

Synthesis and Photochromic Property of *cis*-Azobenzene Complex with a Binuclear η^6 -Areneruthenium(II) Unit

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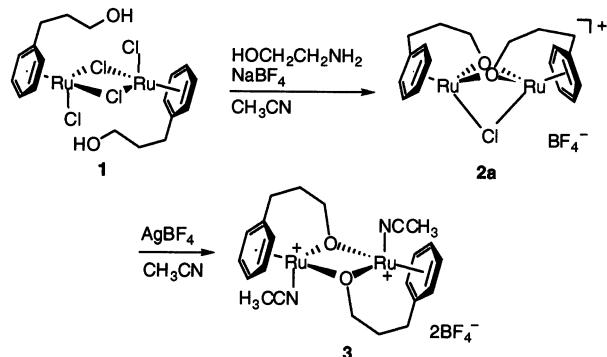
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A *cis*-azobenzene complex with a binuclear ruthenium(II) unit bridged by alkoxy ligands which are tethered to η^6 -arene donors (**4**) was synthesized from corresponding binuclear acetonitrile complex (**3**) and *trans*-azobenzene irradiated by UV light ($300 \text{ nm} < \lambda < 400 \text{ nm}$). On irradiation with visible light ($\lambda > 510 \text{ nm}$) in acetonitrile, **4** mostly dissociated to *trans*-azobenzene and **3** with the photostationary ratio **3**/**4** = 92/8.

A limited number of organotransition metal complexes having azobenzene ligand are known¹ where the thermodynamically less stable *cis*-azobenzene is incorporated in binuclear metal units. We report here synthesis, structure, and photochromic behavior of a binuclear ruthenium(II) *cis*-azobenzene complex. In this system the complexation of azobenzene with the binuclear ruthenium unit can be controlled by the irradiation wavelength.

An arene ruthenium(II) dimer complex having side arm alcohol $[\text{Ru}\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{OH}\}\text{Cl}_2]_2$ (**1**)² was treated with 2-aminoethanol (2 equiv) and NaBF_4 in acetonitrile to give a new binuclear complex $[\text{Ru}_2\{\eta^6\text{-}\mu\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{O}\}_2(\mu\text{-Cl})]\text{BF}_4$ (**2a**)³ in high yield. The molecular structure of $[\text{Ru}_2\{\eta^6\text{-}\mu\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{O}\}_2(\mu\text{-Cl})]\text{PF}_6$ (**2b**) prepared by anion exchange from BF_4 to PF_6 is shown in Figure 1a.⁴ Abstraction of chloride ligand of **2a** in acetonitrile afforded binuclear acetonitrile complex $[\text{Ru}\{\eta^6\text{-}\mu\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{O}\}_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ (**3**)⁵ (Scheme 1) whose structure is shown in Figure 1b.⁴ Binuclear ruthenium complexes of the type **2** with unsubstituted η^6 -benzene ligand have been known,⁶ but complexes of the type **3** are less common.



Scheme 1.

In both CH_2Cl_2 and CH_3CN under dark **3** does not react with *trans*-azobenzene at all. However, when an orange acetonitrile solution of **3** and *trans*-azobenzene was irradiated by a high-pressure Hg lamp (using a UV-D36A filter, $300 < \lambda < 400 \text{ nm}$) for 1 h, a purple solution emerged of which ¹H-NMR spectra indicated quantitative formation of *cis*-azobenzene complex

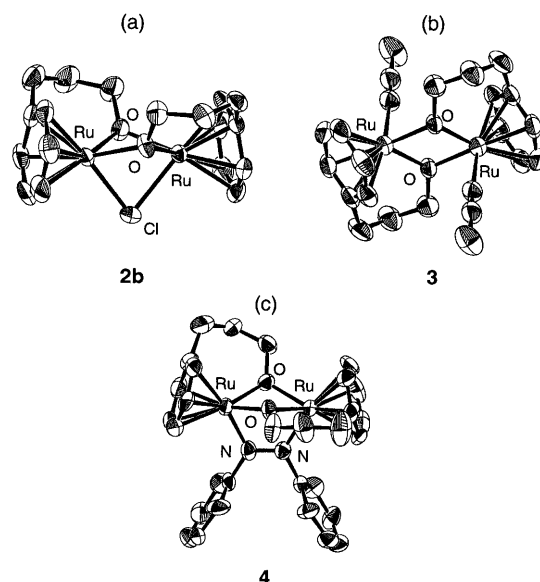
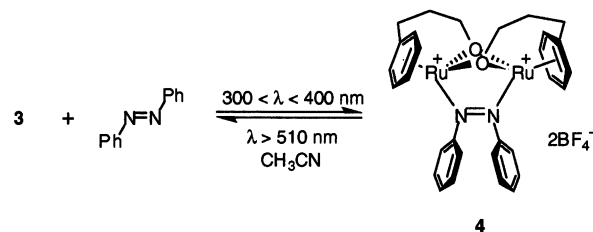


Figure 1. ORTEP drawing of **2b**, **3**, and **4** with ellipsoids at 50% probability levels. Counter anions were omitted for clarity.

