Cleavage of Co-C Bond in a Cobaltathiirane by Hydrogen Chloride and Reformation of Co-C Bond by Tetrabutylammonium Fluoride

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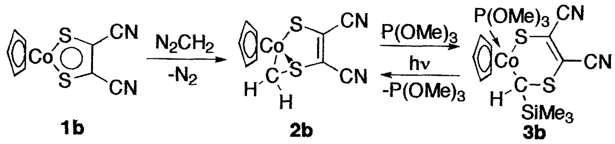
The cobaltadithiolene complex, (η^5-cyclopentadienyl)(1-methoxycarbonyl-1,2-ethenedithiolato)cobalt(III) (**1a**) reacts with trimethylsilyldiazomethane by formal addition of Me_3SiCH to the Co-S bond to afford a cobaltathiirane (**2a**). Addition of hydrogen chloride to **2a** causes the cleavage of the Co-C bond to give chloro(η^5-cyclopentadienyl)[[1-(trimethylsilyl)methylthio-κ*S*]-1-methoxycarbonylethene-2-thiolato-κ*S*]cobalt(III)(**4a**). By the reaction with tetrabutylammonium fluoride in THF, **4a** undergoes loss of Cl and Me_3Si to afford (η^5-cyclopentadienyl)-[(methylene-κ*C*-thio-κ*S*)-1-methoxycarbonylethene-2-thiolato-κ*S*]cobalt(III) (**2c**).

A metalladithiolene ring in $[CpM(S_2C_2XY)]$-type complexes is a very unique metallacycle: a variety of organic species insert into the M-S bond.[1-3] Diazo compounds react by loss of N_2 to give metallathiiranes.[2] These may react further in different ways. By UV-irradiation, thermolysis, and electrochemical oxidation, some metallathiiranes eliminate the alkylene moiety to reform the metalladithiolene complexes, although their reactivities depend on the substituents on the metalladichalcogenolene rings.[2] Another type of reaction is the addition of phosphines or phosphites to the central metal, accompanied by opening of the M-S bond.[4] Scheme 1 summarizes these reactions for the case of the cobaltadithiolene (**1b**). UV-irradiation causes elimination of the phosphite to reform the Co-S bond to give the cobaltathiirane **2b**.[5]

Scheme 1.



We report here another type of bond cleavage in the cobaltathiirane **2a** caused by hydrogen chloride, and also describe a ring reforming reaction of the three-component-adduct $[CpCoCl\{S\{CH_2(SiMe_3)\}C(COOMe){=}CHS\}]$ (**4a**) induced by tetrabutylammonium fluoride (TBAF) to afford **2c** (see Scheme 2). The reactivities of **2a** with HCl or $P(OMe)_3$ was found to strongly depend on the kinds of substituents present.

A solution of **1a** (0.1859 g, 0.683 mmol) and $N_2CHSiMe_3$ (2.46 mmol) in dichloromethane (20 cm^3) was refluxed for 20 h. The color of the solution changed from purple to brown. After the solvent was removed at reduced pressure, the residue was chromatographed on silica-gel (Wako-gel C300, eluent : CH_2Cl_2) to afford **2a** as a brown crystalline solid in 90% yield (0.22 g, 0.615 mmol).[6] Hydrochloric acid (12 mol dm^{-3}, 0.1 cm^3) was added to a solution of **2a** (0.0651 mmol) in CH_2Cl_2 (20 cm^3). The suspension solution was vigourously stirred for 1 h. The reaction was accompanied by a readily observable color change from brown to blue-violet. After the reaction mixture was neutralized by an aquous solution of $NaHCO_3$, and extracted with CH_2Cl_2, a blue-violet solid was obtained by flash-column chromatography on silica-gel (Wako-gel C300). After recrystal-lization from CH_2Cl_2/hexane (v/v=4/1), blue-violet crystals of **4a** were obtained in 72% yield.[7] Figure 1 shows the molecular structure of **4a**.[8] Selected bond lengths and bond angles are given in the caption.

