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Electrochemical Methods: Analyses of Structures and Determination of Properties of the Cobaltadithiolene Derivatives [CpCoX(S_2C_2(COOMe)$_2$)(CHR^{1}R^2)] (X = Cl, Br, and I)

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The electrochemical behavior of cobaltadithiolene derivatives [CpCoX(S_2C_2(COOMe)$_2$)-(CHR^{1}R^2)] (X = Cl, Br, and I, (R^1, R^2) = (H, H), (H, COOEt), (COOMe, COOMe), and (H, SiMe$_3$)) showed the easy elimination of halide, and the formation of an equilibrium system between these complexes and their corresponding cation complexes and eliminated halide. We report a methodology that proves the existence of this equilibrium in solutions together with their redox behavior according to the application and uses of electrochemical measurements.

Introduction

Electrochemistry is the best method to monitor oxidation and reduction reactions. However, aside from Geiger's and a few other groups, not many studies have been done on the electrochemical behavior accompanying dynamic structural changes in organometallic complexes, especially those having complicated structures.[1,2] This can be attributed to the high reactivity of reaction intermediates generated during an electrochemical transformation. In most case, studies on structural changes during a reaction are usually done through in-situ measurements of UV−vis, ESR, and IR[3] spectra. Interpretation and correlation of all spectra can lead to structural information concerning not only reduction or oxidation products but also the neutral complexes.[4] In the electrochemistry of metalladithiolene complexes, aside from the usual redox behavior, much information can be obtained on the existence of equilibria in a solution.

The metalladithiolene[5,6] rings are very intersting conjugated metal chelate rings with 6π electrons. Dithiolene complexes may be regarded as either 16e or 18e complexes, depending upon the absence or the presence of lone pair donation from the sulfur atoms to the metal center.[7] The coexistence of aromaticity[8] and unsaturation[9] is the origin of the unique reactivities of this quasi-aromatic ring. The metalladithiolene complexes react with diazo compounds to give alkylidene-bridged complexes having metallathiirane ring [CpM($S_2C_2Y_2$)-(CR^{1}R^2)] (Cp = η^5-C_5H_5, M = Co, Rh, Y = CN, COOMe, Ph, etc.; (R^1, R^2) = (COOMe, COOMe), (H, COOEt), (H, H), (H, SiMe$_3$), and (Ph, Ph)). The chemical and physical properties of alkylidene-bridged complexes are presently the subject of our intensive investigations. They show interesting reactions. For example, they undergo bond cleavage with Lewis bases[10] and protic acids[11] to give three-component adducts. Here, we use these three-component adducts as model compounds for our electrochemical measurements. In this paper, we wish to

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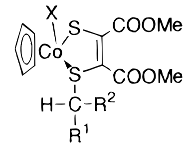
report the application and use of electrochemical measurements in proving the existence of equilibria in solution together with redox behavior. We hope to develop and generalize this electrochemical methodology for product analysis in organometallic chemistry.



1a	X =Cl	(R^1, R^2) = (H, H)
1b		(R^1, R^2) = (H, COOEt)
1c		(R^1, R^2) = (COOMe, COOMe)
1d		(R^1, R^2) = (H, SiMe$_3$)
2a	X = Br	(R^1, R^2) = (H, H)
2b		(R^1, R^2) = (H, COOEt)
2c		(R^1, R^2) = (COOMe, COOMe)
2d		(R^1, R^2) = (H, SiMe$_3$)
3a	X = I	(R^1, R^2) = (H, H)

Experimental Section

Reaction with Protic Acids. Each of the cobaltadithiolene complexes [CpCo(S$_2$C$_2$(COOMe)$_2$)(CR^{1}R^2)] (Cp = η^5-C$_5$H$_5$, (R^1, R^2) = (H, H) (**5a**), (H, COOEt) (**5b**), (COOMe, COOMe) (**5c**), and (H, SiMe$_3$) (**5d**)) (ca 0.3 mmol) was separately suspended in 50 cm^3 of dichloromethane. Concentrated hydrochloric acid solution (2 to 3 drops) was added to each suspension. After stirring for 30 min at room temperature, the reaction mixtures were washed with water and dried over anhydrous sodium sulfate, and the solvent was evaporated in vacuo. The resulting residues were recrystallized from hexane−dichloromethane to yield [CpCoCl(S$_2$C$_2$(COOMe)$_2$)(CHR^{1}R^2)] ((R^1, R^2) = (H, H) (**1a**), (H, COOEt) (**1b**), (COOMe, COOMe) (**1c**), and (H, SiMe$_3$) (**1d**)). Similarly, complexes **5a**, **5b**, **5c**, and **5d** were also made to react with hydrobromic acid under the same reaction conditions and gave products [CpCoBr(S$_2$C$_2$(COOMe)$_2$)(CHR^{1}R^2)] ((R^1, R^2) = (H, H) (**2a**), (H, COOEt) (**2b**), (COOMe, COOMe) (**2c**), and (H, SiMe$_3$) (**2d**)). Likewise [CpCoI(S$_2$C$_2$(COOMe)$_2$)(CH$_3$)] (**3a**) was obtained from the reaction of **5a** using hydroiodic acid as the protic acid.

CV Measurements. All the electrochemical measurements were done in 1 mmol dm^{-3} (CV) or 1.5 mmol dm^{-3} (OTTLE) acetonitrile solutions containing 0.1 mol dm^{-3} (CV) or 0.3 mmol dm^{-3} (OTTLE)[12] tetraethylammonium perchlorate (TEAP) at 25 °C. A stationary platinum disk (1.6 mm in diameter) (CV) or platinum mesh (OTTLE) was used as a working electrode. A coiled platinum wire served as a counter electrode, with the reference electrode as Ag|AgNO$_3$ corrected for junction potentials by being referenced internally to the ferrocene/ferrocenium (Fc|Fc$^+$) couple.

ESR Spectral Measurements. ESR spectra were obtained for ~1 mmol dm^{-3} dichloromethane solutions of the complexes by the electrochemical reductions. Isotropic spectra were obtained from solutions at 293 K, and anisotropic spectra were obtained from frozen solutions at 123 K. The spectra were recorded on a JEOL X-band JES-3X ESR spectrometer. Microwave frequencies and the magnetic field were directly determined by using a microwave counter, ADVANTEST TR5212, and a field measurement unit, JEOL NMR field meter ES-FC-5, respectively.

