced in the Cp ring of ferrocene, the protonation site shifts to the O atom. Superacids protonate acylferrocenes at both O and Fe atoms.[15] The triosmium $(\mu\text{-H})Os_3(\mu\text{-X})(CO)_{10}$ clusters are protonated at the Os—Os bond.[16,17] The protonation site can move from the Os_3 metal ring to the ligands[16—19] if the ligands contain, for example, a lone electron pair or a multiple bond. Data on the protonation of the heterometallic $(\mu\text{-H})Os_3(\mu\text{-O}{=}CC_5Me_4MC_5Me_5)(CO)_{10}$ complexes (M = Fe, Ru, Os) in which the metallocenyl fragments are coordinated by a bridging aldehyde group are documented.[20] In a HBF_4/CF_3COOH mixture, these complexes are protonated at the metal atom of the metallocenyl fragment. The protonated

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$[(\mu\text{-H})Os_3(\mu\text{-O}{=}CC_5Me_4FeHC_5Me_5)(CO)_{10}]^+$ complex, unlike the other two complexes, is unstable and is rapidly converted into the ferrocenium derivative exhibiting paramagnetic properties.[20]

Results and Discussion

Complexes **1** and **2** were protonated by CF_3COOH and CF_3SO_3H. The addition of 2 equiv. of CF_3COOH

