Two-Electron Reduction of a Rh−Mo−Rh Dithiolato Complex To Form a Triplet Ground State Associated with a Change in CO Coordination Mode

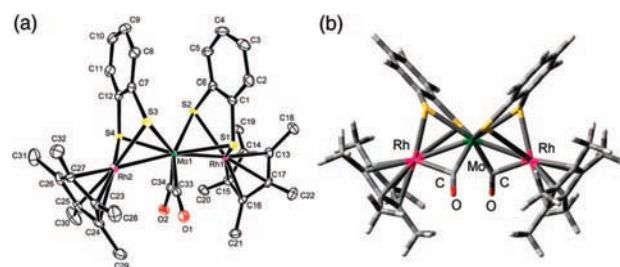Satoshi Muratsugu,[†] Keitaro Sodeyama,[‡] Fusao Kitamura,[§] Manabu Sugimoto,[||] Shinji Tsuneyuki,[‡] Seiji Miyashita,[‡] Tatsuhisa Kato,[⊥] and Hiroshi Nishihara*[,†]

Department of Chemistry and Department of Physics, School of Science, The University of Tokyo, 7-3-1, Hongo, Bunkyo-Ku, Tokyo, 113-0033, Japan, Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4256, Nagatsuta, Midori-Ku, Yokohama, 226-8502, Japan, Department of Applied Chemistry and Biochemistry, Graduate School of Science and Technology, Kumamoto University, 2-39-1, Kurokami, Kumamoto, 860-8555, Japan, and Department of Chemistry, Graduate School of Material Science, Josai University, Sakado, 350-0295, Japan

Received November 19, 2008; E-mail: nisihara@chem.s.u-tokyo.ac.jp

Multielectron transfer reactions are key steps in important biological and artificial catalytic processes, and a mechanistic understanding of these reactions requires comprehensive study of the redox processes and the accompanying structural changes and electronic states.[1] Typically, multinuclear complexes containing electronically coupled equivalent redox units show multistep redox reaction due to the formation of thermodynamically favorable mixed-valence states.[2] To our knowledge, no exceptions have been found to this mechanism among redox reactions in multinuclear metalladithiolene complexes of the late transition metals.[3,4] For example, a successive multistep, one-electron redox reaction with a positive redox potential difference ($\Delta E^{0'}_i > 0$; where $\Delta E^{0'}_i = E^{0'}_{i+1} - E^{0'}_i$, $i = 1, 2$) occurs in the trinuclear complex $[Co_3(\eta^5\text{-}C_5H_5)_3(S_6C_6)]$, in which three cobaltadithiolenes are fused to a π-conjugated phenyl ring,[4a] and in the heterometal trinuclear complex, $[\{(\eta^5\text{-}C_5H_5)Co(S_2C_6H_4)\}_2Mo(CO)_2]$, in which $Mo(CO)_2$ bridges two cobaltadithiolenes generating Co−Mo−Co bonds.[4b]

Here we report the first example of a multinuclear metalladithiolene to show a chemically reversible one-step two-electron ($2e^-$) reduction process (Scheme 1). Complex **1**, $[\{(\eta^5\text{-}C_5Me_5)Rh(S_2C_6H_4)\}_2Mo(CO)_2]$, is a novel trinuclear heterometal complex containing two rhodadithiolene units bridged by $Mo(CO)_2$ and forming Rh−Mo−Rh bonds. The observed negative potential difference ($\Delta E^{0'} < 0$; where $\Delta E^{0'} = E^{0'}_{i+1} - E^{0'}_i$, $i = 1$) suggests a fundamentally different redox process from that found in an analogous complex of cobalt, $[\{(\eta^5\text{-}C_5H_5)Co(S_2C_6H_4)\}_2Mo(CO)_2]$.[4b] Potential inversion of this type is uncommon and usually occurs in metal complexes when internuclear electronic interaction renders a mixed-valence state unstable due to structural changes that occur, for example, as a result of metal−metal bond formation or rotation of ligands.[5] In the case of complex **1**, we

Scheme 1

1
Semibridging C≡O, S = 0

1²⁻
Bridging C≡O, S = 1

† Department of Chemistry, The University of Tokyo.
‡ Department of Physics, The University of Tokyo.
§ Tokyo Institute of Technology.
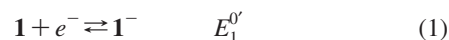|| Kumamoto University.
⊥ Josai University.

