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Accounts

Synthesis and Chemical Properties of Metalladithiolene and Metalladithiazole Rings.
Unique Reactions Due to Coexistence of Aromaticity and Unsaturation

Akira Sugimori,* Takeo Akiyama, Masatsugu Kajitani, and Toru Sugiyama

Department of Chemistry, Faculty of Science and Technology, Sophia University,
Kioi-cho 7-1, Chiyoda-ku, Tokyo 102-8554

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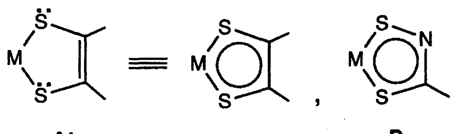
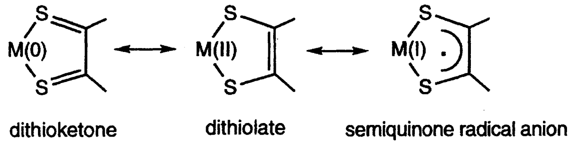
The syntheses and unique chemical properties of metalladithiolene rings (especially in $[CpM(S_2C_2R^1R^2)]$-type complexes) found by our research group are reviewed. The constructions of metalladithiolene rings by one-pot reaction among $[CpM(CO)_n]$, alkyne, and elemental sulfur and by the reaction between $[CpM(CO)_n]$ and sulfur-containing heterocyclic compounds are described. Several ionic and radical substitution reactions are presented. The substitutions by carbon-centered and sulfur-centered radicals occur in the metalladithiolene rings. Benzoyloxy-substitution by dibenzoyl peroxide (BPO) and succinimido-substitution by *N*-halosuccinimides (NXS) proceed via ionic mechanisms induced by the heterolysis of BPO and NXS in the interaction with the lone pair electrons at the sulfur atoms. These substitutions are due to the aromatic character of the metalladithiolene rings. The unique addition reactions due to the unsaturated character of the metalladithiolene rings are also described. Diazo compounds and azides react with $[CpM(S_2C_2R^1R^2)]$-type metalladithiolenes to form alkylidene- and imido-bridges between metal and sulfur. Quadricyclane and dimethyl acetylenedicarboxylate add between metal and sulfur. These addition products undergo a variety of types of dissociation: by heating, illumination, or electrochemical redox.

A metalladithiolene ring consisting of one transition metal atom, two coordinated sulfur atoms, and two unsaturated carbon atoms is a very unique metal chelate ring.[1—6] By using one vacant d orbital of the metal atom, the ring constructs a conjugated system with 6 π-electrons. Thus, we can expect aromaticity for the metalladithiolene rings. As will be described in Chapter 2 of the account, we found a variety of types of substitution reactions which occur in metalladithiolene rings and could give evidence for the aromaticity of each conjugated metal chelate ring on the basis of its reactivities. Thus, we express the valence state of the metalladithiolene ring as Formula **A2** in Eq. 1a. This means that the metalladithiolene ring can be expressed as a hybrid of the resonance structures of Eq. 1b and suggests the ambiguous oxidation state of the central metal atom. The unusual electronic structure gives the metalladithiolene complexes unique reactivities as well as useful functionalities.



A1 **A2** **B** (1a)



(1b)

A metalladithiazole is a nitrogen analog of metalladithiolene and has the structure of **B**.[7,8]

Typical examples of X-ray crystal structures of cobaltadithiolene and cobaltadithiazole complexes are shown in Fig. 1.

The structures of cobaltadithiolene ring and the cobaltadithiazole ring are similar. These rings are planar. The Co–S distances of 2.108(2) and 2.104(2) Å for the complex of $R^1 = R^2 = COOMe$, 2.110(2) and 2.109(2) Å for the complex of $R^1 = R^2 = CN$, and 2.110(4) and 2.0098(4) Å for the complex of $R^1 = R^2 = Ph$ are shorter than the normal bond length of Co(III)–SR (2.25—2.48 Å).[9] Sellmann et al. explained the shorter M–S bond length in the metalladithiolenes by π-electron donation of S to the metal.[10] The π-electron donation contributes to the delocalization of π-electrons, namely to the aromaticity of the metalladithiolene rings.

There are two groups of metalladithiolene complexes: 1)

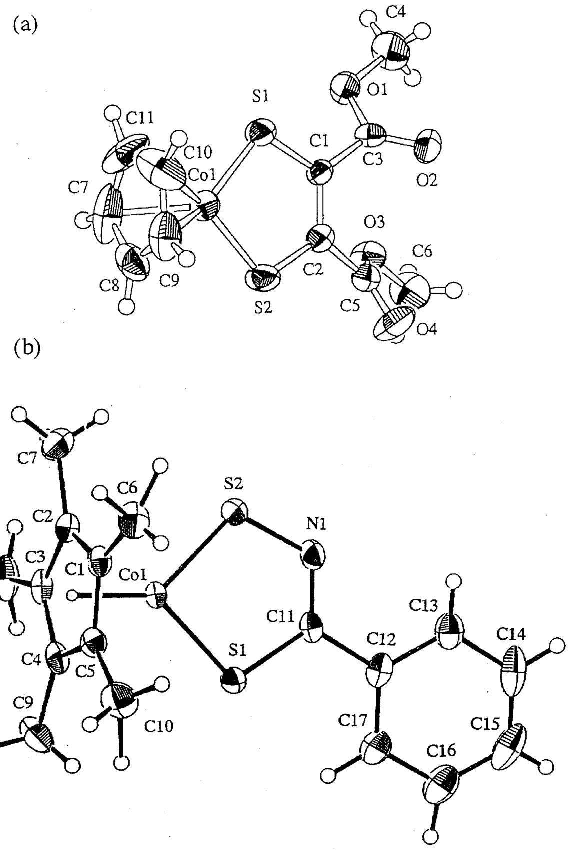
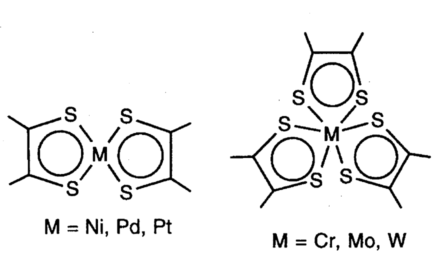


Fig. 1. X-Ray structures of a cobaltadithiolene, $[(Cp)Co\{S_2C_2(COOMe)_2\}]$, and a cobaltadithiazole, $[(Cp^*)Co(S_2CNPh)]$.
a) $[(Cp)Co\{S_2C_2(COOMe)_2\}]$, b) $[(Cp^*)Co(S_2CNPh)]$.

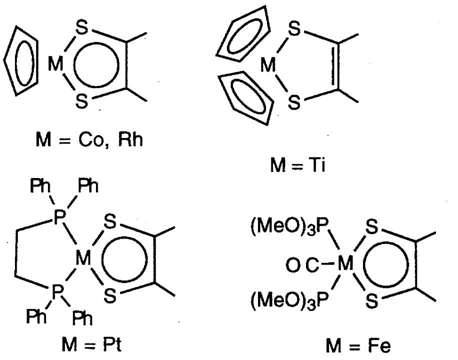
one includes the complexes having only dithiolato as ligand and 2) the other includes the complexes having ligands other than dithiolato (mixed ligand metalladithiolene).

The first type of metalladithiolene complexes are more popular. Typical examples of the $[M(S_2C_2R^1R^2)_n]$-type metalladithiolene complexes are $[Ni(S_2C_2R^1R^2)_2]$, $[Pd(S_2C_2R^1R^2)_2]$, $[Pt(S_2C_2R^1R^2)_2]$, $[Mo(S_2C_2R^1R^2)_3]$ etc. Since the pioneering studies which have been done simultaneously by the three groups (the groups of Schrauzer,[11] Gray,[12] and Davison[13]), the chemistry of metalladithiolenes of this type has been studied extensively.



(2)

Some examples of the second type of mixed-ligand metalladithiolene complexes are shown in Eq. 3.

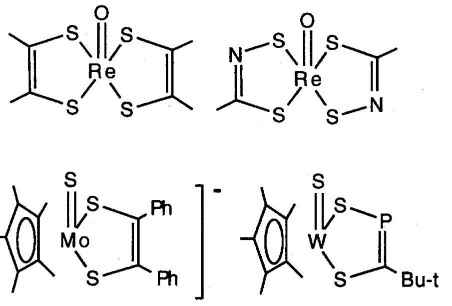


(3)

The most important mixed-ligand metalladithiolene complex is half sandwich metalladithiolene complexes having cyclopentadienyl as another ligand. The $[(Cp)_mM(S_2C_2R^1R^2)]_n$-type mixed ligand metalladithiolene complexes including $[(Cp)Co\{S_2C_2(CF_3)_2\}]$, have been reported as early as 1963 by King,[14] followed by McCleverty[15] and Schrauzer.[16] Typical examples of $[(Cp)_mM(S_2C_2R^1R^2)]_n$-type half sandwich metalladithiolene complexes are $[(Cp)Co(S_2C_2R^1R^2)]$, $[(Cp)Rh(S_2C_2R^1R^2)]$, and $[(Cp)_2Ti(S_2C_2R^1R^2)]$.

Polynuclear metalladithiolene complexes have attracted the interest from the view point of the intramolecular interactions between metal complex moieties. Examples of this type of cobaltadithiolene complexes are a trinuclear cobaltadithiolene fused with a benzene ring,[17] directly bound dinuclear cobaltadithiolenes,[18] and dinuclear cobaltadithiolenes bound at Cp's.[19]

Recently, some other types of metalladithiolenes have been reported. Rhenium and molybdenum dithiolene and dithiazole complexes having oxo group coordinated to the metal atoms have been synthesized.[20—22] A phosphorus analog was also reported.[23]



(4)

We have developed several methods for the construction of the metalladithiolene rings in $[CpM(S_2C_2R^1R^2)]$-type complexes. During these efforts, we could construct a novel metallacyclic system, metalladithiazole. We also found several synthetic routes of metalladichalcogenolene rings through interesting interactions between organic heterocyclic compounds and coordinatively unsaturated transition metal species. We will describe these reactions in Chapter 1.

The aromaticity of metalladithiolene rings has long been discussed. Schrauzer first pointed out the unusual electronic structure of the metalladithiolene ring: the bonding is characterized by extensive delocalization of electrons.[24] ^1H NMR studies revealed the existence of ring currents ascribed to the aromaticity of the metalladithiolene ring.[25,26]

The chemical evidence for the aromaticity should be given by substitution reactions. After the pioneering work of Collman,[27] the electrophilic substitution reactions have been reported in quasi-aromatic metal chelate rings, especially in the acetylacetonatometal complexes.[28—30]

However, there has appeared only one short description which refers to the chemical reaction due to the aromaticity of the metalladithiolene rings. Schrauzer and Mayweg described the Friedel–Crafts alkylation of a molybdadithiolene ring in $[Mo(S_2C_2H_2)_3]$ under the catalysis of anhydrous aluminum chloride.[31] However, the description is very short and the experimental description is lacking. Since then, the electrophilic substitutions of the metalladithiolene rings have not been further investigated.

Thus, we examined the electrophilic reaction for the metalladichalcogenolene complexes. Firstly we have clearly demonstrated the aromatic character of the metalladithiolene rings by the occurrence of electrophilic substitution. Further, we extended the study to the radical substitution and succeeded in the discovery of the first example of radical substitution which occurs in quasi-aromatic conjugated metal rings. In addition, we found another type of substitution reactions initiated by the interaction between the chalcogen atom in the metalladichalcogenolene rings and reactive species such as dibenzoyl peroxide and *N*-halosuccinimides. These substitution reactions in the metalladithiolene rings will be described in Chapter 2.

In parallel to the aromaticity, the metalladichalcogenolene rings have the character of unsaturation. Before our study, very few reports have appeared on the addition reactions in the metalladithiolene rings. We found that a variety of reactive species add to the metalladithiolene rings. In Chapter 3 of the account, we will discuss the addition and elimination reactions in the metalladithiolene rings.

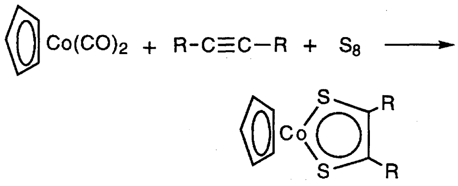
The coexistence of aromaticity and unsaturation should result in the easy bond formation and easy bond cleavage. This character suggests the possibility to use the metalladichalcogenolene complexes as catalysts. In the last chapter of the account, we will give an example of the catalysis by metalladithiolenes.

Recently, the chemistry of metalladithiolene complexes is expanding to various fields. Especially, the applications of the metalladithiolene complexes to the functional materials have become remarkable. Although the functionalities due to the physical and chemical properties of the metalladithiolene complexes are out of the scope of our account, it would be worth while to refer to some important references: electric conductivity[32] or super conductivity,[33] magnetism,[34] photoluminescence,[35] liquid crystals,[36] photochromism,[37] non-linear optical property,[38] and infra red dyes.[39]

1. Construction of Metalladithiolene and Related Metal Chelate Rings

1.1. One-Pot-Reaction among $[(Cp)CoL_n]$, Alkyne, and Elemental Chalcogen.

Bönnemann and a group including one of the authors have discovered a convenient synthesis of $[(Cp)Co(S_2C_2XY)]$-type cobaltadithiolene complexes by one-pot reactions among [(Cp)CoLn] (Ln = $(CO)_2$ and 1,5-cyclooctadiene), alkyne, and elemental sulfur (Eq. 5).[40]

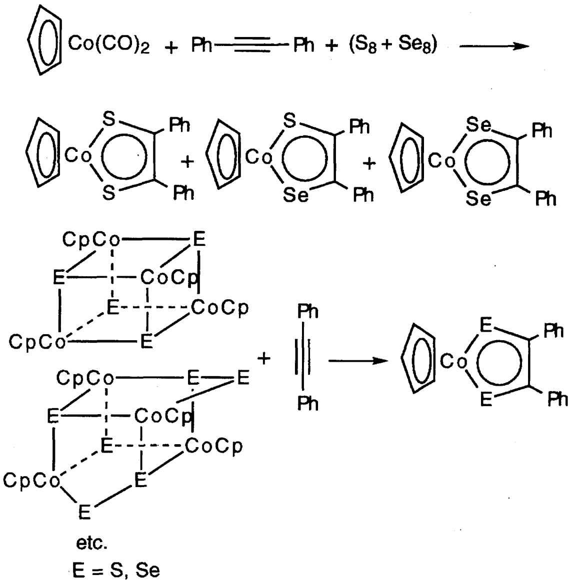


(5)

We have extended the one-pot synthesis of metalladithiolene rings to the metalladichalcogenolene complexes containing selenium. The one-pot reaction of $[(Cp)Co(CO)_2]$, PhC≡CPh, and elemental selenium affords the cobaltadiselenolene complex. The use of a mixture of elemental sulfur and selenium gives a mixture of dithiolene, selenathiolene, and diselenolene complexes. The formation of these cobaltadichalcognolene complexes is explained by the reaction of intermediary-formed cubane-like clusters of CpCo and chalcogen (E) with alkyne (Scheme 1).[41]

For the one-pot syntheses of the cobaltadithiolenes, we use in general alkynes as a component. We found that the alkenes having CHO or COMe instead of the corresponding alkynes can be used as reagents for the one-pot synthesis of the cobaltadithiolenes (Chart 1).[42]

Although the application is limited, the reaction is useful for the preparation of formyl and acetyl cobaltadithiolenes, because the starting enal and enone are more easily available than the corresponding ynal and ynone. The reaction mechanism should involve dehydrogenation by sulfur. But the mechanism has not yet been clarified, except that the non-participation of free radical species was deduced on the basis of the effects of radical initiator and radical scavenger.



Scheme 1.

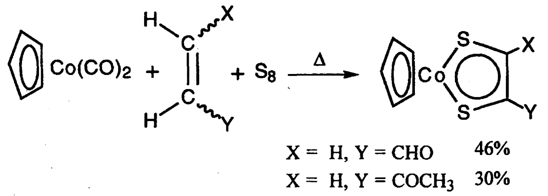
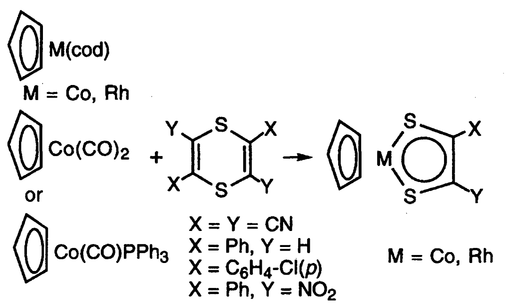


Chart 1.

1.2. Incorporation of a Part of Heterocycles as Ethylenedichalcogenolato Ligand. Another synthetic method of metalladithiolene complexes developed by us is the incorporation of a part of heterocyclic rings into the metal complexes in the reaction with coordinatively unsaturated transition metal species. An example is shown in Eq. 6.[43]



(6)

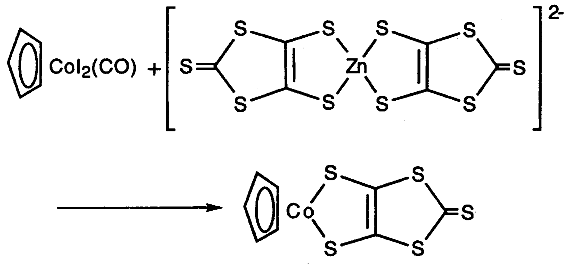
An interesting example of this type of reaction is the formation of cobaltadithiolene complexes via skeletal rearrangement in the heterocyclic compounds. (η^5-Cyclopentadienyl)dicarbonylcobalt(I) reacts with a *meso*-ionic compound, 2,5-diaryl-1,3-dithiolylium-4-olate to give a cobaltadithiolene complex. The *meso*-ionic compound having two different substituents is incorporated as a ethylenedithiolato ligand without scrambling of the substituents. The reaction proceeds effectively by UV-irradiation as well as by heating. A mechanism involving the attack of coordinatively unsaturated [CpCo] species to the sulfur atoms of the *meso*-ionic compound, the rearrangement in the heterocyclic moiety, and the extrusion of CO is proposed (Scheme 2).[45]

Another example is the formation of a rhodadithiolene in the reaction of [(Cp*)Rh(CO)$_2$] with 5-phenyl-3*H*-1,2-dithiol-3-one or its thione. In the reaction with the ketone in a xylene solution under reflux, [(Cp*)Rh(CO)$_2$] affords 4-benzylidene-1,2,5-rhodadithiol-3-one (35% yield) and a rhodadithiolene (8%). In the reaction with the thioketone, [(Cp*)Rh(CO)$_2$] gives selectively the rhodadithiolene. The reaction mechanism should involve some rearrangement. We propose a conceivable mechanism shown as Scheme 3.[46]

The carbonylcobalt complex, [(Cp*)Co(CO)$_2$] (Cp* = pentamethylcyclopentadienyl), gives no 1-oxo-2-benzylidene-1,2-ethylenedithiolato)cobalt(III). The reactions of [(Cp*)Co(CO)$_2$] with either ketone or thioketone afford the cobaltadithiolene complex.

