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Reactions of (η^5-Cyclopentadienyl)(1,5-cyclooctadiene)cobalt(I), Diphenylacetylene, and a Mixture of S_8 and Se_8. Formation of (η^5-Cyclopentadienyl)(1,2-diphenyl-2-selenolatoethylenethiolato-S,Se)cobalt(III) Complex

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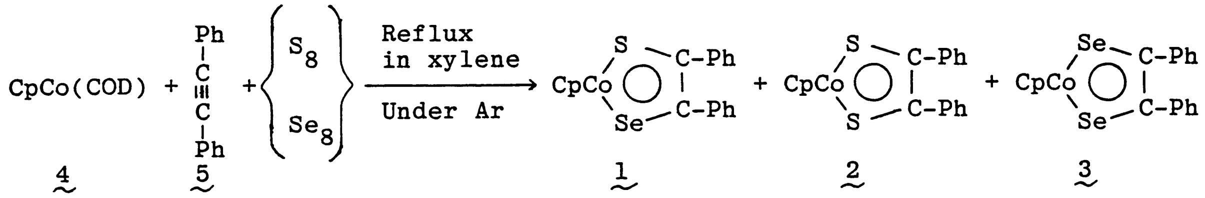
(η^5-Cyclopentadienyl)(1,2-diphenyl-2-selenolatoethylenethiolato-S,Se)cobalt(III) (1) is formed in the reaction of CpCo(1,5-cyclooctadiene) (4), Ph-C≡C-Ph (5), and a mixture of S_8 and Se_8, together with the dithiolato and diselenolato complexes. A possible mechanism for the formation of 1 is the attack of 5 to some S,Se-mixed clusters which are formed in the reaction of 4 with Se_8 and S_8.

The recent increase of interest in the physical and chemical properties of dithiolato- and diselenolato-metal complexes is notable.$^{1)}$ We have reported a convenient one-pot synthesis of (η^5-cyclopentadienyl)(substituted ethylenedithiolato or diselenolato)metal complexes.$^{2,3)}$ We report here that the one-pot reaction of (η^5-cyclopentadienyl)(1,5-cyclooctadiene)cobalt(I) (4), diphenylacetylene (5), and a mixture of elemental sulfur and selenium gives a new selenolatothiolato complex. We discuss the mechanism of the complex formation. Only three reports have appeared on the synthesis of S,Se-mixed complexes.$^{4-6)}$

A mixture of 4 (329 mg, 1.42 mmol), 5 (300 mg, 1.69 mmol), and an any molar mixture of S_8 and Se_8 was refluxed in xylene (25 cm^3) for 24 h under an atmosphere of Ar. The selenolatothiolato complex 1 was obtained as a blue mixture with the corresponding dithiolato- and diselenolato-cobalt complexes (2 and 3). By means of silica gel chromatography [column, Wako gel C-300; developing solvent, n-C_6H_{14}-CH_2Cl_2(1:1,v/v)] and preparative HPLC which employed a column of GPC (developing solvent, $CHCl_3$), the separation of the selenolatothiolato 1 from the diselenolato complex 3 was unsuccessful. The formation of the S,Se-mixed complex 1, however, was confirmed by means of MS and ^{1}H and ^{13}C NMR spectroscopy. The mass spectra of the product mixture (Fig. 1) show the parent peaks of the S,Se-mixed complex: m/z (rel intensity) 416(4.5), 415(4.2), 414(19.2), 412(10.0), 411(3.5), and 410(3.3). The peaks due to the CpCoSSe were also observed at m/z = 238, 237, 236, 234, 233, and 232. The relative intensities of the peaks ascribable to the parent cation and CpCoSSe$^+$

are consistent with the calculated ones on the basis of natural abundance of the isotopes. All the peaks due to the dithiolato (**2**) and diselenolato (**3**) complexes were also observed in the MS of the mixture.

