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A New Azaferrocenophane with an Azobenzene-Containing Ligand. Remote Control of Photoisomerization of the Azobenzene Group by Redox of the Iron Center

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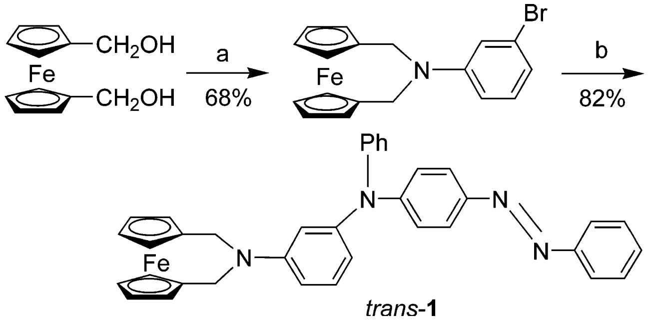
Summary: Azobenzene-introduced azaferrocenophanes have been newly synthesized by coupling reactions catalyzed by transition-metal complexes. The photochemical response of the azobenzene group is controlled by the oxidation state of the molecule.

Organotransition-metal complexes that have azobenzene-containing ligands are of recent interest because they can exhibit photochemical properties which are not achieved by azobenzene and its organic derivatives.[1] Connecting the metal center and azobenzene with an organic linker having suitable length and/or a π-conjugated system enables communication of the electronic states between the metal and the azobenzene group. Nishihara reported the unique properties of *m*-ferrocenylazobenzene, in which azobenzene is directly bonded to a Cp ligand of ferrocene.[2] One-electron oxidation of the compound decreased the thermodynamic stability of the *cis*-azobenzene group bonded to ferrocene. This oxidation led to the formation of a trans-rich mixture in the Fe(III) state under irradiation with a single green light and its conversion to a cis-rich mixture upon electrochemical reduction to Fe(II). This control of photoinduced cis−trans isomerization of the azobenzene by changing the electronic state of the metal center formed a smart on−off switching system.[3] Alternatively, the introduction of a functional group to the organic azobenzene can accelerate or retard the cis−trans isomerization, depending on the kind of group.[4] Thus,the electronic character of the substituent bonded to azobenzene changes the photochemical properties.

Scheme 1. Synthesis of *trans*-1[a]



trans-**1**

[a] Conditions: (a) 3-bromoaniline, $RuCl_2(PPh_3)_3$ (5 mol %), 180 °C, NMP; (b) (4-phenylamino)azobenzene, $Pd_2(dba)_3$ (dba = dibenzylidenacetone, 1.3 mol %), NaO-*t*-Bu (1.5 equiv), P(*t*-Bu)$_3$ (7.5 mol %), 100 °C, toluene.

We recently found that azaferrocenophanes undergo reversible electron transfer between the Fe and N atoms in the electrochemically oxidized state.[5] Electronic communication between the azaferrocenophane, showing reversible redox behavior, and the substituent bonded to azobenzene would provide a new approach for the control of photochemical output of the molecule by electrochemical stimuli. In this paper, we report the preparation of a new azaferrocenophane containing an azobenzene group and its electrochemical control over the photochemical response via intramolecular electron transfer.

Scheme 1 summarizes the preparation of the azaferrocenophane *trans*-**1**, which contains an azobenzene group, via coupling reactions catalyzed by Ru[6] and Pd complexes.[7,8] The N atom, bonded to a phenyl carbon of

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(1) (a) Coe, B. J.; Jones, C. J.; McCleverty, J. A.; Bloor, D.; Kolinsky, P. V.; Jones, R. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1485. (b) Lee, S.-M.; Marcaccio, M.; McCleverty, J. A.; Ward, M. D. *Chem. Mater.* **1998**, *10*, 3272. (c) Barlow, S.; Bunting, H. E.; Ringham, C.; Green, J. C.; Bublitz, G. U.; Boxer, S. G.; Perry, J. W.; Marder, S. R. *J. Am. Chem. Soc.* **1999**, *121*, 3715. (d) Walter, D. G.; Compbell, D. J.; Mirkin, C. A. *J. Phys. Chem. B* **1999**, *103*, 402. (e) Miyaki, Y.; Onishi, T.; Kurosawa, H. *Chem. Lett.* **2000**, 1334. (f) Murata, M.; Yamada, M.; Fujita, T.; Kojima, K.; Kurihara, M.; Kubo, K.; Kobayashi, Y.; Nishihara, H. *J. Am. Chem. Soc.* **2001**, *123*, 12903. (g) Muraoka, T.; Kinbara, K.; Kobayashi, Y.; Aida, T. *J. Am. Chem. Soc.* **2003**, *125*, 5612.

