μ-Acyl Os_3 clusters containing metallocenyl substituents and products of their protonation

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Previously unknown μ-acyl osmium clusters containing simultaneously permethylmetallocenyl and Os_3 cluster fragments were synthesized. The IR, UV, NMR (^1H and ^{13}C), and FAB-MS spectra were examined. Protonation of the clusters proceeds at the metal atom of the metallocenyl fragment.

Key words: osmium, μ-acyl clusters, protonation, permethylmetallocenylcarbaldehydes; IR spectra, UV spectra, FAB mass spectra, NMR spectra.

To extend the range of available permethylated derivatives of metallocenes and their functional derivatives, we studied the reactions of permethylmetallocenylcarbaldehydes **1a—c** (M = Fe, Ru, or Os) with the trinuclear cluster $Os_3(CO)_{10}(MeCN)_2$. The aim of this work is to prepare previously unknown μ-acyl clusters of osmium **2a—c** containing simultaneously the permethylmetallocenyl and cluster fragments. Methyl groups can then serve as a source of carbenium ions. In this work, we also studied protonation of compounds **2a—c** with the aim of comparing their properties with the properties of the initial aldehydes, whose protonation we have studied previously.[1,2]

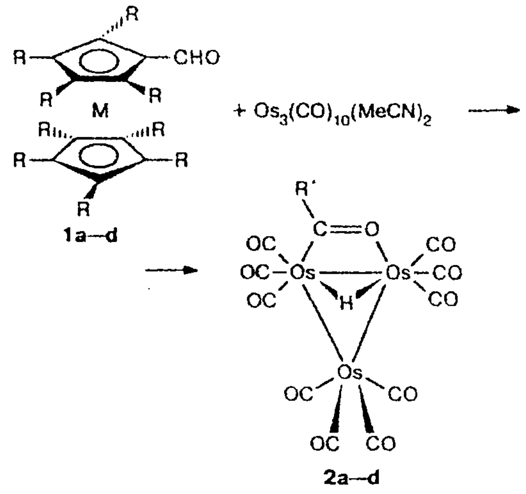
Results and Discussion

Previously,[3—8] the syntheses of μ-acyl clusters **2** containing various organic groups (R′ = Alk, Ar,[3,4] RCH=CH (R = Me or Ph)[5], HC≡C, [6] or residues of heterocycles[7]) as R′ substituents as well as of nonmethylated ferrocenyl (**2d**, R′ = Fc = $C_5H_5FeC_5H_4$)[8] have been reported. These compounds were prepared by the reactions of the corresponding aldehydes with $Os_3(CO)_{10}(MeCN)_2$.

We used aldehydes **1a—c** [9—11] in the reactions with $Os_3(CO)_{10}(MeCN)_2$. Heating of their mixtures in heptane at 80 °C afforded clusters **2a—c** (Scheme 1, R′ = $C_5Me_5MC_5Me_4$; M = Fe (**2a**), Ru (**2b**), or Os (**2c**)).

The compositions and structures of compounds **2a—c** agree with the data of elemental analysis and are confirmed by the fact that the metallocarbonyl regions of the IR spectra of all clusters **2** containing organic substituents are identical to that of the first simplest representative (**2d**) containing the ferrocenyl substituent (R′ = $C_5H_5FeC_5H_4$), which has been studied by X-ray analysis.[8]

Scheme 1



R = Me (**a—c**), H (**d**); R′ = $C_5R_5MC_5R_4$;
M = Fe (**a**, **d**), Ru (**b**), Os (**c**)

Table 1. IR spectra of compounds **2a—c** in the region of vibrations of Os—CO (as Nujol mulls)

