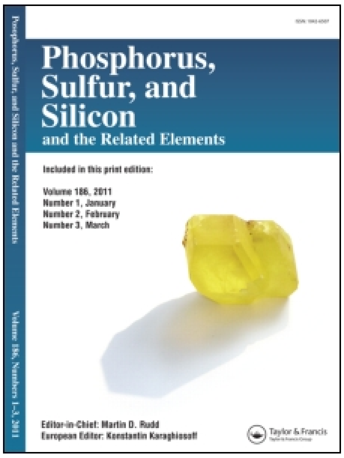

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Sakurada, Masami , Okubo, Joe , Kajitani, Masatsugu , Akiyama, Takeo and Sugimori, Akira(1992) 'Reactions of Cobaltadichalcogenolenes with Diazo Compounds; Reactivities of Sulfur and Selenium in Formation and Dissociation of Alkylidene-Adducts', Phosphorus, Sulfur, and Silicon and the Related Elements, 67: 1, 145 — 150

To link to this Article: DOI: 10.1080/10426509208045831

URL: http://dx.doi.org/10.1080/10426509208045831

Phosphorus, Sulfur, and Silicon, 1992, Vol. 67, pp. 145–150
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REACTIONS OF COBALTADICHALCOGENOLENES WITH DIAZO COMPOUNDS; REACTIVITIES OF SULFUR AND SELENIUM IN FORMATION AND DISSOCIATION OF ALKYLIDENE-ADDUCTS.

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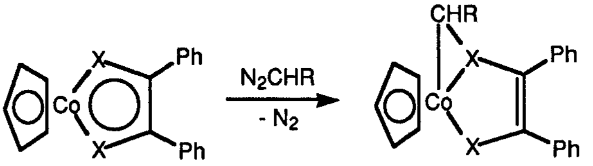
Abstract Dichalcogenolatocobalt complexes $CpCo(X^1X^2C_2Ph_2)$ (**1**: $X^1 = X^2 = S$; **2**: $X^1 = X^2 = Se$; **3**: $X^1 = S$, $X^2 = Se$) react with diazomethane or ethyl diazoacetate to yield 1:1 alkylidene-adducts $CpCo[\eta^3\text{-}(X^1, X^2, C)\text{-}\{X^1C(Ph)\text{-}C(Ph)X^2CHR\}]$ (**4** - **9**) with the evolution of N_2. Thermal reaction of **9** ($X^1 = S$, $X^2 = Se$, $R = CO_2Et$) causes isomerization to **8** ($X^1 = Se$, $X^2 = S$, $R = CO_2Et$). The reactivities and the regioselectivities of S and Se in the formation and dissociation of the alkylidene-adducts are discussed. ^{77}Se NMR spectroscopy of the alkylidene-adducts was also studied.

INTRODUCTION

The dithiolato cobalt or rhodium complexes with a η^5-cyclopentadienyl ligand have unsaturated five-membered metalladithiolene rings which are delocalized π-electron systems.[1] They undergo addition reactions with some organic compounds: phosphines and phosphites,[2] diazo compounds,[3] dimethyl acetylenedicarboxylate,[4] or quadricyclane.[5] The interest in the chemistry of chalcogen compounds is now expanding to those containing selenium and tellurium. We report here the reactivities of selenium and sulfur in the formation and the dissociation of alkylidene-adducts containing selenium and/or sulfur.[6]

RESULTS AND DISCUSSION

Cobaltadichalcogenolenes **1** and **2** react with diazomethane or ethyl diazoacetate to yield 1:1 alkylidene-adducts **4** - **7**, with the evolution of N_2, as shown in eq. 1.



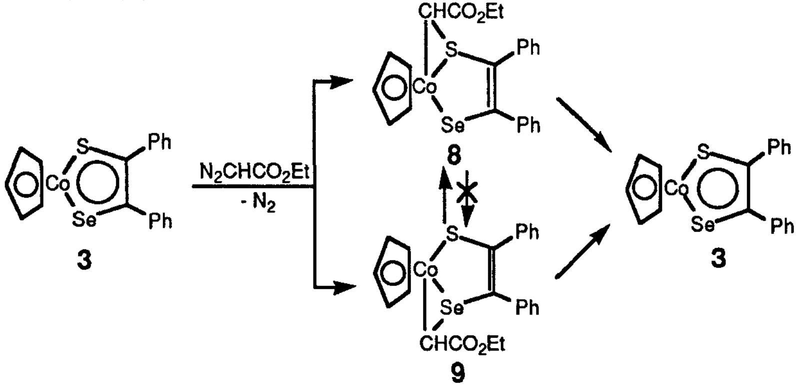
(1)

