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Mendeleev Commun., 2012, **22**, 189–191
Mendeleev Communications

[2+2] Photodimerization of the acenaphthylene ruthenium complex $[(C_5Me_4CH_2OMe)Ru(\eta^6\text{-}C_{12}H_8)]^+$

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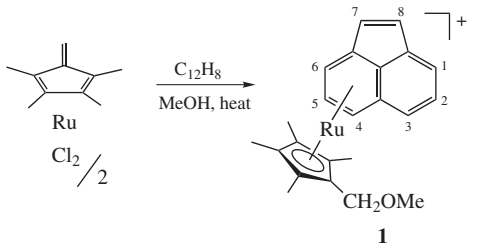
DOI: 10.1016/j.mencom.2012.06.005

The [2+2] photodimerization of the complex $[(C_5Me_4CH_2OMe)Ru(\eta^6\text{-}C_{12}H_8)]^+$ under visible-light irradiation leads to a mixture of the head-to-head heptacyclene products $[(\mu\text{-}\eta^6\text{:}\eta^6\text{-}C_{24}H_{16})Ru_2(C_5Me_4CH_2OMe)_2]^{2+}$ (*syn*- and *anti*-) with the predominant formation of the *syn*-isomer; the structures of both isomers were established by X-ray diffraction analysis.

The photodimerization of acenaphthylene has been thoroughly studied.[1–3] However, the dimerization of transition metal acenaphthylene complexes remained unknown. Here, we report the first example of such a reaction for ruthenium derivatives.

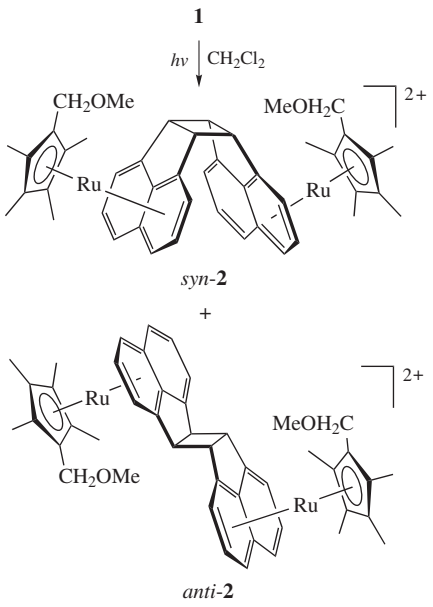
Using a reaction of the fulvene ruthenium complex $[(C_5Me_4CH_2)RuCl_2]_2$ with acenaphthylene in refluxing MeOH, we synthesized the acenaphthylene complex $[(C_5Me_4CH_2OMe)Ru(\eta^6\text{-}C_{12}H_8)]^+$ **1** in high yield (Scheme 1, one of the two enantiomers is displayed).† Earlier we used similar reaction for the preparation of the photoactive anthracene complex $[(C_5Me_4CH_2OMe)Ru(\eta^6\text{-}C_{14}H_{10})]^+$.[4]



Scheme 1

We have found that cation **1** dimerizes under visible-light irradiation giving a mixture of *syn*- and *anti*-complexes $[(\mu\text{-}\eta^6\text{:}\eta^6\text{-}C_{24}H_{16})Ru_2(C_5Me_4CH_2OMe)_2]^{2+}$ **2** in a 4:1 ratio (Scheme 2).‡ *Syn*- and *anti*- isomers were separated by fractional crystallization.

