

Synthesis and properties of conjugated bimetallic ruthenium complexes with σ,σ -bridging azobenzene chains

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Abstract

A versatile synthetic route to conjugated bimetallic ruthenium complexes with σ,σ -bridging azobenzene chains was developed, and new ruthenium complexes with various ligands were synthesized and characterized. These bimetallic complexes showed a remarkable absorption in the visible region (λ_{max} : 452–483 nm), and undergo *trans*-to-*cis* isomerization under UV light irradiation for short time. Electrochemical study showed that the metal centers in bimetallic complexes containing the $\text{CH}=\text{CH}-\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4-\text{CH}=\text{CH}$ bridge interact with each other.

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1. Introduction

Organic azo-compounds have been intensively investigated to clarify the mechanism of isomerization [1] and to understand their applications utilizing alteration of the chemical structure [2] in terms of photoswitching and photo-mode high-density information storage devices [3]. Transition-metal complexes of azobenzene and its derivations have attracted much attention for over half a century because of both theoretical and industrial interests [4].

Azo-conjugated transition metal complexes 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. Some metal complexes with azobenzene and related com-

pounds as a building block have already been synthesized [5], and a number of studies on the photoisomerization of azo-conjugated metal complexes have appeared in recent years [6]. Some of them have shown novel behaviors which are not observed for organic azobenzenes, such as redox-combined single light reversible isomerization, MLCT photoisomerization, and isomerization-promoted photoluminescence switching. It appears from various recent studies that direct metal–carbon σ -linkage of the organic bridge to the metal center usually results in increased electronic delocalization in comparison with connections made through a dative or a π -bond [7]. It is unfortunate, however, to our knowledge, none of bimetallic complexes with σ,σ -bridging azobenzene chains has been reported to date. To study the difference in the properties of organic azo-compounds and bimetallic complexes with σ,σ -bridging azobenzene chains, in this report, several bimetallic complexes with σ,σ -bridging azobenzene chains will be designed and synthesized, and their characterization, electrochemistry and photoisomerization will be described.

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2. Experimental

2.1. General procedures and starting materials

All solvents were used as received. $\text{PdCl}_2(\text{PPh}_3)_2$, 4,4'-diiodoazobenzene and $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ were prepared according to literature procedures [8]. All other chemicals were obtained from commercial sources. ^1H NMR (400 MHz) ^{13}C NMR (100.6 MHz) and ^{31}P NMR (162 MHz) spectra were recorded on a Bruker AC400 spectrometer. Elemental analyses (C, H, N) were performed by the Microanalytical Services, College of Chemistry, CCNU. The syntheses of all complexes were carried out under a dinitrogen atmosphere with standard Schlenk techniques [9].

2.2. Compounds synthesis

2.2.1. Coupling reaction of **1** with TMSA: Synthesis of $(\text{CH}_3)_3\text{SiC}\equiv\text{CC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{C}\equiv\text{CSi}(\text{CH}_3)_3$ (**2**)

A degassed solution of 4,4'-diiodoazobenzene (4.7 g, 10.83 mmol) in 150 mL triethylamine was added to a mixture of $\text{Pd}(\text{PPh}_3)_4$ (0.57 g, 0.82 mmol), copper (I) iodide (0.18 g, 0.94 mmol) and trimethylsilyl acetylene (2.8 g, 27 mmol). The resulting mixture was stirred at 45 °C for 7 h. The reaction mixture was concentrated with a rotary evaporator. The residue was taken up in 50 mL of ether and washed with water, and the water layer was extracted with ether. The ether layers are combined, dried over MgSO_4 , filtered, and concentrated with a rotary evaporator. The crude product was purified by column chromatography (alumina, eluent: petroleum ether/ CH_2Cl_2 , 2:1) to give a red-brown solid. Yield: 2.64 g, 64%. ^1H NMR (400 MHz, CDCl_3) δ 0.28 (s, 18H, SiMe_3), 7.60 (d, 4H, $J(\text{HH}) = 8.8$ Hz, Ar–H), 7.86 (d, 4H, $J(\text{HH}) = 8.8$ Hz, Ar–H). ^{13}C NMR (100.6 MHz, CDCl_3) δ –0.13 (s, SiMe_3), 97.3 (s, $\text{C}\equiv\text{C}$), 104.5 (s, $\text{C}\equiv\text{C}$), 122.8 (s, Ar), 125.9 (s, Ar), 132.8 (s, Ar), 151.7 (s, Ar). Anal. Calc. for $\text{C}_{22}\text{H}_{26}\text{N}_2\text{Si}_2$: C, 70.53; H, 7.00; N, 7.48. Found: C, 70.68; H, 7.23; N, 7.15.