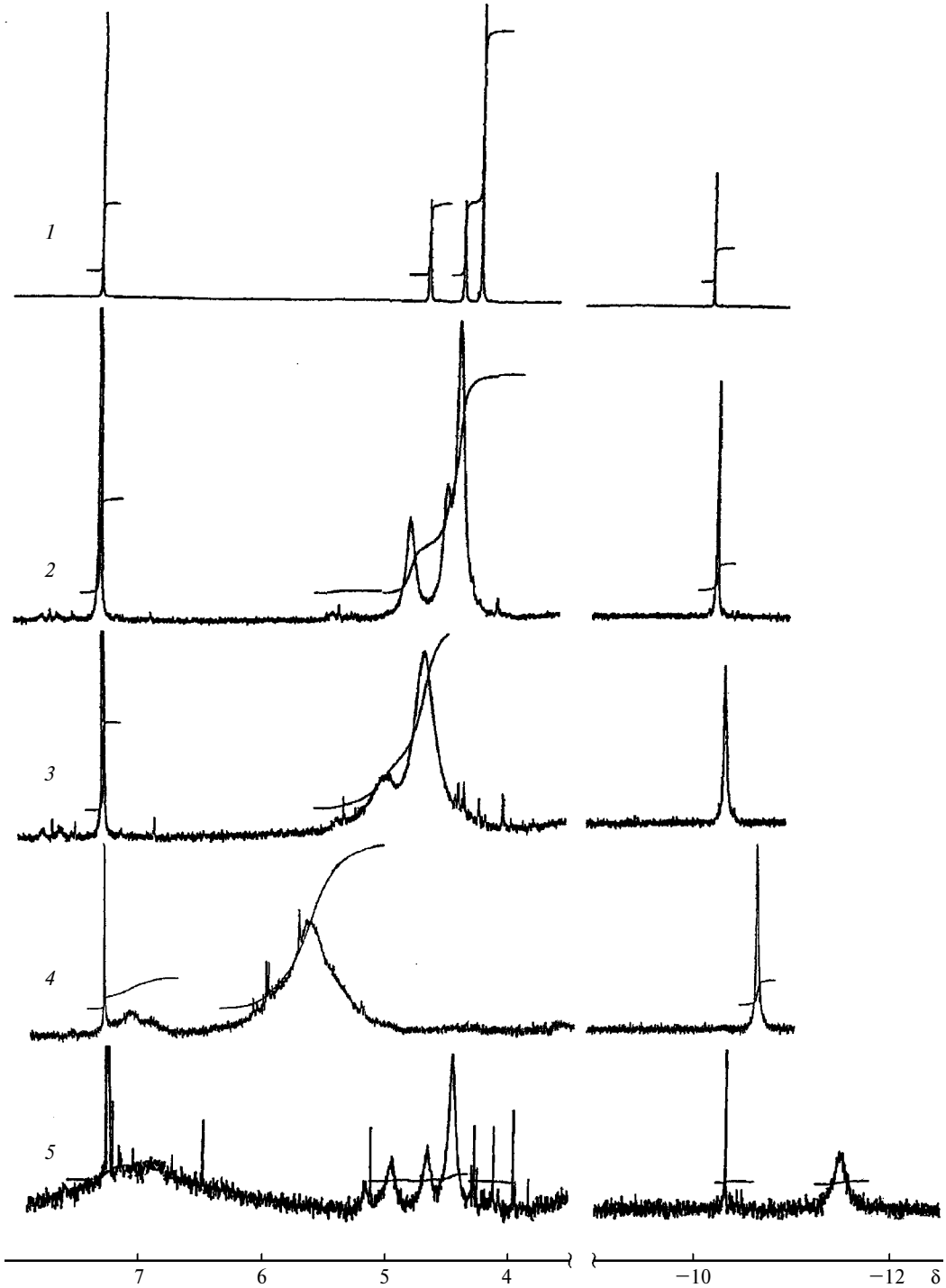


Fig. 1. Changes in the ^1H NMR spectra (250 MHz, $CDCl_3$) of a solution of the $(\mu\text{-H})Os_3(\mu\text{-O}_2CC_5H_4FeCp)(CO)_{10}$ complex (**1**) in $CDCl_3$ in the presence of 2 equiv. of CF_3COOH: spectra *1—3* were recorded at 3-h intervals, spectrum *4* was measured 18 h after the onset of the reaction, and spectrum *5* was recorded after 2 days.

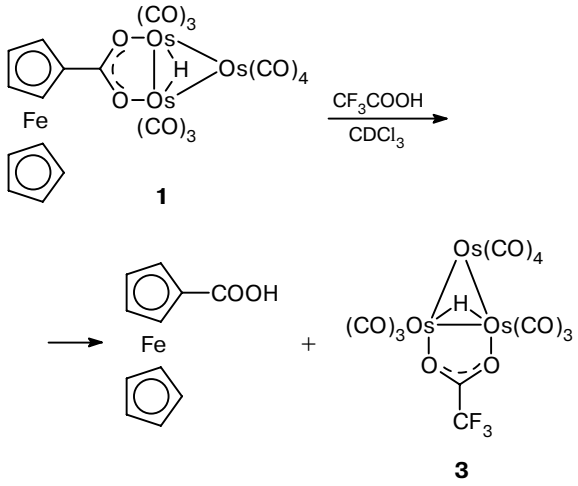
to a solution of $(\mu\text{-H})Os_3(\mu\text{-}O_2CC_5H_4FeCp)(CO)_{10}$ (**1**) in CD_2Cl_2 or $CDCl_3$ induces broadening of ^1H NMR signals and downfield shifts of the signals of the Cp protons and upfield shifts of the μ-H signals (Fig. 1). The signals of Cp protons gradually approach each other and finally coalesce at about δ 5.5. After about 2 days, broadened signals typical of the Cp protons of a monosubstituted ferrocene appear again in the region of δ 4.5; they shift downfield and approach each other with time as described above. In the high-field region, a narrow, intense signal appears (δ −10.3), whose position remains unchanged, and several other weak signals. As the reaction progresses, the color intensity of the solution decreases and a dark solid precipitates. Chromatographic separation of the reaction mixture (elution with hexane—benzene—acetone, 4 : 2 : 1.5) gave the known[16] $(\mu\text{-H})Os_3(\mu\text{-}O_2CCF_3)(CO)_{10}$ cluster (**3**) (30%), which is responsible for a signal with δ −10.30, the $(\mu\text{-H})Os_3(\mu\text{-Cl})(CO)_{10}$ complex[21] (1 to 3% in various experiments), responsible for the μ-H signal with δ −14.25, and ferrocenecarboxylic acid (up to 30%), which was identified from IR and ^1H NMR spectra.[22] As the CF_3COOH concentration increases threefold, all the protons of the Cp ligands in complex **1** appear in the spectrum as a single broad signal. With a 20-fold excess of the acid with respect to complex **1**, no signals for the Cp protons are observed in the spectrum; apparently, they merge with the intense signal of the CF_3COOH protons. An increase in the concentration of the acid markedly accelerates the process.

Analysis of the spectrocopic data indicates that the reaction of complex **1** with CF_3COOH follows two pathways: the acid either reacts with the Cp ligands or protonates the O atom of the carboxylate group. In the former case, the signals for the Cp protons are broadened. The gradual downfield displacement and the subsequent broadening of these signals is apparently due to the oxidative processes that usually take place in CF_3COOH-containing solutions of ferrocene derivatives in air.[23] This results in partial decomposition of the complex. Protonation of the O atoms of the bridging ligand is accompanied by substitution of a trifluoroacetate group for the ferrocenecarboxylate ligand in complex **1** and gives rise to $(\mu\text{-H})Os_3(\mu\text{-}O_2CCF_3)(CO)_{10}$ (**3**) and ferrocenecarboxylic acid, which is also oxidized under the reaction conditions (Scheme 1).

The reaction of CF_3COOH with the $[Os_3(CO)_{10}]$ fragment arising upon decomposition of complex **1** represents an alternative route to cluster **3**. It was shown in a special experiment that in the presence of CF_3COOH, the acetate group in $(\mu\text{-H})Os_3(\mu\text{-}O_2CCH_3)(CO)_{10}$ is replaced by a trifluoroacetate group. Neither in this reaction nor in the reaction of CF_3COOH with complex **1**, the protonation of the Os—Os bond takes place, which indicates a lower basicity of the Os_3 metal ring compared to the O atoms of the carboxylate ligands.