Note that the dimerization of **1** regioselectively leads to head-to-head§ products, only two isomers from six possible for the head-to-head reaction pathway being formed. Similar selectivity was observed for the dimerization of nitroacenaphthylene and



Scheme 2

† $[(C_5Me_5)RuCl_2]_2$ (90 mg, 0.15 mmol) was dissolved in CH_2Cl_2 (15 ml) and stirred for 1 h in air resulting in the formation of the fulvene complex $[(C_5Me_4CH_2)RuCl_2]_2$. The solvent was removed *in vacuo*, and the flask was filled with argon. Acenaphthylene (76 mg, 0.5 mmol) and MeOH (15 ml) were added and the resulting orange suspension was refluxed with stirring for 5 h. The reaction mixture was opened to air and evaporated. The residue was dissolved in H_2O (10 ml) and filtered, and KPF_6 (184 mg, 1 mmol) was added to the aqueous solution producing an orange precipitate, which was collected by filtration. The crude product was eluted through a short alumina column (4 cm) with acetone. Reprecipitation from acetone by Et_2O gives $[\mathbf{1}][PF_6]$ as a bright orange solid. Yield, 135 mg (80%). ^{1}H NMR (acetone-d_6) for $[\mathbf{1}]^+$, δ: 1.46 (s, 3H, Me), 1.50 (s, 3H, Me), 1.59 (s, 3H, Me), 1.65 (s, 3H, Me), 3.29 (s, 3H, OMe), 3.92 (s, 2H, CH_2), 6.30 (t, 1H, H-5, *J* 6.0 Hz), 6.70 (d, 1H, H-4, *J* 6.0 Hz), 6.92 (d, 1H, H-6, *J* 6.0 Hz), 7.28 (d, 1H, H-8, *J* 5.2 Hz), 7.54 (d, 1H, H-7, *J* 5.2 Hz), 7.94 (m, 2H, H-1, H-3), 8.13 (m, 1H, H-2). Found (%): C, 49.57; H, 4.79. Calc. for $C_{23}H_{25}F_6OPRu$ (%): C, 49.03; H, 4.47.

‡ Complex $[\mathbf{1}]PF_6$ (113 mg, 0.2 mmol) was dissolved in CH_2Cl_2 (10 ml) in a Schlenk tube in an inert atmosphere. The reaction mixture was irradiated for 8 h using mercury luminescent lamps with a total power of 650 W. Both the Shlenk tube and the lamps were placed in a water-cooled vessel. Then, the solvent was evaporated *in vacuo*, and the residue was dissolved in a minimal amount of CH_2Cl_2 and eluted through a short alumina column (4 cm; eluent, CH_2Cl_2/Me_2CO). The resulting solution was evaporated *in vacuo*. The resulting mixture of *syn*-**2** and *anti*-**2** complexes (~4:1) was crystallized by slow vapour diffusion of Et_2O into a solution in $MeNO_2$ (0.5 ml). The obtained crystals were suspended in Me_2CO (3 ml), the insoluble residue was collected and twice recrystallized by slow vapour diffusion of Et_2O into a solution in Me_2CO giving light-yellow needles, which were reprecipitated from $C_2H_4Cl_2/Et_2O$ to produce a pale yellow solid of $[anti\text{-}\mathbf{2}](PF_6)_2$. Yield, 19 mg (17%). The remaining filtrate was evaporated *in vacuo* and twice recrystallized by slow vapour diffusion of Et_2O into a solution in 1,2-dichloroethane to form bright-yellow crystals, which were reprecipitated from CH_2Cl_2/Et_2O giving a bright yellow solid of $[syn\text{-}\mathbf{2}](PF_6)_2$. Yield, 57 mg (50%).

^{1}H NMR (acetone-d_6) for $[syn\text{-}\mathbf{2}]^{2+}$: 1.54 (s, 6H, Me), 1.57 (s, 6H, Me), 1.60 (s, 6H, Me), 1.68 (s, 6H, Me), 3.28 (s, 6H, OMe), 3.87 (d, 2H, CH_2, *J* 11.6 Hz), 3.92 (d, 2H, CH_2, *J* 11.6 Hz), 4.99 (m, 2H, H-8), 5.06 (m, 2H, H-7), 5.99 (t, 2H, H-5, *J* 5.6 Hz), 6.39 (d, 2H, H-4, *J* 5.6 Hz), 6.50 (d, 2H, H-6, *J* 5.6 Hz), 7.22 (d, 2H, H-3, *J* 8.8 Hz), 7.51 (d, 2H, H-1, *J* 6.4), 7.61 (dd, 2H, H-2, *J* 8.8 and 6.4 Hz). Found (%): C, 49.18; H, 4.30. Calc. for $C_{46}H_{50}F_{12}O_2P_2Ru_2$ (%): C, 49.03; H, 4.47.

