Dyes and Pigments 92 (2012) 854–860

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Color change of redox-active organometallic dithienylethene complexes by photochemical and redox processes

Huifang Li, Takashi Koike, Munetaka Akita*

Chemical Resources Laboratory, Tokyo Institute of Technology, R1-27, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

ARTICLE INFO

Article history:
Received 25 December 2010
Received in revised form
23 March 2011
Accepted 24 March 2011
Available online 13 April 2011

Keywords:
Dithienylethene
Photochromism
Redox reaction
Organo-iron complex
Organo-ruthenium complex
Mononuclear DTE complexes

ABSTRACT

Photochromic dithienylethene (DTE) derivatives, DTE–$MCpL_2$ {M = Fe, Ru; Cp = η^5-cyclopentadienyl; $L_2 = (CO)_2$, $(CO)PPh_3$, dppe (dppe = $Ph_2PCH_2CH_2PPh_2$)}, with a directly σ-bonded, redox-active organometallic attachment have been prepared and their response to photo- and electrochemical stimuli has been investigated. It turns out that the color of the organometallic derivatives can be controlled not only by photochromic processes but also by one-electron redox processes. The Ru complexes $\mathbf{1^{Ru}}$ and $\mathbf{2^{Ru}}$ exhibit reversible photochromism in a manner similar to organic DTE derivatives, with ring closing and ring opening triggered by UV and visible-light irradiation, respectively. Their photochromic behavior is critically dependent on both of the central metal and ligands. One-electron oxidation of the Fe complex $\mathbf{3^{Fe}}$ gives the corresponding radical cationic species with a visible absorption.

1. Introduction

Photochromic dithienylethenes (DTE) have received considerable attention over the years because of their promising functions such as molecular switch [1–3], molecular mechanics [4–6], and photochromic materials [7–13]. A great variety of DTE derivatives have been developed so far toward various objectives. Combination with other chemical systems would lead to more sophisticated chromic systems. Attachment of organometallic fragments is one of the promising ways of functionalization of the photochromic system, because the metal species are capable of molecular transformation and their redox-active nature would provide further opportunities to functionalize the photochromic system [14–25].

Herein we report synthesis and photochromic properties of DTE derivatives having the iron and ruthenium organometallic fragments, $MCpL_2$ {M = Fe, Ru; Cp = η^5-cyclopentadienyl; $L_2 = (CO)_2$, $(CO)PPh_3$, dppe (dppe = $Ph_2PCH_2CH_2PPh_2$)}, at the 5-position of one of the two thiophene rings, DTE–$MCpL_2$ (Chart 1). We have found that the color of the redox-active organometallic derivatives can be controlled not only by the photochromic processes but also by one-electron redox processes. Comparison with the previously reported dinuclear derivatives will be also made.

2. Experimental

2.1. General procedures

All manipulations were carried out under an inert atmosphere by using standard Schlenk tube techniques. CH_3CN (P_2O_5) and CH_3OH (Mg) were treated with appropriate drying agents, distilled, and stored under N_2 atmosphere. CH_2Cl_2, THF, ether, and toluene were purified through two columns containing alumina and alumina–Cu catalyst and stored under N_2 atmosphere. Dehydrated pentane and hexane were purchased and degassed by supersonic waves. ^1H and ^{31}P NMR spectra were recorded on a Bruker AVANCE-400 spectrometer (^1H, 400 MHz; ^{31}P, 162 MHz) and a JEOL AL-300 (^1H, 300 MHz; ^{31}P, 121 MHz). Chemical shifts (downfield from TMS (^1H) and H_3PO_4 (^{31}P)) and coupling constants are reported in ppm and in Hz, respectively (Chart 2). Solvents for NMR measurements containing 0.5% TMS were dried over molecular sieves, degassed, distilled under reduced pressure, and stored under N_2. IR and UV–vis spectra were obtained on a JASCO FT/IR 4200 spectrometer and a JASCO V-670 spectrometer, respectively. UV and visible-light irradiations were performed with an Ushio high pressure mercury lamp (UM-452; $\lambda < 360$ nm with a U36 cut-off filter) and a Soma Kogaku Xe lamp (150 W; $\lambda > 420$ nm with an L42 cut-off filter), respectively. Electrochemical measurements (CV) were made with a Hokutodenkou HZ-5000 analyzer (observed in CH_2Cl_2; [complex] = $\sim 2 \times 10^{-3}$ M; [NBu_4PF_6] = 0.1 M; Ag/AgCl electrode

---

* Corresponding author. Tel./fax: +81 45 924 5230.
E-mail address: makita@res.titech.ac.jp (M. Akita).

