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Formation of (η-Cyclopentadienyl)(1,2-ethylenedithiolato, 1,2-ethylenediselenolato, and 2-selenolatoethylenethiolato-*S*,*Se*)cobalt(III) Complexes in a One-Pot-Reaction of (η-Cyclopentadienyl)(1,5-cyclooctadiene or dicarbonyl)cobalt(I) with Alkyne and a Mixture of S_8 and Se_8

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A one-pot-reaction of (η-cyclopentadienyl)(1,5-cyclooctadiene or dicarbonyl)cobalt(I) with alkyne (diphenylacetylene and phenylacetylene) and a mixture of S_8 and Se_8 gives (η-cyclopentadienyl)(2-selenolatoethylenethiolato-*S*,*Se*)cobalt(III) complex in addition to the corresponding dithiolato and diselenolato complexes. When phenylacetylene was used as an alkyne, a (2-phenyl-2-selenolatoethylenethiolato-*S*,*Se*)cobalt(III) complex was formed preferentially rather than the (1-phenyl-2-selenolatothiolato-*S*,*Se*)cobalt(III) complex. The separation of the diselenolato and selenolatothiolato complexes from the dithiolato complex was successfully done by utilizing the difference in how these complexes form adducts with tributylphosphine. The dithiolato complexes have more negative reversible half-wave potentials (for reduction) than the diselenolato complexes; the selenolatothiolato complexes have intermediate half-wave potentials.

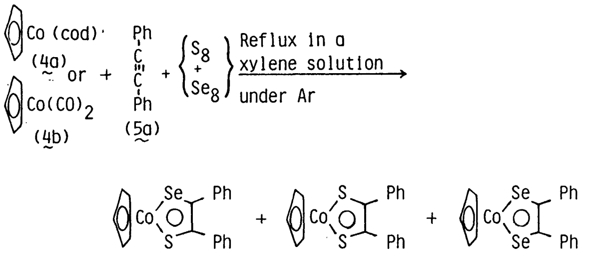
Dithiolatometal complexes have unique electronic structures[1] and show several useful functions,[2] such as catalysts for the synthesis of thiophene derivatives[3] and for isomerization of quadricyclane to norbornadiene.[4] Photocatalysis for hydrogen evolution[5] and quenching of singlet oxygen[6] have been reported, along with electron transport[7] and electric conductivity properties.[8] The interest in the chemistry of chalcogen compounds is now expanding to compounds containing selenium and tellurium.

Owing to the development of a new and facile synthetic method for (η-cyclopentadienyl)(1,2-ethylenedithiolato)cobalt(III) complexes in a one-pot-reaction of [Co(cp)(CO)$_2$] or [Co(cp)(cod)] (cod=1,5-cyclooctadiene) with elemental sulfur and alkynes,[3] dithiolatometal complexes of this type with various substituents can be easily synthesized.

This type of reaction has been applied to the synthesis of diselenolatometal complexes.[9] However, this type of reaction has never been examined by using a mixture of elemental sulphur and elemental selenium. In this paper we report that the one-pot-reactions of η-cyclopentadienylcobalt species with alkyne and a mixture of S_8 and Se_8 give (η-cyclopentadienyl)(2-selenolatoethylenethiolato-*S*,*Se*)cobalt(III), in addition to the corresponding dithiolato and diselenolato complexes.[10] Only three reports have appeared on the synthesis of selenolatothiolatometal complexes.[9,11,12] We also discuss the properties of dithiolato, diselenolato, and selenolatothiolato complexes.

Results and Discussion

Formation of Dithiolato, Diselenolato, and Selenolatothiolato Complexes. When a mixture of (η-cyclopentadienyl)(1,5-cyclooctadiene or dicarbonyl)cobalt(I)([Co(cp)(cod)]: **4a** or [Co(cp)(CO)$_2$]: **4b**), diphenylacetylene, elemental sulfur, and elemental selenium is refluxed in xylene, (η-cyclopentadienyl)(1,2-diphenyl-1,2-ethylenedithiolato)cobalt(III)(**2a**), (η-cyclopentadienyl)(1,2-diphenyl-1,2-ethylenediselenolato)cobalt(III) (**3a**), and (η-cyclopentadienyl)(1,2-diphenyl-2-selenolatoethylenethiolato-*S*,*Se*)cobalt(III) (**1a**) are formed.



