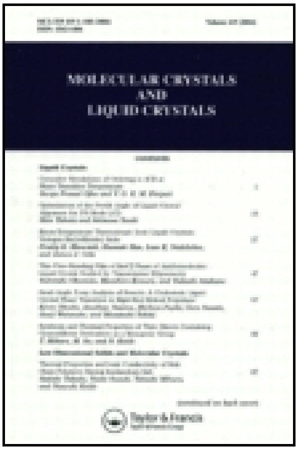

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Synthesis of Bimetallic Ruthenium Complexes with an Azobenzene-Containing Ligand

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Synthesis of Bimetallic Ruthenium Complexes with an Azobenzene-Containing Ligand

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Two novel bimetallic ruthenium complexes with an azobenzene-containing ligand were synthesized. Their photochromic properties were investigated.

Keywords: azobenzene; bimetallic; photochromic; ruthenium complex

Photochromic compounds have attracted remarkable attention because of their potential for optical memory media and optical switching devices [1]. Among them, organic azo-compounds are well-known photochromic compounds, and some have been intensively investigated to clarify the mechanism of isomerization [2] and to understand their applications vitalizing alteration of the chemical structure [3]. Organo-transition-metal complexes with azobenzene-containing ligands are of recent interest. They can provide new molecular functions, due to the combination of photoisomerization of the azo group, and changes in the intrinsic properties, that is, in the optical, redox, and magnetic properties, originating from the d-electrons [4].

Some metal complexes with azobenzene-containing ligands as a building block have already been synthesized, and a number of studies focused on the photoisomerization of azobenzene metal complexes. Some

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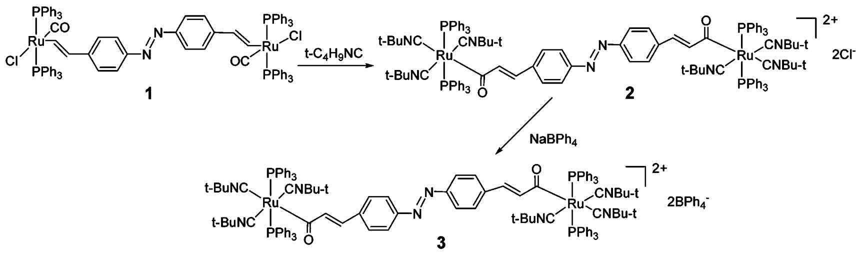
of them have shown novel properties, which are not observed for organic azobenzenes, such as redox-combined single light reversible isomerization, MLCT (metal-to-ligand change transfer) photoisomerization, and isomerization-promoted photoluminescence switching, indicating that the type of attached metal complexes controls such functionalities. Recent studies show that direct metal–carbon σ-linkage of the organic bridge to the metal center usually results in increased electronic delocalization [5,6].

To our knowledge, however, few bimetallic complexes with σ,σ-bridging azobenzene chains have been reported to date. In a previous work, we reported some azo-conjugated bimetallic ruthenium complexes with б,б-bridge azobenzene chains for the first time [7]. However, an additional problem can be circumvented by developing metal complexes systems with azobenzene-containing ligands that employ gated mechanisms or systems that display some novel properties. To further study the photoisomerization of bimetallic ruthenium complexes with an б,б-bridge azobenzene-containing ligand, in this report, two new bimetallic complexes with an б,б-bridge azobenzene-containing ligand have been designed and synthesized, and their characterization and photoisomerization is described.

Azo-conjugated bimetallic ruthenium complexes **1** were prepared according to literature procedures [7]. Ruthenium complex **1** was treated with t-BuNC in CH_2Cl_2. The reaction mixture was stirred at room temperature overnight to give an orange-red solution. The volume of the reaction mixture was then reduced to ca.2 mL under vacuum. Then addition of hexane to the reaction mixture produced a red solid. The solid was collected by filtration, washed with hexane, and dried under vacuum to give complex **2** (Scheme 1). Complex **2** was treated with sodium tetraphenylborate in methanol at room temperature for 20 min to give an orange precipitate. The orange solid was collected by filtration, washed with methanol and hexane, and dried under vacuum to give complex **3**.



SCHEME 1 Synthetic route of bimetallic ruthenium complex **2** and **3**.