Characterization of Complex [CpCoCl(S$_2$C$_2$(COOMe)$_2$)(CH(COOMe)$_2$)], 1c. ^{1}H NMR (CDCl$_3$): δ 3.71 (6H, s, OCH$_3$), 3.76 (3H, s, OCH$_3$), 3.81 (3H, s, OCH$_3$), 3.82 (3H, s, OCH$_3$), 3.87 (3H, s, OCH$_3$), 3.88 (3H, s, OCH$_3$), 3.95 (3H, s, OCH$_3$), 4.31 (1H, s, alkyl H), 4.81 (1H, s, alkyl H), 5.66 (5H, s, C$_5$H$_5$) and 5.74 (5H, s, C$_5$H$_5$). MS (FAB$^+$, 70 eV): *m/z* 497 (M$^+$ + 1), 496 (M$^+$). Anal. Calcd for C$_{16}$H$_{18}$ClO$_8$S$_2$Co: C, 38.68; H, 3.65. Found: C. 38.64; H, 3.56.

Characterization of Complex [CpCoCl(S$_2$C$_2$(COOMe)$_2$)(CH$_2$SiMe$_3$)], 1d. ^{1}H NMR (CDCl$_3$): δ 0.29 (9H, s, SiMe$_3$), 1.44 (1H, d, $^2J_{H-H}$ = 14 Hz, CH), 2.43 (1H, d, $^2J_{H-H}$ = 14 Hz, CH), 3.77 (3H, s, OCH$_3$), 3.85 (3H, s, OCH$_3$), and 5.51 (5H, s, C$_5$H$_5$). MS (EI$^+$, 70 eV): *m/z* (relative intensity) 417 (65.37, M$^+$ − Cl), 344 (12.51, M$^+$ − Cl − SiMe$_3$), 330 (84.41, M$^+$ − Cl − CH$_2$SiMe$_3$), 299 (8.91, M$^+$ − Cl − CH$_2$SiMe$_3$ − OMe), 188 (100.0, CpCoS$_2$$^+$), 124 (31.42, CpCo$^+$), and 59 (21.70, Co$^+$).

Characterization of Complex [CpCoBr(S$_2$C$_2$(COOMe)$_2$)(CH$_2$COOEt)], 2b. ^{1}H NMR (CDCl$_3$): δ 1.34 (3H, m, CH$_3$), 3.75 (3H, s, OMe), 3.85 (3H, s, OMe), 3.98 (1H, d, $^2J_{H-H}$ = 20.8, CH), 4.04 (1H, d, $^2J_{H-H}$ = 20.8, CH), 4.23−.31(2H, q, CH$_2$) and 5.59 (5H, s, C$_5$H$_5$). ^{13}C NMR (CDCl$_3$): δ 14.17 (CH$_2$*C*H$_3$), 42.33 (*C*H$_2$COOEt), 52.43 (OMe), 52.70 (OMe), 66.18 (*C*H$_2$CH$_3$), 87.55 (C$_5$H$_5$), 161.54 (ring C), 165.66 (*C*OOMe), 167.51 (ring C), 169.78 (*C*OOMe), 174.77 (*C*OOEt). MS (FAB$^+$, 70 eV): *m/z* 497 (M$^+$ + 1), 417 (M$^+$ − Br + 1). MS (EI$^+$, 70 eV): *m/z* (relative intensity) 496 (0.82, M$^+$), 417 (7.17, M$^+$ − Br), 330 (77.85, CpCoS$_2$C$_2$(COOMe)$_2$$^+$), 188 (100, CpCoS$_2C_2$$^+$), 124 (32.65, CpCo$^+$). UV−vis(CH$_2Cl_2$): λ_{max} (ϵ) 273.5 (15572), 339 (9200), 367 (8874), 538 nm (1227). Anal. Calcd for C$_{15}$H$_{18}$BrO$_6$S$_2$Co: C, 36.23; H, 3.65. Found: C. 36.16; H, 3.56.

Characterization of Complex [CpCoBr(S$_2$C$_2$(COOMe)$_2$)(CH(COOMe)$_2$)], 2c. ^{1}H NMR (CDCl$_3$): δ 3.72 (6H, s, OCH$_3$), 3.75 (3H, s, OCH$_3$), 3.80 (6H, s, OCH$_3$), 3.86 (6H, s, OCH$_3$), 3.94 (3H, s, OCH$_3$), 4.44 (1H, s, CH), 4.77 (1H, s, CH), 5.62 (5H, s, C$_5$H$_5$), 5.70 (5H, s, C$_5$H$_5$). ^{13}C NMR (CDCl$_3$): δ 40.62 (*C*H(COOMe)$_2$), 45.15 (*C*H(COOMe)$_2$), 52.82 (OMe), 52.96 (OMe), 53.14 (OMe), 53.60 (OMe), 53.89 (OMe), 54.54 (OMe), 55.82 (OMe), 60.29 (OMe), 86.29 (C$_5$H$_5$), 87.69 (C$_5$H$_5$), 97.70 (ring C), 114.05 (ring C), 131.28 (ring C), 143.68 (ring C), 154.32 (*C*OOMe), 156.16 (*C*OOMe), 161.35 (*C*OOMe), 163.33 (*C*OOMe), 165.28 (*C*OOMe), 165.92 (*C*OOMe), 166.38 (*C*OOMe), 177.76 (*C*OOMe). MS (FAB$^+$, 70 eV): *m/z* 542 (M$^+$ + 1), 462 (M$^+$ + 1 − Br), 461 (M$^+$ + 1 − HBr). UV−vis(CH$_2$Cl$_2$): λ_{max} (ϵ) 278 (15170), 370 (6103), 549 nm (1177).

