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# Hydrogen bonding interaction of CpCo(Dithiolene) complex with monocyclic 2-pyridonyl substituent and unexpected formation of dithiolene-fused tricyclic pyridone derivative

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ABSTRACT

One-pot reaction of $[CpCo(CO)_2]$, elemental sulfur with some heterocycle-substituted alkynes (R–C≡C–HET) produced [CpCo(dithiolene)] complexes with $^2$PyOBn (**2**), with both $^2$PyOBn and 2-hydroxy-2-propyl groups ($C(OH)Me_2$) (**5**), both $^2$Py and $C(OH)Me_2$ (**8**), both $^4$Py and $C(OH)Me_2$ (**11**), and with $^4$Py substituent (**13**). A deprotection of benzyl group (Bn) from **2** with trimethylsilyl iodide formed [CpCo(dithiolene)] with 2-pyridonyl substituent (**3**). Heating reaction of **8** without any base resulted in the $C(OH)Me_2$ group elimination to form the 2-pyridylethylenedithiolate complex (**9**), but **11** underwent only dehydration at the $C(OH)Me_2$ under heating. While the preparation of **5**, the benzyl free complex (**6**) was obtained as a main product. **6** has a dithiolene-fused tricyclic pyridone skeleton. The structures of **3**, **5**, **6**, **8**, and **11** were determined by X-ray diffraction studies. Intramolecular OH···N($^2$Py) hydrogen bondings are found in **5** and **8**, and an intermolecular OH···N($^4$Py) one is found in **11** at solid state. In the 2-pyridonyl complex **3**, intermolecular NH···O and CH(dithiolene)···O hydrogen bondings are observed. **8** showed an intermolecular Cp···Cp face-to-face interaction. The tricyclic complex **6** exhibited lower energy electronic absorption ($\lambda_{max}$ = 668 nm) compared with the others ($\lambda_{max}$ = 562–614 nm), due to an extended π-conjugation of aromatic cobaltadithiolene ring.



## 1. Introduction

Metal dithiolene complexes have been extensively investigated due to their combination of functional properties, specific geometries, and intermolecular interactions that confer them an enormous interest in the field of magnetism [1], conductivities [2], and optical properties [3]. On the other hand, metal dithiolene complex biochemically functions as a coenzyme as well [4]. Some model compounds relating to biochemically functional materials have been studied by using oxo-molybdenum and oxo-tungsten bisdithiolene complexes as oxo-transfer sources [5]. Garner and Joule et al. reported some [CpCo(dithiolene)] (Cp = $\eta^5$-cyclopentadienyl) complexes having heterocycles such as 2-quinoxalinyl [6], pteridin-6-yl [7], pyrano[2,3-b]quinoxaline [8], and pyrano[2,3-g]pteridine [9] which can be also model compounds for a proton-transfer (Chart 1). Among them, [CpCo(dithiolene)] with 2-quinoxalinyl group shows $2e^-/2H^+$ reduction system in the presence of a proton source [6]. In addition, the oxo-molybdenum bisdithiolene complex $[Mo(O)(qdt)_2]$ (qdt = quinoxaline-2,3-dithiolate) undergoes thermally driven valence tautomerism by an intramolecular charge transfer (M/L–CT) [10]. Nishihara et al. reported proton and photo responsive [CpCo(dithiolene)], $[M(dithiolene)_2]$ and [(P^P)M(dithiolene)] (M = Ni, Pd, Pt; P^P = diphosphine) complexes with azobenzene unit due to those *cis-trans* isomerizations [11].

On the other hand, 2-pyridone derivatives have been attracted due to their promising features as an important core structure for the development of biologically active molecules [12]. Pharmaceuticals with the 2-pyridone structure have been investigated for antitumor [13], antifungal [14], antibacterial [15], antiviral [16], and antithrombotic agents [17]. In general, 2-pyridone derivatives could be one of strong hydrogen bonding motifs by the NH···O interaction. Dimeric hydrogen bonding interaction (Chart 2, A) has been well known [18]. Wuest reported dipyridonyl acetylenes which show dimeric (Chart 2, B) and polymeric hydrogen bonding networks (Chart 2, C) [19]. Theoretical studies for dipyridonyl acetylenes have been investigated [20].

In this work, we prepared [CpCo(dithiolene)] complex having 2-pyridonyl substituent which can be also an important metal complex as a biochemically functional material and to be a hydrogen bonding network. Furthermore, 2-pyridonyl group may be

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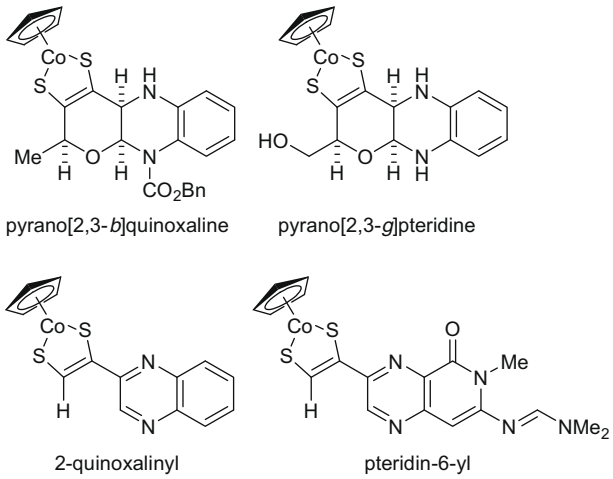



**Chart 1.** CpCo(dithiolene) complexes with heterocycles.

relatively easy to introduce to a molecule compared with pteridine and quinoxaline analogues (Chart 1). Interestingly, we unexpectedly found two different pyridone-containing dithiolene complexes. One is an expected pyridone-substituted dithiolene complex to show a hydrogen bonding interaction, but the other one is the dithiolene-fused *tricyclic pyridone* complex formed by an unexpected intramolecular cyclization. Generally, multicyclic pyridone derivatives are also biologically useful as antibacterial agents [21]. Furthermore, this paper also reports on [CpCo(dithiolene)] complex having 2-pyridyl ($^2$Py) or 4-pyridyl ($^4$Py) substituent for purpose of a comparison.