0143-7208/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2011.03.029

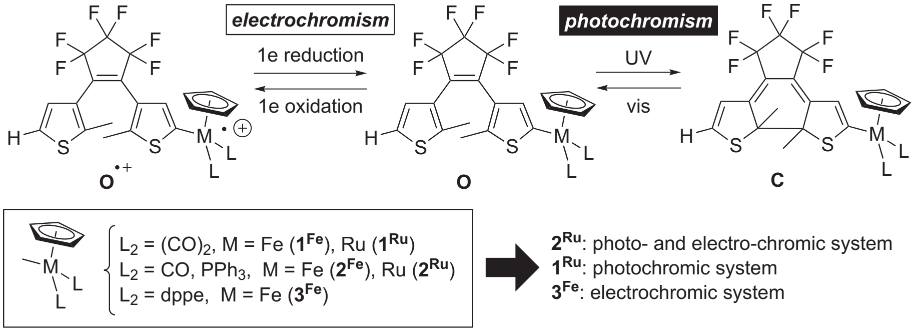

Chart 1. Color change mode of the mononuclear DTE complexes.

(working electrode: Pt; counter electrode: Pt; reference Ag/$AgNO_3$); scan rates were 100 mV/s). After the measurement, ferrocene (Fc) was added to the mixture and the potentials were calibrated with respect to the Fc/Fc^+ redox couple. HRMS (ESI-TOF-MS) spectra were obtained with a Brucker micrOTOF II. Because of the air-sensitivity of the organometallic DTE complexes, analytically pure samples of them could not be obtained. They were characterized on the basis of the spectroscopic data. 1,2-Di(2-methylthien-3-yl)perfluorocyclopentene (DTE) [26], I–FeCp(CO)2 [27], and Cl–RuCp(CO) 2 [28] were prepared according to the published procedures. Other chemicals were purchased and used as received.

2.2. Preparation of DTE–FeCp$(CO)_2$ (1^{Fe})

To a THF solution (2 mL) of DTE (113 mg, 0.308 mmol) cooled at −78 °C, a 1.65 M hexane solution of *n*-BuLi (0.41 mL, 0.677 mmol) was added slowly (5 min.). The resulting mixture was stirred at −78 °C for 30 min and then at room temperature for 20 min. Then a THF solution (2 mL) of I–FeCp$(CO)_2$ (96 mg, 0.317 mmol) was added to the mixture at −78 °C and stirred for 1.5 h. The reaction mixture was gradually warmed to room temperature and quenched by CH_3OH (1 mL). The volatiles were removed under reduced pressure. The residue was extracted with CH_2Cl_2 and passed through a silica plug. Elution with hexane–CH_2Cl_2 (8:2) afforded $\mathbf{1^{Fe}}$ (26 mg, 0.05 mmol, 16% yield) as pale yellow solid. ^1H NMR(300 MHz, C_6D_6): δ 6.98 (d, $^3J_{HH} = 2.6$ Hz, 1H; Hb), 6.93 (s, 1H; Hc), 6.56 (d, $^3J_{HH} = 2.7$ Hz, 1H; Ha), 3.99 (s, 5H; Cp–*H*), 1.83 (s, 3H; CH_3-Th), 1.75 (s, 3H; CH_3-Th). IR(cm^{-1}/KBr): 2030, 1980 (ν(CO)).

2.3. Preparation of DTE–RuCp$(CO)_2$ (1^{Ru})

Complex $\mathbf{1^{Ru}}$ was prepared in a manner similar to the preparation of $\mathbf{1^{Fe}}$ and isolated as colorless solid (19% yield). ^1H NMR(400 MHz, C_6D_6): δ 6.98 (d, $^3J_{HH} = 2.8$ Hz, 1H; Hb), 6.91 (s, 1H; Hc), 6.58 (d, $^3J_{HH} = 2.8$ Hz, 1H; Ha), 4.44 (s, 5H; Cp–*H*), 1.82 (s, 3H; CH_3-Th), 1.77 (s, 3H; CH_3-Th). IR(cm^{-1}/KBr): 2037, 1980 (ν(CO)).

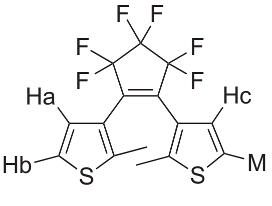

Chart 2. ^1H labels in the mononuclear DTE complexes.

