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

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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; λ < 360 nm with a U36 cut-off filter) and a Soma Kogaku Xe lamp (150 W; λ > 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] = ~2×10^{-3} M; $[NBu_4PF_6] = 0.1$ M; Ag/AgCl electrode

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doi:10.1016/j.dyepig.2011.03.029

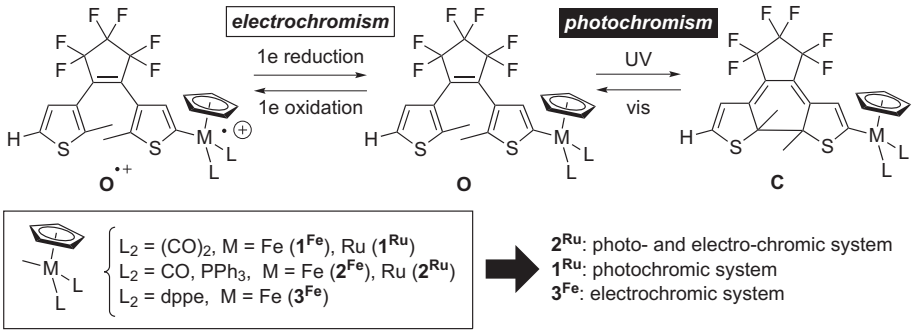


Chart 1. Color change mode of the mononuclear DTE complexes.

(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 **1^{Fe}** (26 mg, 0.05 mmol, 16% yield) as pale yellow solid. ^{1}H 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; C*H*$_3$-Th), 1.75 (s, 3H; C*H*$_3$-Th). IR(cm^{-1}/KBr): 2030, 1980 (ν(CO)).

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

Complex **1^{Ru}** was prepared in a manner similar to the preparation of **1^{Fe}** and isolated as colorless solid (19% yield). ^{1}H 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; C*H*$_3$-Th), 1.77 (s, 3H; C*H*$_3$-Th). IR(cm^{-1}/KBr): 2037, 1980 (ν(CO)).

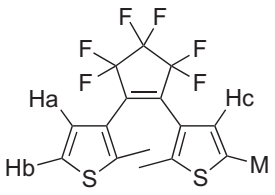


Chart 2. ^{1}H labels in the mononuclear DTE complexes.

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

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 **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 **2^{Fe}** (133 mg, 0.171 mmol, 62% yield) as green crystals. ^{1}H 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; C*H*$_3$-Th), 1.70 (s, 3H; C*H*$_3$-Th). ^{31}P{^{1}H}(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 **2^{Ru}** was prepared in a manner similar to the preparation of **2^{Fe}** (UV irradiation time; 50 h). Recrystallization from ether/hexane gave **1^{Ru}** as green crystals (45% yield). ^{1}H 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; C*H*$_3$-Th), 1.79 (s, 3H; C*H*$_3$-Th). ^{31}P{^{1}H}(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}**)

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 **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 **3^{Fe}** (73 mg, 0.15 mmol, 85% yield) as red crystals. ^{1}H 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; C*H*$_3$-Th), 1.71 (s, 3H; C*H*$_3$-Th). ^{31}P{^{1}H}(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.

NMR spectroscopy: under N_2 atmosphere, the mononuclear complex was dissolved in an appropriate deuterated solvent (2×10^{-2} M), sealed and irradiated by a Xenon lamp with a U36 ($\lambda < 360$ nm) cut-off filter. The progress of the ring-closing process was monitored by appearance of the signals for the closed isomers. After reaching an equilibrium (the photostationary state), the resultant NMR samples were irradiated by a Xenon lamp with a L42 ($\lambda > 420$ nm) cut-off filter and the ring-opening process was monitored on the basis of disappearance of the signals for the closed isomers. Selected ^{1}H NMR data for the closed isomer **1^{Ru}C**: ^{1}H NMR(400 MHz, C_6D_6): δ 6.51 (s, 1H; Hc), 6.12 (d, $^3J_{HH} = 3.0$ Hz, 1H; Hb), 5.97 (d, $^3J_{HH} = 3.0$ Hz, 1H; Ha), 4.35 (s, 5H; Cp–*H*), 2.11 (s, 3H; C*H*$_3$-Th), 2.10 (s, 3H; C*H*$_3$-Th). Selected ^{1}H NMR and ^{31}P NMR data for the closed isomer **2^{Ru}C**: ^{1}H NMR(400 MHz, C_6D_6): δ 7.37–7.01 (30H; Ph–*H*), 6.44, 6.40 (each s, 1H; Hc for the two diastereomers), 6.07 (d, $^3J_{HH} = 2.8$ Hz, 1H; Hb for the two diastereomers), 6.01 (d, $^3J_{HH} = 3$ Hz, 1H; Ha for the two diastereomers), 4.53 (s, 5H; Cp–*H* with diastereomers), 2.17 (s, 3H; C*H*$_3$-Th), 2.13 (s, 3H; C*H*$_3$-Th). ^{31}P {^{1}H}(162 MHz, C_6D_6): δ 54.0.

