Ionic and Radical Substitution in Cobaltadithiolene Ring Induced by Dibenzoyl Peroxide

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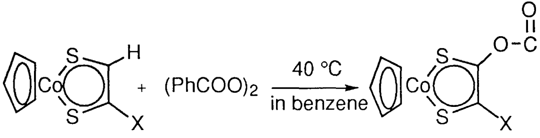
The reaction of (η^5-cyclopentadienyl)(1,2-ethenedithiolato)cobalt(III) complexes with dibenzoyl peroxide at moderate temperature (40 °C) brings about the substitution of a benzoyloxy group for a hydrogen in the cobaltadithiolene ring in an ionic mechanism. At 110 °C in a toluene solution, the substitution of a benzyl group for a hydrogen in the cobaltadithiolene ring in a radical mechanism occurs competitively with benzoyloxylation.

1,2,5-Metalladithiolene rings consist of a transition metal atom, two coordinated sulfur atoms, and two unsaturated carbon atoms is a quasiaromatic conjugated ring with 6 π electrons.[1] Recently we reported that a cobaltadithiolene ring, undergoes a typical aromatic electrophilic Friedel-Crafts acylation.[2] In addition we found a radical substitution in the cobaltadithiolene ring in the reaction with 2,2'-azobis(isobutyronitrile).[2] This is the first example of radical substitution which occurs in quasi-aromatic metal chelate rings. We reported another example of radical substitution in a nickeladithiolene ring.[3] As an extension of this study, we examined the reaction of cobaltadithiolene complexes with dibenzoyl peroxide (BPO) and found that both ionic and radical substitution reactions take place in the cobaltadithiolene ring.

In the reaction of (η^5-cyclopentadienyl)(1,2-ethenedithiolato)cobalt(III) complexes (**1**) having hydrogen in the cobaltadithiolene rings with BPO at 40 °C in benzene, the hydrogen atom in the cobaltadithiolene ring is replaced by a benzoyloxy group.[4,5] The substitution reaction occurs only in the cobaltadithiolene ring; it occurs neither in cyclopentadienyl ring nor in benzene ring (in the case of **1a**). In this reaction, benzoic acid was identified. The results under various conditions are summarized in Table 1. The yields of benzoyloxylation pro-ducts were not high but other products containing cobaltadi-thiolene ring were not identified.



1a: X = Ph
1b: X = COOMe

2a: X = Ph
2b: X = COOMe

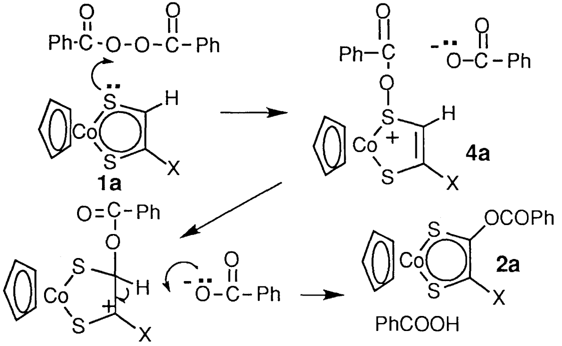
The reaction shows the following features. 1) The reaction is not an addition reaction but a substitution reaction. 2) The group introduced is not a phenyl group but a benzoyloxy group. In normal radical reactions, the benzoyloxy radical eliminates carbon dioxide quickly. If the benzoyloxylation proceeds in a radical mechanism, phenylation should be accompanied. However, this is not the case. 3) The benzoyloxylation occurs at 40 °C, at which BPO does not dissociate thermally to radicals. 4) The large excess of cyclohexene, a radical scavenger, does not inhibit the benzoyloxylation.

Table 1. Substitution in cobaltadithiolene rings by BPO[a]

Com-plex	Additive	Solvent	Temp. °C	Time h	Product yield[b] **2** /%	Product yield[b] **3**/%	Rec.[c] %
1a	----------	Benzene	40	24	19	-----	2
1a	c-C_6H_{12}[d]	Benzene	40	24	13	-----	10
1a	----------	Benzene	80[f]	24	13	-----	14
1a	----------	Hexane	40	24	22	-----	2
1b	----------	Benzene	40	24	5	-----	44
1a	----------	Toluene	40	24	11	0	3
1a	----------	Toluene	111[f]	4	5	23	32
1a	TEMPO[e]	Toluene	111[f]	4	30	0	60

[a]Molar ratio, **1**: BPO = 1 : 2; Amount of **1** = 0.1 mmol; [b]Yield was determined by colorimetry after separating with column chromatography; [c]Recovery of **1** . [d]Cyclohexene, molar ratio to **1a**, 10. [e]2,2,6,6-tetramethylpiperidine-*N*-oxyl, molar ratio to **1a**, 4. [f]To a refluxing solution of **1a**, a solution of BPO was added dropwise during 1 h.

These features of the benzoyloxylation by BPO are different from those of the radical substitution by 2,2'-azobis(isobutyronitrile)[2,3] and suggest that the benzoyloxylation does not proceed in a radical mechanism. We propose the following ionic mechanism.[6] The attack of lone pair electrons at the sulfur atom to BPO causes heterolysis of BPO to give an *S*-benzoyloxy drivative and benzoate anion. The benzoyloxy group migrates to the adjacent carbon atom and then the proton is abstracted by a benzoate anion.



