

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

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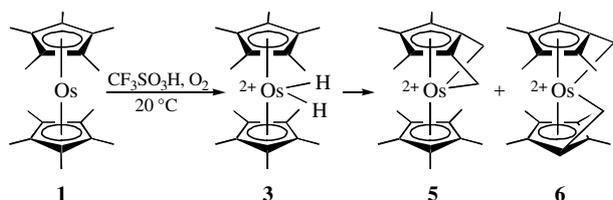
The title dications and trication were generated from decamethylsoscene and $[\text{C}_5\text{Me}_5\text{OsC}_5\text{Me}_4\text{CH}_2]^+$, respectively, by the interaction with dioxygen in $\text{CF}_3\text{SO}_3\text{H}$ solutions.

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

The behaviour of compound **1** in $\text{CF}_3\text{SO}_3\text{H}$ (98%, Fluka) in an inert atmosphere of argon was preliminarily studied by ¹H NMR spectroscopy. It was found that, in contrast to $(\text{C}_5\text{Me}_5)_2\text{Ru}$, which forms the monohydride $[(\text{C}_5\text{Me}_5)_2\text{RuH}]^+$ under these conditions, decamethylsoscene **1** affords dihydride $[(\text{C}_5\text{Me}_5)_2\text{OsH}_2]^{2+}$ **3**. The monohydride $[(\text{C}_5\text{Me}_5)_2\text{OsH}]^+$ is usually formed in weaker acids.¹ In the case of monocation **2** in a $\text{CF}_3\text{SO}_3\text{H}$ solution in an inert atmosphere, dication $[\text{C}_5\text{Me}_5\text{Os}(\text{H})\text{C}_5\text{Me}_4\text{CH}_2]^{2+}$ **4** was formed as the product of monoprotection. The reactions of **1** and **2** with oxygen in $\text{CF}_3\text{SO}_3\text{H}$ solutions were performed in NMR tubes (0.7 ml) with bubbling oxygen[‡] at regular intervals, as described previously³ for the reaction with $(\text{C}_5\text{Me}_5)_2\text{Ru}$. The course of the reaction was monitored by ¹H 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 $[1,2-(\text{CH}_2)_2\text{C}_5\text{Me}_3\text{OsC}_5\text{Me}_5]^{2+}$ **5** and $[1,1'-(\text{CH}_2\text{C}_5\text{Me}_4)_2\text{Os}]^{2+}$ **6**, as well as a new species that corresponds to trication $[1,2-(\text{CH}_2)_2\text{C}_5\text{Me}_3\text{Os}(1'-\text{CH}_2\text{C}_5\text{Me}_4)]^{3+}$ **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 ¹H and ¹³C NMR data.[§] Thus, the ¹H 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



Scheme 1

[†] Complex **2** was prepared from $\text{C}_5\text{Me}_5\text{OsC}_5\text{Me}_4\text{CH}_2\text{OH}$ using HBF_4 etherate.⁴

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

15:1. All signals in the spectrum of dication **4** are broadened ($\Delta\nu_{1/2} \approx 22\text{--}24$ Hz for the signals of Me groups of the C_5Me_4 ring and the CH_2 group, and $\Delta\nu_{1/2} \approx 6\text{--}7$ Hz for the signals of Me groups of the C_5Me_5 ring and the signal of OsH). Similarly to $[\text{C}_5\text{Me}_5\text{Re}(\text{H})\text{C}_5\text{Me}_4\text{CH}_2]^+$,⁷ the protons of the CH_2 group are non-equivalent, as well as the protons of Me groups of the $\text{C}_5\text{Me}_4\text{CH}_2$ ring (four signals of 3H). The ¹H 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 $[1,2-(\text{CH}_2)_2\text{C}_5\text{Me}_3\text{Ru}(1'-\text{CH}_2\text{C}_5\text{Me}_4)]^{3+}$.³ Thus, the spectrum contained three signals of the same intensity (2H) from three CH_2 groups, and the chemical shifts of these signals [$\delta = 5.04$ (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_5Me_5 ring. The equality of $\Delta\delta_{\text{AB}}$ 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 $\text{C}_5\text{Me}_3(\text{CH}_2)_2$ ring of trication **7**. The ¹³C 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 ¹³C NMR spectrum and appear as a triplet with $^1J_{\text{CH}} = 172$ Hz. The carbon atom of the $1'-\text{CH}_2$ group gives an upfield triplet ($\delta = 65.75$ ppm, $^1J_{\text{CH}} = 157$ Hz). Note that two CH_2 groups in the Ru-containing trication exhibit a chemical shift of 88.57 ppm ($^1J_{\text{CH}} = 172$ Hz), whereas the chemical shift and $^1J_{\text{CH}}$ of the third $1'-\text{CH}_2$ group are consistent with the corresponding values for the $1'-\text{CH}_2$ group in trication **7**.