Compound	$\nu(Os—CO)/cm^{-1}$
2a	2105 m, 2064 s, 2052 s, 2022 s, 2016 s, 2006 s, 1986 m, 1974 m
2b	2105 m, 2064 s, 2052 s, 2022 s, 2016 v.s, 2006 m, 1986 m, 1974 m
2c	2106 m, 2064 s, 2052 s, 2024 s, 2016 s, 2006 m, 1990 m, 1974 m
2d[8]	2107 m, 2067 s, 2055 s, 2021 s, 2017 sh, 2008 sh, 1991 m, 1974 m

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The IR spectra of complexes **2a—c**, like that of **2d**,[8] have eight absorption bands each, which correspond to ν(Os—CO) vibrations. Their relative intensities coincide (Table 1). In the case of clusters **2a—c**, the bands are only slightly shifted to the low-frequency region (by 3—9 cm^{-1}) compared to nonmethylated ferrocenyl complex **2d** and the dependence of ν(Os—CO) on the nature of the metal atom is virtually absent.

Previously,[3—8] it has been demonstrated that coordination of the aldehyde group to the Os_3 cluster fragment leads to a sharp decrease in the vibration frequency of this group (1490—1430 cm^{-1}). In compounds **2a—d** under study, bands of the carbonyl C,O-bonded group ($\nu(CO)_{ald}$) are shifted even more substantially to the low-frequency region. Their positions are also independent of the nature of the metal atom but change substantially upon methylation of the rings (see below).

Compound	**1a**	**2a**	**1c**	**2c**
$\nu(CO_{ald})$/cm^{-1}	1660	1328	1672	1330

Table 2. UV spectra of compounds **1** and **2** (in CH_2Cl_2)

Compound	λ_{max}/nm (log ε)
1a	484 (2.87); 384 sh (2.81); 352 sh (3.09)
2a	567 (3.41); 402 (3.96); 351 (3.93); 317 (4.08)
1b	353 (2.9); 277 (3.3)
2b	420 (3.1); 357 (3.4); 322 (3.9)
2c	487 (3.30); 401 (3.81); 303 (4.06)

Table 3. ^1H NMR spectra (δ) of clusters **2** (in CD_2Cl_2)

Compound	Os_3H (s, 1 H)	C_5Me_5 (s, 15 H)	C_5Me_4 (s, 3 H)
2a	−13.27	1.57	1.56, 1.65 1.75, 2.34
2b	−13.34	1.59*	1.65, 2.24
2c	−13.37	1.67	1.62, 1.64 1.68, 2.28

* The integral intensity of 21 H.

Interesting characteristic features of the compounds under study are manifested in the electronic absorption spectra (Table 2). The positions of the long-wavelength bands as well as the color of the compound depend not only on methylation of the rings but also to a larger extent on the nature of the metal atom in the metallocenyl fragment. All clusters **2** containing organic substituents in the μ-acyl ligand are yellow, while for compounds **2a—c** containing metallocenyl substituents, the color becomes deeper and/or changes sharply. In going from cluster **2a** to **2b** and then to **2c**, the color changes from blue to yellow and then to red. Interestingly, all bands in the visible region of the spectra are intense (log ε > 2.5) from which it follows that these allowed transitions are, most likely, associated with the charge transfer from the metallocenyl substituent to the Os_3 cluster fragment.

The structures and compositions of compounds **2a—c** are also confirmed by mass spectrometry. The mass spectra of clusters **2a—c** have groups of peaks at m/z 1180—1198 (the most intense ion peak at m/z 1192), 1233—1244 (1236), and 1318—1332 (1326) for **2a**, **2b**, and **2c**, respectively. These groups consist of isotopically distributed molecular ion peaks $[M]^+$ and peaks of ions formed from $[M]^+$ due to the loss of hydrogen atoms and carbonyl groups (from 1 to 10 CO; for more details, see the Experimental section).