Characterization of Complex [CpCoBr(S$_2$C$_2$(COOMe)$_2$)(CH$_2$SiMe$_3$)], 2d. ^{1}H NMR (CDCl$_3$): δ 0.29 (9H, s, SiMe$_3$), 1.71 (1H, d, $^2J_{H-H}$ = 13.7 Hz, CH), 2.59 (1H, d, $^2J_{H-H}$ = 13.7 Hz, CH), 3.76 (3H, s, OCH$_3$), 3.84 (3H, s, OCH$_3$), and 5.47 (5H, s, C$_5$H$_5$). ^{13}C NMR (CDCl$_3$): δ −1.41 (SiMe$_3$), 27.36 (*C*H$_2$SiMe$_3$), 52.41 (OMe), 53.15 (OMe), 86.99 (C$_5$H$_5$), 121.86 (ring C), 161.77 (*C*OOMe), 165.81 (*C*OOMe), 174.09 (ring C). MS (FAB$^+$, 70 eV): *m/z* 499 (M$^+$ + 1), 498 (M$^+$). UV−vis(CH$_2$Cl$_2$): λ_{max} (ϵ) 258 (14372), 343 (11229), 544 nm (1206). Anal. Calcd for C$_{15}$H$_{22}$BrO$_4$S$_2$SiCo: C, 36.22; H, 4.46. Found: C. 36.20; H, 4.53.

Results and Discussion

We measured the cyclic voltammetry (CV) of nine cobaltadithiolene derivatives [CpCoX(S$_2$C$_2$(COOMe)$_2$)(CHR^{1}R^2)] (X = Cl, (R^1, R^2) = (H, H) (**1a**), (H, COOEt) (**1b**), (COOMe, COOMe) (**1c**), (H, SiMe$_3$) (**1d**), X = Br, (R^1, R^2) = (H, H) (**2a**), (H, COOEt) (**2b**), (COOMe, COOMe) (**2c**), (H, SiMe$_3$) (**2d**), X = I, (R^1, R^2) = (H, H) (**3a**)).[11] The redox potentials of these complexes are shown in Table 1. Most CVs showed two-step reduction processes and two-step oxidation processes in the range from 1.2 to −2.0 V vs Fc|Fc$^+$. Typical CVs of the complexes **1a**, **2a**, and **3a** are shown in Figure 1.

Complex **1a** (Figure 1a) exhibited one-electron reduction and reoxidation waves. These redox waves had a large peak separation (ca. 360 mV). This large peak separation may be ascribed to a quasi-reversible process due to either the slow charge transfer or some chemical reactions accompanied by a fast charge transfer. The

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Table 1. Redox Potentials (vs Fc|Fc$^+$)

	reduction E_p/V	oxidation E_p/V
1a	−0.74	0.72
1b	−0.72	0.89
1c	−0.68	0.96
1d	−0.78	0.70
2a	−0.68	0.64
2b	−0.72	0.73
2c	−0.66	0.76
2d	−0.76	0.54
3a	−0.55[a]	0.23

[a] The potential of complex **4a**$^+$/**4a**.

Table 2. Redox Potentials of Complexes 4 (vs Fc|Fc$^+$)

	reduction **4**/**4**$^-$ E_p/V	1st oxidation **4**/**4**$^+$ E_p/V	rereduction **4**$^+$/**4** E_p/V	2nd oxidation **4**$^+$/**4**$^{2+}$ E_p/V
4a	−1.74	−0.38 (−0.43)[a]	−0.43 (−0.55)[a]	1.18
4b	−1.56	−0.33	−0.39	1.27
4c	−0.97		−0.37	1.33
4d	−1.71	−0.30	−0.38	1.34

[a] The potential using **3a**.

fact that the large peak separation is not dependent on the sweep rate (50−200 mV s^{-1}) indicates that the peak separation is due to the latter reason. This means that the reduction product exhibits a reoxidation wave (eqs 1 and 2).

$$\mathbf{1a} \xrightarrow[+\,e^-]{} \mathbf{1a}^- \qquad (1)$$

$$\mathbf{1a}^- \longrightarrow \mathbf{Q}^- \qquad (2)$$

In situ measurements of the electronic absorption spectra during the electrolytic reduction using an optical transparent thin-layer electrode (OTTLE) cell were also attempted. The electronic absorption spectra during the electrolytic reduction showed the reversibility of the reduction and reoxidation. Figure 2 shows the spectral changes occurring during the controlled potential electrolysis (at −0.9 V) using OTTLE cell. The spectra obtained after the reoxidation agree with the original spectra, although a stepwise reaction occurred (EC reaction). This observation implies that another chemical reaction is accompanied by reoxidation (EC reaction). When complex **1a** underwent a one-electron reduction, it yielded a very unstable reductant **1a**$^-$. This reductant **1a**$^-$ further underwent a sructural change and to yield complex **Q**$^-$. When **Q**$^-$ was reoxidized, it formed **Q**, which reverted back to the original complex **1a**. Equations 3 and 4 illustrate the reversible behavior of the reduction process for complex **1a**.

$$\mathbf{Q}^- \xrightarrow[-\,e^-]{} \mathbf{Q} \qquad (3)$$

$$\mathbf{Q} \longrightarrow \mathbf{1a} \qquad (4)$$

We also examined the electrochemical behavior of complexes **2a** and **3a**. They showed behavior similar to complex **1a**. However, the wave was broader in complex **2a** and reversible in complex **3a**. The reduction potentials were different from that of complex **1a**, but the reoxidation and the second reduction potentials were the same as those of complex **1a**. These results suggest that the reductions of complexes **1a**, **2a**, and **3a** lead to the formation of a common intermediate, called complex **4a** (eq 2) and elimination of halide.

