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Structure Changes Due to Metal−S and Metal−C Bond Cleavages in the Reactions of Alkylidene-Bridged Cobaltadithiolenes with Trimethyl Phosphite

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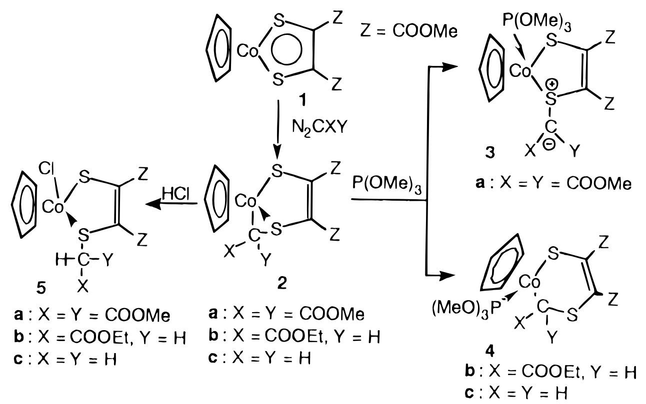
Summary: The reaction of an alkylidene-bridged dithiolene complex, (η^5-cyclopentadienyl){2-[(bis(methoxycarbonyl)methanido)thio-$\kappa C,\kappa S$]-1,2-bis(methoxycarbonyl)ethenethiolato-κS}cobalt(III), with trimethyl phosphite results in the formation of a novel type of sulfonium ylide coordinated to a cobalt atom, (η^5-cyclopentadienyl){2-[(bis(methoxycarbonyl)methylene)-λ^4-thio-κS]-1,2-bis(methoxycarbonyl)ethenethiolato-κS}(trimethyl phosphite)cobalt(III). The structure has been established by X-ray crystallographic analysis.

The metalladithiolene ring in [CpM($S_2C_2Z_2$)]-type complexes is a very unique metallacycle; a variety of organic species, such as alkynes,[1] quadricyclane,[2] and azides,[3] are known to insert into the M−S bond. Diazo compounds N_2CXY react with cobaltadithiolene complexes [CpCo($S_2C_2Z_2$)] to give alkylidene-bridged complexes [CpCo($S_2C_2Z_2$)(CXY)], containing a Co−C−S three-membered ring (cobaltathiirane).[4] We have reported the structural changes in alkylidene-bridged complexes due to two types of bond cleavage, as shown in Scheme 1: one is the cleavage of the Co−C bond in the reactions with protic acids to give a 1:1:1 adduct having an *S*-alkyl moiety;[5] the other is that of the Co−S bond in the reaction of [CpCo($S_2C_2(CN)_2$)(CH_2)] with a Lewis base (P(OMe)$_3$) to give a 1:1:1 adduct, in which the addition of the P(OMe)$_3$ to the Co atom causes ring expansion to give a six-membered metallacycle (see Scheme 1).[6]

Scheme 1



Here we report a novel type of 1:1:1 adduct, (η^5-cyclopentadienyl){2-[(bis(methoxycarbonyl)methylene)-λ^4-thio-κS]-1,2-bis(methoxycarbonyl)ethenethiolato-κS}(trimethyl phosphite)cobalt(III) ([CpCo($S_2C_2Z_2$)(CZ_2)(P(OMe)$_3$)] (Z = COOMe; **3a**).[7] This compound has a sulfonium ylide moiety resulting from the cleavage of a Co−S bond in the reaction of P(OMe)$_3$ with the alkylidene-bridged complex [CpCo($S_2C_2Z_2$)(CZ_2)], which is formed by the reaction of (η^5-cyclopentadienyl)[1,2-bis(methoxycarbonyl)ethenedithiolato-$\kappa S,S'$]cobalt(III) (**1**) with dimethyl diazomalonate.[8] One previous example of a similar ylide complex was reported by Seyferth et al.[9] In this complex, there is a carbon atom between the sulfur and the metal, whereas in our complex the sulfur atom of the sulfonium group is bonded to the metal. To our knowledge, this type of adduct is a very rare example of an organometallic compound with a sulfonium group bonded through sulfur to the metal. In this study, the structure of the novel 1:1:1 adduct was determined by X-ray crystal structure analysis, together with the original alkylidene-bridged complex **2a** and another type of 1:1:1 adduct (a ring-expanded complex, **4b**).