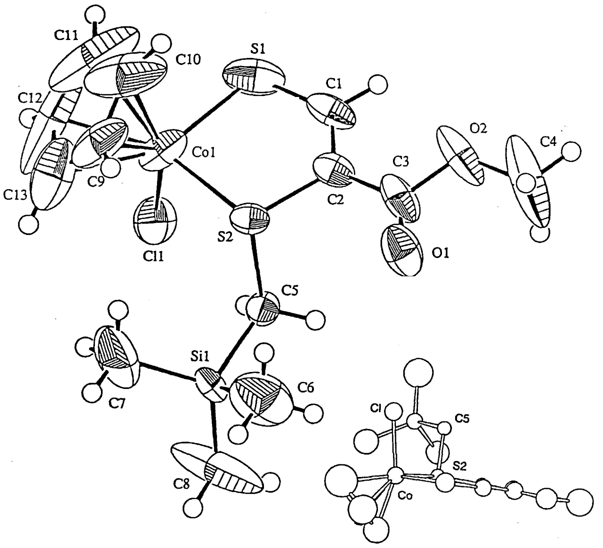


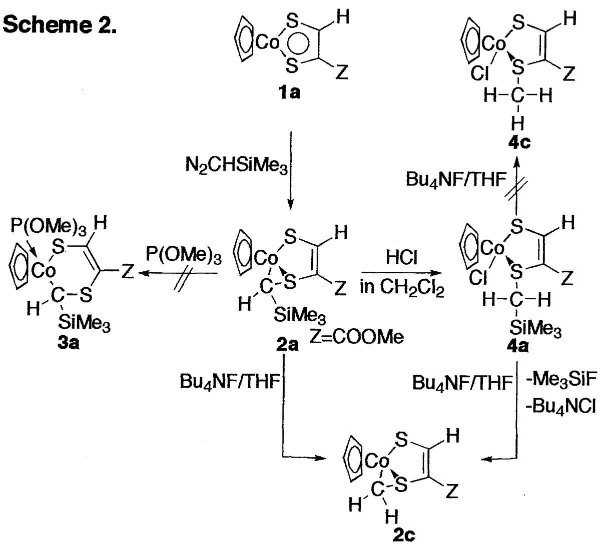
Figure 1. Molecular structure of **4a**.
Selected bond lengths (Å) and angles (deg) are as follows: Co-Cl, 2.238(3); Co-S(1), 2.240(3); Co-S(2), 2.260(2); S(1)-C(1), 1.70(1); S(2)-C(2), 1.770(8); C(1)-C(2), 1.32(1); S(2)-C(5), 1.814(7), Cl-Co(1)-S(1), 93.5(1); Cl-Co(1)-S(2), 97.40(9); S(1)-Co-S(2), 90.1(1); Co-S(1)-C(1), 102.2(3); CO-S(2)-C(2), 102.2(2); S(1)-C(1)-C(2), 125.9(8); C(1)-C(2)-S(2), 119.3(8); Co-S(2)-C(5), 111.6(3); C(2)-S(2)-C(5), 103.6(3).

In contrast to the six-membered trimethylphosphite adduct **3b**,[5] the almost planar five-membered cobaltadithiolene ring is retained in **4a**. The Me_3SiCH_2 group is bonded to S(2) and the Cl atom to the Co atom, as indicated by the short Co-Cl distance (2.238(3) Å). Both Me_3SiCH_2 and Cl groups are almost perpendicular to the plane of the cobaltadithiolene ring. The bond length of Co-S(1) (2.240(3) Å) is shorter than that of Co-S(2) (2.260(2) Å). This differs from the molecular structure of the cobaltathiirane $[CpCo\{CH(COOMe){-}SC(COOMe){=}CHS\}]$,[2] wherein the bond length of CH(COOEt)-bridged Co-S is longer (2.214(3) Å) than that of the non-bridged Co-S (2.185(2) Å) in the cobaltathiirane ring. The bond length (1.32(1) Å) of C(1)-C(2) is typical for the normal C=C bond.

The new hydrogen atom substituted at the Me_3SiCH_2 group comes from the proton of the added HCl: when DCl was used, a deuterium atom appeared at the methylene moiety (*C*DH: δ=23.7, t, *J* (CD)= 22.1 Hz) in the $^{13}C\{^1H\}$ NMR spectra of $[CpCoCl\{S\{CDH(SiMe_3)\}C(COOMe)=CHS\}]$. In the ^{13}C NMR the C5-signal appeared at δ 31.04 (*J* (CH)=144.0 Hz), and was shifted up-field (δ =23.58, *J*(CH)=133.3 Hz) in **4a**. The chemical shifts of carbon and protons in the Cp-ring are shifted down-field (δ=5.45) by the formation of Co-Cl bond.

In the reaction of **2a** with tetrabutylammonium fluoride (TBAF) in THF, the $CHSiMe_3$ group was converted to CH_2 to give the new cobaltathiirane **2c** in ca. 20% yield together with 36% recovery of the original complex **1a**.[9-10] In contrast, **2c** was the only product (75%) when **4a** was reacted with TBAF.[11] This formation of **2c** was unexpected , since it seemed more likely that the $S\text{-}CH_3$ adduct (**4c**) would be obtained. This novel desilylation reaction of **4a** with Bu_4NF is under further investigation.

