Photochemical Reduction of (η^5-Cyclopentadienyl)(1,2-disubstituted 1,2-ethylenedichalcogenolato)cobalt(III) and (η^5-Cyclopentadienyl)-(1,2-benzenedithiolato)cobalt(III) Complexes in the Presence of Triethanolamine

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(Received November 13, 1991)

The title complexes, $[Co(cp)(S_2C_2Y_2)]$(cp=η^5-C_5H_5) (**1**) (**a**: Y=Ph, **b**: Y=2-pyridyl, **c**: Y=4-pyridyl, **d**: Y=$-CO_2Me$, **e**: Y=−CN), $[Co(cp)(S_2C_6H_4)]$ (**2**), $[Co(cp)(Se_2C_2Ph_2)]$ (**3**), and $[Co(cp)(SeSC_2Ph_2)]$ (**4**), are photochemically reduced to give one-electron reduced species, Co(II) complexes, under UV-irradiation in the presence of an electron donor, triethanolamine (TEOA), in acetonitrile solutions. The photoreduction is wavelength dependent. The 313 nm light is the most effective (Φ=0.002—0.018) for all the complexes used, and the light of wavelength longer than 365 nm is ineffective for the photoreduction of **1**—**4**. The irradiation with 254 nm light brings about decomposition of the complexes.

For the square planar bis(dithiolato) metal complexes of Ni triad, some photochemical reactions have been reported. These are: The photochemical oxidations of $[M\{(S_2C_2(CN)_2\}_2]^{2-}$ (M=Ni, Pt, Pd) in polychloromethane solvents[1] and in polymer film supported on SnO_2,[2] and the photochemical reductions of the complexes $[M(S_2C_2Ar_2)_2]^{2-}$ (M=Ni, Pt) by an electron transfer from $\{[Ru(bpy)_3]^{2+}\}^*$, [3,4] from EDTA[5] and from the cation radical of methylviologen.[5] These redox behaviors are one of the characteristics[6] of bis(dithiolato)-metal complexes in photoreactions. However, the photochemical reaction of the mono(dithiolato)metal complex with a cyclopentadienyl ligand has been less investigated than those of the square planar bis(dithiolato)metal complexes because of the difficulties in the synthesis of substituted derivatives. By a convenient synthetic method developed recently by Bönnemann et al.,[7] the syntheses of the complexes of the type $[Co(cp)(E,E'C_2XY)]$ (X,Y=substituents on the 1,2-ethylenedichalcogenolato ligand) (**1**: E=E′=S, **3**: E=E′=Se, **4**: E=S, E′=Se) have become possible. We have reported their characteristic chemical[8—10] and electrochemical[11] behaviors ascribable to the unique electron configuration of the metalladithiolene ring.

We found the first example of the photoreduction of the complexes **1**,**3**,**4**, and their benzenedithiol analog, $[Co(cp)(S_2C_6H_4)]$ (**2**), under UV-irradiation in the presence of an electron donor, triethanolamine (TEOA), and wish to report here the results of the reactions in connection with the excited state involved in this reaction.

Experimental

Measurements. IR spectra were recorded on a Hitachi 260-50 grating spectrophotometer. ^1H NMR spectra were obtained on a JEOL FX-270 spectrometer. Mass spectra were obtained by using a JEOL JMA D-300 spectrometer. The X-band ESR spectra were recorded on a JEOL JES-RE3X spectrometer. Cyclic voltammograms were obtained by using a Huso Polarograph Model 312 and a Huso Potential Scanning Unit Model HECS 321B connected with a Riken Denshi X-Y Recorder F-42DG.

Preparation Methods of the Complexes 1—4. The complexes **1a**—**d**, **3**,[10] and **4**[10] were prepared according to the one-pot method reported by Bönnemann et al.[7] from $[Co(cp)(CO)_2]$ or [Co(cp)(cod)], elemental chalcogen (elemental selenium in the case of **3**, elemental sulfur and elemental selenium in the case of **4**), and disubstituted alkynes. The complex **2** was prepared by the method reported by Heck[12] from $[Co(cp)I_2(CO)]$ and 1,2-benzenedithiol. The complex **1e** was prepared from $[Co(cp)I_2(CO)]$ and disodium salt of *cis*-1,2-dicyano-1,2-ethylenedithiol according to the procedure of Locke and McCleverty.[15] Typical preparation procedures are exemplified by the cases of **1c** and **2**.