## 2. Results and discussion

### 2.1. Syntheses of CpCo(dithiolene) complexes using one-pot reaction

Garner and Joule et al. reported the synthesis of dithiolene's precursor (1,3-dithiol-2-one derivative) related to molybdopterin from diisopropyl xanthogen disulfide and alkynes [22]. On the other hand, many [CpCo(dithiolene)] complexes can be prepared by one-pot reactions of $CpCo^I$ species, elemental sulfur and alkynes, which have been well developed in our research group [23,24]. [$CpCo(CO)_2$], elemental sulfur and 2-(benzyloxy)-6-ethynylpyridine (**1**) reacted in refluxing xylene for 17 h to form the [CpCo(dithiolene)] complex with $^2$PyOBn substituent (**2**) in 26% yield (Scheme 1). A deprotection of the benzyl group was performed by using a conventional way [25]. The treatment of complex **2** with excess trimethylsilyl iodide in refluxing $CH_2Cl_2$ resulted in the dithiolene complex with 2-pyridonyl substituent (**3**) in 56% yield (Scheme 1). Both products **2** and **3** were identified with spectroscopic data and elemental analyses. The $^1$H NMR of **2** and **3** showed dithiolene protons at 9.59 and 9.12 ppm, respectively. In general, a ring current effect due to an aromatic dithiolene leads to a quite lower magnetic shift [26]. In **3**, a broad singlet signal for the NH group was found at 9.60 ppm. This is evidence for an existence of pyridonyl substituent on the cobaltadithiolene ring.

The reaction of [$CpCo(CO)_2$], elemental sulfur with 4-(6-(benzyloxy)pyridin-2-yl)-2-methylbut-3-yn-2-ol (**4**) in refluxing xylene gave the complex (**5**) with both $^2$PyOBn and 2-hydroxy-2-propyl substituents (–C(OH)$Me_2$) on the cobaltadithiolene ring in 18% yield, and formed the tricyclic complex (**6**) in 29% yield as well (Scheme 2). **6** has a 2-pyridonyl substituent but the N atom binds

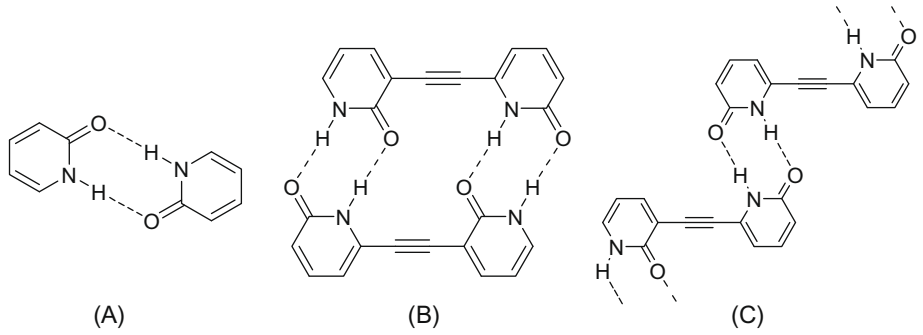
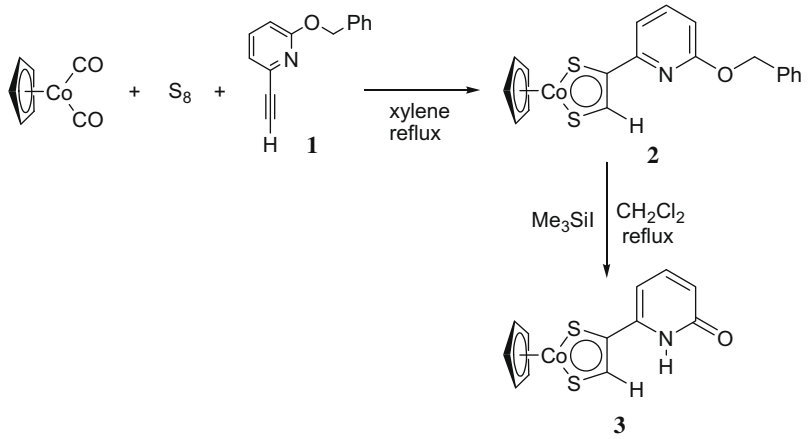
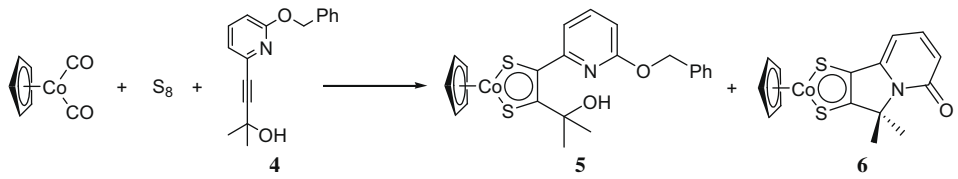



**Chart 2.** Dimeric and polymeric hydrogen bonding in 2-pyridone derivatives.




**Scheme 1.**




**Scheme 2.**

to the carbon on the 2-propyl group. In fact, no NH signal was found in the $^1$H NMR spectrum of **6**. A $^1$H NMR signal at 1.88 ppm (6H) indicates two equivalent Me groups, and evidences that the tricyclic plane in **6** is quite planar. Formally, **6** is formulated as [**5**–PhCH$_2$OH]. Interestingly, the EI$^+$ (70 eV) mass spectrum of **5** resulted in **6**$^+$ (mass number = 346) as a fragment ion. Furthermore, refluxing xylene solution of **5** for 17 h was performed to afford **6** in 25% yield. This result suggests that thermolysis of **5** forms **6** by elimination of PhCH$_2$OH.

Jung and his coworker have reported that Me$_3$SiI reacts with ethers (R–O–R′) to form dealkylated products (R–OH and R′–OH) [25]. An intermediate in this reaction is a silylated oxonium compound (R–O$^+$(SiMe$_3$)–R′) and then one of two alkyl groups eliminates. The silyl group is deprotected during workup process. In the formation of **3**, the reaction process can be explained by the benzyl group elimination from **2** through the silylated oxonium intermediate by Me$_3$SiI. However, the formation of **6** from **5** occurs by benzyl group elimination without Me$_3$SiI. We assume that $^2$Py group in complex **5** can deprotonate from the C(OH)Me$_2$ group through intramolecular OH···N($^2$Py) hydrogen bonding (Fig. 1). After that, an intramolecular cyclization occurs to make a five membered ring for **6**, followed by elimination of benzyl alcohol (PhCH$_2$OH). However, a detailed formation mechanism of cyclization has not been clear yet. Anyway, we thought that the intramolecular hydrogen bonding of the dithiolene complex having $^2$Py group was interesting to make a unique reactivity. Due to this reason, we decided to prepare [CpCo(dithiolene)] complex having $^2$Py group for intramolecular hydrogen bonding, and also synthesized the complex with $^4$Py group for intermolecular hydrogen bonding by purpose of comparison.