These three complexes could not be separated by ordinary chromatographic methods. However, the separation was successfully carried out by the combination of the adduct formation of these complexes with tributylphosphine and chromatography. Complexes **1a** and **3a** form 1 : 1 adducts with tributylphosphine and are separated from **2a** by means of silica-gel chromatography under Ar (**2a** is eluted more easily than the phosphine-adducts of **1a** and **3a**). The complexes **1a** and **3a** can be easily regenerated from the adducts with tributylphosphine by oxidizing the phosphine on exposure to the air.

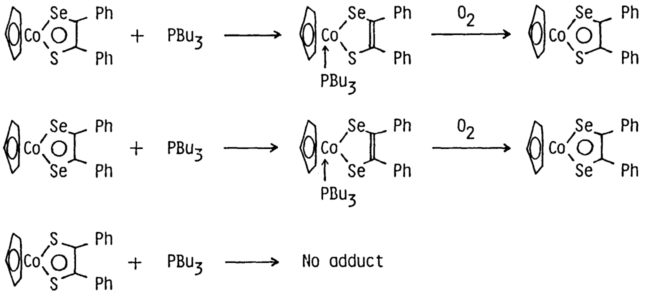
When we choose the compositions of S_8 and Se_8 such that **3a** is not formed (for example, under the condition of S : Se=1 : 6), the selenolatothiolato complex, **1a**, can be obtained in pure form.

The yields of **1a**, **2a**, and **3a** determined by the ^{1}H NMR spectroscopy, are shown in Table 1, together with the initial ratios of sulfur and selenium.

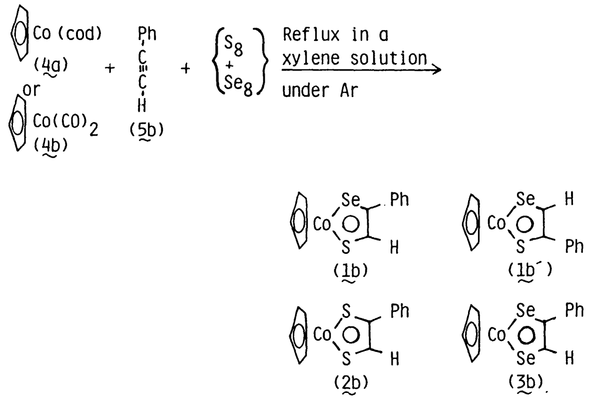
Table 1. Yields of Selenolatothiolato (**1a**), Dithiolato (**2a**), and Diselenolato (**3a**) Complexes in the Reaction of [Co(cp)(cod)] (cod=1,5-cyclooctadiene) (**4a**), Diphenylacetylene (**5a**), and a Mixture of S_8 and Se_8

Molar ratio of S_8 and Se_8 to **5a**		Yield of product/%[a]		
S_8	Se_8	**1a**	**2a**	**3a**
2/8	0	—	16	—
0	2/8	—	—	20
2/8	2/8	18	45	0
2/8	8/8	20	30	1
1/8	1/8	17	16	1
1/8	4/8	27	23	6
1/8	6/8	49	23	7
1/20	4/20	21	9	6

a) Yield=(amount of product/amount of **4a** used) ×100.



When we used phenylacetylene as an alkyne, we obtained (η-cyclopentadienyl)(2-phenyl-2-selenolatoethylenethiolato-*S*,*Se*)cobalt(III) (**1b**) and (η-cyclopentadienyl)(1-phenyl-2-selenolatoethylenethiolato-*S*,*Se*)cobalt(III) (**1b′**) as the complexes containing both S and Se. In this case, the amount of **1b** was greater than that of **1b′**.



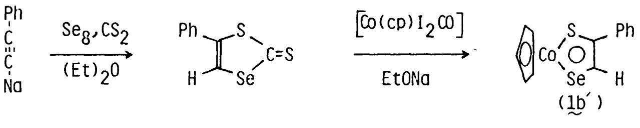
The identification of **1b** and **1b′** was done by the synthesis of **1b′** by the reaction of [Co(cp)I_2CO] and 5-phenyl-1,3-thiaselenole-2-thione in ethanol in the presence of sodium ethoxide. 5-Phenyl-1,3-thiaselenole-2-thione was prepared according to the method of Mayer and Müller.[13]

The dependences of the yields of **1b**, **1b′**, **2b**, and **3b** on the initial ratio of S_8 and Se_8 are shown in Table 2.

