A structural rearrangement on the oxidation of 1,2-bis(ruthenocenyl)ethylene derivatives leads to unprecedented (μ-η^6 : η^6-pentafulvadiene)diruthenium complexes

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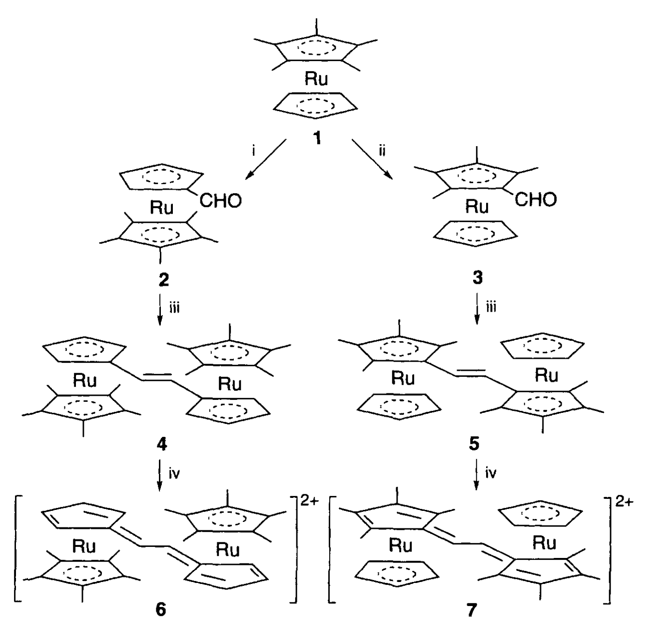
Unprecedentedly stable (μ-η^6 : η^6-pentafulvadiene) diruthenium complexes are obtained upon 2e-oxidation of 1,2-bis(ruthenocenyl)ethylenes, prepared from the reaction of ruthenocenylaldehydes with low-valent titanium.

Much attention has been focused on the structural rearrangement of dinuclear organometallic complexes in connection with studies concerning their electron-transfer reactions.[1–5] Here we report a novel structural rearrangement upon oxidation of bis(ruthenocenyl)ethylenes.

1,2,3,4,5-Pentamethylruthenocene **1** reacted with dimethylformamide and $POCl_3$ to give 1′,2′,3′,4′,5′-pentamethyl-1-formylruthenocene **2** in moderate yield and could be oxidized with activated MnO_2 to give 2,3,4,5-tetramethyl-1-formylruthenocene **3**, although in low yield. Complexes **2** and **3** were treated with $TiCl_4$–Zn in THF to afford *trans*-1,2-bis-(1′,2′,3′,4′,5′-pentamethylruthenocenyl)ethylene **4** and *trans*-1,2-bis(2,3,4,5-tetramethylruthenocenyl)ethylene **5**, respectively, in good yield (Scheme 1).† In agreement with the structures, the Raman spectra of **4** and **5** showed C=C stretching vibrations at 1646 and 1643 cm^{-1}, respectively. The structure of **4** was also confirmed by single-crystal X-ray diffraction (Fig. 1).‡ Half of the molecule is crystallographically unique, with the molecule located on an inversion centre. From the analysis of the difference Fourier synthesis, the C(1) atom in the ethylene moiety of **4** is disordered over two sites [C(1A), C(1B)] in *ca.* 2 : 1 occupancy ratio. This suggests the existence of two orientations of the ethylene moiety as opposite *trans*-forms on the inversion centre. The substituted cyclopentadienyl ring is nearly coplanar with the plane of the ethylene bond. The C(1)–C(1′) distance (1.36 Å) is typical for a conjugated double bond.



