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Photodimerization of the anthracene ruthenium complexes $[(C_5Me_4R)Ru(\eta^6\text{-}C_{14}H_{10})]^+$ (R = Me, CH_2OMe)

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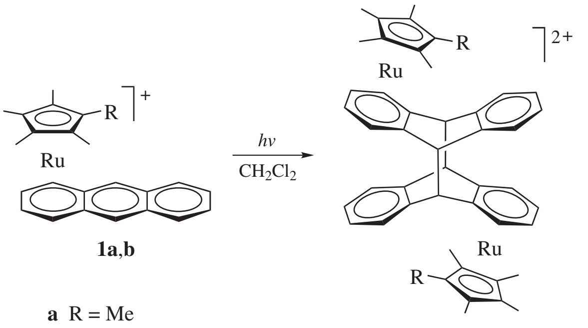
The dimerization of the anthracene ruthenium complexes $[(C_5Me_4R)Ru(\eta^6\text{-}C_{14}H_{10})]^+$ (R = Me, CH_2OMe) under visible-light irradiation gives dications $[(\mu\text{-}\eta^6{:}\eta^6\text{-}C_{28}H_{20})Ru_2(C_5Me_4R)_2]^{2+}$ with the most distant position of the $Ru(C_5Me_4R)$ fragments; the structure of $[(\mu\text{-}\eta^6{:}\eta^6\text{-}C_{28}H_{20})Ru_2(C_5Me_4CH_2OMe)_2](PF_6)_2$ was established by X-ray diffraction.

Polyarenes attract a considerable attention as the precursors of dyes and semiconductors.[1] Particularly, anthracenes possess valuable photochromic properties due to reversible photochemical dimerization.[2] In spite of a great progress in this field,[3] nothing is known of the dimerization of transition metal anthracene complexes. Here we report the first examples of such reactions with ruthenium derivatives.

We found that the cations $[(C_5Me_4R)Ru(\eta^6\text{-}C_{14}H_{10})]^+$ (**1a**, R = Me; **1b**, R = CH_2OMe) dimerize under visible-light irradiation giving in good yields the dicationic complexes $[(\mu\text{-}\eta^6{:}\eta^6\text{-}C_{28}H_{20})Ru_2(C_5Me_4R)_2]^{2+}$ **2a**,**b** with *anti*-orientation of the $Ru(C_5Me_4R)$ fragments (Scheme 1).[†]



1a,**b**

a R = Me
b R = CH_2OMe

2a,**b**

Scheme 1

Cations **2a**,**b** were isolated as salts with the BF_4^- and PF_6^- anions. The ^1H NMR signals of Me groups in **2a** (1.47 ppm) are upfield shifted as compared to $[(C_5Me_5)Ru(C_6H_6)]^+$ (2.08 ppm),[4] apparently due to anisotropic shielding caused by the neighboring non-coordinated benzene ring.[5(a)] Similar effect is observed in **2b**.

The dinuclear complex **2b** can also be prepared by the thermal exchange[5] of anthracene for dianthracene $C_{28}H_{20}$ in cation **1b**. However, this reaction is complicated by the side formation of the mononuclear dianthracene complex $[(C_5Me_4CH_2OMe)Ru(\eta^6\text{-}C_{28}H_{20})]^+$. Indeed, the reaction of $C_{28}H_{20}$ with 2 equiv. of **1b** affords a mixture of cations **2b** and $[(C_5Me_4CH_2OMe)Ru(\eta^6\text{-}C_{28}H_{20})]^+$ in ~2:1 ratio.

Unfortunately, the visible-light irradiation of the parent anthracene complex $[CpRu(\eta^6\text{-}C_{14}H_{10})]^+$ **1c** results only in an inseparable mixture of products. An alternative route, using the reaction of $C_{28}H_{20}$ with 2 equiv. of $[CpRu(MeCN)_3]^+$, affords a mixture of *anti*- and *syn*-isomers **2c** and **3c** in a ~3:2 ratio (Scheme 2).[‡] Note that a minor formation of *syn*-isomers (~10%) was also detected upon the photodimerization of pentasubstituted cations **1a** and **1b**, however, this impurity is easily removed by recrystallization.

