Generation of the metallonium cations [1,2-(CH$_2$)$_2$C$_5$Me$_3$OsC$_5$Me$_5$]$^{2+}$, [1,1′-(CH$_2$C$_5$Me$_4$)$_2$Os]$^{2+}$ and [1,2-(CH$_2$)$_2$C$_5$Me$_3$Os(1′-CH$_2$C$_5$Me$_4$)]$^{3+}$ in the CF$_3$SO$_3$H–O$_2$ system

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The title dications and trication were generated from decamethylosmocene and [C$_5$Me$_5$OsC$_5$Me$_4$CH$_2$]$^+$, respectively, by the interaction with dioxygen in CF$_3$SO$_3$H solutions.

Previously,[1–3] we found that strong protic acids can promote the oxidation of methyl substituents in the decamethylmetallocenes (C$_5$Me$_5$)$_2$M (M = Ru or Os) under certain conditions. Decamethylruthenocene can be oxidised by molecular oxygen in the superacid CF$_3$SO$_3$H to form mono-, di- or even trications. In this work, we examined this reaction by the example of decamethylosmocene **1** and salt† [C$_5$Me$_5$OsC$_5$Me$_4$CH$_2$]$^+$BF$_4^-$ **2** as the product of its one-electron oxidation.

The behaviour of compound **1** in CF$_3$SO$_3$H (98%, Fluka) in an inert atmosphere of argon was preliminarily studied by ^{1}H NMR spectroscopy. It was found that, in contrast to (C$_5$Me$_5$)$_2$Ru, which forms the monohydride [(C$_5$Me$_5$)$_2$RuH]$^+$ under these conditions, decamethylosmocene **1** affords dihydride [(C$_5$Me$_5$)$_2$OsH$_2$]$^{2+}$ **3**. The monohydride [(C$_5$Me$_5$)$_2$OsH]$^+$ is usually formed in weaker acids.[1] In the case of monocation **2** in a CF$_3$SO$_3$H solution in an inert atmosphere, dication [C$_5$Me$_5$Os(H)C$_5$Me$_4$CH$_2$]$^{2+}$ **4** was formed as the product of monoprotonation. The reactions of **1** and **2** with oxygen in CF$_3$SO$_3$H solutions were performed in NMR tubes (0.7 ml) with bubbling oxygen‡ at regular intervals, as described previously[3] for the reaction with (C$_5$Me$_5$)$_2$Ru. The course of the reaction was monitored by ^{1}H NMR spectroscopy. The formation of dihydride **3** (from **1**) and protonated monocation **4** (from **2**) was detected at the first step. Previously described[5,6] dications [1,2-(CH$_2$)$_2$C$_5$Me$_3$OsC$_5$Me$_5$]$^{2+}$ **5** and [1,1′-(CH$_2$C$_5$Me$_4$)$_2$Os]$^{2+}$ **6**, as well as a new species that corresponds to trication [1,2-(CH$_2$)$_2$C$_5$Me$_3$Os(1′-CH$_2$C$_5$Me$_4$)]$^{3+}$ **7**, were identified among the reaction products. The completion of the reaction was judged from the disappearance of dihydride **3** or dication **4** in the oxidation of **1** or **2**, respectively.

A comparison between the ratios of products obtained in the oxidation of **1** demonstrates that dications **5** (62%) and **6** (34%) were primarily formed, and the portion of trication **7** was as low as 4%. The yield of trication **7** cannot be increased by further passing of oxygen (Scheme 1). In the case of oxidation of compound **2** (Scheme 2), trication **7** was the main reaction product (81% on a basis of identified products), whereas dications **5** and **6** were formed in minor amounts (19%) (**5**:**6** ~ 1.4:1) (Scheme 1).

