CpCo^{I}-mediated Diels–Alder Reaction Forming Dimeric 1,3-Dithiol-2-one Derivative with Spiro Structure and Successive Formation of Novel Cobalt Dithiolene Complex

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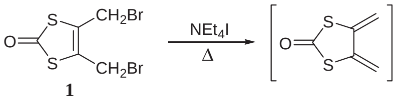
4,5-Bis(bromomethyl)-1,3-dithiol-2-one (**1**) reacts with $CpCo(CO)_2$ (**2**) under thermal condition to undergo a debromination of **1** and to form dimeric 1,3-dithiol-2-one derivative having a spiro structure **3** by the [4 + 2] Diels–Alder reaction, and the resulted **3** further reacts with **2** to afford new CpCo(dithiolene) complex **4**.

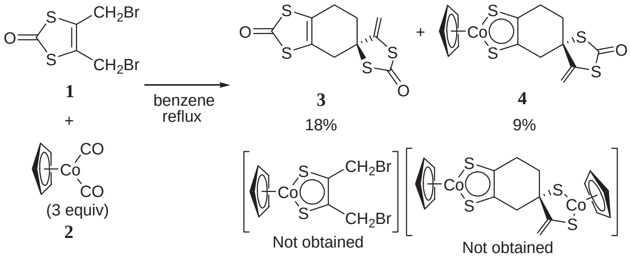
Metalladithiolene rings, which incorporate one metal, two sulfurs, and two unsaturated carbons, are an interesting five-membered metallacycles. The dithiolene metal complexes have been thoroughly investigated from the viewpoint of optical,[1] magnetic,[2] and conductive studies.[3] Some recent topics in dithiolene complexes are their photo catalyses for generating molecular hydrogen from water[4] and selective olefin binding on the dithiolene ligand.[5]

Synthetic procedures for dithiolene complexes have been well developed. Among them, useful dithiolene sources are mostly classified into five categories: (1) 1,2-dithiolate dianion formed from the treatment of 1,3-dithiol-2-one, S-protected dithiolene ligand by $PhCH_2$, PhCO, and $NC(CH_2)_2$ groups, or 1,2-dithiol derivative in the presence of a strong base,[6] (2) 1,2-dithioketone or 1,2-dithiete generated by photolysis and thermolysis of 1,3-dithiol-2-one, or by the reaction of β-diketone with Lawesson's reagent,[7] (3) thiophosphoric esters formed from the reaction of benzoin analogues with diphosphorus pentasulfide or Lawesson's reagent,[8] (4) zinc, titanium, or tin dithiolate as a precursor,[6] (5) stable 1,2-dithiolate salt such as $Na_2(mnt)$ (mnt = maleonitrile-1,2-dithiolate), and (6) metal sulfide while reacted with an alkyne.[6] Among them, using 1,3-dithiol-2-one derivative is the widely useful method to prepare many kinds of dithiolene complex, and as is well-known, this is also a useful precursor for tetrathiafulvalene (TTF) derivatives.[9]

To prepare typical 1,3-dithiol-2-one derivatives, we can usually use substitution of sulfur at the S=C group in 1,3-dithiol-2-thione by treatment with $Hg(OAc)_2$,[10] the reactions of $[Cp_2Ti(dithiolene)]$ or $[Zn(dithiolene)L_n]$ with triphosgene,[11] and cyclization of xanthogenate by treatment with an acid.[12] Furthermore, a direct introduction of 1,3-dithiol-2-one fragment using the [4 + 2] Diels–Alder reaction[13] can be useful but is not well-known. This reaction involves double debromination of 4,5-bis(bromomethyl)-1,3-dithiol-2-one (**1**) while treatment with tetraethylammonium iodide generating the 1,3-diene intermediate shown in Scheme 1. This transient diene itself further undergoes the [4 + 2] Diels–Alder reaction to afford dimeric 1,3-dithiol-2-one compound (**3**, see Scheme 2) or other [4 + 2] adducts in the presence of a dienophile such as *p*-benzoquinone,[13] acrolein,[14] or fullerene.[15] This paper reports on the generation of the 1,3-diene intermediate from the reaction of **1** with $CpCo(CO)_2$ (**2**), but *without iodide*. In addition, the successive formation of new CpCo(dithiolene) complex **4** derived from precursor **3** is described.



