Bis[η^5-(2,4-dimethyl-1-oxapentadienyl)]ruthenium(II): the First Homoleptic Open Ruthenocenes with Non-hydrocarbon Ligands

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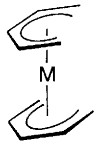
The new stereoisomeric bis(1-oxapentadienyl)ruthenium(II) complexes **3a** and **b** are obtained by reductive dehalogenation of $RuCl_3$·aq. in the presence of 4-methylbuten-2-ones; they have been characterized spectroscopically and their crystal structures have been determined, showing a distorted *syn-gauche* and the unusual *anti*-eclipsed arrangement of the ligands, respectively.

The work by Ernst and co-workers[1] on the preparative and structural aspects of bis(pentadienyl)iron complexes has awakened much interest in these open metallocenes **I**. Bis(dienyl) complexes have been prepared with a number of transition elements, *e.g.* Ti, V, Cr and Mn.[2] Pentadienyl ruthenium compounds have either been obtained by condensation with ruthenium atoms[3] or by reductive complexation[4] starting from substituted pentadienes. Only hydrocarbon ligands have been employed in all these cases. Complexes with heteropentadienyl ligands, on the other hand, are rarely to be found in the literature,[5] all of them being, to our knowledge, non-homoleptic compounds of the general type **II** (X = O, S and NR).

We have found that simple reduction of ruthenium trichloride hydrate ($RuCl_3$·aq.) in the presence of an α,β-unsaturated ketone like mesityloxide **1** leads to a mixture of isomeric, homoleptic oxapentadienyl ruthenium complexes (Scheme 1).[6]

The synthesis can be carried out on the 10 mmolar scale, typically starting from $RuCl_3$·aq. (2.43 g, 10 mmol) in 4-methylbut-3-en-2-one **1** (39.2 g, 0.4 mol) and absolute ethanol (10 ml) at room temperature. A large excess of acid activated zinc dust (4.2 g, 65 mmol) is used as reducing agent. The heterogeneous mixture initially turns grey and later dark yellow in the course of the reaction which after several days finally leads to almost total consumption of the zinc and formation of the ethanolate together with the chloride. After evaporation, the complexes can be continuously extracted from the crude powdered product with boiling hexane. The yellow–brown, crystalline mixture of **3a** and **b** (ratio about 1 : 1) can further be purified by recrystallization from hexane or diethyl ether as well as by sublimation under high vacuum at about 70 °C. The average yield ranges from 50 to 70%. Attempts to accelerate the reaction by sonication using a commercial cleaning bath generally result in lower yields (30–50%) but reduced reaction times of 24–48 h.



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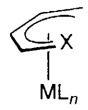
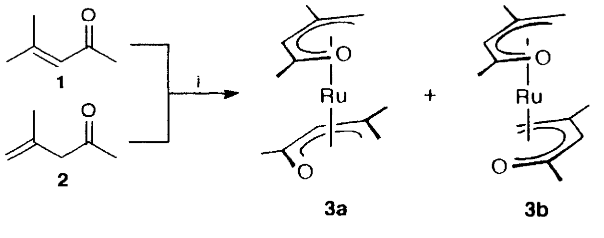


II

Both complexes are moderately air-stable, they decompose upon exposure to air for longer periods. Compound **3a** also slowly decomposes at room temperature even in an inert atmosphere. Interestingly, when the β,γ-unsaturated 4-methylbut-4-en-2-one **2** is used as starting material, the same products are formed in comparable yields, the excess of enone **2** being quantitatively isomerized to **1** in the course of the reaction.

The isomeric mixture of the complexes was separated by column chromatography on silica gel using diethyl ether as solvent under an atmosphere of argon. Pure **3a** and **b** were obtained after a final recrystallization from hexane.



Scheme 1 *Reagents and conditions:* i, $RuCl_3·xH_2O$, Zn, EtOH, 20 °C, with magnetic stirring: 3–10 days, with sonication: 1–2 days

