Reaction of $[Co(\eta^5\text{-}Cp)I(S_2CNMe_2)]$ with Diazomethane - Formation and Structures of 5-Membered 1,2,4-Cobaltadithiolene by Insertion of Methylene and 4-Membered 1,3-Cobaltathietane Formed by Desulfurization and Insertion of Methylene

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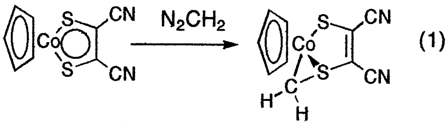
(η^5-Cyclopentadienyl)iodo(*N*, *N*-dimethyldithiocarbamato)-cobalt(III) (**1**) reacts with diazomethane at 0 °C to give two novel complexes: (η^5-cyclopentadienyl)[(dimethylamino)thioxo-κ*S*-methylthiomethanido-κ*C*]iodocobalt(III) having a five-membered 1,2,4-cobaltadithiolene ring and (η^5-cyclopentadienyl)(dimethylaminomethylene-κ*C*-thiomethanido-κ*C*)iodocobalt (III) having a four-membered 1,3-cobaltathiethane ring. The former is formed by insertion of methylene into Co-S bond and the latter by insertion of methylene into Co-S bond, accompanied by desulfurization.

1,1-Dithiocarbamato-,[1] 1,2-ethenedithiolato-,[2] and 1,3-dithioketonatometal[3] complexes are important dithiolatometal complexes with conjugated metallacycles having sulfurs. Among them, 1,2-ethenedithiolatometal complexes have been known to undergo interesting addition-elimination reactions.[4] One of their characteristic reactions is the addition (or insertion) of alkylidenes derived from diazo compounds between the M-S bond in the reaction with diazo compounds.[4] Equation 1 shows an example of this type of reaction.

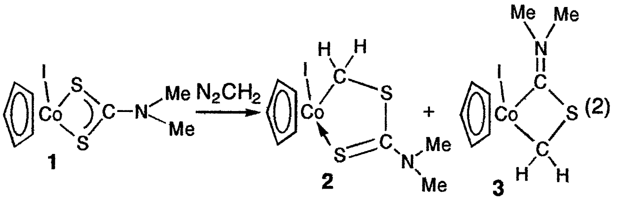


As an extension of this study, we studied the reaction between a four-membered 1,1-dithiolatocobalt complex, (η^5-cyclopentadienyl)(*N*, *N*-dimethyldithiocarbamato)iodocobalt(III) $[Co(Cp)I(S_2CNMe_2)]$ (**1**)[5] and diazomethane (N_2CH_2). No detailed study has been reported on the reactions of dithiocarbamate complexes with diazo compounds, except the report on Mo complexes by Schwarz et al.[6]

An etherial solution of N_2CH_2 (*ca.* 3 mmol) was added to a solution of **1** (0.10 g, 0.26 mmol) in a mixed solvent of ether (45 cm^3) and dichloromethane (30 cm^3) at 0 °C. The color of the solution changed from dark purple to brown within 30 min. The reaction mixture was further stirred for 1 h. After the solvent was removed at reduced pressure, the residue was chromatographed on silica-gel (Wako-gel C300, eluent : CH_2Cl_2) to afford **2** as brown crystalline solid in 18% yield (0.033 g, 0.081 mmol) and **3** as brown crystalline solid in 39% yield (0.036 g, 0.10 mmol) (Eq. 2). Crystals for X-ray structure analysis were obtained by recrystallization (solvent: a mixture of CH_2Cl_2 and hexane).

Their structures were determined by spectral data[7,8] and single crystal X-ray structure analysis.[9,10]

Figures 1 and 2 show the molecular structures of **2** and **3**. Selected bond lengths and bond angles are given in the caption.