(2) Kurihara, M.; Hirooka, A.; Kume, S.; Sugimoto, M.; Nishihara, H. *J. Am. Chem. Soc.* **2002**, *124*, 8800.

(3) Other examples of a dual-response system: (a) de Silva, A. P.; McClenagham, N. D. *J. Am. Chem. Soc.* **2000**, *122*, 3965. (b) Lukas, A. S.; Bushard, P. J.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2001**, *123*, 2440. (c) Alvarez, J.; Ren, T.; Kaifer, A. E. *Organometallics* **2001**, *20*, 3543.

(4) (a) Tsutsumi, O.; Kitsunai, T.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 355. (b) Nishimura, N.; Sueyoshi, T.; Yamanaka, H.; Imai, E.; Yamamoto, S.; Hasegawa, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1381. (c) Nishimura, N.; Kosako, S.; Sueishi, Y. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1617. See also: (d) Nihei, M.; Kurihara, M.; Mizutani, J.; Nishihara, H. *J Am. Chem. Soc.* **2003**, *125*, 2964.

(5) (a) Yamaguchi, I.; Sakano, T.; Ishii, H.; Osakada, K.; Yamamoto, T. *J. Organomet. Chem.* **1999**, *584*, 213. (b) Sakano, T.; Horie, M.; Osakada, K.; Nakao, H. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 2059.

(6) (a) Murahashi, S.-I.; Kondo, K.; Hakata, T. *Tetrahedron Lett.* **1982**, *23*, 229. (b) Tsuji, Y.; Huh, K. T.; Ohsugi, Y.; Watanabe, Y. *J. Org. Chem.* **1985**, *50*, 1365. (c) Tsuji, Y.; Huh, K. T.; Yokoyama, Y.; Watanabe, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 1575.

(7) (a) Hartwig, J. F.; Richards, S.; Barañano, D.; Paul, F. *J. Am. Chem. Soc.* **1996**, *118*, 3626. (b) Hartwig, J. F. *Synlett* **1997**, 329. (c) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 8232. (d) Alcazar-Roman, L. M.; Hartwig, J. F.; Rheingold, A. L.; Liable-Sands, L. M.; Guzei, I. A. *J. Am. Chem. Soc.* **2000**, *122*, 4618.

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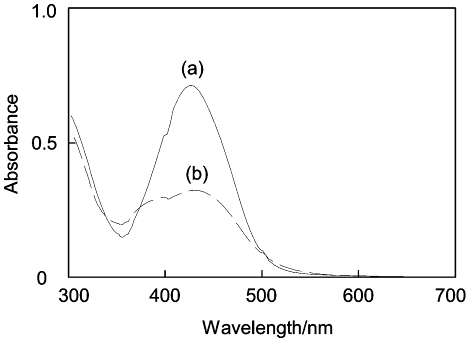

Figure 1. UV−vis spectra of *trans*-**1** in toluene (a) before irradiation and (b) after irradiation at 420 nm from a cutoff-filtered xenon lamp for 1 h at 20 °C (photostationary state).

the azobenzene group, is connected to the N atom of the ferrocenophane group by a *m*-phenylene group.

X-ray crystallography of the azaferrocenophane revealed a structure with a *trans*-azobenzene group.[9] Figure 1 shows the absorption spectra of *trans*-**1**, which exhibits a $\pi-\pi^*$ transition at 420 nm ($\epsilon = 31\,500$ M^{-1} cm^{-1}). Irradiation of the solution at 420 nm decreases the absorption because of photoinduced isomerization of the *trans*-azobenzene group to its cis form. An n−π^* transition of the *cis*-azobenzene group much weaker than the $\pi-\pi^*$ transition of the *trans*-azobenzene group was reported in many organic azobenzene derivatives.[10] This isomerization generates a photostationary state, which contains mainly the compound with a *cis*-azobenzene unit. The azaferrocenophane generated by irradiation undergoes thermal isomerization to regenerate *trans*-**1**. This isomerization is completed in 24 h at 10 °C (0.5 h at 70 °C).