(η^5-Cyclopentadienyl{1,2-Di(4-pyridyl)-1,2-ethylenedithiolato}cobalt (III)[14] (1c). Di(4-pyridyl)acetylene (0.62 g, 3.44×10^{-3} mol), elemental sulfur (0.22 g, 8.6×10^{-4} mol), and [Co(cp)-(cod)] (0.70 g, 3.47×10^{-3} mol) were placed in a 50 cm^3 three necked flask; they were dissolved in 25 cm^3 of xylene under a stream of argon. This xylene solution was refluxed for 4 h. During the reaction, the color of the solution changed from brown to blue. After the reaction, the solvent was removed under reduced pressure and the residue was submitted to flash column chromatography on silica gel (300 mesh). After a brown band was eluted with dichloromethane, a blue band was eluted with ether–acetone (3:1 v/v) and acetone. This fraction was further chromatographed on silica gel (ether–acetone 3:1 v/v). A dark violet crystalline solid was obtained after the evaporation of the solvents. Yield, 185 mg (15%). ^1H NMR ($CDCl_3$) δ=5.47 (5H, s, C_5H_5), 8.48 (4H, m, 2,6-position of 4-pyridyl), and 7.17 (4H, m, 3,5-position of 4-pyridyl). MS(EI, 70 eV) (*m*/*z*, rel intensity), 368 (M^+, 52), 304 (M^+-2S, 5), 188($M^+-C_2(4Py)_2$, 100), 180 ($4PyC_24Py^+$, 6), and 124 ($(Co(cp)^+$, 36).

(η^5-Cyclopentadienyl)(1,2-benzenedithiolato)cobalt(III) (2). The complex was prepared from $[Co(cp)I_2(CO)]$ and 1,2-benzenedithiol. To a methanol solution of disodium 1,2-

benzenedithiol (142 mg, 1 mmol in 10 cm^3) was added dropwise the methanol solution of [Co(cp)I_2CO)] (407 mg, 1 mmol in 90 cm^3) over 30 min. The color of the solution immediately changed to blue-violet. The reaction mixture was stirred for 1 h at room temperature, and then the solvent was removed under reduced pressure. The residue was submitted to flash column chromatography on silica gel (230—400 mesh, eluent: hexane-dichloromethane=1 : 1 v/v). The complex **2** was obtained as a black crystalline solid. Mp 195—196 °C. Yield: 190 mg (70%). Found: C, 50.63; H, 3.52%. Calcd for $C_{11}H_{19}S_2Co$: C, 50.76; H, 3.45%. MS (EI, 70 eV) (*m*/*z*, rel intensity) 264 (M^+, 100), 230 (M^+-SH_2, 62), 199 (M^+ −cp, 24), and 124 $(Co(cp))^+$, 7).

Electrochemistry. The complexes **1**—**4** show reversible waves in their cyclic voltammograms (CV).[11] Reversible half-wave reduction potentials ($E^r_{1/2}$(red)) of the complexes were obtained from the CV's in acetonitrile-0.1 mol dm^{-3} tetraethylammonium perchlorate (TEAP) solutions. The potentials were all measured versus Ag| 0.1 mol dm^{-3} $AgClO_4$ in acetonitrile solutions. Controlled potential electrode reduction of the complex **1e** was carried out at −0.8 V for acetonitrile solution of **1e** by using an OTTLE (optically transparent thin layer electrode) cell. After reduction was completed, electronic absorption spectra of **1e** were measured; then **1e** was reoxidized completely at 0 V, and again absorption spectra were measured. The absorption spectra of **1e** before and after the reduction were already reported in the literature.[11]

Irradiation. An acetonitrile solution of the complexes **1**—**4** (6×10^{-5} mol dm^{-3}) and triethanolamine (TEOA, 1.3×10^{-2} mol dm^{-3}) was placed in a quartz cell (1 cm×1 cm×4 cm) with a long neck fused with a side arm for the solvent reservoir. The sample solution in a cell was degassed by repeated freeze-pump-thaw cycles (5 times), and then it was irradiated with a high pressure Hg lamp (Riko Kagaku Sangyo, UV-L 400P, 400 W, with a Pyrex filter, $\lambda>280$ nm) or with a low pressure Hg lamp (Taika Kogyo, 16 W, for the irradiation of 254 nm light, the quartz cell containing the sample solution was placed in the center of the spiral tube of the lamp). For the determination of quantum yields for photoreduction of the complexes, the monochromatic light (254-, 313-, and 365-nm light) was selected from the light of super high pressure Hg (Osram HBO-200, 200 W) lamp by using a Shimadzu-Bausch & Lomb grating monochrometer. Chemical actinometry was carried out by using potassium ferrioxalate.[15]