The reaction of the dithiolene complex **1** with dimethyl diazonmalonate, to give the alkylidene-bridged

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(7) [CpCo{S_2C_2(COOMe)$_2$C(COOMe)$_2$}(P(OMe)$_3$)] (**3a**): ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 3.63 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.92 (d, 9H, J_{PH} = 10.98 Hz, P(OCH_3)$_3$), 5.22 (s, 5H, C_5H_5); ^{13}C NMR (270 MHz, $CDCl_3$, TMS, −10 °C) δ 14.25 (alkylidene carbon), 49.97 (OCH$_3$), 50.37 (OCH$_3$), 51.59, 52.24 (OCH$_3$), 54.17 (J_{PC} = 7.3 Hz, P(OCH$_3$)$_3$), 90.96 (J_{PC} = 12.4 Hz, C_5H$_5$), 120.13 (J_{PC} = 6.1 Hz, dithiolene ring carbon), 160.66, 166.62, 165.69, 165.86, 166.07; MS (FAB, 70 eV) *m/z* (relative intensity) 585 (M^+ + 1), 584 (M^+); UV−vis (benzene) λ_{max} (ϵ) 288 (14 260), 368 (7460), 584 (3700); IR (KBr) 1736 (s), 1697 (s), 1620 (m), 1528 (m), 1489 (w), 1435 (m), 1350 (m), 1323 (m), 1248 (s), 1182 (m), 1126 (m), 1082 (m), 1028 (s) cm^{-1}.

(8) A solution of **1** and dimethyl diazomalonate (N_2C(COOMe)$_2$) in benzene was refluxed for 24 h with CuI−P(OMe)$_3$ or one of several other Cu catalysts. After the solvent was removed under reduced pressure, the residue was chromatographed on silica gel (Wako-gel C300; eluent dichloromethane) and then the product was further submitted to HPLC (LC-08 produced by Japan Anal. Ind. Co. Ltd.; column JAIGEL-H, eluent $CHCl_3$). The alkylidene-bridged complex **2a** was obtained as a dark purple crystalline solid in 28% yield (Cu powder, 20% yield; $CuSO_4$, trace). P(OMe)$_3$ (3.81 × 10^{-4} mol) was added to a solution of **2a** (2.17 × 10^{-4} mol) in CH_2Cl_2. The suspension was vigorously stirred under an argon atomosphere for 24 h. The color of the solution changed immediately from black to purple. After the reaction, the solvent was removed at reduced pressure and the residue was recrystallized from CH_2Cl_2/hexane (1/1 v/v). Dark purple crystals of **3a** were obtained in 61% yield.

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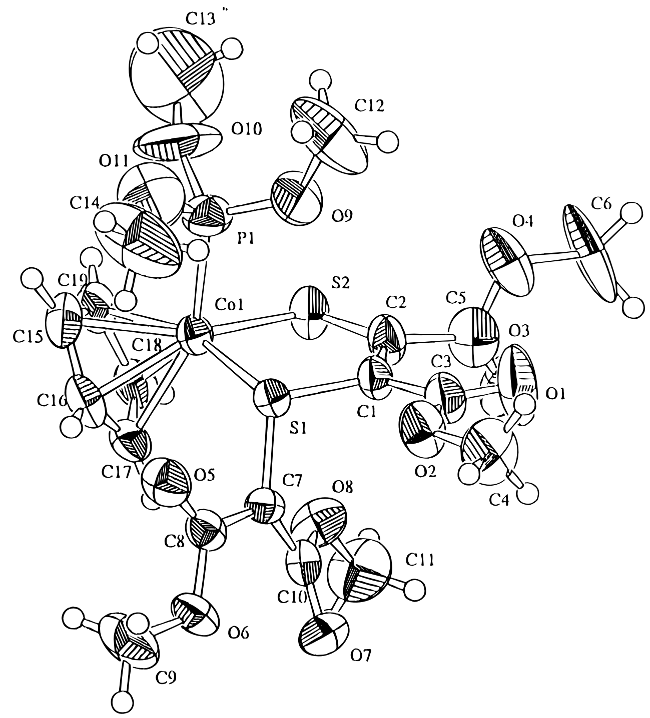