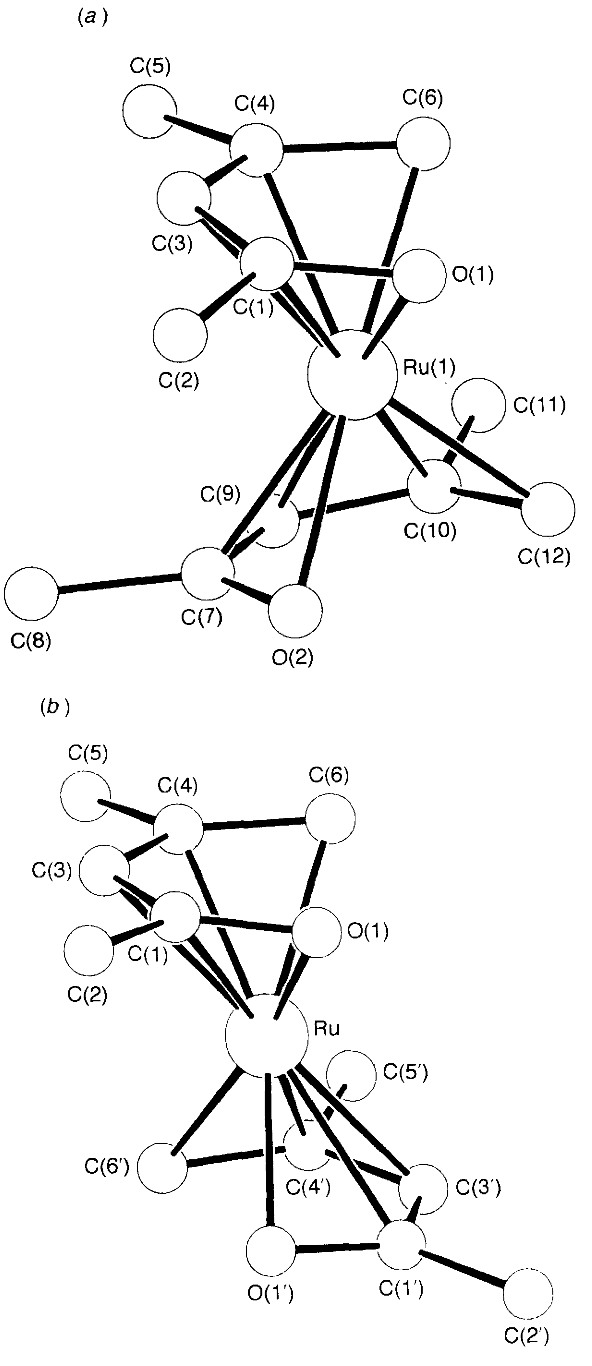


Fig. 1 Molecular structure of one of the two independent molecules of **3a** (*a*) and molecular structure of **3b** (*b*). Hydrogen atoms are omitted for clarity. Selected mean distances (Å) and angles (°) for **3a**: Ru(1)–O(1) 2.13(1), Ru(1)–O(2) 2.17(1), O(1)–C(1) 1.31(2), C(1)–C(3) 1.43(2), C(3)–C(4) 1.43(2), C(4)–C(6) 1.43(2), O(2)–C(7) 1.30(2), C(7)–C(9) 1.44(2), C(9)–C(10) 1.42(2), C(10)–C(12) 1.42(2), O(1)–Ru(1)–O(2) 100.1(4). Selected distances (Å) and angles (°) for **3b**: Ru–O(1) 2.152(4), O(1)–C(1) 1.304(8), C(1)–C(3) 1.424(9), C(3)–C(4) 1.445(9), C(4)–C(6) 1.399(9), O(1)–Ru–O(1') 92.1(2), O(1)–Ru–m[C(4')–C(6')] 172.1(4), where m is the midpoint between C(4') and C(6').

Inspection of the NMR spectra uncovers the higher symmetry of **3b** with respect to **3a**. The former exhibits only one set of ligand signals, the latter two of them. Even at temperatures as low as −80 °C no changes can be observed in the spectra except for a small ($\Delta\delta < 0.1$ ppm) temperature shift of the proton NMR signals. The simplicity of the NMR spectra of **3b** is therefore not the result of a fast dynamic process but shows that the molecule contains either a mirror plane or a twofold axis or both. Mass spectral data and elementary analyses further confirm that **3a** and **b** are isomers. The IR spectra of the isomers are different but give no direct information about the symmetry of the molecules. The melting points differ by about 40 degrees (**3a**: 104–105, **3b**: 145–146 °C).†

As the ligand arrangement in **3a** and **b** could not unequivocally be derived from the above data, their crystal structures were determined by X-ray diffraction methods.‡ The results are shown in Fig. 1. Whereas **3a** has no internal symmetry and a *syn-gauche* arrangement of the two ligands already known for a number of homoleptic bis(2,4-dimethylpentadienyl)-ruthenium(II) complexes, **3b** shows a nearly *anti*-eclipsed conformation of the ligands. Such an arrangement has not been reported for any homoleptic η^5-pentadienyl complex as far as we know. Steric hinderance alone has not been sufficient[4] to stabilize such isomers in the case of hydrocarbon ligands, although the participation of an *anti*-eclipsed structure has been discussed in connection with variable temperature NMR studies of conformer equilibria in bis(cyclohexadienyl)iron complexes (pseudoferrocenes).[7]

