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Reactivities of Sulfur and Selenium in Adduct Formation of (η^5-Cyclopentadienyl)(1,2-diphenyl-1,2-ethylenedichalcogenolato)cobalt(III) Complexes with Ethyl Diazoacetate

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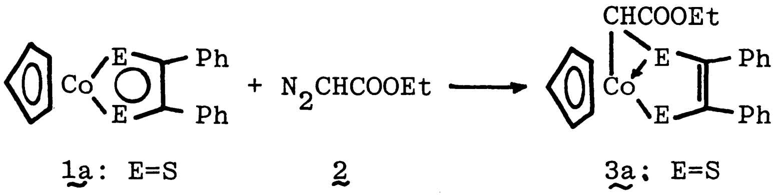
The reactivity and selectivity of S and Se of (η^5-cyclopentadienyl)(1,2-diphenyl-1,2-ethylenedichalchogenolato)cobalt(III) in the alkylidene adduct formation with ethyl diazoacetate were studied. The relative reactivities of dithiolato, selenolatothiolato (**1c**), and diselenolato complexes are 1 : 26 : 400 at 40 °C. In contrast to the large difference in the reactivities in intermolecular competition, S and Se in **1c** reacted with low intramolecular selectivity.

Metalladithiolene rings consisting of one transition metal atom, two sulfur atoms, and two unsaturated carbon atoms have characteristic physical and chemical properties.1) They show reactivities toward some organic compounds, such as diazo compounds,2) dimethyl acetylenedicarboxylate,3) quadricyclane,4) phosphines, and phosphites5) to give the corresponding adducts. The interest in the chemistry of chalcogen compounds is now expanding to compounds containing selenium and tellurium. In the chalcogen chemistry, there remain some important problems as to how the physical and chemical properties of selenium and tellurium compounds differ from those of sulfur compounds. For example, the order of Pauling's electronegativities of S and Se disagrees with that of Allred-Rochow's.6)

Recently, we prepared the dichalcogenolatocobalt(III) complexes containing both sulfur and selenium.7) In this paper, we discuss the reactivities and selectivities of S and Se in the adduct formation of (η^5-cyclopentadienyl)(1,2-diphenyl-1,2-ethylenedichalcogenolato)cobalt(III) (**1a**-**1c**) with ethyl diazoacetate (**2**).

The dichalcogenolatocobalt(III) complexes (1a-1c) reacted with ethyl diazoacetate (2) (in normal procedure: amount of 1 , 80-100 μmol; amount of 2, 450-670 μmol) in benzene solutions (70 cm^3) at room temperature or under reflux. The products were separated by column chromatography on silica gel (C-300 of Wako Junyaku Co.).

The diselenolato complex (1b) reacts with 2 more easily than the dithiolato complex (1a): The complex 1b reacts with 2 at room temperature, while 1a reacts with 2 very slowly at room temperature but reacts smoothly at 80 °C. The results are summarized in Table 1.

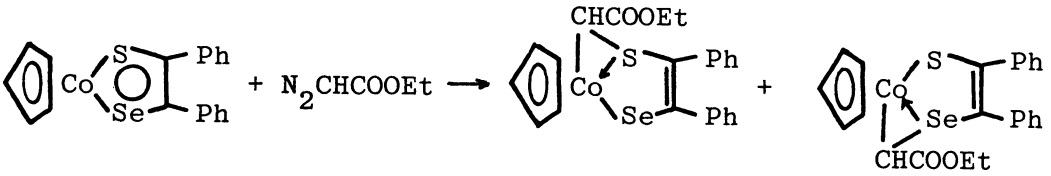


1a: E=S
1b: E=Se
2
3a: E=S
3b: E=Se

Table 1. Formation of Alkylidene Adducts in Reaction between (η^5-Cyclopentadienyl)(1,2-diphenyl-1,2-ethylenedichalcogenolato)cobalt(III) Complexes (1) and Ethyl Diazoacetate (2)

Dichalcogenolato complex			Reaction conditions		Alkylidene adduct	
	E	E'	Temp / °C	Time/h		Yield/%
1a	S	S	80	3	3a	80
1b	Se	Se	20	3	3b	85
1c	S	Se	25	48	3c	30
					3c'	48
1c	S	Se	80	3	3c	38
					3c'	38

The dichalcogenolato complex containing S and Se (1c : (η^5-cyclopentadienyl)(1,2-diphenyl-1-selenolato-2-thiolato-S,Se)cobalt(III)) undergoes a similar addition reaction to give two isomeric alkylidene adducts: 3c in which Co and S are bridged and 3c' in which Co and Se are bridged. The reaction occurs slowly at room temperature but rapidly at 80 °C (Table 1).