2.2.2. Desilylation of **2** with base: synthesis of $\text{HC}\equiv\text{CC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{C}\equiv\text{CH}$ (**3**)

To a flask containing **2** (2 g, 5.35 mmol) in ethanol (40 mL) was added sodium hydroxide (2 g, 50 mmol) in ethanol (90 mL). The resulting mixture were stirred at room temperature for 1 h. To the reaction mixture was added saturated brine, and extracted with hexane. The hexane layers are combined, dried over MgSO_4 , filtered, and concentrated with a rotary evaporator. The crude product was purified by column chromatography (alumina, eluent: petroleum ether/ CH_2Cl_2 , 2:1) to give a red solid. Yield: 1.05 g, 85%. ^1H NMR (400 MHz, CDCl_3) δ 3.24 (s, 2H, $\equiv\text{CH}$), 7.56 (d, 4H, $J(\text{HH}) = 8.4$ Hz, Ar–H), 7.89 (d, 4H, $J(\text{HH}) = 8.4$ Hz, Ar–H).

2.2.3. Synthesis of $[\text{RuCl}(\text{CO})(\text{PPh}_3)_2]_2(\mu\text{-CH}=\text{CH}-\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4-\text{CH}=\text{CH})$ (**4**)

To a suspension of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (3.5 g, 3.68 mmol) in CH_2Cl_2 (90 mL) was slowly added compound **3** (0.42 g, 1.84 mmol) in CH_2Cl_2 (60 mL). The reaction mixture was stirred for 30 min to give a red solution. The reaction mixture was filtered through a column of Celite. The volume of the filtrate was reduced to ca. 10 mL under vacuum. Addition of hexane (60 mL) to the residue produced a red-brown solid, which was collected by filtration, washed with hexane, and dried under vacuum. Yield: 2.25 g, 76%. ^1H NMR (400 MHz, CD_2Cl_2) δ 5.60 (d, 2H, $J(\text{HH}) = 14.0$ Hz, Ar–CH=), 6.74 (d, 4 H, $J(\text{HH}) = 8.4$ Hz, N–Ar–H), 7.05–7.38 (m, 60 H, PPh_3), 7.55 (d, 4 H, $J(\text{HH}) = 8.4$ Hz, N–Ar–H), 8.60 (d, 2H, $J(\text{HH}) = 14.0$ Hz, Ru–CH=). ^{31}P NMR (162 MHz, CD_2Cl_2) δ 30.13 (s, PPh_3). Anal. Calc. for $\text{C}_{90}\text{H}_{72}\text{Cl}_2\text{N}_2\text{O}_2\text{P}_4\text{Ru}_2$: C, 67.12; H, 4.51; N, 1.74. Found: C, 67.45; H, 4.25; N, 1.88.

2.2.4. Synthesis of $[\text{RuCl}(\text{CO})(\text{PMe}_3)_3]_2(\mu\text{-CH}=\text{CH}-\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4-\text{CH}=\text{CH})$ (**5**)