Scheme 1 *Reagents and conditions*: i, DMF–$POCl_3$; ii, MnO_2; iii, $TiCl_4$/Zn, THF; iv, *p*-$C_6H_4O_2$/$BF_3 \cdot OEt_2$

Cyclic voltammety§ of **4** and **5** shows an irreversible redox wave for each at low potential; E_{pa} −0.19, E_{pc} −0.40 V for **4** and E_{pa} −0.03, E_{pc} −0.17, −0.27 V for **5**. Using the Randles–Sevcik equation it was confirmed that each oxidation wave corresponded to a two-electron redox process. The potential of these waves is strikingly lower (ΔE = 0.52 V for **4**, ΔE = 0.36 V for **5**) than that of pentamethylruthenocene (E_{pa} = +0.33 V). Such a remarkable decrease of the redox potential, due to the ruthenocenyl moiety, is also reported for [1,1]ruthenocenophane which is oxidized to the dicationic complex containing a Ru–Ru bond.[6] This suggests that there is a ligand-mediated metal–metal interaction between the two Ru atoms in **4** and **5**.

Complexes **4** and **5** were oxidized with 2 equiv. of *p*-benzoquinone–$BF_3 \cdot OEt_2$ at 0 °C. The two-electron oxidized complexes **6** and **7** were obtained as stable deep-red and orange crystals, respectively, in good yields.† The IR spectrum of **6** showed a very strong absorption of ν_{BF} at 1084 cm^{-1}, suggesting that **6** was a cationic complex. In spite of the increased positive charge in **6** relative to **4**, the olefinic proton shifted upfield from δ 5.92 in the neutral complex **4** to δ 5.44 in the oxidized complex **6**, suggesting coordination of the olefinic carbon to the metal atom. One of the most interesting points is the chemical shift (δ 96.76 for **6**, δ 87.05 for **7**) and the ^1J(CH) coupling constant (167.2 Hz for **6**, 164.7 Hz for **7**) of the carbon atom connecting the two ruthenocenyl moieties. These values are very similar to those of the exomethylene carbon in the η^6-fulvene complex {δ 74.7 and ^1J(CH) = 164.2 Hz in [Ru(η^5-

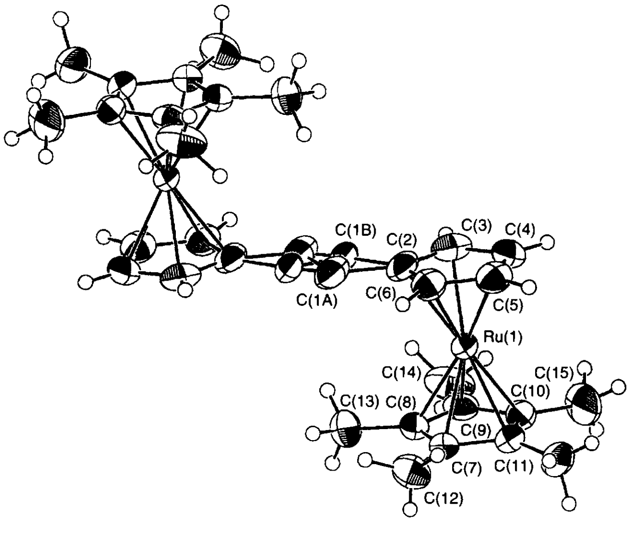


Fig. 1 ORTEP view of complex **4**

$C_5Me_5)(\eta^6\text{-}C_5Me_4CH_2)]^+\}$[7] rather than those of the olefinic carbon [δ 122.2, ^1J(CH) 154 Hz] in **4**. These spectral data suggest that complexes **6** and **7** are (μ-η^6 : η^6-pentafulvadiene)diruthenium complexes.

A single-crystal X-ray analysis of **6**‡ was performed at 150 K and an ORTEP view of **6** is shown in Fig. 2. The cationic molecule of **6** is located on an inversion centre. A disorder of the ethylene moiety similar to that in **4** was found with an occupancy ratio of *ca.* 2 : 1. The influence of the disorder seems to be reflected in the thermal ellipsoids of the carbons in the substituted cyclopentadienyl rings. The Ru–C(2) distance [2.077(5) Å] is somewhat shorter than the Ru–C(3) [2.159(6) Å] and Ru–C(6) distances [2.174(6) Å]. Moreover, the Ru–C(1) distance [av. 2.410 Å] and the bending angle of the C(2)–C(1) bond from the plane of the substituted cyclopentadienyl ring toward to the Ru atom (40.4°) are close to the corresponding values in $[Ru(\eta^5\text{-}C_5Me_5)\ (\eta^6\text{-}C_5Me_4CH_2)]^+$ [2.270(3) Å, 40.3°][8] and the isoelectronic $[(\eta^6\text{-fulvene})Cr(CO)_3]$ [2.352(9) Å, 35°], respectively.[9] The central C–C bond connecting the two halves of the molecule of **6** (1.46 Å) is close to that expected for a sp^2–sp^2 single bond (1.47 Å). These features indicate that each half of the molecule of **6** has the structure of a η^6-fulvene complex and therefore **6** can be regarded as a (μ-η^6 : η^6-pentafulvadiene)diruthenium complex. Complexes **6** and **7**, are as far as we are aware, the first examples of metal-stabilized pentafulvadiene complexes; free pentafulvadiene has been isolated as reactive red–violet crystals by Prinzbach and coworkers in 1977.[10]

