Structural Changes Induced by Electron-Transfer Reactions. Isomerization of an Alkylidene Moiety by Reversible Metal–Carbon Bond Cleavage in an Alkylidene-Bridged Cobaltadithiolene Complex

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Electrochemical investigations concerning the reduction of an alkylidene adduct of a cobaltadithiolene complex are described. $[(Cp)Co\{S_2C_2(COOMe)_2\}\{C(COOMe)_2\}]$ ($Cp = \eta^5$-C_5H_5) exists as an equilibrium mixture of alkylidene-bridged (**2**) and ylide forms (**3**) in solution. Both isomers are reducible by one electron, but the radical anion of the bridged form (**2⁻**) undergoes rapid and irreversible isomerization to the ylide form anion (**3⁻**). Conventional cyclic voltammetry (CV), thin-layer CV, optically transparent thin-layer electrode (OTTLE), and differential pulse polarography (DPP) have been used to establish these mechanisms. In the reaction with trimethyl phosphite, an X-ray structure analysis and CV have also been used to prove the existence of the ylide structure.

Introduction

A metalladithiolene ring is a unique metallacycle which exhibits both aromaticity and unsaturation. It undergoes substitution reactions due to its aromaticity.[1] On the other hand, it also behaves as an unsaturated molecule. Diazo compounds,[2] azides,[3] alkynes,[4] and quadricyclane[5] insert between metal and sulfur atoms in the metalladithiolene ring. In the reactions of the diazo compounds, N_2 is eliminated, and thus alkylidene-bridged complexes which have cobalthathiirane rings are formed. Furthermore, such alkylidene-bridged complexes react with trimethyl phosphite and give a six-membered metallacycle due to the Co–S bond cleavage. Recently, we reported a very unique reaction of the alkylidene-bridged complex **2**, which is formed by the reaction of (η^5-cyclopentadienyl)[1,2-(bis(methoxycarbonyl)ethenethiolato-κS]cobalt(III) (**1**) with dimethyl diazomalonate.[6] This alkylidene-bridged complex reacts with trimethyl phosphite, forming a ylide structure due to the Co–C bond cleavage. This ylide structure is very interesting as a novel type of organometallic complex.
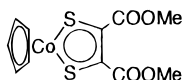
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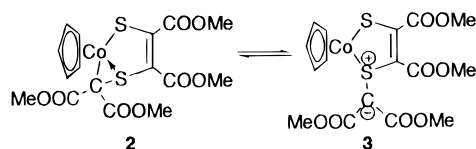
2 ⇌ **3**

Here we examine the reduction behavior of this alkylidene-bridged complex **2** and attempt a comparison with its chemical behavior. Our results indicate that, when the alkylidene-bridged structure is reduced by one electron, it is very unstable and isomerizes rapidly and quantitatively to the ylide form. Furthermore, this complex **2** exists as an equilibrium mixture of alkylidene-bridged form **2** and ylide form **3** in solution. This is the first example of an adduct of a substituent coordinated only to a sulfur atom and of reversible isomerization of the metal–carbon bond in a cobaltadithiolene complex.

Experimental Section

Preparation of Complexes. The cobaltadithiolene complex $[(Cp)Co\{S_2C_2(COOMe)_2\}]$ (**1**),[7] the alkylidene-bridged complex $[(Cp)Co\{S_2C_2(COOMe)_2\}\{C(COOMe)_2\}]$ (**2**),[2] and the trimethyl phosphite adduct $[(Cp)Co\{S_2C_2(COOMe)_2\}$-$\{C(COOMe)_2\}\{P(OMe)_3\}]$ (**4**)[6] were prepared by the literature methods. However, the complex **4** for electrochemical measurement was prepared *in situ* in an electrochemical cell by the addition of 30 equiv of trimethyl phosphite to complex **2**.