Figure 1. Molecular structure of **3a**. Selected bond lengths (Å) and angles (deg) are as follows: Co−S(1), 2.248(1); Co−S(2), 2.215(1); S(1)−C(1), 1.770(4); S(2)−C(2), 1.714(5); C(1)−C(2), 1.331(6); S(1)−C(7), 1.730(4); Cp−Co, 1.707; S(1)−Co−S(2), 90.26(5); Co−S(1)−C(1), 102.8(1); Co−S(2)−C(2), 102.2(2); S(1)−C(1)−C(2), 118.1(4); S(2)−C(2)−C(1), 125.4(4); Co−S(1)−C(7), 116.7(1); C(1)−S(1)−C(7), 105.7(2); S(1)−C(7)−C(8), 111.4(3); S(1)−C(7)−C(10), 123.7(4); C(8)−C(7)−C(10), 124.4(4).

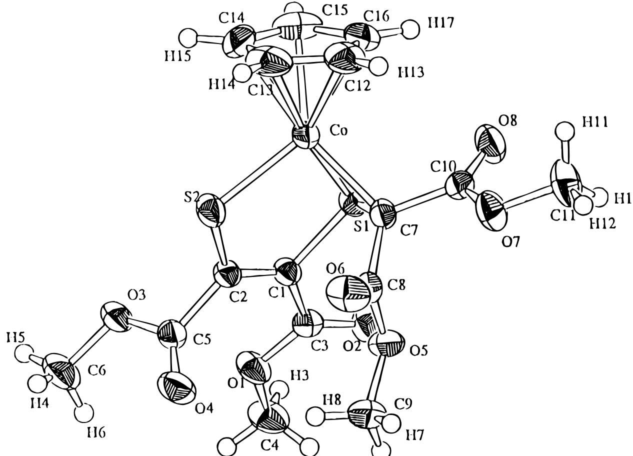

Figure 2. Molecular structure of **2a**. Selected bond lengths (Å) and angles (deg) are as follows: Co−S(1), 2.182(1); Co−S(2), 2.216(1); S(1)−C(1), 1.765(2); S(2)−C(2), 1.703(2); C(1)−C(2), 1.361(3); S(1)−C(7), 1.794(3); Co−C(7), 2.001(2); Cp−Co, 1.681; S(1)−Co−S(2), 91.77(3); Co−S(1)−C(1), 103.29(8); Co−S(2)−C(2), 102.40(8); S(1)−C(1)−C(2), 118.9(2); S(2)−C(2)−C(1), 123.5(2); Co−S(1)−C(7), 59.50(8); C(1)−S(1)−C(7), 105.2(1); S(1)−Co−C(7), 50.56(7).

complex **2a**, requires a catalyst such as CuI−P(OMe)$_3$ or Cu powder (CuI−P(OMe)$_3$, 28% yield; Cu powder, 20% yield); however, other diazo compounds reacted readily with the dithiolene complex **1**. The alkylidene-bridged complex **2a** reacted readily with (P(OMe)$_3$) to give the 1:1:1 adduct **3a** as dark purple crystals in 61% yield.

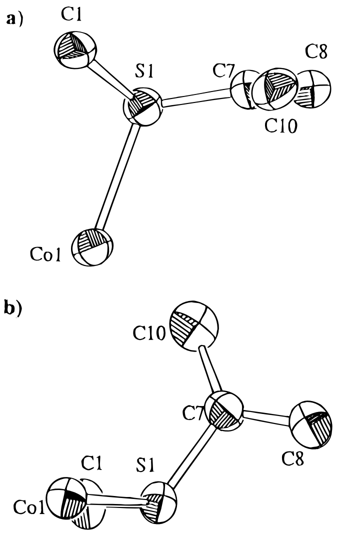

Figure 3. Structure of sulfonium ylide moiety: (a) around carbon atom (planar); (b) around sulfur atom (pyramidal).

The molecular structures of **3a**[10] and the original complex **2a**[11] were determined by X-ray crystal structure analysis and are shown in Figures 1 and 2. Selected bond lengths and bond angles are given in the captions. The nearly planar five-membered cobaltadithiolene ring is retained in **3a**. Coordination of P(OMe)$_3$ to the Co atom causes the cleavage of the Co−C bond of the alkylidene (CZ$_2$) to give the sulfonium ylide structure. As is predictable from the structure of **2a** in Figure 2, the direction of phosphite is perpendicular to the dithiolene ring from the opposite direction of CZ$_2$. The C(1)−C(2) bond length (1.331(6) Å) is slightly shorter than the corresponding value in the original complex **2a** (1.361(3) Å). The S(1)−C(7) bond length (1.730(4) Å) is shorter than the corresponding value in the original complex **2a** (1.794(3) Å).