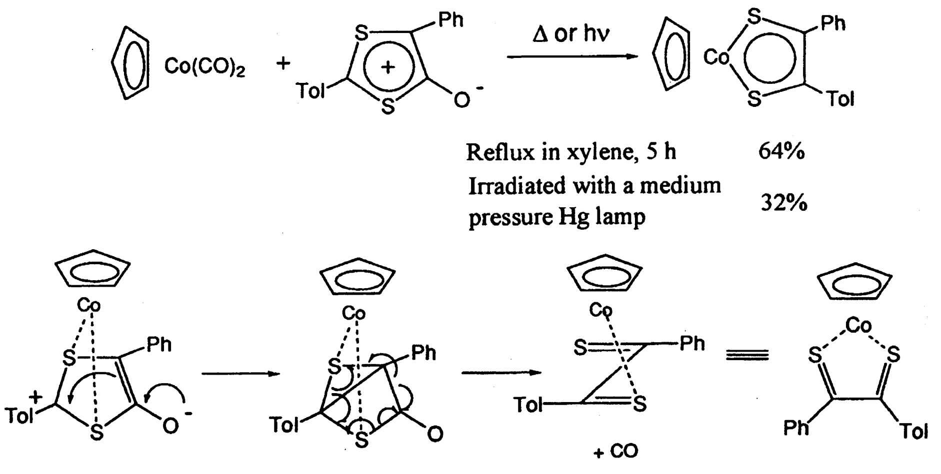
As an extension of the method, we could synthesize a new type metal chelate ring (metallacycle), cobaltadithiazole, in which a carbon atom of the cobaltadithiolene ring is replaced by a nitrogen atom. A metalladithiazole ring is constructed in the reaction of [(Cp)Co(CO)$_2$] with several heterocyclic compounds (Scheme 4).[7,8]

1.3. Exchange of Ethylenedichalcogenolato Ligand. An exchange reaction is also useful for the preparation of metalladithiolene complexes which are difficult to synthesize directly. An example is the synthesis of (η^5-cyclopentadienyl)(dmit)cobalt(III) (dmit = 1,3-dithiole-2-thione-4,5-dithiolato) in the reaction between [(Cp)CoI$_2$(CO)] and [Zn(dmit)$_2$](NEt$_4$)$_2$.[47,48] This reaction occurs easily at room temperature and in high yield.

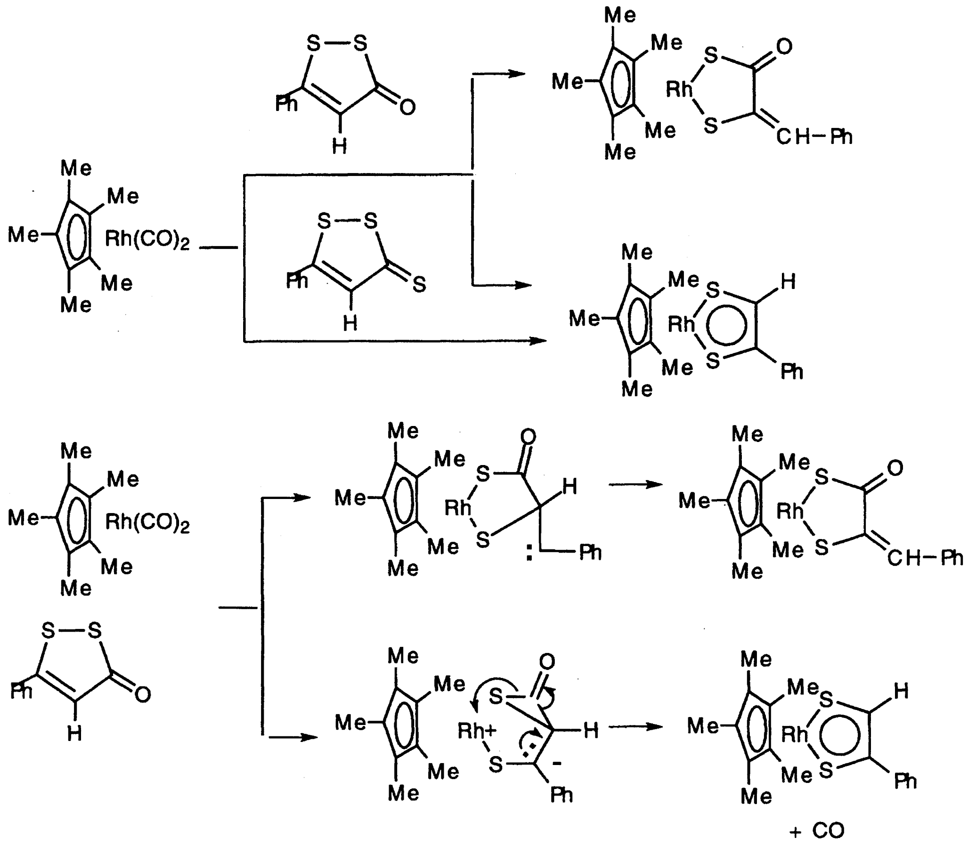


(7)

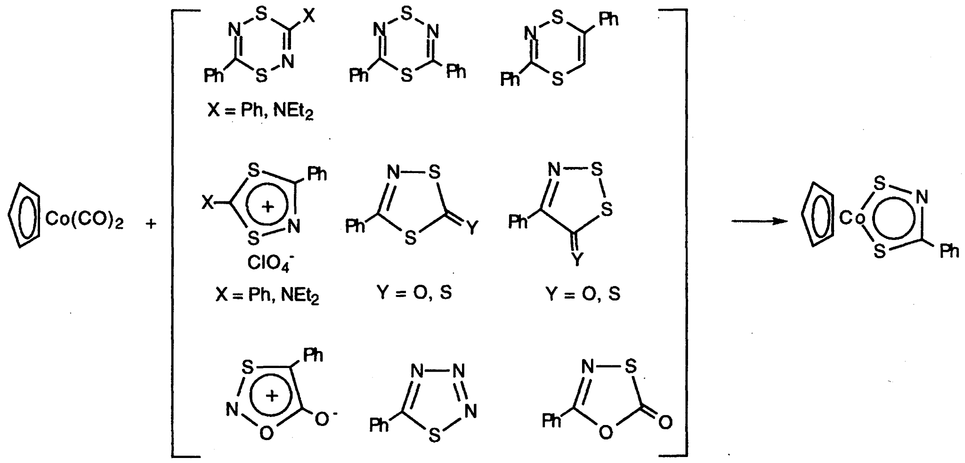
A peculiar exchange of Se by S occurs in the reaction of a cobaltadiselenolene having 2-pyridyl as the substituent with elemental sulfur. One or two selenium atom(s) are replaced by sulfur. The reflux of the diselenolene complex (0.026 mmol) with S$_8$ (0.095 mmol) in 3 cm^3 of toluene at 110 °C for 5 h under Ar gives a mixture of diselenolene, selena-



Scheme 2.

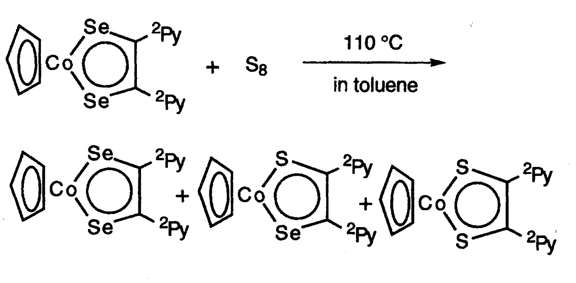


Scheme 3.



Scheme 4.

thiolene, and dithiolene complexes in the ratio of 40 : 28 : 32 (Eq. 8).[49]



(8)

This type of reaction does not occur in the diselenolene complexes having aryl groups as substituents. The unusual behavior of the cobaltadichalcogenolene rings having 2-pyridyl substituent appears in thermolysis. Differently from other cobaltadichalcogenolene complexes, the cobaltadichalcogenolene complexes having 2-pyridyl substituent easily eliminate chalcogen atoms on heating. This should relate to the exchange of chalcogen.

1.4. Formation of Dinuclear Molybdadithiolenes. The one-pot reaction among metalcarbonyl, elemental sulfur, and alkyne and the incorporation of a part of heterocyclic ring as a ligand in the reaction of metalcarbonyl can be applied to the synthesis of metalladithiolene complexes which contain metal atoms other than cobalt and rhodium.

A dinuclear molybdenum complex, bis(cyclopentadienyl)-hexacarbonyldimolybdenum, reacts with a mixture of elemental sulfur and DMAD thermally or photochemically to give several dinuclear molybdadithiolenes. A remarkable difference between thermal and photochemical reaction is observed: Thermal reaction affords solely a bis(cyclopentadienyl)bis(ethylenedithiolato)dicarbonyldimolybdenum in which two CO's are bonded to the same molybdenum atom, while the photoreaction affords mainly the isomeric complex in which two CO's are bonded to the different molybdenum atom (Scheme 5). The other products are the secondary products from these dicarbonyl complexes.[50]

2. Substitution Reactions, Reactions Due to Aromaticity

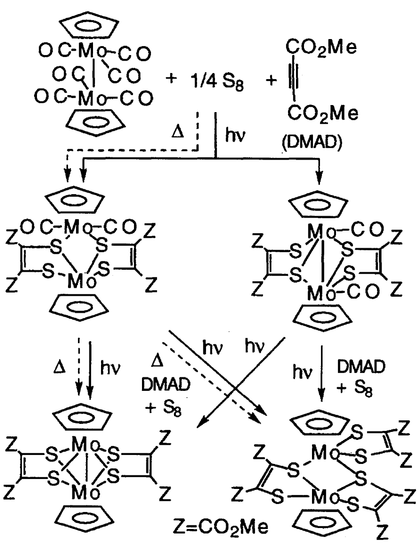
2.1. Electrophilic Substitution. A metal chelate ring in [(Cp)Co(S_2C_2HX)]-type cobaltadithiolene complexes having H in the cobaltadithiolene ring undergoes Friedel–Crafts acylation with acetyl chloride under the catalysis of anhydrous aluminum chloride or with acetic anhydride under the catalysis of phosphoric acid (Chart 2).

In the cobaltadithiolene complex **1c** having Ph in the cobaltadithiolene ring, the acylation occurs only in the cobaltadithiolene ring but neither in the cyclopentadienyl nor in the benzene ring. This indicates the high reactivity of the cobaltadithiolene ring for the electrophilic substitution.[51]

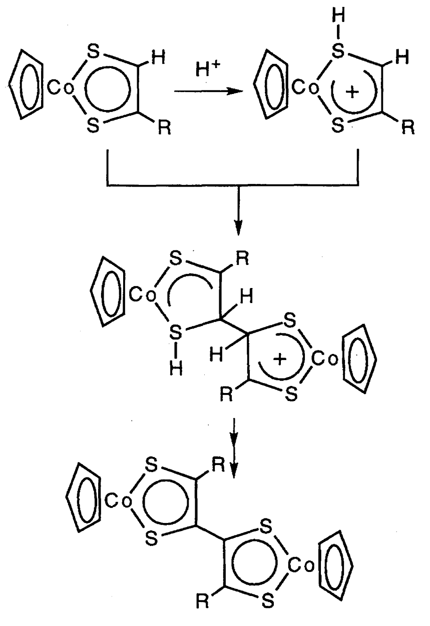
The Friedel–Crafts acylation is accompanied by the coupling of the cobaltadithiolene ring to give a dinuclear complex **3** as a by-product. The coupling reaction also occurs in heating of the cobaltadithiolene in the presence of hydrochloric acid.[52] As will be described later, the coupling product is also obtained as a by-product of succinimido-substitution in the reaction of the cobaltadithiolene complexes with *N*-halosuccinimides. The coupling reaction would be explained by an electrophilic attack of the positively charged protonated cobaltadithiolene to the non-protonated cobaltadithiolene (Scheme 6).

2.2. Radical Substitution. More interesting reactions due to the aromaticity of the metalladithiolene complexes are free radical substitution reactions. The metalladithiolene rings undergo radical substitution reactions by several carbon- and sulfur-centered radicals.

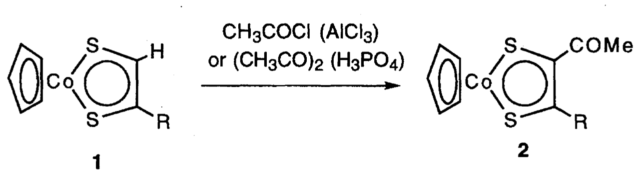
2,2′-Azobis(isobutyronitrile) (AIBN) reacts with [(Cp)Co-



Scheme 5.



Scheme 6.



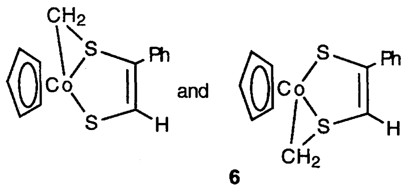
			Yield of 2 %	Recov. of 1 %
1a: R = H	CH_3COCl	$AlCl_3$	10	36
	$(CH_3CO)_2O$	H_3PO_4	15	24
1c: R =Ph	CH_3COCl	$AlCl_3$	7	69
	$(CH_3CO)_2O$	H_3PO_4	22	40
1d: R =COOMe	CH_3COCl	$AlCl_3$	0	not determined

Chart 2.

(S_2C_2HX)]-type cobaltadithiolene complexes to give substitution products in which the hydrogen atom attached to the cobaltadithiolene ring is replaced by 1-cyano-1-methylethyl group derived from AIBN (Chart 3).[50] The substitution would proceed in a mechanism similar to that of the radical substitution of aromatic compounds, i.e. via the addition of the radical to the carbon atom of the metal chelate ring followed by the hydrogen abstraction from the intermediary formed metal complex radical (by a radical).

Differently from the electrophilic Friedel–Crafts acetylation, the radical substitution occurs either in the cobaltadithiolene ring or in the cyclopentadienyl ring. In the case of R = Ph, the substitution in the cobaltadithiolene ring is dominant over that in the Cp ring. The radical substitution shows electrophilic character: The cobaltadithiolene rings having Ph and Me undergo the substitution, while the cobaltadithiolene having electron-attracting COOMe does not undergo the substitution reaction.

The fact that an alkylidene-bridged adduct (**6**) whose metal chelate ring is no longer conjugated does not undergo the substitution indicates that the aromaticity of the ring is essential for the radical substitution.



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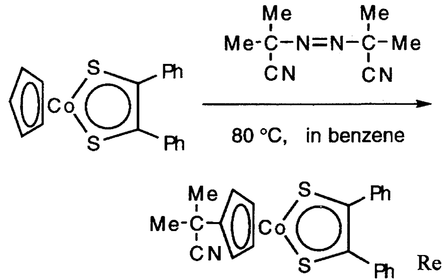
(9)

The substitution reaction which occurs in the metalladithiolene rings by 2,2′-azobis(isobutyronitrile) is the first example of the free radical substitution reaction which occurs in quasi-aromatic metal chelate rings. Although interesting interactions between metal-complex species and free radical species are expected, no one has reported free radical substitution for quasi-aromatic metal chelate rings. Our finding will develop a new field of free radical chemistry on the border between organic and inorganic chemistries.[53]

A peculiar effect of tributyltin hydride was found in the radical substitution. The addition of tributyltin hydride causes a decrease in the substitution in the cobaltadithiolene ring, but at the same time an increase in the substitution in the cyclopentadienyl ring (Chart 3). This can be clearly seen in the reaction of **1c**. In the reaction of **1c** with AIBN (molar ratio, 1 : 1) in the absence of Bu_3SnH, the substitution occurs selectively in the cobaltadithiolene ring. The presence of Bu_3SnH (molar ratio, 0.5) depresses the substitution in the cobaltadithiolene ring but promotes the substitution in the cyclopentadienyl ring. The increase in the total yield and the decrease in the recovery of the starting material (in the reaction in the presence of tributyltin hydride) indicate that tributyltin hydride promotes the reaction as a whole.

The promotion of the radical substitution in the cyclopentadienyl ring by Bu_3SnH is also observed for [(Cp)Co($S_2C_2Ph_2$)] in which no H atom is present in the cobaltadithiolene ring. In the absence of Bu_3SnH, the yield of Cp-substituted product is only 2 and 94% of the starting complex are recovered. However, in the presence of Bu_3SnH, the yield of the Cp-substituted product increases to 28% and the recovery decreases to 38% (Eq. 10).

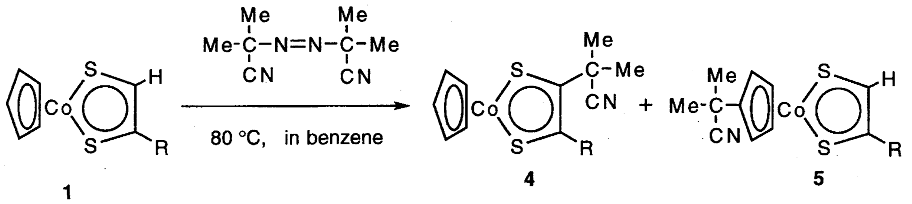


(10)

	7	Recovery of reactant
No additive	2%	94%
Bu_3SnH	28%	38%

The above facts indicate that tributyltin hydride itself or tributyltin radical inhibits the radical substitution in the cobaltadithiolene ring and promotes the substitution in the cyclopentadienyl ring. No similar effect has been observed for tributylsilane and tributylgermane. The mechanism for the effect of tin compounds has not yet been clarified.