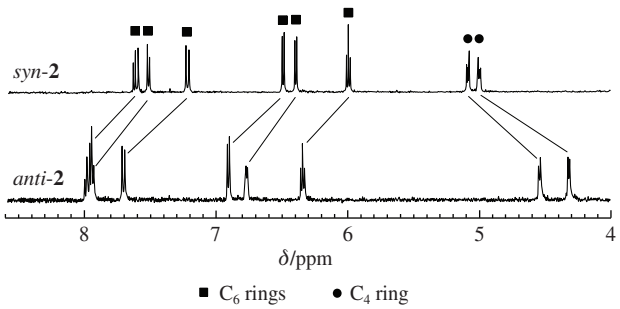


Figure 1 ^{1}H NMR spectra for complexes *syn*-**2** and *anti*-**2** in acetone-d_6. The region of [$C_5Me_4CH_2OMe$] signals is omitted.

coumarine.[5] Presumably, the reaction proceeds through the cation-radical Rydberg excited state.[6]

Cations **1**, *syn*- and *anti*-**2** were isolated as salts with the PF_6^- anion. The ^{1}H NMR signals of Me_{Cp} groups for *syn*- and *anti*-**2** (1.45–1.65 ppm) are upfield shifted, as compared to [($C_5Me_4CH_2$-OMe)Ru(C_6H_6)]$^+$ (2.08 ppm), apparently due to the anisotropic shielding caused by the neighbouring non-coordinated C_6 ring.[4] A similar effect is observed for C_6 and C_4 (cyclobutane) ring protons. Due to the anisotropic shielding caused by opposite arene rings, the C_6 ring protons for *syn*-**2** are upfield shifted *vs*. *anti*-**2**, whereas the C_4 ring protons for *anti*-**2** are upfield shifted *vs*. *syn*-**2** (Figure 1).

The structures of the heptacyclene complexes [*syn*-**2**]$(PF_6)_2$ and [*anti*-**2**]$(PF_6)_2$ were established by single-crystal X-ray diffraction (Figures 2 and 3).¶ The metal-to-ring distances Ru···C_5 (1.802 and 1.799 Å for *syn*- and *anti*-**2**, respectively) and Ru···C_6 (1.724 and 1.733 Å) are almost equal to those for the related mononuclear benzene complex [($C_5Me_4CH_2OMe$)Ru(C_6H_6)]$^+$ (1.805 and 1.706 Å).[7] In accordance with a general tendency for ruthenium arene complexes, the perimeters of the coordinated C_6 rings (8.54 and 8.50 Å) are greater than those of the non-coordinated ones (8.45 and 8.44 Å). It is noteworthy that the

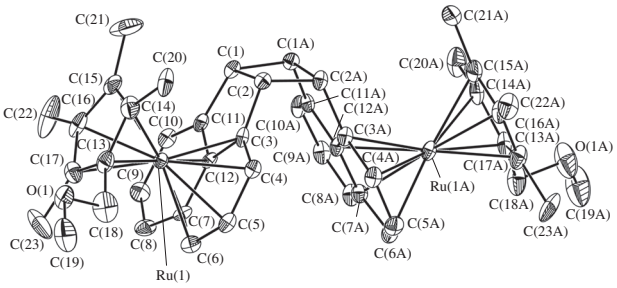


Figure 2 The structure of dication [*syn*-**2**]$^{2+}$ with thermal ellipsoids at a 50% probability level. All hydrogen atoms and the disordered part of the $C_5Me_4CH_2OMe$ ligand are omitted for clarity. Selected distances (Å): Ru(1)–C(3) 2.220(4), Ru(1)–C(4) 2.231(4), Ru(1)–C(5) 2.210(4), Ru(1)–C(6) 2.211(5), Ru(1)–C(7) 2.289(4), Ru(1)–C(12) 2.251(4), Ru(1)–C(13) 2.161(4), Ru(1)–C(14) 2.155(5), Ru(1)–C(15) 2.176(5), Ru(1)–C(16) 2.187(4), Ru(1)–C(17) 2.179(5).