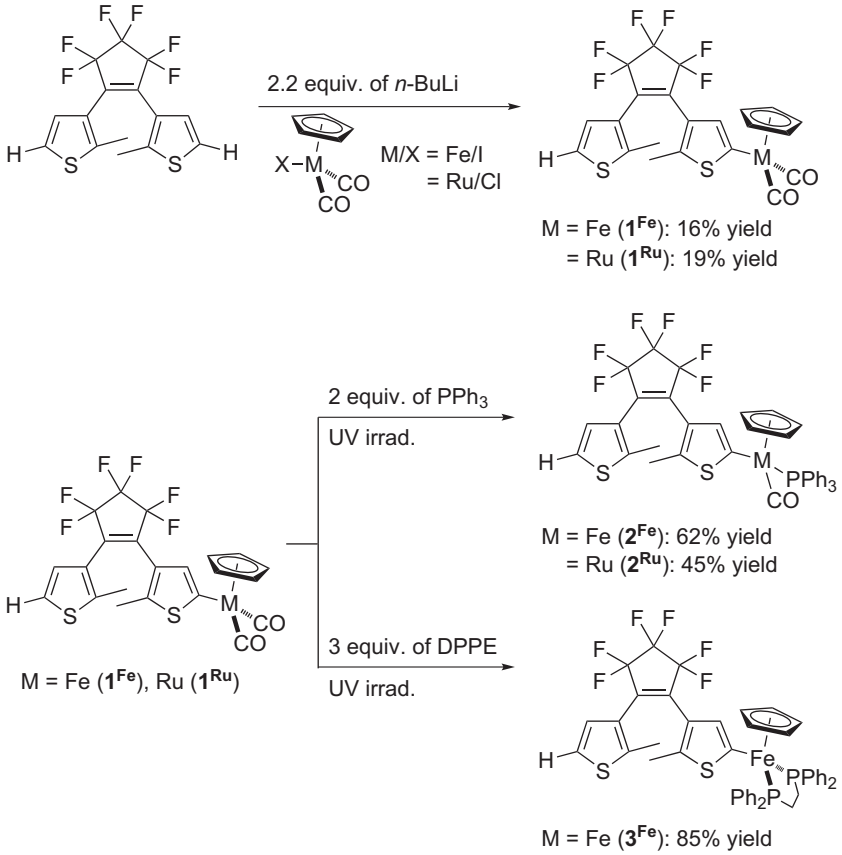
UV–vis spectroscopy: under N_2 atmosphere, the mononuclear complexes were dissolved in an appropriate solvent (2×10^{-5} M) in a cell equipped with a three-way cock and irradiated by a Xenon lamp with a U36 ($\lambda < 360$ nm) cut-off filter. The progress of the ring-closing process was monitored by appearance of the visible absorption for the closed isomers. After reaching the photostationary state, the resultant sample was irradiated by a Xenon lamp with a L42 ($\lambda > 420$ nm) cut-off filter and the ring-opening process was monitored on the basis of disappearance of the visible absorption for the closed isomers. λ_{max} (nm) for the closed isomer in THF were as follows: 345, 547(**1^{Ru}C**), 344, 570(**2^{Ru}C**)