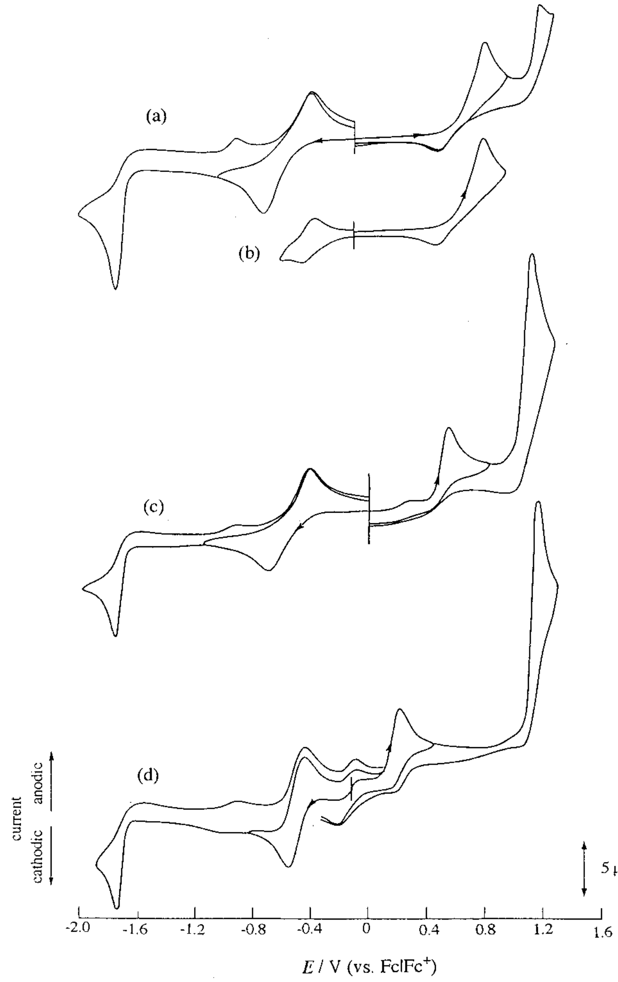

Figure 1. Cyclic voltammograms (v = 100 mV s^{-1}, Φ = 1.6 mm Pt disk) of 1 mM (a) **1a**; initial slope is toward the negative and toward the positive; (b) **1a**; initial slope is toward the positive; (c) **2a**; and (d) **3a** in CH_3CN containing 0.1 M TEAP.

We also measured the ESR spectra of these complexes. The ESR spectra after reduction of complexes **1a**, **2a**, and **3a** are similar to one another. They show eight hyperfine splittings due only to the interaction with the nuclear spin of Co (I = 7/2) and not to that of the halogen (I = 1/2 (Cl), 3/2 (Br), 5/2 (I)). These were observed both in the isotropic spectra (g_{iso} = 2.11, A_{iso} = 2.70 mT) (Figure 3a) and the anisotropic spectra (g_1 = 2.28, a_1 = 7.0 mT) (Figure 4). These results support the fact that the reduction of complexes **1a**, **2a**, and **3a** gives complex **4a**. The hyperfine coupling constants A_{iso} = 2.70 mT, a_1 = 7.0 mT as shown in Figures 3 and 4, respectively, are smaller than those of **6**$^-$ (A_{iso} = 3.84 mT, see Figure 9, a_1 = 9.2 mT, see ref 13). This can be attributed to the delocalization of an unpaired electron to the ligand (Scheme 1).

The reoxidation waves in complexes **1a**, **2a**, and **3a** correspond to the oxidation of **4a**. However, reduction

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(13) Takayama, C.; Kajitani, M.; Sugiyama, T.; Akiyama, T.; Shimizu, K.; Sugimori, A. *Organometallics* **1997**, *16*, 3498.

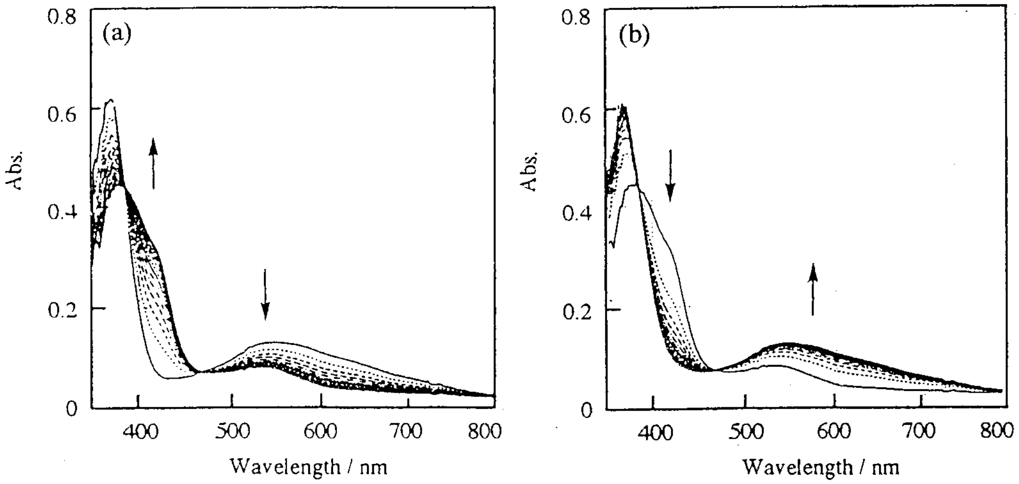


Figure 2. Electronic spectral change of **1a** during (a) reduction and (b) reoxidation: sampling interval, 5 s; potential stepped from (a) −0.1 to −0.9 V and (b) −0.9 to −0.1 V vs Fc|Fc$^+$ using the OTTLE system.

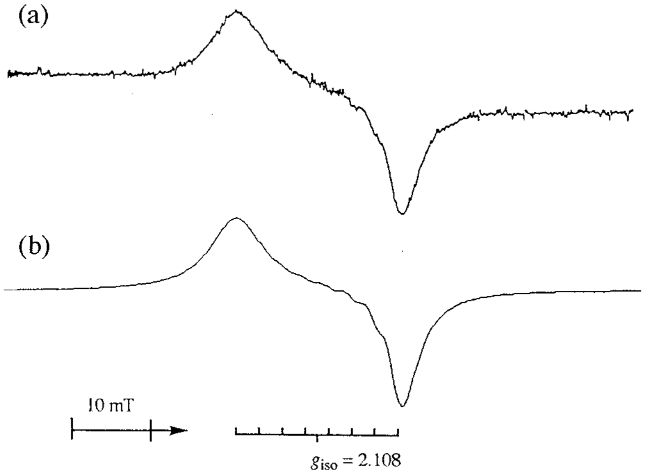


Figure 3. ESR spectra after (a) reduction of **1a** and (b) simulation of (a) at room temperature.