The substitution by the radicals from 2,2′-azobis(isobutyronitrile) and its derivatives also occurs in the nickeladithiolene ring in [Ni(S_2C_2HX)$_2$]-type dithiolene



1 **4** **5**

Molar ratio, 1 : AIBN : Bu_3SnH = 1 : 1 : 0.5

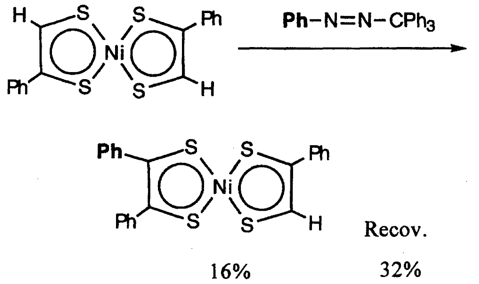
1		Additive	**4**	**5**	Recovery of **1**
1b	R = Me	----------	28%	trace	55%
		Bu_3SnH	15%	12%	31%
1c	R = Ph	----------	8%	4%	74%
		Bu_3SnH	1%	22%	50%
1d	R = COOMe	----------	trace	trace	98%
		Bu_3SnH	trace	11%	51%

Chart 3.

complexes. This type of substitution reaction occurs with several AIBN derivatives (Chart 4).[54]

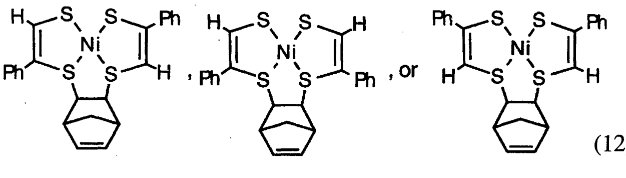
The substitution is completely inhibited by a radical scavenger TEMPO. This is good evidence for a radical mechanism. The carbon radicals having electron-attracting substituents undergo the substitution effectively but the electron-rich alkyl radicals can not cause the substitution. In this reaction, mono and di-substituted products are formed. In the reaction with AIBN, the yield of disubstituted product is higher than that of mono-substituted product. But it does not mean that the mono-substituted product is more reactive for radical substitution than the starting material. This phenomenon can be explained by easy ligand exchange in bis(1,2-ethylenedithiolato)nickel.[55]

(Phenylazo)triphenylmethane (PAT) reacts with [Ni(S_2C_2H,Ph)$_2$], affording phenyl-substituted product.



(11)

The quadricyclane adducts (**11**) of the nickeladithiolene complex, in which the delocalization of electrons is blocked by the substituent at S, do not undergo the substitution reaction. This fact indicates that the aromaticity of the metal chelate ring is essential for the occurrence of radical substitution.



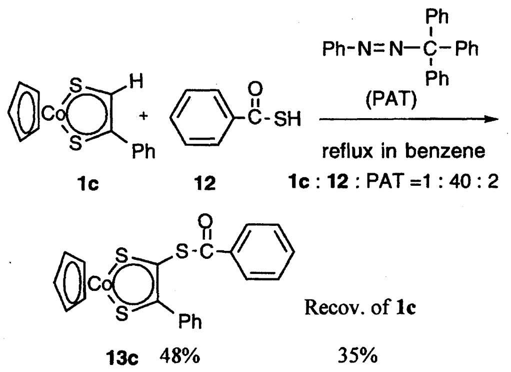
(12)

11

The study on the carbon-centered radicals is extended to the reactions using heteroatom-centered radicals. The substitution reactions are caused by sulfur-centered free radicals.[56,57] The reactions of the cobaltadithiolene complexes with thiobenzoic acid in the presence of radical initiators give benzoylthio-substitution products. The structures of the benzoylthio-substitution products were determined by X-ray crystallographic analysis. As shown in Fig. 2, the sulfur atom of the benzoylthio group is bonded to the carbon atom of the cobaltadithiolene ring.

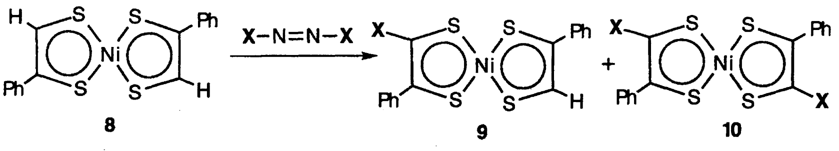
When AIBN is used as a radical initiator, the benzoylthio-substitution product was obtained only in a low yield (2%) even in the presence of large excess of thiobenzoic acid (the molar ratio of **1c** : AIBN : PhCOSH, 1 : 2 : 40). The main product in the reaction using AIBN as a radical initiator is 1-cyano-1-methylethyl-substitution product (35%) (Recovery of **1c**, 32%).

By using (phenylazo)triphenylmethane (PAT) as a radical initiator, one obtains the benzoylthio-substitution product (**13c**) in a higher yield (Eq. 13).[56]



(13)

The reaction among (η^5-cyclopentadienyl)(1,2-ethylenedithiolato)cobalt(III) (**1a**), thiobenzoic acid, and PAT gives benzoylthio-substituted product (**13a**) in 17% yield (recovery of **1a**, 36%). In addition the triphenylmethyl-substituted product (**14a**) was obtained in 26% yield (Eq. 14). The triphenylmethyl-substitution occurs more effectively than ben-



	Additive	9	10	Recovery of 8
X = -CMe$_2$(CN)	-----------	18%	30%	trace
X = -CMe$_2$(CN)	TEMPO	trace	0%	94%
X = -1-Cyanocyclohexyl	-----------	35%	7%	33%
X = -CMe$_2$(COOMe)	-----------	24%	39%	trace

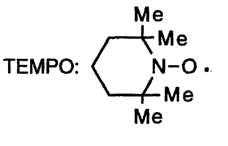


Chart 4.

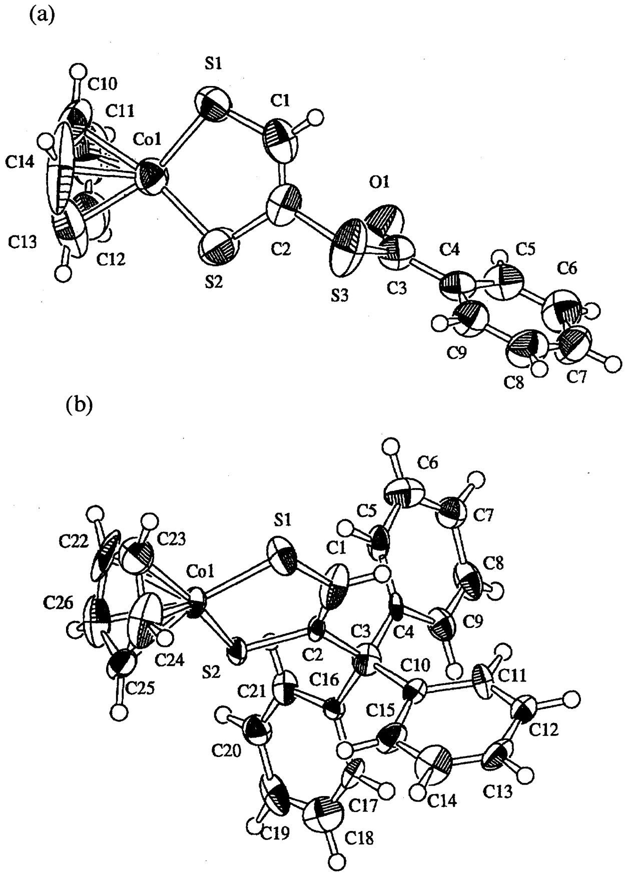
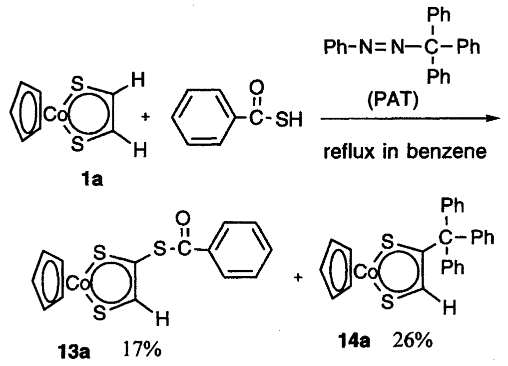


Fig. 2. X-Ray structures of benzoylthio- and triphenylmethyl-substition products of [(Cp)Co($S_2C_2H_2$)].
a) Benzoylthio-substitution product, b) Triphenylmethyl-substitution product.



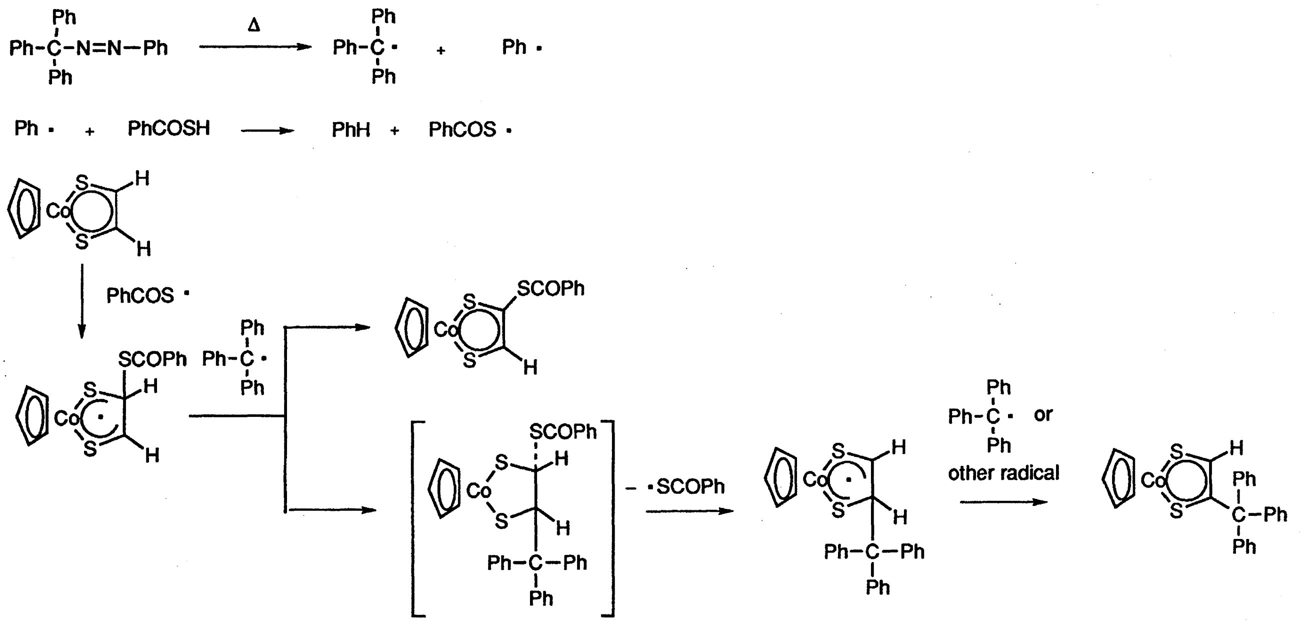
(14)

zoylthio-substitution.

The triphenylmethyl-substitution is an unusual reaction. There have been no reports on the substitution by triphenylmethyl radical, although its addition reactions to benzene,[58)] thiophene,[59)] and furan[60)] have been reported in the reaction of PAT. Formally, a very unreactive triphenylmethyl radical undergoes substitution. We propose a mechanism for the substitution reactions including triphenylmethyl-substitution which are induced by (phenylazo)triphenylmethane.

We propose the mechanism of Scheme 7. In the substitution of cobaltadithiolene by thiobenzoic acid and PAT, the reactive phenyl radical and unreactive triphenylmethyl radical cooperate well for the substitution reactions. The first step is the generation of phenyl and triphenylmethyl radicals. The reactive phenyl radical abstracts hydrogen atom from thiobenzoic acid to give benzoylthio radical. Benzoylthio radical adds to the cobaltadithiolene ring to form a radical intermediate (an adduct between cobaltadithiolene and sulfur radical).

Although the unreactive triphenylmethyl radical can not initiate the reaction by adding to the ring, it would react with the reactive radical intermediate. When the cobaltadithio-



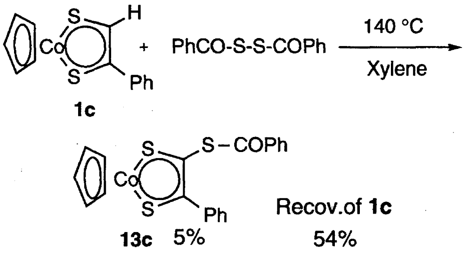
Scheme 7.

lene rings have substituents, triphenylmethyl radical can not combine with the cobaltadithiolene radical because of the large steric hindrance. Thus, it abstracts hydrogen from the metal complex radical and rearomatizes the cobaltadithiolene ring.

The high efficiency of the benzoylthio-substitution induced by PAT is due to the cooperation of phenyl radical and triphenylmethyl radical. On the other hand, 1-cyano-1-methylethyl radical from AIBN has lower ability for hydrogen abstraction. The hydrogen abstraction from thiobenzoic acid competes with the addition to the cobaltadithiolene ring. Thus, the benzoylthio-substitution and 1-cyano-1-methylethyl-substitution occur in parallel.

When the cobaltadithiolene ring has no substituents, triphenylmethyl radical can combine with the cobaltadithiolene radical and kick off the sulfur-centered radical. A feature of sulfur-centered radicals (sulfenyl radicals) is the easy addition and elimination. This feature of the sulfur-centered radical gives rise to the unusual triphenylmethyl-substitution.

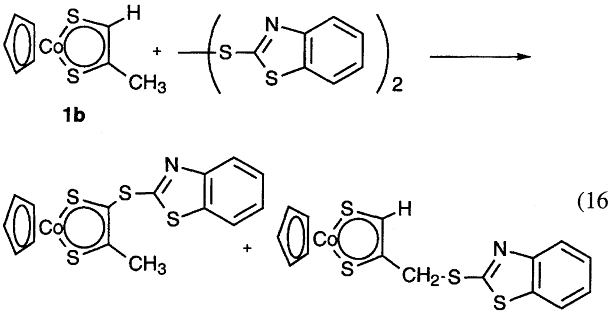
The substitutions by sulfur-centered radicals also occur in the reactions of the cobaltadithiolene complexes with disulfides.[57] The reaction of a cobaltadithiolene complex **1c** with dibenzoyl disulfide causes the benzoylthio-substitution. However, the yield of the benzoylthio-substitution product is low (Eq. 15).



(15)

Other disulfides cause the radical substitution in the cobaltadithiolene ring. Among the disulfides examined, bis(benzo[*d*]-1,3-thiazol-2-yl) disulfide causes the substitution most efficiently. The radical mechanism is proved by the inhibition by TEMPO. The substitution by bis(benzo[*d*]-1,3-thiazol-2-yl) disulfide can also be initiated by UV-irradiation or γ-irradiation in benzene solutions. Photolysis of the disulfide causes the homolytic S–S bond cleavage of the excited disulfides to give benzo[*d*]-1,3-thiazol-2-ylthio radical, which undergoes the substitution. The γ-irradiation of a benzene solution produces the excited benzene and the excitation transfer from the excited benzene to the disulfide occurs to generate the excited disulfide which undergoes the same reaction as photoreaction (Chart 5).

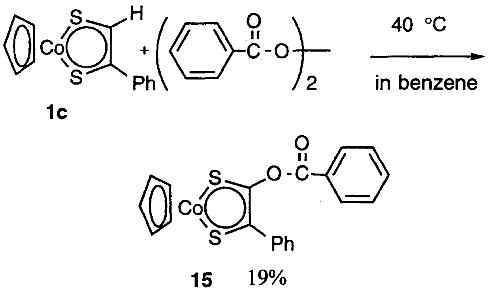
In the cobaltadithiolene ring having a CH_3 group, the substitutions occur both in the cobaltadithiolene ring and at the methyl group (Eq. 16).



(16)

2.3. Other Ionic Substitution Reactions.

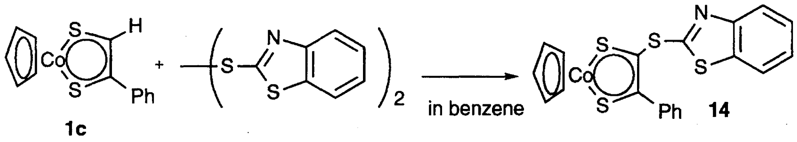
The observation that dibenzoyl disulfide causes the benzoylthio-substitution leads us to a question. "What kind of reaction occurs with dibenzoyl peroxide?" As is expected, the reaction with dibenzoyl peroxide brings about the substitution of the ring hydrogen for benzoyloxy group (Eq. 17).[61]



(17)

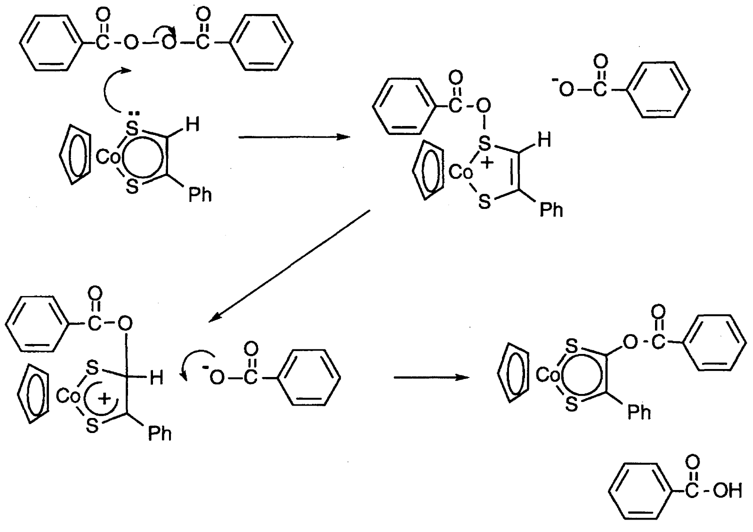
However, the benzoyloxy-substitution can not be explained by a radical mechanism, because the reaction occurs at 40 °C, where dibenzoyl peroxide does not decompose to free radicals and the reaction is not inhibited by radical scavengers. An ionic mechanism as in Scheme 8 has been proposed.

The reactions with some *N*-halosuccinimides are also an unusual substitution reaction. The reaction proceeds at room



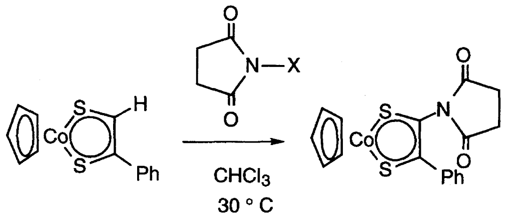
Reaction conditions		Yield of 14 %	Recovery of 1c %
Thermal	80 °C	19	61
	Additive, TEMPO	2	90
Photochemical	Medium pressure Hg lamp	42	29
Radiation-induced	Co-60 γ-rays	11	75

Chart 5.