Sample Solution for the Measurement of ESR Spectra. Irradiated sample. An acetonitrile solution (4 cm^3) of **1e** and TEOA (**1e**: 1.5×10^{-4} mol dm^{-3}; TEOA: 2.3×10^{-2} mol dm^{-3}) in a quartz cuvette (1 cm×1 cm×4 cm) with a stopcock was deaerated under a stream of argon for 2 h. Then it was irradiated with a high pressure Hg lamp (Ushio USH 500D, 500 W; filtered by using Toshiba UV 31 filter, $\lambda>313$ nm)) until the characteristic absorption of **1e** (500—600 nm) reached to about 50% of the initial absorption. Then, about 0.4 cm^3 of the solution was transferred under a stream of argon into the flat cell for ESR measurement, the cell was sealed with a Teflon cap. Into the rest of the solution, air was introduced, and UV-vis spectra of the solution were measured in order to confirm the spectra to be identical with those of **1e** before the irradiation. Electrolyzed sample. The electrochemically reduced **1e** was generated by electrolyzing an acetonitrile solution of **1e** (1×10^{-3} mol dm^{-3}) with a platinum gauze electrode.[11] After the exhaustive electrolysis at −0.8 V, the solution was transferred into the normal ESR sample tube under a stream of argon.

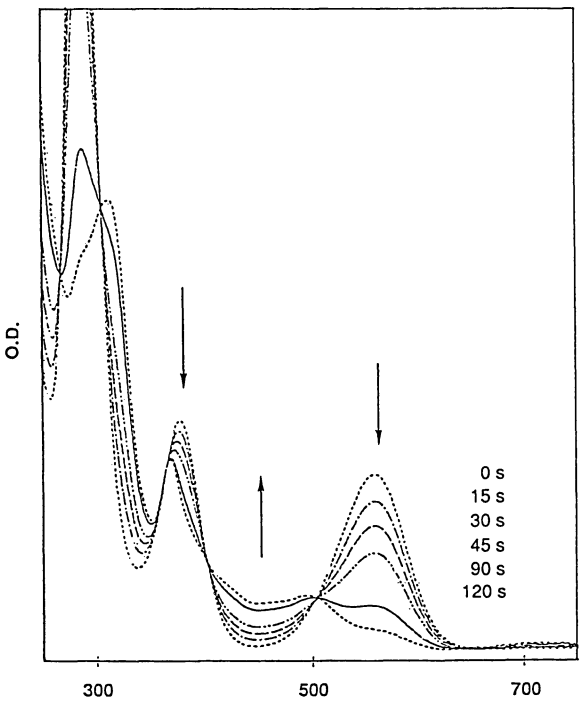


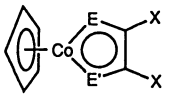
Fig. 1. UV-vis Spectral change of **1e** under irradiation with a high pressure Hg lamp (400 W, with a Pyrex filter). Concentrations: [**1e**]=5×10^{-5} mol dm^{-3}; [TEOA]=1.0×10^{-2} mol dm^{-3} in acetonitrile.

Table 1. Absorption Maxima of the Complexes in Acetonitrile Solutions

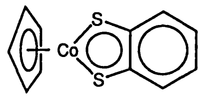
	Complex [Co(cp) (E,E′C_2XY)]	$\lambda_{max}(\varepsilon/mol^{-1}\,dm^3\,cm^{-1})$		
1a	(E=E′=S, X=Y=-Ph)	600 (8550)	424 (sh) (1210)	295 (33500)
1b	(E=E′=S, X=Y=-²Py)	579 (7830)	370 (sh) (4000)	293 (32807)
1c	(E=E′=S, X=Y=-⁴Py)	579 (7500)	370 (sh) (4750)	293 (31000)
1d	(E=E′=S, X=Y=-CO_2CH_3)	550 (7540)	362 (sh) (4990)	280 (28700)
1e	(E=E′=S, X=Y=-CN)	559 (5260)	379 (sh) (7090)	287 (32566)
2	(E=E′=S, XY=C_6H_4)	566 (11702)	—	289 (35108)
3	(E=E′=Se, X=Y=-Ph)	612 (8370)	472 (1980)	304 (34500)
4	(E=S, E′=Se, X=Y=Ph)	610 (8730)	445 (2000)	299 (35600)