To a solution of complex **4** (0.65 g, 0.4 mmol) in CH_2Cl_2 (40 mL) was added a 1 M THF solution of PMe_3 (4.0 mL, 4.0 mmol). The mixture was stirred for 15 h. The volume of the reaction mixture was reduced to ca. 3 mL under vacuum. Addition of hexane (40 mL) to the residue produced a red solid, which was collected by filtration, washed with hexane, and dried under vacuum. Yield: 0.33 g, 80%. ^1H NMR (400 MHz, CD_2Cl_2) δ 1.30 (t, $J(\text{PH}) = 3.2$ Hz, 36H, PMe_3), 1.39 (d, $J(\text{PH}) = 6.8$ Hz, 18H, PMe_3), 6.63 (m, 2H, Ar–CH=), 7.32 (d, 4H, $J(\text{HH}) = 8.0$ Hz, Ar–H), 7.72 (d, 4H, $J(\text{HH}) = 8.0$ Hz, Ar–H), 8.40 (m, 2H, Ru–CH=). ^{13}C NMR (100.6 MHz, CH_2Cl_2): δ 16.59 (t, $J(\text{PC}) = 14.2$ Hz, PMe_3), 19.98 (d, $J(\text{PC}) = 21.4$ Hz, PMe_3), 123.4 (s, Ar), 124.9 (s, Ar), 134.3 (s, =CH), 142.1 (s, Ar), 150.1 (s, Ar), 178.79 (dt, Ru–CH), 202.27 (q, –CO). ^{31}P NMR (162 MHz, CD_2Cl_2) δ –19.5 (t, $J(\text{PP}) = 24.0$ Hz, PMe_3), –7.52 (d, $J(\text{PP}) = 24.0$ Hz, PMe_3). Anal. Calc. for $\text{C}_{36}\text{H}_{66}\text{Cl}_2\text{N}_2\text{O}_2\text{P}_6\text{Ru}_2$: C, 42.48; H, 6.54; N, 2.75. Found: C, 42.15; H, 6.32; N, 2.88.

2.2.5. Synthesis of $[\text{RuCl}(\text{CO})(\text{C}_6\text{H}_5-\text{C}_3\text{H}_4\text{N})(\text{PPh}_3)_2]_2(\mu\text{-CH}=\text{CH}-\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4-\text{CH}=\text{CH})$ (**6**)

To a solution of **4** (1.0 g, 0.62 mmol) in CH_2Cl_2 (35 mL) was added 4-phenylpyridine (0.24 g, 1.5 mmol). The mixture was stirred for 15 h. The reaction mixture was concentrated and added hexane (30 mL) to make it deposit. The solid was collected by filtering, washed with hexane and dried under vacuum to give **6** as a red-brown solid. Yield: 1.00 g, 84%. ^1H NMR (400 MHz, CD_2Cl_2) δ 5.88 (d, 2H, $J(\text{HH}) = 16.8$ Hz, Ar–CH=), 6.75 (d, 4H, $J(\text{HH}) = 5.2$ Hz, $\text{C}_3\text{H}_2\text{H}_2\text{N}$), 6.92 (d, 4H, $J(\text{HH}) = 8.4$ Hz, N–Ar–H), 7.09–7.45(m,

70H, Ph), 7.60 (d, 4H, $J(\text{HH}) = 8.4$ Hz, N–Ar–H), 8.43 (br, 4H, $\text{C}_5\text{H}_2\text{H}_2\text{N}$), 9.16 (d, 2H, $J(\text{HH}) = 16.8$ Hz, Ru–CH=). ^{31}P NMR (162 MHz, CD_2Cl_2) δ 26.5 (s, PPh_3). Anal. Calc. for $\text{C}_{112}\text{H}_{90}\text{Cl}_2\text{N}_4\text{O}_2\text{P}_4\text{Ru}_2$: C, 70.03; H, 4.72; N, 2.92. Found: C, 69.78; H, 4.85; N, 2.65.

2.2.6. Reaction of *KTp* with **4**: synthesis of

$[\text{TpRu}(\text{CO})(\text{PPh}_3)]_2(\mu\text{-CH}=\text{CH}-\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{-CH}=\text{CH})$ (**7**)

To a solution of **4** (0.5 g, 0.31 mmol) in CH_2Cl_2 (20 mL) was added *KTp* (Tp = hydridotris (pyrazolyl) borate, 0.17 g, 0.68 mmol). The mixture was stirred for 15 h. The reaction mixture was concentrated and added hexane (30 mL) to make it deposit. The solid was collected by filtering, washed with hexane and dried under vacuum to give **6** as a red-brown solid. Yield: 0.40 g, 88%. ^1H NMR (400 MHz, CD_2Cl_2) δ 6.51 (d, 2H, $J(\text{HH}) = 16.8$ Hz, Ar–CH=), 6.78 (d, 4H, $J(\text{HH}) = 8.4$ Hz, N–Ar–H), 5.86–7.71 (m, 54 H, Tp, Ph), 8.56 (d, 2 H, $J(\text{HH}) = 16.8$ Hz, Ru–CH=). ^{31}P NMR (162 MHz, CD_2Cl_2) δ 49.0 (s, PPh_3). Anal. Calc. for $\text{C}_{72}\text{H}_{62}\text{B}_2\text{N}_{14}\text{O}_2\text{P}_2\text{Ru}_2$: C, 60.01; H, 4.34; N, 13.61. Found: C, 60.27; H, 4.08; N, 13.28.