The reaction of complex **1** with CF_3SO_3H is similar to that described above except for two points. First, this

Scheme 1



reaction is an order of magnitude faster. Twenty minutes after the introduction of 1.5 equiv. of CF_3SO_3H into a solution of complex **1** in $CDCl_3$, two broad signals (δ 5.18 and 4.77) in a 2 : 7 ratio of integrated intensities and a somewhat broadened high-field singlet with δ −10.14 appear in the ^1H NMR spectrum of the reaction mixture; this virtually reproduces the spectrum shown in Fig. 1, spectrum (*3*). The pattern of subsequent changes in the ^1H NMR spectra of the reaction mixture recorded at 20—30 min intervals is close to that of the corresponding spectra shown in Fig. 1. About 1 h after the beginning of the reaction, the solution starts to darken and after 2.5—3 h, a dark precipitate appears. After 7—9 h (the signals of complex **1** disappear from the ^1H NMR spectra), only a small amount (6—9%) of ferrocenecarboxylic acid can be isolated from the reaction mixture; probably, the bulk of the acid decomposes upon oxidation. The decomposition of complex **1** is apparently due to the fact that the $CF_3SO_3^-$ anion cannot stabilize efficiently the $[HOs_3(CO)_{10}]$ fragment formed in the first stage of the reaction. With a 6-fold excess of CF_3SO_3H, a vigorous reaction takes place accompanied by gas evolution and precipitation of a dark solid. The ^1H NMR spectrum of the reaction mixture recorded 10 min after the onset of the reaction exhibits two broad signals in the region of δ 4.5 and a weak singlet with δ −19.42, which then rapidly disappears. Only traces of ferrocenecarboxylic acid can be detected in the reaction mixture (TLC).

The $Fe\{(\mu\text{-}O_2CC_5H_4)(\mu\text{-H})Os_3(CO)_{10}\}_2$ complex (**2**) contains an additional electron-withdrawing $[(\mu\text{-}CO_2)(\mu\text{-H})Os_3(CO)_{10}]$ cluster group as compared to complex **1**. This decreases the basicity of the ferrocenyl fragment, which appreciably affects the ability of this complex to react with electrophilic reagents. Only with a 40-fold excess of CF_3COOH, do signs of the reactions appear. Within 24 h after beginning of the reaction, new multiplet signals corresponding in structure to the pro-

