# Reactions of Tetracyanoethylene Oxide (TCNEO) with Cobaltadithiolene Complexes

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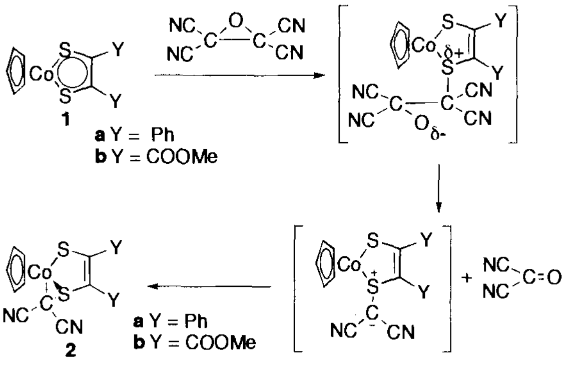
The reactions of cobaltadithiolene complexes bearing phenyl or ester ligands with tetracyanoethylene oxide (TCNEO) result in the formation of dicyanomethylene-bridged complexes, *via* dicyanomethylide intermediates. Furthermore, the reaction of cobaltadithiolene complex bearing 4-pyridyl ligands produces pyridinium dicyanomethylide complexes in good yields.

Metalladithiolene rings exhibit both aromaticity[1] and unsaturation. They undergo addition reactions to the metal and sulfur atoms in the metalladithiolene ring due to their unsaturation; diazo compounds add *via* the nucleophilic reaction to the metal center.[2] Here, we tried the reaction of cobaltadithiolene complexes ($CpCo(S_2C_2Y_2)$: Y = Ph (**1a**), COOMe (**1b**), CN (**1c**), $^4$Py (**1d**)) with tetracyanoethylene oxide (TCNEO). In these reactions, the electrophilic reactions of TCNEO are expected to occur at the nucleophilic sulfur atoms in the dithiolene ring and at the nucleophilic nitrogen atom in the pyridine ring.

TCNEO normally undergoes two types of electrophilic reactions. One is the reaction with pyridine derivatives and dialkyl sulfides to give stable dicyanometylides and carbonyl cyanide.[3] The other is the reaction with multiple C-C bonds, including those in aromatic compounds to give five-membered tetracyanotetrahydrofurans by cleavage of the C-C bond of the epoxide ring.[4]



**Scheme 1.** Conditions: THF, reflux, 3 h.

A mixture of a dithiolene complexes $[CpCo(S_2C_2Y_2)]$ (**1a**, Y = Ph; **1b**, Y = COOMe) and TCNEO (twice as much as **1a** or **1b**) was heated under refluxing in THF for 3 h. In each case, novel dicyanomethylene-bridged cobaltadithiolene complexes (**2a** and **2b**) having a $C(CN)_2$ unit were obtained in 39% and 13% yields (recovery of **1a**; 9% and **1b**; 53%), respectively (Scheme 1).[5] No analogous product was obtained in the reaction with $[CpCo(S_2C_2(CN)_2)]$ (**1c**) (recovery of **1c**; 60%).

The structures of the dicyanomethylene-bridged complexes **2a** and **2b** were determined by X-ray structure analysis: ORTEP drawing of **2a** with the selected bond lengths and angles is shown in Figure 1.[6]

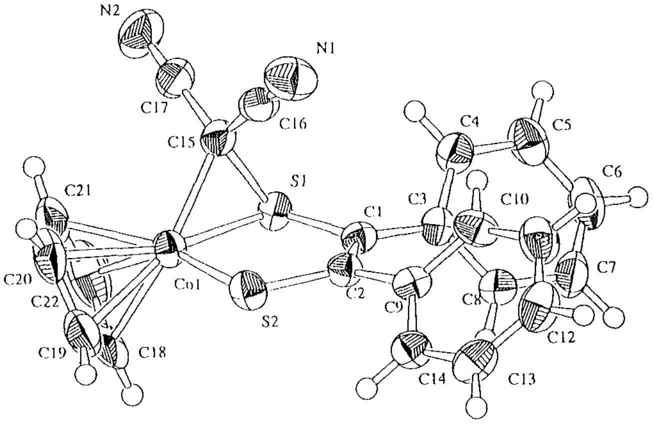
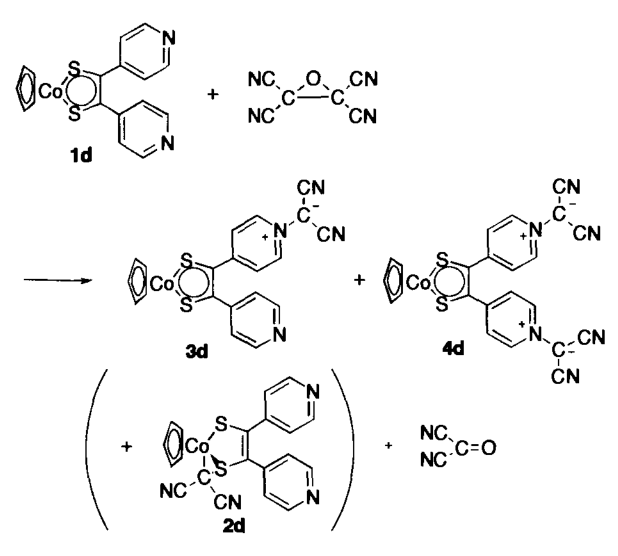