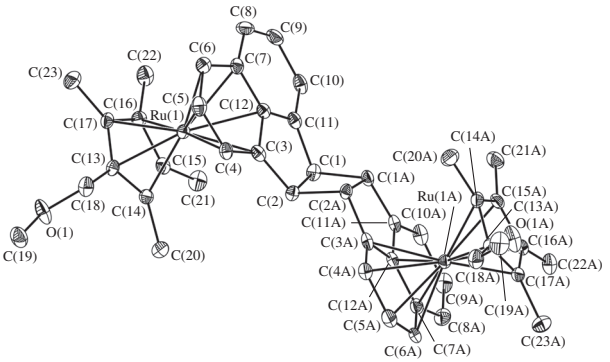


Figure 3 The structure of dication [*anti*-**2**]$^{2+}$ with thermal ellipsoids at 50% probability level. All hydrogen atoms are omitted for clarity. Selected distances (Å): Ru(1)–C(3) 2.238(3), Ru(1)–C(4) 2.224(3), Ru(1)–C(5) 2.203(4), Ru(1)–C(6) 2.230(4), Ru(1)–C(7) 2.292(4), Ru(1)–C(12) 2.243(3), Ru(1)–C(13) 2.143(4), Ru(1)–C(14) 2.180(3), Ru(1)–C(15) 2.177(3), Ru(1)–C(16) 2.176(3), Ru(1)–C(17) 2.174(3).

cyclobutane ring is not planar and has an envelope conformation with a dihedral angle of 9.9° for *syn*-**2** or 10.8° for *anti*-**2**, in contrast to the non-coordinated *Z*- and *E*-heptacyclene (2.9° and 0°, respectively).[9]

To explain the selective formation of *syn*- and *anti*-**2** complexes upon the head-to-head dimerization of **1**, we carried out the DFT calculations (Priroda//PBE/L2)[††] of six isomers, which can be formed from the parent acenaphthylene complex [CpRu-(η^6-$C_{12}H_8$)]$^+$ (**1′**, see Figure S1 and Table S1 in the Online Supplementary Materials). Isomers *syn*- and *anti*-**2′** (analogues of *syn*- and *anti*-**2**) are the most stable, supporting the selectivity of the reaction. Presumably, the higher stability of *syn*- and *anti*-**2′** is the result of a minimal electrostatic repulsion between two [CpRu]$^+$ fragments. Indeed, according to the energy decomposition analysis[‡‡] (EDA), electrostatic repulsion (ΔE_{elstat}) between two [RuCp]$^+$ cations for *syn*-**2′** (38.2 kcal mol^{-1}) and *anti*-**2′**

^{1}H NMR (acetone-d_6) for [*anti*-**2**]$^{2+}$, δ: 1.53 (s, 6H, Me), 1.54 (s, 6H, Me), 1.62 (s, 6H, Me), 1.64 (s, 6H, Me), 3.23 (s, 6H, OMe), 3.88 (m, 4H, CH_2), 4.32 (d, 2H, H-8, *J* 5.2 Hz), 4.52 (d, 2H, H-7, *J* 5.2 Hz), 6.32 (t, 2H, H-5, *J* 5.6 Hz), 6.69 (d, 2H, H-4, *J* 5.6 Hz), 6.89 (d, 2H, H-6, *J* 5.6 Hz), 7.70 (d, 2H, H-3, *J* 8.0 Hz), 7.93 (d, 2H, H-1, *J* 6.4 Hz), 7.98 (dd, 2H, H-2, *J* 8.0 and 6.4 Hz). Found (%): C, 49.18; H, 4.64. Calc. for $C_{46}H_{50}F_{12}O_2P_2Ru_2$ (%): C, 49.03; H, 4.47.