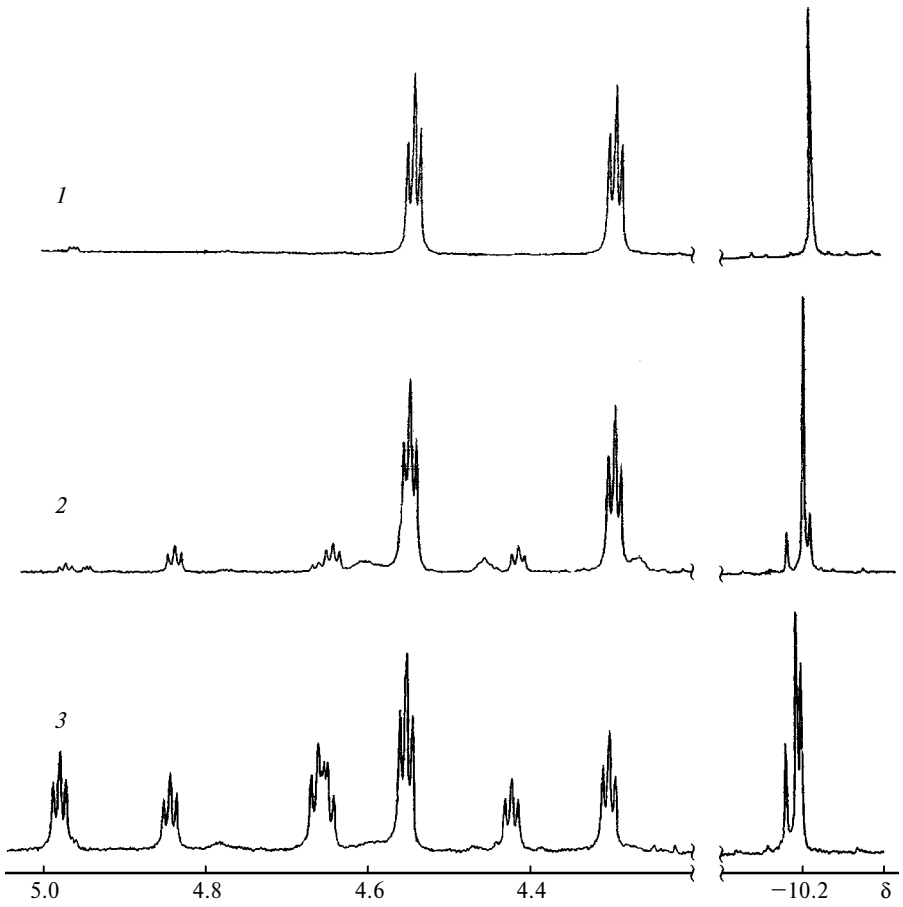
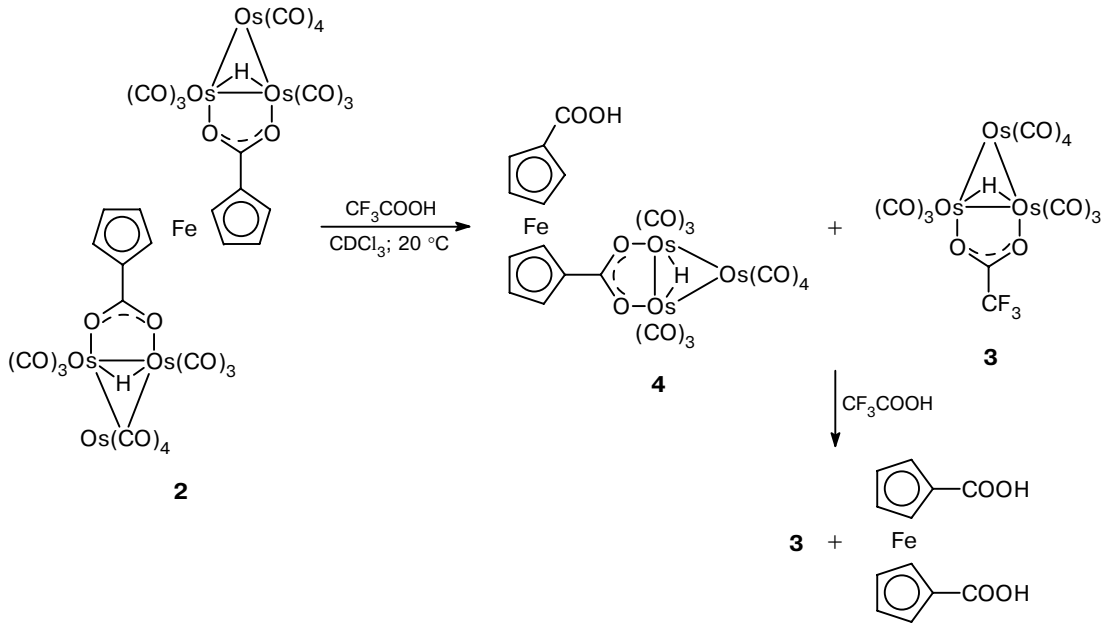


Fig. 2. Changes in the ^{1}H NMR spectra (250 MHz) of a solution of the Fe{(μ-$O_2CC_5H_4$)(μ-H)$Os_3(CO)_{10}$}$_2$ complex (**2**) in CD_2Cl_2 in the presence of a 40-fold excess of CF_3COOH: initial spectrum (*1*), spectra recorded within 1 day (*2*) and 6 days (*3*) after the onset of the reaction.

ton signals of substituted Cp ligands appear at about δ 4.5 in the ^{1}H NMR spectrum of the reaction mixture (Fig. 2). Simultaneously, two signals of the hydride H atoms appear in the high field; their chemical shifts differ from each other and from that of the μ-H signal of complex **2** only by several Hz. The intensity of two other, barely visible analogous multiplet signals gradually increases and after 2 days it reaches the intensity of other signals (see Fig. 2, spectrum *3*). The reaction proceeds slowly; after 10 days, the reaction mixture contains ~40% of the initial complex **2** and ~30% of each of the newly formed compounds with Cp ligands (Scheme 2). The observed changes in the ^{1}H NMR spectrum of the reaction mixture are due to the successive elimination of two [$HOs_3(CO)_{10}$] fragments from the initial complex. Upon the formation of complex **4**, two pairs of multiplets due to the protons of Cp ligands containing different substituents and a new high-field signal (δ −10.20) appear in the ^{1}H NMR spectrum, while the formation of cluster **3** gives rise to the μ-H signal at δ −10.18. The second, slower step involves elimination of the second hydridocarbonyl fragment from complex **4**. The formation of ferrocenedicarboxylic acid entails the appearance of one more pair of multiplet signals in the low field in the ^{1}H NMR spectrum. Chromatographic separation of the reaction mixture on Silufol plates results in slight amounts of complexes **2**, **3**, and **4** and ferrocenedicarboxylic acid, which is consistent with the proposed reaction scheme. The structure of complex **4** was confirmed by its independent synthesis.