The structures of the products were supported by ^{1}H and ^{13}C NMR data.§ Thus, the ^{1}H NMR spectrum of dihydride **3** exhibits two singlet signals, and the ratio between the integral intensities of methyl protons and the signal of an OsH proton is equal to

15:1. All signals in the spectrum of dication **4** are broadened ($\Delta\nu_{1/2} \approx$ 22–24 Hz for the signals of Me groups of the C$_5$Me$_4$ ring and the CH$_2$ group, and $\Delta\nu_{1/2} \approx$ 6–7 Hz for the signals of Me groups of the C$_5$Me$_5$ ring and the signal of OsH). Similarly to [C$_5$Me$_5$Re(H)C$_5$Me$_4$CH$_2$]$^+$,[7] the protons of the CH$_2$ group are non-equivalent, as well as the protons of Me groups of the C$_5$Me$_4$CH$_2$ ring (four signals of 3H). The ^{1}H NMR spectra of dications **5** and **6** are consistent with the spectra of dications obtained by the protonation of corresponding dicarbinols.[5,6] The assignment of signals in the spectrum of trication **7** presented no special problems because all of the signals exhibited the same behaviour as those of the trication [1,2-(CH$_2$)$_2$C$_5$Me$_3$Ru(1′-CH$_2$-C$_5$Me$_4$)]$^{3+}$.[3] Thus, the spectrum contained three signals of the same intensity (2H) from three CH$_2$ groups, and the chemical shifts of these signals [δ = 5.04 (d), 5.66 (d) and 5.49 (s) ppm] are almost equal to the values published for the Ru-containing trication.[3] The appearance of signals due to three CH$_2$ groups as two doublets and a singlet indicates that trication **7** exhibits a plane of symmetry and does not contain a C$_5$Me$_5$ ring. The equality of $\Delta\delta_{AB}$ differences for trication **7** (0.62 ppm) and 1,2-dication **5** (0.62 ppm) is indicative of the 1,2-arrangement of CH$_2$ groups in the C$_5$Me$_3$(CH$_2$)$_2$ ring of trication **7**. The ^{13}C NMR spectra of all complexes also support the structures. Thus, the carbon atoms of two 1,2-CH$_2$ groups of trication **7** exhibit a chemical shift of 71.32 ppm in the ^{13}C NMR spectrum and appear as a triplet with $^1J_{CH}$ = 172 Hz. The carbon atom of the 1′-CH$_2$ group gives an upfield triplet (δ = 65.75 ppm, $^1J_{CH}$ 157 Hz). Note that two CH$_2$ groups in the Ru-containing trication exhibit a chemical shift of 88.57 ppm ($^1J_{CH}$ = 172 Hz), whereas the chemical shift and $^1J_{CH}$ of the third 1′-CH$_2$ group are consistent with the corresponding values for the 1′-CH$_2$ group in trication **7**.

It is known[8] that the great difference between the electronegativities of transition metal complexes and O$_2$ induces the formation of bridging or nonbridging oxo compounds. Com-
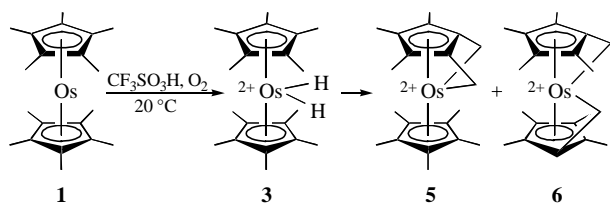
Scheme 1

† Complex **2** was prepared from C$_5$Me$_5$OsC$_5$Me$_4$CH$_2$OH using HBF$_4$ etherate.[4]

‡ A solution of ~0.1 mmol of complex **1** or ~0.02 mmol of complex **2** in CF$_3$SO$_3$H (~3 mmol) was placed in a tube. Oxygen (~1 l) was bubbled through the solution for 2–3 h at ambient temperature.

§ The NMR spectra were measured on a Bruker AMX-400 spectrometer (400.13 and 100.61 MHz for ^{1}H and ^{13}C, respectively). An external standard was used for CF$_3$SO$_3$H solutions (δ C$_6$D$_5$H 7.25 and 127.96 ppm for ^{1}H and ^{13}C, respectively).

3: ^{1}H NMR, δ: 2.68 (s, 30H, C$_5$Me$_5$), –14.58 (s, 2H, OsH). ^{13}C NMR, δ: 8.77 (γ-Me), 106.32 (C$_{Cp}$).