Table 2. Yields of Selenolatothiolato (**1b** and **1b′**), Dithiolato (**2b**), and Diselenolato (**3b**) Complexes in the Reaction of [Co(cp)$(CO)_2$] (**4b**), Phenylacetylene (**5b**), and a Mixture of S_8 and Se_8

Molar ratio of S_8 and Se_8 to **5b**		Yield of product/%[a]			
S_8	Se_8	**1b**	**1b′**	**2b**	**3b**
2/8	0	—	—	28	—
0	2/8	—	—	—	15
2/8	2/8	15	1.7	13	1.1
1/8	6/8	24	3	8	6
6/8	1/8	Trace	0	35	0

a) Yield=(amount of product/amount of **4b** used) ×100.



The addition of sulfur to the [Co(cp)(cod)]-alkyne-Se_8 system causes remarkable decreases in the yields of the diselenolato complexes. But the addition of selenium to the [Co(cp)(cod)]-diphenylacetylene-S_8 system promotes the formation of the dithiolato complex. In the [Co(cp)$(CO)_2$]-phenylacetylene-S_8 system, the addition of selenium lowers the yield of the dithiolato complex, but the inhibiting effect of selenium on the formation of dithiolato complex is much smaller than that of sulfur on the formation of the diselenolato complex in the reaction of [Co(cp)$(CO)_2$], phenylacetylene, and Se_8.

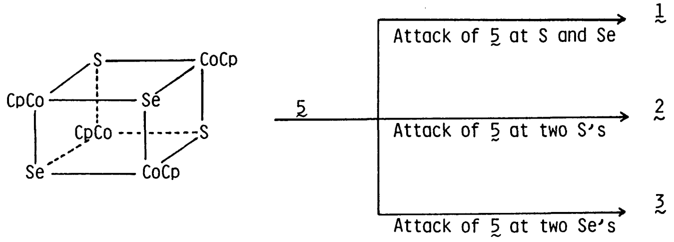
Reaction Mechanism. For the formation of dithiolato, diselenolato, and selenolatothiolato complexes, the intermediacy of "clusters" consisting of η-cyclopentadienylcobalt and chalcogen atoms is presumed. In the absence of alkyne, [Co(cp)(cod)] reacts with a mixture of S_8 and Se_8 (molar ratio of S_8 and Se_8 to **4a** are 1/20 and 1/5 (=4/20), respectively) to give a dark brown solid. The mass spectral analysis of the dark brown solid showed that the solid consists of several S, Se-mixed clusters. A chromatographically separated fraction, which consists of [$Co_4S_2Se_2(cp)_4$], [$Co_4S_3Se(cp)_4$], and [$Co_4S_4(cp)_4$], reacts with **4a** in boiling xylene to afford **1a**, **2a**, and **3a**.

This result indicates that the dithiolato, diselenolato, and selenolatothiolato complexes are formed by the attack of alkyne to the chalcogen atoms of the cluster complexes either in a concerted or in a stepwise process.

One factor in determining the relative amounts of dithiolato, diselenolato, and selenolatothiolato complexes would be the selectivity in the attack of alkyne to the cluster complexes. However, there exists another factor to determine the amounts: the ligand exchange of the primarily formed dichalcogenato complexes. A prolonged heating of a selenolatothiolato complex **1b′** in xylene under reflux (140 °C) brings about the formation of the dithiolato complex

$$[Co(cp)(cod)] \xrightarrow{S_8 + Se_8} \text{Clusters such as } [Co_4SSe_3(cp)_4],\ [Co_4S_2Se_2(cp)_4],\ [Co_4S_3Se(cp)_4],\ [Co_4S_4(cp)_4] \text{ etc.}$$

An example of reaction of the cluster $[Co_4S_2Se_2(cp)_4]$ with 5.



2b. This fact shows the exchange of the chalcogen atoms.

Physical Properties of Dithiolato, Diselenolato, and Selenolatothiolato Complexes. Some important spectroscopic properties as well as the reversible half-wave potentials (for reduction) of the complexes **1**, **2**, and **3** are summarized in Table 3.