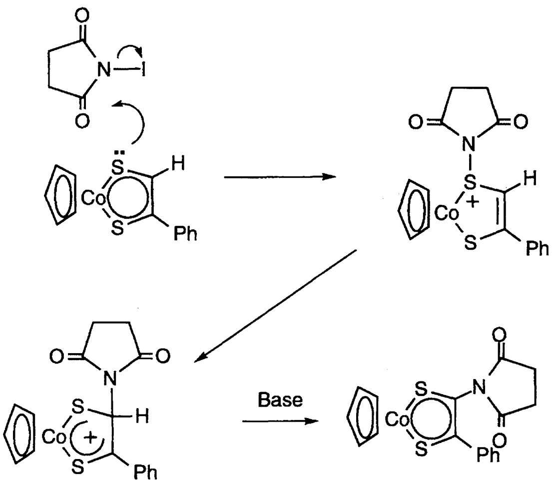
Scheme 8.

temperature and gives no halogenation products but a succinimido-substitution product. When we use excess *N*-iodosuccinimide, we obtain about 50% of the succinimido-substituted product. In the reaction with *N*-bromosuccinimide, the expected bromination does not occur (Eq. 18).[62]



(18)

Although several examples of succinimido-substitution have been reported for aromatic and heteroaromatic compounds,[63—66] the substitution of succinimido group for the hydrogen atom of aromatic rings is exceptional. Thus, the reaction indicates unique reactivity of the quasi-aromatic cobaltadithiolene ring. A similar succinimido-substitution has been reported for Ni, Co, and Cu complexes with salicylaldehyde.[67] The succinimido-substitution takes place more efficiently when *N*-iodosuccinimide is used. The succinimido-substitution should proceed in an ionic mechanism similar to that of benzoyloxylation (Scheme 9).



Scheme 9.

Sometimes the succinimido-substitution accompanies the coupling of the cobaltadithiolene ring. The coupling occurs when the succinimido-substitution is not efficient. Considering that the coupling occurs by the catalysis of protic acid as described earlier, we see that the coupling is effected by hydrogen halide formed in the succinimido-substitution.

In summary, we have clarified that metalladithiolene rings undergo various types of substitution reactions: Friedel–Crafts acylation proceeds in an electrophilic mechanism, 1-cyano-1-methylethyl-substitution reactions by AIBN and benzoylthio-substitution proceed in radical mechanisms, and the benzoyloxy-substitution by dibenzoyl peroxide and succinimido-substitution by *N*-halosuccinimides proceed in ionic mechanisms including the participation of the lone pair electrons at the sulfur atom.

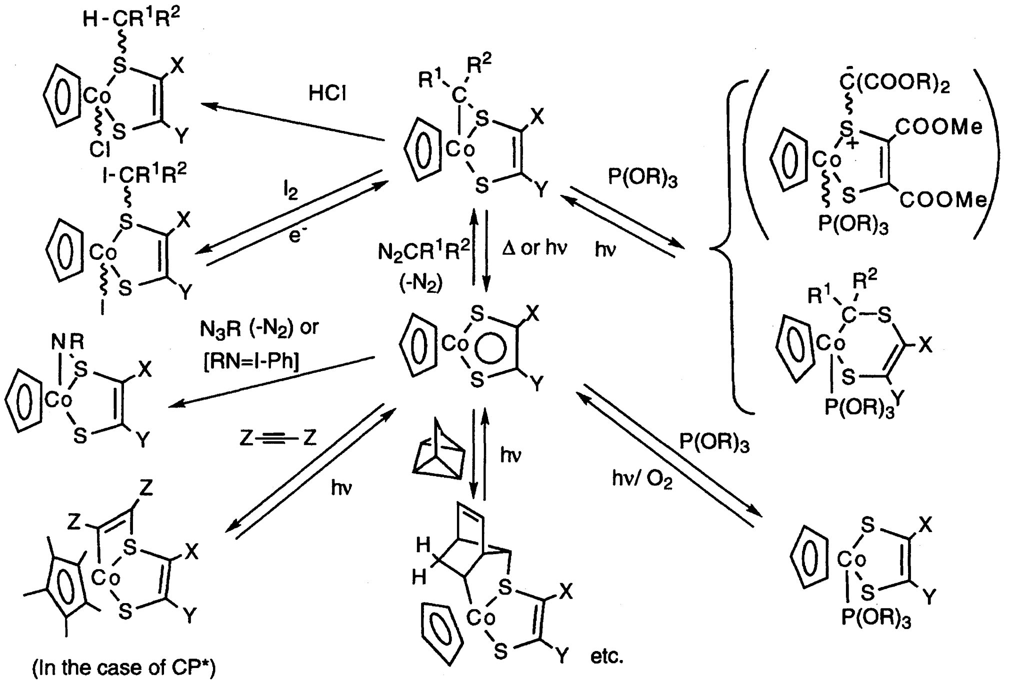
3. Addition and Elimination Reactions Due to Unsaturation

3.1. General Scope. In parallel to the aromaticity, the metalladichalcogenolene rings have the character of unsaturation. We found that a variety of reactive species add to the metalladichalcogenolene rings. Especially interesting addition reactions occur in $[(Cp)M(S_2C_2XY)]$-type metalladithiolene rings. Most addition reactions occur at the metal and the chalcogen atom. Some important examples of the addition reactions in cobaltadithiolene rings are summarized in Scheme 10.

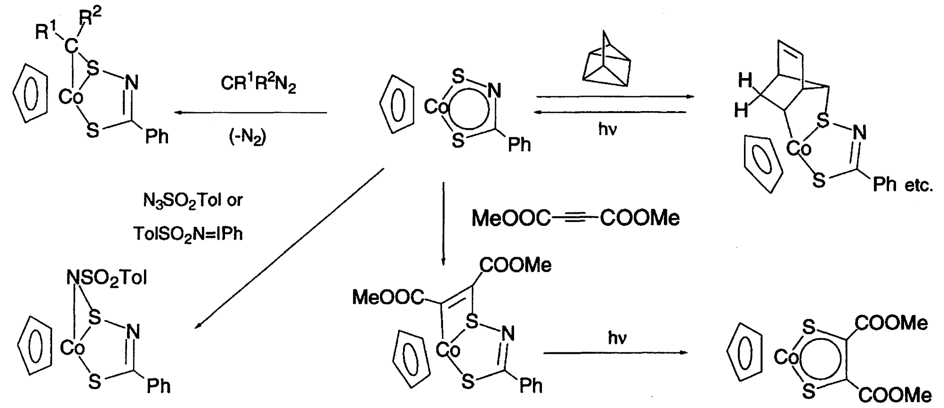
The reactions of the addition products are also interesting. An important reaction of these adducts is the elimination of the added moieties by heating, irradiation of light, or electrochemical redox. The easy elimination of the added parts is probably due to the tendency to regenerate the quasi-aromatic system.

Similar reactions occur in cobaltadithiazole rings. Some typical reactions are shown in Scheme 11.

In the following sections, several important addition and



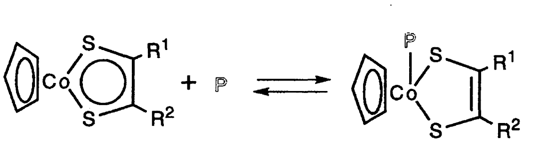
Scheme 10.



Scheme 11.

elimination reactions will be discussed.

3.2. Addition and Elimination of Posphines and Phosphites. In [(Cp)M(S_2C_2XY)]-type cobalta- and rhodadithiolene complexes, phosphines and phosphites add to the metal atoms (Eq. 19).[68—70)]



(19)

ℙ = PMe_3, PEt_3,PBu_3,
$P(OMe)_3$, $P(OEt)_3$,$P(OBu)_3$

The formation of the phosphine and phosphite adducts is an equilibrium reaction. The equilibrium constant K of the reaction is dependent on the reduction potentials ($E^{\mathrm{r}}_{1/2}$(red)) of the metalladithiolenes. The cobaltadithiolene complexes having more positive reduction potentials have larger K values. Logarithmic plots give a fairly good linear relationship (Fig. 3).

The reversible reduction of the cobaltadithiolene complexes occurs mainly at the metal atom. The half-wave potential is a measure of the positive charge at the cobalt atom. Thus, the linear relationship between $E^{\mathrm{r}}_{1/2}$(red) and the equilibrium constant is explained by the affinity of the electronegative phosphorus atom to the electropositive metal atom.

The coordinated phosphine and phosphite are dissociated by UV-irradiation[71)] or electrochemical redox reactions.[69)] The tributylphosphine adduct of a cobaltadithiolene complex **17** itself is photochemically unreactive under Ar, but it gives the free cobaltadithiolene complex in the UV-irradiation under O_2. The reaction under O_2 is inhibited by DABCO. The irradiation of **17** under O_2 in the presence of a triplet sensitizer such as methylene blue also causes the formation of the free cobaltadithiolene complex. The formation of tributylphosphine oxide is confirmed. These facts indicate that the coordinated phosphine is eliminated in the oxidation

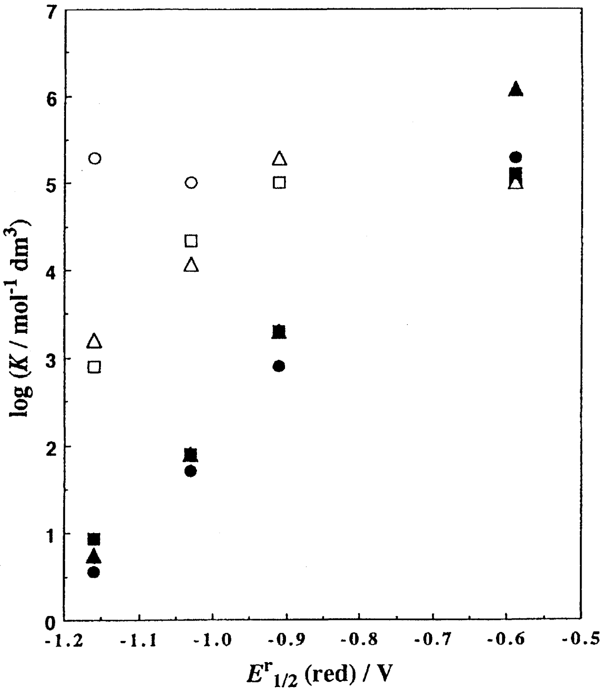
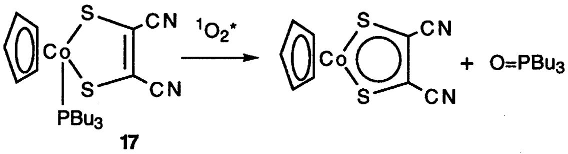


Fig. 3. Correlation between $E^{r}_{1/2}$(red) of metalladithiolene complexes and equilibrium constant K for the adduct formation with phosphine and phosphite.
○ : for PMe_3, □ : for PEt_3, △ : for PBu_3, ● : for $P(OMe)_3$, ■ : for $P(OEt)_3$, ▲ : for $P(OBu)_3$.

by singlet oxygen. The phosphine adduct **17** can act as a triplet sensitizer which produces singlet oxygen (Eq. 20).



17 (20)

Electrochemical reduction and oxidation of the phosphine and phosphite adducts are irreversible and cause the elimination of phosphorus compounds. The reduction causes the elimination of the electrically neutral phosphorus compounds to give the anion of the cobaltadithiolene. The oxidation affords the electrically neutral cobaltadithiolene accompanying the oxidation of the phosphorus compound (Scheme 12).

3.3. Addition and Elimination of Quadricyclane. Quadricyclane reacts with metalladithiolene and metalladithiazole complexes to give 1 : 1 adducts.[72] X-Ray crystal structure analysis (Fig. 4a) of an adduct from the reaction of (η^5-cyclopentadienyl)(benzene-1,2-dithiolato)cobalt(III) (**1h**) and quadricyclane reveals that the hydrocarbon moiety bridges between the metal and sulfur of the cobaltadithiolene ring. The carbon atom at the bridge is bonded to a sulfur atom and an edge-carbon is bonded to the cobalt atom.

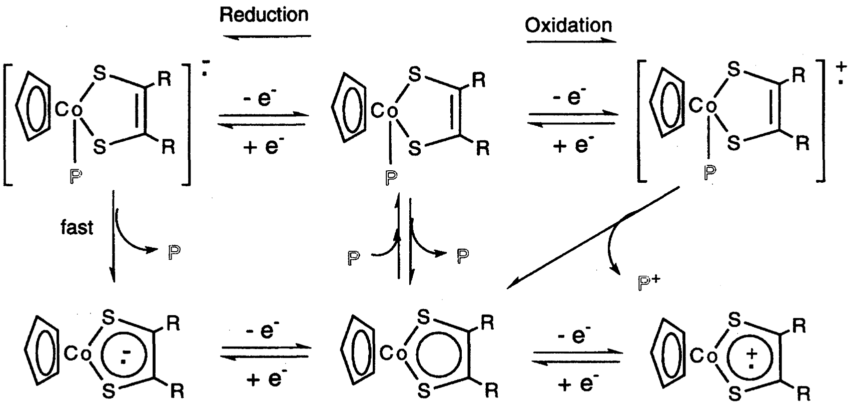
In the formation of adducts, skeletal rearrangement occurs in the hydrocarbon moiety. By a study using a deuterium labeled quadricyclane, the mechanism in Scheme 13 is proposed.

In the reaction with electron-rich quadricyclane, the positively charged cobalt atom attacks to quadricyclane to cause heterolytic bond cleavage in quadricyclane to form a Co–C bond. The carbonium ion of quadicyclane moiety undergoes skeletal rearrangement. At the final stage, the positive center of the hydrocarbon (rearranged quadricyclane) moiety is bonded to a negatively charged sulfur atom.

The adduct is easily dissociated upon photo-irradiation to give norbornadiene and the free cobaltadithiolene complex. A study using deuterium-labeled compound revealed that the abundance of D in norbornadiene formed in the photolysis is identical with that of the norbornadiene used for the preparation of quadricyclane. This indicates that the elimination of norbornadiene takes almost the reverse path for the formation of the quadricyclane adduct. Thus, the mechanism in Scheme 14 can be proposed.

A rhodadithiolene complex also gives a 1 : 1 adduct with quadricyclane.[73,74] The structure of the 1 : 1 adduct between rhodadithiolene and quadricyclane is similar to that of the cobaltadithiolene (Fig. 4b). But in the adducts of rhodadithiolene, the bridge of the bicyclic hydrocarbon is bonded to the metal atom, while in the adduct of cobaltadithiolene, the bridge carbon is bonded to the sulfur atom. The difference in the structures of the cobaltadithiolene and rhodadithiolene can be explained by the difference in the approach of quadricyclane to the metalladithiolene complexes in the initial step of the adduct formation (Scheme 15).

A similar reaction occurs with a cobaltadithiazole com-



Scheme 12.

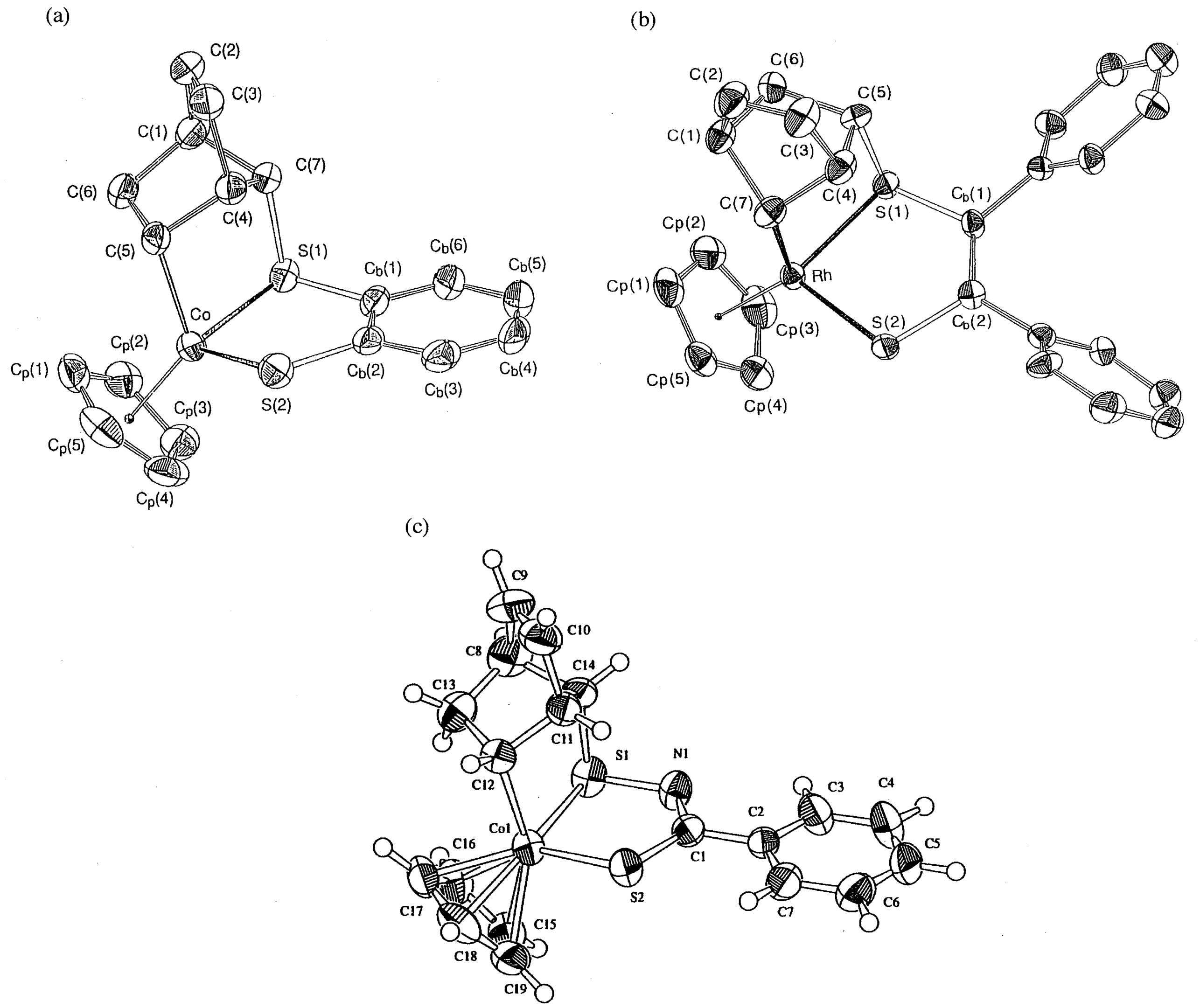
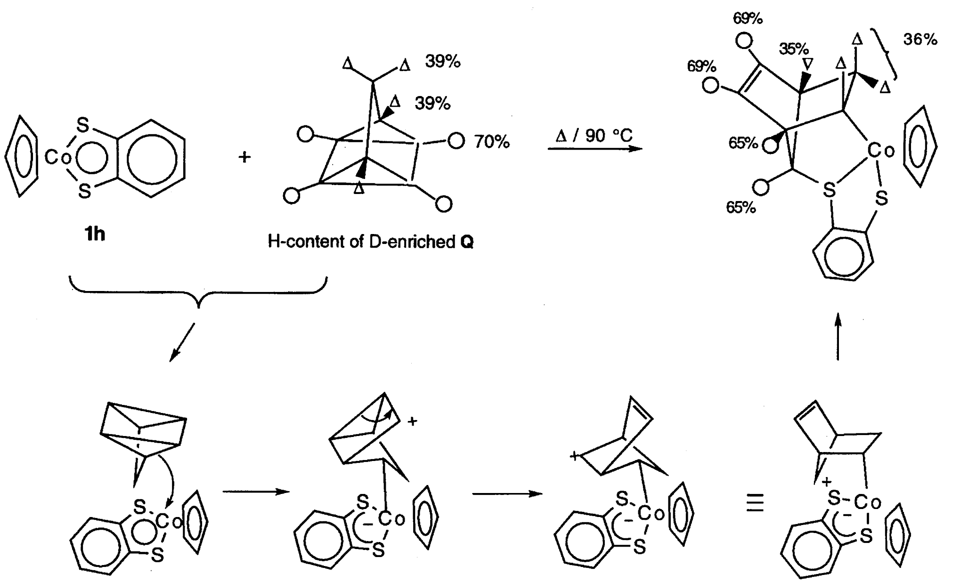
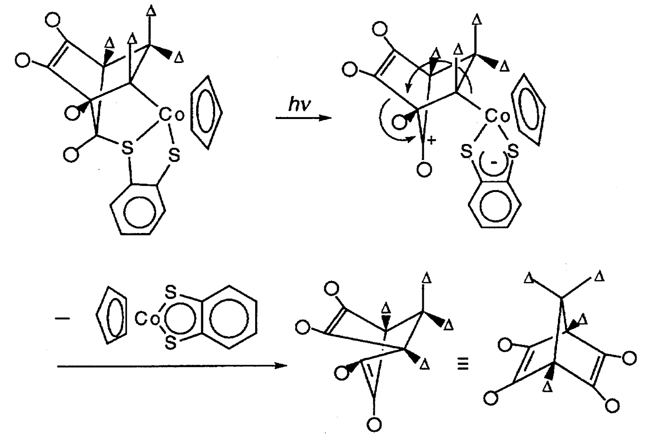