3. Results and discussion

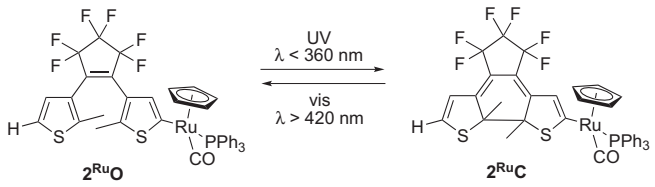
3.1. Synthesis of a series of mononuclear iron and ruthenium complexes bearing a DTE ligand

The DTE complexes, DTE–MCp(CO)$_2$ (M = Fe (**1^{Fe}**), Ru (**1^{Ru}**)), were obtained by the direct lithiation of DTE using 2.2 equiv. of *n*-BuLi followed by treatment with 1.0 equiv. of metal-halides, MCpX(CO)$_2$, (M/X = Fe/I or Ru/Cl) (Scheme 1). It is essential to carefully adjust the amount of *n*-BuLi and metal-halides, because the use of a too much excess amount of the reagent gives the dinuclear complex [20] and an insufficient amount of the reagent causes a lower conversion of the starting materials. After several trials, we have found that the use of 2.2 equiv. of *n*-BuLi leads to the best results, and the desired mononuclear products are separated from the dinuclear products by column chromatography. The monolithium reagent may be selectively generated by lithiation of the corresponding monobromo derivative with *n*-BuLi but selective preparation of the monobromo-DTE derivative turns out to be even more difficult.

Irradiation of UV light to a toluene/CH_3CN solution of **1^{Fe}** or **1^{Ru}** in the presence of PPh_3 induced the ligand exchange between CO and PPh_3 giving DTE–MCp(CO)PPh_3 (M = Fe (**2^{Fe}**), Ru (**2^{Ru}**)). The introduction of diphosphine ligand (dppe) under similar conditions proceeded smoothly in the case of the iron complex leading to DTE–FeCp(dppe) (**3^{Fe}**). The ruthenium complex, however, did not give the corresponding diphosphine complex due to slow



Scheme 1. Synthesis of a series of the mononuclear DTE complexes.



Scheme 2. Photochromic behavior of the mononuclear DTE complexes.

dissociation of the second CO ligand owing to stronger back-donation from the metal center. Thus, a series of mononuclear DTE complexes was synthesized by the above-mentioned methods.

3.2. Photochromic behavior of a series of the mononuclear iron and ruthenium complexes bearing a DTE ligand

As a typical example, photochromic behavior of $\mathbf{2^{Ru}}$ is described (Scheme 2). UV irradiation ($\lambda < 360$ nm) of a THF solution of $\mathbf{2^{Ru}O}$ caused appearance of the characteristic absorption signal at 570 nm in UV–vis spectra, which was assignable to the closed isomer $\mathbf{2^{Ru}C}$, as shown in Fig. 1. Upon visible-light irradiation to the resultant reaction mixture, disappearance of the visible band was observed. The ring-closing and ring-opening processes could be repeated without any degradation more than 7 times. UV irradiation of a C_6D_6 solution of $\mathbf{2^{Ru}O}$ gave new sets of ^{1}H NMR signals due to two diastereomers of the closed isomers $\mathbf{2^{Ru}C}$. The ratio, 58:42, of the open isomer $\mathbf{2^{Ru}O}$ to the closed isomers $\mathbf{2^{Ru}C}$ at the photostationary state was determined by ^{1}H NMR spectroscopy. Similar changes of the signals were observed for the ^{31}P NMR spectra.