The structure of $[\mathbf{2b}](PF_6)_2$ was established by single-crystal X-ray diffraction (Figure 1).[§] Interestingly, the planes of the coor-

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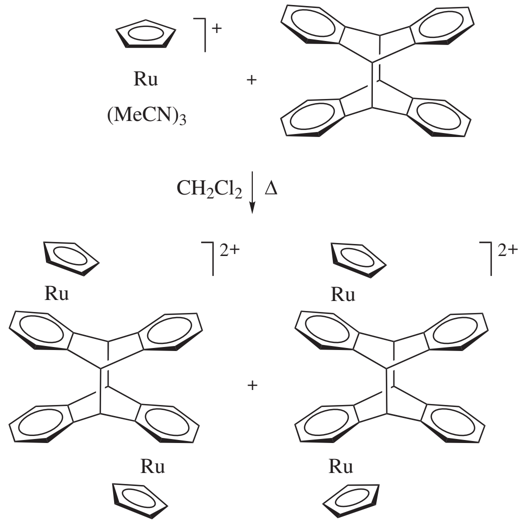
[†] $[(C_5Me_5)Ru(C_{14}H_{10})]BF_4$ ($[\mathbf{1a}]BF_4$)[10] (56 mg, 0.1 mmol) was dissolved in CH_2Cl_2 (3 ml) in a Schlenk tube in an inert atmosphere. The reaction mixture was irradiated using mercury luminescent lamps with a total power of 650 W until it became colorless (12 h). Both the Schlenk tube and the lamps were placed in a vessel of an appropriate volume; cooling was accomplished by running water. The resulting colorless crystals were separated, washed with Et_2O (3×5 ml) and reprecipitated from $MeNO_2$ by Et_2O giving white solid of $[\mathbf{2a}](BF_4)_2$. Yield, 32 mg (57%). ^1H NMR (acetone-d_6) δ: 1.47 (s, 30H, Me), 4.72 (s, 4H, CH_{bridge}), 5,65 (m, 4H), 5.84 (m, 4H), 7.11 (m, 4H), 7.20 (m, 4H). Found (%): C, 57.16; H, 4.99. Calc. for $C_{48}H_{50}B_2F_8Ru_2$ (%): C, 57.50; H, 5.03.

$[(C_5Me_4CH_2OMe)Ru(C_{14}H_{10})]PF_6$ ($[\mathbf{1b}]PF_6$)[5(a)] (118 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 until it became colorless (for ~12 h) and evaporated *in vacuo*. The residue was washed with Et_2O (3×5 ml) and recrystallized by slow vapour diffusion of Et_2O into its solution in 1,2-dichloroethane (1 ml). Colorless crystals of $[\mathbf{2b}](PF_6)_2$ were collected and dried *in vacuo*. Yield 90 mg (76%). ^1H NMR (acetone-d$_6$) δ: 1.49 (s, 12H, Me), 1.55 (s, 12H, Me), 3.17 (s, 6H, OMe), 3.55 (s, 4H, CH_2), 4.76 (s, 4H, CH_{bridge}), 5,73 (m, 4H), 5.93 (m, 4H), 7.17 (m, 4H), 7.26 (m, 4H). Found (%): C, 51.28; H, 4.70. Calc. for $C_{50}H_{54}F_{12}O_2P_2Ru_2$ (%): C, 50.93; H, 4.62.