2.3. X-ray structure determination of

$(\text{CH}_3)_3\text{SiC}\equiv\text{CC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{C}\equiv\text{CSi}(\text{CH}_3)_3$ (**2**)

Crystals suitable for X-ray diffraction was grown by slow diffusion of hexane into a solution of **2** in CH_2Cl_2 at room temperature. A crystal was mounted on a glass fiber, and the diffraction intensity data were collected on a Bruker CCD 4K diffractometer with graphite-monochromatized Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). Lattice determination and data collection were carried out using SMART version 5.625 software. Data reduction and absorption corrections were performed using SAINT version 6.45 and SADABS version 2.03. Structure solution and refinement were performed using the SHELXTL version 6.14 software package. The space group $P_4(2)/m$ was determined base on systematic absences and intensity statistics. All non-hydrogen atoms were refined anisotropic. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Further crystallographic details were summarized in Table 1, and selected bond distances and angles are given in Table 2.

2.4. Physical measurements

UV/Vis spectra were recorded with Shimadzu UV-2550 spectrometer. Photoisomerization measurements were carried out under a HPK 125 W mercury lamp as an irradiation source. The distance between the sample and the lamp is 10 cm; in front of the sample there is a quartz cell with water.

Table 1
Crystal date and structure refinement for $[(\text{CH}_3)_3\text{SiC}\equiv\text{CC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{C}\equiv\text{CSi}(\text{CH}_3)_3]$

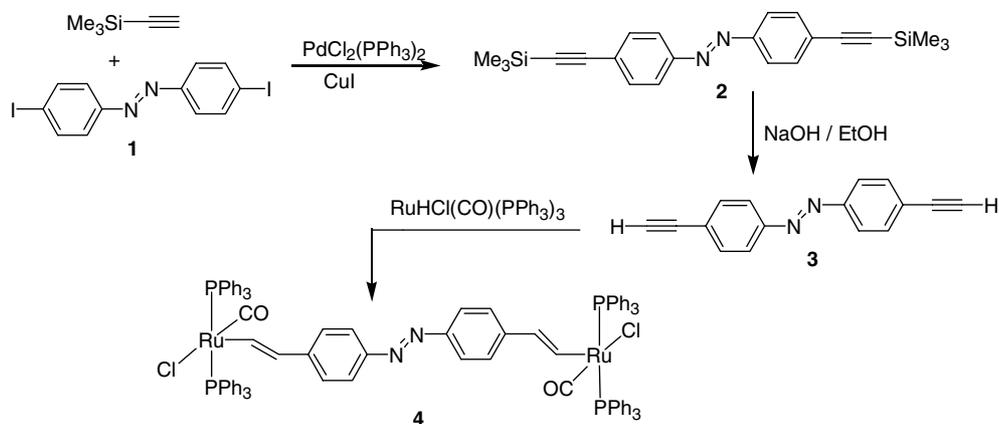
Compound	2
Empirical formula	$\text{C}_{22}\text{H}_{26}\text{N}_2\text{Si}_2$
Molecular weight	374.62
Wavelength (Å)	0.71073
Temperature (K)	293(2)
Crystal system	Tetragonal
Space group	$P_4(2)/m$
<i>a</i> (Å)	10.5296(9)
<i>c</i> (Å)	10.280(1)
<i>V</i> (Å ³)	1139.8(2)
<i>Z</i>	4
<i>D</i> _{calc} (Mg m ⁻³)	1.092
μ (mm ⁻¹)	0.163
<i>F</i> (000)	400
θ (min–max) (°C)	1.93–28.26
Reflections collected	5692
Independent reflection	1321
<i>R</i> _{int}	0.0684
Crystal size (mm)	0.28 × 0.26 × 0.26
Weighting scheme	$\omega = 1/[\sigma^2(F_o^2) + (0.0429P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$
<i>R</i> indices [$I > 2\sigma$] <i>R</i> ₁ , ωR ₂	0.0501, 0.0954
<i>R</i> indices (all data) <i>R</i> ₁ , ωR ₂	0.0979, 0.1100
Goodness-of-fit on <i>F</i> ²	0.824