The patterns of the electronic spectra of the diselenolatocobalt(III) complexes are similar to those of the dithiolato complexes. Each complex has four absorptions in the UV-vis. region. The absorption maxima of the diselenolatocobalt(III) complexes are situated at wavelengths longer than those of the corresponding dithiolato complexes. The absorption maxima of the selenolatothiolato complexes are located between those of the dithiolato and diselenolato complexes. The weak absorptions around 750—820 and 420—480 nm shift more sensitively dependent on the kinds and number of the chalcogen atoms than the strong absorptions around 600—620 and 290—300 nm.

The reversible half-wave potentials (for reduction) of the diselenolato complexes are higher than those of the corresponding dithiolato complexes: thus the diselenolato complexes are reduced more easily than the dithiolato complexes. The selenolatothiolato complexes have intermediate half-wave potentials between the dithiolato and diselenolato complexes.

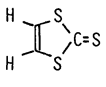
The fact that the $E^r_{1/2}$ values of the diselenolato complexes are higher than those of the dithiolato complexes suggests that the central cobalt atoms in the diselenolato complexes are charged more positively than those in the dithiolato complexes. There is a contradiction in the values of electronegativities of selenium and sulfur: according to Pauling, the electronegativity of sulfur (2.5) is larger than that of selenium (2.4),[14] while according to Allred-Rochow, the electronegativity of sulfur (2.4) is smaller than that of selenium (2.5).[15] The observed half-wave potentials of diselenolato and dithiolato complexes suggest that the selenium behaves in dichalcogenatometal complexes as a more electronegative element than sulfur does.

The delta value of chemical shifts in ^{1}H NMR spectra for the proton attached to the diselenolene ring in **3b** is larger than that for the proton attached to the dithiolene ring in **2b**. The chemical shifts ascribed to H in selenathiolene rings in **1b** and **1b′** are interme-

Table 3. Spectral Properties and Half-Wave Potentials (for Reduction) of Selenolatothiolato (**1**), Dithiolato (**2**), and Diselenolato (**3**) Complexes

	2a	**1a**	**3a**	**2b**	**1b**	**1b′**	**3b**
^{1}H NMR (δ)							
Cp	5.39	5.37	5.35	5.37	5.36	5.36	5.35
Ring[a]	—	—	—	9.00	9.15	9.74	9.85
^{13}C NMR (δ)							
Cp	79.62	78.80	77.97	79.28	78.42	78.51	77.61
Ring[a]	168.80	165.95	169.14	155.23	158.72	150.62	154.23
		171.93		172.47	169.74	176.60	174.00
UV-vis. λ_{max}/nm (ε[b])	750 (770)	772 (970)	812 (1050)	748 (725)	765 (1040)	764 (760)	812 (1060)
	600 (8550)	610 (8730)	612 (8370)	558 (7250)	602 (7450)	601 (5660)	608 (7340)
	424 (1210)	445 (2000)	472 (1980)	424 (1100)	444 (1550)	438 (1410)	471 (1730)
	295 (33500)	299 (35600)	304 (34500)	292 (24000)	298 (27800)	297 (21600)	303 (30000)
Half-wave potential $E^r_{1/2}$(red)/V	−1.16	−1.12	−1.08	−1.17	−1.13	−1.13	−1.09
Formation of adduct with PBu$_3$	No	Yes	Yes	No	Yes	Yes	Yes

a) Dithiolene, diselenolene, or thioselenolene ring. b) ε/mol^{-1} dm^3 cm^{-1}.



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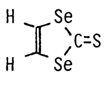

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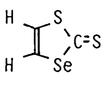

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diate. A similar tendency has been reported for 1,3-dichalcogenolene-2-thiones and selones (**6**, **7**, and **8**).[16] (Delta-values of ^{1}H NMR in **6** and **7** are 7.17 and 7.92, respectively. Those in **8** are 7.26 and 7.80.) These facts seem to agree with the results of $E^{\mathrm{r}}_{1/2}$: The more positive selenium attracts electrons more strongly than sulfur does.

The chemical shifts of the ^{1}H and ^{13}C NMR in the cyclopentadienyl ring are influenced much less by the chalcogen atoms than those of H in the dichalcogenolene rings. However, an opposite effect of chalcogen is observed: The signals due to ^{1}H and ^{13}C in the cyclopentadienyl ring in diselenolato complexes appear in higher magnetic field than those in the dithiolato complexes.

The chemical shifts of ^{1}H and ^{13}C NMR in the selenolatothiolato complexes are situated between those of the dithiolato complexes and those of the diselenolato complexes.