The reaction of [CpCo(CO)$_2$], elemental sulfur with 2-methyl-4-(pyridin-2-yl)but-3-yn-2-ol (**7**) in refluxing xylene formed the complex (**8**) with both $^2$Py and C(OH)Me$_2$ substituents on the cobaltadithiolene ring in 23% yield, and CpCo 2-pyridylethylenedithiolate complex (**9**) in 3% yield as a byproduct (Scheme 3). **9** has been synthesized from 1,3-dithiol-2-thione derivative by Garner and Joule [6b], but been not characterized. The $^1$H NMR of **9** showed a dithiolene proton at 9.66 ppm. The mass spectrum **8** resulted in the fragmentation of **9**$^+$ (mass number = 291). Thermal reaction of **8** in refluxing xylene (140 °C) produced **9** in low yield but the reaction in refluxing *trans*-decahydronaphthalene (b.p. 185 °C) gave **9** in higher yield (39%). This result indicates that **8** eliminates one acetone fragment from **9**. We assume that the $^2$Py group deprotonates from the hydroxyl group on C(OH)Me$_2$, because an OH···N($^2$Py) intramolecular hydrogen bonding is observed (see Fig. 2 and Table 1). As previously reported, the C(OH)Me$_2$ group is deprotected by treatment with a strong base such as NaOH [27], but a weak base such as pyridine can not make it. However, most probably, the intramolecular deprotonation by $^2$Py group mediates the C(OH)Me$_2$ group elimination to form **9**. In fact, no reaction occurred in thermal reaction of **8** in the presence of H$_2$SO$_4$. In this case, H$_2$SO$_4$ might protonate the $^2$Py group. Here we assume that the protonated $^2$Py (pyridinium) can make an intramolecular hydrogen bonding such as NH($^2$Py)···OH in an acidic condition. Accordingly, this intramolecular hydrogen bonding prevents the protonation of OH group by H$_2$SO$_4$. Normally, dehydration of alcohol is hard to occur without protonation of OH group.

The reaction of [CpCo(CO)$_2$], elemental sulfur with 2-methyl-4-(pyridin-4-yl)but-3-yn-2-ol (**10**) in refluxing xylene formed the complex (**11**) with both $^4$Py and C(OH)Me$_2$ substituents on the cobaltadithiolene ring in 22% yield, and the complex (**12**) with both $^4$Py and 2-propenyl substituents in 4% yield (Scheme 4). A 2-propenyl free complex (**13**, Scheme 4) was not obtained at all. The $^1$H NMR of **12** exhibited an olefinic proton at 5.05 ppm (singlet, 2H), and revealed absence of the OH proton. This result suggested existence of C=CH$_2$ moiety. A dehydration of **11** plausibly gives **12**. In fact, the thermal reaction of **11** in refluxing *trans*-decahydronaphthalene for 18 h formed **12** in 79% yield but did not give 2-propenyl free complex **13**. The dehydration reaction of **11** in the presence of H$_2$SO$_4$ in refluxing xylene gave higher yield of **12** (89%). One reason for no formation of **13** may be absence of an intramolecular OH···N hydrogen bonding or intermolecular OH···N($^4$Py) hydrogen bonding in **11** (see Fig. 3 or Table 1) is not enough effective for deprotonation of C(OH)Me$_2$ group.

A deprotection of C(OH)Me$_2$ group with NaOH from alkyne **10** formed 4-ethynylpyridine [27]. The 2-propenyl free complex (**13**) was obtained by the reaction of [CpCo(CO)$_2$], elemental sulfur with 4-ethynylpyridine in refluxing xylene in 30% yield (Scheme 4). **13** was characterized by spectroscopic data and elemental analysis. However, treatment of **11** with NaOH resulted in decomposition of the product. In addition, no reaction was confirmed by the reaction of **11** in xylene solution containing excess pyridine.

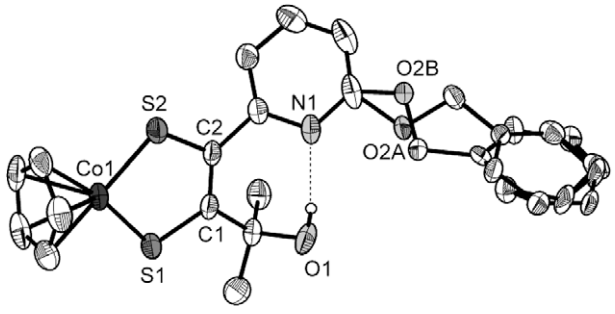
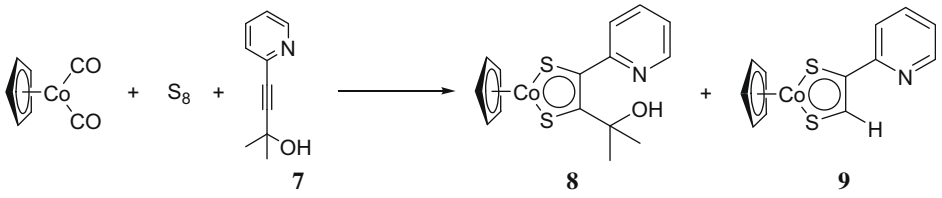



**Fig. 1.** The ORTEP drawing of **5** with intramolecular OH···N hydrogen bonding (thermal ellipsoids 30% probability). Two oxybenzyl groups A and B are disordered (A:B = 54:46).

### 2.2. X-ray structures of CpCo(dithiolene) complexes

Molecular and crystal structures of **3**, **5**, **6**, **8**, and **11** were determined by single crystal X-ray structure analyses. Those ORTEP drawings and crystal packing diagrams are shown in Figs. 1–5. The selected bond lengths, bond angles in the cobaltadithiolene moiety, hydrogen bonding distances and dihedral angles are summarized in Table 1.

The Co–S bond lengths are 2.08–2.10 Å except for **6**. In typical, the Co–S lengths in [CpCo(dithiolene)] complexes are almost 2.1 Å. Sellmann et al. explained that a strong π-donation from




**Scheme 3.**

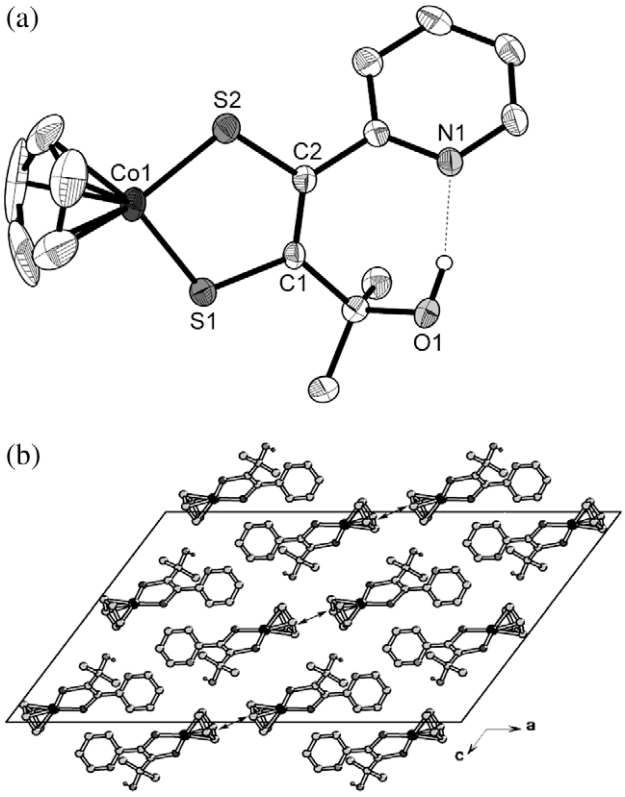



**Fig. 2.** (a) The ORTEP drawing of **8** with intramolecular OH···N hydrogen bonding (dotted line). The thermal ellipsoids are drawn at 30% probability level. (b) Projection view along the *b*-axis of the unit cell of **8** exhibiting intermolecular Cp···Cp interaction (shown by an arrow).