Scheme 1.

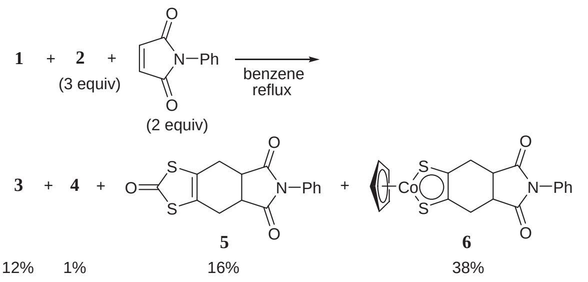


Scheme 2.

1 reacted with 3 equiv of **2** in refluxing benzene for 24 h to obtain the dimeric 1,3-dithiol-2-one with a spiro structure **3** and the new CpCo(dithiolene) complex **4** in 18% and 9% yields, respectively (Scheme 2). This reaction also occurred at room temperature to form **3** in 21% yield but formed only trace amount of **4**. For a comparison, a previous paper has reported that the reaction of **1** with tetraethylammonium iodide (3 equiv) gives **3** in 30% yield under thermal conditions in acetonitrile.[13] Unexpectedly, CpCo(dithiolene) complex having two bromomethyl groups, $[CpCo(S_2C_2(CH_2Br)_2)]$, was not obtained at all (Scheme 2). To explain this reason, a bromine abstraction by CpCo^{I} is proposed, and then the 1,3-diene intermediate noted in Scheme 1 should be formed. Accordingly, slight excess **2** (3 equiv) is necessary to obtain **4**.

Furthermore, isolated compound **3** directly reacted with **2** for 24 h to form complex **4** in 4% yield under refluxing benzene, in 19% yield under refluxing toluene and in 34% yield under refluxing xylene. These results indicate that higher temperature accelerates decarbonylation of **3** to generate 1,2-dithioketone or 1,2-dithiete intermediate.[7] No formation of a dinuclear CpCo(dithiolene) complex in Scheme 2 suggests that only one of two 1,3-dithiol-2-one fragments is thermally activated for decarbonylation.

The reaction of **1** with tetraethylammonium iodide (3 equiv) for 3 h in the presence of *N*-phenylmaleimide in refluxing acetonitrile was carried out, and this reaction resulted in **3** in 5% yield and the Diels–Alder cycloadduct **5** in 75% yield, respectively. This result indicates that *N*-phenylmaleimide is



Scheme 3.

an effective dienophile. Moreover, the reaction shown in Scheme 2 in the presence of *N*-phenylmaleimide was performed (Scheme 3), and produced **3** in 12% yield, **4** in 1% yield, **5** in 16% yield, and new dithiolene complex **6** in 38% yield. Lower yields of **3** and **4** were found than those in Scheme 2 upon the absence of any dienophiles. This result proves that the dienophile effectively combines with the 1,3-diene intermediate to avoid the formation of dimeric cycloadduct **3**. Therefore, the formation of **5** reveals that CpCo^{I} can mediate the [4 + 2] Diels–Alder reaction with **3** and the resulting **5** successively reacts with **2** to form **6** under thermal conditions.

Some new compounds **4**–**6** were identified with spectroscopic data and elemental analysis (Supporting Information).[18] Single crystals of **3** and **4** were obtained by recrystallization from dichloromethane/*n*-hexane.[16,17] Analytical data for **3** has been reported previously,[13] but has been not structurally characterized yet. The ORTEP drawings of **4** is shown in Figure 1 together with selected bond lengths and angles, respectively. The ORTEP of **3** is shown in Supporting Information.[18]

In complex **4**, the Cp plane is located at an almost perpendicular position with respect to the cobaltadithiolene plane because the dihedral angle of Cp/cobaltadithiolene is equal to 83.972°. This result suggests a typical two-legged piano-stool geometry. The dihedral angle between the C3–C4–C5 and S3–C4–C8 is almost 90° indicating a general spiro structure. The C1–C2 bond length in cobaltadithiolene is 1.353 Å. This is intermediary between a typical C–C single bond (ca. 1.5 Å) and C=C double bond (ca. 1.3 Å) relating to an aromaticity of the cobaltadithiolene ring.[7a] The cobaltadithiolene plane is quite planar due to negligible mean deviation from the plane (0.0314 Å). This fact also supports the aromaticity of the cobaltadithiolene ring. In compound **3**, there is also a spiro structure centered at the C4 carbon (Supporting Information).[18] The C1–C2 bond length in the dithiolene ring is 1.333 Å, which is close to the bond length of the vinylene moiety at C8–C9 (1.316 Å). These results show the C1–C2 bond becomes olefinic by lack of aromaticity. Interestingly, while comparing **3** and **4**, the 1,3-dithiol-2-one fragments containing S3 and S4 are located contrarily to each other (Figures 1 and S1 in Supporting Information).