Chemical Reduction of Complex 2. Chemical reduction was carried out under an atmosphere of argon. Complex **2** (92.8 mg, 0.20 mmol) and sodium tetrahydroborate ($NaBH_4$; 0.80 mg, 0.021 mmol) were stirred in an ethanol–benzene (1:1) mixture solution for 10 min. After the reaction, the solution was exposed to dry O_2. The solvent was removed under reduced pressure, and the residue was chromatographed on a

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(2) Sakurada, M.; Kajitani, M.; Dohki, K.; Akiyama, T.; Sugimori, A. *J. Organomet. Chem.* **1992**, *423*, 144.
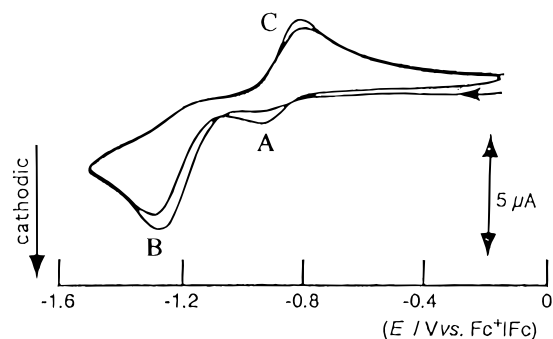
(3) (a) Sakurada, M.; Kajitani, M.; Akiyama, T.; Sugimori, A. *Chem. Express* **1991**, *6*, 759. (b) Katsuta, H.; Noguchi, N.; Inomata, Y.; Kajitani, M.; Akiyama, T.; Sugimori, A. *Chem. Lett.* **1994**, *1165*.
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Figure 1. Continuous cyclic voltammogram ($v = 100$ mV s^{-1}, $\Phi = 1.6$ mm, Pt disk) of 1 mM alkylidene-bridged complex **2** in CH$_3$CN containing 0.1 M TEAP.

silica gel column to give the following two fractions: the first band yielded dithiolene complex **1** (in 10% yield; 6.2 mg, 0.019 mmol), and the second band afforded starting complex **2** (in 89% yield; 82.2 mg, 0.18 mmol).

Measurements. The voltammetric equipment and the suitable optically transparent thin-layer electrochemical electrode (OTTLE) cell used here were described previously.[8,9] All the electrochemical measurements were undertaken in acetonitrile solutions containing 0.1 mol dm^{-3} tetraethylammonium perchlorate (TEAP) at 25 °C. A stationary platinum disk (1.6 mm in diameter; CV), platinum gauze (DPP), or platinum mesh (OTTLE) was used as a working electrode. A coiled platinum wire served as a counter electrode, with the reference electrode Ag$^+$/Ag corrected for junction potentials by being referenced internally to the ferrocenium/ferrocene (Fc$^+$/Fc) couple. ESR spectra were obtained for ~1 mM solutions of the complex obtained either synthetically (by excess NaBH$_4$) or electrochemically as described above. Anisotropic spectra were obtained from frozen solutions of a 1:1 ethanol−toluene mixture at 77 K (synthetically) or frozen solutions of acetonitrile at 123 K (electrochemically). 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.

Results and Discussion

CV. Complex **2** exhibits a one-electron reduction wave (B) and a reoxidation wave (C). These redox waves have a large peak separation (ca. 500 mV). This large peak separation may be ascribed to a quasi-reversible process either due to the slow charge transfer or due to some chemical reactions accompanied by fast charge transfer (Figure 1).

The fact that the large peak separation is not dependent on the sweep rate (50−200 mVs^{-1}) (Table 1) indicates that the peak separation is attributable to the latter reason and suggests the presence of another reduction product which exhibits a reoxidation wave (C; EC reaction) (Scheme 1). A cyclic voltammetric scan (Figure 1) displays, in addition to the major cathodic wave (B) for **2** and anodic wave (C), another cathodic feature (A) at more positive potentials. This wave (A) and anodic wave (C) are separated by the Nernstian value of 60 mV. The presence of A and C suggests (a) that the solution of **2** contains a minor component (**3**) and (b) that the reduced form of **2** changes rapidly and

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Table 1. Electrochemical Data of Complex 2 (vs Fc$^+$/Fc)

sweep rate	$E_{1/2}$/V^a	ΔE/mV^b	ΔE_p/mV^c	I_{pa}/I_{pc}^{d}
200	−1.26	104	567	0.6
100	−1.25	103	550	0.6
100^e	−1.33	100	576	0.6
50	−1.25	103	516	0.6
20	−1.25	102	508	0.6