1; X = S
2; X = Se

4; X = S, R = H
5; X = Se, R = H
6; X = S, R = CO_2Et
7; X = Se, R = CO_2Et

Adducts **4**, **6**, and **7** were isolated as air-stable microcrystalline solids and were spectroscopically characterized, and they satisfied the elemental analysis. Adduct **5** was isolated as a green solid, but it dissociated slightly at room temperature and rapidly on silica-gel to re-generate the parent complex **2**. Adduct **5** was spectroscopically characterized by ^1H NMR. The adduct showed Cp (δ 5.06), CH_2 (δ 2.90 and 4.60), and Ph (δ 7.03 - 7.31) resonances in the expected 5:2:10 intensity ratio in its ^1H NMR, but no parent ion in its EI mass spectra.

The reaction of selenolatothiolato complex **3** with N_2CHCO_2Et under the reflux in benzene gives the two expected adducts **8** and **9** as air-stable crystalline solids in the ratio of **8** / **9** = 36 / 39, but we observed that this ratio increased with the progress of the reaction. The change of the ratio is mainly due to the isomerization of **9** to **8** and to differences of the stabilities of the adducts at that temperature (Scheme 1); the thermal reaction of **9** at 80 °C for 17 h gave **8** (5%), **3** (22%), and **9** (73%), although the reaction of **8** under the same conditions gave **3** (8%) and **8** (92%) (Scheme 1).

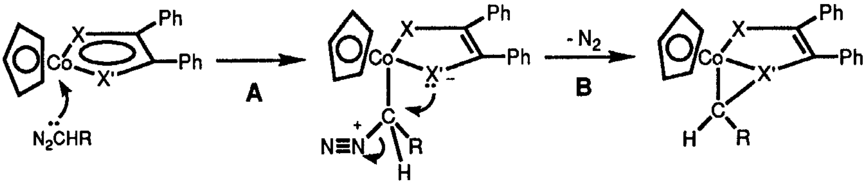


Scheme 1

Compared with the small intramolecular regioselectivity of **3** with N_2CHCO_2Et, there are large differences in intermolecular reactivities for the cycloadditions of **1**, **2**, and **3** with N_2CHCO_2Et. The dichalcogenolene containing more selenium atoms is more reactive. The relative reaction rates of complexes **1**, **3**, and **2** with N_2CHCO_2Et at 40 °C were found to be 1:26:400.

Mechanism for the Addition Reactions.

We have proposed a description for the mechanism of addition reaction of dithiolenes with diazo compounds.[3] The central metal of the dithiolato complexes accepts an electron pair from the carbon atom of the diazo compounds; this is followed by the elimination of N_2, which occurs by nucleophilic attack of sulphur at the alkylidene carbon. The addition reactions of selenium-analogues with diazo compounds can be explained by a similar mechanism.



Scheme 2

The first step (step A) in the reaction is the nucleophilic attack of the negatively charged carbon of the diazo compound to the positively charged Co atom of the complex (Scheme 2). This process determines the intermolecular competition. The reversible half-wave potentials for the one-electron reduction steps of **1**, **2**, and **3**, which are the measures of the positive charges at the cobalt atoms in the dichalcogenolatocobalt(III) complexes, are -1.16, -1.08, and -1.12 V, respectively.[7-8] The dichalcogenolato complex with more positively charged Co atom reacts more easily.

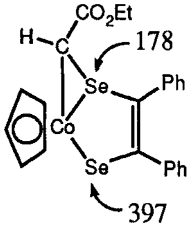
The low regioselectivity in the reaction of the selenolatothiolato complex **3** can be explained by the similar reactivities of S and Se in the second step: nucleophilic attack of the chalcogen to the carbon atom of the diazo compound moiety.

