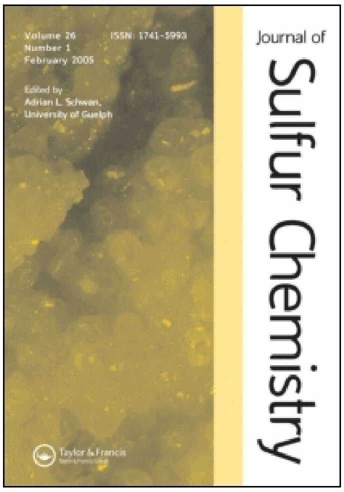

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Electrochemistry of [(Cp)M($S_2C_2R_2$)]-Type Metalladithiolene Complexes and their Derivatives

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ELECTROCHEMISTRY OF [(Cp)M($S_2C_2R_2$)]-TYPE METALLADITHIOLENE COMPLEXES AND THEIR DERIVATIVES

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Our studies on the electrochemical properties and electrochemical reactions of the [(Cp)M($S_2C_2R^1R^2$)]-type metalladithiolene complexes (M = Co and Rh) and their derivatives are reviewed. We discuss on (1) the dependences of redox potentials of the metalladichalcogenolene complexes on the components (metal, chalcogen, and substituents) of the complexes, (1′) the electrochemical properties of dinuclear metalladithiolene complexes, (2) the relationship between redox potentials and the reactions of the metalladithiolenes (addition of phosphorus compounds and catalysis for isomerization of quadricyclane to norbornadiene), and (3) the reactions of some addition products of the metalladithiolenes (phosphine or phosphite adducts, alkylidene adducts, and "three-component-adducts" among [(Cp)M($S_2C_2R_2$)]-type metalladithiolene, alkylidene, and hydrogen halide, elemental halogen, phosphine, or phosphite) induced by electrochemical reduction or oxidation. These studies have been done by means of ESR and UV-visible spectral measurement by the use of optically transparent thin layer electrodes (OTTLE) as well as by means of the electrochemical measurements.

Keywords: Cobaltadithiolene; rhodadithiolene; 1,2-ethylenedithiolatometal complex; dinuclear cobaltadithiolene; adduct of metalladithiolene; alkylidene-bridged cobaltadithiolene; redox potential; addition reaction; electrochemical dissociation

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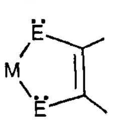
1 INTRODUCTION

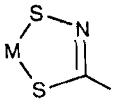
1.1 Types of Metalladichalcogenolenes

A metalladichalcogenolene (**A**)[1-6] is a heterocyclic ring consisting of one metal atom, two coordinated chalcogen atoms (sulfur and/or selenium), and two unsaturated carbon atoms. When the metal is cobalt and the chalcogen is sulfur, the ring is called cobaltadithiolene. According to the rules of inorganic nomenclature, the chelate ring is called 1,2-ethylenedichalcogenolatometal. A metalladithiazole ring (**B**) which was first synthesized by us is a nitrogen analog of the metalladithiolene ring.[7,8]



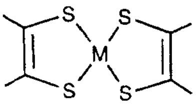
E = S, Se

A

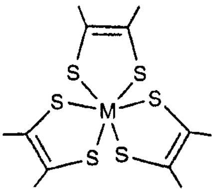


B

There are two types of metalladithiolene complexes: one includes the complexes having only 1,2-ethylenedithiolato as the ligand and the other (mixed ligand metalladithiolene) includes the complexes having ligand(s) other than 1,2-ethylenedithiolato. The first type of metalladithiolene complex is more popular. Several pioneering works have been done on the first type of metalladithiolene complexes.

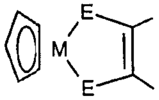


M = Ni, Pd, Pt



M = Cr, Mo, W

Examples of metalladithiolenes having only ethylenedithiolato as ligand



M =Co, Rh

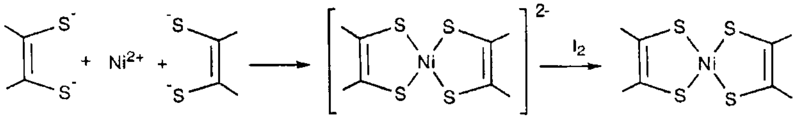
An example of mixed ligand metalladithiolene

In spite of the early synthesis of the second type of metalladithiolene complexes having cyclopentadienyl as another ligand (half-sandwiched metalladithiolene),[9-11] the chemisty of the second type of metalladithiolene complexes has been poorly investigated.

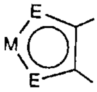
We have started a detailed study on the $[(Cp)M(S_2C_2R^1R^2)]$-type metalladithiolene complexes from the view point of organic chemistry and have found that the metalladithiolene rings show a variety of interesting reactions: substitution reactions due to their aromaticity and addition reactions due to their unsaturation. These reactions of metalladithiolene and metalladithiazole rings have recently been reviewed.[6] The present review describes mainly the electrochemical properties and electrochemical reactions of the $[(Cp)M(S_2C_2R^1R^2)]$-type metalladithiolene complexes. Before describing the electrochemistry, the valence state, functionalities, and characteristic reactions of the metalladithiolene rings will be summarized in the following sections of the Introduction.

1.2 *Electronic Structure of $[(Cp)M(S_2C_2R_2)]$-Type Metalladithiolenes*

As early as 1966, Schrauzer pointed out the unique valence state of the metalladithiolene ring.[12] The peculiar electronic state (valence state) appears in the very peculiar oxidation state of bis(1,2-ethylenedithiolato)nickel complex. The dithiolato ligand is formally, dianionic ($^-S{-}CR{=}CR{-}S^-$) and the stable oxidation state of nickel is 2+. Thus, $[Ni(S_2C_2R_2)_2]^{2-}$ should be stable, as is found to be the case. However, electrically neutral $[Ni(S_2C_2R_2)_2]$, in which the formal oxidation state of nickel is 4+, is also stable in air. Moreover, the neutral complex is diamagnetic.



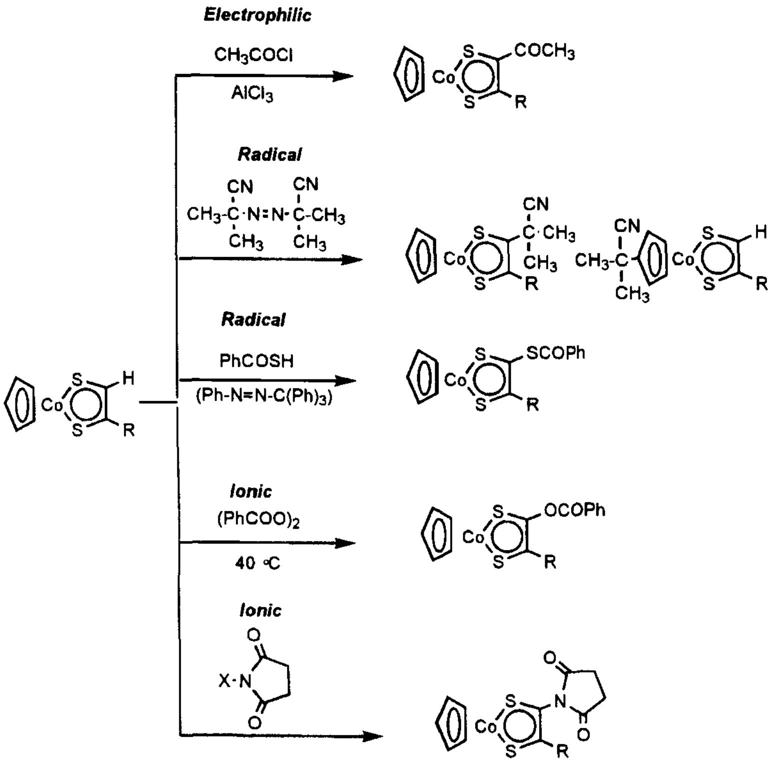
A metalladithiolene ring has a unique electronic structure. A metalladithiolene ring is planar. The chelate ring is a conjugated ring system with 6 π-electrons. Metalladichalcogenolene rings are characterized by the delocalization of π-electrons. It gives rise to aromaticity as well as an intense $\pi{-}\pi^*$ absorption in the visible region.[12,13] The ring current in ^1H NMR supports the aromaticity of the metalladithiolene rings.[14] Thus, we express the metalladichalcogenolene ring as **A2**.



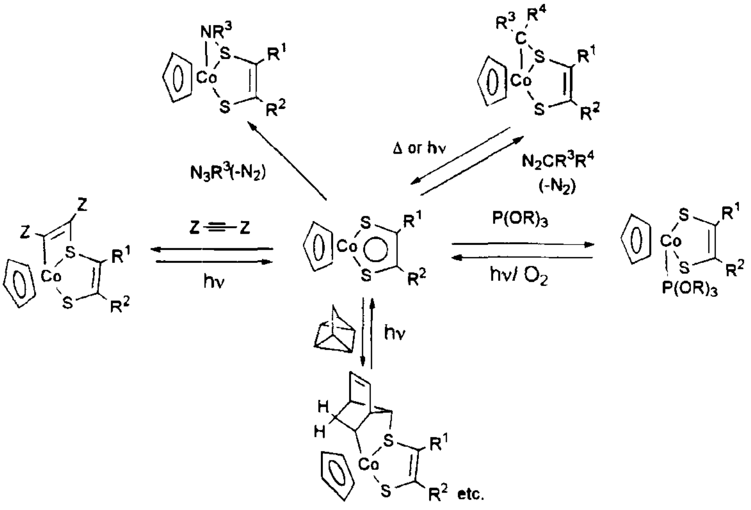
A2

1.3 Overview of Characteristic Reactions of $[(Cp)M(S_2C_2R_2)]$-Type Metalladithiolenes

Compared with the large amount of interest in their useful physical properties, interest in the chemical properties (reactivities) of the metalladichalcogenolene complexes is only recently growing. During last ten years, we have engaged in extensive studies on the reactions of metalladichalcogenolene complexes, especially $[(Cp)M(E_2C_2R^1R^2)]$-type mixed ligand metalladichalcogenolene complexes. We have clarified the unique reactivities of the metalladichalcogenolene rings i.e. the coexistence of substitution reactions due to aromaticity and addition reactions due to unsaturation. Typical examples of the substitution and addition reactions are shown in Schemes 1 and 2.



SCHEME 1



SCHEME 2

1.3.1 Substitution reactions due to aromaticity

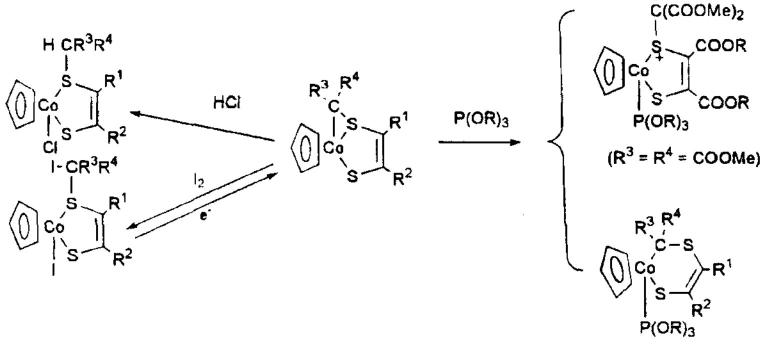
With respect to the reactions due to aromaticity, we have found several types of substitution reactions: electrophilic substitution,[15] radical substitution,[15,16] and substitution by other ionic mechanisms[17] (Scheme 1).

1.3.2 Addition reactions due to unsaturation

In contrast to the substitution reactions due to aromaticity, the metalladithiolene rings undergo a variety of addition reactions due to unsaturation.[6] Typical examples of addition reactions in [(Cp)M($S_2C_2R^1R^2$)]-type metalladithiolene complexes are shown in Scheme 2.

Most of addition reactions occur between metal and chalcogen. Diazo compounds react easily (at 0 °C) with [(Cp)M($S_2C_2R^1R^2$)]-type metalladithiolene complexes to give alkylidene adducts in which the alkylidene group bridges between metal and chalcogen. Azides react similarly to afford imido-bridged complexes. Quadricyclane addition to the metalladithiolenes is accompanied by a rearrangement of the hydrocarbon skeleton. Phosphines and phosphites are coordinated to the central metal atom.