^{a} $E_{1/2} = (E_p + E_{p/2})/2$, as half-wave potential. ^{b} $\Delta E = E_p - E_{p/2}$. ^{c} $\Delta E_p = |E_{pa} - E_{pc}|$. ^{d} I_{pa} = anodic peak current; I_{pc} = cathodic peak current. ^{e} In CH$_2$Cl$_2$ solution.
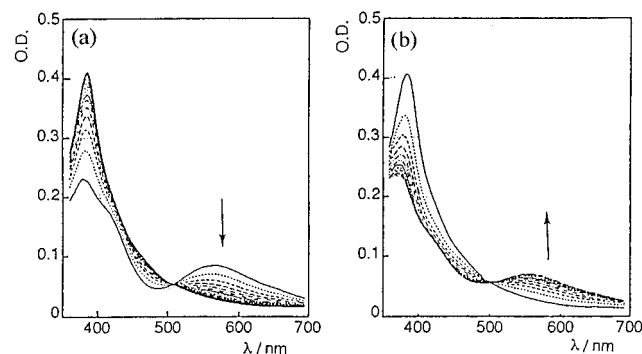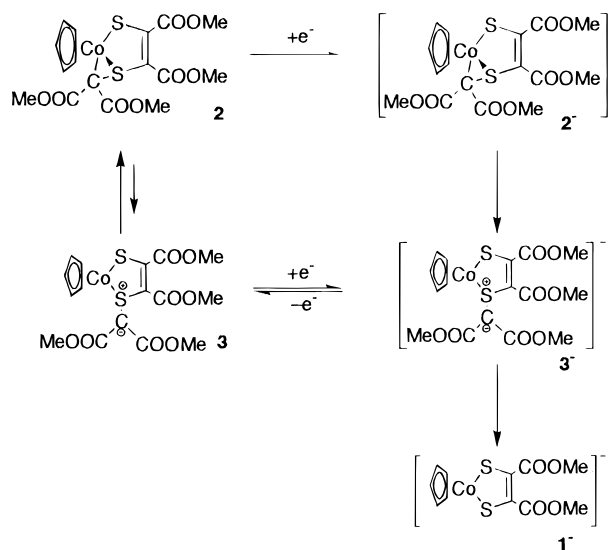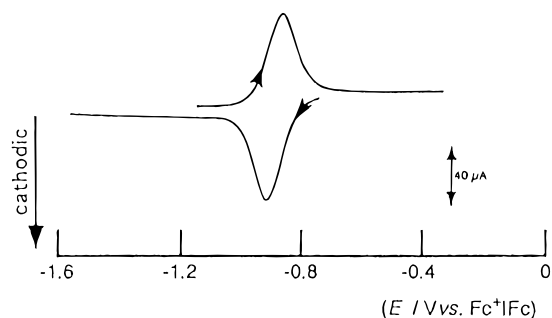

Figure 2. Electronic spectrum change of **2** during (a) reduction and (b) reoxidation; (sampling interval 1 s); potential stepped from (a) −0.5 to −1.5 V and (b) −1.5 V to −0.5 V using the OTTLE system.

Scheme 1

quantitatively to that of **3**. The enhanced cathodic wave (A) of the minor component on an immediate second scan (Figure 1) reveals that the solution near the electrode is enriched in the minor component after the reduction/reoxidation cycle. The cathodic wave A in the second scan becomes larger than that in the single scan. The cathodic behavior of this complex was also studied in CH$_2$Cl$_2$ (Table 1). The overall behavior was similar in both solvents, and no solvent effect was seen.

OTTLE. An *in situ* measurement of the electronic absorption spectrum during the electrolytic reduction using an optically transparent thin-layer electrode (OTTLE) showed the reversibility of the reduction and reoxidation. Figure 2 shows the spectral changes during the controlled-potential electrolysis (at −1.40 V) using OTTLE. The spectra obtained after the reoxidation

Figure 3. Thin-layer cyclic voltammograms of 1 mM alkylidene-bridged complex **2** in CH_3CN containing 0.1 M TEAP ($v = 1$ mV s^{-1}, Pt gauze).
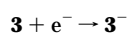
agree with the original spectra, in spite of the occurrence of a following chemical reaction. This observation implies that another chemical reaction is accompanied by reoxidation (EC reaction); when complex **2** was reduced by one electron, it was very unstable and underwent a structure change, but when it was reoxidized, it reverted to the original alkylidene-bridged complex **2**. Namely, complex **2** showed reversible behavior of the reduction process (Scheme 1).