Adduct Formation with Tributylphosphine. A remarkable difference in chemical properties among dithiolato, diselenolato, and selenolatothiolato complexes with phenyl group as the substituent is the adduct formation with phosphine. Complexes **1a** and **3a** form 1 : 1 adduct with tributylphosphine, while **2a** does not react with tributylphosphine. A similar difference in the reactivities was observed for **1b**, **1b′**, **2b**, and **3b**. In a separate report,[17] we have described that the adduct formation of dithiolatocobalt complexes with phosphines and phosphites is dependent on the (reversible) half-wave potentials of reduction of the dithiolato complexes: The dithiolato complexes, the $E^{\mathrm{r}}_{1/2}$'s of which are higher than −1.13 V, form an adduct with tributylphosphine. The $E^{\mathrm{r}}_{1/2}$ values of the dithiolato, diselenolato, and selenolatothiolato complexes are accidentally distributed across the critical $E^{\mathrm{r}}_{1/2}$ value. This is the reason why we could separate these complexes by the adduct formation with tributylphosphine.

Experimental

Materials. Commercially available diphenylacetylene, elemental sulfur, and elemental selenium were used as purchased. Phenylacetylene was purified by distillation.

Spectroscopy and Elemental Analysis. NMR spectra were recorded on a JEOL GX-270 instrument and mass spectra on a JEOL JMS-D300 instrument. UV-vis. spectra were measured with a Hitachi spectrometer Model 228. Elemental analysis was carried out with a Perkin-Elmer Model 240 C apparatus.

Reaction of η-Cyclopentadienylcobalt(I) Species, Alkyne, and Elemental Chalcogen. A mixture of [Co(cp)(cod)] or [Co(cp)(CO)$_2$] (ca 1.4 mmol), alkyne (ca 1.7 mmol), and a mixture of S$_8$ and Se$_8$ in xylene (25 cm^3) was refluxed for 24 h under an atmosphere of Ar.

Separation and Identification of Products. After the evaporation of the solvent under reduced pressure, the residue was extracted with dichloromethane. The extract was concentrated and the product mixture was submitted to the column chromatography (column, silica gel C-300 made by Wako Pure Chemical Co.; eluent, hexane-dichloromethane). The complexes **1**, **2**, and **3** were eluted together.

In order to obtain pure **1a**, the following procedure was followed. The reaction mixture from the reaction under the condition of S : Se=1 : 6 (the conditions under which only a small amount of **3a** was formed) was preliminarily separated by the procedure described above. The composition of the mixture of **1a**, **2a**, and **3a** was determined by means of ^{1}H NMR. Then, to the mixture under Ar was added tributylphosphine, the amount of which was equal to the sum of the amounts of **1a** and **3a**. Then the mixture was submitted to the column chromatography using a column packed with silica gel C-300. After the elution of **2a** with a mixture of dichloromethane and hexane, the column was exposed to the air and **1a** and **3a** were regenerated by the oxidative elimination of tributylphosphine. By the elution with dichloromethane-hexane, **1a** was obtained in analytically pure form. A similar method was applied to the separation of **1b**, **1b′**, **2b**, and **3b**.

(η-Cyclopentadienyl)(1,2-diphenyl-1,2-ethylenedithiolato)cobalt(III) (2a) was identified by reference to the spectra reported by Bönnemann.[18] Blue crystals; mp 235—238 °C; IR (KBr disk) 3098, 764, 743, and 698 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=5.39 (5H, s, cp) and 7.12—7.26 (10H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=79.62 (cp), 127.1 (Ph), 127.8m (Ph), 129.0 (Ph), 142.0 (Ph), and 168.8 (dithiolene ring); MS (70 eV) *m*/*z* (rel intensity) 368 (5, M$^+$), 367 (11, M$^+$), 366 (49, M$^+$), 190 (9), 189 (7), 188 (100), 178 (16), 124 (26), and 59 (7). Found: C, 62.51; H, 3.95%.