Some adducts react further. Interesting ring opening reactions take place in the reaction with phosphorus compounds, hydrogen halide,



SCHEME 3

or dihalogen. Some examples of the ring opening reactions of the alkylidene-bridged complexes are shown in Scheme 3.

The electrochemical reactions which will be described in the succeeding chapters are mainly the reactions of these adducts.

1.4 Importance of Electrochemistry in Metalladichalcogenolene Chemistry

In order to understand the unique physical and chemical properties of the metalladichalcogenolene complexes, the electrochemical data give fundamental information. For the design of superconducting materials, the electrochemical measurements are indispensable. The spectral properties of the metalladichalcogenolene complexes are related to the redox properties.

Some of the unique reactions of the metalladichalcogenolene complexes can be understood after the consideration on their electrochemical properties. Sometimes the electrochemical measurements afford information on the structures of the reacting molecules in a solution. In addition, we found that in some cases the electrochemical reduction and/or oxidation induces interesting reactions.

In this article, we will describe:

(1) basic electrochemical data of the metalladichalcogenolene complexes,

(2) the current state of the understanding of unique reactions of the metalladichalcogenolene complexes on the basis of electrochemical data, and

(3) reactions caused by electrochemical reduction or oxidation.

An important feature of our study is the analysis of the electrochemical reactions on the basis of identification and quantification of the products. Another feature of our electrochemical study is the cooperative use of UV–visible spectra obtained using optically transparent thin-layer electrode (OTTLE) and ESR. These give firm grounds to the conclusions derived from the electrochemical measurements.

Here we ask for the understanding of the readers. We use in this article three sorts of potential values: the potential values relative to ferrocene/ferrocenium (Fc/Fc^+), relative to Ag/0.1 mol dm^{-3} $AgClO_4$, and relative to Ag/AgCl. Our study on electrochemistry continues over 10 years and we made the electrochemical measurements using several reference electrodes. This gives rise to the lack of unity in the potential values. In this review, we did not try to normalize the potential values. Instead, we describe the references in each case. [The potential values based on Fc/Fc^+ are almost the same as those based on $Ag/AgClO_4$ (the difference is 0.025 V) but the potential values based on Ag/AgCl are different from other potential values by several hundred mV.]

1.5 Functionalities of Metalladichalcogeolene Complexes

The unique electronic state gives interesting and useful functionalities to the metalladichalcogenolene complexes. The applications of metalladichalcogenolene complexes as functional materials are out of the scope of this review. But it is worth citing some important articles in these fields. Several groups are studying the electric properties of the metalladichalcogenolene complexes, aiming at the development of conducting[18] and superconducting material.[19] Their magnetic properties also attract interest.[20]

The optical and photochemical functionalities of the metalladichalcogenolene complexes have large potential for practical application. Some of them have already been used commercially. A typical example is the use of [M($S_2C_2R_2$)$_2$]-type metalladithiolene complexes as inhibitors against photodegradation of cyanine dyes used for CD ROM.[21,22] In spite of extensive application, the mechanism of the protecting effect has not been satisfactorily elucidated. Efficient quenching of singlet oxygen has been proposed for the mechanism. But a recent study on the protecting effect against photodegradation by [(Cp)Co($S_2C_2R_2$)]-type cobaltadithiolenes revealed that this type of cobaltadithiolene complexes act as efficient triplet quenchers as well as quenchers for singlet oxygen.[23]

Another important optical feature of metalladichalcogenolene complexes is the intense absorption in the visible to ultraviolet region.[24] Application as Q-switches for laser has been proposed.[24] Recently, the application of these materials as non-linear optical materials has been claimed.[25] There have been some studies on the application of metalladithiolene complexes as materials for photoluminescence,[26] liquid crystals,[27] photochromism,[28] and infra red dyes.[29]

2 ELECTROCHEMICAL PROPERTIES OF [(Cp)M($S_2C_2R_2$)]-TYPE METALLADICHALCOGENOLENES

2.1 *Mononuclear Metalladichalcogenolenes*[30–32]

A typical example of the cyclic voltammogram of [(R^3–Cp)Co-($E_2C_2R^1R^2$)]-type cobaltadichalcogenolene complexes is shown in Figure 1 (for the complex with R^3 = H, E = S, and R^1 = R^2 = CN). In Table I, the half-wave potentials of [(R^3–Cp)Co($E_2C_2R^1R^2$)]-type

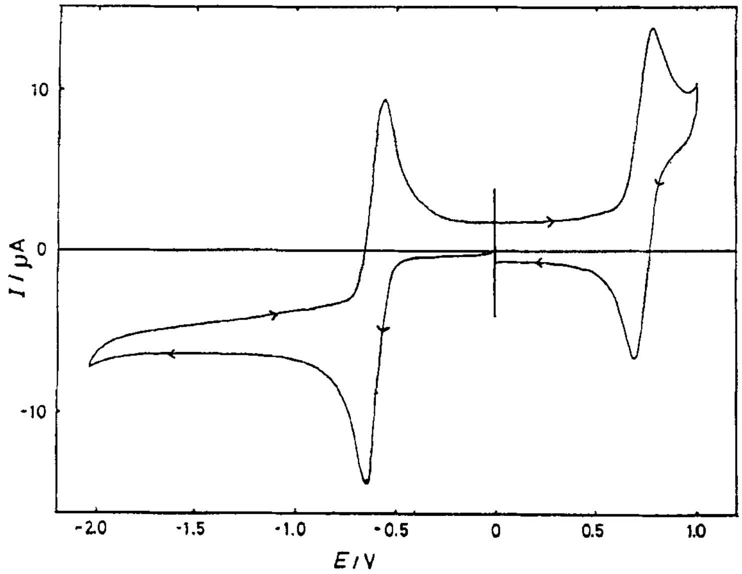
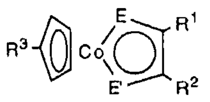


FIGURE 1 Cyclic voltammogram of [(Cp)Co{$S_2C_2(CN)_2$}] measured in an acetonitrile solution in the presence of 0.1 mol dm^{-3} of Et_4N ClO_4 at 25 °C. Reference electrode, Ag/0.1 mol dm^{-3} Ag ClO_4; test electrode, stationary platinum disk, 2 mm diameter; scan rate, 100 mV s^{-1}.

cobaltadichalcogenolenes are summarized.



1 : E = E'= S; R^3 = H;
2 : E = E'= S; R^3 =substituent;
3 : E = E'= S or Se; R^3 = H;

TABLE I Reversible half-wave potentials (vs. Ag/0.1 mol dm^{-3} $AgClO_4$) of half-sandwich type metalladichalcogenolene complexes and sum of field parameters ($\sum\chi_F$) of the substituents in the metalladichalcogenolene rings

Complex	R^3	*E*	*E'*	R^1	R^2	*Field parameter* $\sum\chi_F$	*Half-wave potential* $E^{r}_{1/2}(red)$	*Half-wave potential* $E_{1/2}(ox)$
Dithiolato complexes with unsubstituted Cp								
1a	5H	S	S	H	H	0	−1.21	ir
1b	5H	S	S	H	Ph	0.05	−1.19	0.30*
1c	5H	S	S	H	$C_6H_4NO_2(p)$		−1.07	ir
1d	5H	S	S	H	^{2}Py		−1.13	ir
1e	5H	S	S	H	^{3}Py		−1.11	ir
1f	5H	S	S	H	COOMe	0.23	−1.02	0.41*
1g	5H	S	S	Ph	Ph	0.12	−1.16	0.30*
1h	5H	S	S	Ph	$C_6H_4NH_2(p)$		−1.19	ir
1i	5H	S	S	Ph	$C_6H_4NO_2$		−1.07	0.36*
1j	5H	S	S	Ph	Ac	0.25	−1.04	ir
1k	5H	S	S	Ph	COOEt	0.29	−1.04	0.41*
1l	5H	S	S	Ph	NO_2	0.72	−0.81	0.52*
1m	5H	S	S	^{2}Py^a	^{2}Py^a		−1.11	ir
1n	5H	S	S	^{4}Py^b	^{4}Py^b		−1.03	ir
1o	5H	S	S	^{2}Py^a	^{4}Py^b		−1.07	ir
1p	5H	S	S	COOMe	COOMe	0.46	−0.91	ir
1q	5H	S	S	CN	CN	0.90	−0.59	0.70
Dithiolato complexes with substituted Cp								
2a	5Me	S	S	COOMe	COOMe	0.41	−1.21	ir
2b	3H, C_3H_6	S	S	COOMe	COOMe	0.44	−1.02	—^{c}
2c	4H, Me	S	S	COOMe	COOMe	0.45	−0.96	ir
2d	4H, Et	S	S	COOMe	COOMe	0.45	−0.96	ir
2e	4H, Ac	S	S	COOMe	COOMe	0.65	−0.67	ir
2f	5Me	S	S	Ph	Ph	0.07	−1.55	—^{c}
2g	4H, Ac	S	S	Ph	Ph	0.31	−0.93	—^{c}
2h	4H, Ac	S	S	H	Ph	0.25	−0.95	—^{c}
2i	5Me	S	S	CN	CN	0.85	−0.93	0.54
Selenolatothiolato and diselenolato complexes								
3a	5H	S	Se	H	Ph	0.06	−1.13	ir
3b	5H	S	Se	Ph	H	0.06	−1.13	ir
3c	5H	S	Se	Ph	Ph	0.12	−1.12	—^{c}
4a	5H	Se	Se	H	Ph	0.06	−1.09	ir
4b	5H	Se	Se	Ph	Ph	0.12	−1.08	—^{c}
4c	5H	Se	Se	COOMe	COOMe	0.46	−0.85	—^{c}

[a] ^{2}Py: 2-Pyridyl. [b] ^{4}Py: 4-Pyridyl. [c] Not determined. *Midpoint of the cathodic and anodic potentials is listed.

Each [(R^3-Cp)Co($E_2C_2R^1R^2$)]-type cobaltadichalcogenolene complex listed in Table I except **2f** shows a reduction step and an oxidation step. (Oxidation waves were observed for **2g**, **2h**, **3c**, **4b**, and **4c**, but the half-wave potentials were not determined.)

The reduction step is a reversible process. Normal-pulse, hydrodynamic, and/or triangular-wave voltammetric results indicate that every reduction step is mass-transfer controlled. Each reduction is a Nernstian one-electron process without any complications owing to following reactions. The reversibility of the reaction was confirmed by the measurement of UV–visible spectra using OTTLE.

The ESR spectrum observed after one-electron reduction of [(Cp)Co{$S_2C_2(CN)_2$}] (Figure 2) consisted of 8 hyperfine lines with equal spacing; the *g*-value is 2.087. The spectrum shows that the unpaired electron is localized around a nucleus of nuclear spin 7/2, namely cobalt.

The oxidation process, on the other hand, is less simple. Some complexes (complexes **1q** and **2i**) show Nernstian one-electron steps; **1b**, **1g**, **1i**, **1k**, and **1l** show a couple of oxidation and reduction peaks with peak separations of 100–190 mV in the triangular-wave voltammograms; **2f** gives no oxidation step. The oxidation processes of the remaining complexes are quite complicated. The normal-pulse and hydrodynamic voltammograms are drawn-out or ill-defined. The triangular-wave

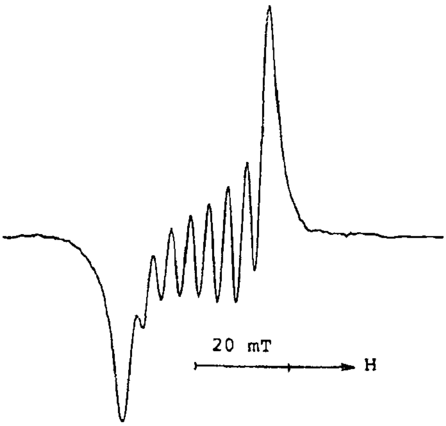


FIGURE 2 ESR spectrum of on-electron reduction product of [(Cp)Co{$S_2C_2(CN)_2$}] in acetonitrile at room temperature.

voltammograms show only ill-defined or overlapping anodic peaks or humps accompanied by either a small cathodic peak at a remote negative potential or none at all.

