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One-pot method for the generation of the trication $[1,2\text{-}(CH_2)_2C_5Me_3RuC_5Me_4CH_2]^{3+}$ from decamethylruthenocene

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The title trication was generated for the first time by the interaction of decamethylruthenocene with oxygen in CF_3SO_3H.

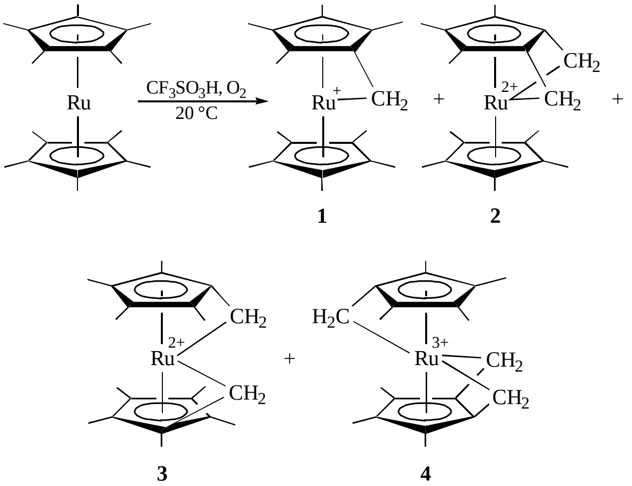
Previously,[1–3] multistage methods were developed for the synthesis of metalonium monocations $[CH_2C_5Me_4MC_5Me_5]^+$ **1** and homoannular and heteroannular dications $[1,2\text{-}(CH_2)_2C_5Me_4\text{-}MC_5Me_5]^{2+}$ **2** and $[1,1'\text{-}(CH_2C_5Me_4)_2M]^{2+}$ **3** (where M = Fe, Ru or Os), respectively. Single-stage methods based on permethylmetallocenes[4–7] were also proposed for the synthesis of cations **1**–**3**. Simple and convenient methods with the use of strong protic acids exhibited the most promise.[6,7] The generation of a mixture of dications **2** and **3** on dissolving $(C_5Me_5)_2Ru$ in oleum at 20 °C was of prime interest.[7]

The dications are readily formed and exhibit reasonably high thermodynamic stability due to the donor–acceptor interactions between the carbocationic sites CH_2^+ and two lone electron pairs of the metal atom. This suggested that structurally similar trications can also be generated because a transition metal atom in metallocenes has three lone electron pairs (d_{xy}, $d_{x^2-y^2}$, d_{z^2}). It seemed reasonable to generate trications under similar conditions with the use of strong protic acids.

We examined the behaviour of $(C_5Me_5)_2Ru$ in a CF_3SO_3H solution both in an inert atmosphere and in air. According to the ^1H NMR spectra, the protonation product $[(C_5Me_5)_2RuH]^+$ and monocation **1** were formed in argon, whereas dications **2** and **3** along with a small amount of new cationic species **4** were detected in the reaction mixture in air in addition to the above products. Thus, we discovered that oxygen of the air in the presence of a strong protic acid can oxidise one, two or even three methyl groups in $(C_5Me_5)_2Ru$. With the use of oxygen in this reaction, we found that the concentration of $[(C_5Me_5)_2RuH]^+$ decreased with a simultaneous increase in the amounts of cations **1**–**3** and new species **4**. The ^1H and ^{13}C NMR data allowed us to describe this species as trication $[1,2\text{-}(CH_2)_2C_5Me_3Ru\text{-}C_5Me_4CH_2]^{3+}$ **4**. To monitor the reaction, we performed it in a 0.7 ml NMR tube, which was filled with new portions of oxygen at regular intervals. This ^1H NMR monitoring demonstrated that monocation **1** completely disappeared after twice flushing the tube with oxygen. After the flushing with oxygen was repeated three times, the distribution of reaction products was as follows: **2**, 21%; **3**, 22%; **4**, 57%. In this case, the content of either of cations **2** and **3** decreased by ~6%. These data indicate that cations **1**–**3** are precursors of trication **4**, and this fact together with the NMR data substantiates the structure of **4**.

Note that the use of monocation **1** in place of $(C_5Me_5)_2Ru$ in this reaction also resulted in the generation of a mixture of dications **2** and **3** and trication **4**.