(η-Cyclopentadienyl)(1,2-diphenyl-1,2-ethylenediselenolato)cobalt(III) (3a): Green crystals; mp 250—255 °C (lit,[9] mp 237 °C); IR (KBr disk) 3095, 762, 727, and 697 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=5.35 (5H, s, cp) and 7.10—7.23 (10H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=77.97 (cp), 126.84 (Ph), 127.74 (Ph), 129.22 (Ph), 143.83 (Ph), and 169.14 (diselenolene ring); MS (70 eV) *m*/*z* (rel intensity) 462 (6, M$^+$), 460 (6, M$^+$), 459 (2, M$^+$), 458 (3, M$^+$), 286 (12), 284 (43), 282 (37), 281 (12), 280 (23), 178 (100), 124 (43), and 59 (7).

Found: C, 49.57; H, 3.26%. Calcd for C$_{19}$H$_{15}$CoSe$_2$: C, 49.59; H, 3.29%.

(η-Cyclopentadienyl)(1,2-diphenyl-2-selenolatoethylenethiolato-*S*,*Se*)cobalt(III) (1a): Green crystals; mp 234—236 °C; IR (KBr disk) 3098, 763, 734, and 698 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=5.37 (5H, s, cp) and 7.10—7.25 (10H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=78.80 (cp), 126.84 (Ph), 127.15 (Ph), 127.78 (Ph), 127.85 (Ph), 128.73 (Ph), 129.56 (Ph), 142.57 (Ph), 143.75 (Ph), 165.95 (thiaselenolene ring), and 171.93 (thiaselenolene ring); MS (70 eV) *m*/*z* (rel intensity) 416 (8, M$^+$), 415 (7, M$^+$), 414 (32, M$^+$), 412 (16, M$^+$), 411 (6, M$^+$), 410 (6, M$^+$), 238 (22), 237 (8), 236 (100), 234 (49), 233 (17), 232 (19), 178 (57), 124 (55), and 59 (11)

Found: C, 54.87; H, 3.89%. Calcd for C$_{19}$H$_{15}$CoSSe: C, 55.07; H, 3.62%.

(η-Cyclopentadienyl)(phenyl-1,2-ethylenedithiolato)cobalt(III) (2b) was identified by reference to the spectra reported by Bönnemann.18) Blue crystals; mp 85—87 °C; IR (KBr disk) 3098, 757, and 697 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=5.37 (5H, s, cp), 7.24—7.80 (5H, m, Ph), and 9.00 (1H, s, H in dithiolene ring); ^{13}C NMR (CDCl$_3$) δ=79.28 (cp), 126.47 (Ph), 127.53 (Ph), 128.62 (Ph), 140.14 (Ph), 155.23 (dithiolene ring attached to H), and 172.47 (dithiolene ring attached to Ph); MS (70 eV) m/z (rel intensity) 292 (6, M$^+$), 291 (10, M$^+$), 290 (64, M$^+$), 190 (9), 189 (7), 188 (100), 124 (36), 102 (8), 59 (16).

Found: C, 55.09; H, 3.79%. Calcd for $\mathrm{C_{13}H_{11}CoS_2}$: C, 53.79; H, 3.79%.

(η-Cyclopentadienyl)(phenyl-1,2-ethylenediselenolato)-cobalt(III) (3b): Blue crystals; mp 116—118 °C; IR (KBr disk) 3096, 763, 740, and 696 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=5.35 (5H, s, cp), 7.29—7.71 (5H, m, Ph), and 9.85 (1H, s, diselenolene ring); ^{13}C NMR (CDCl$_3$) δ=77.61 (cp), 126.96 (Ph), 127.28 (Ph), 128.39 (Ph), 150.70 (Ph), 154.23 (diselenolene ring), 174.00 (diselenolene ring); MS (70 eV) m/z (rel intensity) 338 (9, M$^+$), 386 (29, M$^+$), 384 (26, M$^+$), 383 (10, M$^+$), 382 (15, M$^+$), 380 (6, M$^+$), 286 (31), 285 (6), 284 (100), 282 (86), 281 (29), 280 (51), 279 (14), 278 (20), 124 (99), 102 (33), and 59 (18).

Found: C, 40.93; H, 2.84%. Calcd for $\mathrm{C_{13}H_{11}CoSe_2}$: C, 40.66; H, 2.87%.