Fig. 4. X-Ray structures of quadricyclane adducts of cobaltadithiolene (a), rhodadithiolene (b), and cobaltadithiazole (c).
a) Quaricyclane adduct of a cobaltadithiolene [(Cp)Co($S_2C_6H_4$)], b) Quaricyclane adduct of a rhodadithiolene [(Cp)Rh($S_2C_6H_4$)], c) Quaricyclane adduct of a cobaltadithiazole [(Cp*)Co(S_2CNPh)].

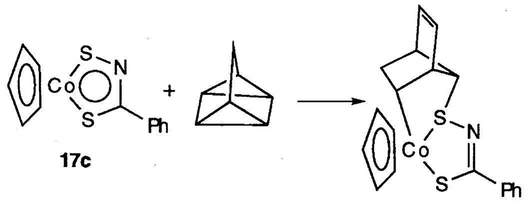


Scheme 13.



Scheme 14.

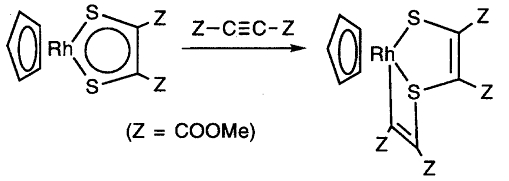
plex. A cobaltadithiazole complex **17c** reacts with Q to give several adducts (Eq. 21).74) The main product has the structure similar to the quadricyclane-adduct of the cobaltadithiolene complex (Fig. 4c). The bridge carbon is bonded to the sulfur atom. It is noted that the sulfur atom bonded to the hydrocarbon moiety is the sulfur atom attached to N and not the sulfur atom attached to C. Between the two sulfur atoms in the cobaltadithiazole ring, the sulfur atom adjacent to the nitrogen atom is more electron-rich, because the electrons at the other sulfur atom are withdrawn by the conjugation with N=C. At the final stage of the addition, the positively charged carbon atom of the hydrocarbon moiety chooses the more electron-rich sulfur atom.



17c

(21)

3.4. Addition and Elimination of Dimethyl Acetylenedicarboxylate (DMAD). A rhodadithiolene complex having a cyclopentadienyl ligand forms a 1 : 1 adduct with dimethyl acetylenedicarboxylate (DMAD) (Eq. 22).76)

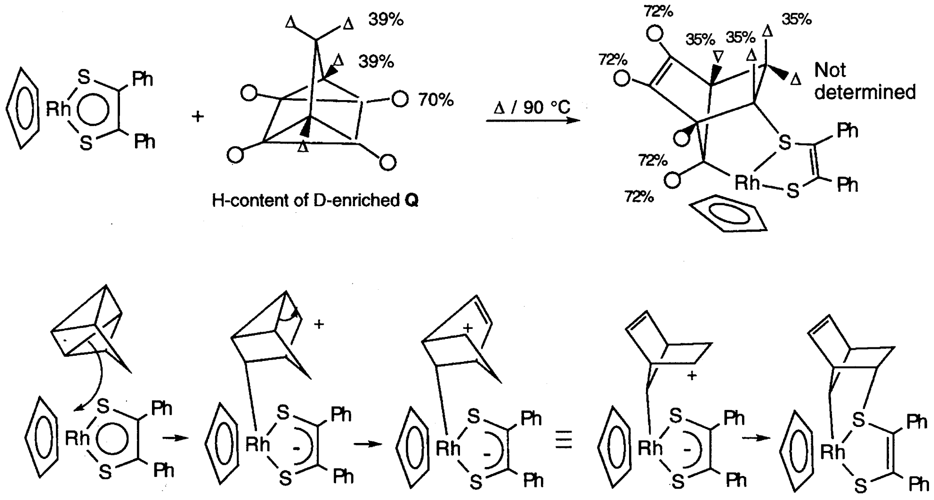


(22)

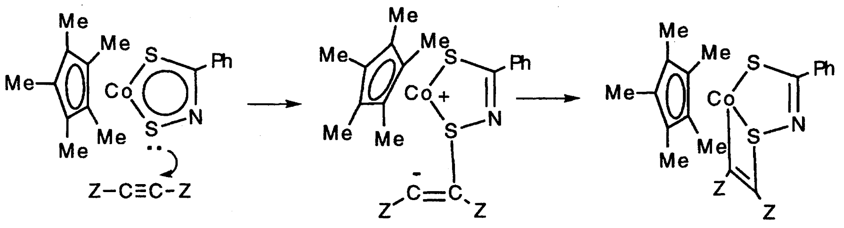
Most $[(Cp)Co(S_2C_2R_2)]$-type cobaltadithiolene complexes do not react with DMAD, while the cobaltadithiolene complexes having pentamethylcyclopentadienyl or methylcyclopentadienyl as a ligand instead of cyclopentadienyl form 1 : 1 adducts with DMAD. Electrophilic DMAD adds to a cobaltadithiazole having Cp* (Cp* = pentamethylcyclopentadienyl) ligand to afford an adduct. In that case, the more electron-rich sulfur atom adjacent to N is selectively reacted.77) These facts suggest that the formation of DMAD adducts is initiated by the electrophilic attack of DMAD to the sulfur atom of the cobaltadithiolene. The mechanism for the formation of DMAD adduct is shown in Scheme 16.

This is in sharp contrast to the adduct formation with quadricyclane. The reaction with quadricyclane is initiated at the positively charged metal atom, while the reaction with DMAD is initiated at the more negatively charged sulfur atom. Thus, the metalladithiolene rings can react either with electron-rich compounds or with electron-poor compounds. Both reactions lead finally to the same type of reaction namely the bridging between the metal and sulfur.

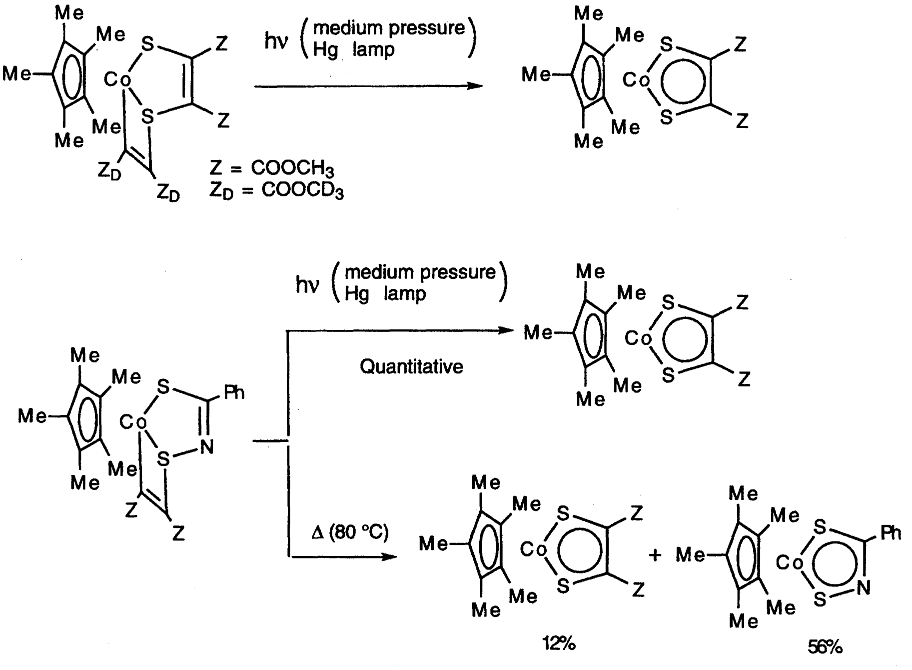
With respect to the photochemical and the thermal elimination, there is an interesting difference between the cobaltadithiolene and cobaltadithiazole complexes. In the irradiation with a medium pressure mercury lamp, the DMAD adduct of the cobaltadithiolene complex eliminates the bridging DMAD. In contrast, the UV-irradiation of the DMAD adduct of the cobaltadithiazole complex causes the selective elimination of benzonitrile to give cobaltadithiolene complex. The thermolysis of the DMAD adduct of the cobaltadithiazole complex, however, causes the elimination of DMAD and benzonitrile in parallel (Scheme 17).



Scheme 15.



Scheme 16.

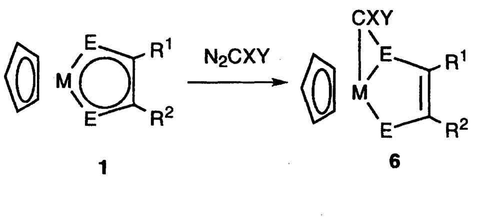


Scheme 17.

3.5. Formation of Alkylidene Adducts. Among the addition reactions, the reactions with diazo compounds are most versatile. Several interesting reactions of diazo compounds with chalcogen-containing metal complexes have been reported. Herrmann found that methylene bridges between Cr and Se in the reaction of diazo compounds with a selenium coordinated chromium complex and ascribed the reaction to the double bond character of the Cr=Se bond.[78]

Mathur et al. described the formation of a methylene-bridged double butterfly shaped complex in the reaction of $[Fe_2(CO)_6Te_2]$ with diazomethane.[79] Diazomethane reacts also with $[Ni(S_2C_2Ph_2)_2]$, resulting in the replacement of dithiolato ligand by methylene via a methylene-coordinated complex.[80]

We found that diazo compounds react with cobalta- and rhoda-dichalcogenolene complexes to form alkylidene bridges between metal and chalcogen (Eq. 23).[81,82] The reaction with diazomethane occurs at 0 °C at which no carbene species is generated.



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(23)

The electron-attracting groups in the diazo compounds lowers the reactivity. The reaction with dimethyl diazomalonate occurs in refluxing benzene under the catalysis of CuI–P(OMe)$_3$. The reactions of the metalladichalcogenolene complexes with diazo compounds are summarized in Table 1.

A typical example of the X-ray structure of the alkylidene adduct is shown in Fig. 5a. The five-membered metalladichalcogenolene ring is almost planar like non-bridged complexes. The Co–S distance of the bridged moiety is almost the same as the Co–S distance of the non-bridged moiety. The three-membered metallathiirane ring is almost perpendicular to the metalladithiolene ring.

The bridging reaction with diazomethane proceeds smoothly at 0 °C, at which diazo compounds do not decompose to carbene. It suggests that the diazo compounds react not as carbene but as a dipolar species.

The reactivities and selectivities of the bridging give useful information for the reaction mechanism. As was mentioned above, the electron-attracting groups in diazo compounds retard the reaction. On the other hand, the electron-attracting groups in metalladichalcogenolene rings facilitate the reaction, although the effect of the substituents in the cobaltadithiolene ring is smaller than that in the diazo compounds. These facts indicate that the initial step is the attack of negative center (carbon atom) of diazo compounds to the positive center (metal atom) of the metalladithiolene ring.

Table 1. Formation of Alkylidene Adducts in the Reaction of Metalladichalcogenolene Complexes with Diazo Compounds

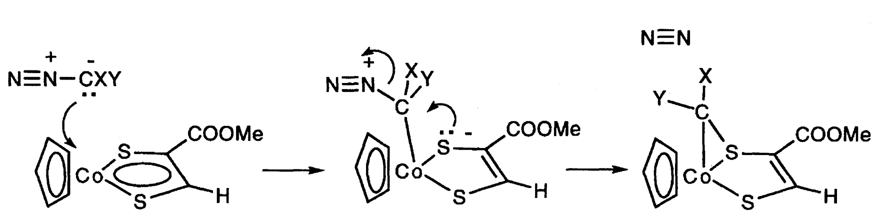
Metalladichalcogenolene					Diazo compound		Conditions		Yield of adduct
M	E	E′	R^1	R^2	X	Y	Temp	Time	%
							°C	h	
Co	S	S	H	H	H	H	0	a)	50
Co	S	S	Ph	Ph	H	H	0	a)	50
Co	S	S	COOMe	COOMe	H	H	0	a)	92
Co	S	S	CN	CN	H	H	0	a)	84
Co	S	S	COOMe	H	H	H	0	a)	45
Co	S	S	COOMe	H	H	H	0	a)	45
Co	S	S	Benzo		H	H	0	a)	70
Co	S	S	1,4-Dichlorobenzo		H	H	0	a)	70
Co	S	S	Tetrachlorobenzo		H	H	0	a)	64
Co	Se	Se	Ph	Ph	H	H	0	a)	2.3
Rh	S	S	COOMe	COOMe	H	H	0	a)	56
Rh	S	S	COOMe	H	H	H	0	a)	28
Rh	S	S	Benzo		H	H	0	a)	65
Co	S	S	Ph	Ph	COOEt	H	80	3	80
Co	S	S	COOMe	COOMe	COOEt	H	80	3	87
Co	S	S	COOMe	H	COOEt	H	80	5	59
Co	S	S	Benzo		COOEt	H	80	a)	15
Co	Se	Se	Ph	Ph	COOEt	H	80	3	49
Co	S	Se	Ph	Ph	COOEt	H	80	3	36c) 39d)
Rh	S	S	COOMe	COOMe	COOEt	H	80	0.083	76
Rh	S	S	COOMe	H	COOEt	H	Room temp	0.083	63
Co	S	S	COOMe	COOMe	COOMe	COOMe	80	24	5
Co	S	S	COOMe	COOMe	COOMe	COOMe	80b)	24	40
Rh	S	S	COOMe	COOMe	COOMe	COOMe	80	24	31

a) The reaction occurs immediately at 0 °C. b) Reflux in benzene in the presence of $CuI–P(OMe)_3$. c) The complex in which ethoxycarbonylmethylene bridges between Co and S. d) The complex in which ethoxycarbonylmethylene bridges between Co and Se.

In the reaction of the cobaltadithiolene having one methoxycarbonyl group with diazomethane, the S atom adjacent to the methoxycarbonyl group is selectively bridged. In the reaction of cobaltadithiolene ring having one phenyl substituent, the bridging of either S atom occurs in parallel. In the reaction of the cobaltadithiazole complex with diazomethane, the S atom adjacent to N is preferentially reacted. The S atoms to be bridged are more electron-rich than the other S atoms. The electrons at the latter S atoms are withdrawn by the electron-attracting COOMe or N through conjugation. These facts suggest that the succeeding process is the attack of negatively charged S atom to the positively charged C of diazo compound moiety to cause S_N2-type elimination of N_2 (Scheme 18).

In the reaction of cobaltaselenathiolene with ethyl diazoacetate, the bridgings between selenium and metal and between sulfur and metal occur in parallel. The yields of S-bridged product and Se-bridged product are similar. But the ratio of the sulfur bridged product is increasing as the reaction time increases. This is explained by the thermal isomerization via the switching of bridge from Se to S. The reverse reaction does not occur (Scheme 19).[83)]

Most of the alkylidene-bridged cobaltadithiolene complexes have a rigid structures and normally structural changes are not observed in solutions. But there are three exceptions: One is the switching of bridging in selenathiolene described above, the second is the stereoisomerization, and the third is an equilibrium between the alkylidene-bridged form and ylide form in the bis(methoxycarbonyl)methylene-bridged adduct.



Scheme 18.