In both **3a** and **b** the backbones of the oxapentadienyl ligands are almost planar (rms deviation: 0.027 Å for **3a**, 0.045 Å for **3b**) and lie almost parallel to one another on each side of the Ru atoms (angle between mean planes: 13° for **3a** and 1° for **3b**). The compounds can thus be satisfactorily described as open sandwich complexes. If one assumes a possible restricted rotation of one ligand relative to another the question arises: why does **3a** not adopt the *anti*-eclipsed geometry apparently favoured by **3b**? Apart from the obvious effect of packing in the solid state a possible reason may be found in the positions of the O atoms. If **3a** were to adopt an *anti*-eclipsed geometry the O atoms would be approximately *trans* to one another relative to the Ru atom. In both isomers the Ru–O bonds are,

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† Satisfactory elemental analyses were obtained for compounds **3a** and **b**. ^{13}C NMR signal multiplicities are listed in brackets as detected in DEPT experiments. *Spectroscopic data:* **3a**: IR ν/cm^{-1} (KBr): 3050, 3035, 2990, 2978, 2955, 2918 (ν_{CH}); 1479, 1434, 1396, 1344; ^{1}H NMR (CD_2Cl_2, 200.133 MHz) δ 5.36 (s, 1H), 4.57 (s, 1H), 3.83 (s, 1H), 2.52 (s, 1H), 2.24 (s, 3H), 1.98 (s, 3H), 1.89 (s, 1H), 1.78 (s, 3H), 1.57 (s, 3H), 1.25 (s, 1H); ^{13}C NMR (50.323 MHz) δ 150.9 (s, C–O), 147.1 (s, C–O), 108.9 (s), 96.4 (s), 87.8 (d), 75.8 (d), 55.2 (t), 50.1 (t), 25.5 (q), 24.9 (q), 24.6 (q), 22.1 (q); MS (EI) *m*/*z* (rel. intensity) 296 (M^+, 100%), 198 ($M^+ - C_6H_{10}O$, 22%), 167 (58%), 43 [C(O)Me$^+$, 30%].

3b: IR ν/cm^{-1} (KBr) 3060, 2992, 2960, 2920 (ν_{CH}); 1480sh, 1470, 1455, 1435, 1414, 1400, 1365, 1354; ^{1}H NMR (CD_2Cl_2, 200.133 MHz) δ 5.73 (d, $J_{HH} < 1$ Hz, 1H), 2.31 (s, 3H), 2.14 (br s, 1H), 1.60 (s, 1H), 1.44 (s, 3H); ^{13}C NMR (50.323 MHz) δ 160.2 (s, C–O), 95.9 (s), 78.8 (d), 44.4 (t), 24.9 (q), 22.6 (q); MS (EI) *m*/*z* (rel. intensity) 296 (M^+, 100%), 198 (22%), 167 (52%), 43 (29%).

‡ *Crystal data*: **3a**: $C_{12}H_{18}O_2Ru$, $M = 295.3$, orthorhombic, space group $Pca2_1$, $a = 16.229(5)$, $b = 10.815(2)$, $c = 13.783(3)$ Å, $V = 2419.2$ Å^3, $T = -170$ °C, $D_c = 1.62$ g cm^{-3}, $Z = 8$, μ(Mo-Kα) = 12.50 cm^{-1}, 6109 measured reflections ($\pm h$, $+k$, $+l$), 3671 independent and 3070 observed reflections [$I > 2\sigma(I)$], 270 refined parameters, $R = 0.040$, $R_w = 0.041$, final difference Fourier $\rho = 1.77$ eÅ^{-3}. Refinement of the enantiopol parameter ($k = 0.07$) indicated the chosen polar axis to be correct. **3b**: $C_{12}H_{18}O_2Ru$, $M = 295.3$, orthorhombic, space group *Pccn*, $a = 5.916(1)$, $b = 13.078(1)$, $c = 15.266(1)$ Å, $V = 1181.1$ Å^3, $T = 20$ °C, $D_c = 1.66$ g cm^{-3}, $Z = 4$, μ(Mo-Kα) = 12.80 cm^{-1}, 8802 measured reflections ($\pm h$, $\pm k$, $\pm l$), 1350 independent and 1124 observed reflections [$I > 2\sigma(I)$], 69 refined parameters, $R = 0.058$, $R_w = 0.059$, final difference Fourier $\rho = 2.67$ eÅ^{-3}. The residual electron density lies on the twofold axis and is related to the Ru atom by [x, y, $0.5 - z$]. An attempt was made to measure the crystal structure of **3b** at the same low temperature as **3a**. However, the crystal undergoes a phase change on cooling. The unit cell became monoclinic, $P2_1/c$, but presumably because of disorder caused by the phase change $R = 0.136$. The unit cell dimensions are $a = 5.864(4)$, $b = 12{,}960(8)$, $c = 15.148(3)$ Å, $\beta = 90.42(3)°$, $V = 1151(1)$ Å^3, $T = -173$ °C. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

however, approximately orthogonal to one another [**3a:** O(1)–Ru(1)–O(2) 100.1(4)°, **3b:** O(1)–Ru–O(1′) 92.1(2)°].

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