$[\text{Ru}_2\{\eta^6\text{-}\mu\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{O}\}_2(\text{PhN=NPh})](\text{BF}_4)_2$ (**4**)⁷ (Scheme 2). The solid state structure of **4** is shown in Figure 1c.⁴ The N=N bond distance of **4** is 1.28(2) Å comparable to common N=N bond distances. It should be noted that a similar irradiation ($300 < \lambda < 400 \text{ nm}$) of *trans*-azobenzene alone in the same solvent afforded a photostationary mixture of *cis* (50%) and *trans* (50%) azobenzene. Enhancement of photostationary distribution of the *cis* form of azobenzenes owing to the more favorable metal complexation in this form was reported before.⁸



Scheme 2.

A UV-vis spectrum of **3** and **4** is shown in Figure 2, which indicated $\lambda_{\text{max}} = 530 \text{ nm}$ ($\epsilon = 3300 \text{ M}^{-1} \text{ cm}^{-1}$) with respect to **4**. On irradiation with a tungsten lamp (using an O-54 filter, $\lambda > 510 \text{ nm}$) of a CD_3CN solution of **4** for 90 min, the solution color turned from purple to red-orange. ¹H-NMR measurements showed the formation of **3** and *trans*-azobenzene in a ratio of **4** : **3** : *trans*-azobenzene = 8 : 92 : 92.⁹ Thus, the inter-conversion between **3** and **4** can be controlled by the irradiation

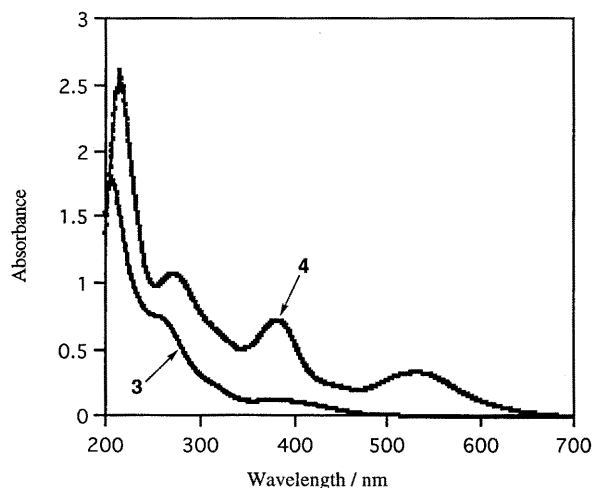


Figure 2. UV-vis spectra of **3** and **4** in CH_3CN at 25°C (10^{-4} M).

wavelength. Further studies are in progress to synthesize other complexes related to **4** and reveal more details of their photochemistry.