The reversible half-wave potentials of the reduction steps, $E^r_{1/2}$(red), correlate with the electronic parameter of the substituents.

As shown in Figure 3, the reversible half-wave potentials are linearly dependent on the sum of the field parameters χ_F (a Hammett's σ

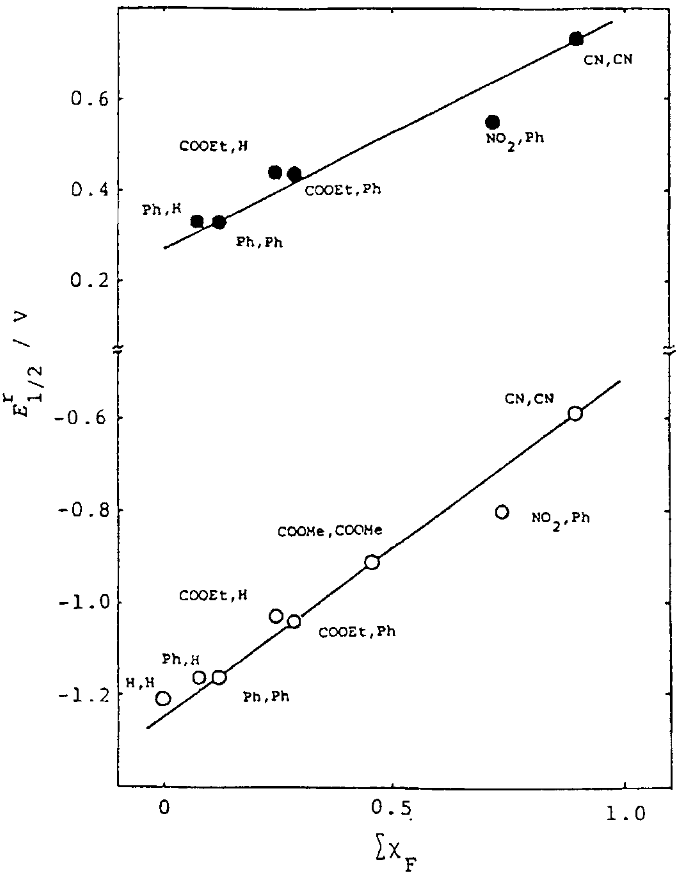


FIGURE 3 Plots of reversible half-wave potentials of against the sums of field parameter of the substituents (a Hammett's plot) in [(R^3–Cp)Co($E_2C_2R^1R^2$)]-type cobaltadichalcogenolene complexes. ●: For the first one-electron oxidation step; ○: For the first one-electron reduction step.

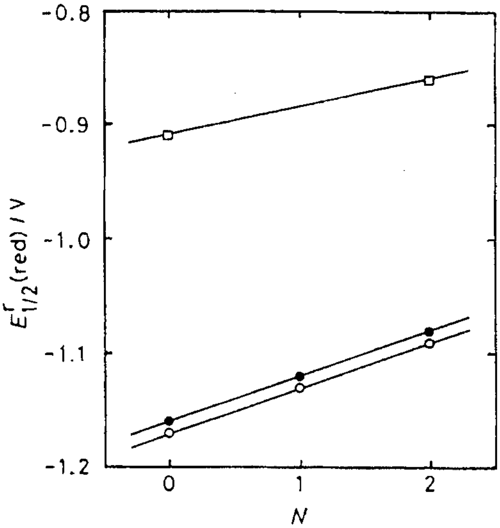


FIGURE 4 Plot of $E_{1/2}$(red) against the number of Se atoms for [(R^3-Cp)-Co($E_2C_2R^1R^2$)]-type cobaltadichalcogenolene complexes. □: $R^1 = R^2 =$ COOMe; ●: $R^1 = R^2 =$ Ph; ○: $R^1 =$ H, $R^2 =$ Ph.

which takes into the account the direct through-space transmission of the inductive effect of the substituents to the particular site considered [33,34]).

The replacement of S by Se causes a positive shift of $E^{r}_{1/2}$(red) (Figure 4). This may be explained partly by the higher electronegativity of Se (2.5) than that of S (2.4) (according to Allred–Rochow's electronegativity[35]).[36] However, the difference in electronegativity is not large enough to explain the difference in the reduction potentials. Another explanation is by the difference in delocalization of electron in metalladichalcogenolene rings. The atomic radius of Se is larger than that of S and, therefore, the double bond character of Co=Se should be smaller than that of Co=S. The delocalization of selenium-containing metalladichalcogenolenes would be lower than that of sulfur-containing metalladithiolenes. The decrease of conjugation of the ring results in the decrease of the supply of electrons to the metal atom. Thus, the cobalt atom adjacent to Se would be more positive than that adjacent to S. The positive shift caused by the replacement of S by Se may be partly due to the less effective conjugation of the selenium-containing metalladichalcogenolene rings.

Cobaltadithiazole complexes, in which the carbon atom of a cobaltadithiolene ring is replaced by a nitrogen atom, show similar electrochemical behavior. They undergo a reversible one-electron reduction which is ascribed to the reduction of Co(III) to Co(II).[7,8]

Next, we describe the electrochemical behavior of [CpCo(dmit)] (dmit = 1,3-dithiole-2-thione-4,5-dithiolato) and its ketone (dmio) analog which are of interest as superconducting materials.[37,38] Each thioketone **5** and ketone **6** exhibits a reversible reduction process and two reversible oxidation processes in spite of the fact that the complex has only one metal atom (Figure 5). These results suggest that the complex may be able to store and transfer electrons effectively.

Analysis of normal-pulse and hydrodynamic voltammograms of **5** reveal that the first and second oxidation processes as well as reduction process are Nernstian one-electron processes with the limiting current controlled by diffusion or convective diffusion, but they have some subsequent chemical reactions. A yellow insoluble solid is deposited on the working electrode by electrolytic oxidation of **5**

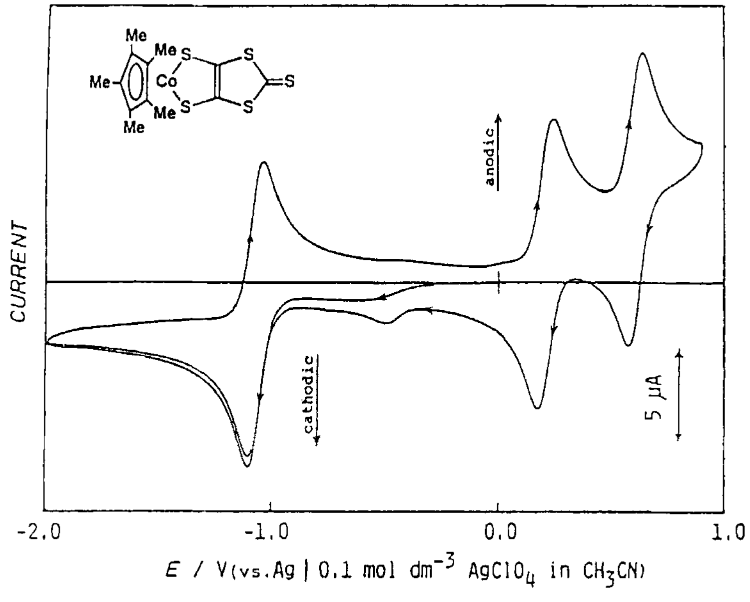
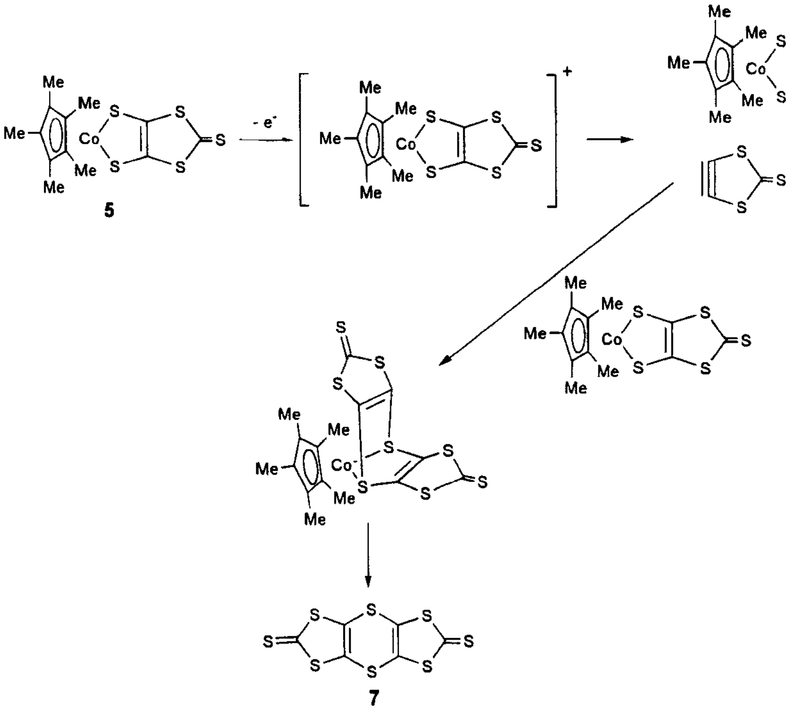


FIGURE 5 Cyclic voltammogram of [CpCo(dmit)] in an acetonitrile solution. Reference electrode, Ag/Ag Cl; scan rate, 100 mV s^{-1}.

at the first oxidation potential. High resolution MS of the yellow solid shows a peak attributable to C_6S_8 (Found: *m/z* 327.7767; Calcd. for C_6S_8M, 327.7766). An EC mechanism is postulated for the electrolytic oxidation process in Scheme 4.

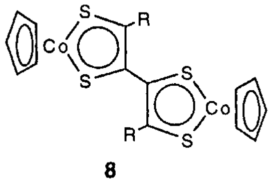


SCHEME 4

2.2 *Dinuclear Metalladithiolene Complexes*

Recently the mixed-valence states derived from the intramolecular interaction between two (or more) metal-complex-moieties have attracted increasing interest owing to attempts to produce high temperature superconducting organometallic materials or organometallic catalysts due to the cooperative behavior of the metals. We examined the intramolecular interaction between two cobaltadithiolene moieties in two systems: (1) the dinuclear complexes in which two metalladithiolene rings are bound directly (**8**: Type-I dinuclear cobaltadithiolene) and

(2) the dinuclear complexes in which two cyclopentadienyl rings are bonded together via another group X (**9**: Type-II dinuclear cobaltadithiolene).



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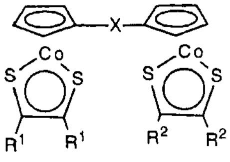
Type-I Dinuclear Cobaltadithiolene



9

Type-II Dinuclear Cobaltadithiolene

2.2.1 Type-I dinuclear cobaltadithiolene complexes[39]

The Type-I dinuclear complexes show two reduction waves as exemplified by the cyclic voltammogram of **8** ($R = CH_3$) (Figure 6).

The potentials of the first reduction wave of these Type-I dinuclear cobaltadithiolenes are almost the same as those of the corresponding mononuclear cobaltadithiolene complexes. This shows the very small intramolecular interactions between two cobaltadithiolene rings in the electrically neutral state. This can be understood after considering configuration of the two cobaltadithiolene rings in the dinuclear complexes: the two cobaltadithiolene rings are almost perpendicular with each other and we can expect only a small conjugation between the two cobaltadithiolene rings.

The half-wave potentials of the 1st and 2nd reduction are dependent on the substituents: the complexes having electron-attracting substituents have more negative half-wave potentials.

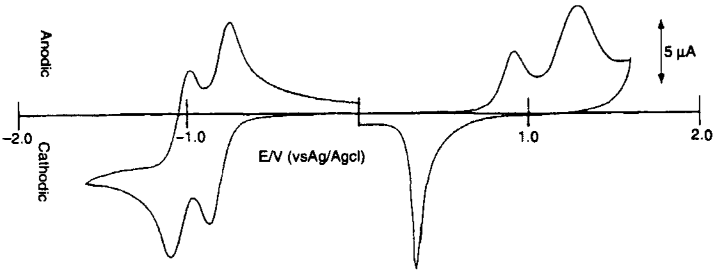


FIGURE 6 Cyclic voltammogram of a Type-I dinuclear cobaltadithiolene complex **8** ($R = CH_3$) measured in a dichloromethane solution at 25 °C. Reference electrode, Ag/ 0.1 mol dm^{-3} Ag ClO_4; scan rate, 100 mV s^{-1}.