Figure 1. (a) ORTEP view of **1** with thermal ellipsoids set at the 50% probability level. Hydrogen atoms are omitted for clarity. (b) Optimized structure of **1²⁻** by the DFT(B3LYP) method.

found that a novel reversible change in the CO coordination mode—from semibridging to bridging—accompanies the redox process, giving a triplet ground spin state in **1²⁻** (Scheme 1).

Complex **1** was prepared by the reaction of rhodadithiolene $[(\eta^5\text{-}C_5Me_5)Rh(S_2C_6H_4)]$ and $[Mo(CO)_3py_3]$ in the presence of $BF_3 \cdot Et_2O$ in toluene (see Supporting Information). In the single crystal X-ray structure (Figure 1a and Supporting Information Tables S1−S3), the average O−C−Mo bond angle is 167.65°, the average Mo−C bond length is 1.955 Å, and the average Rh−C length is 2.670 Å, suggesting the presence of weak π-back-donation from Rh to CO in addition to a Mo−CO single bond. The coordination mode of CO is classified as semibridging closer to terminal according to the asymmetric parameter $\alpha = 0.37$.[6] Two ν(CO) stretching bands were observed in the IR spectrum: 1862 and 1797 cm⁻¹ in a KBr pellet, and 1869 and 1802 cm⁻¹ in a THF solution (Figure S1). These spectra strongly suggest a weakening of CO bond strength due to π-back-donation not only from the Mo site but also from the Rh sites. Complex **1** was diamagnetic (NMR active), indicative of a singlet ground state ($S = 0$).

A cyclic voltammogram (CV) of **1** in Bu_4NClO_4−MeCN/toluene (1:1 v/v) at 253 K (Figures 2a and S3) showed only one reversible redox wave at $E^{0'} = -1870$ mV vs ferrocenium/ferrocene (Fc⁺/Fc) with a peak separation ΔE_p of 38 mV (where $\Delta E_p = E_{pa} - E_{pc}$). The number of electrons transferred in the reduction of **1** was determined to be 2.01 by coulometry (Figure S5), confirming that **1** undergoes one-step $2e^-$ redox reaction. The potential inversion was supported by the results of CV simulation that gave two redox potentials of $E^{0'}_1 = -1891$ mV and $E^{0'}_2 = -1851$ mV vs Fc⁺/Fc. Thus, $\Delta E^{0'} = E^{0'}_2 - E^{0'}_1 = -40$ mV according to the following equations:
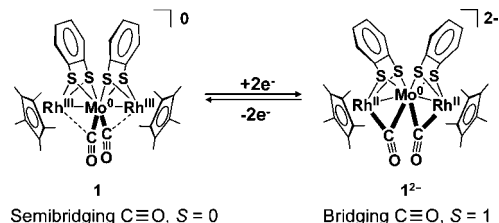
$$\mathbf{1} + e^- \rightleftharpoons \mathbf{1}^- \qquad E^{0'}_1 \qquad (1)$$
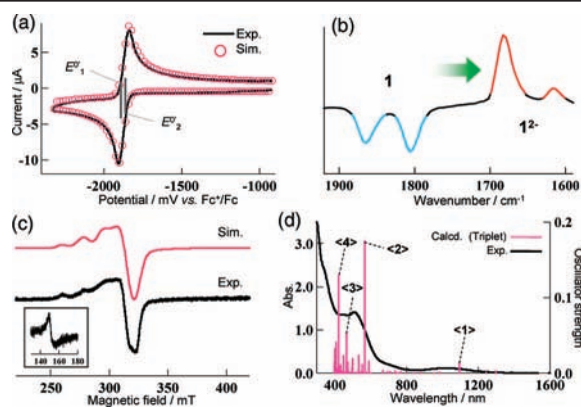
Figure 2. (a) Cyclic voltammogram of **1** at 100 mVs^{-1} in 0.1 M Bu$_4$NClO$_4$–MeCN/toluene (1:1 v/v) at 253 K and its simulated voltammogram. (b) IRAS differential spectrum of **1** after electrochemical reduction by application of −1.85 V vs Fc$^+$/Fc in 0.1 M NaBPh$_4$–THF at 298 K. Blue peaks disappeared and red peaks appeared upon the reduction of **1** to **1**$^{2-}$. (c) EPR spectrum of **1**$^{2-}$ in 2-MeTHF at 4.2 K and its simulated spectrum. (Inset) spectrum of the $\Delta M_s = 2$ region. (d) UV–vis–NIR spectrum of **1**$^{2-}$ in 2-MeTHF and oscillator strength calculated by TDDFT. Numbered oscillator strengths are given in Table S12.