The pathway of the reaction of CF_3SO_3H with complex **2** depends on the ratio of the reactant concentrations. When the CF_3SO_3H concentration is low (**2** : CF_3SO_3H = 3 : 1), the first step of the reaction involves elimination of one cluster fragment to give the (μ-H)Os_3(μ-$O_2CC_5H_4FeC_5H_4COOH$)$(CO)_{10}$ (**4**) complex. The chemical shifts of protons of complex **4** in the ^{1}H NMR spectrum of the reaction mixture ($CDCl_3$, δ: 4.98, 4.84, 4.69, 4.52 (all m, 2 H each, CH); −10.24 (s, 1 H, μ-H)) differ substantially from the chemical shifts of signals in the spectrum of pure complex **4** recorded in acetone (see Experimental). However, if the IR and ^{1}H NMR spectra of this complex isolated from the reaction mixture in a pure state and similar spectra of complex **4** are recorded under the same conditions, they

Scheme 2



are virtually identical. The intensity of proton signals of complex **4** in the ^{1}H NMR spectrum of the reaction mixture reaches a maximum after 2.5 h and then gradually decreases. After 1.5 days, only signals of the initial complex **4** remain in the spectrum. The $[HOs_3(CO)_{10}]$ cluster fragment, formed inevitably both in the first (formation of complex **4**) and second (reaction of complex **4** with the acid) steps is apparently destroyed because it cannot be stabilized efficiently under the reaction conditions. Subsequently, CF_3SO_3H seems to react mainly with complex **4**, which results in the destruction of the complex. As a consequence, after 1.5 days the ^{1}H NMR spectrum of the reaction solution exhibits mainly the proton signals of the initial complex **2** and weak signals due to ferrocenedicarboxylic acid. The reaction stops apparently after CF_3SO_3H has been completely exhausted.

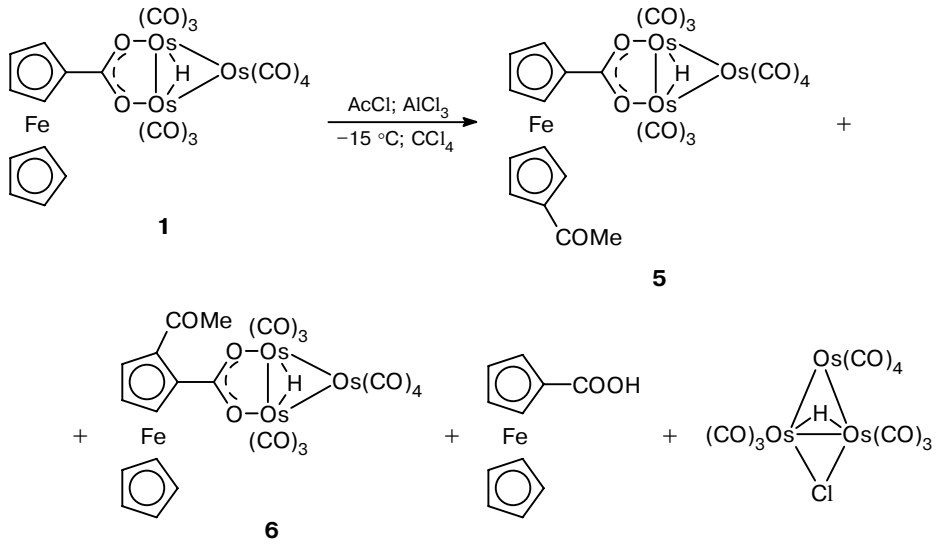
When a 15-fold excess of CF_3SO_3H is added to a solution of cluster **2** in CD_2Cl_2, both metal cluster fragments are protonated to give the $[Fe\{(\mu\text{-}O_2CC_5H_4)(\mu\text{-}H)_2Os_3(CO)_{10}\}_2]^{2+}$ dication. As a consequence, the cyclopentadienyl protons in the ^{1}H NMR spectrum shift downfield by ~0.7 ppm and two new, somewhat broadened singlets (δ −15.25 and −17.67) appear in the high field. Broadening of the signals of the hydride H atoms is due, most likely, to the intramolecular exchange between these atoms. The high-field region also contains a weak broadened multiplet with δ −9.3 and a singlet with δ −14.25 (the signal of $(\mu\text{-}H)Os_3(\mu\text{-}Cl)(CO)_{10}$), which disappear after 2 h. Subsequently, no changes take place in the ^{1}H NMR spectrum of the reaction mixture. Within 7 h after the onset of the process, the reaction mixture was concentrated *in vacuo* with addition of acetone three times and the solid residue was separated on Silufol plates. The initial complex **2** was recovered in 60% yield probably due to its parallel protonation at the O atoms of the carboxylate ligands as shown in Scheme 2.

Among reactions of ferrocene and its derivatives with electrophilic reagents, alkylation and acylation are as characteristic as protonation. Acylation is performed most often using acyl halides or carboxylic acid anhydrides and aluminum chloride as the catalyst.[11] Acylation using these procedures mainly yields diketones having heteroannular structures. Monoacylferrocenes are formed when the reactants are taken in strictly equivalent amounts. Electron-donating substituents in ferrocene facilitate acylation of the substituted Cp ring, while in the presence of electron-withdrawing substituents, *e.g.*, the $[-CO_2Os_3(\mu\text{-}H)(CO)_{10}]$ fragment, acylation involves the unsubstituted ring.