Thin-Layer CV. Thin-layer cyclic voltammetry with slow scan rates provided more definite evidence about this chemical reaction. Figure 3 shows the thin-layer CV of complex **2** obtained at a slow scan rate (1 mV s^{-1}) using OTTLE. As is seen in Figure 3, only a pair of redox waves were obtained at ca. −0.92 V. They correspond to the small reduction wave (A) and reoxidation wave (C) in the conventional CV. This suggests that the chemical reaction prior to the electrochemical reaction (CE reaction) or electron-transfer catalysis (ETC reaction)[10] occurs in the case of the slow sweep scan. However, the latter was excluded by the chemical reduction experiment (as described later).
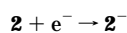
Therefore, an equilibrium exists between complexes **2** and **3**, and the equilibrium lies to the side of the chemical reaction product **3** due to the reduction. Thus, species **2** and **3** are in equilibrium, with **2** being the thermodynamically more stable isomer. However, the radical anion **2**$^-$ is very unstable and is rapidly converted to the radical anion **3**$^-$, which is reoxidized at ca. −0.8 V.

The reduction of complex **2** with 0.1 equiv of sodium tetrahydroborate (NaBH$_4$) gave two complexes. One is the starting complex **2** (in 88% yield), and the other is dithiolene complex **1** (in 10% yield). These results exclude the participation of electron-transfer catalysis (ETC). Also, the formation of complex **1** creates a

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(10) CE and ETC reactions are described as follows. CE reaction:

$$2 \rightarrow 3$$

$$3 + e^- \rightarrow 3^-$$

ETC reaction:

$$2 + e^- \rightarrow 2^-$$

$$2^- \rightarrow 3^-$$

$$3^- \rightarrow 2 + e^- \text{ and/or } 3^- + 2 \rightarrow 3 + 2^-$$

A way to check could be to react complex **2** with a small amount (e.g. 5%) of a homogeneous outer-sphere reducer and examine if **2** is converted to **3**. If one obtains only 5% conversion to **3**, there is no ETC reaction; if the yield of **3** is larger than 5%, there is an ETC reaction.

(11) Kajitani, M.; Igarashi, A.; Hatano, H.; Akiyama, T.; Sugimori, A.; Matsumoto, S.; Iguchi, Y.; Boennemann, H.; Shimizu, K.; Sato, G. P. *J. Organomet. Chem.* **1995**, *485*, 31.
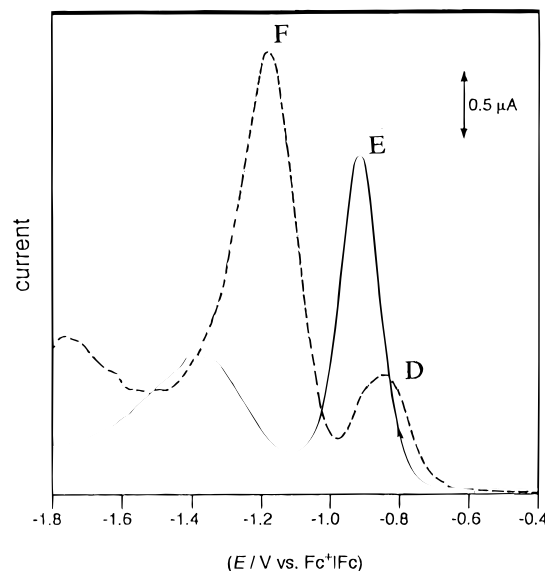

Figure 4. Differential pulse polarograms of complex **2**: (- - -) before reduction; (—) after reduction at −1.5 V (*vs* Fc$^+$/Fc).

question of whether complex **3** is complex **1** or not. The reduction potential obtained from CV cannot answer the question. Therefore, we performed differential pulse polarography in order to obtain more detailed information about this chemical reaction.

Differential Pulse Polarography (DPP). Figure 4 shows the DPP of complex **2** (broken line) and of the compound obtained after the controlled-potential reduction at −1.5 V (solid line). Two peaks (F and D) corresponding to the reductions of the complex **2** and **3** disappeared during the controlled-potential reduction, and a new peak (E) corresponding to the reduction of the original dithiolene complex **1** appeared at ca. −0.9 V. These results signify that complex **2** dissociates to the original dithiolene complex **1** via complex **3** by reduction (Scheme 3). Thus, the results of DPP can differentiate complex **3** from complex **1**.