In the ^{1}H NMR (JEOL FX-200, in $CDCl_3$) of the products, there exist three absorptions of the protons in the cyclopentadienyl rings at δ = 5.340, 5.364, and 5.379. The authentic dithiolato (**2**) and diselenolato (**3**) complexes have the absorptions at δ = 5.340 and 5.379, respectively. Thus, the absorption at δ = 5.349 can be assigned to the protons of the S,Se-mixed complex. ^{13}C NMR spectra of the cyclopentadienyl rings of **2** and **3** appear at δ = 77.962 and 79.641, respectively. An absorption at δ = 78.789 which is situated at the middle of the corresponding absorptions of **2** and **3** can safely be ascribed to the cyclopentadienyl ring of **1**.



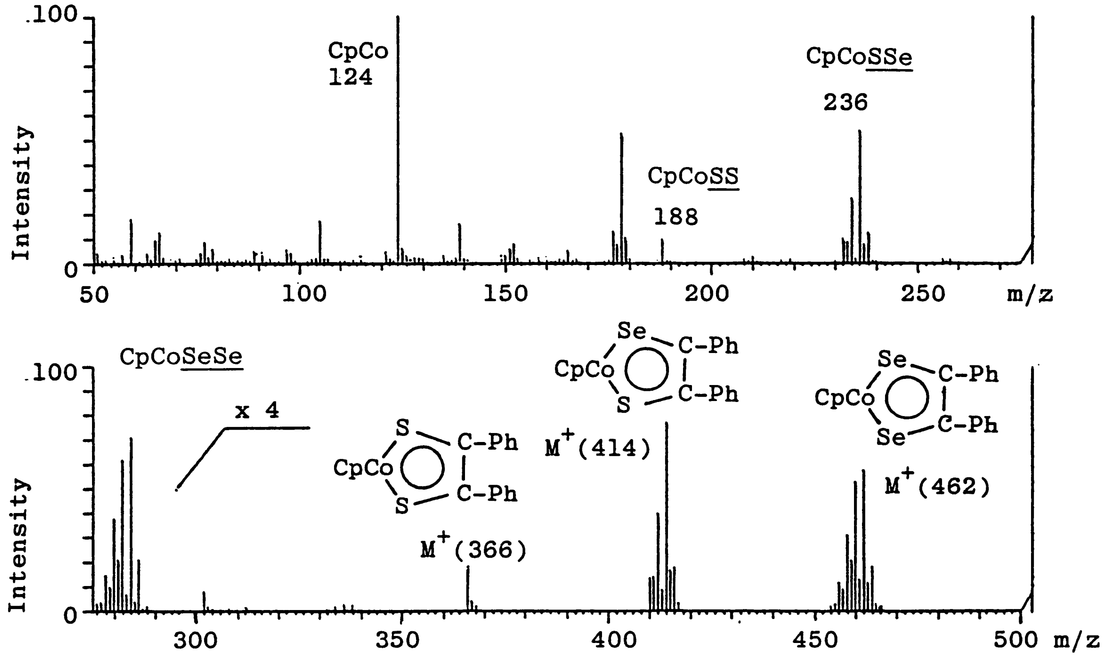


Fig. 1. Mass spectra (EI, 70 eV) of mixture of **1**, **2**, and **3**.

The yields of **1**, **2**, and **3**, which are calculated from the ^{1}H NMR, are shown in Table 1 together with the correlation with the composition of sulfur and selenium in the starting mixtures.

Table 1. Yields of **1**, **2**, and **3** in reaction of **4**, **5**, and mixture of S_8 and Se_8 in various ratios
Amount of **4**, 1.42 mmol; Amount of **5**, 1.69 mmol; Solvent, 25 cm^3 of xylene; Reaction conditions, Reflux for 24 h.

Run	Molar ratio of S_8 and Se_8 to **4**		Yield of product[a)] %		
	S_8	Se_8	**1**	**2**	**3**
1	2/8	2/8	18	45	0
2	2/8	8/8	20	30	1
3	1/8	1/8	17	16	1
4	1/8	4/8	27	23	6
5	1/20	4/20	21	9	6
6	2/8	-	-	16	-
7	-	2/8	-	-	20

a) Yield = (Amount of product/Amount of **4** used) x 100.

