Formation of Cobaltadithiolene in a One-Pot Reaction among $[Co(Cp)(CO)_2]$, α,β-Unsaturated Carbonyls, and Elemental Sulfur

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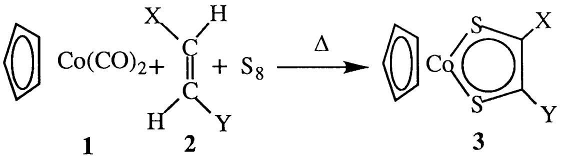
A one-pot reaction among $[(Cp)Co(CO)_2]$, some α,β-unsaturated carbonyls, and elemental sulfur gives cobaltadithiolene complexes, $[(Cp)Co(S_2C_2XY)]$. The reaction affords a convenient synthesis of the cobaltadithiolene rings having aldehyde and ketone groups. The reaction involves the formal dehydrogenation of alkene presumably *via* cooperative interactions with sulfur and [(Cp)Co] species.

A class of metalladithiolene complexes, $[(Cp)M(S_2C_2XY)]$, was first prepared by the reaction of [(Cp)MLn] with 1,2-dithiete[1] or 1,2-ethenedithiolate.[2] Another method is the incorporation of a part of sulfur-containing heterocyclic compounds in the reaction with [(Cp)MLn].[3,4] One-pot reaction among [(Cp)MLn], alkyne, and elemental sulfur has been developed as a convenient preparative method of (η^5-cyclopentadienyl)(1,2-ethenedithiolato)metal(III) complexes (metal = Co and Rh).[5-7]

We found the formation of cobaltadithiolene complexes using alkenes as starting material in place of alkyne *via* formal dehydrogenation of alkene to alkyne. The reaction is characterized by the simultaneous occurrence of chelate ring formation and dehydrogenation of alkene to alkyne.

There have appeared several reports on the formation of dithiolatometal complexes in similar reaction conditions. The formation of dinuclear dithiolatoiron complexes has been reported in the reaction among iron carbonyl, several alkenes, and elemental sulfur.[8] The reaction of μ-*S* molybdenum complex with alkene affords binuclear dithiolatomolybdenum complexes.[9] But in these reactions dehydrogenation does not take place.

Benzene solutions of $[(Cp)Co(CO)_2]$ (**1**), α,β-unsaturated carbonyl (**2**), and elemental sulfur (normally in the ratio of 1 : 10 : 4 (as S)) were heated under stirring under Ar for several hours. In some cases, the reaction yielded (η^5-cyclopentadienyl)(carbonyl substituted 1,2-ethenedithiolato)cobalt(III) complexes (**3**).[10] Results are summarized in Table 1.



1 **2** **3**

a: X=CHO, Y=H; **b**: X=CHO, Y=Me; **c**: X=COMe, Y=H;
d: X=COMe, Y=Me; **e**: X=COOMe, Y=H; **f**: X=CN, Y=H

When we use propenal (**2a**) or butenone(**2c**) as an alkene, we obtain cobaltadithiolene complexes in moderate yields. The alkyl group attached to alkene lowers the formation of **3**. Ethyl acrylate and acrylonitrile afford **3** but in very low yields. Neither acrylamide nor cinnamaldehyde gives cobaltadithiolene complex.

Table 1. Formation of cobaltadithiolene complexes (**3**) in one-pot reaction among $[(Cp)Co(CO)_2]$ (**1**), α,β-unsaturated carbonyl (**2**), and elemental sulfur[a]

Alkene	Additive	Reaction conditions			Yield of 3[b]
		Solvent	Temp °C	Time h	%
2a		benzene	50	4	46
2b		benzene	80	4	7
2c		benzene	80	24	30
2c	AIBN[c]	benzene	80	24	11
2c	cyclohexene[d]	benzene	80	24	30
2c		benzene	40	24	13
2c		chloroform	61	24	14
2c		acetonitrile	82	24	28
2d		benzene	80	4	2
2e		benzene	80	4	2
2f		benzene	80	4	1

[a] Ratio of amounts, **1** : **2** : elemental sulfur (as S) = 1 : 10 : 4; [b] Yields are based on the amount of **1**; [c] Ratio of amounts, **1** : AIBN = 1: 10; [d] Ratio of amounts, **1** : cyclohexene = 1: 10.

Although the applicability of this reaction is limited, the reaction is useful for the preparation of formyl and acetyl cobaltadithiolenes,[11] because the starting enal and enone are more easily available than the corresponding ynal and ynone.