The results of the photochromic behavior of the other DTE complexes, DTE–$MCp(CO)_2$ (M = Fe ($\mathbf{1^{Fe}}$), Ru ($\mathbf{1^{Ru}}$)), DTE–FeCp(CO)PPh_3 ($\mathbf{2^{Fe}}$), DTE–FeCp(dppe) ($\mathbf{3^{Fe}}$), are summarized in Table 1. It is revealed that the structure of the metal fragments dramatically affected the photochromic properties. The photochromic data of the corresponding dinuclear DTE complexes, L_2CpM–DTE–$MCpL_2$ ($L_2 = (CO)_2$, M = Fe ($\mathbf{4^{Fe}}$), Ru ($\mathbf{4^{Ru}}$), $L_2 = (CO)PPh_3$, M = Fe ($\mathbf{5^{Fe}}$), Ru ($\mathbf{5^{Ru}}$), L_2 = dppe, Cp′ = methylcyclopentadienyl, M = Fe ($\mathbf{6^{Fe}}$)), which were reported previously [20], was also listed in Table 1. The stability of the Ru complexes during the photoreaction turns out to be superior to that of the corresponding Fe complexes. The order can be interpreted in terms of the decarbonylation process leading to decomposition. The ruthenium center with a stronger back-donation ability hinders photochemical decarbonylation to retard decomposition. The ruthenium complexes showed the reversible photochromism in a manner similar to organic DTE irrespective of the nuclearity of the complexes. Noticeably, the conversion of the mononuclear complexes to the closed isomer at the

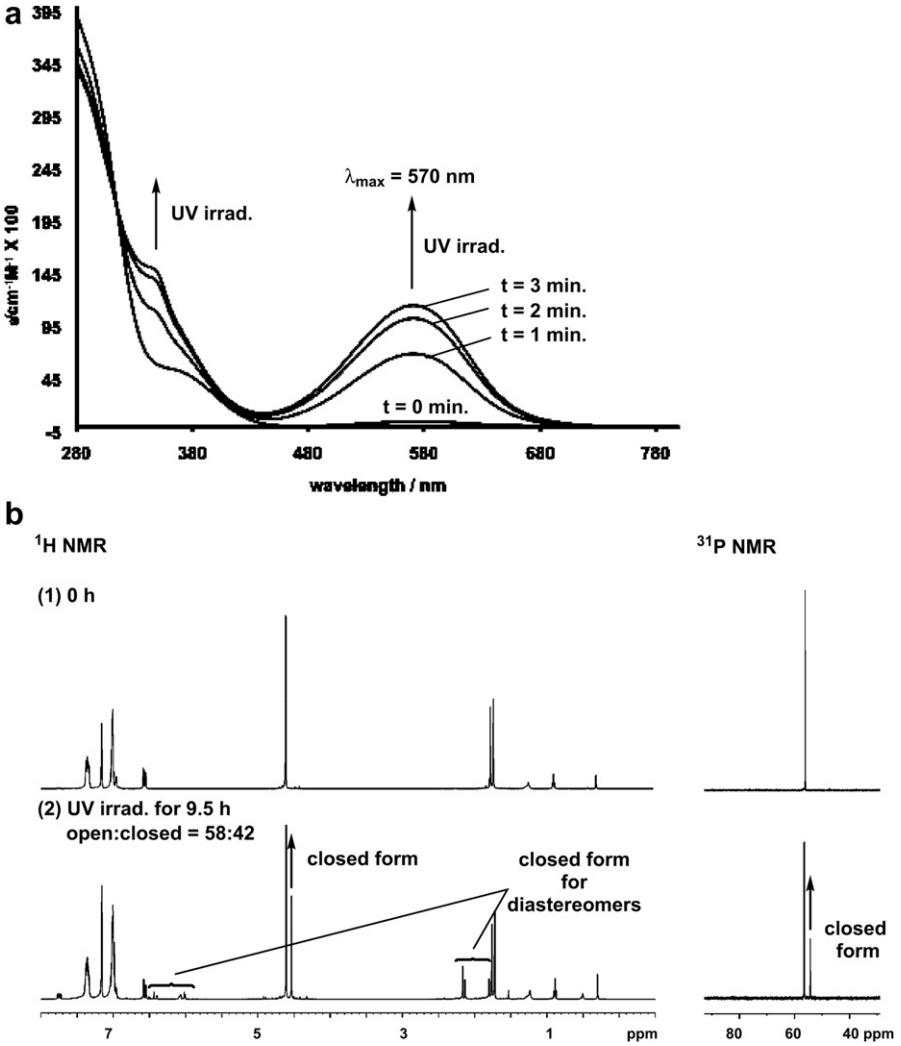
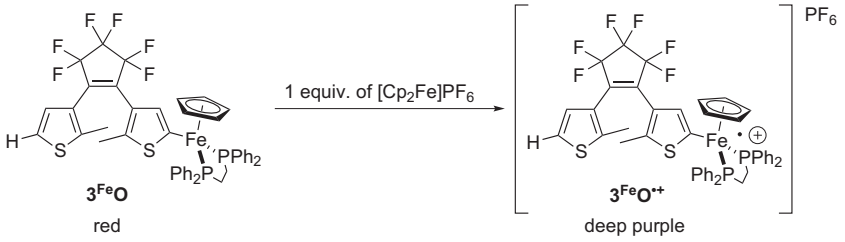