sulfur to metal shortens the M–S bond [28]. However, the Co–S bond length in **6** is longer than those of the others (Table 1, 2. 13–2.14 Å). We consider that the π-extended system in **6** can delocalize the whole π-electrons in the plane. In this case, π-electron donation from S to M can be weaker than those of less π-extended complexes **3**, **5**, **8**, and **11**. Therefore, there is an extended π-conjugation between cobaltadithiolene ring and pyridonyl group in **6**. In fact, the tricyclic pyridone plane is quite planar (Fig. 5). In addition, the long Co–S bond in **6** slightly modifies the bond angles in cobaltadithiolene ring (Table 1). According to dihedral angles of Cp/cobaltadithiolene, the Cp rings are located at perpendicular position with regards to the cobaltadithiolene ring.

Figs. 1–3 display the molecular structures of **5**, **8** and **11**. In **5**, two oxybenzyl groups are disordered (Fig. 1). **5** and **8** have intramolecular OH···N($^2$Py) hydrogen bondings whose distances are 1.958(33) and 1.830(3) Å, and **11** has an intermolecular OH···N($^4$Py) one whose distance is 1.856(3) Å. Those hydrogen bondings result in difference of dihedral angle between cobaltadithiolene and pyridyl rings. The cobaltadithiolene/$^2$Py angles in **5** and **8** are 50.490° and 40.843° but the cobaltadithiolene/$^4$Py angle in **11** is almost right angle (Table 1, 92.946°). In the crystal packing of **8**, there is an intermolecular Cp···Cp interaction (Fig. 1). The face-to-face distance is c.a. 3.5 Å. Some previous paper have reported similar Cp···Cp interactions in the paramagnetic [CpNi(bdt)] (bdt = benzene-1,2-dithiolate) [29], [CpNi(bds)] (bds = benzene-1,2-diselenolate) [29], [CpNi(adt)] (adt = acrylonitrile-2,3-dithiolate) [30]. Those π−π interactions are weak bonding but undergo strong magnetic interactions [31].

Figs. 4 and 5 exhibit the ORTEP drawings of **3** and **6**. Dimeric intermolecular hydrogen bonding interactions are found in the crystal packing of **3** (Fig. 4). There are NH···O (1.908(13) Å) bonding between 2-pyridonyl groups and CH···O (2.283(16) Å) hydrogen bonding between dithiolene ring and 2-pyridonyl group. The latter result suggests that the dithiolene proton could be somewhat acidic. In actual, an aromatic dithiolene proton appears around 9 ppm in $^1$H NMR spectra [26] whose $\delta$ value is lower magnetic field than that of a typical aromatic compound. This dimeric hydrogen bonding makes a slightly flat geometry. Actually, the dihedral angle of cobaltadithiolene/pyridonyl is 22.4° (Fig. 4 and Table 1). We consider that this is an interesting two-dimensional hydrogen bonding involving the dithiolene proton. Furthermore, the dihedral angle of that in the tricyclic pyridone complex **3** is 0.9° due to direct binding of the N atom to the carbon on the 2-propyl group. A remarkable structural feature of **6** is short C–C bond length in the five-membered ring moiety. In general, average C–C single bond length is 1.54 Å as well known. The C1–C8 and C2–C3 bond lengths are shorter than 1.54 Å. This fact indicates that the five-membered ring is conjugated with dithiolene and pyridone rings.

### 2.3. Electronic absorption spectra and electrochemical behavior

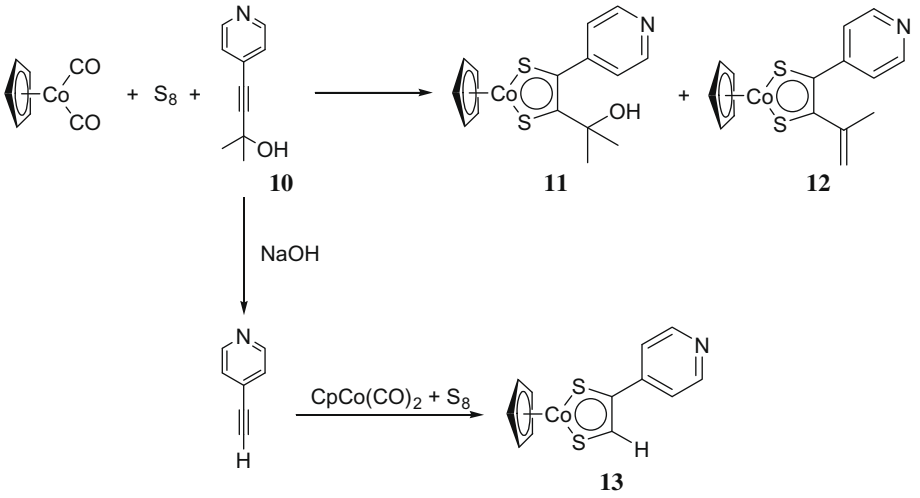
UV–Vis spectral data and CV data were obtained in dichloromethane solution. Those absorption maxima ($\lambda_{max}$/nm) and redox potentials (vs. Fc/Fc$^+$) are summarized in Table 2. The UV–Vis spectra and cyclic voltammograms of **5** and **6** are shown in Figs. 6 and 7. Most [CpCo(dithiolene)] complexes prepared in this work showed $\lambda_{max}$ around 560–610 nm in dichloromethane solution in visible region, except for **6**. These $\lambda_{max}$ results are similar to those of typical [CpCo(dithiolene)] [31,32] and [Cp$^*$Co(dithiolene)] (Cp$^*$ = $\eta^5$-pentamethylcyclopentadienyl) [33] complexes previously reported. On the other hand, **6** resulted in the $\lambda_{max}$ at 668 nm (Table 2). While compared **6** with its precursor **5**, interestingly there are 95 nm differences (Fig. 6). Most probably, the lower energy absorption caused by an extended π-conjugation of tricyclic pyridone plane. According to some previous reports, some π-extended [CpCo(dithiolene)] complexes show lower energy absorption at 678 nm for [CpCo(dmit)] [32] and at 677 nm for [Cp$^*$Co(dmit)] (dmit = $C_3S_5$, 1,3-dithiol-2-thione-4,5-dithiolate).[33] The dinuclear [Cp$^*$Co(btt)CoCp$^*$] (btt = benzene-1,2,4,5-tetrathiolate) exhibits visible absorption at 677 nm [33].