The reaction is characterized by that the dehydogenation in the alkene moiety occurs but no redox reaction occurs in carbonyl moiety. How and at what stage dehydrogenation occurs? We examined the feature of the reaction using **2c** as a substrate.

An important observation is that hydrogen sulfide was detected in the evolved gas during the reaction, although its amount was 20% to the amount of the cobaltadithiolene complex **3c** formed. If we take it into consideration that H_2S adds easily to α,β-unsaturated carbonyls, we can suggest that sulfur acts as dehydrogenation reagent as well as the source of the component of the dithiolene ring.

In order to obtain further information, we tried a stepwise reaction: At first alkene and S_8 were reacted for 24 h under reflux in benzene and then the resulting reaction mixture was reacted with $[(Cp)Co(CO)_2]$ at 80 °C. In the first process, we observed the formation of H_2S and detected. However, the yield of the cobaltadithiolene complex by this sequential reactions was only 0.3%.

In the one-pot reaction among **1**, **2**, and S_8, cubane-like cluster complexes, $[\{(Cp)Co)\}_mS_n]$ (m = 4, n = 4; m = 4; n = 5 *etc.*) may play important role, because they are easily formed in the reaction between $[(Cp)Co(CO)_2]$ and S_8 and have been proven to give the cobaltadithiolene complexes in the reaction with alkyne.[7]

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The reaction of a mixture of cluster complexes, $[\{(Cp)Co)\}_mS_n]$ with **2c** at 80 °C afforded the cobaltadithiolene **3c** but only in a low yield (0.5%). The raise of temperature to 140 °C (in the reaction in xylene) causes only a small increase in the yield of **3c** to 0.8%. However, the addition of elemental sulfur improves the yield to 4% at 80 °C and 19% at 140 °C.

The two step reaction performed by adding S_8 to the reaction mixture from **1** and **2c** gave no cobaltadithiolene.

The participation of free radical species was examined by the effects of radical scavenger and radical initiator in the reaction. The presence of a radical scavenger, cyclohexene, does not inhibit the formation of a cobaltadithiolene complex. The addition of 2,2'-azobis(isobutyronitrile) rather lowered the yield of the cobaltadithiolene complex. These facts suggest that the radical intermediates play no important role for the reaction.

These facts suggest that some cooperative interactions among three components are important for the formation of the cobaltadithiolene complexes. However, the mechanism for the formation of the cobaltadithiolene complexes is not yet clear.

A similar dehydrogenation has been found in a one-pot reaction among $[(Cp)Co(CO)_2]$, 2-propynol, and elemental sulfur. In this case, the oxidation of primary alcohol to CHO takes place.

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10 **3a**: Mp, 162 °C; UV (CH_2Cl_2) 294 (ε, 26400), 364 (6800), and 561 nm (7300); IR (KBr disk) 1670 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) $\delta = 5.50$ (5H, s, Cp), 9.34 (1H, s, H in the cobaltadithiolene ring), 9.99 (1H, s, CHO); MS (70 eV) *m/z* (rel intensity) 242 (M^+, 100), 188 (16), 124 (24), 59 (7). Found: C, 39.56; H, 2.93%. Calcd for $C_8H_7CoOS_2$: C, 39.67; H, 2.91%.

3c: Black crystals; mp 131-133 °C; UV (CH_2Cl_2) 292 nm (ε, 25370), 365 nm (3878), 558 nm (6787), and 725 nm (501) ; IR (KBr disk) 1653 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) $\delta = 2.26$ (3H, s, $COCH_3$), 5.45 (5H, s, Cp), and 9.43 (1H, s, H in the cobaltadithiolene ring); MS (70eV) *m/z* (rel intensity) 256 (M^+, 100), 213 (34), 188 (65), 124 (27), and 59 (17). Found: C, 42.21; H, 3.45%. Calcd for $C_9H_9CoOS_2$: C, 42.19; H, 3.54%. Other complexes were identified by comparing their spectral data with those of **3a** and **3c**.

11 The character of the carbonyl groups attached to the cobaltadithiolene ring is somewhat different from that of normal aliphatic or aromatic carbonyls. The C=O stretching vibrations of cobaltadithiolenes (1670 and 1653 cm^{-1} for CHO and COMe, respectively) appear lower wave number region than those in normal carbonyls. We failed the benzoin condensation for **2a**.