The above results suggest an extensive charge delocalization of the carbanion in the C−S bond of the sulfonium ylide. The C(7)−S(1) bond length (1.73 Å)

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(10) Crystal structure data for **3a**: dark purple prismatic crystal, $C_{19}H_{26}S_2O_{11}CoP$ (fw = 584.43), monoclinic, space group $P2_1/a$ (No. 14), $a = 9.816(3)$ Å, $b = 17.271(4)$ Å, $c = 14.689(3)$ Å, $\beta = 93.57(2)°$, $V = 2485(1)$ Å^3, $Z = 4$, $D_c = 1.562$ g cm^{-3}, μ(Mo Kα) = 9.78 cm^{-1}, $F_{000} = 1208.00$, $R = 0.042$ ($R_w = 0.030$) on 2528 intensities ($|F_o| > 3.00\sigma|F_o|$).

(11) Crystal structure data for **2a**: dark purple cubic crystal, $C_{16}H_{17}S_2O_8Co$ (fw = 460.36), triclinic, space group $P\bar{1}$ (No. 2), $a = 7.989(5)$ Å, $b = 15.861(6)$ Å, $c = 7.616(4)$ Å, $\alpha = 95.09(4)°$, $\beta = 100.68(4)°$, $\gamma = 98.89(4)°$, $V = 930.0(9)$ Å^3, $Z = 2$, $D_c = 1.644$ g cm^{-3}, μ(Mo Kα) = 11.89 cm^{-1}, $F_{000} = 472.00$, $R = 0.036$ ($R_w = 0.029$) on 3624 intensities ($|F_o| > 3.00\sigma|F_o|$).

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(14) [Co(Cp){$S_2C_2(COOMe)_2$(CHCOOEt)(P(OMe)$_3$)}] (**4b**): mp 136−138 °C dec; ^{1}H NMR (270 MHz, CDCl$_3$, TMS) δ 1.34 (t, 3H, $J_{HH} = 7.3$ Hz, CH$_2$CH_3), 3.05 (d, 1H, $J_{PH} = 7.3$ Hz, CH), 3.74 (d, 9H, $J_{PH} = 10.38$ Hz, P(OCH_3)$_3$), 3.75 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 4.15−4.34 (m, 2H, CH_2CH$_3$), 4.94 (s, 5H, C$_5H_5$); ^{13}C NMR (270 MHz, CDCl$_3$, TMS) δ 14.50 (CH$_2$$CH_3$, $J_{CH} = 127$ Hz), 28.04 (alkylidene carbon, $J_{PC} = 25.6$ Hz, $J_{CH} = 58.1$ Hz), 52.36 (OCH$_3$, $J_{CH} = 147.7$ Hz), 53.05 (OCH$_3$, $J_{CH} = 147.7$ Hz), 54.31 (P(OCH$_3$)$_3$, $J_{PC} = 8.5$ Hz, $J_{CH} = 147.7$ Hz), 60.52 (CH$_2$CH$_3$, $J_{CH} = 294.2$ Hz), 91.21 (C_5H$_5$, $J_{PC} = 2.4$ Hz, $J_{CH} = 180.7$ Hz), 122.53 (dithiolene ring carbon, $J_{PC} = 6.1$ Hz), 46.27 ($J_{PC} = 4.9$ Hz), 164.69, 169.84 ($J_{PC} = 3.7$ Hz), 180.15 ($J_{PC} = 2.5$ Hz); MS (FAB, 70 eV) *m/z* (relative intensity) 541 ($M^+ + 1$), 540 (M^+); UV−vis (benzene) λ_{max} (ϵ) 300 (10 225), 345 (12 299), 520 (974). Anal. Calcd for $C_{18}H_{26}S_2O_9PCo$: C, 40.01; H, 4.85. Found: C, 40.09; H, 5.02.