TABLE II Reduction half-wave potentials (vs. Ag/AgCl) of directly bound dinuclear cobaltadithiolenes (**8**) and the corresponding mononuclear cobaltadithiolenes

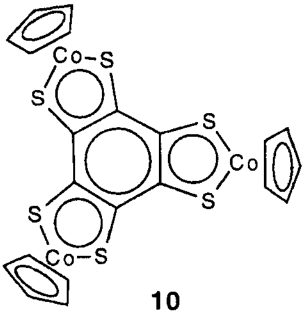
	$E^{r}_{1/2}$(*red.* 1) mV	$E^{a}_{p}-E^{c}_{p}$ mV	$E^{r}_{1/2}$(*red.* 2) mV	$E^{a}_{p}-E^{c}_{p}$ mV	$\Delta E^{r}_{1/2}$ mV
Dinuclear cobaltadithiolene					
8a (R = H)	−665	95	−950	100	285
8b (R = CH_3)	−818	84	−1040	85	222
8c (R = $SiMe_3$)	−828	90	−1090	100	262
8d (R = Ph)	−720	80	−880	70	160
8e (R = C_6H_4-$COCH_3$-*p*)	−682	70	−876	72	192
8e (R = C_6H_4-NO_2-*p*)	−610	90	−810	73	200
Mononuclear cobaltadithiolene					
8a (R = H)	−790	110	—	—	—
8b (R = CH_3)	−810	100	—	—	—
8d (R = Ph)	−760	310	—	—	—
8e (R = C_6H_4-NO_2-*p*)	−630	104	—	—	—

Half-wave reduction potentials were obtained from cyclic voltammograms measured in CH_2Cl_2 at 25 °C. Scan rate, 100 mV s^{-1}.

The separation between the 1st and 2nd reduction potentials suggests that the two cobaltadithiolene rings interact more strongly, when one cobaltadithiolene ring is reduced. The mixed-valence states would be stabilized. The stability of mixed-valence states in dinuclear complexes is evaluated in terms of $\Delta E^{r}_{1/2}$(red) values [$\Delta E^{r}_{1/2}$(red) = $E^{r}_{1/2}$(red. 1) − $E^{r}_{1/2}$(red. 2)].

The $\Delta E^{r}_{1/2}$(red) values of the Type-I dinuclear cobaltadithiolenes range between 160 and 285 mV as shown in Table II.

Nishihara *et al.* reported that the $E^{r}_{1/2}$(red. 1) − $E^{r}_{1/2}$(red. 2) value of the planar trinuclear cobaltadithiolene complex **10** is 0.24 V.[40] This value is similar to the $\Delta E^{r}_{1/2}$(red) values of the directly bound dinuclear cobaltadithiolene complexes in which two cobaltadithiolene rings cannot be coplanar.[40]



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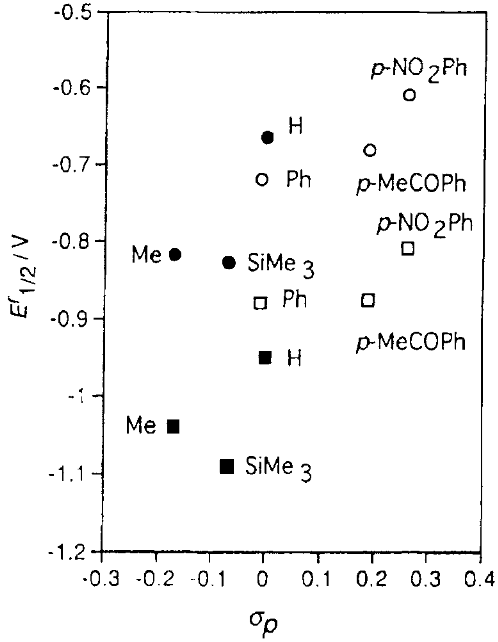


FIGURE 7 Hammett's plots for $E^{r}_{1/2}$(red. 1) and $E^{r}_{1/2}$(red. 2) of Type-I dinuclear cobaltadithiolene complex **8**. ○: $E^{r}_{1/2}$(red. 1) for **8** having aryl substituent; ●: $E^{r}_{1/2}$(red. 1) for **8** having non aryl substituent; □: $E^{r}_{1/2}$(red. 2) for **8** having aryl substituent; ■: $E^{r}_{1/2}$(red. 2) for **8** having non aryl substituent.

There seems to be no clear difference in the effects of aryl substituted and non-aryl substituted complexes in the Hammett's plots of $E^{r}_{1/2}$(red. 1) and $E^{r}_{1/2}$(red. 2) (Figure 7). On the other hand, the plots of $\Delta E^{r}_{1/2}$(red) (= $E^{r}_{1/2}$(red. 1) − $E^{r}_{1/2}$(red. 2)) vs. σ_p show two different linear relationships: one is for the complexes having non-aryl substituents and the other is for the complexes having aryl substituents (Figure 8).

The mixed-valence state of the anionic dinuclear cobaltadithiolene complexes is stabilized by the delocalization of an extra electron in the two cobaltadithiolene rings bound directly. The complexes having non-aryl substituents show larger $\Delta E^{r}_{1/2}$(red) and larger dependence on the σ_p values, while the complexes having aryl substituents show smaller $\Delta E^{r}_{1/2}$(red) and weaker dependence on the σ_p values. This suggests that in mono-anionic states the conjugation between two metalladithiolene

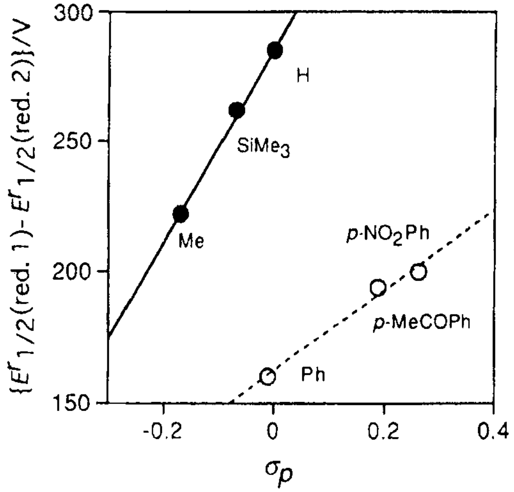


FIGURE 8 Hammett's plots for $\Delta E^r_{1/2}(\text{red})(= E^r_{1/2}(\text{red. }1) - E^r_{1/2}(\text{red. }2))$ of Type-I dinuclear cobaltadithiolene complex **8**. ○: **8** having aryl substituent; ●: **8** having non-aryl substituent.

rings becomes more important for the stabilization than in electrically neutral states. The inhibition of the conjugation by more bulky aryl groups may cause the lower $\Delta E^r_{1/2}(\text{red})$ values. The electron-attracting substituents would contribute to the stabilization of the mono-anionic complexes more effectively.

2.2.2 Type-II dinuclear cobaltadithiolene complexes[41]

Interestingly, the dinuclear cobaltadithiolene complex (**9**) bound at the cyclopentadienyl rings by methylene show larger interactions than the Type-I directly bound cobaltadithiolenes.[39] In contrast to the two-step reversible reduction of the latter complexes, the dinuclear complex having methylene-bridged Cp rings (**9**) shows one reversible and one irreversible reduction. This shows the strong interaction between the reduced cobaltadithiolene moiety and the electrically neutral cobaltadithiolene moiety. The $\Delta E_{1/2}(\text{red})$ value (in this case, the second reduction is irreversible) is 670 mV. This value is much larger than the values (160–285 mV) of the directly bound cobaltadithiolenes.

The dinuclear cobaltadithiolenes having C=O-bridged Cp rings show no similar behavior. The two reduction waves are reversible and the $\Delta E_{1/2}$(red) value is 220 mV.

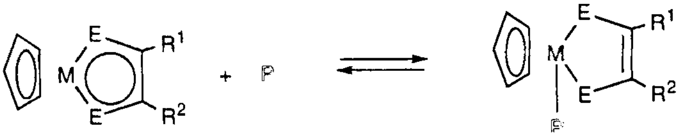
The dinuclear cobaltadithiolenes having silanediyl-bridged cyclopentadienyl rings are different from that having methanediyl-bridged cyclopentadienyl rings. The two reduction waves are reversible and the $\Delta E_{1/2}$(red) values are in the range of 120–170 mV.

3 RELATIONSHIP BETWEEN ELECTROCHEMICAL PROPERTIES AND REACTIVITIES

As described in Section 1.3.2, the metalladichalcogenolene complexes undergo a variety of addition reactions. The reactivities of some reactions are controlled by the redox potentials of the metalladithiolene complexes. As examples of such reactions, adduct formation with phosphines or phosphites and the catalyzed isomerization of quadricyclane to norbornadiene will be discussed.

3.1 Adduct Formation with Phosphines and Phosphites[42]

Some [(Cp)M($E_2C_2R^1R^2$)]-type metalladichalcogenolene complexes (M = Co and Rh, E = S and Se) form 1 : 1 adducts with phosphines or phosphites. The phosphorus compounds are coordinated to the metal atom. The reaction is an equilibrium reaction.



P = PR_3 (R = Me, Et, Bu); $P(OR)_3$ (R = Me, Et, Bu)

There is a good correlation between the equilibrium constants for the formation of these adducts and the $E^r_{1/2}$(red) values of the cobaltadithiolene complexes. When the logarithm of the formation constants, log(K(mol^{-1} dm^3)), is plotted against the reversible half-wave potentials for reduction $E^r_{1/2}$(red) of the free cobaltadithiolene complexes, the points lie along an almost straight line for a given phosphorus

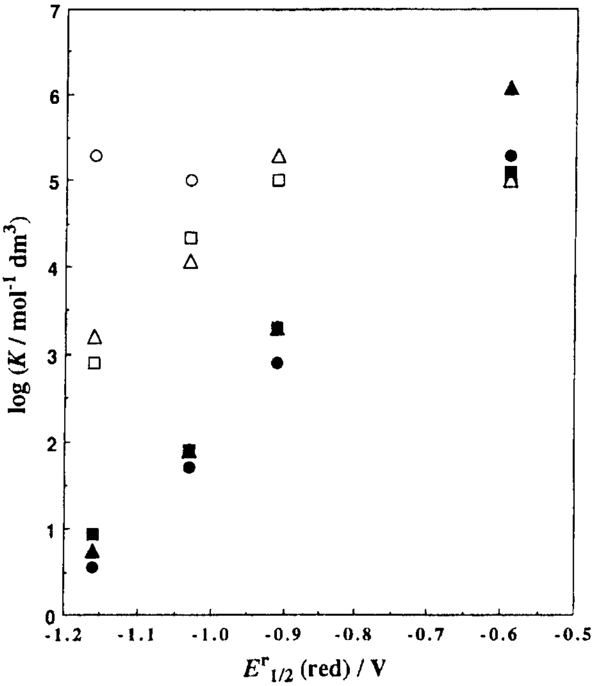


FIGURE 9 Dependence of log$K$ for the formation of phosphine or phosphite adducts on $E^r_{1/2}$(red. 1) of the cobaltadithiolenes. ○: For the adduct formation with PMe_3; □: For the adduct formation with PEt_3; △: For the adduct formation with PBu_3; ●: For the adduct formation with $P(OMe)_3$; ■: For the adduct formation with $P(OEt)_3$; ▲: For the adduct formation with $P(OBu)_3$.

ligand (Figure 9). The electron-attracting substituents in the cobaltadithiolene ring make $E^r_{1/2}$(red) more positive and thus increase the positive charge at the cobalt atom. This facilitates the coordination of the phosphorus compounds to the cobalt atom.

3.2 *Catalysis of Isomerization of Quadricyclane to Norbornadiene*[43]

Owing to the coexistence of aromaticity and unsaturation, the metalladithiolene rings undergo both addition and elimination easily: unsaturated character causes the facile addition reaction, while aromaticity causes the regeneration of conjugated system by facile elimination. The bonds formed between an atom in the metalladithiolene ring and an atom of the added group would be neither too strong nor too weak.