(η-Cyclopentadienyl)(2-phenyl-2-selenolatoethylenethiolato-*S,Se*)cobalt(III) (1b): Violet crystals; mp 86—88 °C; IR (KBr disk) 3098, 755, and 696 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=5.36 (5H, s, cp) and 9.15 (1H, s, thiaselenolene ring); ^{13}C NMR (CDCl$_3$) δ=78.50 (cp), 126.49 (Ph), 127.29 (Ph), 128.70 (Ph), 141.88 (Ph), 158.72 (thiaselenolene ring), and 169.74 (thiaselenolene ring); MS (70 eV) m/z (rel intensity) 340 (10, M$^+$), 339 (7, M$^+$), 338 (43, M$^+$), 336 (22, M$^+$), 335 (8, M$^+$), 334 (8, M$^+$), 238 (22), 237 (7), 236 (100), 235 (4), 234 (49), 233 (17), 232 (19), 124 (71), 102 (12), and 59 (22).

Found: C, 45.88; H, 3.22%. Calcd for $\mathrm{C_{13}H_{11}CoSSe}$: C, 46.32; H, 3.27%.

(η-Cyclopentadienyl)(2-phenyl-2-selenolatoethylenethiolato-*S,Se*)cobalt(III) (1b′) was identified by the synthesis in the reaction of [Co(cp)I$_2$CO] with 5-phenyl-1,3-thiaselenole-2-thione. Violet crystals; mp 98—100 °C; IR (KBr disk) 3096, 764, 746, and 698 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=5.36 (5H, s, cp), 9.74 (1H, s, H in the dithiolene ring); ^{13}C NMR (CDCl$_3$) δ=78.51 (cp), 127.06 (Ph), 127.56 (Ph), 128.39 (Ph), 140.74 (Ph), 150.62 ($\underline{\mathrm{C}}$H in the dithiolene ring), and 176.60 ($\underline{\mathrm{C}}$Ph in the dithiolene ring); MS (70 eV) m/z (rel intensity) 340 (11, M$^+$), 339 (7, M$^+$), 338 (48, M$^+$), 336 (24, M$^+$), 335 (9, M$^+$), 334 (9, M$^+$), 238 (22), 237 (7), 236 (100), 235 (4), 234 (49), 233 (16), 232 (19), 124 (80), 102 (17), and 59 (29).

Found: C, 45.72; H, 3.09%. Calcd for $\mathrm{C_{13}H_{11}CoSSe}$: C, 46.32; H, 3.27%.

Determination of Yields of Products. The fraction containing **1**, **2**, and **3**, which resulted from the column chromatography of the products, was submitted to the measurement of ^{1}H NMR in a CDCl$_3$ solution. The contents of **1a**, **2a**, and **3a** from the reaction among diphenylacetylene, [Co(cp)(CO)$_2$], S$_8$, and Se$_8$ were calculated from the areas of the ^{1}H NMR peaks ascribed to cp rings (δ=5.37 for **1a**, δ=5.39 for **2a**, and δ=5.35 for **3a**).

The composition of the mixtures from the reaction among phenylacetylene, [Co(cp)(CO)$_2$], S$_8$, and Se$_8$ were calculated from the areas of the ^{1}H NMR peaks ascribed to the protons in the dithiolene ring (δ=9.15 for **1b**, δ=9.74 for **1b′**, δ=9.00 for **2b**, and δ=9.85 for **3b**).

Formation, Separation, and Identification of Cluster Complexes. A mixture consisting of [Co(cp)(cod)] (4.3 mmol), Se$_8$ (0.54 mmol), and S$_8$ (0.54 mmol) in xylene (35 cm^3) was heated under reflux (140 °C) under Ar for 24 h. After the evaporation of the solvent under reduced pressure, the residue was extracted with dichloromethane and the dichloromethane-insoluble substances were removed by filtration. The dichloromethane-soluble substances were separated by column chromatography (column, silica gel C-300 made by Wako Pure Chemical Co.; eluent, dichloromethane–diethyl ether). Black solid was eluted with dichloromethane (3)–diethyl ether (1). The mass-spectral measurement showed it to be a mixture of cluster complexes of [Co$_4$S$_2$Se$_2$(cp)$_4$], [Co$_4$S$_3$Se(cp)$_4$], and [Co$_4$S$_4$(cp)$_4$] (the mass spectra of the mixture (70 eV): m/z (rel intensity) 720 (0.42, M$^+$ of [Co$_4$S$_2$Se$_2$(cp)$_4$]), 718 (0.36, M$^+$ of [Co$_4$S$_2$Se$_2$(cp)$_4$]), 674 (1.07, M$^+$ of [Co$_4$S$_3$Se(cp)$_4$]), 672 (3.46, M$^+$ of [Co$_4$S$_3$Se(cp)$_4$]) 670 (1.71, M$^+$ of [Co$_4$S$_3$Se(cp)$_4$]), 626 (2.52, M$^+$ of [Co$_4$S$_4$(cp)$_4$]), 624 (11.87, M$^+$ of [Co$_4$S$_4$(cp)$_4$], 124 (10.09, Co(cp)), and 66 (100, cpH)).

