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Photochemical reactions of several adducts of metalladithiolenes and metalladithiazoles---Dissociation and rearrangement--

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ABSTRACT

The addition products of metalladithiolene and metalladithiazole complexes undergo interesting photochemical dissociation reactions accompanied by rearrangement. Three examples are discussed. Upon irradiation with a medium pressure mercury lamp, the quadicyclane adducts of cobaltadithiolene and rhodiadithiolene dissociate to the free metalladithiolenes and norbornadiene accompanied by the skeletal rearrangement in the hydrocarbon moieties. The tributylphosphine adduct of a cobaltadithiolene eliminates photochemically the coodinated phosphine via the attack of singlet oxygen. In the photoreaction with 254 nm light, the phosphine adduct itself acts as a triplet sensitizer to produce singlet oxygen. The DMAD adducts of 1,2,5-cobaltadithiolene and 1,2,5,3-cobaltadithiazole behave differently upon irradiation: DMAD adduct of the cobaltadithiolene eliminates selectively the alkyne moiety which bridges between Co and S, while DMAD adduct of the cobaltadithiazole eliminates carbonitrile to give the cobaltadithiolenes.

INTRODUCTION

A metalladithiolene ring consisting of one metal atom, two coordinated sulfur atoms, and two unsaturated carbon atoms is a very interesting ring system. It is not a simple inorganic coodination compound but a cojugated metallacycle with 6 π electrons [1].

Metalladithiolene rings undergo both substitution reactions due to their aromaticity and addition reactions due to their unsaturation.

Recently we found that typical electrophilic substitution reactions such as Friedel-Crafts acylation and nitration occur in the rings [2].

On one side, metalladithiolene rings undergo addition reactions due to their unsaturation. A variety of organic species add to the ring, especially between metal and sulfur. Phospines and phosphites are coordinated to the metal [3]. Diazo compounds react with cobaltadithiolenes with the elimination of N_2 to form alkylidene-bridged compounds [4]. Azides undergo similar reactions [5].

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Alkyne inserts between metal and S [6]. Quadicyclane adds to the cobaltadithiolene to give norbornene-5,7-diyl adduct [7].

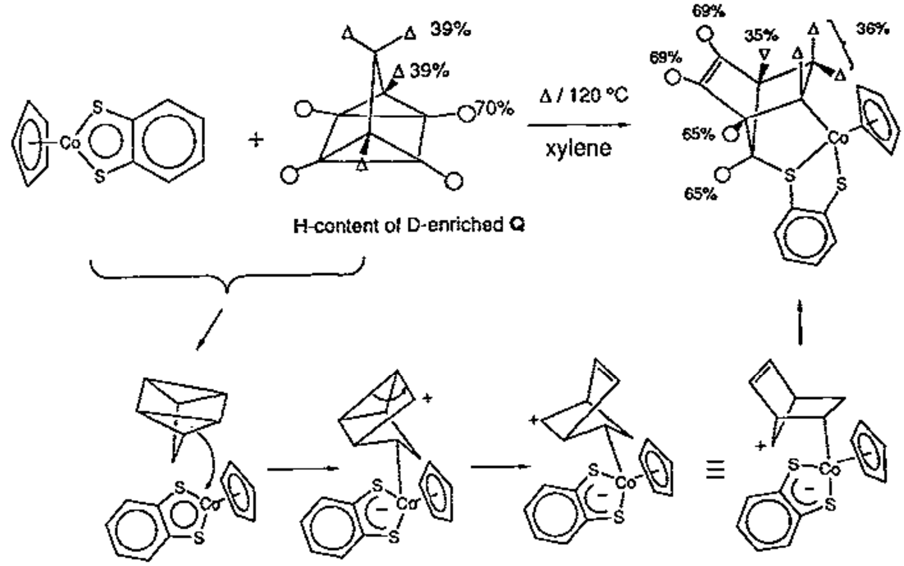
A common reaction of these addition products is the photochemical elimination to regenerate the free metalladithiolenes. In addition, several other types of photoreaction have been observed.

Here we discuss three examples of the photoreactions of the adducts of the metalladithiolenes and their analog, metalladithiazole, which contains one nitrogen atom instead of a carbon atom [8].