Easy bond formation and easy bond cleavage give rise to a catalytic process.

We found that the cobaltadithiolene complexes (**1**) catalyze the isomerization of quadricyclane (Q) to norbornadiene (NBD).[43] As mentioned in the Introduction, cobaltadithiolene complexes form adducts with quadricyclane (**11**).[44] Parallel to the adduct-formation, isomerization of quadricyclane to norbornadiene occurs. The isomerization is dominant over the adduct-formation. In some cases the ratios of the isomerization to the adduct-formation reach to several thousands.

The catalytic activities of the cobaltadithiolene complexes (expressed as turnover number) are dependent on the half-wave potentials for reduction of the complexes (namely on the positive charge on the metal atom) as shown in Figure 10. This suggests that the electron transfer from quadricyclane to the cobaltadithiolene plays an important role for the catalytic isomerization of quadricyclane to norbornadiene. The cobaltadithiazole complex also catalyzes the reaction. The plot of catalytic activity against $E_{1/2}$(red) for the cobaltadithiazole complex (○) lies on the line for the plot for the cobaltadithiolene complexes. However, the charge transfer interaction cannot explain the catalytic isomerization completely. A titanium dithiolene complex (**12**) with a half-wave potential of −1.13 V does not catalyze the isomerization of quadricyclane to norbornadiene. (The cobaltadithiolene with a half-wave potential of −1.13 V should catalyze the isomerization

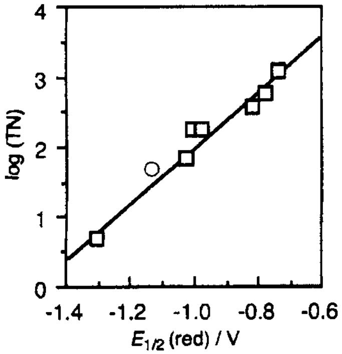
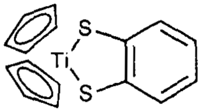


FIGURE 10 Relation between catalytic activity of the cobaltadithiolene and cobaltadithiazole (○) for the isomerization of Q to NBD and $E^{r}_{1/2}$(red. 1).

of quadricyclane effectively.) These titanium dithiolene complexes do not form adducts with quadricyclane.



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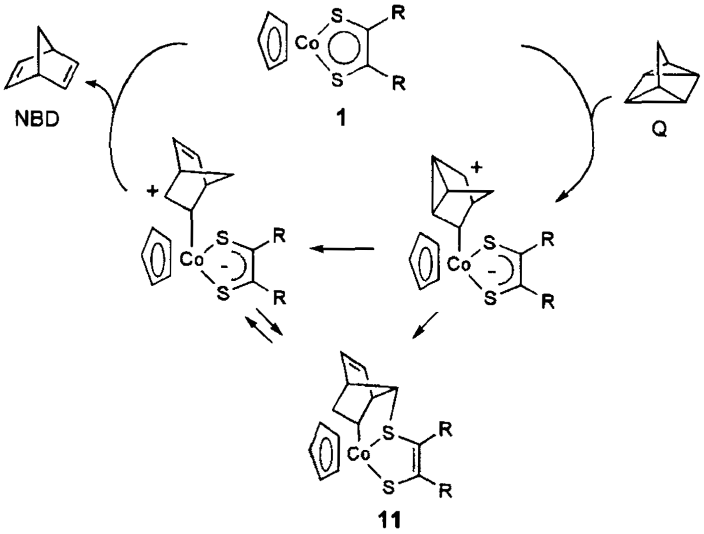
These facts indicate that partial bond formation between the metal of the dithiolene complex and a carbon atom of quadricyclane is essential for the catalytic reaction. Thus, the following mechanism including the intermediary bonding between Co and hydrocarbon moiety can be postulated (Scheme 5).[43]



SCHEME 5

4 REACTIONS OF ADDITION PRODUCTS INDUCED BY ELECTROCHEMICAL REDUCTION OR OXIDATION

Some addition products of metalladichalcogenolene complexes shown in Schemes 2 and 3 display interesting behavior, when they are reduced or oxidized. We have studied the reactions induced by electrochemical reduction or oxidation.

An electron is the simplest chemical reagent. It is very useful to learn how the addition or removal of an electron or electrons induces structure changes or reactions. However, beside Geiger's and a few other groups, studies of electrochemical behavior accompanying dynamic structural change in organometallic complexes, especially those having complicated structures, are still rare.[45–53]

The careful examination of cyclic voltammograms affords more detailed information on the dynamic behavior of the species formed in the electron transfer. In addition, *in situ* measurement of electronic absorption spectra is possible by the use of OTTLE. *In situ* measurement of ESR is also possible. By analyzing the data from these experiments as a whole, we can know the structural changes and reactions following the electrochemical redox reaction in more detail.

The electrochemical reaction of the addition products is a good model for the analysis of the dynamic behavior induced by the electron uptake or removal.

4.1 Adducts with Phosphines and Phosphites[54,55]

As described in Section 3.1, [(Cp)M($S_2C_2R^1R^2$)]-type metalladithiolene complexes form 1 : 1 adducts with phosphines and phosphites.[42] The reaction between the metalladithiolene complex and phosphorus compound is essentially an equilibrium reaction. But several combinations of metalladithiolene and phosphorus compound afford systems in which the equilibrium favors the adducts. The cobaltadithiolene having two CN groups (**1q**) forms stable (isolable) adducts (**13**) with phosphines or phosphites.

Either by electrochemical reduction or by oxidation, these adducts eliminate phosphorus compounds. A cyclic voltammogram (for tributylphosphine adduct of the dicyanocobaltadithiolene) is shown in Figure 11.

By analyzing carefully the cyclic voltammogram, the existence of reactions induced by electrochemical reduction or oxidation can be concluded. The peak separation of the anodic process is 62 mV, reflecting the Nernstian nature of the process. However, the cathodic current is slightly smaller than the anodic peak current, and the difference is

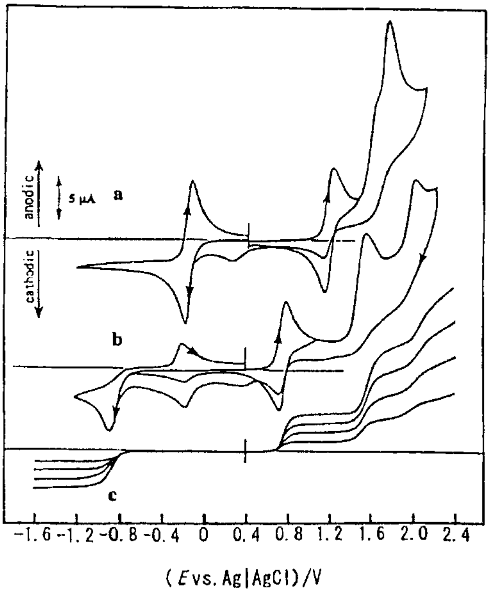


FIGURE 11 Cyclic and hydrodynamic voltammograms of dicyanocobaltadithiolene (**1p**) and its PBu_3 adduct (**13**) in an acetonitrile sution (1 mmol dm^{-3}) at 25 °C. (a) Cyclic voltammogram of **1p**: [**1p**] = 1 mmol dm^{-3}; scan rate, 100 mV s^{-1}; (b) Cyclic voltammogram of **13**: [**13**] = 1 mmol dm^{-3}; scan rate, 100 mV s^{-1}; (c) Hydrodynamic voltammogram of **13**: [**13**] = 1 mmol dm^{-3}; rotation rate, 400, 900, 1600, and 2500 rev min^{-1}.

more pronounced at lower scan rates. This indicates the presence of a chemical reaction after the electron transfer. When the potential scan is swept back to negative, a new cathodic wave is observed at −0.15 V vs. Ag/AgCl, a potential is very close to that of the reduction peak of **1q**, suggesting that the product is the free cobaltadithiolene complex.

The results obtained by controlled-potential coulometry confirm the formation of the free cobaltadithiolene. Thin-layer cyclic voltammetry (in which diffusion is strongly limited) with slow scan rates and *in situ* measurement of the electronic absorption spectrum during oxidation using OTTLE provide more definite evidence for the identity of the final oxidation product Figure 12.

Thus, the oxidative dissociation of the phosphine adducts of the cobaltadithiolene to the electrically neutral free cobaltadithiolene has been concluded.

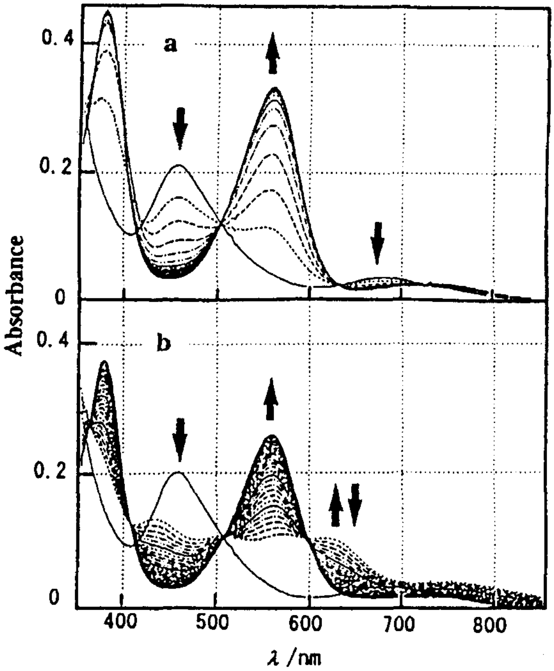
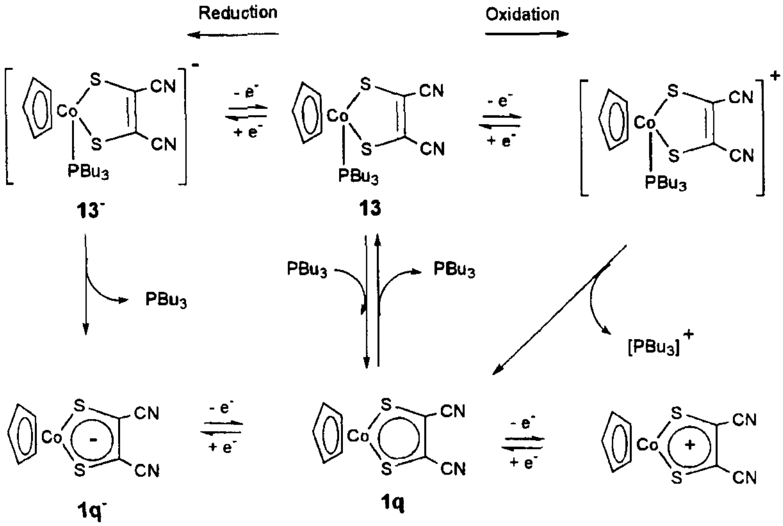


FIGURE 12 Electronic spectrum change **13** during oxidation obtained by the use of OTTLE. Sampling time, 0–1500 s; sampling interval, 50 s; potential stepped from (a) 0.3–0.65 V and (b) 0.3–0.80 V vs. Ag/AgCl.

Electrochemical reduction also causes the elimination of the phosphorus ligands. As seen in Figure 11 the reduction of adduct **13** is a Nernstian one-electron process. Nevertheless, the corresponding re-oxidation peak is not observed even at a high scan rate (10 V s^{-1}). Instead, a new oxidation peak appears at −0.12 V vs. Ag/AgCl. The latter is attributed to the re-oxidation of the reduced form of the free complex **1q**$^-$. When multi-cyclic voltammetry was carried out between 0.4 and −1.2 V with a scan rate of 10 V s^{-1}, the reduction wave of the free complex, which should be generated at the electrode surface on the positive sweep was not observed. These facts would lead to the conclusion that the dissociation of the reduced adduct, **13**$^-$, dissociates very rapidly to the anion of the free cobaltadithiolene (**1q**$^-$) and phosphine and that **1q** reacts very rapidly with phosphine, when **1q**$^-$ is re-oxidized. The results of the OTTLE experiment confirm the conclusion drawn



SCHEME 6

from voltammetric observations. Thus, the electrochemical reactions of a phosphine adduct **13** can be summarized in Scheme 6.