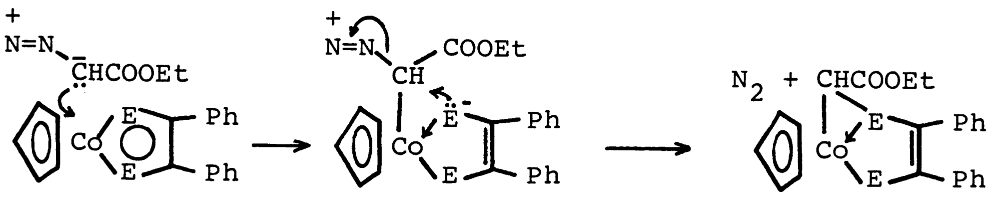
1c 2 3c 3c'

The relative reaction rates of **1a**, **1c**, and **1b** are found to be 1 : 26 : 400 at 40 °C.

In contrast to the large difference in the reactivities among dithiolato, diselenolato, and selenolatothiolato complexes, the intramolecular selectivity of S and Se in the alkylidene adduct formation is small. The adducts **3c** and **3c'** are formed in similar yields. The ratios of **3c** to **3c'** in low conversion at 20, 50, and 80 °C are 1 : 1.7, 1 : 1.6, and 1 : 1.3, respectively.$^{8)}$

At 20 °C, the ratio of **3c** to **3c'** did not change during the progress of the reaction. However, at elevated temperatures, the ratios of **3c'** to **3c** decrease as the reaction time increases. This suggests some secondary reactions. In fact, the heating of **3c'** at 80 °C for 17 h gave a mixture of **3c** (5%), **3c'** (73%), and **1c** (22%). The heating of **3c** under the same conditions gave a mixture of **3c** (92%) and **1c** (8%). The decrease of the ratios **3c'** to **3c** at prolonged heating should be due to the easier dissociation of **3c'** to **1c** than **3c** and the isomerization of **3c'** to **3c**.

The large difference in the reactivities of S and Se in the intermolecular competition and the small selectivities of S and Se in the intramolecular competition are consistent with the mechanism proposed in the preceding paper (Scheme 1).$^{2)}$



Scheme 1.

The first step in the reaction is the nucleophilic attack of negatively charged C of the diazo compound to the positively charged Co atom of the complex. This process determines the reactivities of the dichalcogenolatocobalt complexes. The half-wave potentials of **1a**, **1b**, and **1c**, which are the measures of the positive charge of the cobalt atom in the dichalcogenolatocobalt(III) complexes, are -1.16, -1.08, and -1.12 V, respectively.$^{7,9)}$ The dichalcogenolato complex with more positively charged Co atom reacts more easily.

The low regioselectivity in the reaction of selenolatothiolato complex can be explained by the similar reactivities of S and Se in the second step (nucleophilic attack of the chalcogen to the carbon atom of the diazo compound moiety).

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8) The structures of the adducts **3c** and **3c'** were determined by the comparison of ^{1}H and ^{13}C NMR of the bridging alkylidene. The chemical shifts of ^{1}H and ^{13}C NMR in the alkylidene are influenced by the neighboring chalcogen atom. The adduct **3c** which gives NMR signals similar to those of **3a** can be assigned to the adduct in which S and Co are bridged by CHCOOEt. The similality of NMR between **3c'** and **3b** should be due to the similality of their structures (bridge between Se and Co).

Adduct	^{1}H NMR for CHCOOEt	^{13}C NMR for CHCOOEt
3a	δ = 2.21	δ = 32.0 (J_{CH} = 174.6 Hz)
3c	δ = 2.51	δ = 32.1 (J_{CH} = 174.6 Hz)
3c'	δ = 2.77	δ = 43.1 (J_{CH} = 174.6 Hz)
3b	δ = 3.11	δ = 43.8 (J_{CH} = 173.3 Hz)

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