^{77}Se NMR

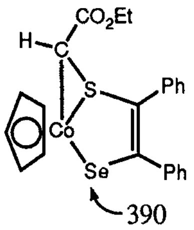
The ^{77}Se NMR showed a dynamic change of chemical shifts through the addition reaction of diselenolene **2** and selenolatothiolato complex **3**. The resonances of two Se nuclei of adduct **7** appear at 178 and 397 ppm; the upfield resonance can be assigned to Se bridged by alkylidene group, because the ^{13}C NMR resonance of the dithiolene ring carbon adjacent to the bridge in the adducts lies significantly upperfield to that of the other carbon.[3, 5] In the same way, the signals at 148 and 390 ppm are assigned to the resonances of Se in **9** and **8**, respectively.

TABLE I ^{77}Se NMR Data of the complexes, in $CDCl_3$ (51.55 MHz; in ppm)

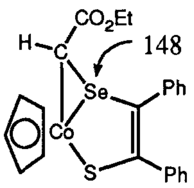
Complexes	Chemical Shift [a]
2; $CpCo(Se_2C_2Ph_2)$	1379
3; $CpCo(SSeC_2Ph_2)$	1387



7



8



9

[a] In ppm from internal diphenyl diselenide (464.1 ppm), measured at room temperature in $CDCl_3$.

EXPERIMENTAL SECTION

General. All reactions were conducted under a pure argon atmosphere with the use of standard Schlenk techniques. All NMR spectra were recorded on a JEOL JNM-GX270 spectrometer. The dithiolatometal complexes **1**- **3** were synthesized according to the literature methods.[7] The adducts **4** and **6** were prepared by the method previously reported.[3] Other solvents and reagents were dried prior to use when necessary with appropriate drying agents.

Preparation of $CpCo(Se_2C_2Ph_2)(CH_2)$ *(5).* A 10-fold excess of N_2CH_2 in ether was added to a solution of **2** (155.6 mg, 0.337 mmol) in ether (100 ml) at 0 °C. The color of the solution changed from green to orange immediately. Removal of the solvent at reduced pressure and recrystallization of the residue from ether gave **5** as an orange solid. This solid was promptly chromatographed on silica-gel to afford **5** in 2.3% yield (3.7 mg, 0.0077 mmol) as a slightly sensitive solid that did not give satisfactory analysis. ^{1}H NMR ($CDCl_3$): δ 2.90 (1 H, d, *J* 1.90 Hz, CH_2), 4.60 (1 H, d, *J* 1.90 Hz, CH_2), 5.06 (5 H, s, Cp), 7.03 - 7.31 (10 H, m, Ph). MS (EI, 70eV): *m/z* (relative intensity) 462 {9, $CpCo(Se_2C_2Ph_2)$}, 284 (58, $CpCoSe_2$), 178 (100, Ph_2C_2), 124 (58, CpCo).

Preparation of $CpCo(Se_2C_2Ph_2)(CHCO_2Et)$ (7). A solution of complex **2** (60.1 mg, 0.130 mmol) and N_2CHCO_2Et (76.0 mg, 0.667 mmol) in benzene (70 cm^3) was refluxed for 3 h, during which time the color changed from blue to green. Removal of solvent at reduced pressure and chromatography of the residue on silica-gel gave **7** as a green crystalline solid in 49% yield (34.8 mg, 0.064 mmol). Decomp. 159 - 164 °C. Anal. Calcd for $C_{23}H_{21}O_2Se_2Co$: C, 50.36; H, 3.83. Found: C, 50.40; H, 3.92. IR (KBr): ν(CO) 1668 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.37 (3 H, t, *J* 7.19 Hz, CH_2CH_3), 3.11 (1 H, s, alkylidene proton), 4.25 (2 H, q, *J* 7.19 Hz, CH_2CH_3), 5.08 (5 H, s, Cp), 7.01 - 7.12 (10 H, m, Ph). ^{13}C NMR ($CDCl_3$): δ 14.7 (CH_2CH_3), 43.8 (J_{CH} 173.3 Hz, alkylidene carbon), 61.1 (CH_2-CH_3), 83.7 (Cp), 122.3 (dithiolene ring), 126.7, 127.3, 127.7, 128.0, 128.5, 129.6, 139.2, 141.7, 156.2 (dithiolene ring), 180.8. MS (EI, 70eV): *m/z* (relative intensity) 548 (3, M^+), 462 (14, M - $CHCO_2Et$), 284 (76, $CpCoSe_2$), 178 (95, Ph_2C_2), 124 (100, CpCo).