Fig. 1. (a) UV–vis in THF monitoring of photochromic behavior of $\mathbf{2^{Ru}}$ induced by UV irradiation (<360 nm, [complex] = 2×10^{-5} M). (b) ^{1}H NMR and ^{31}P NMR in C_6D_6 monitoring of photochromic behavior of $\mathbf{2^{Ru}}$ induced by UV irradiation (<360 nm, [complex] = 2×10^{-2} M). (1) $\mathbf{2^{Ru}O}$ (2) A photoequilibrated mixture of $\mathbf{2^{Ru}O}$ and $\mathbf{2^{Ru}C}$.

Table 1
Photochromic properties of the DTE complexes.

$MCpL_2$ and $(MCpL_2)_2$	$\mathbf{1}^{Fe}$	$\mathbf{4}^{Fe}$	$\mathbf{1}^{Ru}$	$\mathbf{4}^{Ru}$	$\mathbf{2}^{Fe}$	$\mathbf{5}^{Fe}$	$\mathbf{2}^{Ru}$	$\mathbf{5}^{Ru}$	$\mathbf{3}^{Fe}$	$\mathbf{6}^{Fe}$[c]
Open:closed[a]	–	61:39	62:38	36:64	–	90>:<10	58:42	30:70	–	–
Ring closure (UV)/min.[b]	–	16	2.5	24	–	–	3	30	–	–
Ring opening (vis)/min.[b]	–	4	2	4	–	–	3	8	–	–
Closed λ_{max}/nm	–	560	547	553	–	–	570	584	–	–
Recycl.	Decomp.	Decomp.	70%(2)	50%(5)	Decomp.	Decomp.	>90%(7)	70%(10)	–	–

[a] A ratio of photoequilibrated mixture in C_6D_6.
[b] A necessary time under UV/vis irradiation in THF.
[c] $\mathbf{6}^{Fe}$: $MCpL_2 = (\eta^5\text{-}C_5H_4(CH_3))Fe(dppe)$.



Scheme 3. Oxidation of the complex $\mathbf{3}^{Fe}\mathbf{O}$.

photostationary state is lower than that of the dinuclear derivatives. Especially, UV irradiation on the iron complexes bearing phosphine ligands ($\mathbf{3}^{Fe}$ and $\mathbf{6}^{Fe}$) did not induce any photoreaction including decomposition and the ring-closure reaction. These results indicated that the metal attachments strongly affect the photochromic properties of the DTE derivatives despite their distant location from the reaction site [17]. The reason for the different photoreactivities has not been clarified yet.

3.3. One-electron oxidation of the open isomers $\mathbf{3}^{Fe}\mathbf{O}$ and $\mathbf{2}^{Ru}\mathbf{O}$

It would be possible to cause a big change in a tone of color based on the redox reaction of the metal fragments. In fact, the oxidation of the red solution of $\mathbf{3}^{Fe}\mathbf{O}$ with 1 equivalent of $[Cp_2Fe]PF_6$ gave a deep purple paramagnetic radical cation species $\mathbf{3}^{Fe}\mathbf{O}^{\cdot+}$ with a visible band at 676 nm assigned to LMCT [29] (Scheme 3). CV charts of $\mathbf{3}^{Fe}\mathbf{O}$ and $\mathbf{2}^{Ru}\mathbf{O}$ as shown in Fig. 2 contained single reversible redox waves at −450 mV and 335 mV, respectively. These results suggested that the one-electron redox processes might induce reversible color change of the mononuclear DTE complexes.