The determination of the structure of trication **4** presented no serious problems because its ^1H NMR spectrum was similar to that of $CH_2C_5Me_4$ and $1,2\text{-}(CH_2)_2C_5Me_3$ units in cations **1**–**3** with downfield shifted signals.[†] Trication **4** has a plane of symmetry and does not contain the C_5Me_5 ring. Thus, isomers with the arrangement of CH_2 groups at the 1,2,3- or 1,2,4-positions of the same ring cannot exist. To compare the chemical shifts in the ^1H NMR spectra with those in the spectra[2] of dications **2** and **3**, CD_2Cl_2 was added. The signals of protons of dication **3** in CF_3SO_3H without solvent are broadened and shifted downfield. The difference between the signals of protons of cations **2** and **4** is insignificant.



Scheme 1

The structure of trication **4** was also supported by ^{13}C NMR data. In the $^{13}C\{^1H\}$ NMR spectrum, three carbon atoms of CH_2 groups appear as triplets, and both carbon atoms of $1,2\text{-}(CH_2)_2$ groups with the chemical shift 88.57 ppm exhibit the constant $^1J_{CH}$ 172 Hz, which is close to that of dication **2** ($^1J_{CH}$ 171 Hz).[2,7] The signal of the carbon atom of the third CH_2 group is upfield (65.66 ppm, $^1J_{CH}$ 157 Hz). In this case, the constant is close to the constant obtained for monocation **1** ($^1J_{CH}$ 167 Hz).[‡][2]

Thus, we found that a metal atom in Group VIII element metallocenes can stabilise three carbocationic centres on the formation of trication **4**, which is the first example of organometallic onium complexes (note that in contrast to the salt of monocation **1**,[6] the salts of cations **2**–**4** are sensitive to trace water and were not isolated as individual compounds). It is unusual that three lone electron pairs of the metal atom participate in the formation of Ru–CH_2 bonds. The procedure developed for the oxidation of methyl groups can also be helpful in the case of other transition metal complexes. The only example similar to the reaction considered is the recently reported[8] oxidation of methane with oxygen in concentrated H_2SO_4 in the presence of Pt^{II} catalysts to form methanol derivatives.

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[†] The NMR spectra were measured on a Bruker AMX-400 spectrometer (400.13 and 100.61 MHz for ^1H and ^{13}C, respectively). C_6D_6 was used as an external standard for acid solutions (δ C_6D_5H 7.25 and 127.96 ppm for ^1H and ^{13}C, respectively). ^{13}C NMR data for **4**, δ ($^1J_{CH}$/Hz): 9.22 (133) (2Me), 9.28 (131) (2Me), 10.09 (132) (3Me), 65.66 (157) (CH_2), 88.57 (172) (2CH_2), 99.51, 107.16, 110.35, 114.01, 128.44, 138.50 (C_{Cp}).

[‡] ^1H NMR spectra of the ruthenium cations complexes (δ/ppm). The chemical shifts in CF_3SO_3H are given in parentheses, the other values were measured upon addition of CD_2Cl_2 to a CF_3SO_3H solution.

1: (1.96) (C_5Me_5), (1.71) (α-Me), (2.04) (β-Me), (4.56) (s, CH_2).

2: 2.35 (2.31) (C_5Me_5), 2.22 (2.18) (α-Me), 2.55 (2.51) (β-Me), 4.86 (4.82) and 5.26 (5.27) (2d, CH_2^{AB}, $^2J_{HH}^{gem}$ 2.0 Hz).

3: 2.28 (2.01) and 2.33 (2.23) (α,α'-Me), 2.47 (2.32) and 2.59 (2.55) (β,β'-Me), 4.99 (5.26 s) and 5.41 (5.86 s) (2d, CH_2^{AB}, $^2J_{HH}^{gem}$ 2.0 Hz).

4: 2.29 (2.28) and 2.31 (2.33) (2×6H, α,α'-Me), 2.48 (2.47) and 2.62 (2.59) (6H and 3H, β,β'-Me), 5.51 (5.50) (s, 2H, CH_2), 5.07 (5.03) and 5.49 (5.51) (2d, 2×2H, CH_2^{AB}, $^2J_{HH}^{gem}$ 1.9 Hz).

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