RESULTS AND DISCUSSION

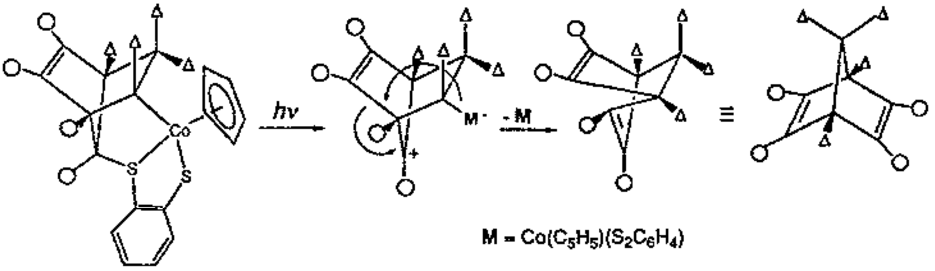
1) Photochemical dissociation of quadricyclane adducts accompanying rearrangement in the hydrocarbon moiety [7,9]

Cobaltadithiolenes and rhodiadithiolenes react with quadricyclane to give adducts in which norbornene-5,7-diyl group bridges between the metal atom and one of the sulfur atoms. A remarkable observation is that quadricyclane insert between the metal-S bond accompanyinig skeletal rearrangements. Furthermore, the skeletal rearrangement in the cobalt complex is different from that in the rhodium complex. A mechanistic study using D-labeled quadricyclane (Q-D) revealed that the metal atom of the metalladithiolene attacks electrophilically to quadricyclane to give a carbenium ion intermediate, which combines with a sulfur atom after skeletal rearrangement. The mechanism for the reaction of cobaltadithiolene is shown below. The quadricyclane adduct of the rhodiadithiolene forms in a similar mechanism.

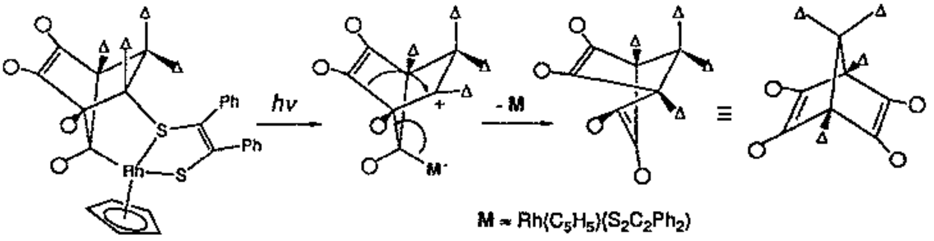


The adducts between metalladithiolene and quadricyclane dissociate upon UV-irradiation. The irradiation of an acetonitrile solution of the adduct of the cobaltadithiolene or a dichloromethane solution of the adduct of the rhodiadithiolene with a medium pressure mercury lamp gives rise to the formation of the free metaladitiolene and norborndiene. The reaction proceeds quantitatively.

A study using D-labeled adduct revealed that the norbornadiene is formed in a mechanism involving reverse skeletal rearrangement.



M = Co(C_5H_5)($S_2C_6H_4$)



M = Rh(C_5H_5)($S_2C_2Ph_2$)

The photodissociation of the quadricyclane adducts is wavelength dependent. The quantum yields of the photoreactions are listed in Table 1.

Table 1. Quantum yields of photoreactions of quadricyclane adducts of cobalta- and rhodiadithiolene

Wavelength / nm	254nm	313 nm	365 nm
Adduct of cobalt complex	0.017	0.018	0.007
Adduct of rhodium complex	(0.41)[a]	(0.01)[a]	0.005

a) Quantum yield of decomposition

The photodissociation of the cobalt complex at 254 and 313 nm is twice more efficient than that at 365 nm. The types of photoreaction of the rhodium complex change depending on the wavelengths of the irradiating light. The irradiation with longer wavelength light brings about the dissociation, whereas the irradiation with shorter wavelength light causes the decomposition of the complex.

2) Photochemical reactions of tributylphosphine adduct of cobaltadithiolene [3]

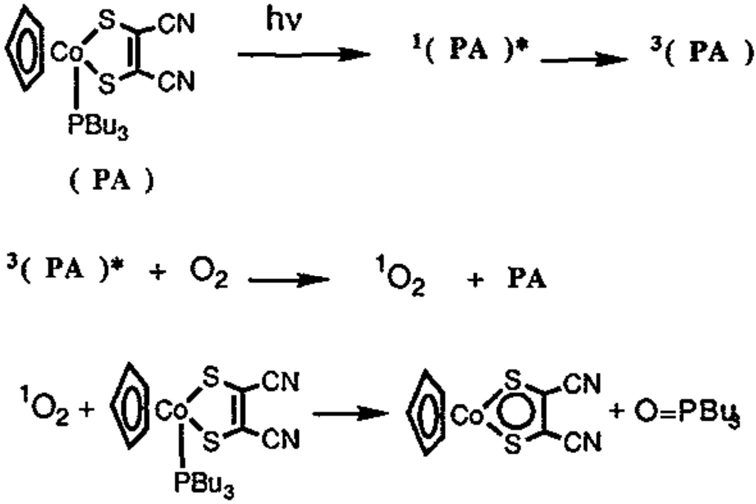
The tributylphosphine adduct of (η^5-cyclopentadienyl)(1,2-dicyano-1,2-ethenedithiolato)cobalt exhibits a unique photoelimination of the phosphine ligand: singlet oxygen abstracts the phosphine ligand and in the irradiation with the shorter wavelength region the adduct acts as a triplet sensitizer to produce $^1O_2$.