The above result suggests that this chemical reaction is due to the cleavage of the Co−C or Co−S bond, which accompanies the dissociation of the alkylidene moiety. Apparently, one-electron reduction of **2** for several minutes produces anion radicals with a isomer. However, the radicals still contain a dithiolene ring and alkylidene moiety: [(Cp)Co{S$_2$C$_2$(COOMe)$_2$}{C(COOMe)$_2$}]$^-$.

ESR. The brown solutions of **2**$^-$ exhibited strong ESR signals. The ESR in frozen 1:1 ethanol-toluene solutions exhibits hyperfine splittings of a cobalt-centered radical (Figure 5, top). Judging from the lifetime of **2**$^-$, we ascribe the spectrum to the anion radical **3**$^-$ or **1**$^-$. The largest cobalt splitting is along the low-field g component ($g_1 = 2.28$, $A_{Co}(1) = 7.015$ mT). Because this spectrum is different from that of **1**$^-$ ($g_1 = 2.2240$, $g_2 = 2.0320$, $g_3 = 1.9895$, $A_{Co}(1) = 9.200$ mT, $A_{Co}(2) = -0.486$ mT, $A_{Co}(3) = 2.800$ mT; (Figure 5, middle), it seems to depend on the anion radical **3**$^-$. Pending a complete simulation of the spectrum, it can be stated with confidence that there is an appreciable cobalt(II) contribution to the half-filled orbital of the monoanion. Further, this spectrum (Figure 5, top) contains the spectrum of a small amount of **1**$^-$ (dashed lines). These spectra (**1**$^-$) grow with time when such
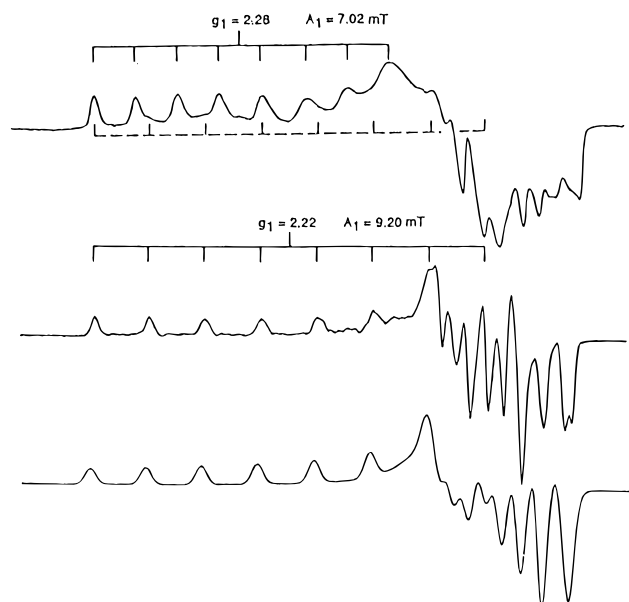
Scheme 2

Figure 5. ESR spectrum after reduction of complex **2** (top) and that of complex **1** (middle) in frozen 1:1 ethanol−toluene solutions and the simulated ESR spectrum of complex **1**$^-$ (bottom).

Figure 6. Cyclic voltammograms ($v = 100$ mV s^{-1}, $\Phi = 1.6$ mm, Pt disk) of 1 mM complex **4** in CH$_3$CN containing 0.1 M TEAP; initial slope is (a) to the negative side and (b) to the positive side.

solutions are kept at ambient temperature, and at last, they agree with that of **1**$^-$. These results agreed with the results of DPP and are ascribed to the formation of **1**$^-$ from **2**$^-$ *via* **3**$^-$.
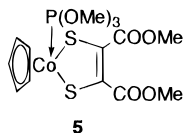
The electrochemical measurements gave important information about the reduced complex but offered no direct information about the geometry. That information came from the study of the reaction with trimethyl phosphite.

Reaction of the Alkylidene-Bridged Complex 2 with Trimethyl Phosphite. The reaction of alkylidene-bridged complex **2** with trimethyl phosphite results in the formation of sulfonium ylide **4** (Scheme 2).[6] Its structure has been established by X-ray crystallographic analysis.

CV. Cyclic voltammograms of complex **4** (solid line) and **2** (broken line) measured in acetonitrile solution are shown in Figure 6.