$$\mathbf{1}^- + e^- \rightleftharpoons \mathbf{1}^{2-} \qquad E_2^{0\prime} \qquad (2)$$

While the ΔE_p values and redox potentials showed an obvious solvent–electrolyte dependence (Figures S3 and S4, Tables S5 and S6), **1** showed a one-step 2e$^-$ reduction wave with potential inversion under all experimental conditions. From the electrochemical results and EPR studies (vide infra), the reduction of **1** can be attributed to the reduction of both Rh sites, from Rh^{III}Mo^{0}Rh^{III} to Rh^{II}Mo^{0}Rh^{II}.

To investigate the structural changes that accompany the reduction of **1** to **1**$^{2-}$, DFT calculations of **1** and **1**$^{2-}$ were carried out in which all the geometries were optimized while including solvent effects as a CPCM model. In the optimized structure of **1**$^{2-}$ (Figures 1b and S10), the triplet ground-state is more favorable than the singlet ground state (Tables S7–S9). The O–C–Mo angle is 151.64°, the Mo–C bond length is 2.018 Å, and the Rh–C length is 2.157 Å (Table S10), strongly indicating that the two CO groups bridge between the Rh and Mo sites. The IR frequencies of the two CO groups in **1**$^{2-}$ are calculated to be 1705 and 1664 cm^{-1}, smaller than the calculated values of 1839 and 1792 cm^{-1} in **1**.[7]

The predicted change in the mode of CO coordination following 2e$^-$ reduction of **1** was studied by examination of the ν(CO) frequency shifts in infrared reflection absorption spectroscopy (IRAS) while controlling the reduction state electrochemically (Figure 2b). Two ν(CO) peaks for **1** at 1864 and 1806 cm^{-1} shifted to lower frequencies (1682 and 1617 cm^{-1}) upon reduction of **1** to **1**$^{2-}$. This frequency shift suggests strong π-back-donation from the electron-rich Rh^{II} sites to the CO groups. These results are consistent with the theoretical expectation that the two CO groups bridge the Rh and Mo sites in **1**$^{2-}$, following change in the mode of CO coordination from semibridging to bridging during the 2e$^-$ reduction of **1** (vide supra). Reoxidation from **1**$^{2-}$ to **1** recovered the original spectrum (Figure S6), indicating that the switching of CO coordination mode during the redox reaction is reversible.

Broad signals in the $\Delta M_s = 1$ region were observed in an EPR spectrum of **1**$^{2-}$ at 4.2 K (Figure 2c), generated by chemical reduction of **1** with Na in 2-MeTHF under vacuum (Figure S7). A simulation yielded the EPR parameters $g_{xx} = 2.15$, $g_{yy} = 2.25$, $g_{zz} = 2.37$, $D = 7.2$ mT, and $E = 3.8$ mT for an $S = 1$ electronic spin; and $A_{xx} = 4.0$ mT, $A_{yy} = 6.0$ mT, and $A_{zz} = 19.5$ mT for two Rh^{II} nuclear spins ($I = {}^1/_2$). This analysis is consistent with reduction

occurring at both Rh sites. There is a signal in the "spin-forbidden" $\Delta M_s = 2$ region,[8] and the spin intensity of the signal decreases linearly with increasing temperature, strongly supporting the theoretical expectation that **1**$^{2-}$ possesses a triplet ground state (Figures S8 and S9).

In the UV–vis–NIR spectrum of **1**$^{2-}$ in 2-MeTHF, a characteristic peak appears at around 1100 nm in the NIR region (Figure 2d). TDDFT calculations (Figures 2d, S11–13, Tables S11 and S12) based on the optimized structure reproduced the obtained UV–vis–NIR spectra reasonably well, including the absorption in the NIR region. These observations provide additional support for the validity of the CO-bridging structure and the triplet spin state of **1**$^{2-}$.

In conclusion, complex **1** exhibited a novel one-step 2e$^-$ reduction coupled with an intramolecular chemical reaction (an ECE reaction[9]), which was revealed to be a structural change in the coordination mode of two COs from semibridging to bridging. Accompanying this reduction process was the change in the ground spin state, from spin singlet of **1** to spin triplet of the generated dianion **1**$^{2-}$.