2.4. Preparation of DTE–FeCp(CO)(PPh_3) (2^{Fe})

$\mathbf{1^{Fe}}$ (150 mg, 0.276 mmol) and PPh_3 (223 mg, 0.851 mmol) were dissolved in a mixture of toluene (13 mL) and CH_3CN (0.7 mL) and irradiated by a UV lamp for 3 h. After consumption of $\mathbf{1^{Fe}}$ was confirmed by TLC (alumina), CH_3I (0.5 mL) was added to the mixture to remove the remaining PPh_3 as salts by filtration and the volatiles were removed under reduced pressure. Recrystallization from ether/hexane afforded $\mathbf{2^{Fe}}$ (133 mg, 0.171 mmol, 62% yield) as green crystals. ^1H NMR(300 MHz, $CDCl_3$): δ 7.67–7.32 (15H; Ph–*H*), 7.07 (d, $^3J_{HH} = 2.7$ Hz, 1H; Hb), 6.98 (d, $^3J_{HH} = 2.7$ Hz, 1H; Ha), 6.27 (s, 1H; Hc), 4.46 (s, 5H; Cp–*H*), 1.79 (s, 3H; CH_3-Th), 1.70 (s, 3H; CH_3-Th). $^{31}P\{^1H\}$(121 MHz, $CDCl_3$): δ 74.6. IR(cm^{-1}/KBr): 1943 (ν(CO)).

2.5. Preparation of DTE–RuCp(CO)(PPh_3) (2^{Ru})

Complex $\mathbf{2^{Ru}}$ was prepared in a manner similar to the preparation of $\mathbf{2^{Fe}}$ (UV irradiation time; 50 h). Recrystallization from ether/hexane gave $\mathbf{1^{Ru}}$ as green crystals (45% yield). ^1H NMR(400 MHz, $CDCl_3$): δ 7.36–7.20 (15H; Ph–*H*), 7.02 (d, $^3J_{HH} = 2.6$ Hz, 1H; Hb), 6.95 (d, $^3J_{HH} = 2.6$ Hz, 1H; Ha), 6.16 (s, 1H; Hc), 4.90 (s, 5H; Cp–*H*), 1.83 (s, 3H; CH_3-Th), 1.79 (s, 3H; CH_3-Th). ^{31}P $\{^1H\}$(162 MHz, $CDCl_3$): δ 56.4. IR(cm^{-1}/KBr): 2035, 1939 (ν(CO)). HRMS(ESI, *m*/*z*) calcd for $C_{39}H_{29}F_6OPRuS_2$ $[M]^+$: 824.0349, found 824.0326.

2.6. Preparation of DTE–FeCp(dppe) (3^{Fe})

$\mathbf{1^{Fe}}$ (53 mg, 0.098 mmol) and dppe (120 mg, 0.29 mmol) were dissolved in a mixture of toluene (5 mL) and CH_3CN (0.3 mL) and irradiated by a UV lamp for 5 h. After consumption of $\mathbf{1^{Fe}}$ was confirmed by TLC (alumina), CH_3I (0.5 mL) was added to the mixture to remove the remaining dppe as salts by filtration and the volatiles were removed under reduced pressure. Recrystallization from ether/hexane afforded $\mathbf{3^{Fe}}$ (73 mg, 0.15 mmol, 85% yield) as red crystals. ^1H NMR(400 MHz, C_6D_6): δ 7.41–7.01 (20H; Ph–*H*), 6.95 (d, $^3J_{HH} = 2.8$ Hz, 1H; Hb), 6.61 (d, $^3J_{HH} = 2.8$ Hz, 1H; Ha), 5.51 (s, 1H; Hc), 4.26 (s, 5H; Cp–*H*), 1.74 (s, 3H; CH_3-Th), 1.71 (s, 3H; CH_3-Th). $^{31}P\{^1H\}$(162 MHz, C_6D_6): δ 111.8. IR(cm^{-1}/KBr): 1943 (ν(CO)). ESI-MS (*m*/*z*): calcd for $[M]^+$: 886.1. found: 886.2. HRMS(ESI, *m*/*z*) calcd for $C_{46}H_{38}F_6FeP_2S_2$ $[M]^+$: 886.1139, found 886.1117.

2.7. Studies on photochromic processes of the DTE complexes 1^{Ru} and 2^{Ru}

The photochromic processes were followed by NMR and UV–vis spectroscopy.