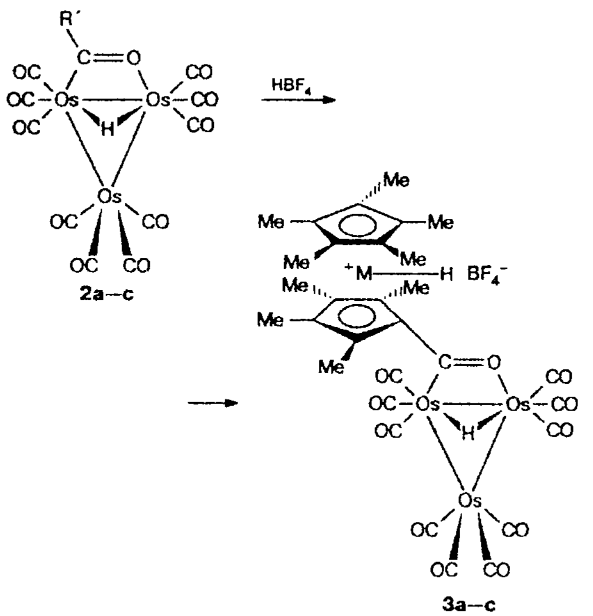
The structures of compounds **2a—c** agree also with the data of ^1H and ^{13}C NMR spectroscopy (Tables 3 and 4). The ^1H NMR spectra of compounds **2a—c** have four singlet signals of the nonequivalent groups of the substituted cyclopentadienyl ring and a signal of the bridging hydrogen atom along with a singlet of five methyl groups of the free cyclopentadienyl ring. The nonequivalence of the protons of the Me groups is caused by asymmetry of the μ-acyl Os_3 cluster fragment, whose free rotation is hindered by the α- and α′-methyl groups. The nonequivalence of the methyl groups of the substituted ring is also observed in the ^{13}C NMR spectra of clusters **2a—c** (see Table 4).

As mentioned above, we studied also protonation of complexes **2a—c** with the aim of comparing their properties with the properties of the initial aldehydes **1**.

Table 4. ^{13}C NMR spectra (δ) of clusters **2** (in CD_2Cl_2).

Compound	$C_5\underline{Me}_5$	$C_5\underline{Me}_4$	$\underline{C}_5Me_5$	$\underline{C}_5Me_4$	$M\underline{C}O$
2a	9.62	9.51, 9.82, 12.12, 12.80	80.95	79.50, 86.43, 86.61, 87.63, 88.80	174.57, 175.84, 176.14, 176.73, 177.14, 177.96, 178.48, 183.12, 183.31
2b	10.13	9.59, 9.57, 12.71, 13.30	85.16	82.97, 86.28, 88.88, 90.07, 90.32	174.47, 176.00, 176.07, 176.49, 177.08, 177.83, 178.02, 178.27, 183.04, 183.56
2c	10.46	9.89, 10.22, 13.04, 13.70	81.14	75.34, 77.34, 78.55, 82.84, 84.12	174.32, 175.94, 176.41, 177.10, 177.74, 177.89, 178.36, 183.06, 183.75

Scheme 2



$R' = C_5Me_5MC_5Me_4$; M = Fe (**a**), Ru (**b**), Os (**c**)

Using compounds **1** as an example, we demonstrated that *O*-protonation products were formed.[1,2] However, unlike aldehydes **1**, μ-acyl clusters **2a—c** underwent protonation at the metal atom of the metallocenyl fragment to form cationic hydride complexes **3a—c** (Scheme 2).

For comparison, we performed protonation of decamethylmetallocenes (Table 5). The ^1H NMR spectra of complexes **3a—c** have signals of hydride protons, which are similar in positions to the analogous signals of protonated decamethylmetallocenes,[12] along with signals of the Me groups and of the bridging hydrogen atom, which are slightly shifted compared to the corresponding signals of the initial clusters **2a—c**. This is indicative of the formation of the $M^+—H$ bond in the metallocenyl fragments of clusters **3a—c**.