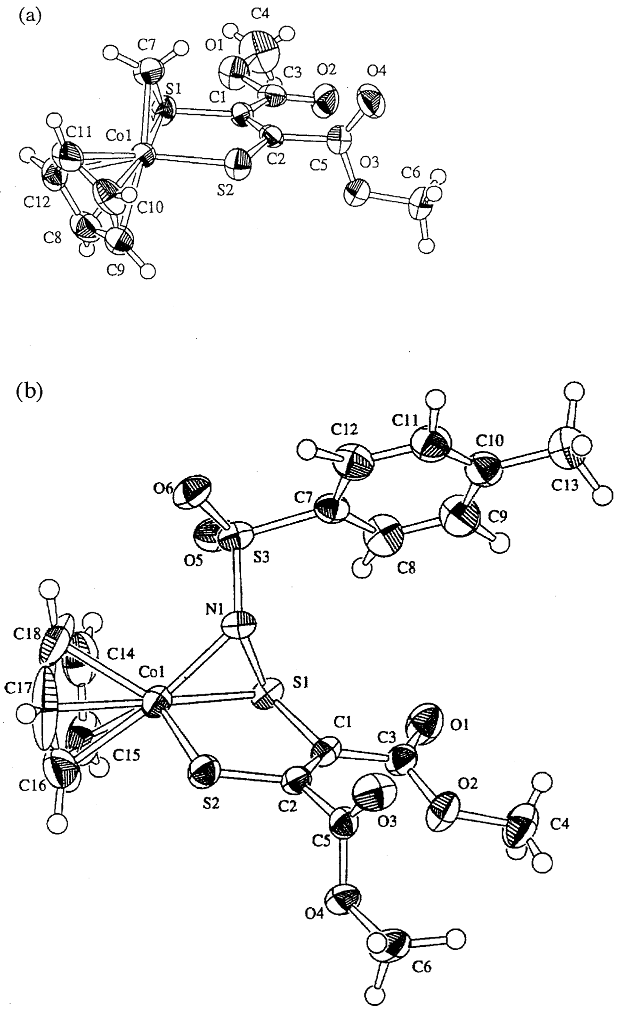
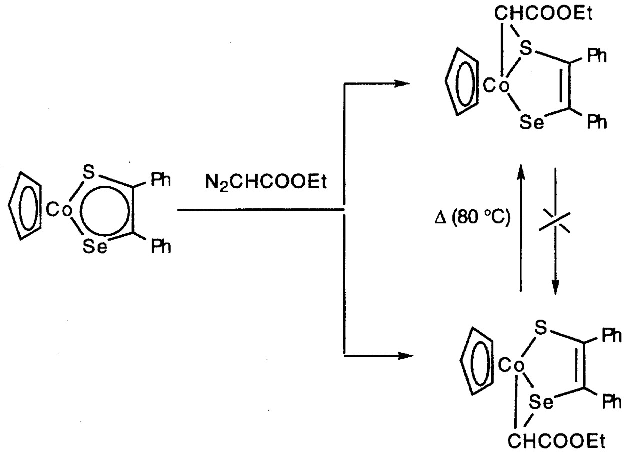


Fig. 5. X-Ray structures of alkylidene- and imido-bridged cobaltadithiolenes.
a) Methylene-bridged adduct of $[(Cp)Co(CH_2)\{S_2C_2(COOMe)_2\}]$, b) *p*-Tolylsulfonylimido-bridged adduct of $[(Cp)Co(NSO_2\ Tol)\{S_2C_2(COOMe)_2\}]$.



Scheme 19.

An example of the stereoisomerization is the case of (trimethylsilyl)methylene-bridged cobaltadithiazole. A cobaltadithiazole complex, **17c**, reacts with trimethylsilyldiazomethane to give stereoisomeric trimethylsilylmethylene-bridged complex. In this case, thermal stereochemical isomerization takes place and an equilibrium is attained. For the isomerization, the S–C bond cleavage should be involved (Scheme 20).[84)]

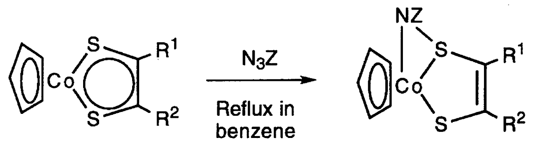
The third case is the equilibrium between three-membered cobaltadthiirane form and *S*-ylide form. This will be discussed in 3.7.2.

3.6. Formation of Imido Adducts. Similar to diazo compounds, some azides (*p*-tolylsulfonyl azide, methylsulfonyl azide, and ethyl azidoformate) react with cobaltadithiolene complexes to afford imido-bridged cobaltadithiolenes (Chart 6).[85)] The reaction proceeds in boiling benzene.

The structure of the *p*-tolylsulfonylimido-bridged cobaltadithiolene (Fig. 5b) is similar to that of alkylidene-bridged cobaltadithiolene. Considering the similarity to the reaction of diazo compounds and the difference from reaction by the nitrene species (Section 3.10), the mechanism of the imido-bridging should be similar to that of the alkylidene-bridging by diazo compounds.

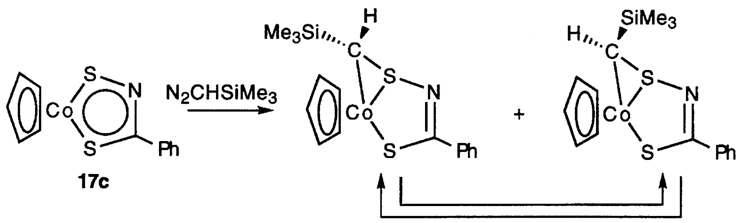
The same type of *p*-tolylsulfonylimido-bridged complex is synthesized in the reaction of the cobaltadithiolene with *N*-(*p*-tolylsulfonylimino)phenyliodinane (Chart 7).[84)]

N-(*p*-Tolylsulfonylimino)phenyliodinane is considered to

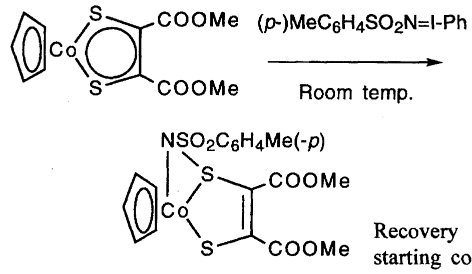


Cobaltadithiolene $R^1 = R^2$	Azide Z	Reaction time h	Yield %
COOMe	(*p*-) Me-$C_6H_4SO_2$-	2	78
	Me-SO_2-	5	76
	-COOEt	24	64
Ph	(*p*-) Me-$C_6H_4SO_2$-	24	59
	-COOEt	24	67

Chart 6.



Scheme 20.



Catalyst		Recovery of starting complex
----------	27%	64%
$Cu(OCOCF_3)_2$	27%	71%

Chart 7.

form a nitrenoid with copper. By heating in the presence of copper compound as a catalyst, it generates nitrene.86) However, the imido-bridging reaction takes place even in the absence of the catalyst at low temperature. Therefore, the participation of nitrene species is excluded. An ionic mechanism is more probable for the imido-bridge formation with *N*-(*p*-tolylsulfonylimino)phenyliodinane. We propose the mechanism in Scheme 21.

3.7. Reactions of Methylene and Imido Adducts. The methylene and imido adducts show also a variety of interesting reactions. The reactions of these addition products are classified into two types:

1. Two bond-cleavage (the elimination of the bridging moiety).
2. One bond-cleavage (opening of three-membered ring).

These reactions are caused by various types of activations of the adducts: thermolysis, photolysis, electrochemical redox, or attack of reagents.

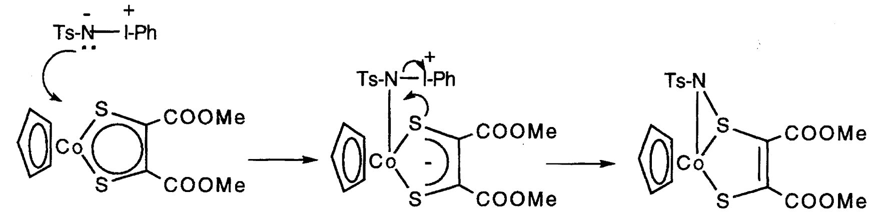
3.7.1. Elimination of Bridging Moiety. In many cases, thermolysis, photolysis, or electrochemical reduction or oxidation of methylene and imido adducts leads to the elimination of the added group to regenerate the original cobaltadithiolene complexes.

An important point in the elimination of the bridging moieties is what types of reactive species are formed in the dissociation. The alkylidene- and imido-adducts may eject carbene and nitrene species, because the adducts have the structures in which the cobaltadithiolenes trap carbene and nitrene.

A methylene adduct **6a** dissociates either thermally or photochemically. The thermolysis of **6a** in the presence of cyclohexene gives the free cobaltadithiolene and bicyclo[4.1.0]heptane (52% based on the methylene adduct). This suggests the formation of singlet methylene.

The irradiation of **6a** in a benzene solution with a medium pressure mercury lamp affords the free cobaltadithiolene complex. However, in the photoreaction in the presence of cyclohexene, no bicyclo[4.1.0]heptane is detected (Chart 8). The photochemical dissociation of **6a** is inhibited by 1,3-cyclohexadiene. These facts suggest that the photochemical dissociation occurs not from a excited singlet state but from a triplet excited state of the methylene-bridged cobaltadithiolenes.

This conclusion is supported by the photolysis of another adduct **6b**. The adduct **6b** itself does not dissociate upon irradiation. However, the presence of a triplet sensitizer, benzophenone, causes the photodissociation. In the presence of benzophenone and dimethyl sulfide which is a scavenger of singlet carbene, no *S*-ylide ($Me_2S^+{-}C^-(COOMe)_2$) which is the expected product from singlet carbene is detected. Instead dimethyl malonate is obtained (52%).86) These facts support the mechanism of photochemical elimination of al-



Scheme 21.

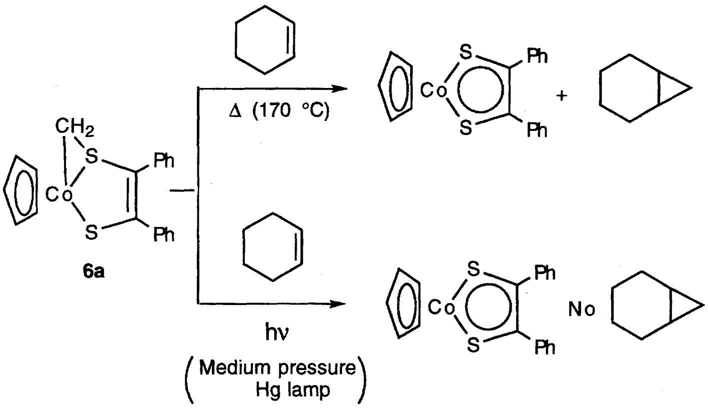


Chart 8.

kylidenes via excited triplet state (Chart 9).[82]

Electrochemical redox reactions also cause the elimination of the bridging alkylidene moiety. The methylene-bridged cobaltadithiolene complex **6c** displays a reversible reduction under the conditions for the CV measurement. However, the anion decomposes slowly (with a lifetime of a few minutes) to give the anionic form of the free cobaltadithiolene complex. On the other hand, in oxidation, the methylene-bridged cobaltadithiolene complex shows an irreversible oxidation peak. A study based on CV and spectral measurement using OTTLE (optically transparent thin layer electrode) revealed that the cation radical has only a few seconds of lifetime to give the electrically neutral free cobaltadithiolenes via several intermediates (Scheme 22).[87]

The adduct between $[(Cp)Co\{S_2C_2(COOMe)_2\}]$ and $C(COOMe)_2$, which has two electron-attracting groups at the bridging part, exhibits different electrochemical behavior. As described earlier, the complex exists as an equilibrium mixture of alkylidene-bridged (**6b**) and ylide forms (**6b′**) in a solution. Both isomers are reducible by one-electron uptake, but the radical anion of the bridged form undergoes rapid and irreversible isomerization to the anion of the ylide form. The anion of the ylide form eliminates bis(methoxycarbonyl)methylene group to give the anion of the free cobaltadithiolene complex. The reaction mechanism of the electrochemical redox reactions is shown in Scheme 23.

3.7.2. Opening of Metallathiirane Ring. The metallathiirane rings in the alkylidene-bridged metalladithiolenes show interesting reactions. The actions of hydrogen halide, phosphines, and phosphites to the alkylidene-bridged cobaltadithiolene complexes cause the opening of three-membered cobaltathiirane ring. Ring opening occurs either at the metal–carbon bond or at the metal–sulfur bond (Scheme 24).

The Co–S bond of the three-membered cobaltathiirane ring is easily cleaved by hydrogen halides. The halogen atom is bonded to the cobalt atom and the hydrogen atom is bonded to the bridging methylene carbon to give three-component-adducts among cobaltadithiolene, alkylidene, and hydrogen halide, (η^5-cyclopentadienyl)(halo)(1-methylthio-$\varkappa S$-ethylene-2-thiolato-$\varkappa S$)cobalt(III) (Scheme 24).[88] Trifluoroacetic acid causes the same type of reaction. The ring opening does not occur, when sodium iodide is reacted. This suggests that the driving force for the ring opening is supplied by the interaction of the methylene-bridged complex with a proton. The proton may either attack directly to the bridging carbon

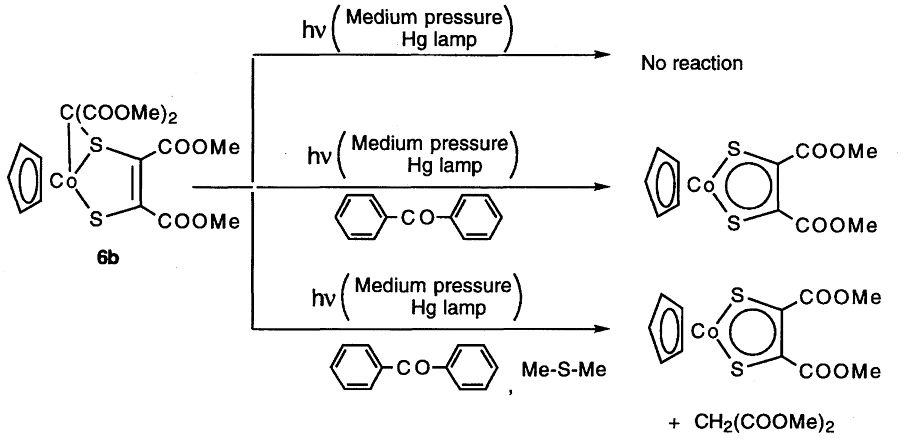
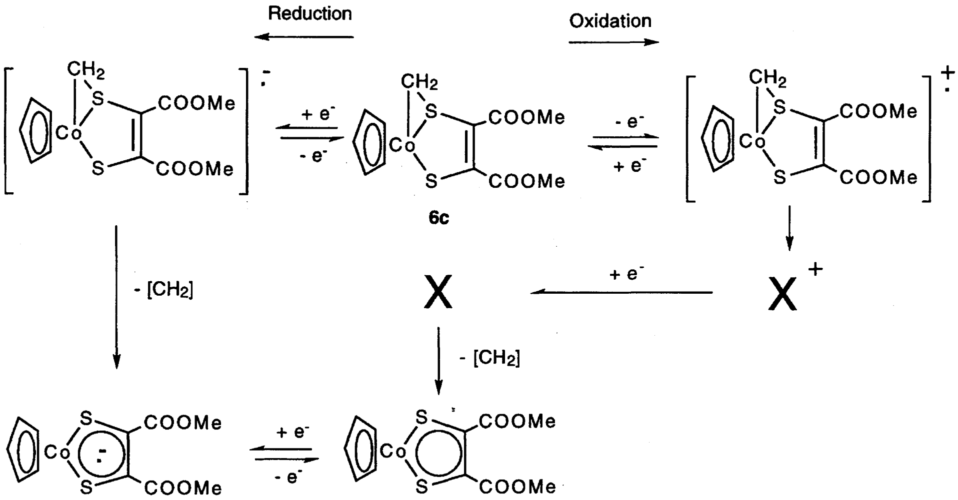
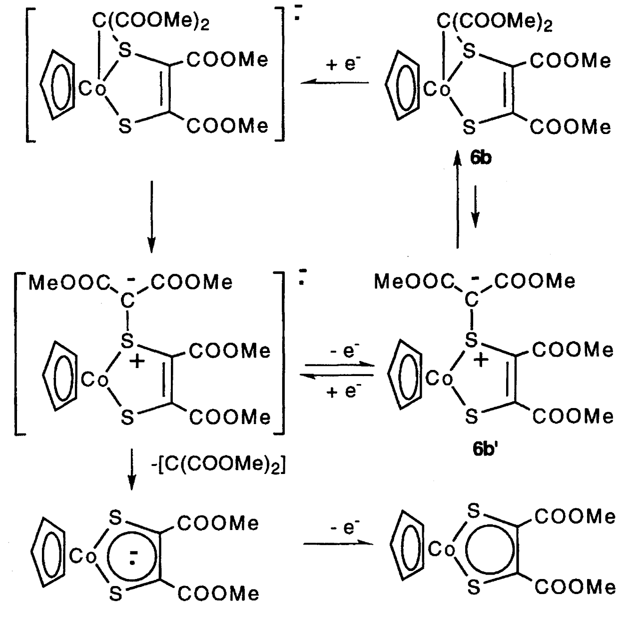


Chart 9.



Scheme 22.

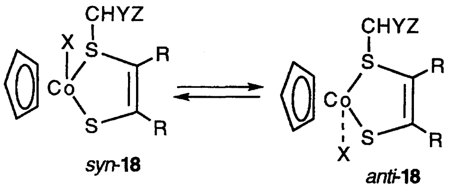


Scheme 23.

or may attack to the basic sulfur atom at first and then migrate to the bridging carbon.

The three-component-adducts take either *syn*- or *anti*-configuration with respect to the anionic group attached to the metal atom and the group attached to the sulfur atom. We have determined the X-ray crystal structure of 12 kinds of the three-component-adducts. Typical examples of the X-ray structures of each stereoisomer are shown in Fig. 6. It is noteworthy that the three-component-adducts having bulky groups are not always in *anti*-configuration. As exemplified by *syn*-**18** (Fig. 6a), the three-component-adduct having two bulky groups, trifluoroacetato attached to Co and trimethylsilylmethyl group attached to S, takes *syn*-conformation. On the contrary, *anti*-**18** having small groups attached to the metal atom and the sulfur atom takes *anti*-conformation (Fig. 6b).

In solutions the situation is more complex. Some three-component-adducts exist solely in *syn*-form. Some exist solely in *anti*-form. Several three-component-adducts exist in equilibria between the *syn*- and *anti*-stereoisomeric forms. In solutions, the exchange of the coordinated anions occurs rapidly and thus the isomerization occurs very easily (Eq. 24).