The cyclic voltammogram of *trans*-**1** shows one reversible redox and one irreversible oxidation, as shown in Figure 2. The first wave is assigned to electrochemical oxidation and reduction of the Fe center, while the second wave at a higher potential is due to the electrochemical oxidation of the organic moiety.[11,12] Electrochemical oxidation of **1** in the photostationary state at 0.4 V (vs Ag$^+$/Ag) led to a solution whose spectrum is similar to that of *trans*-**1**. This result is rationalized by assuming a significant acceleration of the thermal isomerization of the *cis*-azobenzene to the trans form. Electrochemical oxidation of a toluene solution of *trans*-**1** at 0.4 V (vs Ag$^+$/Ag) by a flow electrolysis method and subsequent irradiation of this solution at 420 nm caused a slight decrease of the absorption due to photoisomerization of the *trans*-azobenzene to the cis isomer,[13] and the spectrum rapidly returned to that of *trans*-**1**, as a result of the rapid thermal isomerization of the *cis*-azobenzene group. The thermal isomerization was monitored by the spectroscopic change at 10 °C. Completion of the isomerization required a time shorter than 5 min at that temperature. Figure 3 shows a comparison of first-order plots of the reaction to those of the thermal isomerization of the isomer mixture of **1** in the photostationary state to pure *trans*-**1**. The first-order rate constant of the thermal reaction of **1** after the electrochemical oxidation (1.0×10^{-2} s^{-1}; 283 K) is much faster than that without electrochemical oxidation (1.4×10^{-4} s^{-1}). Thus, the *cis*-azobenzene group of the oxidized form of **1** undergoes much more rapid isomerization to the trans form than does compound **1** without electrochemical oxidation.

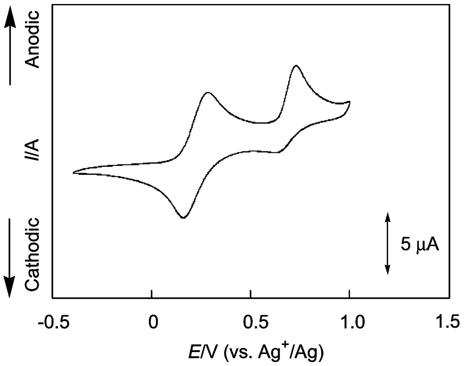

Figure 2. Cyclic voltammogram of *trans*-**1** (1.0 mM) in CH_2Cl_2 containing 0.10 M *n*-Bu_4NPF_6 and 25 °C. Sweep rate: 0.10 V s^{-1}. $E_{1/2} = 0.22$ V and $E_{pa} = 0.73$ V.

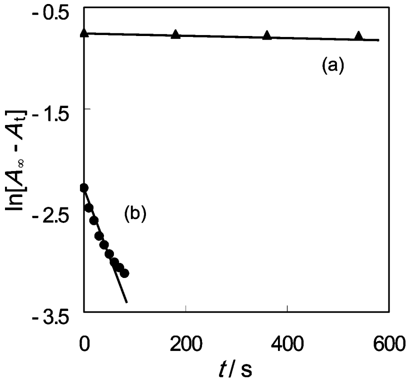

Figure 3. First-order plots of thermal isomerization (283 K) of *cis*-**1** in the photostationary state (a) without oxidation and (b) after oxidation at 0.4 V. A_t denotes the absorption at *t*.

Scheme 2 summarizes a mechanism that accounts for rapid isomerization of the oxidized species. A one-electron oxidation of *cis*-**1** would form the Fe(III) complex, which could easily be converted into *cis*-**A** and *cis*-**B**, having an Fe(II) center and a cation radical at the N atom,[11] via electron transfer among the Fe and two N atoms.[5] *cis*-**B** is responsible for the rapid isomeriza-

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[8] (a) Guram, A. S.; Rennels, R. A.; Buchwald, S. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1348. (b) Wolfe, J. P.; Wagaw, S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 7215. (c) Wagaw, S.; Rennels, R. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 8451. (d) Singer, R. A.; Sadighi, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 213. (e) Old, D. W.; Harris, M. C.; Buchwald, S. L. *Org. Lett.* **2000**, *2*, 1403.

[9] Crystal data for *trans*-**1**: $C_{36}H_{30}FeN_4$, $M_r = 574.51$, red prisms ($0.70 \times 0.50 \times 0.40$ mm), triclinic, $P1$, $a = 10.362(2)$ Å, $b = 18.639(4)$ Å, $c = 7.399(2)$ Å, $\alpha = 97.97(2)°$, $\beta = 102.67(2)°$, $\gamma = 86.58(2)°$, $V = 1380.1(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.382$ g/cm^3, $\mu = 5.79$ cm^{-1}, minimum/maximum transmission 0.9169/1.0000, $2\theta_{max} = 55.0°$, λ(Mo Kα) = 0.710 69 Å, $T = 293$ K, 5457 total reflections (R(int) = 0.051), R1 = 0.047, wR2 = 0.033 ($I > 3.0\sigma(I)$), GOF (F^2) = 1.65.

