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

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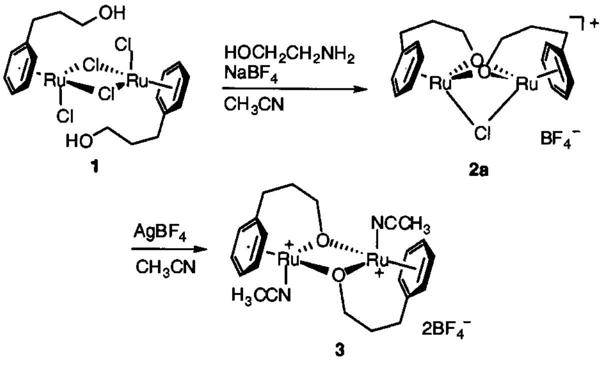
A *cis*-azobenzene complex with a binuclear ruthenium(II) unit bridged by alkoxo ligands which are tethered to η^6-arene donors (**4**) was synthesized from corresponding binuclear acetonitrile complex (**3**) and *trans*-azobenzene irradiated by UV light (300 nm < λ < 400 nm). On irradiation with visible light (λ > 510 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 known[1] 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 $[Ru\{\eta^6\text{-}C_6H_5(CH_2)_3OH\}Cl_2]_2$ (**1**)[2] was treated with 2-aminoethanol (2 equiv) and $NaBF_4$ in acetonitrile to give a new binuclear complex $[Ru_2\{\eta^6:\eta^1:\mu\text{-}C_6H_5(CH_2)_3O\}_2(\mu\text{-}Cl)]BF_4$ (**2a**)[3] in high yield. The molecular structure of $[Ru_2\{\eta^6:\eta^1:\mu\text{-}C_6H_5(CH_2)_3O\}_2(\mu\text{-}Cl)]PF_6$ (**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 $[Ru\{\eta^6:\eta^1:\mu\text{-}C_6H_5(CH_2)_3O\}(CH_3CN)]_2(BF_4)_2$ (**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 < λ < 400 nm) for 1 h, a purple solution emerged of which ^{1}H-NMR spectra indicated quantitative formation of *cis*-azobenzene complex $[Ru_2\{\eta^6:\eta^1:\mu\text{-}C_6H_5(CH_2)_3O\}_2(PhN{=}NPh)](BF_4)_2$ (**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 < λ < 400 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]

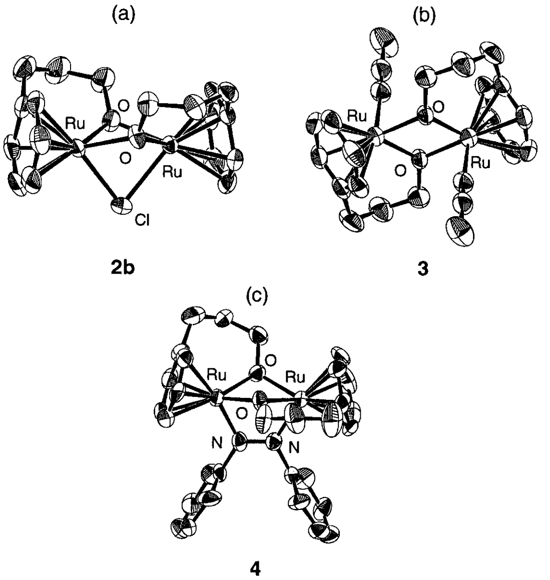
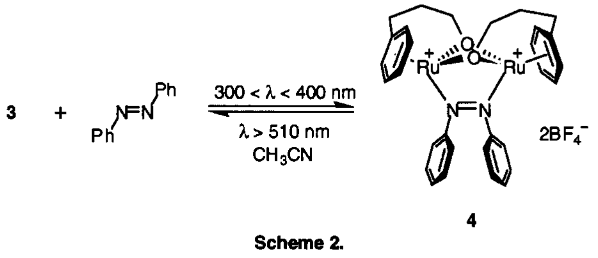


Figure 1. ORTEP drawing of **2b**, **3**, and **4** with ellipsoids at 50% propability levels. Counter anions were omitted for clarity.



Scheme 2.

A UV–vis spectrum of **3** and **4** is shown in Figure 2, which indicated λ_{max} = 530 nm (ε = 3300 M^{-1} cm^{-1}) with respect to **4**. On irradiation with a tungsten lamp (using an O-54 filter, λ > 510 nm) of a CD_3CN solution of **4** for 90 min, the solution color turned from purple to red-orange. ^{1}H-NMR measurements showed the formation of **3** and *trans*-azobenzene in a ratio of **4** : **3** : *trans*-azobenzene = 8 : 92 : 92.[9] Thus, the interconversion between **3** and **4** can be controlled by the irradiation

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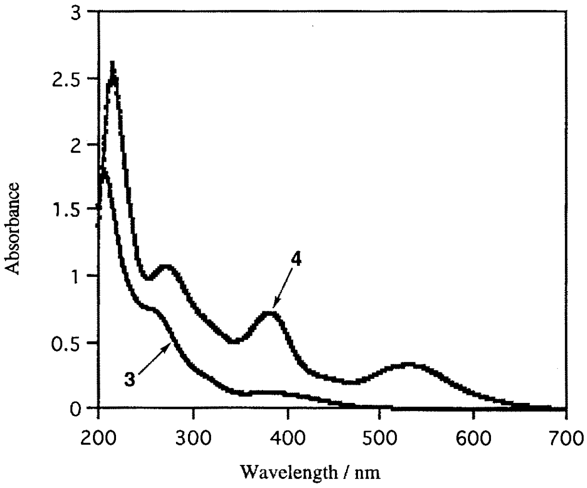

Figure 2. UV-vis spectra of **3** and **4** in CH_3CN at 25 °C (10^{-4} M).

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}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 $C_{18}H_{22}BClF_4O_2Ru_2$: C, 36.35; H, 3.73%. Found: C, 36.49; H, 3.53%.

4 Crystal data for **2b**: $C_{18}H_{22}ClF_6O_2PRu_2$, 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, β = 106.37(2)°, V = 2083.3(7) Å^3, Z = 4, F(000) = 1280, D_c = 2.082 g/cm^3, μ(Mo Kα) = 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**: $C_{22}H_{28}B_2F_8N_2O_2Ru_2$, 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, α = 113.446(4)°, β = 106.37(2)°, γ = 82.047(3)°, V = 803.5(2) Å^3, Z = 1, F(000) = 382, D_c = 1.590 g/cm^3, μ(Mo Kα) = 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**: $C_{30}H_{32}B_2F_8N_2O_2Ru_2{\cdot}CH_2Cl_2$, 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) Å^3, Z = 4, F(000) = 1816, D_c = 1.771 g/cm^3, μ(Mo Kα) = 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}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 $C_{22}H_{28}B_2F_8N_2O_2Ru_2{\cdot}H_2O$: 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}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 $C_{30}H_{32}B_2F_8N_2O_2Ru_2{\cdot}CH_2Cl_2$: 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).