4.2 Adducts with Alkylidene

The [(Cp)M($E_2C_2R^1R^1$)]-type metalladichalcogenolenes react with diazo compounds with the loss of N_2 to afford the complexes in which (substituted) methylene groups bridge between metal and chalcogen.[56] The methylene (alkylidene) adducts [(Cp)Co($S_2C_2R^1R^1$)(CR^3R^4)] show a variety of reactions after electrochemical reduction and oxidation depending mainly on the electronic states at the bridging alkylidene.

4.2.1 Methylene-bridged cobaltadithiolene complexes

Most of the alkylidene-bridged cobaltadithiolenes eliminate the bridging moiety after electrochemical reduction or oxidation.[57] In the reduced form, the elimination of the alkylidene occurs. As a typical example, the cyclic voltammogram of the methylene-adduct of [(Cp)Co{$S_2C_2(COOMe)_2$}] (**14**) is shown in Figure 13.

A methylene-bridged complex **14** displays a reversible reduction wave (-160 V vs. Fc/Fc$^+$) which is situated at a more negative potential

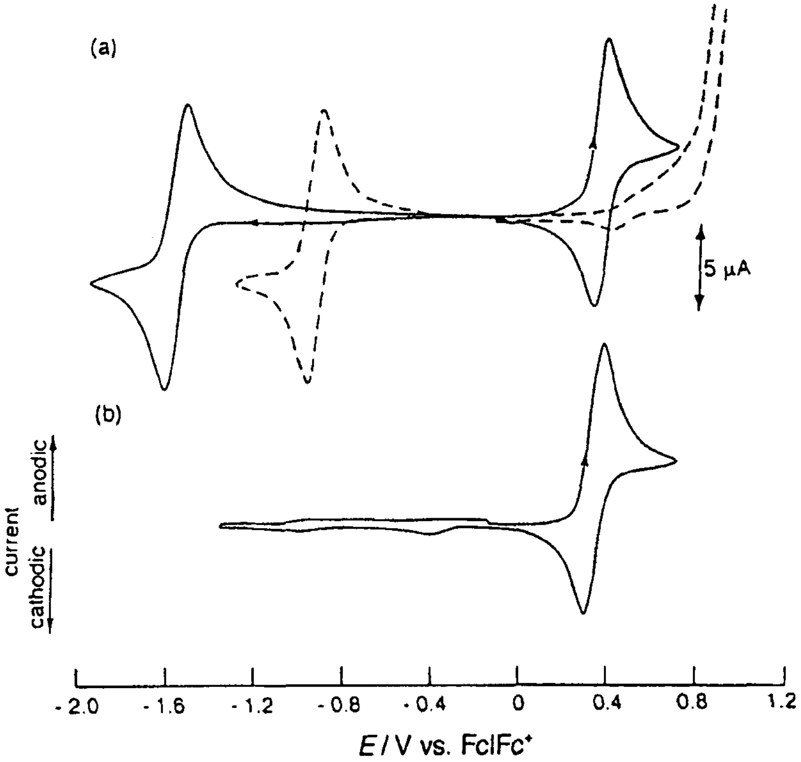
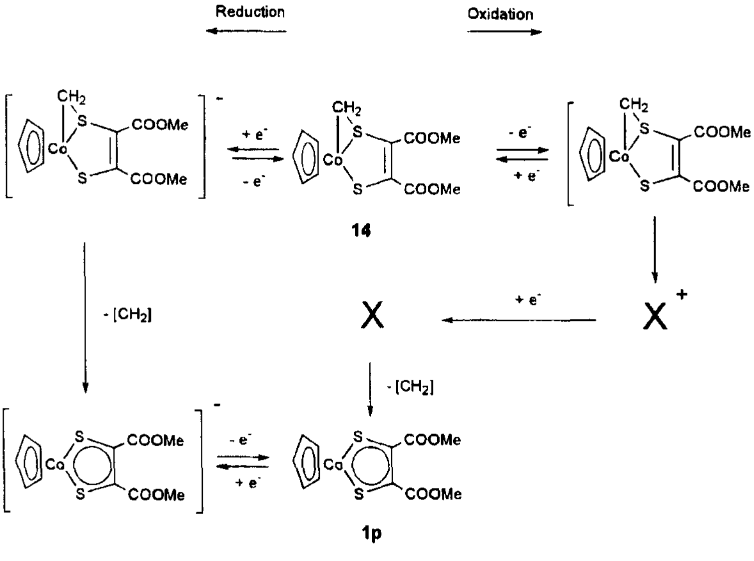


FIGURE 13 Cyclic voltammograms of [(Cp)Co{$S_2C_2(COOMe)_2$}] (**1p**) (broken line) and its methylene-adduct (**14**) (solid line) in an acetonitrile solution in the presence of 0.1 mol dm^{-3} of $Et_4N\ ClO_4$. (a) Initial sweep was done either toward the negative potential (for the measurement of reduction side) or toward the positive potential (for the measurement of oxidation side). (b) Initial sweep was done toward the positive potential.

than that for the free cobaltadithiene complex **1p** (−0.94 V). There is no scan rate dependence in the sweep rate range of 20–200 mV s^{-1} and the voltammogram exhibits a current ratio of ($i_{pa}/i_{pc} \sim 1$). In the time scale of cyclic voltammetry, the process is reversible. *In situ* measurement of the electronic absorption spectra during the electrolytic reduction using an optically transparent thin-layer electrode shows also the reversibility of the reduction and re-oxidation. However, the spectral change observed during the controlled potential electrolysis at −1.70 V using OTTLE shows the formation of the anionic form of the free cobaltadithiolene complex. One-electron reduction products of the alkylidene-bridged complexes have a few minutes of lifetime and then they lose the alkylidene moieties to give the stable anion radicals of the original dithiolene complexes.

The electrochemical oxidation shows more complicated behavior. The cyclic voltammogram of **14** gives an apparently reversible oxidation peak. However, the detailed examination of the spectral change using OTTLE during the controlled potential electrolysis reveals that the cation of alkylidene-bridged complex has a few seconds of lifetime, and then it is converted to some species X (an unidentified intermediate). When X is re-reduced, the corresponding original dithiolene complex is formed rapidly. This unidentified species X is stable in the cationic form, but very unstable in the electrically neutral form to regenerate the original complex.

The electrochemical processes of the methylene-bridged cobaltadithiolene complex are summarized in Scheme 7.



SCHEME 7

4.2.2 *Bis(methoxycarbonyl)methylene-bridged cobaltadithiolene complex*[58]

An alkylidene-bridged complex **15** which has two electron-attracting COOMe's at the bridge behaves differently from the unsubstituted methylene-bridged complex on electrochemical reduction and oxidation.[58]

The bis(methoxycarbonyl)methylene-bridged complex **15** exhibits a one-electron reduction wave (B) and a re-oxidation wave (C) in its cyclic voltammogram (Figure 14).

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. The fact that the large peak separation is not dependent on the sweep rate (50–200 mV s^{-1}) indicates that the peak separation is attributable to the latter reason and suggests the presence of another reduction product which exhibits a re-oxidation wave (C: EC reaction). A cyclic voltammetric scan (Figure 14) displays, in addition to the major cathodic wave (B) and anodic wave (C), another cathodic wave (A) at more positive potentials. This wave (A) and anodic wave (C) are separated by the Nernstian value of 60 mV. This suggests (a) that a minor species (**15′**) is formed slowly from the parent complex, (b) that the waves A and C correspond to the reduction and oxidation of the species **15′**, and (c) that the reduced form of the parent bis(methoxycarbonyl)methylene-bridged complex changes

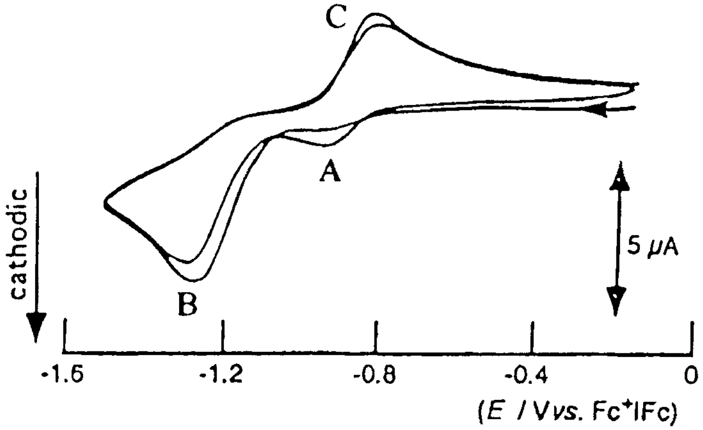


FIGURE 14 Continuous cyclic voltammogram of bis(methoxycarbonyl)methylene-bridged cobaltadithiolene (**15**) in an acetonitrile solution (1 mmol dm^{-3}) in the presence of 0.1 mol dm^{-3} of $Et_4N\ ClO_4$. Test electrode, stationary platinum disk, 1.6 mm diameter; scan rate, 100 mV s^{-1}.

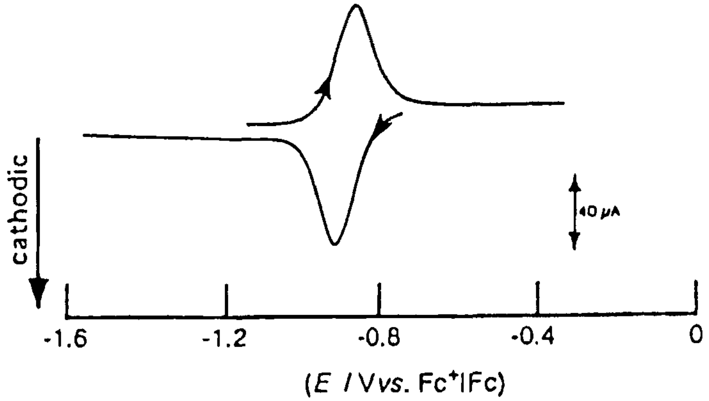


FIGURE 15 Cyclic voltammogram of bis(methoxycarbonyl)methylene-bridged cobaltadithiolene (**15**) using a thin-layer electrode cell (with Pt gauge) in an acetonitrile solution (1 mmol dm^{-3}) in the presence of 0.1 mol dm^{-3} of $Et_4N\ ClO_4$. Scan rate, 1 mV s^{-1}.

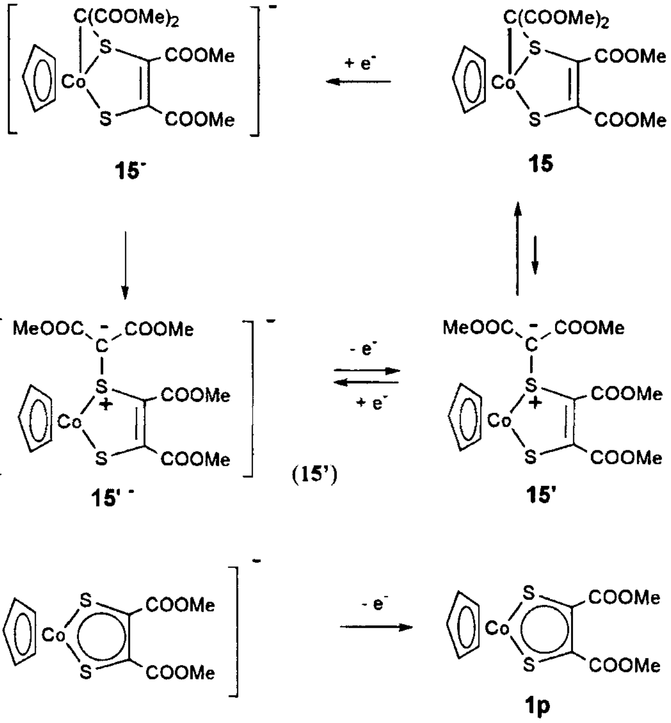
rapidly and quantitatively to the reduced form of species **15′** namely **15′**$^-$. The cathodic wave A and anodic wave C in the second scan become larger than those in the first scan. It suggests that the solution near the electrode is enriched by the minor component after the reduction/oxidation cycle.

