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Electrophilic and Radical Substitution of 1,2,5-Cobaltadithiolenes

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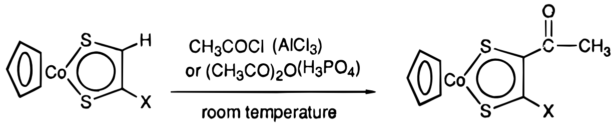
The aromaticity of chelated metal complexes with conjugated π-electronic systems is an interesting problem from the viewpoints of organic as well as inorganic chemistry. Several chelated metal complexes have been claimed to show aromatic character. 1,3-Diketonatometal rings and their nitrogen and sulfur analogs are well-studied metallacycles having aromaticity. The chemical evidence of the aromaticity of these metallacycles is the occurrence of electrophilic substitution reactions such as Friedel−Crafts alkylation and acylation, nitration, and halogenation.[1,2]

Metalladithiolene rings[3] consist of one metal atom, two coordinated sulfur atoms, and two unsaturated carbon atoms; their aromaticity has long been discussed. Schrauzer first pointed out their unusual electronic structure: the bonding is characterized by extensive ground-state delocalization.[4] ^{1}H NMR studies revealed the existence of a ring current which is ascribed to the aromaticity of the metalladithiolene ring.[5,6]

However, there has appeared only one short description which refers to a 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 aluminum chloride.[5] This is the only description which has evidenced the aromatic character of the metalladithiolene ring on the basis of chemical reactions. Since then, however, electrophilic substitutions of metalladithiolene ring have not been further investigated. Characteristic reactions of metalladithiolene rings reported to date are mostly the addition reactions which are ascribable to the unsaturation of the ring.[7]

We report here electrophilic substitution in the cobaltadithiolene rings in $[Co(Cp)(S_2C_2HX)]$-type dithiolatocobalt complexes. In addition we describe a substitution reaction in the metalladithiolene rings induced by free radical species. It constitutes a new type of reaction in organometallic chemistry, because radical substitution has scarcely been reported in conjugated metallacycles.

A typical example of the electrophilic substitution is Friedel−Crafts acetylation. The results are summarized in Table 1.



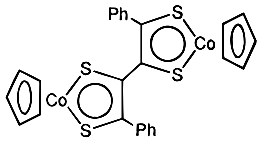
1a : X = H
1b : X = Ph

2a : X = H
2b : X = Ph

(η^5-Cyclopentadienyl)(1-phenyl-1,2-ethenedithiolato)cobalt(III) (**1b**) reacts with acetyl chloride under the catalysis of aluminum chloride or with acetic anhydride under the catalysis of phosphoric acid at room temperature in dichloromethane to give (η^5-cyclopentadienyl)(1-acetyl-2-phenyl-1,2-ethenedithiolato)cobalt(III) (**2b**). It should be noted that in this case acetylation occurs neither in the cyclopentadienyl ring nor in the benzene ring but only in the cobaltadithiolene ring. This shows the higher reactivity of the cobaltadithiolene ring in electrophilic acetylation than of cyclopentadienyl and phenyl groups.

(η^5-Cyclopentadienyl)(1,2-ethenedithiolato)cobalt(III) (**1a**) undergoes monoacetylation. No diacetylated compound was obtained. (η^5-Cyclopentadienyl)[1-(methoxycarbonyl)-1,2-ethenedithiolato]cobalt(III) (**1c**), which has an electron accepting methoxycarbonyl group in the ring, was not acetylated. This shows that acetylation proceeds in an electrophilic process.

The reaction of **1b** with acetyl chloride under the catalysis of aluminum chloride gave the acetylation product in 7% yield and a coupling product, μ-(1,4-diphenyl-1,3-butadiene-1,2,3,4-tetrathiolato)bis[(η^5-cyclopentadienyl)cobalt(III)] (**3b**) in 2% yield.[8] In this case, 69% of the substrate **1b** was recovered. The high recovery may come from the deactivation of the cobaltadithiolene ring for electrophilic reaction due to the coordination of a Lewis acid to the cobaltadithiolene ring (presumably at the sulfur atom).



3b

The cobaltadithiolene ring also undergoes radical substitution. The reflux of a benzene solution of **1b** and 2,2′-azobis(isobutyronitrile) (AIBN) resulted in the replacement of a ring hydrogen by the 1-cyano-1-methylethyl group which derives from AIBN.

The radical substitution reaction occurs not only in the cobaltadithiolene ring but also in the cyclopentadienyl ring, but that in the cobaltadithiolene ring is dominant. The reaction of 0.34 mmol of **1b** with 0.70 mmol of AIBN in a benzene solution at 80 °C for 22 h gave **4b** as the main product [0.118 mmol (34%)], which is formed by the substitution in the cobaltadithiolene ring. As a byproduct we obtained **5b** (5%), in which the cyclopentadienyl ring is substituted. The recovery of the starting material **1b** was 55%.

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[8] The coupling product is formed in the reaction of **1b** with aluminum chloride without acetyl chloride. The mechanism of the formation of the coupling product has not been elucidated.

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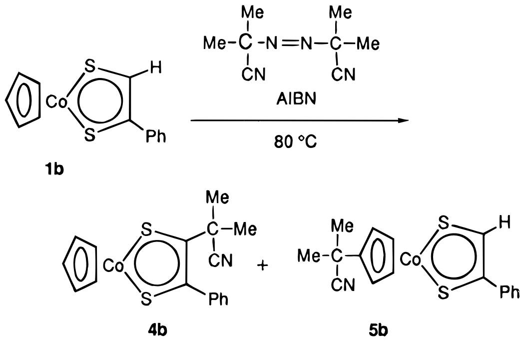
Table 1. Friedel−Crafts Acetylation of Cobaltadithiolene Ring[a]

cobaltadithiolene			acetyl compd, mmol		catalyst, mmol			
R	X	mmol					yield of **2**, %	recovery of **1**, %
H	H	0.31	CH_3COCl	1.55	$AlCl_3$	1.55	10	36
H	H	0.23	$(CH_3CO)_2O$	150	H_3PO_4	1.17	15	24
H	Ph	0.10	CH_3COCl	0.52	$AlCl_3$	0.52	7	69
H	Ph	0.19	$(CH_3CO)_2O$	140	H_3PO_4	0.95	22	40
H	$COOCH_3$	0.20	CH_3COCl	1.00	$AlCl_3$	1.00	0	not determined

[a] Reaction conditions: solvent, CH_2Cl_2 for the reaction with acetyl chloride, without other solvent for the reaction with acetic anhydride; temperature, room temperature; reaction time, 1 h.



1b **4b** **5b**

These substitution reactions are completely inhibited by a radical scavenger, TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl). This shows that the substitution reaction proceeds in a radical mechanism. Radical substitution reactions have been reported in aromatic and heteroaromatic compounds, but no report has appeared on radical substitution at the carbon atoms in metallacycles. Radical substitution in a cobaltadithiolene ring is a novel type of radical reaction in metallacycles.

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Supporting Information Available: Experimental details and spectral data (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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