Results and Discussion

Photochemical Behavior of Complex. The complexes used in this study are shown below. The absorption maxima in UV-vis spectra of the complexes **1a**—**e**, **2**, **3**, and **4** are listed in Table 1. When a degassed acetonitrile solution of the complex (6×10^{-5} mol dm^{-3}) and triethanolamine (TEOA) (1.3×10^{-2} mol dm^{-3}) was irradiated with a high pressure mercury lamp ($\lambda>280$ nm) for 2—10 min, a drastic change of UV-vis spectra was observed, as exemplified by the case of **1e** (Fig. 1). Similar spectral changes were observed in the cases of **1a**—**d**, **2**,**3**, and **4**.



1:E=E'=S; a:X=Ph, b:X=^{2}Py, c:X=^{4}Py, d:X=CO_2Me, e:X=CN
3:E=E'=Se, X=Ph
4:E=Se,E'=S,X=Ph



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These spectral changes have the following common features: (i)during the irradiation, the UV-vis absorption spectra change with some isosbestic points and the characteristic absorption bands of the original complex (550—600 nm) decrease, and (ii) when air is introduced into the system after the irradiation, the absorptions around 550—600 nm region regenerate and the whole spectra become almost identical with those of the complex before the irradiation (recovery of the original complex, 93—99%). These spectral changes are not observed in any system which does not contain triethanolamine or in any system which was kept in the dark. Neither acetonitrile nor TEOA absorbs light of the wavelength longer than 313 nm. The UV-vis[11] and ESR spectra of the species generated by controlled potential reduction are identical with those of photochemically produced species. These results strongly suggest that the photochemically produced species is a reduced form of the original complex. The ESR spectra of electrochemically reduced **1e** and the photoproduct are shown in Fig. 2 (a and b). They are assigned as Co(II) species, since this species has paramagnetic d^7 electron configuration.[16] These results strongly suggest that an electron is localized on the cobalt atom in the reduced form of **1e**. Based on the results described above, the following sequence of processes are suggested for the redox behavior of the complexes, **1**—**4**: (i) in the excited state of the complexes, their reduction potentials become positive enough to accept an electron from the ground state TEOA, (ii) an electron transfer from the ground state TEOA to the excited state of the complex occurs to produce Co(II) species, and (iii) an electron transfer from the Co(II) species to oxygen regenerates the original Co(III) complex. These processes are schematically shown in Scheme 1.

Wavelength Dependency of the Photoreduction of the Complex. Although all of the complexes, **1**—**4**, have absorptions in the wavelength region of 550—600 nm, the irradiation of the light of wavelength longer than 365

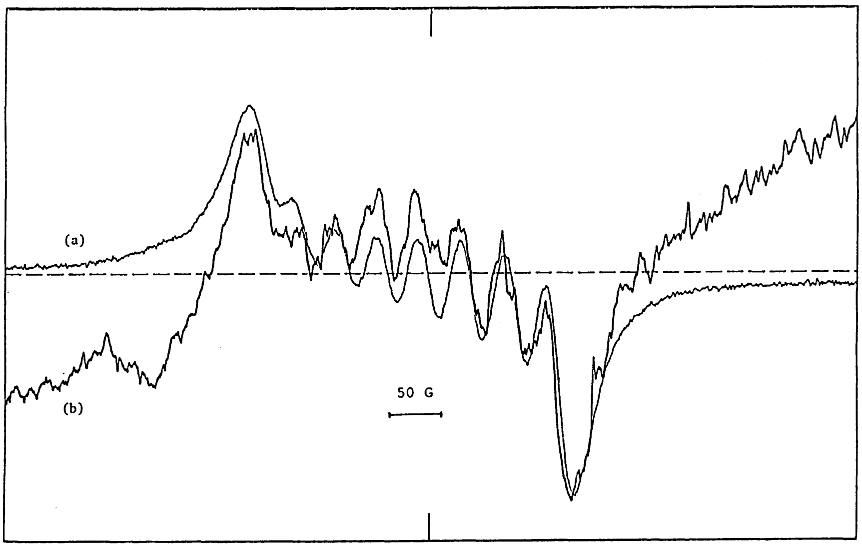
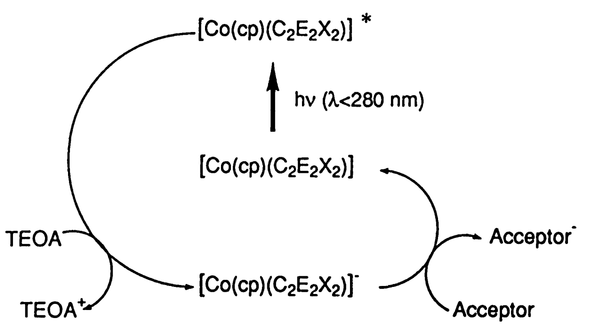