Scheme 2.



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6 $[CpCo\{CH(SiMe_3)SC(COOMe)=CHS\}]$ **2a**: Mp 96-98 °C, ^1H NMR (270 MHz, $CDCl_3$, TMS): δ=0.16 (s, 9H, $Si(CH_3)_3$), 1.22 (d, 1H, C*H*, ^5J (HH)=1.48 Hz), 3.67 (s, 3H, OCH_3), 5.05 (s, 5H, C_5H_5) and 7.87 (d, 1H, C=C*H*, ^5J (HH)=1.48 Hz). ^{13}C NMR (67.94 MHz, $CDCl_3$, TMS): δ=0.27 ($Si(CH_3)_3$), 30.36 (alkylene carbon), 51.77 (OCH_3), 81.97 (C_5H_5), 119.68(*C*=CH), 163.27 (*C*OOMe), and 171.37 (C=*C*H). IR (KBr): 1688(s), 1478(s), 1255(s), 1183(m), 1049(s), 861(m), and 748(m) cm^{-1}. MS (EI, 70 eV): m/z (relative intensity) 358(71, M^+), 272(11, $M^+\text{-}CHSiMe_3$), 188(15, $CpCoS_2^+$), and 73(100, $SiMe_3$). UV/VIS(CH_2Cl_2): λ_{max}(log ε) 513.2 nm(3.10), 384.8(3.31), and 255.2 (4.15). Found: C, 39.55; H, 5.09%. Calcd for $C_{13}H_{19}O_2SiCoS_2$: C, 39.54, H, 5.11%.

7 $[CpCoCl\{S\{CH_2(SiMe_3)\}C(COOMe)=CHS]$ **4a**: Mp 112-115 °C(decomp.), ^1H NMR(270 MHz, $CDCl_3$, TMS): δ=0.31(s, 9H, $Si(CH_3)_3$), 1.58(d, 1H, ^2J (HH)=13.43 Hz), 2.39(d, 1H, ^2J (HH)=13.43 Hz), 3.79(s, 3H, OCH_3), 5.45(s, 5H, C_5H_5), and 7.77(s, 1H, C=C*H*). ^{13}C NMR(67.94 MHz, $CDCl_3$, TMS): δ= -1.40($Si(CH_3)_3$), 23.58(CH_2SiMe_3), 52.08(OCH_3), 86.74 (C_5H_5), 123.22 (dithiolene ring carbon), 162.84 (*C*OOMe), 169.90(dithiolene ring carbon, C=*C*H). IR(KBr): 1691(s), 1510(s), 1503(s), 1433(m), 1260(s), 1220(s), 1053(m), and 845(s) cm^{-1}. MS(EI, 70eV) m/z(relative intensity): 396(trace, $M^+(^{37}Cl)$), 394(trace, $M^+(^{35}Cl)$), 359(100, $M^+\text{-}Cl$), 272(81, $M^+\text{-}CH_2ClSiMe_3$), 188(73, $CpCoS_2^+$), 124(27, $CpCo^+$), and 73(100, $SiMe_3^+$). UV/VIS(CH_2Cl_2): λ_{max}(log ε) 534.4 nm (3.12), 334.0(4.17) and 238.0(4.16). Found: C, 39.55; H, 5.09%. Calcd for $C_{13}H_{20}O_2SiCoS_2Cl$: C, 39.54; H, 5.11%.

8 Crystal structure data for adduct **2a**: A dark-brown prismatic crystal of $C_{13}H_{20}SiS_2ClCoO_2$ (F.W.=394.89), triclinic, space group $P\bar{1}$, a=9.903(1) Å, b=10.251(1) Å, c=9.636(1) Å, α=91.964(9)°, β=112.646(9)°, γ= 85.85(5)°, V=886.6(2) $Å^3$, Z=2, Dc=1.48 $g.cm^{-3}$, $\mu(CuK\alpha)=118.09\ cm^{-1}$, F_{000}=408.00, R =0.068 (R_w = 0.094) on 1784 intensities ($|F_o| > 3\sigma|F_o|$).

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11 Reaction of **4a** with TBAF: To a solution of **4a** (72.8 mg, 0.185 mmol) in THF (20 cm^{-3}) was added a solution of TBAF(156 mg, 0.6 mmol) in THF (0.6 cm^3). After the mixture was stirred at room temperature for 10 min, the solvent was removed at reduced pressure and the residue was chromatographed on silica gel (Wako-gel C-300) to afford the known methylene adduct **2c**[2] in 75% yield (39.7 mg, 0.139 mmol).