Table 2

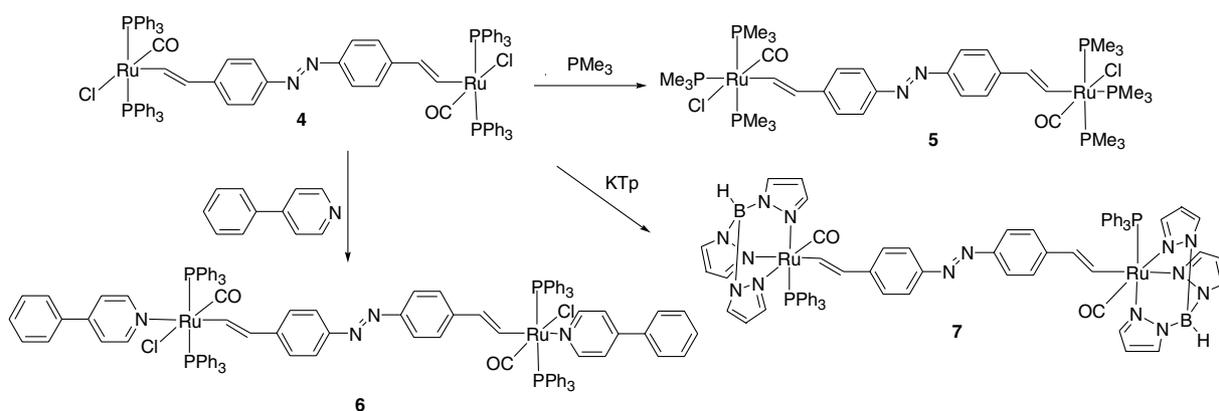
Selected bond lengths (Å) and angles (°) of compound **2**

Si(1)–C(6)	1.844(3)
Si(1)–C(7)	1.853(2)
Si(1)–C(8)	1.862(3)
N(1)–N(1B)	1.230(5)
N(1)–C(1)	1.67(4)
C(1)–C(2)	1.723(18)
C(2)–C(3)	1.368(3)
C(3)–C(4)	1.392(2)
C(4)–C(5)	1.434(4)
C(5)–C(6)	1.192(4)
C(1)–N(1)–N(1B)	172.6(16)
N(1)–C(1)–C(2)	81.5(12)
C(6)–Si(1)–C(7)	109.01(10)
C(6)–Si(1)–C(8)	106.40(18)
C(7)–Si(1)–C(8)	111.24(11)
C(1)–C(2)–C(3)	114.0(13)
C(2)–C(3)–C(4)	120.5(2)
C(3)–C(4)–C(5)	120.60(13)
C(4)–C(5)–C(6)	176.9(3)
C(5)–C(6)–Si(1)	173.9(3)

The electrochemical measurements were performed with Autolab PGSTAT 30. A three-component electrochemical cell was used with a glassy-carbon electrode as the working electrode, a platinum wire as the counter electrode, and a Ag/AgCl electrode as the reference electrode. The cyclic voltammograms were collected with a scan rate of 100 mV/s in CH_2Cl_2 containing 0.10 M *n*-Bu₄NClO₄ as the supporting electrolyte. The peak potentials reported are referenced to Ag/AgCl. The ferrocene/ferrocenium redox couple was located at 0.50 V under our experimental conditions.



Scheme 1.



Scheme 2.

3. Results and discussion

3.1. Synthesis

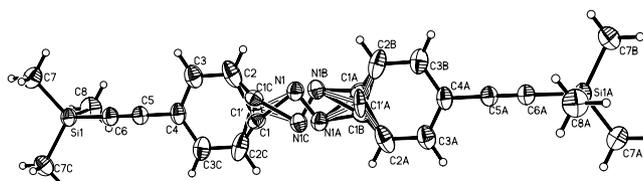
The synthetic route to compounds **2**, **3** and **4** is shown in [Scheme 1](#). Compound **2** was prepared in 64% yield by palladium-catalyzed coupling reaction [10] of trimethylsilyl acetylene with 4,4'-diiodoazobenzene which was obtained by oxidative coupling of 4-iodoaniline with MnO_2 [8d]. Treatment of **2** with NaOH produced **3**, which was isolated as a red solid in 85% yield. Reaction of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ with $\text{HC}\equiv\text{CR}$ are known to give $\text{RuCl}((E)\text{-CH=CHR})(\text{CO})(\text{PPh}_3)_2$ [11]. The insertion reaction of **3** with $\text{RuHCl}(\text{CO})(\text{PPh}_3)_4$ gave bimetallic ruthenium complex **4** in 76% yield. Because of instability of the five-coordinated complex **4** in the solution, it reacted with PMe_3 , 4-phenylpyridine and KTp