In the reduction, complex **4** exhibited a reversible redox peak at −1.0 V (H and I) and a small reversible peak at −0.8 V (G and J) similar to those of complex **2**. These former peaks (H and I) correspond to the redox peaks of complex **4**, and the latter peaks (G and J) correspond to the redox peaks of complex **3**. These peaks indicate the existence of an equilibrium between complex **4** and chemical reaction product **3**, just as complex **2** exists as an equilibrium mixture of **2** and **3** in solution.

The reduction potential of complex **4** (−1.01 V *vs* Fc$^+$/Fc) is more positive than that of complex **2** (−1.25 V *vs* Fc$^+$/Fc) and trimethyl phosphite complex [(Cp)Co{S$_2$C$_2$-(COOMe)$_2$}{P(OMe)$_3$}] (**5**)[11] (−1.38 V *vs* Fc$^+$/Fc). This

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result shows that the ylide moiety has strong electron-withdrawing abilities. This is explained by the fact that
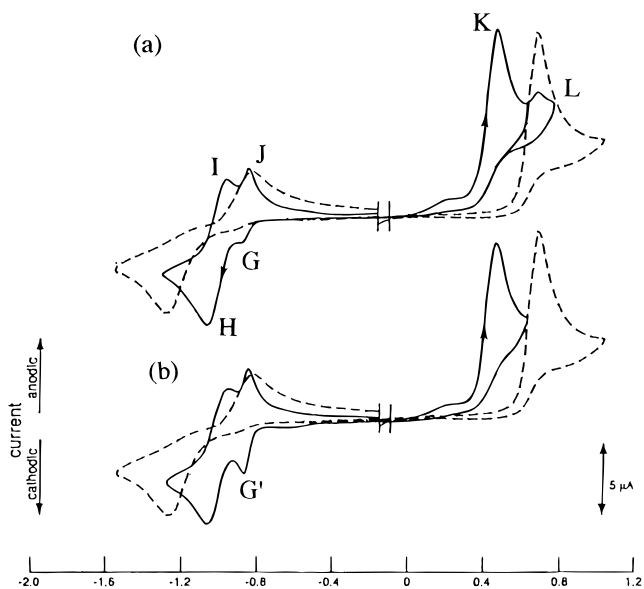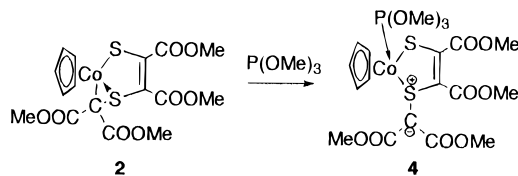
the carbon in the ylide form is found to be planar in structure, according to the sp^2 hybrid orbital of the carbon atom. Consequently, because the conjugated system is extended from the ester groups to the sulfur atom of the dithiolene ring, the reduction potential may shift to become more positive by reflecting the effect of electron-withdrawing properties in the esters.

This complex showed an irreversible oxidation peak (K). Also, if one continued the potential scan to a more positive range, one more small anodic peak (L) corresponding to the oxidation of complex **2** appeared. The formation of complex **2** thus accompanies the elimination of phosphite cation by the oxidation of complex **4**. Moreover, when the potential scan was swept back to the negative side, the cathodic peak at −0.8 V (D′) became much larger. This result supports the conclusion that the chemical reaction product has an ylide structure. The equilibrium in [(Cp)Co{S$_2$C$_2$(COOMe)$_2$}-{C(COOMe)$_2$}] is between the alkylidene-bridged triangle structure **2** and the ylide structure **3** formed by the cleavage of the Co−C bond (Scheme 3).

Other Odd-Electron Compounds Including Structural Changes. Some topics have been recently described in general reviews of redox-induced structural changes.[12−15]

With the exception of metal sandwich compounds such as cobaltocene[16] and [(η^6-arene)FeCp],[17] very few