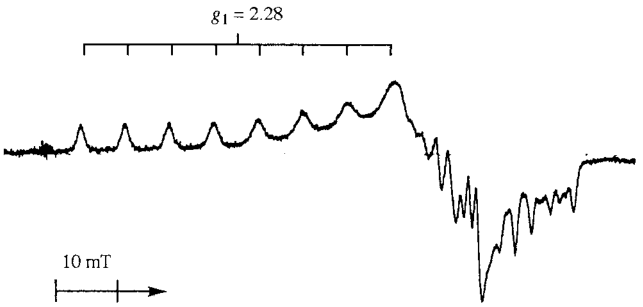
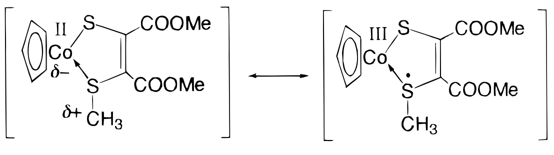


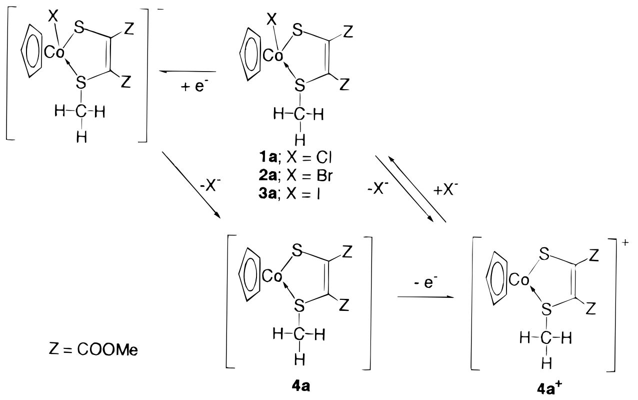
Figure 4. ESR spectra after reduction of **1a** at −150 °C.

Scheme 1



4a

Scheme 2



and reoxidation waves are reversible in complex **3a**. This is attributed to the redox of **4a**/**4a**$^+$. It means that all or a portion of complex **3a** eliminated the iodide and formed complex **4a** in solution. On the other hand, the equilibria **1a** $\rightleftharpoons$ (**4a**$^+$ + chloride) and **2a** $\rightleftharpoons$ (**4a**$^+$ + bromide) are expected because the reduction waves are broader. We also propose the existence of the equilibria **1a** $\rightleftharpoons$ (**4a**$^+$ + chrolide), **2a** $\rightleftharpoons$ (**4a**$^+$ + bromide), and **3a** $\rightleftharpoons$ (**4a**$^+$ + iodide).[14] The reduction potential of each complex (**1a**, **2a**, and **3a**) is more negative than the cation complex **4a**$^+$. For the equilibrium system of complex **1a**, only **1a** was observed in the reduction. However, for the equilibrium system of **2a**, the reduction wave for **2a** included a small reduction wave for the cation complex **4a**$^+$. This is evident because of the broader reduction wave. Furthermore, for the equilibrium system of complex **3a**, only the reduction wave of **4a**$^+$ was seen (Scheme 2).

We also tried CV measurements at slow rates using the OTTLE cell to provide more definite evidence about this chemical reaction. The thickness of the thin layer in the cell is 0.4 mm. The use of this OTTLE cell makes it possible to measure CV at a very slow rate (≥1 mV s^{-1}). It can also determine approximately the yields of products, because the thin-layer cell can prevent diffusion of the solution. Figure 5 shows the thin-layer CV of complexes **1a** and **2a** obtained at a slow scan rate (1−10 mV s^{-1}). As seen in Figure 5, the CV of complex **1a** evidences little change; however the waves become broader at 1 mV s^{-1}. In complex **2a**, a small shoulder appears at 10 mV s^{-1}, and only a pair of redox waves is obtained at 1 mV s^{-1}.[15] These correspond to the redox

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[14] Oxidation potentials (vs Fc|Fc$^+$) of halides are as follows: Cl$^-$, 0.63 V; Br$^-$, 0.35 V, 0.65 V; I$^-$, −0.12 V, 0.23 V.

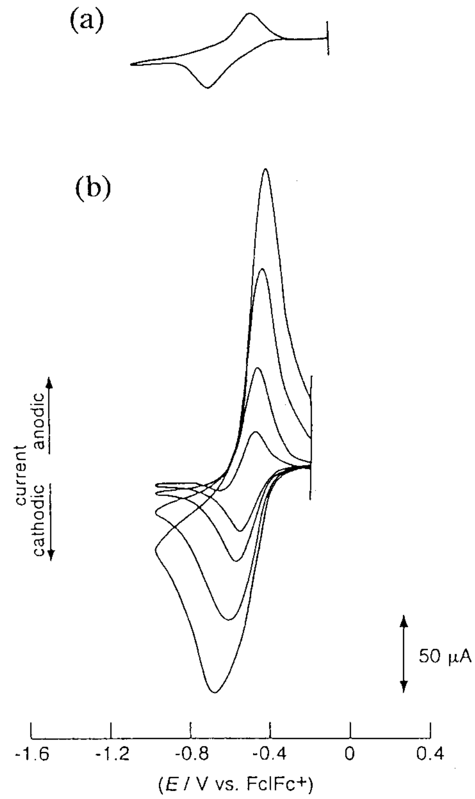


Figure 5. Cyclic voltammograms using the OTTLE cell of 1.5 mM (a) **1a** ($v = 1$ mV s^{-1}) and (b) **2a** ($v = 1$, 2, 5, and 10 mV s^{-1}) in CH_3CN containing 0.3 M TEAP.

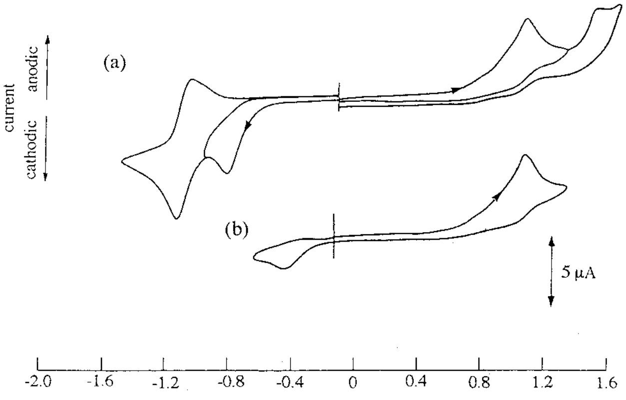


Figure 6. Cyclic voltammograms ($v = 100$ mV s^{-1}, $\Phi =$ 1.6 mm Pt disk) of 1 mM **1c** in CH_3CN containing 0.1 M TEAP; initial slope is (a) toward the negative and toward the positive and (b) toward the positive.

of **4a**/**4a**$^+$. This suggests the elimination of halide prior to the electrochemical reaction. From these results, we propose the redox mechanism wherein a one-electron reductant immediately eliminates the halide to give complex **4a**. This product **4a** is reoxidized at -0.35 V to give cation complex **4a**$^+$, which immediately regenerates the corresponding complexes **1a**, **2a**, and **3a**, accompanied by the addition of halide. Therefore, an equilibrium exists between complexes **1a** and **4a**$^+$ and chloride. Likewise **2a** or **3a** are also in equilibrium with **4a**$^+$ and their corresponding halides. The equilibria lie to the side of product **4a** due to the reduction.[16] The ease of elimination of the halide occurs in the order of $I^- > Br^- > Cl^-$.