Table 5. ^1H NMR spectra (δ) of clusters **3a—c** and protonated decamethylmetallocenes (in $CD_2Cl_2/HBF_4/CF_3COOH$)

Compound	Os_3H (s, 1 H)	M—H (s, 1 H)	C_5Me_5 (s, 15 H)	C_5Me_4 (s, 3 H)
3a	—	-22.05^a	-32.09^a	-43.71^a
$(C_5Me_5)_2FeH^+$	—	−3.70	1.67	-38.34^b
$(C_5Me_5FeC_5Me_4CHO)^{\cdot +}$	—	-20.18^c	-31.27^c	-41.24^c
3b	−13.53	−6.80		1.49, 1.80, 1.83, 2.00
$(C_5Me_5)_2RuH^+$	—	-8.32^d	1.88^d	
3c	−13.50	−14.24		1.70, 1.86, 1.89, 2.31
$(C_5Me_5)_2OsH^+$	—	-15.57^d	1.97^d	

[a] Resonance signals of the 2,5-, 3,4-, and 1′-Me groups of the paramagnetic cluster.

[b] The signal of $(C_5Me_5)_2Fe^{\cdot +}$; see Ref. 13.

[c] The signals of the 2,5-, 3,4-, and 1′-Me groups of the product of oxidation and protonation of **1a**; see Ref. 13.

[d] *Cf.* Ref. 12.

The specificity of the behavior of decamethylferrocene and μ-acyl complex **2a** under the above-mentioned conditions should also be noted. The initially formed protonation products, $C_5Me_5Fe^+HC_5Me_5$ and cationic complex **3a**, converted very rapidly to the ferrocenium derivatives $C_5Me_5Fe^{\cdot +}C_5Me_5$ and $C_5Me_5Fe^{\cdot +}C_5Me_4CO[Os_3(CO)_{10}H]$ (**4**), which is manifested in the ^1H NMR spectra as broad signals typical of paramagnetic compounds (see Table 5). Note that the ^1H NMR spectral pattern of complex **4** is very similar to that of $C_5Me_5Fe^{\cdot +}C_5Me_4CHO$.[13]

Experimental

The ^1H and ^{13}C NMR spectra were recorded in CD_2Cl_2 on a Bruker WP-200SY instrument operating at 200.13 and 50.31 MHz and on a Bruker AMX 400 instrument operating at 400.13 and 100 MHz for ^1H and ^{13}C, respectively. The IR spectra were obtained on a Specord M-40 instrument as Nujol mulls. The UV spectra (in CH_2Cl_2) were obtained on a Specord 82 instrument. The FAB mass spectra were measured on a Kratos Concept instrument; *m*-nitrobenzyl alcohol was used as the matrix.

Elemental analysis was carried out at the Laboratory of Microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences. The complex organometallic compounds containing simultaneously Fe and Os or Ru and Os atoms were analyzed according to a special procedure developed previously.[14] Aldehydes **1a**,[9] **1b**,[10] and **1c** [11] have been prepared by us previously. The complex $Os_3(CO)_{10}(MeCN)_2$ was synthesized according to a known procedure.[15] Protonation was carried out in an NMR tube with the use of the HBF_4/CF_3COOH mixture at 20 °C. The HBF_4/CF_3COOH mixture was prepared by the reaction of HBF_4 with $(CF_3CO)_2O$ (1 : 8). It is convenient to use this mixture for studying protonation by NMR spectroscopy because the solution does not give resonance signals for protons, which may overlap with signals of the compound under study.

Synthesis of clusters 2a—c (general procedure). A mixture of the cluster $(MeCN)_2Os_3(CO)_{10}$ (0.46 g, 0.51 mmol) and the corresponding aldehyde **1a—c** (~1 mmol) taken in a ratio of 1 : 2 was heated in heptane at 80 °C under argon with intense stirring using a magnetic stirrer for 4 h. The solution was filtered off, concentrated, and chromatographed on a column (20×2 cm) with silica gel (Chemapol L 40/100 μm). $Os_3(CO)_{12}$ (yellow band), clusters **2a** (blue band), **2b** (yellow-orange band), and **2c** (bright red band) were eluted with petroleum ether. By-products were eluted with a 1 : 1 petroleum ether—benzene mixture. The initial unconsumed aldehydes **1a—c** were eluted with a 5 : 1 benzene—ether mixture; m.p. of **2a—c** (from a benzene—hexane mixture) 200—205 °C (with decomp.).