The UV/Vis absorption spectra of complexes **2** and **3** in CH_2Cl_2 show the intense MLCT (metal-to-ligand charge transfer) bands at 394 nm and 393 nm, respectively, which are about 26 nm red-shifted compared with λ_{max} of organic azobenzene compound that we previously have reported for the compound $(CH_3)_3SiC{\equiv}CC_6H_4N{=}NC_6H_4C{\equiv}CSi(CH_3)_3$ [7]. The spectral changes, which are similar to those of azobenzene-conjugated Ru bis(terpyridine) complexes and Fe complexes [8–10], were suggested to result from the effect of conjugation between the $[RuL_n]$ moiety and the azo group in complexes **2** and **3**. In addition, the complexes **2** and **3** are about 57–90 nm blue-shifted compared with the λ_{max} of some complexes that we previously have reported (azo-conjugated bimetallic ruthenium complexes with б, б-bridge azobenzene chains [7]), which is due to the effect of the changes of the ligands and decrease of conjugation. Complex **3** exhibits obvious spectral changes upon irradiation with the light of wavelength 365 nm in CH_2Cl_2 as shown in Fig. 1, and well-defined isosbestic point at 370 and 585 nm were observed. A new absorption maxima (λ_{max}) at

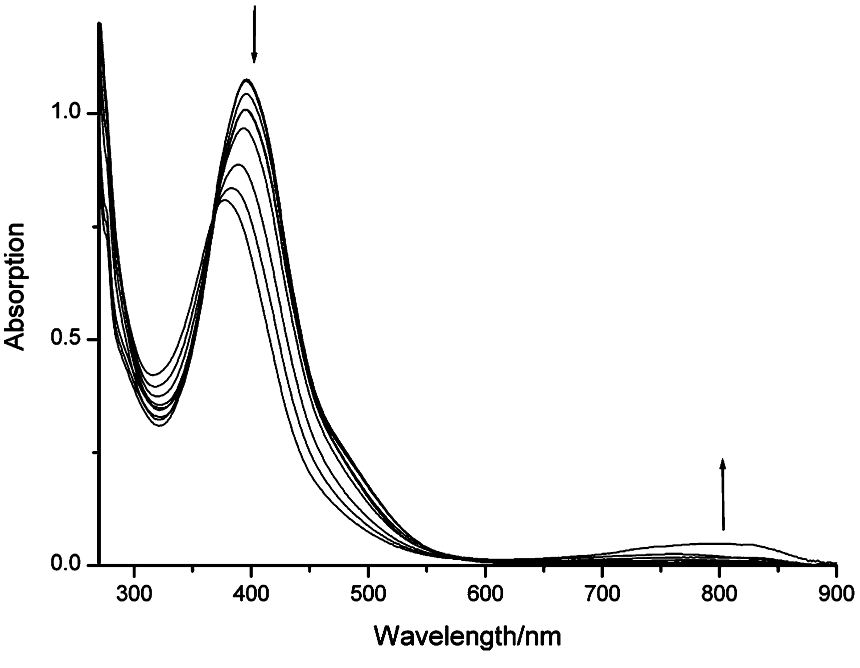


FIGURE 1 UV/Vis absorption spectral change of compound **3** in CH_2CI_2 $(5.0\text{–}10^{-5})$ upon the UV light irradiation at 0, 30, 60, 90, 120, 150, 180, 210, and 240s.

798 nm was observed because of the photoisomerization from *trans*-form to *cis*-form.

Further research efforts will focus on illustrating the effect of different length of conjugating system and transition metal to the photoisomerization. These results will be reported in due course.

DATA

Compound **2**: Yield 85%. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 1.21 (18H, s, CH_3); δ 1.25 (18H, s, CH_3), δ 1.38 (18H, s, CH_3), δ 5.74 (2H, m, Ar–CH=), δ 6.33 (2H, m, –COCH=), δ 7.05 (4H, m, N–Ar–H), δ 7.04 – 7.74 (60H, m, ph), δ 7.91 (4H, m, N–Ar–H). ^{31}P NMR (CD_2Cl_2, 121.5 MHz). δ 36.97 (s, PPh_3). Compound **3**: ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 0.96 (18H, s, CH_3), δ 0.99 (18H, s, CH_3), δ 1.13 (18H, s, CH_3), δ 5.49 (2H, m, s, Ar–CH=), δ 6.10 (2H, m, –COCH=), δ 6.95 (4H, m, N–Ar–H), δ 7.26–7.53 (100H, m, ph), δ 7.67 (4H, m, N–Ar–H). ^{31}P NMR (CD_2Cl_2, 121.5 MHz), δ 36.98 (s, PPh_3). ^{13}C NMR ($CDCl_3$ 100.6 MHz), δ 29.60 (m, –CH_3), δ 57.86 [m, –$C(CH_3)_3$], δ 121.477 (s, –CN), δ 122.95 (S, Ar), δ 124.05 (s, Ar), δ 125.40 (s, Ar), δ 130.75 (s, Ar), δ 133.76 (s, Ar), δ 136.32 (s, Ar), δ 139.70 (s, Ar–CH=), δ 152.18 (s, Ar), δ 164.30 (dt, –CH=), δ 209.32 (s, C=O).

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