Reaction of a Mixture of Cluster Complexes with Diphenylacetylene. Diphenylacetylene (30 mg) and the mixture of the cluster complexes (30 mg) described above were reacted in xylene (30 cm^3) under Ar at 140 °C for 24 h. After the reaction, the products were separated in the procedure described above. The yields of **1a** and **2a** are 54 mmol and 46 mmol, respectively. The complex **3a** was formed in a trace amount.

Cyclic Voltammetry. All the electrochemical measurements were carried out in acetonitrile solutions containing 0.1 mol dm^{-3} tetraethylammonium perchlorate at 25 °C with a Yanaco Polarographic Analyzer P-1100. A platinum disk electrode (ϕ=2 mm) served as both a stationary working electrode and a rotating electrode. The potential of the working electrode was measured against a silver–silver ion electrode (Ag| 0.1 mol dm^{-3} AgClO$_4$ in acetonitrile).

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References

1) Recently, Hoffmann et al. analyzed the structural electronic features by MO method: S. Alvarez, R. Vicente, and R. Hoffmann, *J. Am. Chem. Soc.*, **107**, 6253 (1985).

2) A review: A. Sugimori and M. Kajitani, *Kagaku, Zokan*, **115**, 113 (1988).

3) H. Bönnemann, B. Bogdanovic, W. Brijoux, R. Brinkmann, M. Kajitani, R. Mynott, G. S. Natarajan, and M. G. Y. Samson, "Transition-Metal-Catalyzed Synthesis of Heterocyclic Compounds," in "Catalysis in Organic Reactions," ed by J. R. Kosak, Marcel Dekker (1984), pp. 31—62; M. Kajitani, T. Suetsugu, R. Wakabayashi, A. Igarashi, T. Akiyama, and A. Sugimori, *J. Organomet. Chem.*, **293**, C15 (1985).

4) R. B. King and S. Ikai, *J. Mol. Catal.*, **4**, 361 (1978).

5) R. Henning, W. Schlamann, and H. Kisch, *Angew. Chem.*, **92**, 604 (1980).

6) M. Kajitani, Y. Yoshida, T. Akiyama, and A. Sugimori, *Nippon Kagaku Kaishi*, **1987**, 1464.

7) J. J. Grimaldi and J. M. Lehn, *J. Am. Chem. Soc.*, **101**, 1333 (1979).

8) A. Kokayashi, Y. Sasaki, H. Kobayashi, A. E.

Underhill, and M. M. Ahmad, *J. Chem. Soc., Chem. Commun.*, **1982**, 390.

9) E. J. Miller, S. J. Landon, and T. B. Brill, *Organometallics*, **4**, 533 (1985).

10) We have preliminarily reported that the reaction of [Co(cp)(cod)] diphenylacetylene, and a mixture of S_8 and Se_8. (M. Kajitani, R. Ochiai, N. Kobayashi, T. Akiyama, and A. Sugimori, *Chem. Lett.*, **1987**, 245).

11) E. Fanghanel and H. Poleschner, *Z. Chem.*, **19**, 192 (1979).

12) D. J. Sandman, J. C. Stark, L. A. Acampora, L. A. Samuelson, G. W. Allen, S. Jansen, M. T. Jones, and B. M. Foxman, *Mol. Crtst. Liq. Cryst.*, **107**, 1 (1984).

13) R. Mayer and A. K. Müller, *Z. Chem.*, **4**, 384 (1964).

14) L. Pauling, "The Nature of Chemical Bond," 3rd ed, Cornell University Press, NY (1960), p. 93.

15) A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 264 (1958).

16) E. M. Engler and V. V. Patel, *J. Org. Chem.*, **40**, 387 (1975).

17) M. Kajitani, A. Igarashi, T. Aritomo, T. Akiyama, K. Shimizu, A. Sugimori, and H. Bönnemann, *J. Organomet. Chem.*, submitted.

18) H. Bönnemann, private communication.