The CV of [CpCo(dithiolene)] complexes displayed a reversible reduction wave and some irreversible oxidation waves. Those reductions are attibuted to the central metal, formally Co$^{III}$/Co$^{II}$ couple. Namely, those reduction potentials correlate with a substituent effect on the cobaltadithiolene ring. The reduction potentials

**Table 1**
Selected bond lengths (Å), bond angles (°), hydrogen bonding distances (Å) and dihedral angles (°).

| | 3 | 5 | 6 | 8 | 11 |
|---|---|---|---|---|---|
| *Bond length* | | | | | |
| Co1–S1 | 2.108(2) | 2.0837(9) | 2.143(3) | 2.0863(17) | 2.094(3) |
| Co1–S2 | 2.107(2) | 2.0813(9) | 2.129(3) | 2.0885(14) | 2.106(3) |
| S1–C1 | 1.694(8) | 1.707(3) | 1.709(10) | 1.719(5) | 1.709(11) |
| S2–C2 | 1.719(7) | 1.718(3) | 1.719(10) | 1.716(5) | 1.723(11) |
| C1–C2 | 1.351(10) | 1.361(4) | 1.36(1) | 1.375(5) | 1.389(15) |
| *Bond angle* | | | | | |
| S1–Co1–S2 | 90.89(9) | 89.95(3) | 93.4(1) | 90.43(6) | 89.98(13) |
| Co1–S1–C1 | 105.6(3) | 107.74(11) | 102.8(3) | 106.69(16) | 106.3(4) |
| Co1–S2–C2 | 105.5(2) | 107.24(11) | 102.2(4) | 107.79(13) | 108.8(3) |
| S1–C1–C2 | 119.7(6) | 117.3(2) | 120.4(8) | 118.7(4) | 121.0(8) |
| S2–C2–C1 | 118.2(6) | 117.8(2) | 121.1(8) | 116.4(3) | 113.8(8) |
| *Hydrogen bonding* | | | | | |
| OH···N | – | 1.958(33)[b] | – | 1.830(3)[b] | 1.856(11)[a] |
| NH···O | 1.908(13)[a] | – | – | – | – |
| CH···O | 2.283(16)[a] | – | – | – | – |
| *Dihedral angle* | | | | | |
| Cp/$CoS_2C_2$ | 90.9 | 90.144 | 87.6 | 89.342 | 91.990 |
| $CoS_2C_2$/pyridyl | – | 50.490 | – | 40.843 | 92.946 |
| $CoS_2C_2$/pyridonyl | 22.4 | – | 0.9 | – | – |

[a] Intermolecular hydrogen bonding.
[b] Intramolecular hydrogen bonding.




**Scheme 4.**

of complexes having electron-donating C(OH)$Me_2$ group (**8** at −1.30 V and **11** at −1.31 V) are more negative than those of comparable complexes without the substituent (**9** at −1.25 V and **13** at −1.25 V). The reduction potentials of complexes with pyridyl group (**2** at −1.23 V and **5** at −1.29 V) are more negative than those of comparable complexes with pyridonyl group (**3** at −1.06 V and **6** at −1.03 V) (Fig. 7).

## 3. Conclusion

This work aimed to synthesize [CpCo(dithiolene)] complexes bearing pyridonyl derivative followed some previous works by Garner and Joule [6–9]. [CpCo(dithiolene)] complexes with 2-pyridonyl substituent (**3**) revealed intermolecular NH···O and CH(dithiolene)···O hydrogen bondings. Some early works reported [Ni(dithiolene)$_2$] and [CpCo(dithiolene)] bearing amide and carboxylic acid groups, and these complexes have NH···O, NH···S(dithiolene) and OH···O hydrogen bondings [34,35]. Our case is more interesting because it is rare hydrogen bonding incorporating a dithiolene proton. This result really indicates that the dithiolene proton is not only an aromatic ring proton involving ring current effect but also an acidic one. In future, asymmetric dithiolene complexes involving a dithiolene proton, which formulated as [$M(S_2C_2(R, H))_n$], will be good materials to make a hydrogen bonding network. As also one of interesting results in this work, we unexpectedly obtained dithiolene-fused tricyclic pyridone derivative (**6**) by an intramolecular cyclization and its extended π-conjugation was observed.

## 4. Experimental

### 4.1. Materials and instrumentation

All reactions were carried out under an argon atmosphere by means of standard Schlenk techniques. All solvents for chemical reactions were dried and distilled by Na-benzophenone for xylene and *trans*-decahydronaphthalene or $CaH_2$ for dichloromethane before use. 2-(benzyloxy)-6-ethynylpyridine (**1**) [36], 2-methyl-4-

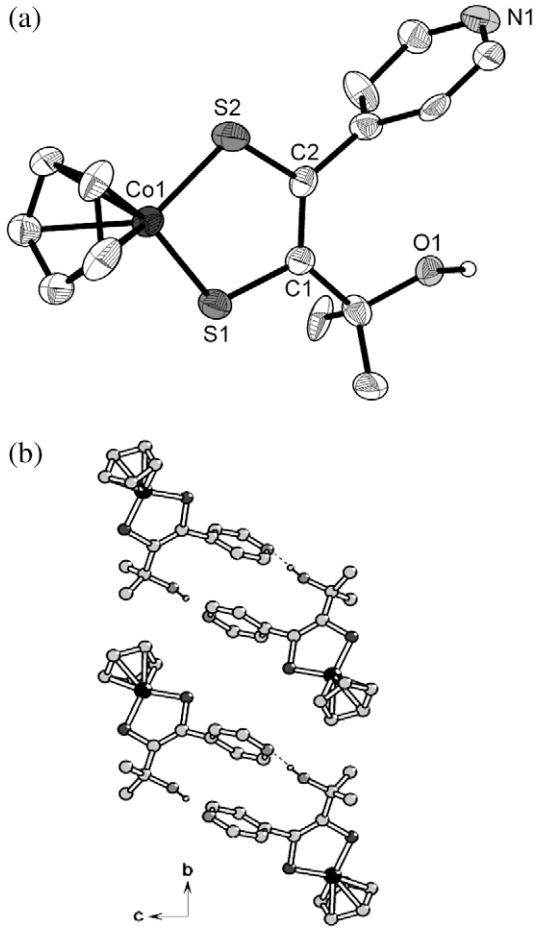



**Fig. 3.** (a) The ORTEP drawing of **11**. The thermal ellipsoids are drawn at 30% probability level. (b) Projection view along the *a*-axis of **11** showing intermolecular OH···N hydrogen bonding.