(Tp = hydridotris (pyrazolyl) borate) to give six-coordinated bimetallic ruthenium complexes **5**, **6** and **7** in 80–88% yields ([Scheme 2](#)).

3.2. Description and character of structure

3.2.1. Structure of compounds **2** and **3**

The ^1H NMR spectrum of **2** in CDCl_3 showed one SiMe_3 signal at 0.28 ppm and two Ar–H signals at 7.60 and 7.86 ppm; the ^{13}C NMR spectrum (in CDCl_3) showed the acetylenic carbon signals at 97.3 and 104.5 ppm and aromatic ring carbon signals at 122.8, 125.9, 132.8, 151.7 ppm. The ^1H NMR spectrum of **3** in CDCl_3 showed acetylenic hydrogen signal at 3.24 ppm and two Ar–H signals at 7.56 and 7.89 ppm. [Fig. 1](#) showed the ORTEP drawing of molecular structure of **2**. The crystal structure consists of discrete

Fig. 1. Molecular structure of **2** with atom numbering scheme.

monomeric molecules of $[(\text{CH}_3)_3\text{SiC}\equiv\text{CC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{C}\equiv\text{CSi}(\text{CH}_3)_3]$, which is in *trans*-form. The azobenzene group was disordered. The structural features within the azo group can be discussed by comparing the data with those of the related azobenzene derivative. The angles of $\text{N}(1)\text{--C}(1)\text{--C}(2)$ and $\text{C}(1)\text{--N}(1)\text{--N}(1\text{B})$ are $81.5(12)^\circ$ and $172.6(16)^\circ$. The $\text{N}=\text{N}$ bond length in azobenzenes was estimated to be 1.26–1.27 Å. The small $\text{N}=\text{N}$ bond length 1.230(5) Å, is comparable with those reported in $[\text{H}_3\text{CC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{CH}_3]$ [1.251(2) Å] [12].

3.2.2. Structure of bimetallic ruthenium complexes 4, 5, 6 and 7

Complex **4** ($[\text{RuCl}(\text{CO})(\text{PPh}_3)_2]_2(\mu\text{-CH}=\text{CH}\text{-C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{-CH}=\text{CH})$) has been characterized by NMR and elemental analysis. The ^{31}P NMR spectrum of complex **4** in CD_2Cl_2 displayed a singlet at 30.1 ppm, which indicated that the two phosphine ligands are equivalent and *trans* to each other. The ^1H NMR spectrum showed resonances for the two vinylic hydrogen atoms at 8.6 and 5.6 ppm with $J(\text{HH}) = 14$ Hz. The magnitude of the coupling constants indicated that the two vinylic protons are *trans* to each other.

The six-coordinated complex **5**, **6** and **7** have also been characterized by NMR and elemental analysis. Their ^1H NMR spectra showed that the two vinylic protons are *trans* to each other. The geometry of complex **5**, **6** and **7** around ruthenium was assigned by analogy to those of complexes $[\text{RuCl}(\text{CO})(\text{PMe}_3)_3]_2(\mu\text{-CH}=\text{CHCH}=\text{CHCH}=\text{CH})$ [13], $[\text{RuCl}(\text{PhPy})(\text{CO})(\text{PPh}_3)_2]_2(\mu\text{-CH}=\text{CH}\text{-Ar}\text{-CH}=\text{CH})$ [7b], $[\text{TpRu}(\text{CO})(\text{PPh}_3)_2]_2(\mu\text{-CH}=\text{CHCH}=\text{CH}\text{-Ar}\text{-CH}=\text{CH}\text{-CH}=\text{CH})$ [14]. In the ^{13}C NMR spectrum of complex **5**, the signals of carbons attached to ruthenium atoms were observed at 178.79 ppm, which appear at lower magnetic fields than those of $=\text{CH}$ observed at 115.6 ppm in 4,4-divinylazobenzene [15], due to the electron-withdrawing effects of the metal atoms.