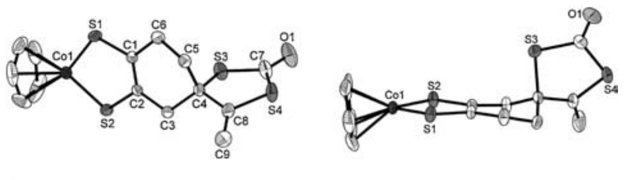


Figure 1. ORTEP drawing of **4** (thermal ellipsoids 30% probability). Selected bond lengths (Å): Co1–S1 2.1108(15), Co1–S2 2.1150(17), S1–C1 1.720(4), S2–C2 1.721(4), C1–C2 1.353(5), C8–C9 1.302(8), O1–C7 1.190(8). Selected bond angles (°): S1–Co1–S2 91.07(7), Co1–S1–C1 105.61(15), Co1–S2–C2 105.39(14), S1–C1–C2 118.8(3), S2–C2–C1 119.0(3). Dihedral angles: Cp/dithiolene = 83.972°, C3–C4–C5/S3–C4–C8 = 90.988°.

This paper reported a CpCo^{I}-mediated a debromination of **1** to form 1,3-diene intermediate without the conventional use of iodide and eventually underwent [4 + 2] Diels–Alder reactions. The resulting 1,3-dithiol-2-one derivative is generally useful for syntheses of TTF derivatives and metal dithiolene complexes as well. An important point in this work is that CpCo^{I} species facilitates the Diels–Alder reaction and successively forms CpCo(dithiolene) complex. Finally, the target CpCo(dithiolene) complex **4** or **6** can be obtained in one-step reaction of **1** with **2** or in the presence of *N*-phenylmaleimide.

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16 Crystal data for **4**: ($C_{14}H_{13}CoOS_4$): blue crystal, crystal size: $0.23 \times 0.15 \times 0.02\,\text{mm}^3$, fw $384.45\,\text{g·mol}^{-1}$, monoclinic, space group Pa(#7), $a = 10.9508(11)$ Å, $b = 6.3141(9)$ Å, $c = 11.1090(13)$ Å, $\beta = 94.2048(19)°$, $V = 766.06(16)$ Å^3, $Z = 2$, $T = 298\,\text{K}$, $D_{\text{calc}} = 1.667\,\text{g·cm}^{-3}$, $\mu(\text{Mo}\,K\alpha) = 1.658\,\text{mm}^{-1}$, 5334 reflections measured, 2793 unique ($R_{\text{int}} = 0.023$), $R(I > 2\sigma(I)) = 0.0343$ and $wR = 0.0971$, goodness-of-fit = 1.046, CCDC No. 693392.

17 Crystal data for **3**: ($C_{10}H_8O_2S_4$): colorless crystal, crystal size: $0.42 \times 0.12 \times 0.10\,\text{mm}^3$, fw $288.41\,\text{g·mol}^{-1}$, monoclinic, space group $P2_1/n$(#14), $a = 7.750(2)$ Å, $b = 15.616(4)$ Å, $c = 9.586(3)$ Å, $\beta = 97.6871(13)°$, $V = 1149.7(5)$ Å^3, $Z = 4$, $T = 298\,\text{K}$, $D_{\text{calc}} = 1.666\,\text{g·cm}^{-3}$, $\mu(\text{Mo}\,K\alpha) = 0.804\,\text{mm}^{-1}$, 8764 reflections measured, 2594 unique ($R_{\text{int}} = 0.016$), $R(I > 2\sigma(I)) = 0.0332$ and $wR = 0.0978$, goodness-of-fit = 1.052, CCDC No. 693393.

18 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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