[‡] A mixture of $[CpRu(MeCN)_3]BF_4$ (43 mg, 0.1 mmol)[11] and dianthracene (14 mg, 0.04 mmol) was dissolved in CH_2Cl_2 (5 ml). The reaction mixture was refluxed until it became colorless (4 h). The solvent was removed *in vacuo,* and the residue was reprecipitated twice from $MeNO_2$ by Et_2O giving a mixture of **2c**/**3c** isomers (~3:2) as a white solid. Yield, 24 mg (85%). ^1H NMR (acetone-d_6) for $[\mathbf{2c}]^{2+}$ δ: 4.67 (s, 10H, Cp), 4.91 (s, 4H, CH_{bridge}), 5.99 (m, 4H), 6.35 (m, 4H), 7.19 (m, 4H), 7.33 (m, 4H); for $[\mathbf{3c}]^{2+}$ δ: 4.69 (s, 10H, Cp), 4.90 (s, 4H, CH_{bridge}), 6.10 (m, 4H), 6.54 (m, 4H), 7.03 (m, 4H), 7.16 (m, 4H).

[§] *Crystallographic data.* X-ray diffraction data were collected using a Bruker SMART APEX2 CCD diffractometer [λ(MoKα) = 0.71073 Å, graphite monochromator]. The obtained images were integrated. The precise unit cell dimensions and errors were determined. The absorption correction was applied semiempirically using the SADABS program. Crystals of $[\mathbf{2b}](PF_6)_2$ ($C_{52}H_{60}F_{12}N_2O_6P_2Ru_2$, M = 1301.10) are triclinic, space group $P\bar{1}$, at 100(2) K: a = 10.0526(12), b = 11.4080(13) and c = = 11.5078(13) Å, α = 96.474(3)°, β = 91.925(2)°, γ = 90.911(2)°, V = = 1310.3(3) Å^3, Z = 1, d_{calc} = 1.649 g cm^{-3}, μ(MoKα) = 0.732 cm^{-1}, F(000) = 660. Intensities of 15710 reflections were measured and 6954 independent reflections (R_{int} = 0.0266) were used in the further refinement. Initially spherical atom refinements were undertaken with SHELXTL



2c **3c**

Scheme 2

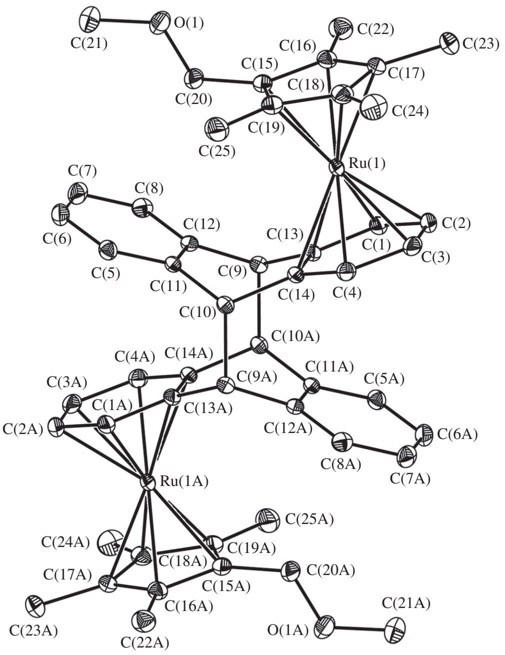


Figure 1 Structure of cation **2b** with thermal ellipsoids at a 50% probability level. Selected distances (Å): Ru(1)–C(1) 2.231(2), Ru(1)–C(2) 2.213(2), Ru(1)–C(3) 2.206(2), Ru(1)–C(4) 2.214(2), Ru(1)–C(13) 2.2664(18), Ru(1)–C(14) 2.2431(18), Ru(1)–C(15) 2.188(2), Ru(1)–C(16) 2.197(2), Ru(1)–C(17) 2.1836(19), Ru(1)–C(18) 2.175(2), Ru(1)–C(19) 2.184(2).