3.2.3. Physical properties

Fig. 2 shows the UV/Vis absorption spectra of compound **2**, **5**, **6** and **7** in CH_2Cl_2 . Before irradiation, compound **2** showed the absorption maxima (λ_{max}) at 367 nm. Compound **5**, **6** and **7** showed the intense MLCT bands at 451, 479, 483 nm, respectively, which are about 84–116 nm red-shifted compared with the λ_{max} of **2**. The spectral changes which are similar to those of azobenzene-conjugated Ru bis (terpyridine) complex and Fe complex [16], were suggested to result from the effect of conjugation between the $[\text{RuL}_n]$ moiety and the azo group in complex **5**, **6** and **7**.

Figs. 3–5 show the UV/Vis absorption spectra of **2** and **5** in CH_2Cl_2 upon the UV light irradiation. Compound **2** exhibits slight spectral changes after UV light irradiation as shown in Fig. 3. Upon irradiation of a solution of compound **5** in 10 s, spectral changes with

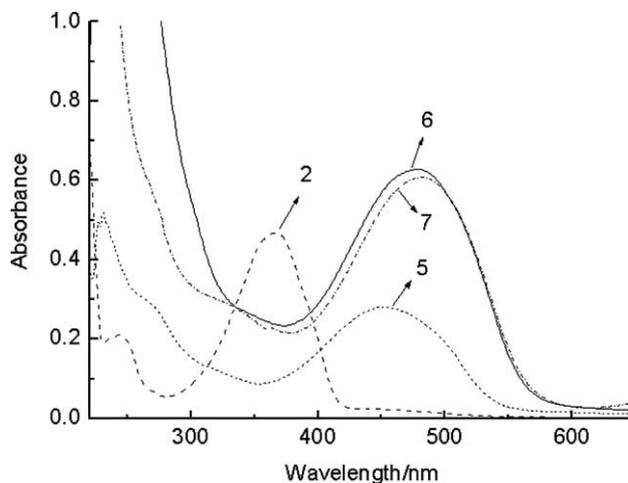


Fig. 2. UV/Vis absorption spectra of compound **2**, **5**, **6** and **7** in CH_2Cl_2 .

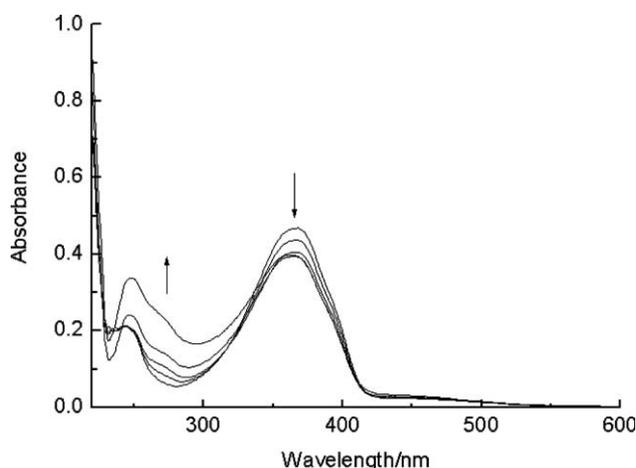


Fig. 3. UV/Vis absorption spectral change of compound **2** (5.4×10^{-5} M) in CH_2Cl_2 upon the UV light irradiation at 0, 10, 20, 240, 540 s.

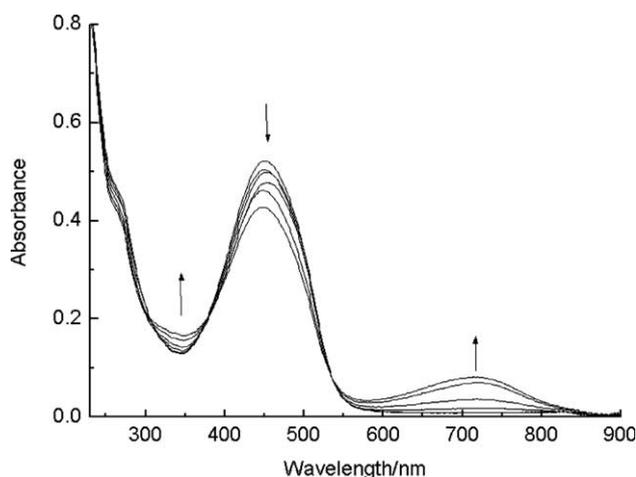


Fig. 4. UV/Vis absorption spectral change of compound **5** (4.2×10^{-5} M) in CH_2Cl_2 upon the UV light irradiation at 0, 2, 4, 6, 8, 10 s.