Supporting Information Available: Synthetic procedures and characterization data for **1** (CIF), CV and simulated parameters of **1**, IRAS and EPR spectral data for **1**$^{2-}$, and theoretical calculation data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Yandulov, D. V.; Schrock, R. R. *Science* **2003**, *301*, 76. (b) McEvoy, J. P.; Brudvig, G. W. *Chem. Rev.* **2006**, *106*, 4455. (c) Meyer, T. J.; Huynh, M. H. V.; Thorp, H. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 5284. (d) Collman, J. P.; Devaraj, N. K.; Decréau, R. A.; Yang, Y.; Yan, Y.-L.; Ebina, W.; Eberspacher, T. A.; Chidsey, C. E. D. *Science* **2007**, *315*, 1565.
(2) (a) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278. (b) Creutz, C. *Prog. Inorg. Chem.* **1983**, 1. (c) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107. (d) Crutchley, R. J. *Adv. Inorg. Chem.* **1994**, *41*, 273. (e) Nishihara, H. *Adv. Inorg. Chem.* **2002**, *53*, 41. (f) D'Alessandro, D. M.; Keene, F. R. *Chem. Soc. Rev.* **2006**, *35*, 424. (g) Kaim, W.; Sarkar, B. *Coord. Chem. Rev.* **2007**, *251*, 584.
(3) (a) *Dithiolene Chemistry; Synthesis, Properties, and Applications*; Stiefel, E. I., Ed.; Progress in Inorganic Chemistry, Vol. 52; Wiley: Hoboken, NJ, 2004. (b) Fourmigué, M. *Coord. Chem. Rev.* **1998**, *178–180*, 823. (c) Sugimori, A.; Akiyama, T.; Kajitani, M.; Sugiyama, T. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 879. (d) Tanaka, H.; Okano, Y.; Kobayashi, H.; Suzuki, W.; Kobayashi, A. *Science* **2001**, *291*, 285. (e) Kato, R. *Chem. Rev.* **2004**, *104*, 5319. (f) Liu, S.; Han, Y.-F.; Jin, G.-X. *Chem. Soc. Rev.* **2007**, *36*, 1543.
(4) (a) Nishihara, H.; Okuno, M.; Akimoto, N.; Kogawa, N.; Aramaki, K. *J. Chem. Soc., Dalton Trans.* **1998**, 2651. (b) Nihei, M.; Nankawa, T.; Kurihara, M.; Nishihara, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 1098. (c) Nakagawa, N.; Yamada, T.; Murata, M.; Sugimoto, M.; Nishihara, H. *Inorg. Chem.* **2006**, *45*, 14. (d) Murata, M.; Habe, S.; Araki, S.; Namiki, K.; Yamada, T.; Nakagawa, N.; Nankawa, T.; Nihei, M.; Mizutani, J.; Kurihara, M.; Nishihara, H. *Inorg. Chem.* **2006**, *45*, 1108.
(5) (a) Astruc, D.; Lacoste, M.; Toupet, L. *J. Chem. Soc., Chem. Commun.* **1990**, 558. (b) Lacoste, M.; Rabaâ, H.; Astruc, D.; Ardoin, N.; Varret, F.; Saillard, J.-Y.; Le Beuze, A. *J. Am. Chem. Soc.* **1990**, *112*, 9548. (c) Baik, M.-H.; Ziegler, T.; Schauer, C. K. *J. Am. Chem. Soc.* **2000**, *122*, 9143. (d) Evans, D. H. *Chem. Rev.* **2008**, *108*, 2113.
(6) An asymmetric parameter α is defined as α = $(d_2 − d_1)/d_1$, where d_1 and d_2 are the short and long distances, respectively, in M–C(O) : Curtis, M. D.; Han, K. R.; Butler, W. M. *Inorg. Chem.* **1980**, *19*, 2096.
(7) Vibrational frequencies were multiplied by the scale factor $\omega = 0.9614$ for B3LYP/6-31G(d) Merrick, J. P.; Moran, D.; Radom, L. *J. Phys. Chem. A* **2007**, *111*, 11683.
(8) The signal at the $\Delta M_s = 2$ region can be observed without large splitting on the signal at the $\Delta M_s = 1$ region. See Supporting Information.
(9) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods; Fundamentals and Applications*, 2nd ed.; Wiley: Hoboken, NJ, 2001; Chapter 12.