dinated C_5 and C_6 rings are non-parallel (the dihedral angle is 6.9°), presumably due to a steric repulsion of the CH_2OMe group and the neighboring non-coordinated benzene ring. The metal-to-ring distances Ru···C_5 (1.814 Å) and Ru···C_6 (1.720 Å) for cation **2b** are slightly longer than those for the related mononuclear benzene complex $[(C_5Me_4CH_2OMe)Ru(C_6H_6)]^+$ (1.805, 1.706 Å).[6] In accordance with a general tendency for ruthenium arene complexes,[7] the perimeter of the coordinated C_6 ring (8.532 Å) is considerably greater than that of the non-coordinated one (8.367 Å). The distances between centroids of opposite coordinated and non-coordinated C_6 rings (av. 3.491 Å), as well as the C(9)–C(10A) and C(9A)–C(10) distances (av. 1.608 Å) are shorter than those for the free anthracene dimer (av. 3.672 Å and 1.620 Å, respectively)[8] possibly due to the favorable intramolecular π-stacking of coordinated and non-coordinated rings. There are no distinct intermolecular contacts between cation **2b** and PF_6^- anions.

Table 1 Energy decomposition analysis of complexes **2c** and **3c** in terms of interactions between the $[RuCp]^+$ and $[CpRu(C_{28}H_{20})]^+$ fragments at BP86/TZ2P.[a]

Compound	ΔE_{int}	ΔE_{Pauli}	ΔE_{elstat}	ΔE_{orb}
2c (*anti*)	–46.2	218.3	–88.3 (33.3%)	–176.2 (66.7%)
3c (*syn*)	–42.9	219.2	–85.0 (32.4%)	–177.1 (67.6%)

[a] The values in parentheses give the percentage contributions to the total attractive interactions.

To explain the predominant formation of *anti*-isomers in the above reactions, we carried out the energy decomposition analysis (EDA)[9,¶] for the parent *anti*- and *syn*-isomers **2c** and **3c** in terms of interactions between the $[RuCp]^+$ and $[CpRu(C_{28}H_{20})]^+$ fragments (Table 1).[††] The attractive interactions in both cases are ~67% covalent and 33% electrostatic. The total bonding energy ΔE_{int} for *anti*-isomer **2c** is 3.3 kcal mol^{-1} greater than that for *syn*-isomer **3c** in accordance with higher electrostatic attraction ΔE_{elstat} (3.3 kcal mol^{-1}), which is caused by decrease in repulsion between two $[RuCp]^+$ cations due to a larger Ru···Ru distance (**2c**, 7.69 Å and **3c**, 6.89 Å, see Table S1 in the Online Supplementary Materials). It explains the predominant formation of the *anti*-isomers.

Thus, we found that anthracene ruthenium complexes **1a**,**b** undergo dimerization under visible-light irradiation with the predominant formation of isomers with the most distant position of the $Ru(C_5Me_4R)$ fragments.

Online Supplementary Materials

Supplementary data associated with this article (atomic coordinates for optimized geometry and energy data for complexes **2c** and **3c** as well as energy decomposition analysis for the interaction between two $[RuCp]^+$ cations in the $[Ru_2Cp_2]^{2+}$ moiety with the geometry it has in complexes **2c** and **3c**) can be found in the online version at doi:10.1016/j.mencom.2011.11.005.

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PLUS 5.0 using the full-matrix least-squares method. All non-hydrogen atoms were allowed to have an anisotropic thermal motion. The refinement converged to $wR_2 = 0.0785$ and GOF = 1.000 for all independent reflections [$R_1 = 0.0305$ was calculated against F for 6171 observed reflections with $I > 2\sigma(I)$].

CCDC 823137 contains 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, 2011.

[¶] According to the EDA method,[12] the interaction energy between the bonding fragments ΔE_{int} can be divided into three main components:

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

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. The $\Delta E_{elstat}/\Delta E_{orb}$ ratio indicates the electrostatic/covalent character of the bond.

[††] Geometry optimizations were performed without constraints using the PBE exchange-correlation functional,[13] the scalar-relativistic Hamiltonian,[14] atomic basis sets of generally-contracted Gaussian functions,[15] and a density-fitting technique[16] as implemented in a recent version of Priroda[17] code. The all-electron triple-ζ basis set L2 augmented by two polarization functions was used for light elements (H, C) whereas ruthenium atoms were described by the all-electron double-ζ basis set L1 augmented by one polarization function.[18]

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