Preparation of $CpCo(SSeC_2Ph_2)(CHCO_2Et)$ (8 and 9). A solution of complex **3** (35.7 mg, 0.0982 mmol) and N_2CHCO_2Et (53.0 mg, 0.465 mmol) in benzene (70 cm^3) was refluxed for 3 h, during which time the color changed from blue to green. Removal of solvent at reduced pressure and chromatography of the residue on silica-gel gave two green bands. The first band afforded **8** as a green crystalline solid in 36% yield (15.6 mg, 0.0312 mmol), and the second band yielded **9** as a green crystalline solid in 39% yield (16.6 mg, 0.0332 mmol). **8**: mp 162 - 164 °C. Anal. Calcd for $C_{23}H_{21}O_2SSeCo$: C, 55.32; H, 4.24. Found: C, 55.24; H, 4.17. IR (KBr): ν(CO) 1676 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.38 (3 H, t, *J* 7.20 Hz, CH_2CH_3), 2.51 (1 H, s, alkylidene proton), 4.26 (2 H, q, *J* 7.20 Hz, CH_2CH_3), 5.09 (5 H, s, Cp), 7.01 - 7.16 (10 H, m, Ph). ^{13}C NMR ($CDCl_3$): δ 14.7 (CH_2CH_3), 32.1 (J_{CH} 174.6 Hz, alkylidene carbon), 61.0 (CH_2CH_3), 84.1 (Cp), 122.0 (dithiolene ring), 126.3, 127.5, 127.8, 128.0, 128.8, 129.8, 138.3, 141.1, 158.5 (dithiolene ring), 179.2. MS (EI, 70eV): *m/z* (relative intensity) 500 (8, M^+), 414 (29, M - $CHCO_2Et$), 236 (100, CpCoSSe), 178 (89, Ph_2C_2), and 124 (70, CpCo). **9**: mp 152 - 154 °C. Anal. Calcd for $C_{23}H_{21}O_2SSeCo$: C, 55.32; H, 4.24. Found: C, 55.23; H, 4.27. IR (KBr): ν(CO) 1675 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.37 (3 H, t, *J* 7.20 Hz, CH_2CH_3), 2.77 (1 H, s, alkylidene proton), 4.25 (2 H, q, *J* 7.20 Hz, CH_2CH_3), 5.13 (5 H, s, Cp), 6.99 - 7.08 (10 H, m, Ph). ^{13}C NMR ($CDCl_3$): δ 14.7 (CH_2CH_3), 43.1 (alkylidene carbon), 61.1 (CH_2CH_3), 84.3 (Cp), 117.6 (dithiolene ring), 126.3, 127.5, 127.8, 128.0, 128.8, 129.8, 138.3, 141.1, 162.9 (dithiolene ring), 180.0. MS (EI, 70eV): *m/z* (relative intensity) 414 (20, M - $CHCO_2Et$), 236

(76, CpCoSSe), 178 (100, Ph_2C_2), 124 (56, CpCo).

Thermal Reactions of Adduct 8 and 9; Isomerization of the adducts. A solution of the adduct (**8** or **9**: 0.001 mmol, each) and mesithylene as a standard sample in toluene-d_8 was sealed in NMR sample tube; this was heated at 80 °C. The yields of the products were decided by measuring the integral of the Cp ring proton peak (C_5H_5) of the corresponding complexes by ^1H NMR.

Relative Rates of the Reaction of Dichalchogenolenes with Ethyl Diazoacetate. A solution of complex **1**, **2**, or **3** (0.004 mmol), ethyl diazoacetate (0.030 mmol), and cyclohexane as a standard sample in $CDCl_3$ was sealed in NMR sample tube, and was heated at 40 °C. The relative reaction rates were obtained by measuring the integral of the alkylidene proton peak ($CoCHCO_2Et$) of corresponding adducts by ^1H NMR.

ACKNOWLEDGMENT

This work was supported in part by Grant-in-Aid for Scientific Research on Priority Areas on Organic Unusual Valency No. 02247102 and by Grant-in-Aid for Scientific Research No. 03640464 from the Ministry of Education, Science and Culture, and by Asahi Glass Foundation.

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