Thin-layer cyclic voltammetry at slow scan rates provides more definitive evidence about the chemical reaction. Figure 15 shows the thin-layer cyclic voltammogram of the complex **15** obtained at a slow scan rate (1 mV s^{-1}). Here we observe only a pair of redox waves at *ca.* −0.92 V which correspond to the redox couple of A and C.

An *in situ* measurement of the electronic absorption spectrum during the electrolytic reduction using OTTLE shows the reversibility of the reduction and re-oxidation.

Thus, we can postulate an ylide as an isomer which exists in an equilibrium with the alkylidene-bridged complex. In the electrically neutral state, the equilibrium lies to the side of the bridged form, while in the reduced form the equilibrium lies to the isomeric non-bridged form. The reactions are summarized in Scheme 8.

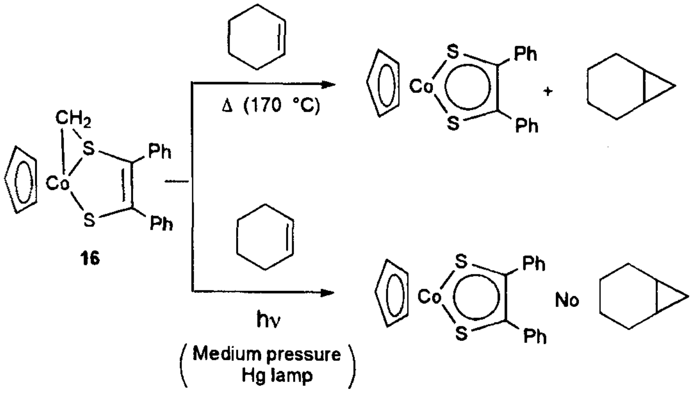
Here comparison of the electrochemical reaction of the alkylidene-bridged metalladithiolene with its thermal and photochemical reactions is worth mentioning.[56] The alkylidene-bridge is easily eliminated



SCHEME 8

either by heating or by UV-irradiation and the free cobaltadithiolene is regenerated (Scheme 9).

An important point in the dissociation of the alkylidene group, is whether the alkylidene is eliminated as singlet or triplet carbene species. The thermolysis of a methylene-bridged cobaltadithiolene **16** at 170 °C in the presence of cyclohexene (a scavenger of singlet carbene) affords bicyclo[4.1.0]heptane. On the other hand, after photolysis of **16** in the presence of cyclohexene, no bicyclo[4.1.0]heptane is detected. The photochemical dissociation of **16** is inhibited by 1,3-cyclohexadiene. These facts suggest that the thermolysis gives singlet carbene but the photolysis gives triplet carbene, indicating that the photochemical dissociation of the alkylidene-bridged cobaltadithiolenes occurs not from a singlet excited state but from a triplet excited state.



SCHEME 9

4.3 *Three-Component-Adducts among [(Cp)M($S_2C_2R_2$)]-Type Metalladithiolene, Alkylidene, and HX (Hydrogen Halide), X_2 (Elemental Halogen), Phosphine, or Phosphite*

As shown in Scheme 3, the alkylidene-bridged cobaltadithiolenes react further with protic acids, phosphines, phosphites, and dihalogen to give complexes containing the cobaltadithiolene, alkylidene, and the third reactants. In this review, we call them "three-component-adducts." These three-component-adducts show also various electrochemical reactions. Here we will discuss the electrochemical behavior of three kinds of "three-component-adduct": (a) three-component-adduct among [(Cp)Co($S_2C_2R_2$)], alkylidene, and hydrogen halide; (b) three-component-adduct among [(Cp)Co($S_2C_2R_2$)], alkylidene, and dihalogen, and (c) three-component-adduct among [(Cp)Co($S_2C_2R_2$)], alkylidene, and phosphite.

4.3.1 *Three-component-adducts among [(Cp)M($S_2C_2R_2$)], alkylidene, and hydrogen halides*[59]

The electrochemical reaction of a three-component-adduct among [(Cp)M{$S_2C_2(COOMe)_2$}], alkylidene, and hydrogen halides (**17**) is a good model to analyze the dynamic behavior of the meta-stable reduced or oxidized species.

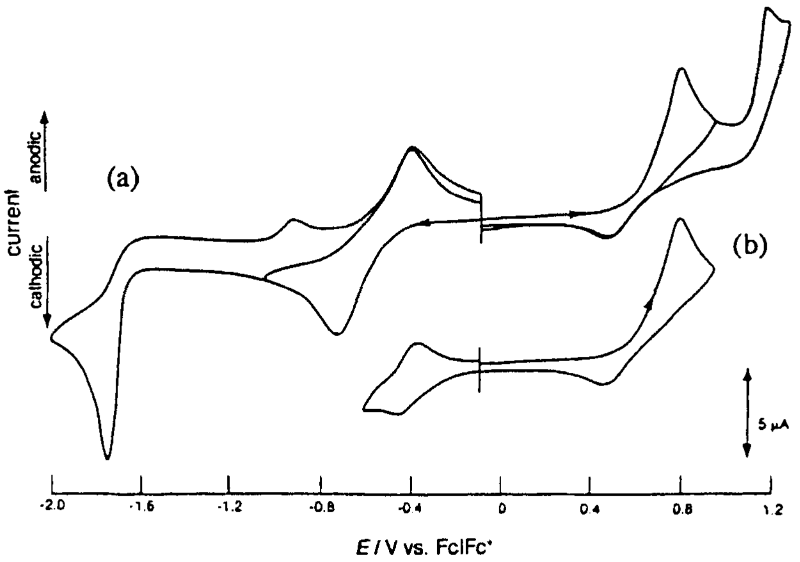


FIGURE 16 Cyclic voltammogram of a three-component-adduct among [(Cp)M-{$S_2C_2(COOMe)_2$}], methylene, and HCl (**17a**) in an acetonitrile solution (1 mmol dm^{-3}) in the presence of 0.1 mol dm^{-3} of $Et_4N\ ClO_4$. (a) Initial sweep was done either toward the negative potential (for the measurement of reduction side) or toward the positive potential (for the measurement of oxidation side). (b) Initial sweep was done toward the positive potential.

Both electrochemical reduction and oxidation causes the elimination of halogen; in the reduction, halide anion is dissociated, while in the oxidation, halogen atom is dissociated. In some cases, succeeding reactions occur.

As shown in Figure 16, a three-component-adduct among [(Cp)M{$S_2C_2(COOMe)_2$}], methylene, and HCl (**17a**: $R^3 = R^4 = R^5 = H$) shows two-step reduction processes and two-step oxidation proceses.

Firstly we discuss the one-electron reduction. The large peak separation of reduction and re-oxidation waves in the first reduction suggests that some reaction occurs after one-electron reduction. The ESR spectra (Figure 17) observed for the one-electron reduction product show 8 hyperfine splitting due to Co(II) but no splitting by Cl^-. These facts suggest that the one-electron reduction product rapidly eliminates the chloride anion to form electrically neutral

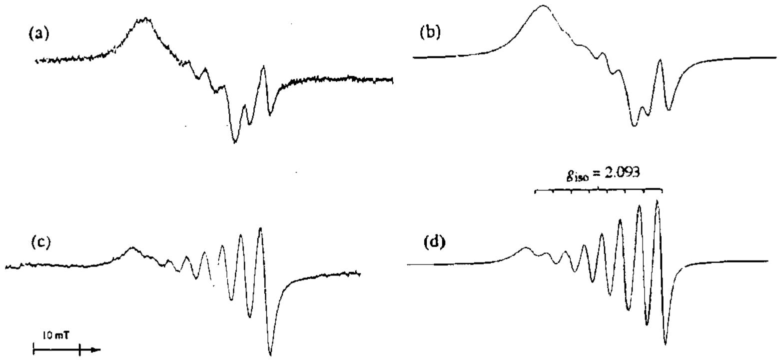


FIGURE 17 ESR spectra obtained (a) after reduction of **18a** ($R^3 = R^4 = R^5 = H$), (b) simulation for (a), presuming a mixture of **18a** and **1p**, (c) after reduction of **1p** and (d) simulation for **1p**$^-$.

S-methyl-cobaltadithiolene **18a**. However, *in situ* measurement of electronic absorption spectra during the electrolytic reduction and re-oxidation using OTTLE shows the reversibility of the reaction: the spectra obtained after re-oxidation agree with those of **17a**. This indicates rapid recombination of the **18a**$^+$ with chloride anion occurs.

Two-electron reduction of **17a** causes the elimination of the *S*-methyl group. This can be concluded from the following experimental result. After the second reduction, the re-oxidation wave corresponding to the oxidation of the reduced form of the free cobaltadithiolene complex appears. The ESR spectra obtained for the second reduction product (two-electron-reduction product) agree with those of the anion of the free cobaltadithiolene complex, $[(Cp)Co\{S_2C_2(COOMe)_2\}]^-$.

The three-component-adducts having electron attracting groups in the *S*-alkyl moiety behave somewhat differently after electrochemical reduction. The first reduction wave of the three-component-adduct having two electron-attracting COOMe's in the *S*-alkyl group is irreversible and no corresponding re-oxidation wave is observed. Instead, after reduction a reversible redox couple is observed at a more negative potential. This wave is assigned to the reduction of the free cobaltadithiolene **1p**. The formation of **1p** is confirmed by the observed spectral change using an OTTLE cell. This suggests the elimination of bis(methoxycarbonyl)methyl radical from **18**.

The three-component-adduct (containing hydrogen halide) having one COOEt in the *S*-alkyl moiety does not undergo elimination of the *S*-alkyl group after the first reduction. But the two-electron-reduction product (**18**$^-$) eliminates a hydrogen atom to give an anion-radical of the alkylidene-bridged complex (**16**$^-$). This conclusion is supported by the observation of the redox couple of **16**$^-$/**16**.

The electrochemical oxidation of **17a** causes the succeeding reactions. The cyclic voltammogram shows two one-electron oxidations (Figure 16). When the potential scan is reversed after the first oxidation, a reversible redox couple appears at *ca.* −0.4 V. The re-oxidation wave in the redox couple agrees with the re-oxidation wave corresponding to the product of reduction of *S*-methyl-cobaltadithiolene (**18a**). Thus, this re-oxidation wave is assigned to the oxidation of the anion of the *S*-methyl-cobaltadithiolene (**18a**). In order to explain the formation of **18a**, we postulate the elimination of chlorine atom from the mono-cation of the three-component-adduct.

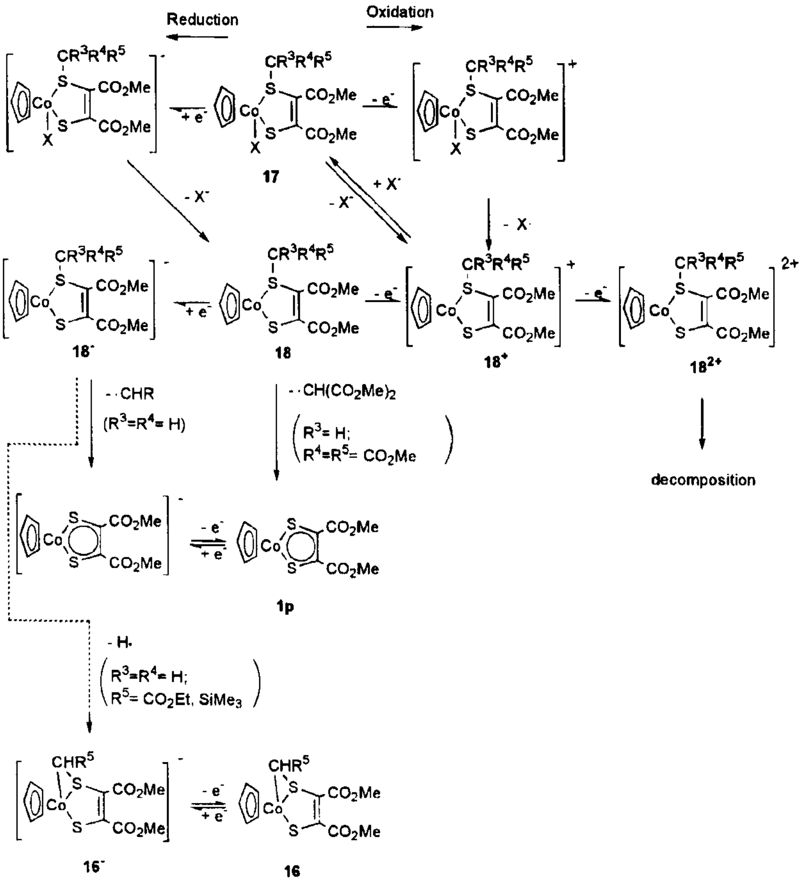
The second oxidation of **18a** is irreversible and we observe no definite re-reduction wave, indicating the rapid decomposition of **18a**$^{2+}$.