There have been some reports that additional color change can be induced by combination with other stimulus including oxidation [20,22,24,25,30–36]. For example, Irie and Matsuda revealed that one-electron oxidation of the open form of the organic DTE leads to the closed form [35]. If the balance of the redox properties of the open and closed isomers are matched, the ring closure can proceed in a catalytic manner with respect to the oxidant. But, as far as the color is concerned, color change occurs only between those of the original open and closed isomers. Our group recently reported that 2e-oxidation of the DTE derivatives with two redox-active organometallic fragments, $L_2CpM\text{–}DTE\text{–}MCpL_2$ ($L_2 = (CO)PPh_3$, M = Fe ($\mathbf{5}^{Fe}$), Ru ($\mathbf{5}^{Ru}$)), leads to the ring closure giving the dicationic closed isomer $\mathbf{C}^{2+}$ [20]. Rigaut [22] and Humphrey [24] also reported on the chromic behavior induced by two-electron redox processes of the DTE derivatives with two metal fragments. These results suggest that more than three states with respect to the color can be formed in the system of the dinuclear DTE complexes. This two-electron redox process is not reversible as shown in Scheme 4 (our previous work). It is notable, in the present mononuclear

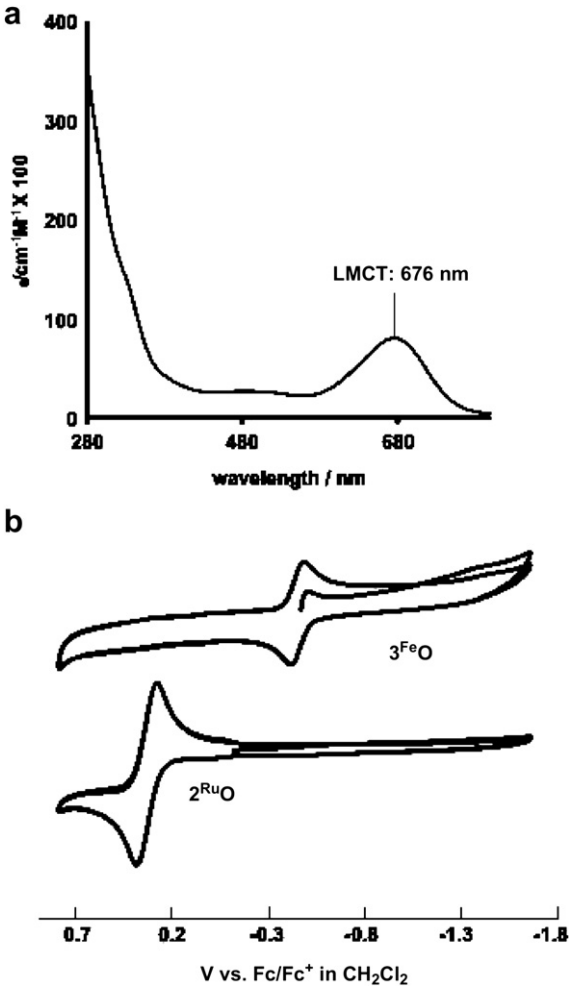
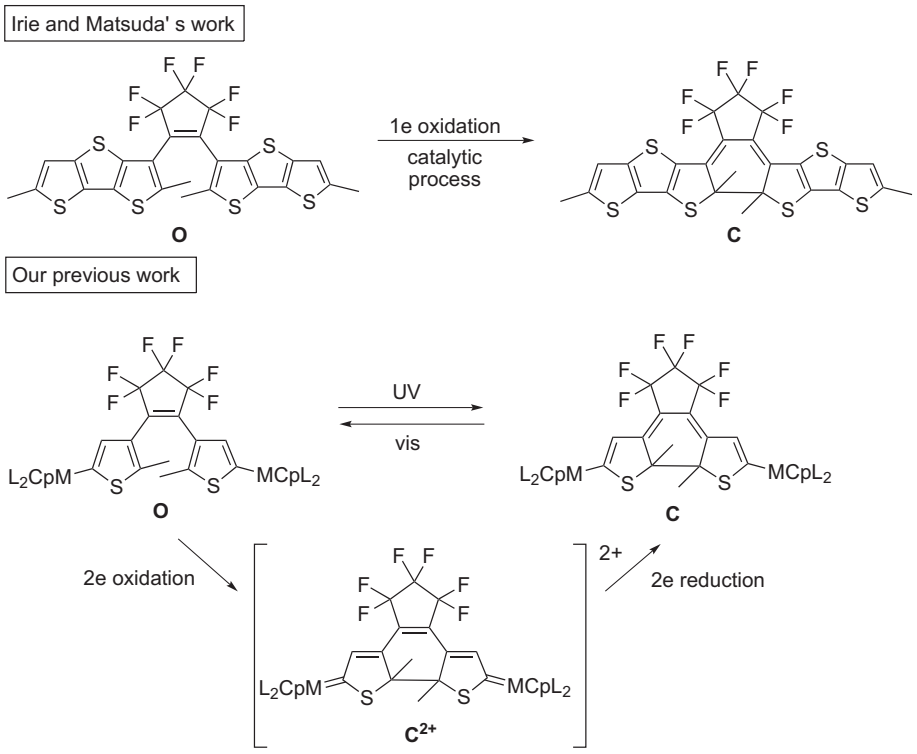