**Figure 1.** Molecular structure of **2a**. Selected bond lengths (Å) and angles (deg) are as follows: Co-S(1), 2.164(1); Co-S(2), 2.210(1); S(1)-C(1), 1.747(4); S(2)-C(2), 1.727(4); C(1)-C(2), 1.376(5); S(1)-C(15), 1.832(4); Co-C(15), 2.006(4); S(1)-Co-S(2), 90.44(5); Co-S(1)-C(1), 106.1(2); Co-S(2)-C(2), 103.6 (1); S(1)-C(1)-C(2), 117.6(3); S(2)-C(2)-C(1), 122.0(3); Co-S(1)-C(15), 59.6(1); C(1)-S(1)-C(15), 105.5(2); S(1)-Co-C(15), 52.0(1); S(2)-Co-C(15), 94.9(1); Co-C(15)-S(1), 68.5(2).

As shown in Figure 1, dicyanomethylene adds to the Co-S bond in the cobaltadithiolene ring to form a Co-S-C triangle structure. These structures are as same as those of alkylidene-bridged complexes synthesized in the reactions of dithiolene complexes with diazo compounds.[2] The bond lengths in the Co-S-C ring are within the range normally observed for other complexes.[7] The five-membered ring (dithiolene ring), which consists of Co, two S, and two C, is almost planar (mean derivation of **1a**; 0.0178 Å and **1b**; 0.0064 Å), the planarity of the five-membered ring is similar to those of original dithiolene complexes.[8]

In these reactions, carbonyl cyanide was detected by GC-MS. The yield of the dicyanomethylene-bridged complexes decreased markedly from **1a** *via* **1b** to **1c**. Namely, with decreasing of electron-attracting ability of substituents Y in the dithiolene ring, the reactivity of dithiolene complexes increases. These results suggest that the dicyanomethylene-bridged complexes **2** are obtained by the electrophilic reaction of the electron-poor carbon in TCNEO with a sulfur atom in dithiolene ring, *via* dicyanomethylide. These intermediates are presumably unstable and change rapidly to species with a bridging structure. The reactions to give alkylidene-bridged adducts from diazo compounds proceed *via* the nucleophilic reaction to the metal center. The example for electrophilic reaction is very rare and very interesting.[9]

The reaction of the dithiolene complex bearing 4-pyridyl ligands $[CpCo(S_2C_2(C_5H_4N)_2)]$ (**1d**) with TCNEO under refluxing in THF afforded green powder of **3d** in 21% yield and yellow-brown powder of **4d** in 59% yield.[10] In the FAB MS the molecular ions (*m/z* = 432 and 497) were observed, indicating that **3d** must be derived from one molecule of **1d** and one $C(CN)_2$ unit and that **4d** must be derived from one molecule of **1d** and two $C(CN)_2$ units. This reaction was also proceeded at room temperature in THF for 24 h to give **3d** and **4d** in 12% and 38% yields, respectively. The reactions giving the dicyanomethlene-bridged complexes **2a** and **2b** did not proceed at room temperature. Namely, these results suggest that novel types of dicyanomethylene adducts which had pyridinium dicyanomethylide moieties were formed (Scheme 2). $^1H$ NMR spectra of **4d** are indicative of symmetrical structure. Signals of Cp rings in **3d** (δ 5.52) and **4d** (δ 5.56) occurred at somewhat lower field than that of the original complex **1d** (δ 5.47). On the other hand, those of pyridine rings in pyridinium dicyanomethylide moieties of **4d** appeared at δ 7.40 (4H, d, *J* = 7.32 Hz) and 8.27 (4H, d, *J* = 7.32 Hz), and those of free pyridine rings of **1d** were shown at δ 7.12 (4H, d, *J* = 6.10 Hz) and 8.47 ( 4H, broad). Complex **3d** showed both pyridine ring in pyridinium dicyanomethylide moieties (δ 7.37 (2H, d, *J* = 7.32 Hz), 8.16 (2H, d, *J* = 7.32 Hz)) and free pyridine ring protons (δ 7.14 (2H, d, *J* = 6.10 Hz), 8.58 (2H, broad)). These results suggest that the structures of **3d** and **4d** have one and two pyridinium dicyanomethylide structures (Scheme 2) and dicyanomethylene-bridged complex **2d** is not formed.