References and Notes

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- 3 To a suspension of **1** (400 mg, 0.65 mmol) in CH_3CN (100 mL) was added 2-aminoethanol (79 mg, 1.3 mmol) and NaBF_4 (143 mg, 1.3 mmol) in the presence of Molecular Sieves 4A. After stirred for 48 h at room temperature, the mixture was filtered and the filtrate was evaporated. The residue was dissolved in CH_2Cl_2 and the suspension was filtered. The orange filtrate was evaporated to give 308 mg of orange powders of **2a** (0.52 mmol, 80%). $^1\text{H-NMR}$ (CD_3CN , 270 MHz): δ 2.29 (m, 4H), 2.36 (m, 2H), 2.66 (m, 2H), 4.04 (m, 2H), 4.32 (m, 2H), 5.09 (d, $J = 5.9$ Hz, 2H), 5.31 (d, $J = 5.9$ Hz, 2H), 5.34 (t, $J = 6.1$ Hz, 2H), 5.61 (t, $J = 5.9$ Hz, 2H), 5.70 (t, $J = 5.5$ Hz, 2H). Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{BClF}_4\text{O}_2\text{Ru}_2$: C, 36.35; H, 3.73%. Found: C, 36.49; H, 3.53%.
- 4 Crystal data for **2b**: $\text{C}_{18}\text{H}_{22}\text{ClF}_6\text{O}_2\text{PRu}_2$, MW = 652.93, monoclinic, space group $P2_1/c$ (No. 14), $a = 10.092(3)$ Å, $b = 17.182(3)$ Å, $c = 12.522(2)$ Å, $\beta = 106.37(2)^\circ$, $V = 2083.3(7)$ Å³, $Z = 4$, $F(000) = 1280$, $D_c = 2.082$ g/cm³, $\mu(\text{Mo K}\alpha) = 17.21$ cm⁻¹, 271 variables refined with 4085 reflections with $I > 3\sigma(I)$ to $R = 0.046$, $R_w = 0.055$. Crystal data for **3**: $\text{C}_{22}\text{H}_{28}\text{B}_2\text{F}_8\text{N}_2\text{O}_2\text{Ru}_2$, MW = 769.27, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.073(1)$ Å, $b = 10.633(1)$ Å, $c = 9.000(1)$ Å, $\alpha = 113.446(4)^\circ$, $\beta = 106.37(2)^\circ$, $\gamma = 82.047(3)^\circ$, $V = 803.5(2)$ Å³, $Z = 1$, $F(000) = 382$, $D_c = 1.590$ g/cm³, $\mu(\text{Mo K}\alpha) = 10.11$ cm⁻¹, 199 variables refined with 3393 reflections with $I > 3\sigma(I)$ to $R = 0.074$, $R_w = 0.080$. Crystal data for **4**: $\text{C}_{30}\text{H}_{32}\text{B}_2\text{F}_8\text{N}_2\text{O}_2\text{Ru}_2 \cdot \text{CH}_2\text{Cl}_2$, MW = 913.28, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 18.670(1)$ Å, $b = 18.718(1)$ Å, $c = 9.8025(5)$ Å, $V = 3425.6(4)$ Å³, $Z = 4$, $F(000) = 1816$, $D_c = 1.771$ g/cm³, $\mu(\text{Mo K}\alpha) = 11.14$ cm⁻¹, 443 variables refined with 2589 reflections with $I > 3\sigma(I)$ to $R = 0.055$, $R_w = 0.069$.
- 5 To a solution of **2a** (220 mg, 0.37 mmol) in CH_3CN (35 mL) was added AgBF_4 (74 mg, 0.38 mmol) dissolved in CH_3CN (5 mL). After stirred for 2 h at room temperature, the reaction mixture was filtered and the filtrate was evaporated. The residue was recrystallized with CH_3CN and ether to give 189 mg (0.22 mmol, 72%) of orange crystalline product **3**. **3** was hardly soluble in common organic solvents except for acetonitrile. $^1\text{H-NMR}$ (CD_3CN , 270 MHz): δ 1.97 (m, 4H), 2.36 (m, 4H), 3.72 (m, 4H), 5.15 (d, $J = 6.5$ Hz, 4H), 5.43 (t, $J = 5.8$ Hz, 2H), 5.79 (t, $J = 6.1$ Hz, 4H). Anal. Calcd for $\text{C}_{22}\text{H}_{28}\text{B}_2\text{F}_8\text{N}_2\text{O}_2\text{Ru}_2 \cdot \text{H}_2\text{O}$: C, 35.41; H, 4.05; N, 3.75%. Found: C, 35.45; H, 3.71; N, 3.87%.
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- 7 **3** (96 mg, 0.13 mmol) and *trans*-azobenzene (24 mg, 0.13 mmol) were dissolved in 10 mL of CH_3CN , and the solution was irradiated through a TOSHIBA UV-D36A filter ($300 < \lambda < 400$ nm) by a high-pressure Hg lamp for 1 h. The solvent was removed and the residue was recrystallized with CH_2Cl_2 and hexane to give 108 mg of purple powders of **4** (0.13 mmol, 99%). $^1\text{H-NMR}$ (CD_3CN , 270 MHz): δ 1.97 (m, 2H), 2.35 (m, 2H), 2.56 (m, 4H), 4.14 (m, 2H), 4.28 (m, 2H), 4.84 (t, $J = 5.8$ Hz, 2H), 5.10 (d, $J = 6.5$ Hz, 2H), 5.49 (t, $J = 5.7$ Hz, 2H), 6.03 (d, $J = 5.7$ Hz, 2H), 6.22 (t, $J = 5.8$ Hz, 2H), 6.99 (m, 2H), 7.30–7.50 (m, 8H). Anal. Calcd for $\text{C}_{30}\text{H}_{32}\text{B}_2\text{F}_8\text{N}_2\text{O}_2\text{Ru}_2 \cdot \text{CH}_2\text{Cl}_2$: C, 40.77; H, 3.75; N, 3.07%. Found: C, 40.48; H, 3.77; N, 2.90%.
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- 9 Irradiation with the light ($\lambda > 510$ nm) of a CH_3CN solution of free azobenzene (*cis* : *trans* = 50 : 50) for 80 min afforded a photostationary mixture (*cis* : *trans* = 22 : 78).