This mechanism is similar to that for the benzoyloxylation of phenol proposed by Walling and Hodgdon[7] and confirmed by Denney and Denney.[8] Their mechanism involves the heterolytic cleavage of peroxide, the formation of a phenyl ester of perbenzoic acid, and the migration of benzoyloxy group to the *o*-position. The heterolytic cleavage of O-O bond in peroxide by sulfur has been reported by Horner and Jürgens.[9]

Does BPO always undergo ionic reaction with cobaltadithiolenes? We examined the reaction at elevated temperatures where BPO dissociates to free radicals. A benzene solution of BPO was added dropwise during 1 h to a refluxing benzene solution of **1a**. In this case, we obtained only **2a** as the substitution product. We changed the solvent from benzene to toluene. The reaction under similar procedure at 111 °C

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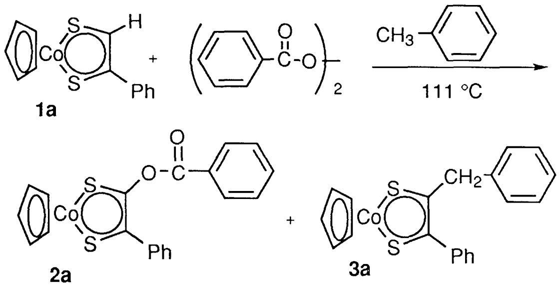
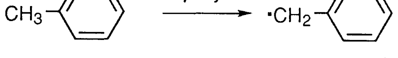
afforded two substitution products: benzoyloxy substituted product **2a** and benzyl substituted product, (η^5-cyclopentadienyl)(1-benzyl-2-phenyl-1,2-ethenedithiolato)cobalt(III) (**3a**).[10] The results are shown in Table 1.



At 40 °C in toluene, only benzoyloxylation occurs but no benzylation takes place. The presence of excess amount of a radical scavenger, 2,2,6,6-tetramethyl-piperidine-*N*-oxyl (TEMPO), completely inhibits benzylation but not benzoyloxylation.

These facts indicate that the substitution of a benzyl group is effected by benzyl radical formed in the hydrogen abstraction by benzoyloxy or phenyl radical from toluene. The substitution by benzyl radical is confirmed by radiation-induced reaction of **1a** in toluene.[11] In the radiation-induced reaction, **3a** was obtained. In this case, radiolytically produced benzyl radical causes the benzyl substitution.



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4 **2a** (η^5-Cyclopentadienyl)(1-benzoyloxy-2-phenyl-1,2-ethenedithiolato)cobalt(III): Blue crystals; Mp, 177-179 °C; UV (CH_2Cl_2): 290 (ε, 55080) and 593 nm (15310); ^{1}H NMR ($CDCl_3$) δ = 5.40 (5H, s, Cp), 7.20-7.61 (3H, m, H in Ph at the *m*- and *p*-position), and 8.04 (2H, dd J = 8.54 and 1.22 Hz, H in benzoyloxy at the *o*-position); MS (70 eV) *m*/*z* (rel intensity): 410 (M^+, 46), 124 (3, CpCo), 105 (100, PhCO). Found: C, 58.58; H, 3.85%. Calcd for $C_{20}H_{15}O_2CoS_2$: C, 58.53; H, 3.68%.
2b (η^5-Cyclopentadienyl)(1-benzoyloxy-2-methoxycarbonyl-1,2-ethenedithiolato)cobalt(III): Blue crystals; Mp, 195-196 °C; ^{1}H NMR ($CDCl_3$)δ= 3.74 (3H, s, Me), 5.44 (5H, s, Cp), 7.46-7.52 (3H, m, H in Ph at the *m*- and *p*-position), and 8.04 (2H, m, H in Ph at the *o*-position); UV (CH_2Cl_2) 235 (ε, 29500), 288 (42700), 347 (3080), and 560 nm (9040); MS (70 eV) *m*/*z* (rel intensity) 392 (M^+, 26), 188 (4,$CpCoS_2$) 124 (10, CpCo), and 105 (100, PhCO). Found: C, 48.44; H, 3.24%. Calcd for $C_{16}H_{13}O_4CoS_2$: C, 48.98; H, 3.34%.

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10 **3a** (η^5-Cyclopentadienyl)(1-benzyl-2-phenyl-1,2-ethenedithiolato)cobalt(III): Blue crystals; Mp, 167-170 °C; UV (CH_2Cl_2) 290 (ε, 31000), 419 (1700), and 581 nm (9400) ; ^{1}H NMR ($CDCl_3$) δ= 4.09 (2H, s, CH_2), 5.30 (5H, s, Cp), and 7.1-7.4 (5H, m, Ph); MS (70 eV) *m*/*z* (rel intensity) 380 (100, M^+), 188 (100, $CpCoS_2$), 124 (18, CpCo), and 91(12, $PhCH_2$). Found: C, 62.90; H, 4.78%. Calcd for $C_{18}H_{17}CoS_2$: C, 63.15; H, 4.50%.

11 The γ-irradiation facility equipped with a 193 kCi (7000 TBq) of ^{60}Co source at Japan Atomic Energy Research Institute in Takasaki was used for radiation-induced reaction. The dose rate was 2.58×10^2 C kg^{-1} h^{-1}. The solutions were irradiated for 3 h. The yield of **3a** was 6% (recovery of **1a**, 61%).