For acylation of complex **1**, we chose the procedure[24] proposed for the reactions of esters of ferrocenemonocarboxylic acids with AcCl, because the electron-withdrawing properties of the ester group appear to be rather close to those of the $[-CO_2(\mu\text{-}H)Os_3(CO)_{10}]$ fragment in complex **1**. When the **1** : AcCl : $AlCl_3$ ratio was 1 : 4 : 4, as in the published procedure,[24] the reaction did not proceed in CCl_4. Acylation of complex **1** becomes possible only in the presence of a large excess of AcCl and $AlCl_3$. The optimal yields of the acylation products (Scheme 3) were obtained with **1** : AcCl : $AlCl_3 \approx 1 : 11 : 16$.

The main reaction product was the $(\mu\text{-}H)Os_3(\mu\text{-}Cl)(CO)_{10}$ cluster (~30%), whose formation is associated with the appearance of HCl in the reaction medium

Scheme 3



upon acylation of the initial complex. Hydrogen chloride protonates the O atoms of the carboxylate bridges of both the initial complex and the acylation products, resulting in elimination of $[HOs_3(CO)_{10}]$ fragments, which then add the Cl^- ion. This process reduced appreciably the yield of the major acylation products of complex **1**. Ferrocenecarboxylic acid formed in the reaction is apparently protonated by HCl and forms a complex with $AlCl_3$, which is removed from the reaction. In the separation of the reaction mixture on Silufol plates, this complex remains at the application point and decomposes partially only when some acetone is added to the solvent system. The structures of acylated complexes **5** and **6** can be judged reliably based on the IR and NMR spectra. The four multiplet signals with equal integrated intensities in the low-field region of the ^{1}H NMR spectrum of complex **5** (Fig. 3) are typical of 1,1′-disubstituted ferrocenes whose substituents differ in donor-acceptor properties.[11] The signal of the Me group of the acyl fragment has a typical chemical shift (δ 2.39). A new band corresponding to stretching vibrations of the acyl CO bond appears in the IR spectrum at 1681 cm^{-1}, while the band at ~1110 cm^{-1} peculiar to unsubstituted Cp rings of ferrocene[25] is not recorded. In the IR spectrum of complex **6**, a similar band is observed at 1108 cm^{-1}. The low-field region of the ^{1}H NMR spectrum of this complex is typical of 1,2-disubstituted ferrocenes containing two electron-withdrawing groups. Two lowest-field multiplets correspond to the H atoms attached to carbon atoms closest to electron-withdrawing groups. The third signal having a somewhat smaller chemical shift is due to the remaining H atom. In addition, the ^{1}H NMR spectrum of complex **6** contains the signals due to the protons of the unsubstituted Cp ring, the acyl group, and the μ-H ligand. This ratio of acylation products of complex **1** is usually observed for ferrocenes containing an electron-withdrawing substituent in one Cp ligand.

Experimental data obtained in this work indicate that the behavior of complexes **1** and **2** in an acidic medium is mainly governed by the basicity of the O atoms of the carboxylate groups and the electron-withdrawing properties of the $[-CO_2Os_3(\mu\text{-}H)(CO)_{10}]$ cluster fragments. The electron-withdrawing properties of the cluster fragment determine also the conditions and the pattern of the acylation of complex **1**.

Experimental

Acylation of complex **1** and synthesis of complex **4** were carried out under Ar. The solvents were purified by standard procedures and removed from reaction mixtures under reduced pressure. Analytical chromatography was performed on Silufol plates; preparative chromatography was performed on Silufol plates and on a column with Silica gel 100/160. Complexes **1**,[7] **2**,[7] $Os(CO)_{11}NCMe$,[26] and $(\mu\text{-}H)Os_3(\mu\text{-}O_2CCH_3)(CO)_{10}$ [16] were prepared by known procedures. IR spectra were recorded on a Specord IR-75 spectrometer, and ^{1}H NMR spectra were registered on Bruker DPX-250 (250.13 MHz) and Tesla BS-567 (100 MHz) spectrometers using Me_4Si as the internal standard. Mass spectra (EI) were obtained on MKh-1310 (70 eV) and Finnigan MAT 8200 (70 eV) spectrometers. The masses of Os-containing compounds and fragments are given for the ^{192}Os isotope, those for iron-containing compounds are given for ^{56}Fe.

Protonation of complexes **1**, **2**, and $(\mu\text{-}H)Os_3(\mu\text{-}O_2CMe)(CO)_{10}$ was performed in air. The course of reactions of complexes **1** and **2** with acids was monitored by following the changes in the ^{1}H NMR spectra. For this purpose, a known amount of the acid or a solution of the acid in a deuterated solvent with a known concentration was introduced in an NMR tube with solution of the complex in a CD_2Cl_2 or $CDCl_3$, and the ^{1}H NMR spectra were recorded at definite time intervals.