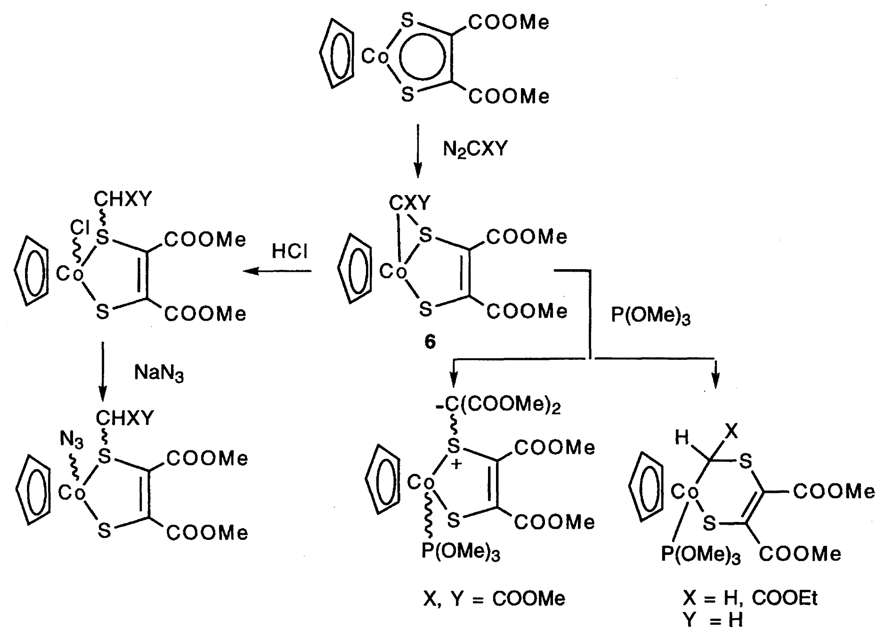


(24)

The attack (coordination) of phosphines and phosphites to the metal atom causes either the Co–C bond cleavage or Co–S bond cleavage. The former reaction leads to the formation of *S*-ylides and the latter reaction leads to the ring expansion to give six-membered 1,2,5-cobaltadithiine ring (Scheme 24).

Which type of reaction occurs depends on the electronic state of the bridging group and on the coordinated phosphorus compounds. The methylene-bridged complex undergoes the cleavage of the Co–S bond to give the ring expansion product. The bis(methoxycarbonyl)methylene-bridged complex undergoes the cleavage of the Co–C bond to give an ylide.[89] The methoxycarbonyl group at the methylene bridge stabilizes the ylide form and thus facilitates the cleavage of the Co–C bond. The complex which has one electron-attracting ethoxycarbonyl group at the bridge is on the border.[90] When it reacts with trimethyl phosphite, the Co–S bond cleavage occurs selectively. When it reacts with trimethylphosphine, both Co–C bond cleavage and Co–S bond cleavage occur in parallel.

Relating to the opening of three-membered cobaltathi-



Scheme 24.

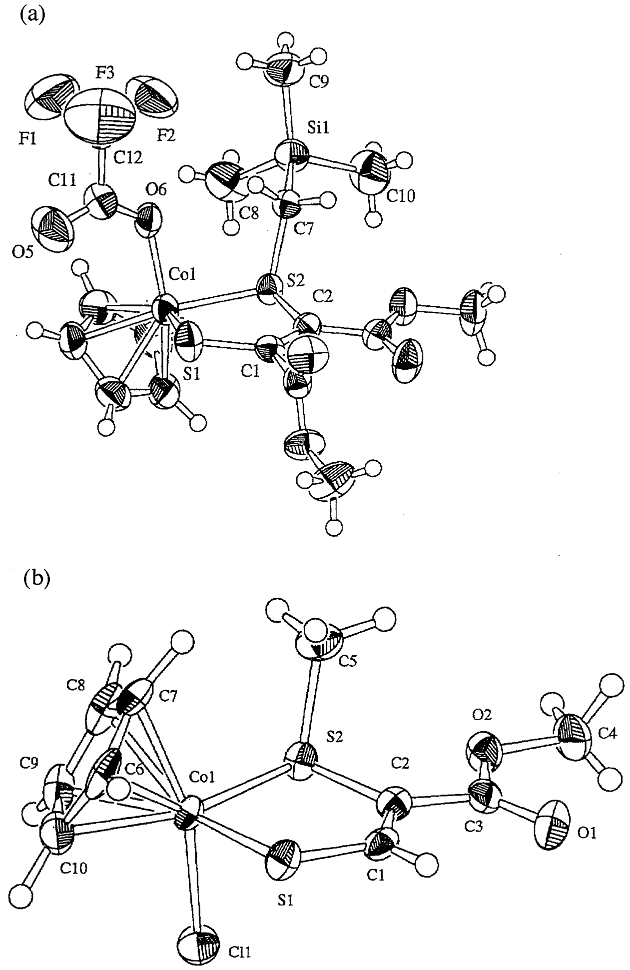
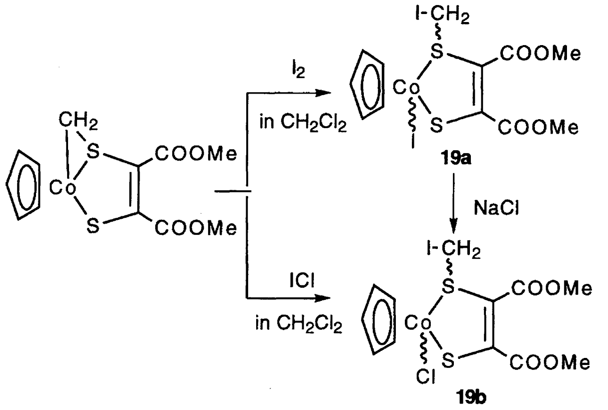


Fig. 6. X-Ray structures of three-component adducts among cobaltadithiolene, alkylidene, and protic acid having *syn*- and *anti*-configuration.
a) a typical example of the complex having *syn*-configuration ([(Cp)Co(CF$_3$COO){S(SiMe$_3$)C(COOMe)=C-(COOMe)S}], b) a typical example of the complex having *anti*-configuration ([(Cp)Co(Cl){S(Me)C-(COOMe)=CHS}].

irane ring by hydrogen halide, the ring opening and closure by halogen are interesting.[91] The Co–C bond of cobaltathiirane ring is cleaved by dihalogens (Cl$_2$, Br$_2$, and I$_2$) to give (η^5-cyclopentadienyl)(halo)[1-(halomethylthio)-κS-1,2-bis(methoxycarbonyl)ethylene-2-thiolato-κS]cobalt(III) (Scheme 25). The reactions of chlorine and bromine are vigorous and are difficult to control. The reaction with I$_2$ occurs at room temperature in a dichloromethane solution.

An important question concerning this reaction is whether the dihalogens act as nucleophiles or electrophiles. The answer can be obtained in the reaction with iodine chloride (ICl). The reaction yields (η^5-cyclopentadienyl)(chloro)-[1-(iodomethylthio)-κS-1,2-bis(methoxycarbonyl)ethylene-2-thiolato-κS]cobalt(III) (**19b**) and (η^5-cyclopentadienyl)-(iodo)[1-(iodomethylthio)-κS-1,2-bis(methoxycarbonyl)ethylene-2-thiolato-κS]cobalt(III) (**19a**) (Scheme 25).

The important point is the fact that iodine is bonded solely to the bridging methylene carbon. This indicates that the attack of positively charged iodine to the carbon induces the Co–C bond cleavage and the succeeding coordination of halide ion to the cobalt atom gives finally the products (Scheme 26). In this case, the exchange of coordinated halide ions occurs very easily. Thus, the iodo complex **19a** is considered to be a secondary product.

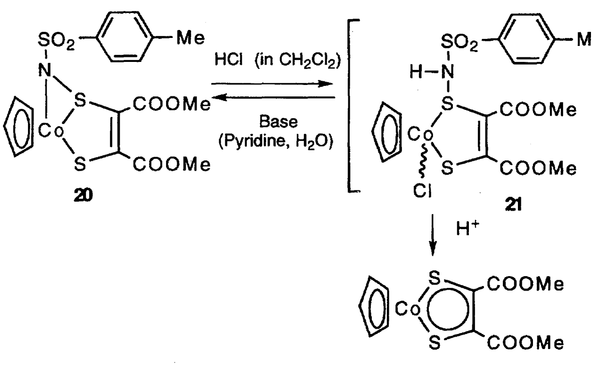


Scheme 25.

An interesting reaction of the dihalogen adducts is the reforming of the cobaltathiirane ring in the one-electron reduction. The reaction was deduced by the analysis of the cyclic voltammetry and was confirmed by the reduction with NaBH$_4$. The reaction should involve the elimination of I_2^- (or $I^- + I^\bullet$). A conceivable mechanism is shown in Scheme 27.

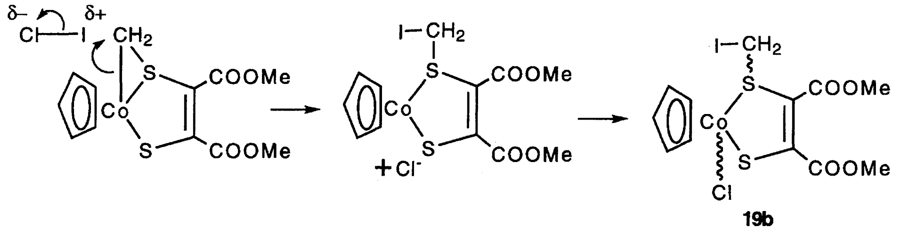
3.8. Reactions of Imido Adducts. The reactions of (*p*-tolylsulfonylimido and methylsulfonylimido)-bridged cobaltadithiolene complexes are similar to those of the bis(methoxycarbonyl)methylene-bridged cobaltadithiolene complex.

On the treatment with protic acid, the sulfonylimido-bridged complexes (**20**) undergo the Co–N bond cleavage affording **21**. A feature of ring opening product **21** is its strong acidity. Complex **21** reacts even with a very weak base such as water to eliminate proton. This results in the regeneration of sulfonylimido-bridged complexes. A more strong base, pyridine, causes of course the same reaction. Complex **21** is not stable enough in an acidic solution. It eliminates gradually the sulfonylimido moiety to give the free cobaltadithiolene complex (Eq. 25).[85]

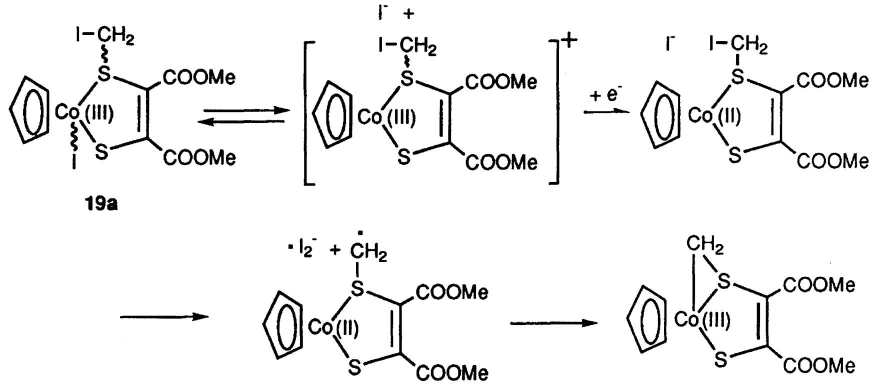


(25)

In the reaction with phosphorus compounds, the sulfonyl-

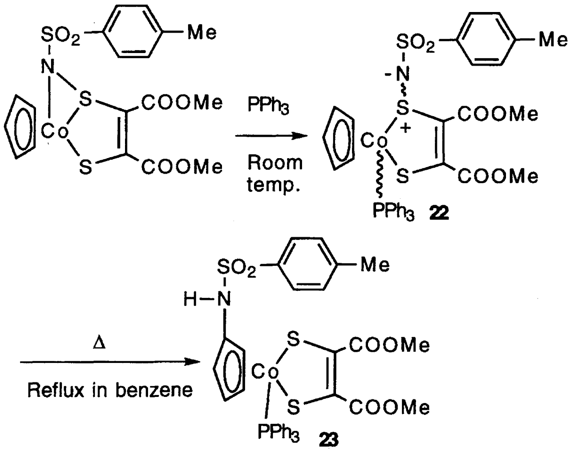


Scheme 26.



Scheme 27.

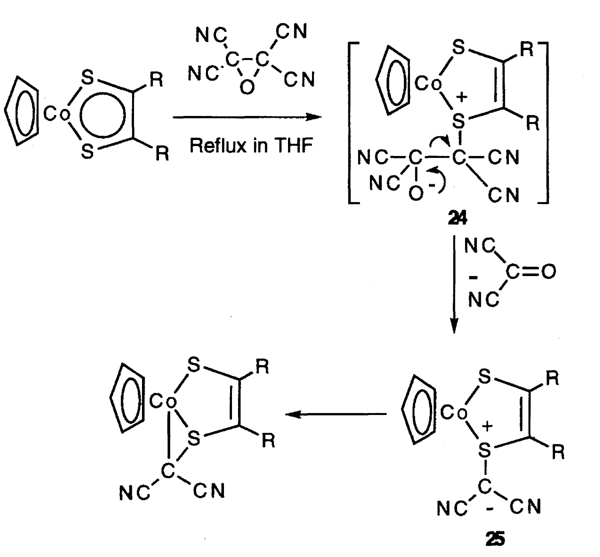
imido-bridged complex shows an interesting reaction which is not observed for the alkylidene-bridged complexes. The coordination of phosphine at room temperature causes the Co–C bond cleavage to give an ylide. The ylides from the sulfonylimido-bridged complexes are more reactive than the ylides from the methylene-bridged complexes. If one heats the ylide at 80 °C in benzene, the migration of sulfonylimido group from S to cyclopentadienyl ring occurs to give [(*p*-tolylsulfonylimino)cyclopentadienyl](triphenylphosphine)(1,2-ethylenedithiolato)cobalt(III). Two different mechanisms are conceivable. One mechanism involves the intermediary formation of nitrene species and the other involves the intramolecular migration of the sulfonylimido group (Eq. 26).[85] We can not yet decide the mechanism.



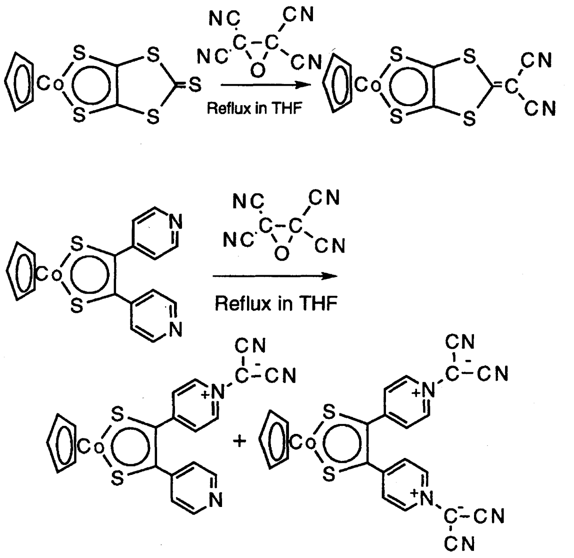
(26)

3.9. Reaction with Tetracyanoethylene Oxide (TCNEO). Tetracyanoethylene oxide (TCNEO) reacts with the cobaltadithiolene complexes to give the dicyanomethylene-bridged complexes. The structures of dicyanomethylene-bridged complexes are similar to those of the alkylidene-bridged complexes derived from the reactions of diazo compounds. However, the mechanism for the reaction of diazo compounds is different from that of TCNEO. The reaction of TCNEO would be initiated by the nucleophilic attack of the lone pair electrons at the sulfur atom to the positively charged carbon of TCNEO. Through the intermediacy of **24** and an ylide **25**, the dicyanomethylene-bridged complexes would be formed (Scheme 28).[92]

In the reaction with cobaltadithiolene complex having 4-pyridyl group, TCNEO reacts preferentially at the nitrogen atom and *N*-dicyanomethylene compounds are formed. In the reaction of a cobaltadithiolene having dmit (1,3-dithiole-2-thione-4,5-dithiolato) ligand with TCNEO, the C=S group reacts selectively (Scheme 29).[93]



Scheme 28.



Scheme 29.

3.10. Reactions with Nitrene and Germylene.

The reactions of aryl azides with cobaltadithiolene are different from those of sulfonyl azides. Aryl azides do not react with cobaltadithiolene complexes at room temperature. The reaction occurs at the temperature where they give nitrene species. In this case, the imido-bridging reaction does not occur but the replacement of one or two S atom(s) by arylimido-group (nitrene species) occurs. In addition the replacement of S–C(CN)=C(CN) group by the aryl nitrene (in a biradical form) to give (η^5-cyclopentadienyl)(2-imido-κN-arene-1-thiolato-κS)cobalt(III) (Chart 10). The mechanism shown in Scheme 30 is proposed.[94]

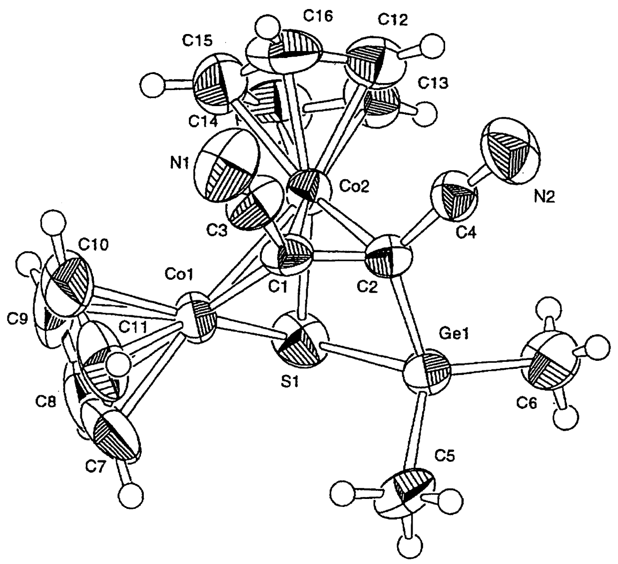
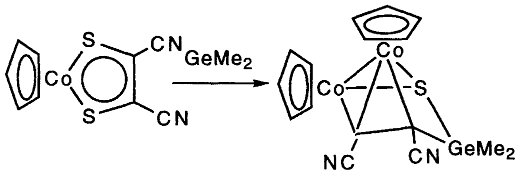


Fig. 7. X-Ray structures of a product formed in the reaction of a cobaltadithiolene with germylene.