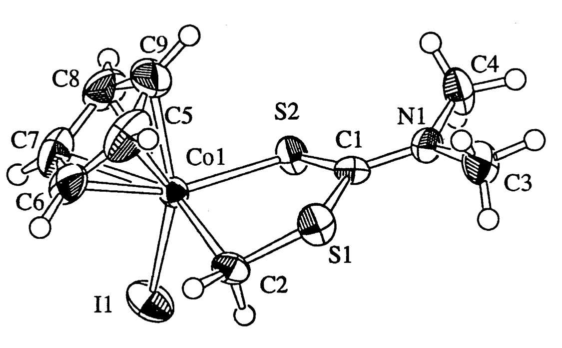


Figure 1. Molecular structure of **2**.
Selected bond lengths (Å) and angles (deg) are as follows: Co(1)-I(1), 2.6100(9); Co(1)-C(2), 1.974(5); Co(1)-S(2), 2.217(1); C(2)-S(1), 1.788(5); S(1)-C(1), 1.738(4); S(2)-C(1), 1.694(5); I(1)-Co(1)-C(2), 92.7(1); I(1)-Co(1)-S(2), 94.92(4); C(2)-Co(1)-S(2), 87.0(1); Co(1)-C(2)-S(1), 112.5(2); C(2)-S(1)-C(1), 99.4(2); S(1)-C(1)-S(2), 118.8(3); C(1)-S(2)-Co(1), 103.3(2); Cp-Co, 1.700.

The minor product, complex **2**, consists of a Cp ring, a coordinated I, and a five-membered 1,2,4-cobaltadithiolene ring.

The bond length of 2.6100(9) Å for Co(1)-I(1) suggests that I is coodinated to Co, although it is somewhat longer than that of the starting complex **1** (2.597(1) Å) reported by Manning et al.[11] The bond length of S(2)-C(1) is 1.694(5) Å, which shows its double-bond character. The length of Co(1)-C(2) (1.974(5) Å) is shorter than that of the six-membered 1,2,5-cobaltadithiin, $CpCo[P(OMe)_3][\eta^2\text{-}(S, C')\text{-}SC(CN){=}C(CN)S\text{-}C'H_2]$ (2.011(8) Å);[4] both complexes are nevertheless ring-expanded complexes due to the CH_2 insertion into the Co-S bond.

Complex **2** is regarded as a methylene insertion product. Methylene inserts between Co and S. This type of reaction is fundamentally similar to that between a cobaltadithiolene complex and diazomethane, although in the latter case a cobaltathiirane ring is formed.[4]

The major product, complex **3** $[CpCoI(C(NMe_2)SCH_2)]$, consists of a Cp ring, a coordinated I, and a four-membered 1,3-cobaltathiethane ring.

Complex **3** has the following structural features. The bond length of Co(1)-C(2) (1.892(4) Å) is somewhat shorter than that of Co(1)-C(1) (2.000(4) Å) near to that of Co(1)-C(2) (1.974(5)

Å) of complex **2**. Although the C(2) carbon may be regarded as the carbene carbon atom in "Fischer-type" carbene complex, its chemical shift (δ = 224.7) of ^{13}C NMR does not agree with this expectation. The C(2)-N(1) bond (1.308(5) Å) shows its double bond character. The Co(1)-I(1) (2.5629(7) Å) bond is coordinative.

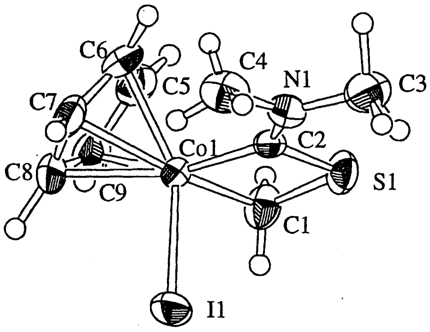


Figure 2. Molecular structure of **3**.
Selected bond lengths (Å) and angles (deg) are as follows: Co(1)-I(1), 2.5629(7); Co(1)-C(1), 2.000(4); Co(1)-C(2), 1.892(4); C(1)-S(1), 1.796(5); S(1)-C(2), 1.717(4); C(2)-N(1), 1.308(5); N(1)-C(3), 1.452(6); N(1)-C(4), 1.459(6); I(1)-Co(1)-C(1), 93.2(1); I(1)-Co(1)-C(2), 91.3(1); C(1)-Co-C(2), 76.4(2); Co(1)-C(1)-S(1), 95.1(2); C(1)-S(1)-C(2), 86.6(2); S(1)-C(2)-Co(1), 101.9(2); Cp-Co, 1.719.

As an interesting ^{13}C NMR behavior, the ^{13}C NMR signal of methylene (CH_2) in the cobaltathietane ring appears at very high field (δ = -25.0), while that of complex **2** shows normal chemical shift (δ = 10.60).

Complex **3** is a new type product which has not been obtained in the reaction of cobaltadithiolene with diazomethane and is formed by the insertion of methylene accompanied by desulfurization.

Our attempt to obtain **3** from **2** with N_2CH_2 in a mixed solvent of Et_2O and CH_2Cl_2 was unsuccessful. Although the formation mechanism of **3** is not yet clear, both a desulfurization and an insertion of methylene into Co-S bond should occur in the formation of **3**.