Fig. 2. (a) a UV–vis spectrum of $\mathbf{3}^{Fe}\mathbf{O}^{\cdot+}$ observed in THF ([complex] = 8×10^{-6} M). (b) Cyclic voltammograms of $\mathbf{3}^{Fe}\mathbf{O}$ and $\mathbf{2}^{Ru}\mathbf{O}$ observed in CH_2Cl_2 ([complex] = 1.0×10^{-3} M; $[Bu_4N{\cdot}PF_6] = 0.1$ M).



Scheme 4. Redox reactions of the DTE derivatives.

systems, the color of the open isomer **O** can be changed into two directions in reversible manners, i.e. photochemical ring closure/opening process of DTE moiety between **O** and **C** in $\mathbf{1}^{Ru}$ and $\mathbf{2}^{Ru}$ and 1e-redox process of the organometallic fragment between **O** and $\mathbf{O}^{\bullet+}$ in $\mathbf{2}^{Ru}$ and $\mathbf{3}^{Fe}$, as described above.

4. Conclusion

The synthesis of a series of DTE derivatives, DTE–$MCpL_2$ {M = Fe, Ru; Cp = η^5-cycopentadienyl; L_2 = $(CO)_2$, $(CO)PPh_3$, dppe (dppe = $Ph_2PCH_2CH_2PPh_2$)}, with a directly σ-bonded, redox-active organometallic attachment has been achieved using conventional transmetalation of the thienyllithium reagent with metal-halides and subsequent ligand exchange under UV irradiation. Their photochromic behavior is dramatically dependent on the central metal, nuclearity and ligands, meaning that the metal units can affect the reactivity of the DTE moiety in spite of the long distance between the metal terminal and the DTE core. The mononuclear ruthenium complexes exhibited photochromic performance better than the corresponding iron complexes. Electrochemical investigation of $\mathbf{2}^{Ru}$ and $\mathbf{3}^{Fe}$ showed the reversible redox behavior in contrast to the corresponding dinuclear complexes, which underwent the ring closure upon oxidation. As a result, the redox-active mononuclear DTE complexes show two different chromic behavior, i.e. photochromic and electrochromic behavior. Thus, the mononuclear systems turn out to be a triplet coloring system.

Acknowledgments

We are grateful to Dr. S. Nakamura (Science & Technology Research Center Inc., Mitsubishi Chemical Group) for helpful discussion on the reaction mechanism. This research was financially supported by the Ministry of Education, Culture, Sports, Science and Technology of the Japanese Government (the Grants-in-Aid for Scientific Research on Priority Areas, "New Frontiers in Photochromism (No. 471)"), which is gratefully acknowledged. H. Li is grateful to the G-COE (Tokyo Institute of Technology Global COE Program) "Education and Research Center for Emergence of New Molecular Chemistry" and Akimoto Tatsunoko International Scholarship Foundation. A generous gift of perfluorocyclopentene, the starting compound for DTE, from ZEON Corporation is gratefully acknowledged.

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