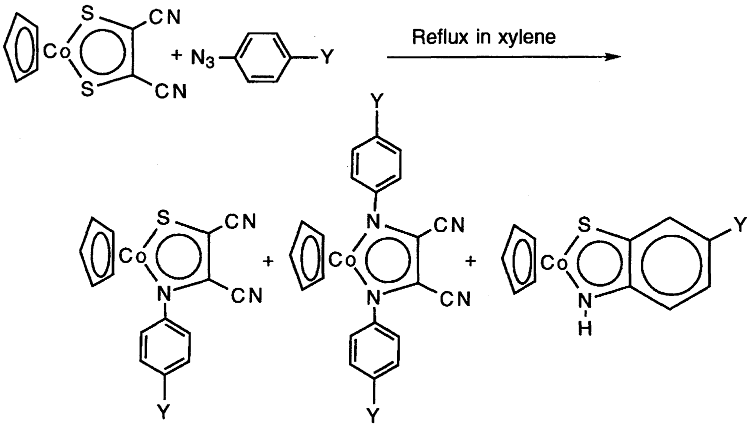
Germylene generated from the thermolysis of 1,4,5,6-tetraphenyl-2,3-benzo-7,7-dimethyl-7-germanorborna-2,3-diene reacts with the cobaltadithiolenes to give binuclear cobalt complexes containing a bridging dimethylgermylene moiety (Fig. 7). In this reaction, two molecules of the cobaltadithiolene and one germylene molecule should participate in the reaction (Eq. 27).[95] The mechanism has not been elucidated.



(27)

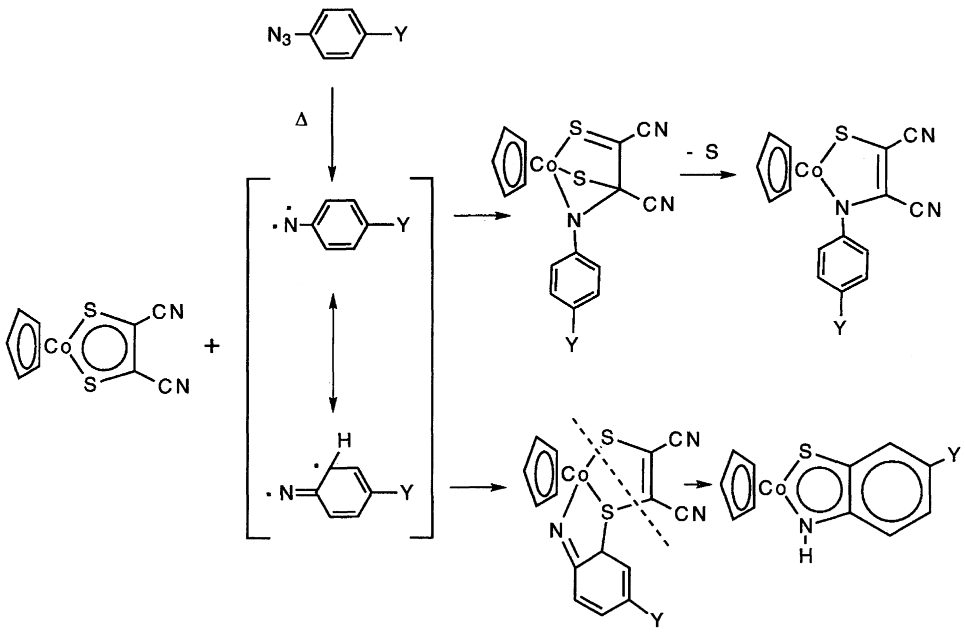
3.11. Adduct Formation and Dissociation in $[\mathrm{M}(\mathrm{S_2C_2XY})_2]$-Type Metalladithiolenes.

The $[\mathrm{M}(\mathrm{S_2C_2XY})_2]$-type metalladithiolene complexes (M = Ni, Pd, and Pt) undergo another type of addition-elimination reaction. As early as 1965, Schrauzer and his co-workers reported the formation of a 1 : 1 adduct and a dihydro-1,4-dithiine derivative in the reaction between $[\mathrm{M}(\mathrm{S_2C_2XY})_2]$-type metalladithiolene and norbornadiene.[96—98] We found that $[\mathrm{M}(\mathrm{S_2C_2XY})_2]$-type metalladithiolenes react with quadricy-



Y = H	12%	6%	3%
Y = Me	17%	3%	4%
Y = NO_2	2%	1%	0%

Chart 10.



Scheme 30.

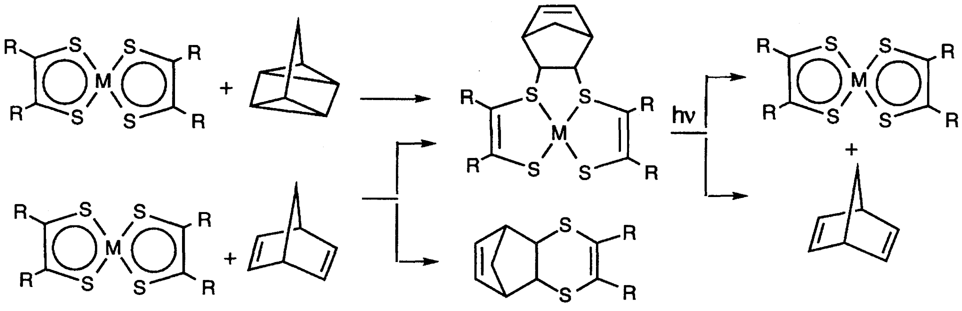
clane (Q) much more rapidly (10^3—10^4 times faster) and selectively to give the same 1 : 1 adducts. In the reaction with quadricyclane, no dihydro-1,4-dithiine derivative is formed. The order of the reactivity is Pd complex > Ni complex > Pt complex. The relation between the reactivity and reduction half-wave potential reveals that the more electro-positive complexes react with Q faster. The photochemical dissociation proceeds effectively. In contrast to a large effect of metal and substituents in the formation of the adducts, there is only a small dependence of the quantum yield of photodissociation on the metal and substituents (Scheme 31).[99)]

Schrauzer et al. also reported the formation of *S*,*S*′-dibenzyl derivatives[100)] of [$M(S_2C_2XY)_2$]-type metalladithiolene complexes (M = Ni, Pd, and Pt) and they described also the photodissociation of the *S*,*S*′-dibenzyl derivatives and the formation of benzyl radical.[97)] However, the details of this photoreaction have not been studied.

We found that the photolysis of the *S*,*S*′-dialkyl derivatives produces metal-complex-radicals having unusually long lifetimes in a benzene solution at room temperature.[101—103)] The irradiation of *S*,*S*′-dibenzyl derivatives of the [$M(S_2C_2XY)_2$]-type metalladithiolenes (M = Ni, Pd, Pt) causes the homolysis of C–S bond to give a benzyl radical and a metalladithiolene radical having a long lifetime of ca. 10 min. The half-lives of the metal-complex-radicals are 1500, 5000, and 1200 s for Ni, Pd, and Pt complexes, respectively. A time-resolved ESR study identified benzyl radical and a metal complex radical and concludes that these radicals originate from an excited triplet state of the *S*,*S*′-dibenzyl derivative.

The unique change of the ligand character from a dithiolato type to a dithiolato–dithiolene resonance type is suggested as a possible source for stabilities of the intermediate radicals. The spin densities estimated from the anisotropic part of the *g* factor Δg_u are 0.19, 0.06, and 0.23 for Ni, Pd, and Pt complex radicals, respectively. The remaining 77—94% of the unpaired electrons in the metal-complex-radicals are considered to be delocalized over the ligand.

The metalladithiolene radical eliminates the other alkyl radical in the dark to give finally [$M(S_2C_2XY)_2$]. We can follow the thermal dissociation process of the metal complex radicals by the simultaneous measurement of ESR and UV-visible spectra using a rapid scan UV-visible spectrometer. A typical example of *S*,*S*′-dibenzyl derivative of [$Ni\{S_2C_2(p\text{-}Cl\text{-}C_6H_4)_2\}_2$] is shown in Fig. 8.[104)] The first order plot of the disappearance of the metal-complex-radi-



Scheme 31.

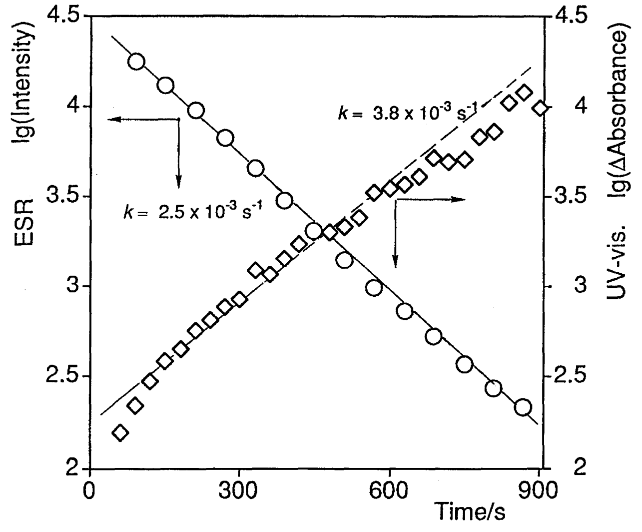


Fig. 8. Correlation between the decay of ESR of the metal-complex-radical from *S*,*S*′-dibenzyl derivative of $[Ni\{S_2C_2(p\text{-}Cl\text{-}C_6H_4)_2\}_2]$ and the rise of absorption of the free nickeladithiolene First order plots of ESR intensity ($k = 2.5\times10^{-3}$ s^{-1}) of the metal-complex-radical and of the increase of absorbance ($k = 3.8\times10^{-3}$ s^{-1}) due to the formation of free nickeladithiolene complex.

cal (measured by ESR) agrees well with that of the appearance of the free nickeladithiolene (measured by UV-visible spectroscopy). The reaction path of the photodissociation is shown in Scheme 32.

4. Catalysis Due to Coexistence of Aromaticity and Unsaturation

The coexistence of aromaticity and unsaturation results in the easy addition and easy elimination in the metalladithiolene rings. Namely, the bonds formed between an atom in the metalladithiolene ring and an atom of the added group may be neither too strong nor too weak. This characteristic may give rise to the catalytic activities.

We found that the cobaltadithiolene complexes catalyze the isomerization of quadricyclane to norbornadiene.[105] As mentioned earlier, cobaltadithiolene complexes form adducts with quadricyclane. Accompanying the adduct formation, the isomerization of quadricyclane to norbornadiene occurs. In some cases, the ratios of quadricyclane to form the adduct to the isomerized norbornadiene reach to several thousands.

The catalytic activities of the cobaltadithiolene complexes are dependent on the half-wave potentials for reduction of the complexes (namely on the positive charge on the metal atom) as shown in Fig. 9. A titanium dithiolene complex **27** with a half-wave potential of −1.13 V does not catalyze the isomerization of Q to NBD. The titanium dithiolene complex does not form an adduct with quadricyclane. These facts indicate that the partial bond formation between Co of

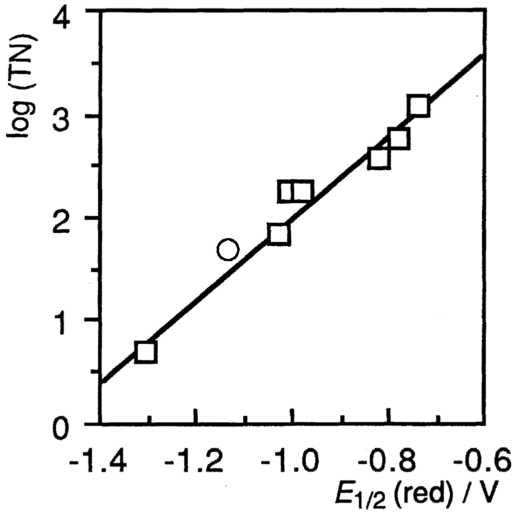
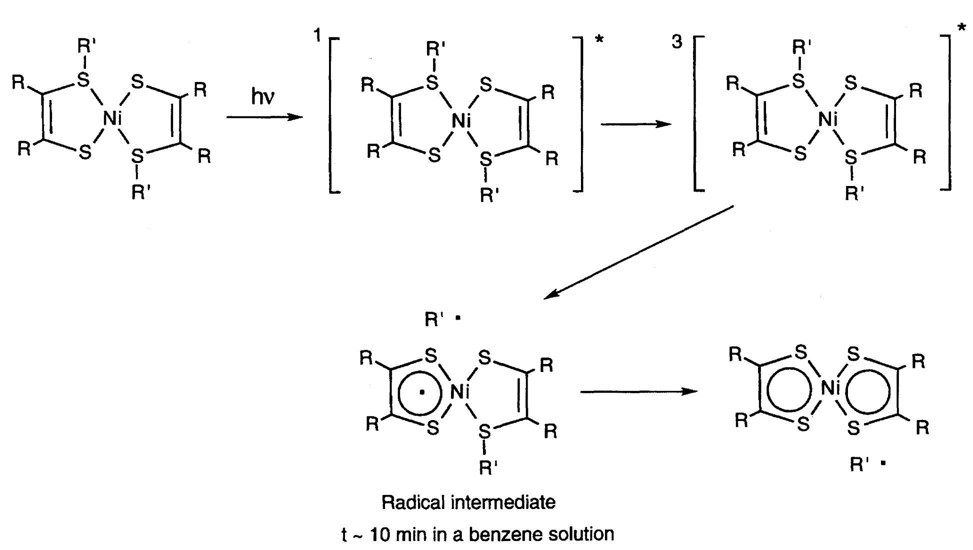
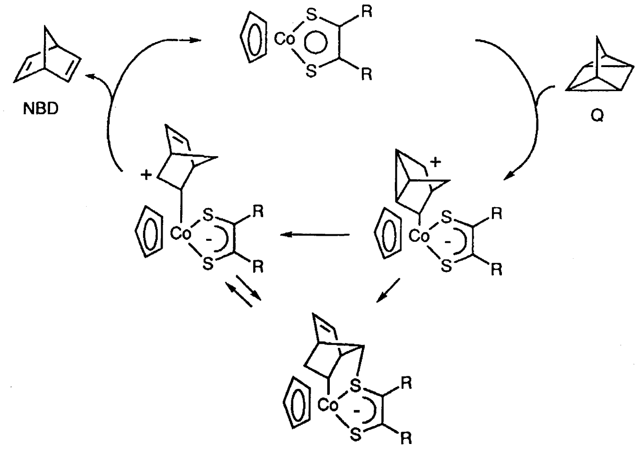


Fig. 9. Correlation between catalytic activity (for isomerization of Q to NBD) and $E^{r}_{1/2}$ of metalladithiolene complexes. □: for cobaltadithiolene, ○: for cobaltadithiazole. Catalytic activity is expressed in turnover number (TN) for the isomerization on the basis of the amount of metal complex in 2 h of reaction. For the measurement of $E^{r}_{1/2}$, Ag/0.1 mol dm^{-3} $AgClO_4$ is used as a reference electrode.



Scheme 32.



Scheme 33.

the dithiolene complex and carbon atom of quadricyclane is essential for the catalytic reaction. Thus, a mechanism (Scheme 33) can be postulated.

The catalyses of metalladithiolenes in other reactions also have been reported. Recently, homolytic activation of H_2 at transition metal sulfur sites in coordinatively unsaturated $\{Rh(L)(``S4")\}[BF_4]$ ("S4" = 1,2-bis[2-mercapto-3,5-di-*t*-butylphenylthio]ethane) has been reported.[106)]

Using molybdadithiolene as a model compound, extensive studies on Moco (molybdenum-containing cofactor) have been developed. Here we cite recent papers.[107—111)]

Catalysis of the metalladithiolene complexes in photoreactions is an interesting theme. Several reports have appeared on the quenching by metalladithiolenes.[112—114)]

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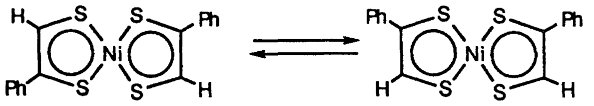

Chart 11.

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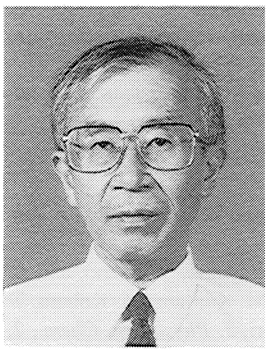
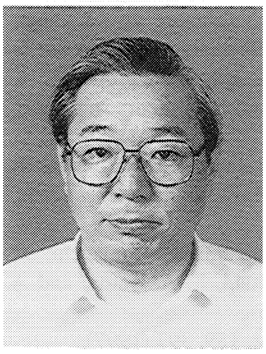
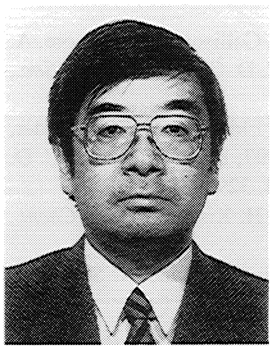


Dr. Akira Sugimori was born in 1933 in Tokyo. He was graduated from the University of Tokyo in 1956 and finished master course there in 1958. After 5 years work in Japan Atomic Energy Research Institute as a researcher (radiation chemistry), he joined Department of Chemistry at Sophia University in 1963 as associate professor. He obtained Ph. D. degree from the University of Tokyo in 1963. He was promoted to full professor in 1972. His research interests include thermal, electrochemical, and radiation-induced reactions of metal complexes and heteroatom compounds. He aims at the development of metal complex chemistry through organic methodology.



Takeo Akiyama, born in 1939 in Tokyo, received Ph. D. degree from Tokyo Metropolitan University in 1975. He joined the Department of Chemistry, Faculty of Science & Technology, Sophia University from 1967 to 1996. He was a professor of organic chemistry in Sophia University from 1989 to 1996, and is now a director of Nishiki Shokai Co., since April 1996. He was a visiting researcher at Max-Planck Institut Muelheim in 1979—1980. His research interests include the photochemical behavior of organometallic compounds and the syntheses and the reactions of catalytically active transition-metal organometallic compounds.

Masatsugu Kajitani, Dr. of Science, Associate Professor of Department of Chemistry, Faculty of Science and Technology, Sophia University: Born in 1944 in Tokyo, Japan, studied chemistry at Sophia University under the late Prof. Y. Urushibara and Prof. A. Sugimori. After he graduated from the doctor's course, he has been worked in the Prof. Sugimori's laboratory at Sophia University. He was promoted to a associate professor in 1998. He was a visiting researcher under Prof. Boennemann at Max-Planck-Institute füer Kohlenforschung (1978—1980). His current research interests include chemistry of metalladichalcogenolene complexes: syntheses, structures, reactivities, electrochemical and photochemical natures, and application as functional materials.



Toru Sugiyama, Research associate of Department of Chemistry, Faculty of Science and Technology, Sophia University: Born in 1948 in Nagasaki, Japan, studied chemistry at Sophia University under the late Y. Urushibara and Prof. A. Sugimori. He has been worked in the Prof. A. Sugimori's laboratory at Sophia University. His research interests include the photochemical behavior of organometallic compounds and the synthesis, structures, and reactivities of metalladichalcogenolene complexes.