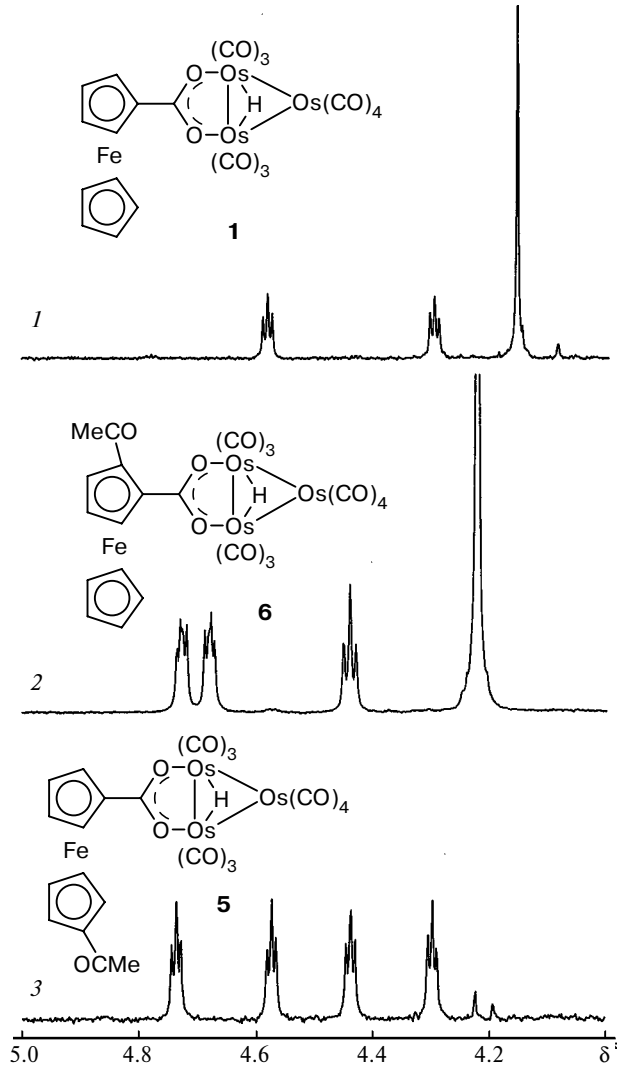


Fig. 3. Low-field region of the ^1H NMR spectra (250 MHz, $CDCl_3$) of $(\mu\text{-H})Os_3(\mu\text{-}O_2CC_5H_4FeCp)(CO)_{10}$ (**1**) (*1*), $(\mu\text{-H})Os_3\{\mu\text{-}O_2CC_5H_3C(O)MeFeCp\}(CO)_{10}$ (**6**) (*2*), and $(\mu\text{-H})Os_3\{\mu\text{-}O_2CC_5H_4FeC_5H_4C(O)Me\}(CO)_{10}$ (**5**) (*3*).

Reaction of the $(\mu\text{-H})Os_3(\mu\text{-}O_2CC_5H_4FeCp)(CO)_{10}$ complex (1) with AcCl. A solution of complex **1** (100 mg, $9.2 \cdot 10^{-5}$ mol) in 12 mL of CCl_4 was added with vigorous stirring and cooling to −15 °C over a period of 2 h to a suspension of $AlCl_3$ (200 mg, $1.5 \cdot 10^{-3}$ mol) and a solution of AcCl (80 mg, $1 \cdot 10^{-3}$ mol) in 6 mL of CCl_4. The reaction mixture was warmed to ~20 °C and H_2O (30 mL) was added with vigorous stirring. The organic layer was separated from the aqueous one; the latter was washed with ether (4×10 mL). The organic phases were combined, dried with $CaCl_2$, concentrated *in vacuo*, and chromatographed on Silufol plates using a 4 : 1 hexane—ether solvent system to give the following products:

— the initial complex **1** (10 mg, 10%);[7,8]

— a yellow-orange solid (22 mg, 30%), whose IR and ^1H NMR spectra completely coincided with the corresponding spectra of $(\mu\text{-H})Os_3(\mu\text{-Cl})(CO)_{10}$;[21]

— 1-{1,2-μ,η²-(*O*,*O*′)-carboxylato-(1,2-μ-hydrido)-1,1,1,1,2,2,2,3,3,3-decacarbonyl-*triangulo*-triosmium}-2-acetylferrocene (**6**) (9.2 mg, 9.7%), an orange crystalline solid. IR (hexane), ν/cm^{-1}: 2114 w, 2075 vs, 2063 s, 2027 vs, 2015 s, 2009 sh, 1987 m, 1984 sh, 1982 sh (CO); 1684 w (—C(O)Me); 1543 w (—CO_2—), 1108 w (Cp). ^1H NMR (250 MHz, $CDCl_3$), δ: 4.73 (m, 1 H, C_5H_3); 4.68 (m, 1 H, C_5H_3); 4.44 (m, 1 H, C_5H_3); 4.22 (m, 5 H, Cp); 2.35 (s, 3 H, MeCO—); −10.25 (s, 1 H, μ-H). The mass spectrum contained a molecular ion peak $[M]^+$ with m/z = 1128 (I_{rel} ~26%) and peaks with variable intensities (16 to 100%) corresponding to abstraction of ten CO groups from the cluster fragment;