(15) Crystal structure data for **4b**: dark purple prismatic crystal of $C_{18}H_{26}S_2O_9CoP$ (fw = 540.42), monoclinic, space group $P2_1/n$ (No. 14), $a = 12.961(4)$ Å, $b = 8.085(3)$ Å, $c = 22.111(2)$ Å, $\beta = 90.48(1)°$, $V = 2316(1)$ Å^3, $Z = 4$, $D_c = 1.549$ g cm^{-3}, μ(Mo Kα) = 10.36 cm^{-1}, $F_{000} = 1120.00$, $R = 0.049$ ($R_w = 0.031$) on 2228 intensities ($|F_o| > 3.00\sigma|F_o|$).

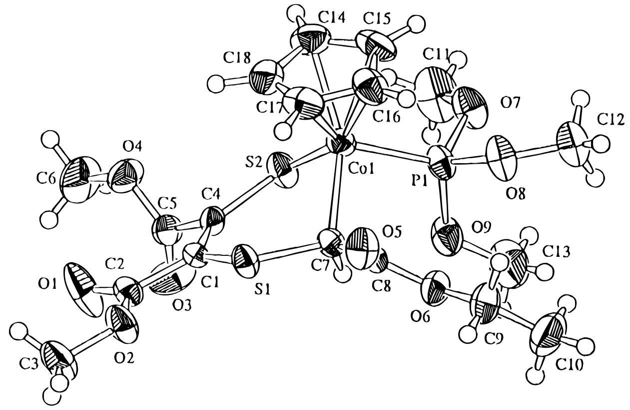
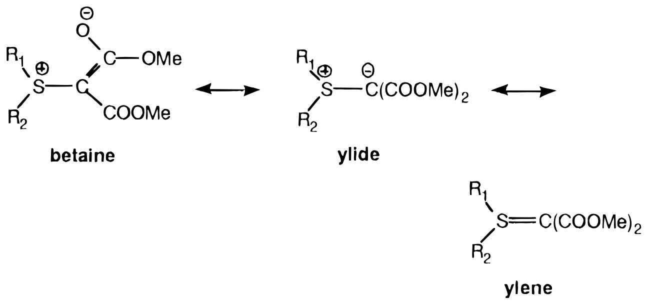


Figure 4. Molecular structure of **4b**. Selected bond lengths (Å) and angles (deg) are as follows: Co−S(2), 2.234(2); Co−C(7), 2.019(6); S(1)−C(7), 1.799(5); S(1)−C(1), 1.751(6); S(2)− C(4), 1.721(6); Co−P, 2.155(2); Cp−Co, 1.693; S(2)−Co−C(7), 87.7(2); C(1)−S(1)−C(7), 103.6(3); Co−S(2)−C(4), 111.8(2); Co−C(7)−S(1), 112.3(3); S(2)−Co−P(1), 94.67(7); P(1)−Co−C(7), 92.3(2).

lies between the normal C−S single-bond length (1.81 Å) and the normal C=S double-bond length (1.66 Å).[12] The S−CC$_2$ group is found to be planar, and the sulfur atom displays a pyramidal structure (see Figure 3).[13,14]

When the COOMe group was used as the substituent on the dithiolene ring, the reactivities of the alkylidene-bridged complexes with P(OMe)$_3$ were found to be strongly dependent on the alkylidene moiety substituents. When X = Y = H and X = H, Y = COOEt were used as substituents on the alkylidene moiety, the ring-expanded 1:1:1 adducts were obtained selectively. The structure of the latter adduct, [CpCo(S$_2$C$_2$Z$_2$)(CHCOOEt)(P(OMe)$_3$)] (**4b**), was determined by an X-ray crystal structure analysis (see Figure 4).[15]

Scheme 2



The 1:1:1 adduct having a sulfonium ylide moiety is obtained selectively when X = Y = COOMe. The ylide structure is visualized as a hybrid resonance between betaine and ylene structures. This fact provides evidence that extensive delocalization of the negative charge is caused by the electron-withdrawing methoxycarbonyl group; this leads to the predominance of a betaine structure stabilizing the ylide structure. Therefore, the stabilization of the sulfonium ylide structure by the addition of P(OMe)$_3$ is important in forming this stable sulfonium ylide adduct which contains strong electron-withdrawing substituents.

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Supporting Information Available: Tables giving crystal data and refinement details, positional and thermal parameters, and bond distances and angles for **2a**, **3a**, and **4b** (32 pages). Ordering information is given on any current masthead page.

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