4: ^{1}H NMR, δ: 2.57 (s, 15H, C$_5$Me$_5$), 2.17, 2.31, 2.51 and 2.98 (4s, 4×3H, α- and β-Me), 5.17, 5.79 (2s, 2×1H, CH$_2$), –15.40 (s, 1H, OsH). ^{13}C NMR, δ: 9.29 (γ-Me), 8.55 (α-Me), 9.35 (β-Me), 66.50 (CH$_2$), 107.06 (C$_1$), 96.39, 102.74, 108.4 (C$_{Cp}$), 105.53 (γ-C$_{Cp}$).

5: ^{1}H NMR, δ: 2.57 (s, 15H, C$_5$Me$_5$), 2.14 (s, 6H, α-Me), 2.57 (s, 3H, β-Me), 4.90 and 5.52 (2d, 2×2H, CH$_2^{AB}$, $^2J_{HH}^{gem}$ 2.7 Hz); *cf.* ref. 5. ^{13}C NMR, δ: 10.00 (γ-Me), 9.41 (α-Me), 10.23 (β-Me), 70.92 (CH$_2$, $^1J_{CH}$ 171 Hz), 134.66 (C$_1$), 105.53, 115.06 (C$_{Cp}$), 107.58 (γ-C$_{Cp}$); *cf.* ref. 5.

6: ^{1}H NMR, δ: 2.19, 2.31, 2.41 and 2.83 (4×6H, α,α′,β,β′-Me), 5.43, 5.87 (2d, 2×2H, CH$_2$); *cf.* ref. 6. ^{13}C NMR, δ: 6.83, 8.64 (α,α′-Me), 8.89, 10.90 (β,β′-Me), 73.31 (CH$_2$, $^1J_{CH}$ 170 Hz), 99.86, 105.71, 111.51, 116.07, 116.53 (C$_{Cp}$).

7: ^{1}H NMR, δ: 2.19, 2.50, 2.71 and 3.03 (3×6H, 3H, α,α′,β,β′-Me), 5.04, 5.66 (2d, 2×2H, CH$_2^{AB}$, $^2J_{HH}^{gem}$ 2.3 Hz), 5.49 (s, 2H, CH$_2$). ^{13}C NMR, δ: 8.67, 8.71, 9.28 (3×2Me), 9.47 (Me), 65.75 (CH$_2$, $^1J_{CH}$ 157 Hz), 71.32 (2CH$_2$, $^1J_{CH}$ 172 Hz), 93.20, 102.70, 106.93, 108.45, 116.80, 135.12 (C$_{Cp}$).
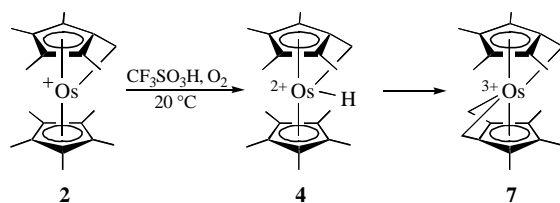
Scheme 2

plexes having a free coordination site let O_2 bind the metal in end-on and edge-on modes. The unprecedented mode of C–H activation of permethyl ligands (for example, η^6-arene) implies a monoelectronic transfer from an organometallic complex to O_2 followed by the deprotonation of $O_2^{\cdot-}$, a ligand activated by the cationic metal moiety:[9]

$$MRH + O_2 \longrightarrow MRH^+O_2^{\cdot-} \xrightarrow{-HO_2} MR$$

The transformation of O_2 into the radical anion is due to a low redox potential of this passage ($E_{1/2} = -0.7$ V/SCE).[8]

Now, we can only say that dication $[C_5Me_5Os(H)C_5Me_4CH_2]^{2+}$ **4** is an obligatory synthon on the way to trication **7** because the protonation of $[C_5Me_5OsC_5Me_4CH_2]^+BF_4^-$ **2** and the formation of trication **7** in the $CF_3CO_2H–O_2$ system do not take place.

Thus, trication **7** can be generated by the oxidation of monocation **2** with oxygen in CF_3SO_3H. At the same time, the oxidation of osmocene **1** with O_2 in CF_3SO_3H can be considered as a method for generating dications **5** and **6**.

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