The irradiation of the phosphine adduct with a medium pressure mercury lamp in an acetonitrile solution in the presence of methylene blue under air causes the formation of the free cobaltadithiolene complex and tributylphosphine oxide.

The irradiation with 254 nm light under air brings about the formation of the free cobaltadithiolene, whereas that under Ar causes no formation of the free cobaltadithiolene but the decomposition of the complex.

The participation of singlet oxygen was proved by the quenching of the photoelimination by a specific quencher of singlet oxygen, DABCO (1,4-diazobicyclo[2.2.2]octane). The photoreaction of the adduct in the absence of oxygen was completely inhibited by a triplet quencher, 1,3-cyclohexadiene.

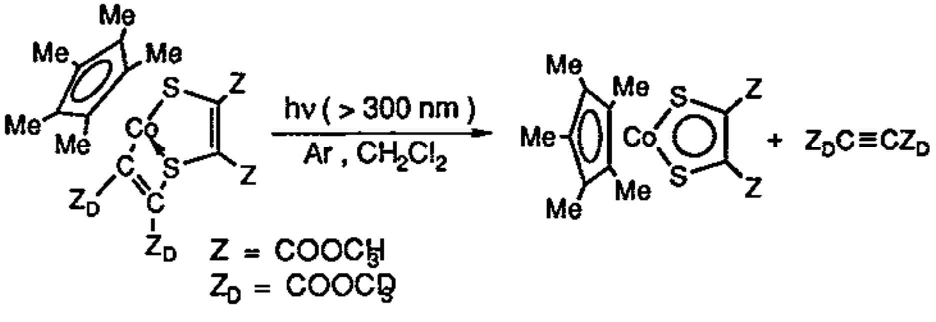
The above facts indicate the following reaction mechanism.



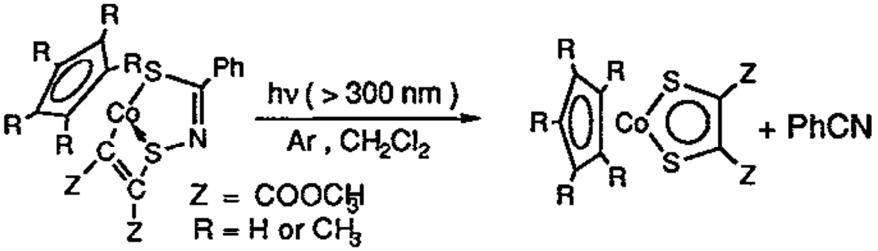
3) Dissociation and replacement in the dithiolene ligand in the alkyne adducts [6, 10, 11]

The akyne adducts of cobaltadithiolenes and cobaltadithiazoles show an interesting difference in the photoreaction. In the reaction with dimethyl acetylenedicarboxylate (DMAD), both cobaltaditiolenes and cobaltadithiazole form adducts in which Co and S are bridged by alkene-1,2-diyl group.

The DMAD adduct of the cobaltadithiolene with two methoxycarbonyl groups as the substituents eliminates selectively the DMAD moiety bridging between Co and S. This can be confirmed by the use of D-labeled DMAD.



On the other hand, the UV-irradiation of a benzene solution of the adduct between cobaltadithiazole and dimethyl acetylenedicarboxylate (DMAD) with a medium pressure mercury lamp causes the elimination of benzonitrile to give the cobaltadithiolene with DMAD moiety in the ligand.



The photoreactions are almost quantitative (yield of dithiolene, 70% and recovery of adduct, 30% for the complex with cp ; yield of dithiolene, 60% and recovery of the adduct , 40% for the complex with cp* for 3 h irradiation) .

As is discussed above, the adducts of the metalladithiolenes exhibit the common photochemical behavior of dissociation to regenerate the free metalladithiolenes. However, the mechanisms for the dissociation are manifold depending on the structure of theadducts. The elimination should be due to the potential tendency of the metalladithiolenes to recover the stable conjugated electronic system with 6 π electrons.

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