The unique electrochemical and chemical oxidation behaviour of complexes **4** and **5** is probably due to the conjugation between two ruthenocenyl moieties connected *via* the ethylene unit. Details of the mechanism for the electronic communication between two Ru atoms and the resulting structural rearrangement based on MO studies are now being studied.

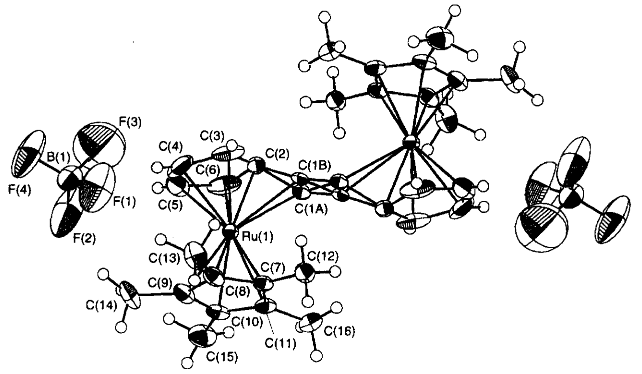


Fig. 2 ORTEP view of complex **6**

Footnotes

† All new compounds were fully characterized by elemental analyses, ^{1}H, ^{13}C NMR, IR, and Raman spectra.

‡ *Crystal data* for **4**, $C_{32}H_{40}Ru_2$, M = 626.80, triclinic, space group $P\bar{1}$, a = 7.820(1), b = 8.573(3), c = 10.803(3) Å, α = 93.83(2), β = 91.76(2), γ = 102.00(2)°, U = 706.1(3) Å^3, Z = 1 ($\bar{1}$ molecular symmetry), D_c = 1.47 Mg m^{-3}, μ = 10.662 cm^{-1}, T = 298 K. 3581 measured reflections, 3239 unique reflections, 2511 reflections with $I \geqslant 3\sigma(I)$ used in refinement, empirical absorption correction (ψ-scan), R = 0.0213, R_w = 0.0278.

For **6**, $C_{32}H_{40}B_2F_8Ru_2$, M = 800.42, monoclinic, space group $P2_1/a$, a = 13.905(3), b = 15.026(3), c = 7.900(1) Å, β = 102.77(2)°, U = 1609.6(5) Å^3, Z = 2 ($\bar{1}$ molecular symmetry), D_c = 1.65 Mg m^{-3}, μ = 9.618 cm^{-1}, T = 150 K. 4208 measured reflections, 3683 unique reflections, 3094 reflections with $I \geqslant 3\sigma(I)$ used in refinement, empirical absorption correction (ψ-scan), R = 0.0395, R_w = 0.0454.

The data were collected using a Mac Science MXC18K diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073) by the ω–2θ scan method in the range $2 < 2\theta < 55°$. The structure was solved by SIR92 in the CRYSTAN GM (software package for structure determination) and refined anisotropically for non-hydrogen atoms with H-atoms isotropic. Atomic coordinates bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ Cyclic voltammetry was performed in dichloromethane solutions containing 0.1 mol dm^{-3} NBu_4ClO_4 under nitrogen at 25 °C, using a standard three-electrode cell and a BAS CV-27 analyser. The potentials are relative to that of the Fc/Fc$^+$ couple.

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Received, 27th July 1995; Com. 5/05000F