It is known⁸ that the great difference between the electro-negativities of transition metal complexes and O_2 induces the formation of bridging or nonbridging oxo compounds. Com-

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

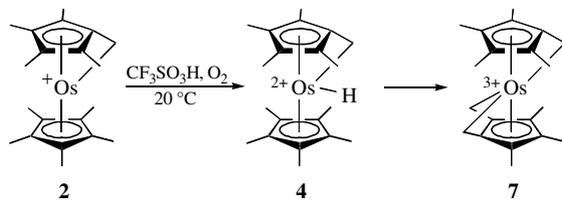
3: ¹H NMR, δ : 2.68 (s, 30H, C_5Me_5), –14.58 (s, 2H, OsH). ¹³C NMR, δ : 8.77 (γ -Me), 106.32 (C_{Cp}).

4: ¹H NMR, δ : 2.57 (s, 15H, C_5Me_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). ¹³C 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: ¹H NMR, δ : 2.57 (s, 15H, C_5Me_5), 2.14 (s, 6H, α -Me), 2.57 (s, 3H, β -Me), 4.90 and 5.52 (2d, 2×2H, CH_2^{AB} , $^2J_{\text{HH}}^{\text{gem}} = 2.7$ Hz); cf. ref. 5. ¹³C NMR, δ : 10.00 (γ -Me), 9.41 (α -Me), 10.23 (β -Me), 70.92 (CH_2), $^1J_{\text{CH}}$ 171 Hz), 134.66 (C_1), 105.53, 115.06 (C_{Cp}), 107.58 (γ - C_{Cp}); cf. ref. 5.

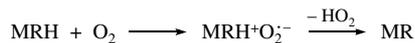
6: ¹H NMR, δ : 2.19, 2.31, 2.41 and 2.83 (4×6H, $\alpha, \alpha', \beta, \beta'$ -Me), 5.43, 5.87 (2d, 2×2H, CH_2); cf. ref. 6. ¹³C NMR, δ : 6.83, 8.64 (α, α' -Me), 8.89, 10.90 (β, β' -Me), 73.31 (CH_2 , $^1J_{\text{CH}}$ 170 Hz), 99.86, 105.71, 111.51, 116.07, 116.53 (C_{Cp}).

7: ¹H NMR, δ : 2.19, 2.50, 2.71 and 3.03 (3×6H, 3H, $\alpha, \alpha', \beta, \beta'$ -Me), 5.04, 5.66 (2d, 2×2H, CH_2^{AB} , $^2J_{\text{HH}}^{\text{gem}} = 2.3$ Hz), 5.49 (s, 2H, CH_2). ¹³C NMR, δ : 8.67, 8.71, 9.28 (3×2Me), 9.47 (Me), 65.75 (CH_2 , $^1J_{\text{CH}}$ 157 Hz), 71.32 (2 CH_2 , $^1J_{\text{CH}}$ 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^- , a ligand activated by the cationic metal moiety:⁹



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

Now, we can only say that dication $[\text{C}_5\text{Me}_5\text{Os}(\text{H})\text{C}_5\text{Me}_4\text{CH}_2]^{2+}$ **4** is an obligatory synthon on the way to trication **7** because the protonation of $[\text{C}_5\text{Me}_5\text{OsC}_5\text{Me}_4\text{CH}_2]^+\text{BF}_4^-$ **2** and the formation of trication **7** in the $\text{CF}_3\text{CO}_2\text{H}-\text{O}_2$ system do not take place.

Thus, trication **7** can be generated by the oxidation of monocation **2** with oxygen in $\text{CF}_3\text{SO}_3\text{H}$. At the same time, the oxidation of osmocene **1** with O_2 in $\text{CF}_3\text{SO}_3\text{H}$ can be considered as a method for generating dications **5** and **6**.

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