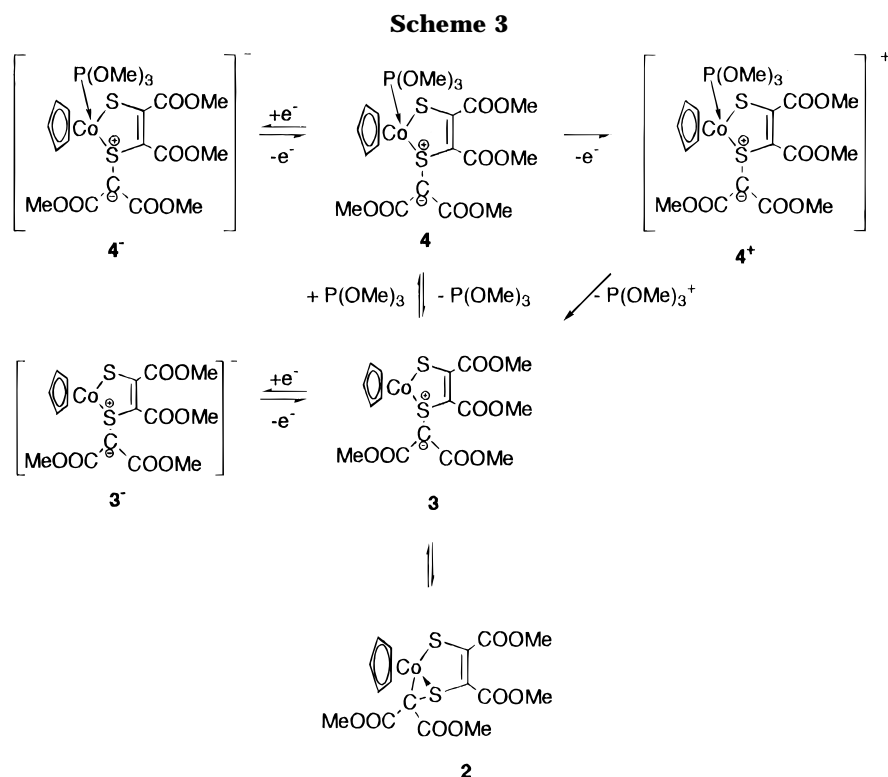(12) Astruc, D. *Chem. Rev.* **1988**, *88*, 1189.
(13) Tyler, D. R. *Acc. Chem. Res.* **1991**, *24*, 325.
(14) Geiger, W. E. *Acc. Chem. Res.* **1995**, *28*, 351.
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(16) (a) Pfab, W.; Fisher, E. O. *Z. Anorg Allg. Chem.* **1953**, *274*, 316.
(b) Wilkinson, G. *J. Am. Chem. Soc.* **1952**, *74*, 6148.

Scheme 3

4⁻ ⇌ (+e⁻ / −e⁻) **4** → (−e⁻) **4⁺**

+ P(OMe)₃ ‖ − P(OMe)₃   / − P(OMe)₃⁺

3⁻ ⇌ (+e⁻ / −e⁻) **3**

2

odd-electron complexes have been adequately characterized by physical methods.[18] Isolation and X-ray characterization of odd-electron complexes are carried out by the formation of a salt with a countercation, but they are usually difficult because the complexes have only a limited lifetime or are susceptible to air oxidation. Examples of well-characterized electronic and geometric structures of odd-electron complexes are rare because NMR analysis, which is a general method of structural analysis, is unavailable for odd-electron complexes.

Although the reversible isomerization between the alkylidene-bridged structure and ylide structure seems to be without precedent, we noted two other relevant studies which focused on the reversible structural changes caused by the reduction. In 1979, Moraczewski and Geiger reported reversible electrochemical isomerization of [(Cp)Co(COT)] (**6**, **7**)[19] (Scheme 4). This complex shows CV behavior very similar to that of complex **2**; the existence of isomers is proved by ^{1}H NMR spectra.

An argument in favor of such partial delegation is found in the results mentioned above by Krusic and co-workers on [(CO)$_3$Fe(diolef)]⁻ analogues.[20] When (CO)$_3$Fe(η^4-butadiene) (**8**) is reduced with 1 equiv of sodium naphthalenide, a high-resolution ESR spectrum of a radical with proton hyperfine splittings consisting of a doublet of triplets is obtained. This evidence is consistent with the presence of a η^2-butadiene ligand in anion **9**⁻ (Scheme 5).