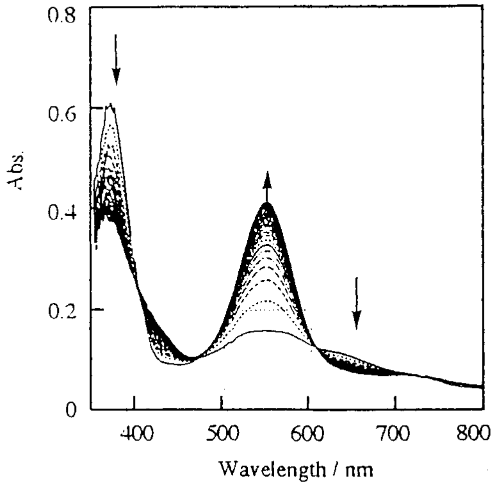
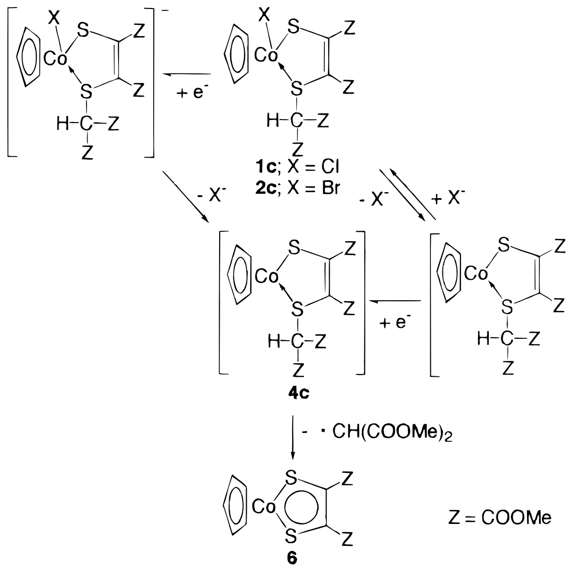
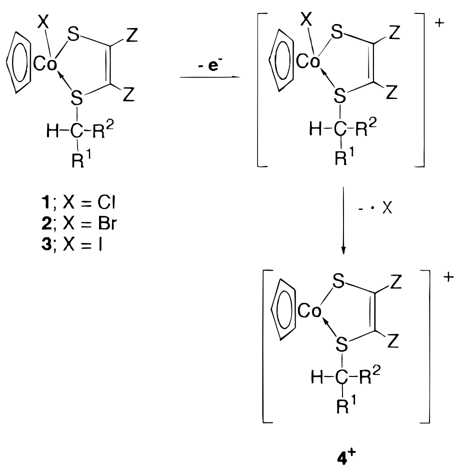


Figure 7. Electronic spectral change of **1c** during reduction: sampling interval, 2 s; potential stepped from -0.1 to -0.9 V vs Fc|Fc$^+$ using the OTTLE system.

Scheme 3



Scheme 4



We also measured CVs of other complexes. A similar behavior was observed in the reduction of complexes **1b**,

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(15) (a) Moraczewski, J.; Geiger, W. E. *J. Am. Chem. Soc.* **1981**, *103*, 4779. (b) Richards, T. C.; Geiger, W. E. *J. Am. Chem. Soc.* **1994**, *116*, 2028.

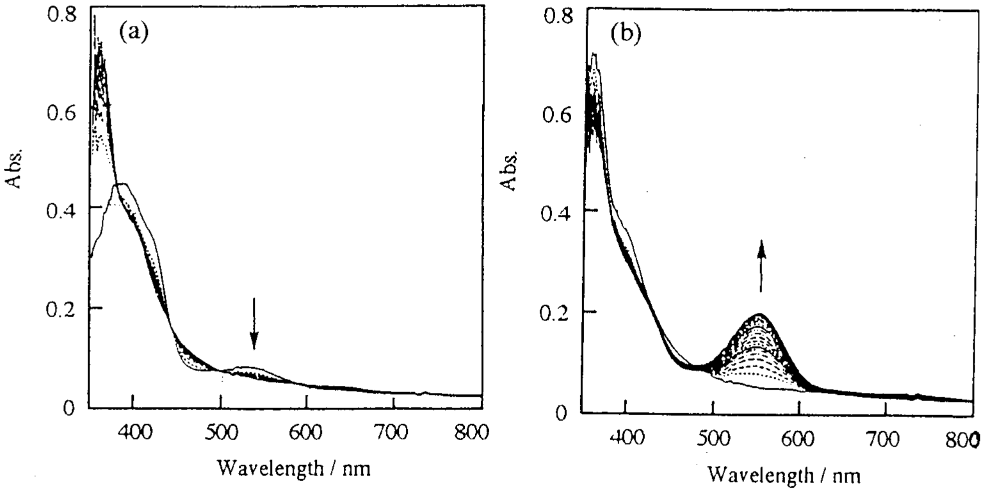


Figure 8. Electronic spectral change of **4a** during (a) reduction and (b) reoxidation: sampling interval, 5 s; potential stepped from (a) −1.1 to −1.9 V and (b) −1.9 to −0.7 V vs Fc|Fc$^+$ using the OTTLE system.