From these considerations, we propose a reaction schemes (Scheme 10) for the electrochemical reactions of a three-component-adduct among [(Cp)Co{$S_2C_2(COOMe)_2$}], alkylidene, and hydrogen halide.

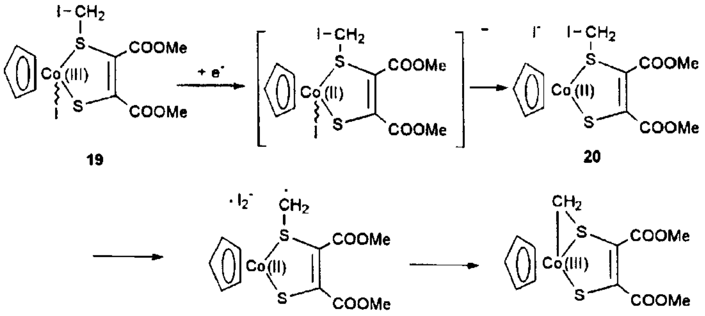
4.3.2 *Three-component-adducts among [(Cp)M($S_2C_2R_2$)], alkylidene, and I_2*

The attack of elemental halogens on an alkylidene-bridged cobaltadithiolene complex causes the cleavage of the Co–C bond. The three-component-adducts among [(Cp)M($S_2C_2R_2$)], alkylidene, and I_2 (**19**) shows an interesting ring closure.

The one-electron reduction of **19** results in the elimination of I_2^- to give the methylene-bridged cobaltadithiolene. The reaction proceeds probably by a two-step mechanism: addition of an electron to the three-component-adduct (**19**) induces the elimination of iodide anion coordinated to Co. The iodide anion liberated in the above reaction abstracts the iodine atom attached to the *S*-(iodomethyl) group (Scheme 11). The abstraction of iodine by iodide and the reforming of strained three-membered ring are interesting reactions.



SCHEME 10



SCHEME 11

4.3.3 Three-component-adducts among [(Cp)M($S_2C_2R_2$)], alkylidene, and phosphine or phosphite

As shown in Scheme 3, the alkylidene-bridged cobaltadithiolene complexes undergo two types of ring opening reactions depending on the electronic states at the bridges in the reaction with phosphines and phosphites. One is the cleavage of the Co–S bond to give six-membered metallacycles and the other is the cleavage of the Co–C bond to give *S*-ylides in the alkylidene-bridged complex having electron-attracting COOMe groups at the bridge. These reactions afford three-component-adducts consisting of the cobaltadithiolene, alkylidene, and phosphorus compound.[60,61]

These three-component-adducts containing phosphorus compounds show interesting electrochemical behavior.[62,58]

We discuss first the electrochemistry of the ylide type three-component-adducts (containing phosphorus compounds).[62] The cyclic voltammograms of [(Cp)Co{$S_2C_2(COOMe)_2$}]–[$C(COOMe)_2$]–$P(OMe)_3$ (**21**) (solid line) and its parent alkylidene adduct, [(Cp)Co{S_2C_2-$(COOMe)_2$}]–[$C(COOMe)_2$] (**15′**) (broken line) are shown in Figure 18.

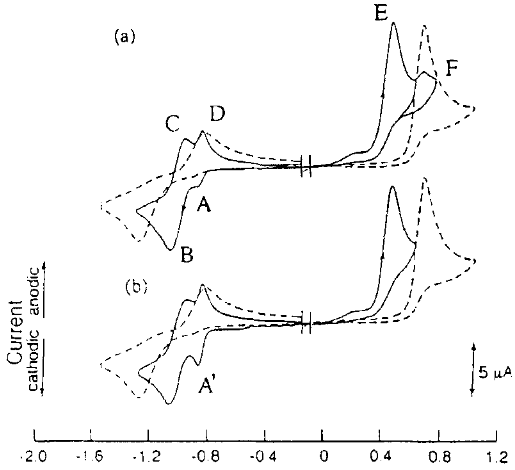
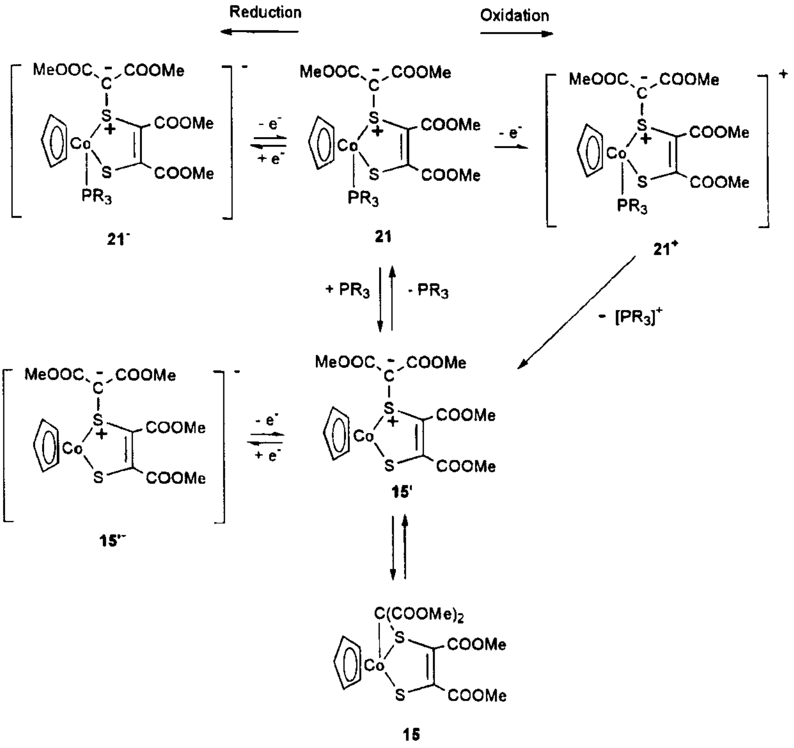


FIGURE 18 Cyclic voltammograms of a three-component-adduct [(CP)CO{S_2C_2-$(COOMe)_2$}–[$C(COOMe)_2$]–P(OMe) (**21**: R = OMe) (solid line) and the binary adduct between [(Cp)Co{$S_2C_2(COOMe)_2$}] and [$C(COOMe)_2$] (**15**) (broken line). Solvent, acetonitrile; concentration of **21** and **15**; 1 mmol dm^{-3}; scan rate, 100 mV s^{-1}. (a) The isolated samples were used for the measurement. (b) *In situ* measurement.

On reduction, **21** exhibits a reversible redox peak at −1.0 V (B and C) and a small reversible peak at −0.8 V (A and D). The former peaks, B and C, correspond to the redox peaks of the three-component-adduct **21** and the latter peaks, A and D, correspond to the redox peaks of the ylide-structured alkylidene-adduct **15′** (without the coordinated phosphite). These facts indicate the existence of an equilibrium between **21** and **15′** as well as an equilibrium between **15** and **15′** (Scheme 12).

The ESR spectrum measured after the one-electron reduction of **21** in an ethanol/benzene (1 : 1) solution exhibits isotropic signals at 20 °C. The spectra show hyperfine splittings arising from coupling to both cobalt ($I = 7/2$) and, phosphorus ($I = 1/2$). This shows that the phosphite is coordinated to the cobalt atom.

The three-component-adduct **21** shows an irreversible oxidation peak (E). Subsequently, if we continue the potential scan to a more



SCHEME 12

positive range, one more small anodic peak (F) corresponding to the oxidation of **15′** appears. This suggests the elimination of the phosphite as a cation from the oxidized three-component-adduct **21**$^+$.

Next we discuss the electrochemistry of a six-membered metallacyclic three-component-adduct **22**. The cyclic voltammogram of **22a** ($R^3 = H$; $R^4 = COOEt$; $R = Me$) is shown (solid line) in Figure 19, together with that of the corresponding alkylidene-bridged complex **23a** ($R^3 = H$; $R^4 = COOEt$). The complex **22a** displays irreversible reduction and oxidation waves. When the potential is reversed after reduction, a re-oxidation wave that was seen in the cyclic voltammogram of the corresponding alkylidene-bridged complex **23a** was detected. This shows that rapid elimination of the phosphorus compound from the reductant **22**$^-$ occurs.

The electrochemical oxidation of **22** is also irreversible. When the potential scan is continued to a more positive range, an oxidation wave

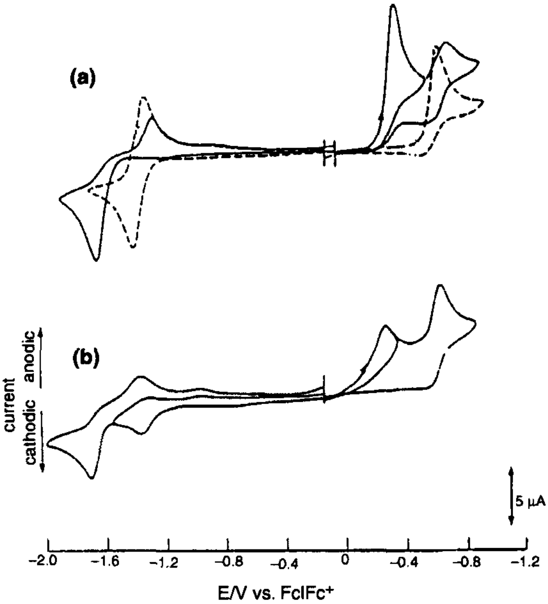
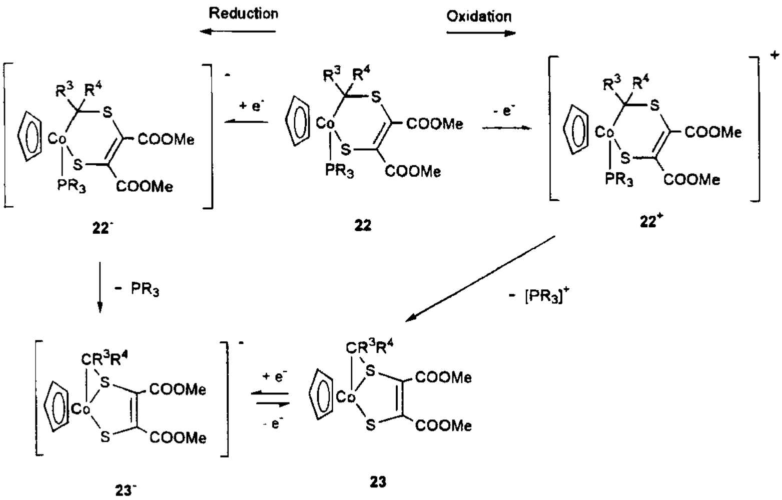


FIGURE 19 Cyclic voltammograms of a three-component-adduct [(Cp)Co{S_2C_2-$(COOMe)_2$}]-[CHCOOEt]-P(Me) (**22a**: R = Me) (solid line) and the binary adduct between [(Cp)Co{$S_2C_2(COOMe)_2$}] and [CH(COOEt] (**15**) (broken line). Solvent, acetonitrile; concentration of **22a** and **15**; 1 mmol dm^{-3}; scan rate, 100 mV s^{-1}. (a) The isolated samples were used for the measurement. (b) *In situ* measurement.



SCHEME 13

corresponding to the oxidation of the alkylidene-bridged complex **23a** appears. This shows that the mono-catioic **22**$^+$ eliminates rapidly the phosphorus compound as a cation to give an electrically neutral alkylidene-bridged complex **23a**.

The electrochemical processes of the six-membered metallacyclic three-component-adduct are summarized in Scheme 13.

The general reactions of the two types of three-component-adducts containing phosphine or phosphite are elimination of the phosphorus compounds following reduction and elimination of the cationic phosphorus compounds following oxidation to give alkylidene-bridged complexes.

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