These complexes are stabilized by the delocalization of the extra electron of the conjugated systems which

Scheme 4

6 → (+e⁻) **6⁻**

‖   ↓

7 ⇌ (+e⁻ / −e⁻) **7⁻**

Scheme 5

8 ⇌ (+e⁻ / −e⁻) **9⁻**
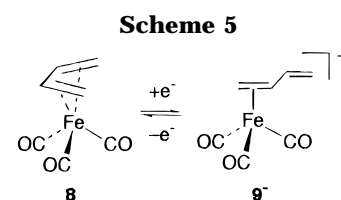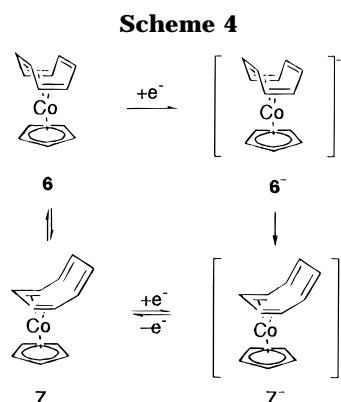
are formed by the structural change and show a reversible structural change due to the reoxidation.

Conclusion

From the results of this study, the electrochemical behavior of [(Cp)Co{S₂C₂(COOMe)₂{C(COOMe)₂}] is summarized, as shown in Scheme 1. When the alkylidene-bridged structure **2** is reduced by one electron, it is very unstable and isomerizes rapidly and quantitatively to the ylide form. Furthermore, this complex **2** exists as an equilibrium mixture of alkylidene-bridged form **2** and ylide form **3** in solutions. It causes some unusual behavior of complex **2**. An increase in the number of the electrons at the cobalt, because of reduction or addition, displaces the equilibrium to the ylide form.

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(19) (a) Moraczewski, J.; Geiger, W. E. *J. Am. Chem. Soc.* **1979**, *101*, 3407. (b) Geiger, W. E.; Rieger, P. H.; Corbato, C.; Edwin, J.; Fonseca, E.; Lane, G. A.; Mevs, J. M. *J. Am. Chem. Soc.* **1993**, *115*, 2314.

(20) Krusic, P. J.; San Filippo, J., Jr., *J. Am. Chem. Soc.* **1982**, *104*, 2645.

Scheme 6
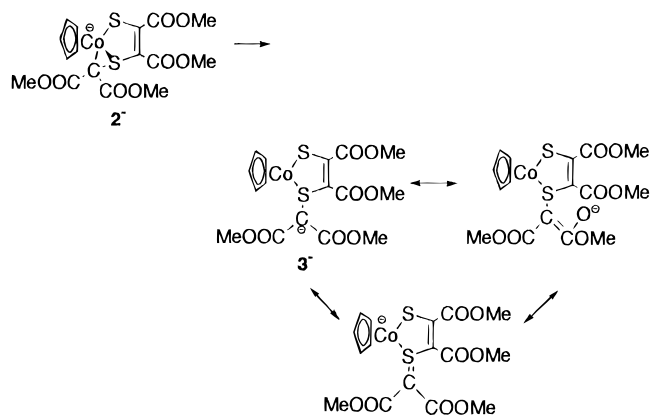
Clearly, the bridged form is the more stable one in the neutral compounds, but the ylide form is favored in the anion. The shift in stability may be due to the ability of an ylide isomer to delocalize the extra electron of the anion among the planar sulfur-bound alkylidene carbons (Scheme 6). It is apparent from these results that the nature of the metal−alkylidene carbon bond may be sensitive to the formal oxidation state of the metal and that electrochemical methods may prove useful in designing ways to alter the nature of the metal−alkylidene bond reversibly.

One more finding worth mentioning is the novel adduct of the substituent coordinated only to the sulfur atom in the cobaltadithiolene complex. Such adducts of substituent coordinated sulfur atoms have been synthesized in $M(dth)_2$ complexes (M = Ni, Pt, Pd; dth = $S_2C_2R_2$)[21] but not in CpM(dth) complexes, in which substituents coordinated to metal or metal- and sulfur-bridged adducts such as alkylidene have been synthesized. This structure is thought to cause the many unique properties in this complex. This finding will make a great contribution to future dithiolene chemistry. The structure of the odd-electron complex has been found by using a combination of electrochemical techniques and chemical reactivity. We hope that this paper will contribute to deducing the structure of odd-electron complexes.

(21) (a) Schrauzer, G. N.; Rabinowitz, H. N. *J. Am. Chem. Soc.* **1968**, *90,* 4297. (b) Zhang, C.; Reddy, H. K.; Schlemper, E. O.; Schrauzer, G. N. *Inorg. Chem.* **1990**, *29,* 4100.