(pyridin-2-yl)but-3-yn-2-ol (**7**) [37], 2-methyl-4-(pyridin-4-yl)-but-3-yn-2-ol (**10**) [27], 4-ethynylpyridine [27], 2-ethynylpyridine [38], 2-(benzyloxy)-6-bromopyridine [39], and $[CpCo(CO)_2]$ [40] were prepared by literature method. 2-Methylbut-3-yn-2-ol and trimethylsilyl iodide were obtained from Tokyo Chemical Industry Co., Ltd. $(PPh_3)_2PdCl_2$, CuI, Silica gel (Wakogel C-300) and aluminum oxide were purchased from Wako Pure Chemical Industries, Ltd. Mass and IR spectra were recorded on a JEOL JMS-D300 and a Shimadzu Model FTIR 8600PC instruments, respectively. UV–Vis spectra were recorded on a Hitachi Model UV-2500PC spectrometer. Elemental analyses were determined by using a Shimadzu PE2400-II instrument.

### 4.2. Synthesis of CpCo(dithiolene) complex with $^2$PyOBn group (*2*)

$[CpCo(CO)_2]$ (1.5 ml, $d = 1.278$ g ml$^{-1}$, 10.7 mmol), elemental sulfur (0.60 g, 18.75 mmol) and 2-(benzyloxy)-6-ethynylpyridine (**1**) (1.89 g, 9.03 mmol) were reacted in refluxing xylene (50 ml) for 17 h. Solvent was removed under reduced pressure, and the residue was separated by column chromatography on silica gel (eluent: *n*-hexane/dichloromethane = 1:1(v/v)) to obtain a dark blue component. A product was further purified by recrystallization from *n*-hexane/dichloromethane (3:1(v/v)). A dark blue product (**2**) was obtained in 26% (dark blue solid, 0.937 g, 2.36 mmol) yield.

**Complex 2.** Mass ($EI^+$, 70 eV) *m/z* (rel. intensity) 397 ($[M^+]$, 93), 331 ($[M^+ - CpH]$, 21), 320 ($[M^+ - Ph]$, 10), 306 ($[M^+ - CH_2Ph]$, 18), 188 ($[CpCoS_2^+]$, 22), 124 ($[CpCo^+]$, 13), 91 ($CH_2Ph^+$, 100). $^1$H NMR ($CDCl_3$, 500 MHz, vs. TMS) $\delta = 9.59$ (s, 1H, dithiolene-H), 7.78 (d, $J = 7.6$ Hz, 1H, Py), 7.57 (t, $J = 7.6$ Hz, 1H, Py), 7.49 (d, $J = 7.3$ Hz, 2H, Ph), 7.37 (t, $J = 7.3$ Hz, 2H, Ph), 7.27 (t, $J = 7.3$ Hz, 1H, Ph), 6.79 (d, $J = 7.6$ Hz, 1H, Py), 5.45 (s, 2H, $CH_2$), 5.41 (s, 5H, Cp). $^{13}$C NMR ($CDCl_3$, 125 MHz, vs. TMS) $\delta = 169.8$, 162.7, 159.6, 153.7, 139.5, 137.6, 128.4, 128.2, 127.8, 112.8, 109.6, 79.4 (Cp), 67.4 ($CH_2$). UV–Vis ($CH_2Cl_2$) $\lambda_{max}$/nm ($\varepsilon$) 338 (11300), 599 (11000). IR (KBr disk) 1585, 1568, 1454, 1427, 1265, 1211, 1049, 984, 835, 795 cm$^{-1}$. Anal. Calcd. For $C_{19}H_{16}CoNOS_2$: C, 57.42; H, 4.06; N, 3.52. Found: C, 57.50; H, 4.05; N, 3.48%.

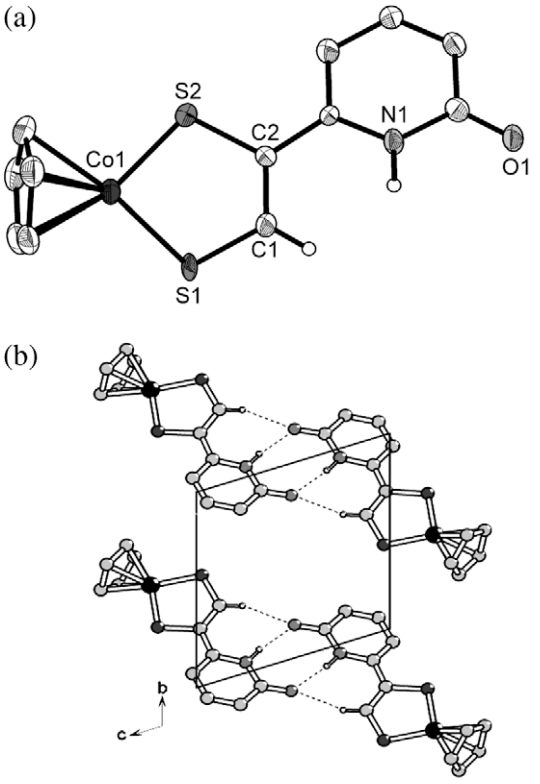



**Fig. 4.** (a) The ORTEP drawing of **3** (thermal ellipsoids 30% probability). (b) Projection view along the *a*-axis of the unit cell of **3** showing intermolecular OH···N and CH···N hydrogen bondings.

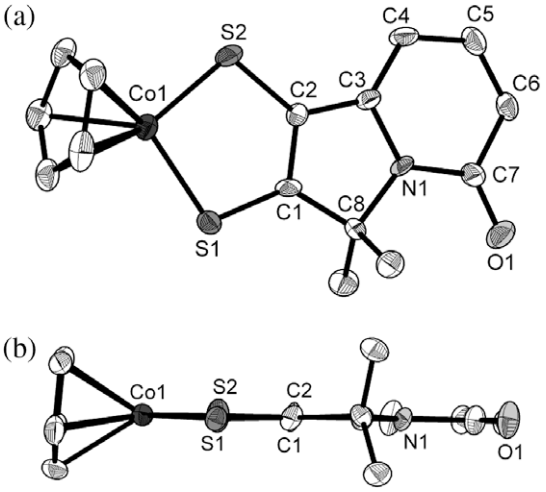



**Fig. 5.** The ORTEP drawings of **6** for (a) top view and (b) side view. (thermal ellipsoids 30% probability). Selected bond lengths except for dithiolene moiety: C1–C8 1.49(1), C2–C3 1.45(1), C3–C4 1.37(1), C4–C5 1.39(1), C5–C6 1.37(1), C6–C7 1.45(1), N1–C7 1.41(1), N1–C8 1.52(1).