The formation of the dithiolato complex **2** is always dominant over that of the diselenolato complex **3**. However, the formation of the selenolatothiolato complex **1** is comparable to that of the dithiolato complex **2**. When the molar ratio of sulfur/**4** is less than 1, the formation of the S,Se- mixed complex is favored.

The exchange of S and Se in the metal complexes which occurs in the reaction of (η^5-cyclopentadienyl)[1,2-(2-pyridyl)-1,2-ethylenediselenolato]cobalt(III) with S_8[7)] does not occur in the reaction of **2** with Se_8 or in the reaction of **3** with S_8.

It was found that in the absence of diphenylacetylene, **4** reacts with the mixture of S_8 and Se_8 (molar ratio of S_8 and Se_8 to **4** are 1/20 and 1/5(=4/20), respectively) to give a dark brown solid which reacts further with **5** to afford a mixture of **1**, **2**, and **3**. From the mass spectral analyses of the dark brown solid, it turns out that the solid consists of several S,Se-mixed clusters such as $Cp_4Co_4SSe_3$, $Cp_4Co_4S_2Se_2$, and $Cp_4Co_4S_3Se$ (m/z(rel intensity) 768(1), 720(2), and 672(2)[8)]).

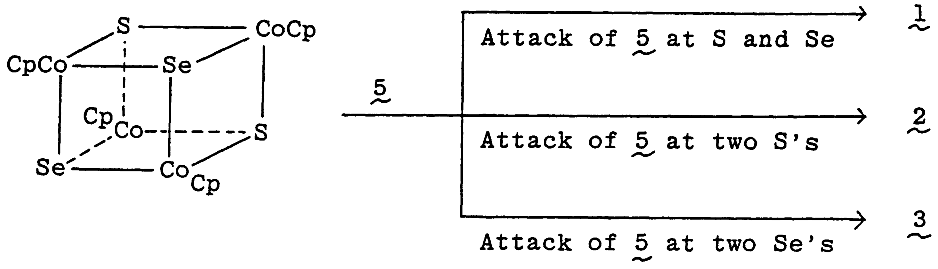
The above results indicate that the S,Se-mixed complex is formed by the attack of diphenylacetylene to the S and Se in the S,Se-mixed clusters.

An intersting observation is that the reaction of **4**, **5**, and a mixture of sulfur and selenium gives the dithiolato complex in much higher yields than those of **4**, **5**, and sulfur. But the reason has not yet been clarified.

The pathways for the formation of **1**, **2**, and **3**, from **4**, **5**, and a mixture of S_8 and Se_8 are illustrated in Scheme 1.

$CpCo(COD) \xrightarrow{S_8 \text{ and } Se_8}$ Clusters such as $Cp_4Co_4SSe_3$, $Cp_4Co_4S_2Se_2$, $Cp_4Co_4S_3Se$ etc.

An example of reaction of the cluster $Cp_4Co_4S_2Se_2$ with 5.



Scheme 1.

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8) Besides these S,Se-mixed clusters, of which the values of m/z were determined by using the isotopes of ^{32}S and ^{80}Se, the following typical peaks were observed at m/z(rel intensity) 624(1, $Cp_4Co_4S_4^+$), 532(2, $Cp_3Co_3Se_2^+$), 484(11, $Cp_3Co_3SSe^+$), 436(23, $Cp_3Co_3S_2^+$), 189(67, Cp_2Co^+),160(16,Se_2^+), 124(10, $CpCo^+$), 66(100, CpH^+), 65(65, Cp^+), and 64(12, S_2^+).
A fraction most of which consists of $Cp_4Co_4S_2Se_2$ was separated by silica gel column chromatography method [column, Wako gel C-300; developing solvent, CH_2Cl_2-Et_2O (3:1,v/v)] from the dark brown solid. The resulting cluster reacted with Ph-C≡C-Ph in boiling xylene for 4 h to afford the S,Se-mixed complex 1, 2, and 3 in the ratio of 1:2:3=68:29:3.

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