— 1-{1,2-μ,η²-(*O*,*O*′)-carboxylato-(1,2-μ-hydrido)-1,1,1,1,2,2,2,3,3,3-decacarbonyl-*triangulo*-triosmium}-1′-acetylferrocene (**5**) (21 mg, 22%), an orange crystalline solid. IR (hexane), ν/cm^{-1}, 2114 w, 2075 vs, 2064 s, 2028 vs, 2026 sh, 2017 s, 2014 sh, 2008 m, 1987 m, 1984 sh (CO); 1681 w (—C(O)Me); 1545 w (—CO_2—). ^1H NMR (250 MHz, $CDCl_3$), δ: 4.73, 4.58, 4.44, 4.30 (all m, 2 H each, 2 CH); 2.39 (s, 3 H, —C(O)Me); −10.18 (s, 1 H, μ-H). The mass spectrum contained a molecular ion peak $[M]^+$ with m/z = 1128 (I_{rel} ~37%) and peaks with variable intensities (21 to 100%) corresponding to the abstraction of ten CO groups from the cluster fragment; and

— a brick-orange solid (4 mg, 19%), whose IR spectrum coincided with the spectrum of ferrocenecarboxylic acid.[22]

Reaction of the $Fe\{(\mu\text{-}O_2CC_5H_4)(\mu\text{-H})Os_3(CO)_{10}\}_2$ complex (2) with CF_3SO_3H. A solution (0.2 mL) of CF_3SO_3H (1 mg, $7 \cdot 10^{-6}$ mol) in CD_2Cl_2 was added to a solution of complex **2** (82 mg, $4.2 \cdot 10^{-5}$ mol) in 1 mL of CD_2Cl_2 and ^1H NMR spectra of the reaction mixture were recorded every 20 min. After 2.5 h, the mixture was concentrated *in vacuo* and separated on Silufol plates using a 1 : 1.5 hexane—ether solvent system to give two major fractions. The first fraction (38 mg, 46%) was complex **2** according to IR and ^1H NMR spectra.[8] The second fraction (38 mg, 26%) was an orange-brown solid, whose IR and ^1H NMR spectra were virtually identical with the corresponding spectra of complex **4**. A trace amount of ferrocene-1,1′-dicarboxylic acid, identified by chromatography, was also isolated.

1-{1,2-μ,η²-(*O*,*O*′)-Carboxylato-(1,2-μ-hydrido)-1,1,1,1,2,2,2,3,3,3-decacarbonyl-*triangulo*-triosmium}-1′-carboxyferrocene (4). A solution of $Me_3NO \cdot 2H_2O$ (40 mg, $3.6 \cdot 10^{-4}$ mol) in 4 mL of anhydrous MeOH was added dropwise with stirring over a period of 1 h to a suspension of $Os(CO)_{11}NCMe$ (135 mg, $1.7 \cdot 10^{-4}$ mol) in 65 mL of MeCN. Then the reaction mixture was passed through a column with Silica gel, the $Os(CO)_{10}(NCMe)_2$ complex was eluted with benzene, and the solvent was removed *in vacuo*. The solid residue was dissolved in 35 mL of THF and ferrocene-1,1′-dicarboxylic acid (80 mg, $2.9 \cdot 10^{-4}$ mol) was added. The reaction mixture was refluxed for 1 h, the solvent was removed *in vacuo*, and the solid residue was chromatographed on a column with Silica gel 40/100 using a hexane—ether mixture (1 : 1.5) as the eluent to give an orange-brown solid (17 mg, 3%) whose IR and ^1H NMR spectra were similar to the corresponding spectra of complex **2**[7,8] and $(\mu\text{-H})Os_3(\mu\text{-}O_2CC_5H_4FeC_5H_4COOH)(CO)_{10}$ (**4**), an orange-brown solid (68 mg, 41%); IR (hexane), ν/cm^{-1}: 2113 w, 2072 vs, 2062 s, 2027 vs, 2016 s, 2005 m, 1985 m, 1981 m (CO); 1686 w (—COOH); 1537 w (—CO_2^-). ^1H NMR (100 MHz, acetone-d_6), δ: 4.80, 4.69, 4.49, 4.40 (all m, 2 H each, CH); −9.98 (s, 1 H, μ-H). Found (%): C, 22.88; H, 1.01; Fe, 4.19; Os, 50.14. $C_{22}H_{10}FeO_{14}Os_3$. Calculated (%): C, 22.40; H, 0.89; Fe, 4.98; Os, 50.76.

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