**Table 2**
UV–Vis spectral data ($\lambda_{max}$/nm) and redox potentials (vs. $Fc/Fc^+$) of [CpCo(dithiolene)] complexes taken from cyclic voltammetry.

| | Absorption maxima $\lambda_{max}$/nm ($\varepsilon M^{-1}\,cm^{-1}$) | $E_{1/2}$ (red)/V | $E_p$ (ox)/V |
|---|---|---|---|
| **2** | 338 (11300), 599 (11000) | −1.23 | 0.56 |
| **3** | 362 (15600), 614 (9000) | −1.06 | 0.61 |
| **5** | 300 (27100), 573 (7700) | −1.29 | 0.62 |
| **6** | 289 (12800), 343 (6300), 364 (8700), 374 (7500), 668 (5800) | −1.03 | 0.60 |
| **8** | 406 (1600), 574 (10300) | −1.30 | 0.61 |
| **9** | 294 (19600), 356 (3700), 589 (7200) | −1.25 | 0.58 |
| **11** | 413 (1600), 562 (9200) | −1.31 | 0.62 |
| **12** | 417 (1500), 587 (9900) | −1.22 | 0.75 |
| **13** | 364 (5200), 583 (9900) | −1.25 | 0.65 |

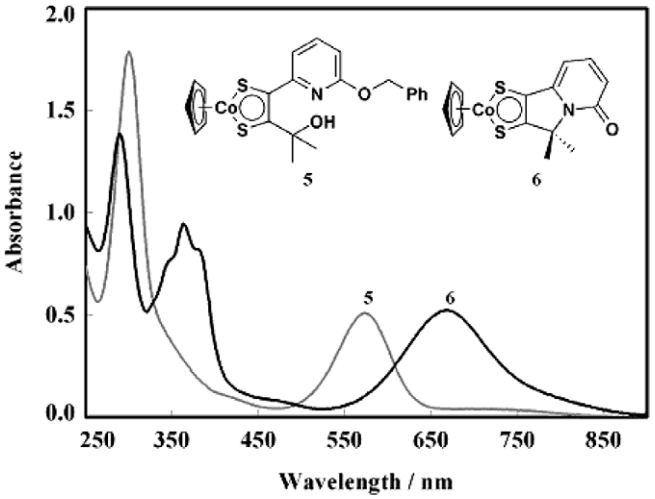



**Fig. 6.** UV–Vis spectra of **5** and **6** in dichloromethane solution ($c$ = c.a. $5.0 \times 10^{-5}$ mol dm$^{-3}$) at room temperature.

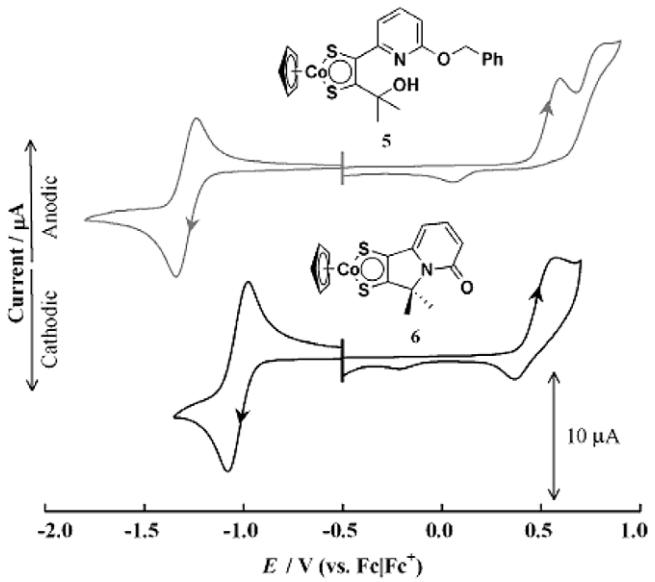



**Fig. 7.** Cyclic voltammograms of **5** and **6** ($c = 1 \times 10^{-3}$ mol dm$^{-3}$, $v$ = 100 mV s$^{-1}$, $\Phi$ = 1.6 mm Pt disk) in dichloromethane solution containing 0.1 mol dm$^{-3}$ tetra-*n*-butylammonium perchlorate at room temperature.

### 4.3. Synthesis of CpCo(dithiolene) complex with 2-pyridonyl substituent (*3*)

A conventional conversion from benzyloxypyridine to pyridone derivative written in literature [25] was performed for following reaction. Complex **2** (0.203 g, 0.511 mmol) reacted with trimethylsilyl iodide (0.3 ml, 2.19 mmol) in refluxing $CH_2Cl_2$ (10 ml) for 4 h. Silica gel was added into the reaction mixture. The resulted mixture was replaced to column chromatography on silica gel, and a blue component was separated with ethyl acetate. All solvents were removed under reduced pressure. A blue solid was further purified by recrystallization from *n*-hexane/dichloromethane (1:1(v/v)). A blue product (**3**) was obtained in 56% (greenish blue solid, 88 mg, 0.286 mmol) yield.

**Complex 3.** Mass ($EI^+$, 70 eV) *m/z* (rel. intensity) 307 ([$M^+$], 100), 241 ([$M^+$ –CpH], 30), 188 ([$CpCoS_2^+$], 65), 124 ([$CpCo^+$], 26). $^1H$ NMR ($CDCl_3$, 500 MHz, vs. TMS) δ = 9.60 (br-s, 1H, NH), 9.12 (s, 1H, dithiolene-H), 7.36 (dd, $J$ = 7.0, 6.5 Hz, 1H, Pyridone), 6.59–6.62 (m, 2H, Pyridone), 5.46 (s, 5H, Cp). $^{13}C$ NMR ($CDCl_3$, 125 MHz, vs. TMS) δ = 160.1, 157.8, 144.0, 141.4, 118.8, 103.6, 77.2 (Cp). UV–Vis ($CH_2Cl_2$) $\lambda_{max}$/nm (ε) 362 (15600), 614 (9000). IR (KBr disk) 1643, 1591, 1539, 1464, 980, 833, 787 cm$^{-1}$. Anal. Calcd. For $C_{12}H_{10}CoNOS_2$: C, 46.90; H, 3.28; N, 4.56. Found: C, 47.12; H, 3.09; N, 4.27%.