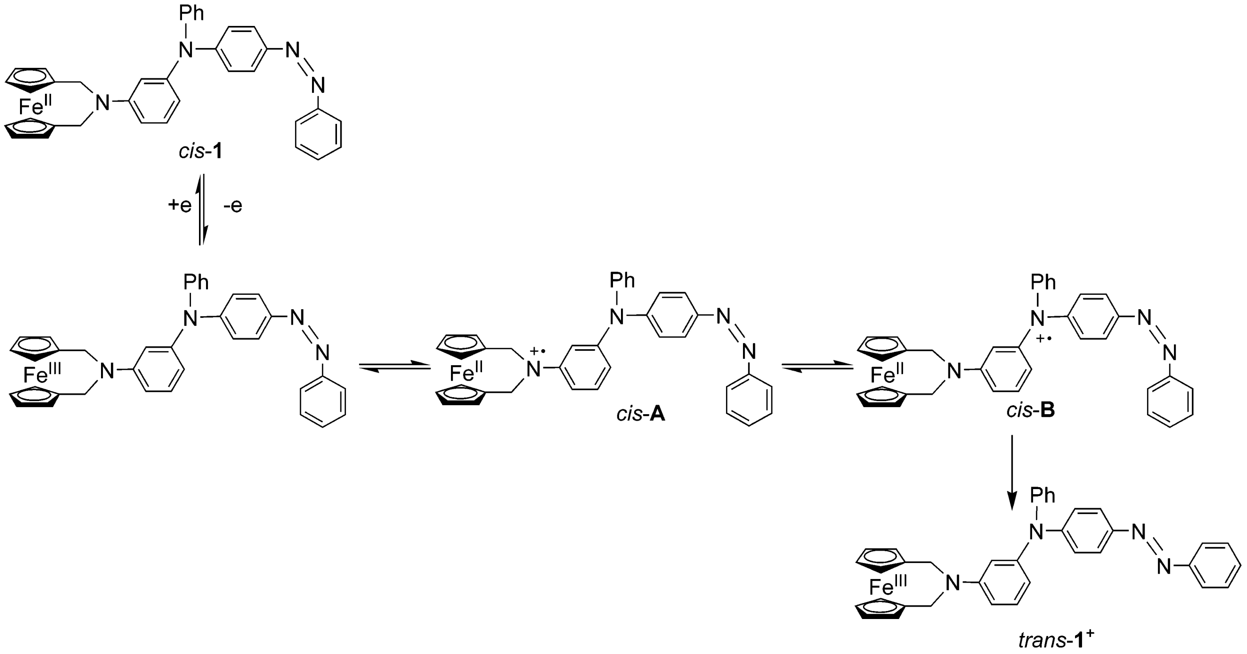
[10] (a) Delaire, J. A.; Nakatani, K. *Chem. Rev.* **2000**, *100*, 1817. (b) Ichimura, K. *Chem. Rev.* **2000**, *100*, 1847.

[11] (a) Somoano, R.; Hadek, V.; Yen, S. P. S.; Rembaum, A. *J. Chem. Phys.* **1975**, *62*, 1061. (b) Yamaguchi, J.; Fujita, H. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2928.

[12] (a) McDiarmid, A. G.; Chiang, J.-C.; Halpern, M.; Huang, W.-S.; Mu, S.-L.; Somasiri, N. L. D.; Wu, W.; Yaniger, S. I. *Mol. Cryst. Liq. Cryst.* **1985**, *121*, 173. (b) Awano, H.; Murakami, H.; Yamashita, T.; Ohigashi, H.; Ogata, T. *Synth. Met.* **1991**, *39*, 327. (c) Kang, E. T.; Neoh, K. G.; Tan, K. L. *Prog. Polym. Sci.* **1998**, *23*, 277.

[13] The degree of change of the absorption peak by irradiation is 17% of the difference between (a) and (b) in Figure 1. It can be ascribed to rapid thermal isomerization of the azobenzene and shift of the trans/cis equilibrium in the photostationary state of the oxidized azaferrocenophane.

Scheme 2



tion of *cis*- to *trans*-azobenzene. The positive charge at the N atom attached to the azobenzene unit enhances the isomerization of the N═N bond significantly, due to the N−N bond rotation of the oxidized form of *cis*-**B** being more rapid than that of the unoxidized form of *cis*-**1**. In summary, the azaferrocenophane in this study undergoes photoinduced isomerization of the *trans*-azobenzene group to the cis form, and the UV−vis spectrum of a photostationary state has been established. Upon electrochemical oxidation, the spectroscopic signature of the photostationary state becomes smaller, due to acceleration of the thermal isomerization. The control of the photochemical output of this molecule by the oxidation state results from an electronic communication between the Fe atom and the organic ligand.

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Supporting Information Available: Text, tables, and figures giving experimental procedures for synthesis of the complexes, results of X-ray crystallography for *trans*-**1**, and kinetics data; X-ray data are also available in electronic form as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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