Scheme 2. Conditions: THF, reflux, 3 h.

To summarize, in the reaction of dithiolene complexes **1a** and **1b** with TCNEO, dicyanomethylene-bridged complexes are produced. In this reaction, the existence of dicyanomethylide intermediate is suggested. On the other hand, in the reaction of **1d**, one and two pyridinium dicyanomethylide complexes are formed in good yields. Namely, TCNEO is more reactive to the N atom of the pyridine ring than to the S atom of the dithiolene ring.

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5 Selected data for **2a**: mp 185-188 °C (decomp. to **1a**); $^1H$ NMR ($CDCl_3$) δ5.48 (5H, s, $C_5H_5$), and 7.04~7.23 (10H, m, Ph); $^{13}C$ NMR ($CDCl_3$) δ-10.84 (*C*(CN)$_2$), 87.17 (*C*$_5$H$_5$), 113.04 (*C*N), 115.67 (*C*N), 119.80, 179.33(dithiolene); EI-MS 70 eV) *m/z* (% relative intensity) 430 (15.90, M+) and 366 (74.71,dithiolene+); Found: C, 61.39; H, 3.51; N, 6.51%. Calcd for $C_{22}H_{15}CoN_2S_2$: C, 60.68; H, 3.45; N, 6.79%; IR(KBr): ν(CN) 2201 and 2210 $cm^{-1}$. For **2b**: mp 195-198 °C (decomp. to **1b**); $^1H$ NMR ($CDCl_3$): δ3.80, 3.86 (3H, s, $CH_3$), and 5.53 (5H, s, $C_5H_5$); $^{13}C$ NMR ($CDCl_3$): δ-7.42 (*C*(CN)$_2$), 87.89 (*C*$_5$H$_5$), 111.61 (*C*N), 112.04 (*C*N), 118.46 , 186.49 (dithiolene); EI-MS (70 eV) *m/z* (% relative intensity): 394 (23.46, M+) and 330 (52.05, dithiolene+); Found: C, 42.72; H, 2.77; N, 7.11; S, 15.82%. Calcd for $C_{14}H_{11}CoN_2O_4S_2$: C, 42.65; H, 2.81; N, 7.11; S, 16.26%; IR(KBr): ν(CN) 2205 and 2213 $cm^{-1}$.

6 Crystal structure data for **2a**: $C_{22}H_{15}S_2O_4N_2Co$ (F.W. = 430.43), monoclinic, space group $P2_1$(#4), $a$ = 7.626(2) Å, $b$ = 13.551(2) Å, $c$ = 9.503(2) Å, $\beta$ = 103.52(2) °, $V$ = 954.9(3) Å$^3$, $Z$ = 2, $Dc$ = 1.497 g $cm^{-3}$, $R$ = 0.033 ($Rw$ = 0.024) on 1838 intensities ($|Fo| > 3.00\sigma|Fo|$). For **2b**: $C_{14}H_{11}CoN_2O_4S_2$ (F.W. = 394.31), triclinic, space group $P1$(#2), $a$ = 9.037(5) Å, $b$ = 11.170(5) Å, $c$ = 8.778(5) Å, $\alpha$ = 113.85(4) °, $\beta$ = 113.85(4) °, $\gamma$ = 91.07(5) °, $V$ = 802.0(8) Å$^3$, $Z$ = 2, $Dc$ = 1.633 g $cm^{-3}$, $R$ = 0.063 ($Rw$ = 0.052) on 1676 intensities ($|Fo| > 3.00\sigma|Fo|$).

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10 Selected data for **3d**: mp 285 °C (decomp.); $^{13}C$ NMR (DMSO): δ 60.2 (*C*(CN)$_2$), 81.2 (*C*$_5$H$_5$), 118.3(*C*N), 123.3, 126.4, 127.5, 132.7, 132.7, 144.8, 147.7, 149.9(Py), 158.8, 165.8(dithiolene); Found: C, 55.43; H, 2.93; N, 12.66%. Calcd for $C_{20}H_{13}CoN_4S_2$: C, 55.56; H, 3.03; N, 12.96%; IR(KBr): ν(CN) 2183 and 2145 $cm^{-1}$; Selected data for **4d:** mp > 300 °C; $^{13}C$ NMR (DMSO) δ 58.4 (*C*(CN)$_2$), 81.6(*C*$_5$H$_5$), 118.2(CN), 126.7, 132.8, 144.0(Py), 161.3(dithiolene); Found: C, 55.09; H, 2.53; N, 16.43; S, 12.81%. Calcd for $C_{23}H_{13}CoN_6S_2$: C, 55.65; H, 2.64; N, 16.93; S, 12.92%; IR(KBr): ν(CN) 2185 and 2149 $cm^{-1}$.