Cluster 2a: yield 68%. Found (%): C, 29.38; H, 2.38; Os, 48.34; Fe, 4,63. $C_{30}H_{28}FeO_{11}Os_3$. Calculated (%): C, 30.75; H, 2.37; Os, 47.91; Fe, 4.69.

MS,* *m/z* (the most intense peak, I_{rel} (%)) 1180—1196 $[\mathrm{M}]^+$ (1192 (45)), 1158—1168 $[\mathrm{M} - \mathrm{CO}]^+$ (1164 (56)), 1074—1080 $[\mathrm{M} - 4\,\mathrm{CO}]^+$ (1178 (25)), 1040—1050 $[\mathrm{M} - 5\,\mathrm{CO}]^+$ (1050 (45)), 1018—1030 $[\mathrm{M} - 6\,\mathrm{CO}]^+$ (1024 (22)), 992 $[\mathrm{M} - 7\,\mathrm{CO}]^+$, 996 $[\mathrm{M} - 8\,\mathrm{CO}]^+$, 940 $[\mathrm{M} - 9\,\mathrm{CO}]^+$, 912 $[\mathrm{M} - 10\,\mathrm{CO}]^+$.

Cluster 2b: yield 67%. Found (%): C, 29.25; H, 2.27; Os, 45.55. $C_{30}H_{28}O_{11}Os_3Ru$. Calculated (%): C, 29.15; H, 2.28; Os, 46.16. MS,* *m/z* (the most intense peak, I_{rel} (%)): 1133—1144 $[\mathrm{M}]^+$ (1236 (65)), 1205—1212 $[\mathrm{M} - \mathrm{CO}]^+$ (1209 (42)), 1120—1125 $[\mathrm{M} - 4\,\mathrm{CO}]^+$ (1123 (60)), 1068—1096 $[\mathrm{M} - 5\,\mathrm{CO}]^+$ (1090 (10)), 1058—1067 $[\mathrm{M} - 6\,\mathrm{CO}]^+$ (1063 (100)), 1031—1039 $[\mathrm{M} - 7\,\mathrm{CO}]^+$ (1134 (85)), 1006 $[\mathrm{M} - 8\,\mathrm{CO}]^+$ (85), 977 $[\mathrm{M} - 9\,\mathrm{CO})^+$ (100).

Cluster 2c: yield 66%. Found (%): C, 26.74; H, 2.22; Os, 57.89. $C_{30}H_{28}O_{11}Os_4$. Calculated (%): C, 27.18; H, 2.13; Os, 57.40. MS,* *m/z* (the most intense peak, I_{rel} (%)): 1318—1332 $[\mathrm{M}]^+$ (1326 (60)), 1292—1304 $[\mathrm{M} - \mathrm{CO}]^+$ (1298 (40)); 1264—1278 $[\mathrm{M} - 2\,\mathrm{CO}]^+$ (1270 (20)), 1230—1246 $[\mathrm{M} - 3\,\mathrm{CO}]^+$ (1235 (15)), 1190—1200 $[\mathrm{M} - 4\,\mathrm{CO} - \mathrm{Me}]^+$ (1198 (100)), 1160—1174 $[\mathrm{M} - 5\,\mathrm{CO} - \mathrm{Me}]^+$ (1171 (65)).

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* The ion peaks $[\mathrm{M} - n\,\mathrm{CO} - m\,\mathrm{H}]^+$ in the mass spectra are given, where $m = 1$—4 and $n = 1$—10. Because Ru and Os are polyisotopic elements, it is difficult to determine the exact value of *m* and the exact values of the relative intensities.

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