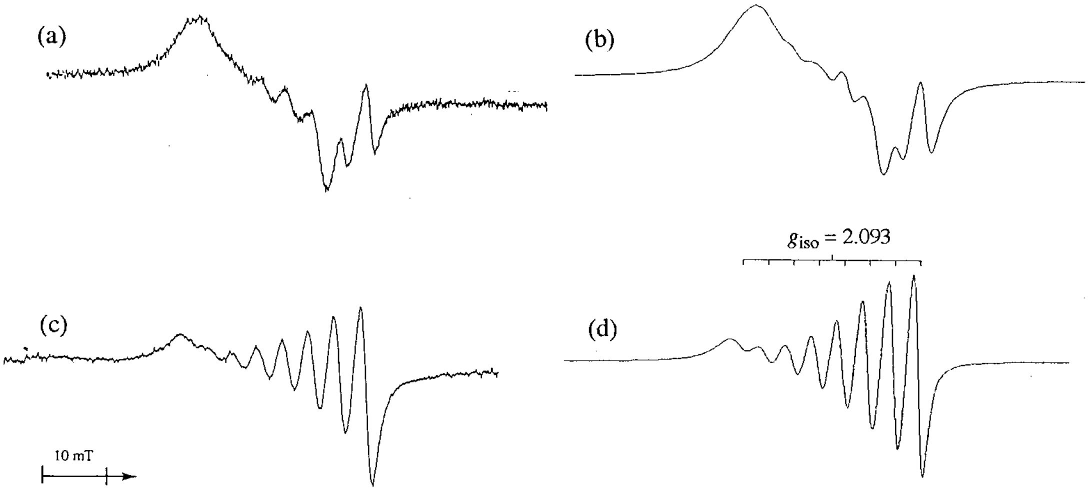
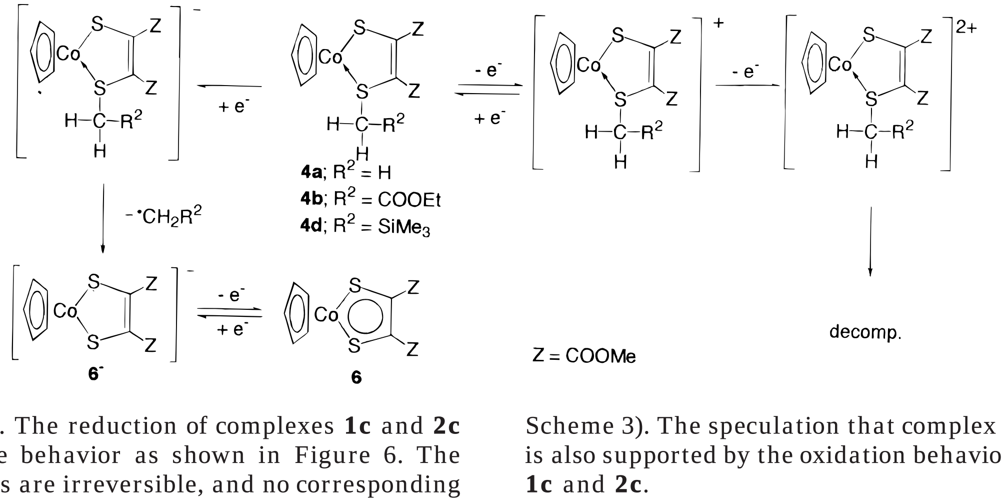


Figure 9. ESR spectra after (a) reduction of **4a**, (b) after simulation of (a), showing a mixture of **4a** (see Figure 3b) and of **6**$^-$ (Figure 9d), (c) after reduction of **6**, and (d) after simulation of (c) at room temperature.

Scheme 5



1d, **2b**, and **2d**. The reduction of complexes **1c** and **2c** exhibits unique behavior as shown in Figure 6. The reduction waves are irreversible, and no corresponding reoxidation wave is observed. After reduction, a reversible redox couple was observed at a more negative potential. This wave is assigned to the reduction wave of dithiolene complex **6**.[12] Thus, a one-electron reduction causes elimination of the halide anion and forms an electrically neutral complex **4c**. Complex **4c** is unstable and eliminates an alkyl radical to form complex **6** (see Scheme 3). The speculation that complex **4c** is unstable is also supported by the oxidation behavior of complexes **1c** and **2c**.

The formation of complex **6** by the reduction of complexes **1c** and **2c** was confirmed by the observed

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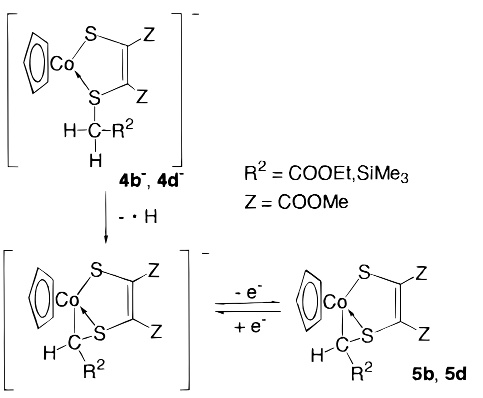
(16) (a) Geiger, W. E.; Salzer, A.; Edwin, J.; Philipsborn, W.; Piantini, U.; Rheingold, A. L. *J. A.m Chem. Soc.* **1990**, *112*, 7113. (b) Moulton, R.; Weidman, T. W.; Vollhardt, K. P. C.; Bard, A. *J. Inorg. Chem.* **1986**, *25*, 1846. (c) Richards, T. C.; Geiger, W. E. *Organometallics* **1994**, *13*, 4494. (d) Chin, T. T.; Geiger, W. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 5002.

Scheme 6



spectral change using the OTTLE cell. Figure 7 shows the spectral changes during the controlled potential electrolysis at −0.69 V. During reduction, the appearance of an absorption due to the dithiolene complex **6** was observed.

We measured the ESR spectra of complexes **1c** and **2c**. The isotropic and anisotropic ESR spectra after reduction at −1.6 V (vs Fc|Fc$^+$) are the same as those of complex **6**$^-$ at ambient temperature ($g_{\mathrm{iso}} = 2.11$, $A_{\mathrm{iso}} = 3.84$ mT) and −150 °C ($g_1 = 2.22$, $g_2 = 2.03$, $g_3 = 1.99$, $A_{\mathrm{Co(1)}} = 9.20$ mT, $A_{\mathrm{Co(2)}} = -0.49$ mT, $A_{\mathrm{Co(3)}} = 2.80$ mT).[13] These results also support the formation of complex **6** on the reduction of complex **1c** and **2c**.