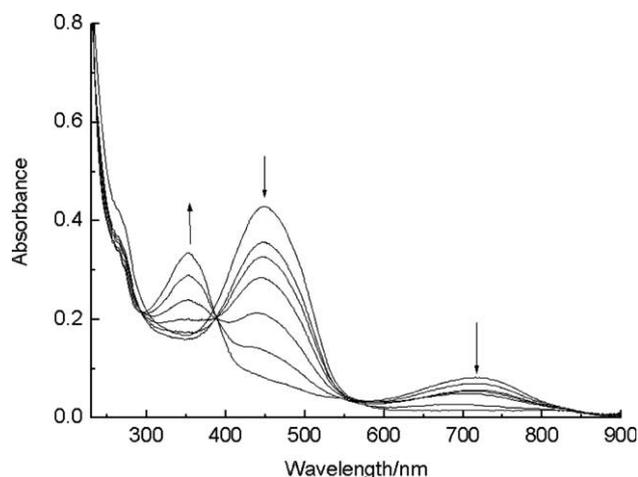


Fig. 5. UV/Vis absorption spectral change of compound **5** (4.2×10^{-5} M) in CH_2Cl_2 upon the UV light irradiation at 10, 20, 30, 40, 60, 80, 100 s.

a clean and well defined isosbestic point at 380 and 534 nm were observed (Fig. 4). The spectral changes are similar to those of azobenzene-conjugated Rh bis(terpyridine) complex [16], indicative of the occurrence of a *trans*-to-*cis* photoisomerization of the azobenzene moiety in the complex. But the absorptions at 450 and 715 nm were weakened, and the absorptions at 350 nm were boosted up if the solution of compound **5** were irradiated for longer time (Fig. 5). LC-MS spectrum of the solution irradiated for 100 s showed that bimetallic complex **5** was decomposed. The changes in the UV/Vis absorption spectra of **6** and **7** in CH_2Cl_2 upon UV light irradiation are similar to those of **5**.

Electrochemistry has often been used to probe metal-metal interactions in bimetallic complexes with σ,σ -bridging hydrocarbon chains. In this work, we have collected cyclic voltammograms of complexes **5**, **6** and **7** in dichloromethane containing 0.10 M *n*-Bu₄NClO₄ as the supporting electrolyte. The cyclic voltammograms of complexes **5**, **6** and **7** have similar features. The complexes **5**, **6** and **7** exhibited two partially reversible oxidation waves at 0.88 and 0.99 V, 0.62 and 0.85 V, 0.64 and 0.79 V versus Ag/AgCl, respectively. The peak separations of the two oxidation waves for complexes **5**, **6** and **7** are dependent on ligands and are at 0.11, 0.23, and 0.15 V, respectively. The peak separations of **5** and **7** are smaller than that reported for Fc-N=N-Fc (0.21 V) [7b]. Observation of two oxidation waves for complexes **5**, **6** and **7** may imply that the two metal centers can interact with each other.

4. Conclusion

We have prepared conjugated bimetallic ruthenium complexes with σ,σ -bridging azobenzene chains. Bime-

talic complexes **5**, **6** and **7** possess λ_{max} at 451, 479, 483 nm, respectively, which are about 84–116 nm red-shifted compared with the λ_{max} of azobenzene **2**. The bimetallic complexes undergo *trans*-to-*cis* isomerization under UV light irradiation for short time, but were decomposed upon the UV light irradiation for long time. Electrochemical study shows that metal centers in bimetallic complexes containing the HC=CH-C₆H₄N=NC₆H₄-CH=CH bridge interact with each other.

5. Supplementary data

The crystallographic data have been deposited with Cambridge Crystallographic Data Centre, CCDC No. 254359 for compound **2**. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1123 336033; e-mail: deposit@ccdc.ac.uk, or <http://www.ccdc.cam.ac.uk>.)

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