§ 'Head' is the double-bond carbon atom attached to the metal-coordinated C_6 ring in **1**.

¶ *Crystallographic data* for [*syn*-**2**]$(PF_6)_2 \cdot C_2H_4Cl_2$ and [*anti*-**2**]$(PF_6)_2$.

Crystals of [*syn*-**2**]$(PF_6)_2 \cdot C_2H_4Cl_2$ ($C_{48}H_{54}Cl_2F_{12}O_2P_2Ru_2$, M = 1225.89) are monoclinic, space group $P2_1$, at 100(2) K: a = 16.521(7), b = 8.854(4) and c = 17.221(8) Å, β = 109.742(10)°, V = 2370.8(19) Å^3, Z = 2, d_{calc} = = 1.717 g cm^{-3}, μ(MoKα) = 9.05 cm^{-1}, F(000) = 1236.

Crystals of [*anti*-**2**]$(PF_6)_2$ ($C_{46}H_{50}F_{12}O_2P_2Ru_2$, M = 1126.94) are monoclinic, space group $C2/c$, at 100(2) K: a = 12.2731(12), b = 12.9235(13) and c = 27.893(3) Å, β = 101.576(2)°, V = 4334.2(7) Å^3, Z = 4, d_{calc} = = 1.727 g cm^{-3}, μ(MoKα) = 8.62 cm^{-1}, F(000) = 2272.

Intensities of 16398 (*syn*-**2**) and 15955 (*anti*-**2**) reflections were measured with a Bruker SMART APEX2 CCD diffractometer and 6670 (*syn*-**2**) and 5751 (*anti*-**2**) independent reflections [R_{int} = 0.0288 (*syn*-**2**) and 0.0332 (*anti*-**2**)] were used in further refinement. The refinement converged to wR_2 = 0.0812 and GOF = 1.002 for all independent reflections [R_1 = = 0.0314 was calculated against F for 6192 observed reflections with $I > 2\sigma(I)$] for *syn*-**2** and to wR_2 = 0.0690 and GOF = 1.731 for all independent reflections [R_1 = 0.0429 was calculated against F for 3349 observed reflections with $I > 2\sigma(I)$] for *anti*-**2**. All calculations were performed using SHELXTL PLUS 5.0.

CCDC 867093 and 867094 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2012.

†† Geometry optimizations were performed without constraints using PBE exchange-correlation functional,[10] the scalar-relativistic Hamiltonian,[11] atomic basis sets of generally-contracted Gaussian functions,[12] and a density-fitting technique[13] as implemented in a recent version of the Priroda[14] code. The all-electron triple-ζ basis set L2 augmented by two polarization functions was used for all elements (H, C, O, Ru).[15]

‡‡ According to EDA, the interaction energy between the bonding fragments ΔE_{int} can be divided into three main components:[16]

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb},$$

where ΔE_{elstat} is the electrostatic interaction energy between the fragments with a frozen electron density distribution, ΔE_{Pauli} presents the repulsive four-electron interactions between occupied orbitals (Pauli repulsion), and ΔE_{orb} is the stabilizing orbital interactions.

(36.2 kcal mol^{-1}) is lower than that in other head-to-head isomers (40.8–61.3 kcal mol^{-1}) due to a larger Ru···Ru distance (7.48 Å for *syn*-**2′**, 8.12 Å for *anti*-**2′**, 5.15–7.25 Å for other isomers).

Thus, we have found that acenaphthylene ruthenium complex **1** undergoes selective dimerization under visible-light irradiation to afford a mixture of head-to-head complexes *syn*- and *anti*-**2** with the predominant formation of the *syn*-isomer.

This work was supported by the Presidium of the Russian Academy of Sciences (programme no. P7), the Russian Foundation for Basic Research (grant no. 110301153a), and the President of the Russian Federation (grant for young scientists no. MK-684.2011.3).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2012.06.005.

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Received: 17th February 2012; Com. 12/3877