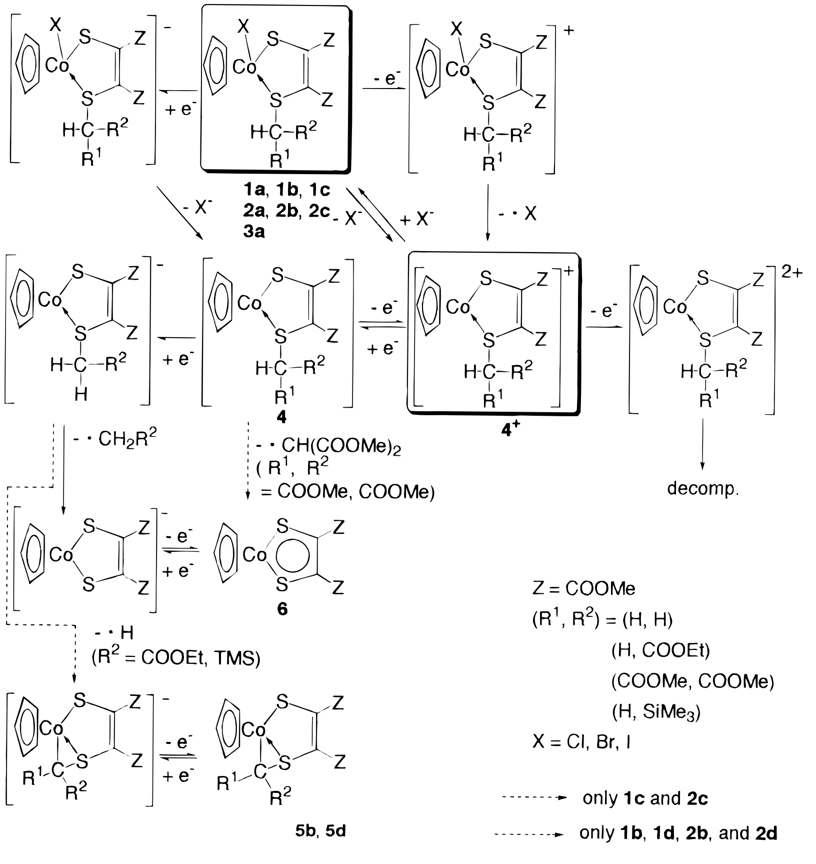
Furthermore, the CV of complex **1a** shows a one-electron oxidation wave (Figure 1a). This oxidation wave is irreversible. When the potential scan was reversed after the oxidation, a reversible redox couple appeared at −0.4 V. This reoxidation wave is the same as the reoxidation wave that was observed after the reduction. The cationic complex **4a**$^+$ is generated through the elimination of the chlorine atom by oxidation (Scheme 4). Other complexes showed the same behavior as that of complex **1a**. However, the reduction wave of complex **4c**$^+$ generated by the oxidation of complexes **1c** and **2c** is irreversible. This result agrees with the argument that forms complex **4c** as an unstable intermediate during reduction.

On the other hand, the second reduction process of complexes **1a**, **2a**, and **3a** can be attributed to the reduction of complex **4a**. Complex **4a** exhibits an irreversible reduction wave. After this reduction, CV shows the same wave observed in the reoxidation of **6**$^-$. The generation of reductant **6**$^-$ by the reduction of complex **4a** was also confirmed by the spectral change using the OTTLE cell. Figure 8b shows the spectral changes during the controlled potential electrolysis at −0.7 V after reduction of **4a**. Accompanying the reoxidation, the absorption due to the dithiolene complex **6** appears.

Figure 9 shows the ESR spectrum of complex **4a** after reduction. The spectrum shows a pattern similar to that of complex **6**$^-$. It shows the concentration of **4a** to that of **6**$^-$ to be 7:3. Thus, the reduction of complex **4a** leads to the formation of **6**$^-$ (Scheme 5).

A similar behavior was observed in the reduction of **4b** and **4d**, except for appearances of the small reoxidation waves of **5b**$^-$ and **5d**$^-$ after reduction.[12] The reduction of **4b** and **4d** gives the reductant of the dithiolene complex **6**$^-$ and alkylidene-bridged complexes **5b**$^-$ or **5d**$^-$. Thus one more step should be added to the proposed redox mechanism (Scheme 6).

Scheme 7



The oxidations of complexes **4a**, **4b**, and **4d** are reversible to give **4a**$^+$, **4b**$^+$, and **4d**$^+$. Complex **4c** was too unstable to observe; however, cation complex **4c**$^+$, which was generated by the oxidation of complex **1c** or **2c**, could be observed by CV. The oxidations of **4a**$^+$, **4b**$^+$, **4c**$^+$, and **4d**$^+$ are irreversible. The cationic complexes **4a**$^{2+}$, **4b**$^{2+}$, **4c**$^{2+}$, and **4d**$^{2+}$ are observed to rapidly decompose.

Conclusions

The reactions of alkylidene-bridged complexes with protic acids cause the Co–C bond cleavage of the three-membered rings to give new adducts **1**–**3** in which a halide coordinates to the Co atom. In solution, a part of the halide anion is eliminated, thus forming an equilibrium between the complexes and cationic complexes **4**$^+$. The order of reactivity of the halides toward elimination is iodide > bromide > chloride. The reductions of these complexes cause the elimination of the halide anions to give neutral complexes **4**. After reoxidation, the original three-component complexes **1**, **2**, and **3** are regenerated through the addition of the halide anion. Furthermore, the reduction of **4** leads to the formation of **6**$^-$. The oxidations also form cationic complexes **4**$^+$ through elimination of halogen radicals. These cationic complexes are intermediates in the formation of the three-component complexes. In general, the product analysis of chemical reactions is typically carried out by conventional methods which make use of spectroscopy and X-ray sturucture analyses. For electrochemical reaction products that are stable enough to be isolated, comparison of the potentials and spectra in situ can give much information about thier structures.[17] In this present work, the reaction products we obtained were too unstable to be isolated.[18] However, we succeeded in analyzing the structures of the products by comparing some common and different points in the electrochemical and ESR behavior whenever substituents in the complexes are changed. We were also able to observe the changes of structures of the complexes in solution and the existence of an equilibrium system. These were made possible by monitoring the electrochemical behavior of these complexes in solution.

Electrochemistry is arguably the most suitable method to monitor redox reactions. The behavior of an electron, being the simplest chemical reagent, in the reaction of complexes provide much important information on the nature of the complex under investigation.

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(18) Geiger, W. E.; Gennett, T.; Mavicar, W. K. *Organometallics* **1987**, *6*, 1634.