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7 [Co(Cp)I{$S_2C(NMe_2)CH_2$}] **2**: Brown crystals, Mp 153 °C (decomp.), ^{1}H NMR(270 MHz, $CDCl_3$, TMS): δ= 4.81 (d, 1H, CH_2, ^2J(HH)=7.63 Hz), 5.63(d, 1H, CH_2, ^2J (HH)=7.63 Hz), 2.39(d, 1H, ^2J (HH)=13.43 Hz), 3.34 (s, 3H, CH_3), 3.51(s, 3H, CH_3), and 5.00(s, 5H, C_5H_5). ^{13}C NMR(67.94 MHz, $CDCl_3$, TMS): δ=10.60 (CH_2), 44.46(CH_3), 47.55(CH_3), 84.69 (C_5H_5), and 212.27 (CN). UV/VIS (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ 625 nm (597), 514 (1042), 264 (19243), and 208 (2945). IR(KBr): 3099 (s), 2903(s), 1526(s), 835(s), and 554(s). MS(EI, 70 eV): m/z 257 (41.5, M^+) and 212(63.3, M^+-I-S). MS (FAB, 70 eV): m/z 386(M^++1), 258(M^+-I), and 244(M^+-I-CH_2), 212(M^+-I-CH_2S). Found: N, 3.47; C, 28.28; H, 3.43. Calcd for $C_9H_{13}NS_2ICo$: N, 3.64; C, 28.06; H, 3.4.

8 [Co(Cp)I{$C(NMe_2)SCH_2$}] **3**: Brown crystals, Mp 163 °C, ^{1}H NMR (270 MHz, $CDCl_3$, TMS): δ=1.82 (d, H, ^2J(HH)=3.41 Hz), 2.59 (d, H, ^2J(HH)=3.41 Hz), 3.21 (s, 3H, CH_3), 3.76 (s, 3H, CH_3), and 4.87 (s, 5H, C_5H_5). ^{13}C NMR (67.94 MHz, $CDCl_3$, TMS): δ=-25.0 (CH_2), 42.3 (CH_3), 48.0 (CH_3), 85.8 (C_5H_5), and 224.6(CN). IR (KBr): 2930(s), 1553(s) (C=N), 1406(s), 1157(s), 1008(s), 810(s), and 540 (s) cm^{-1}. UV/VIS (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ 478 nm(1455), 245(2010), and 215 (2395). MS(EI, 70 eV): m/z 353(96.6, M^+), 307(66.9, M^+-SCH2), 226 (74.9, M^+-I), 212(20.3, M^+-I-CH2), 127(13.9, I), and 124(65.2, CpCo). MS (FAB, 70 eV): m/z 354(M^++1), 353(M^+), and 226(M^+-I). Found: N, 3.91; C, 30.65; H, 3.91%. Calcd for $C_9H_{13}NSICo$: N, 3.97; C, 30.59, H, 3.68%.

9 Crystal structure data for **2**: A dark-brown prismatic crystal of $C_9H_{13}NS_2ICo$ (F.W.=385.17), monoclinic, space group $P2_1/n$(#14), a=6.209(2) Å, b=19.276(3) Å, c=10.478(3) Å, β=98.55(3)°, V=1240.1(5) Å^3, Z=4, Dc= 2.063 g cm^{-3}, $\mu(MoK\alpha)$=41.74 cm^{-1}, F_{000}=744.00, R= 0.035 (Rw=0.025) on 2110 intensities ($|F_o| > 3s|F_o|$).

10 Crystal structure data for **3**: A dark-brown prismatic crystal of $C_9H_{13}NCoIS$ (F.W.=353.11), monoclinic, space group $P2_1/n$(#14), a=7.330(2) Å, b=12.348(2) Å, c=12.932(2) Å, β=93.16(2)°, V=1168.7(4) Å^3, Z=4, Dc=2.007 g cm^{-3}, $\mu(MoK\alpha)$=42.47 cm^{-1}, F_{000}=680.00, and R=0.031 (R_w=0.032) on 2235 intensities ($|F_o| > 3s|F_o|$).

11 Selected bond lengths of **1** in E. P. Cullen, J. Doherty, and A.R. Manning, *J. Organomet. Chem.*, **348**, 109 (1988): Co-I, 2.597(1); Co-S, 2.49(1) and 2.255(1); S-C, 1.716(5) and 1.697(5); C-N, 1.473(8).