Fig. 2. ESR Spectra of the electrochemically reduced **1e** (a) and photochemically produced species from **1e** (b). Concentrations: (a) [**1e**]=1.0×10^{-3} mol dm^{-3} in acetonitrile (measured at room temperature. Conditions of reduction, see text and Ref. 11); (b) [**1e**]= 1.5×10^{-4} mol dm^{-3}, [TEOA]= 2.3×10^{-2} mol dm^{-3} in acetonitrile {measured at room temperature after the irradiation with a high pressure Hg lamp (400 W, with a Pyrex filter) for 2 h}. The signal was accumulated (10 times).



Scheme 1.

nm gave no reduction product. Therefore, the excitation of the transition in the visible region does not contribute to the photoreduction of the complexes. As TEOA has low absorption (ε_{254}: 60 $dm^3\,mol^{-1}\,cm^{-1}$) in the wavelength region shorter than 260 nm, more than 95% of the incident light is absorbed by TEOA under the conditions (**1e**: 1.4×10^{-4} $mol\,dm^{-3}$, TEOA: 5×10^{-1} $mol\,dm^{-3}$) used in this experiment. However, the irradiation of 254 nm light onto this system gave reduced **1e**. When the concentration of TEOA is low enough to absorb nearly 50% (**1e**: 5×10^{-5} $mol\,dm^{-3}$; TEOA: 1.0×10^{-2} $mol\,dm^{-3}$) of the incident light, the photoreduction was drastically reduced and the decomposition of **1e** was observed. Therefore, the excitation of **1e** with 254 nm light mainly brings about the decomposition of **1e** (quantum yield for disappearance at 254 nm is 0.9). The processes in which excited TEOA reduces **1e** also exist only under the condition that most 254 nm light is absorbed by TEOA. The wavelength dependences of the quantum yields for the photoreduction of complexes **1**—**4** were determined for the light of wavelength 254-, 313-, and 365 nm. The results are listed in Table 2, together with the reversible half-wave reduction potentials ($E^r_{1/2}$(red)) of the complexes. The data in Table 2 show that the 313 nm light is the most effective for the photoreduction for all the complexes used and the 254 nm light causes the fast decomposition of the complexes. If the oxidation potential of TEOA is energetically sufficient to reduce the excited state of the complexes, a linear relationship between the reduction half-wave potentials of the complexes and the quantum yield of photo-reduction at 313 nm should be established. Except for **1e**, a general tendency that the complex having more positive $E_{1/2}$ value shows higher quantum yield can be observed. The fact that the relationship between the quantum yield at 313 nm and $E^r_{1/2}$(red) is not linear (Fig. 3) suggests that the efficiency of the electron transfer process from TEOA to the excited complexes is not solely governed by the reduction potential of the complex and, thus that another

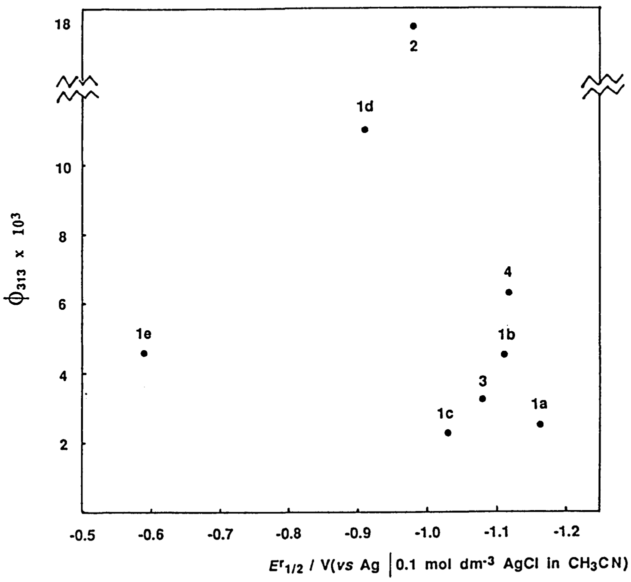


Fig. 3. Correlation between the quantum yields for reduction at 313 nm and the reduction half-wave potentials of the complexes (**1a**—**4**).

Table 2. Wavelength Dependence of Quantum Yields for the Photoreduction[a)] and Half-Wave Reduction Potentials of the Complexes **1**—**4**

Complex [Co(cp) ($E_2C_2X_2$)][b)]			Quantum yield			$E^r_{1/2}$(red)
	E	X	254 nm	313 nm	365 nm	V[c)]
1a	S	Ph	d)	0.0025	0	−1.16
1b	S	²Py	d)	0.0045	2×10^{-5}	−1.11
1c	S	⁴Py	—	0.0023	3×10^{-5}	−1.03
1d	S	CO_2Me	—	0.011	0	−0.91
1e	S	CN	d)	0.0046	8×10^{-5}	−0.59
2	S	C_6H_4	—	0.018	6×10^{-4}	−0.98
3	Se	Ph	d)	0.0032	0	−1.08
4	Se/S	Ph	—	0.0063	0	−1.12

a) The amount of reduction product was obtained for the irradiation of 30 min where the linear relationship between irradiation time and the amount of reduction product was established. b) Concentration of complex: [**1a**], [**1b**], [**3**], and [**4**]: 2.5×10^{-5}, [**1c**]: 2.42×10^{-5}; [**1d**]: 2.52×10^{-5}, [**1e**]: 3.30×10^{-5}, [**2**]: 3.25×10^{-5} $mol\,dm^{-3}$ in CH_3CN. [TEOA]: 1.4×10^{-3} $mol\,dm^{-3}$. c) Volt vs. Ag| 0.1 M $AgClO_4$ in CH_3CN. For the conditions of measurements, see Ref. 11. d) Decomposition. The quantum yield for disappearance was about 0.9 for **1e**. Concentrations: [**1e**], 7.91×10^{-5} $mol\,dm^{-3}$; [TEOA], 1.4×10^{-3} $mol\,dm^{-3}$.

factor governing the electron transfer reaction between TEOA and the excited complex may exist.

Excited State of the Complex Involved in the Photoreduction. The complexes **1**—**4** have at least 4 absorption bands in the wavelength region of 700—250 nm. The absorption in the region of 550—600 nm (ε 300—7500 mol dm^{-3} cm^{-1} for **1**,**3**,**4**, and 1200 dm^3 mol^{-1} cm^{-1} for **2**) can be attributed to the π–π^* transition of the metalladithiolene ring,[17] since this band is not present in their reduced form or in the 1 : 1 adducts of the complex **1** or **2** with alkyne,[8] with alkylidene,[9] and with quadricyclane (these adducts have piano-stool structures around Co), and is substituent dependent (electron-attracting substituent causes the blue-shift of this band[7]). The excitation of these transitions do not contribute to the photoreduction of the complexes. The excited states of **1**—**4** responsible for the photoreduction can be considered as LMCT transitions of the cobaltadithiolene ring which lies in the 280—320 nm region. However, it is difficult to assign this band exactly by comparison of the spectra of **1**—**4** with those of square planar bis(1,2-ethylenedithiolato)nickel complex, since in the latter complex there are many transitions in this region.[17] The absorption around 250 nm contains π–π^* transitions of the cyclopentadienyl ring and the higher energy π–π^* of dithiolene ring, and the production of these excited states causes decomposition of the complex. The absorption in the region of 350—400 nm only slightly contributes to the photoreduction. This absorption band may contain, to a small extent, charge transfer transition (L–M*, M–L*) of both σ and π types.[17]

The authors are grateful for financial support from the Ministry of Education, Science and Culture (Grant-in-Aid for Scientific Research on Priority Areas on Organic Unusual Valancy Nos. 02247102 and 03233102, and Grant-in-Aid for Scientific Research Nos. 02640406 and 03640464), and from the Asahi Glass Foundation.

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