### 4.4. Synthesis of 4-(6-(benzyloxy)pyridin-2-yl)-2-methylbut-3-yn-2-ol (*4*)

2-(Benzyloxy)-6-bromopyridine (0.50 ml, 3.6 mmol) and 2-methylbut-3-yn-2-ol (0.40 ml, 4.0 mmol) were reacted in the presence of $(PPh_3)_2PdCl_2$ (50 mg, 0.07 mmol) and CuI (7 mg, 0.04 mmol) in diethylamine (15 ml) at room temperature for 17 h. After the reaction, solvent was removed under reduced pressure. 100 ml of water was added and then organic component was extracted with 200 ml of diethyl ether. The resulted organic layer was dried with magnesium sulfate, and then it was filtered. The resulted filtrate was evaporated under reduced pressure. The mixture was separated by column chromatography on aluminum oxide with diethyl ether. An oily pale yellow product was obtained in 75% (720 mg, 2.69 mmol) yield. $^1H$ NMR ($CDCl_3$, 500 MHz, vs. TMS) δ = 7.54 (t, $J$ = 7.6 Hz, 1H, Py), 7.33–7.47 (m, 5H, Ph), 7.06 (d, $J$ = 7.6 Hz, 1H, Py), 6.76 (d, $J$ = 7.6 Hz, 1H, Py), 5.40 (s, 2H, $CH_2$), 1.67 (s, 6H, Me). HR-Mass Calcd. For $C_{17}H_{17}NO_2$: 267.1259. Found: 267.1263%.

### 4.5. Reaction of [CpCo(CO)$_2$], elemental sulfur with 4-(6-(benzyloxy)pyridin-2-yl)-2-methylbut-3-yn-2-ol (*4*)

[$CpCo(CO)_2$] (0.4 ml, 2.86 mmol), elemental sulfur (0.174 g, 5.44 mmol) and 4-(6-(benzyloxy)pyridin-2-yl)-2-methylbut-3-yn-2-ol (**4**) (0.695 g, 2.60 mmol) were reacted in refluxing xylene (20 ml) for 17 h. Solvent was removed under reduced pressure, and the residue was separated by column chromatography on silica gel. A first product (**5**) was separated with *n*-hexane/dichloromethane = 1:1(v/v) and a second product (**6**) was separated with dichloromethane/diethyl ether = 1:1(v/v). These products were further purified by recrystallization from *n*-hexane/dichloromethane = 1:1(v/v). Complexes **5** and **6** were obtained in 18% (purple

solid, 0.217 g, 0.477 mmol) and 29% (dark grren solid, 0.263 g, 0.758 mmol) yields, respectively.

**Complex 5.** Mass ($EI^+$, 70 eV) *m/z* (rel. intensity) 455 ($[M^+]$, 5), 437 ($[M^+–H_2O]$, 9), 397 ($[M^+–Me_2CO]$, 3), 346 ([**7**$^+$–1], 100), 332 ([**7**$^+$–Me], 31), 281 ([**7**$^+$–CpH], 36), 188 ($[CpCoS_2^+]$, 5), 124 ($[CpCo^+]$, 6), 91 ($[CH_2Ph^+]$, 68). $^1H$ NMR ($CDCl_3$, 500 MHz, vs. TMS) δ = 7.70 (t, *J* = 7.6 Hz, 1H, Py), 7.55 (d, *J* = 7.6 Hz, 1H, Py), 7.28–7.41 (m, 5H, Ph), 7.20 (s, 1H, OH), 6.85 (d, *J* = 7.6 Hz, 1H, Py), 5.37 (s, 5H, Cp), 5.25 (s, 2H, $CH_2$), 1.62 (s, 6H, Me). UV–Vis ($CH_2Cl_2$) $\lambda_{max}$/nm (ε) 300 (27100), 573 (7700). IR (KBr disk) 3271, 1417, 1296, 1198, 833, 745 $cm^{-1}$. Anal. Calcd. For $C_{22}H_{22}CoNO_2S_2$: C, 58.01; H, 4.87; N, 3.08. Found: C, 57.80; H, 4.81; N, 2.96%.

**Complex 6.** Mass ($EI^+$, 70 eV) *m/z* (rel. intensity) 347 ($[M^+]$, 100), 332 ($[M^+–Me]$, 75), 281 ($[M^+–CpH]$, 62), 188 ($[CpCoS_2^+]$, 5), 124 ($[CpCo^+]$, 9). $^1H$ NMR ($CDCl_3$, 500 MHz, vs. TMS) δ = 7.28 (dd, *J* = 8.2, 6.0 Hz, 1H, Pyridone), 6.71 (d, *J* = 6.0 Hz, 1H, Pyridone), 6.47 (d, *J* = 8.2 Hz, 1H, Pyridone), 5.45 (s, 5H, Cp), 1.88 (s, 6H, Me). UV–Vis ($CH_2Cl_2$) $\lambda_{max}$/nm (ε) 343 (6300), 364 (8700), 374 (7500), 668 (5800). IR (KBr disk) 1651, 1558, 1531, 1456, 1099, 793 $cm^{-1}$. Anal. Calcd. For $C_{15}H_{14}CoNOS_2$: C, 51.87; H, 4.06; N, 4.03. Found: C, 51.70; H, 4.00; N, 3.86%.

### *4.6. Reaction of [CpCo(CO)$_2$], elemental sulfur with 2-methyl-4-(pyridin-2-yl)but-3-yn-2-ol (**7**)*

[$CpCo(CO)_2$] (0.88 ml, 6.21 mmol), elemental sulfur (0.40 g, 12.4 mmol) and 2-methyl-4-(pyridin-2-yl)but-3-yn-2-ol (**7**) (1.0 g, 6.21 mmol) were reacted in refluxing xylene (50 ml) for 17 h. Solvent was removed under reduced pressure, and the residue was separated by column chromatography on aluminum oxide. Two different fractions were separated with *n*-hexane/dichloromethane = 2:5(v/v). Both products were further purified by recrystallization from *n*-hexane/dichloromethane = 1:1(v/v). Complexes **8** and **9** were obtained in 23% (purple solid, 0.499 g, 1.43 mmol) and 3% (dark blue solid, 0.074 g, 0.25 mmol) yields, respectively.

Complex **9** was directly prepared by the reaction of [$CpCo(CO)_2$] (1.37 ml, 9.7 mmol), elemental sulfur (0.621 g, 19.4 mmol) with 2-ethynylpyridine (1.0 g, 9.7 mmol). This reaction mixture was reacted in refluxing xylene (50 ml) for 17 h. The product was isolated in 26% (0.717 g, 2.464 mmol) yield by the same way as noted above.

**Complex 8.** Mass ($EI^+$, 70 eV) *m/z* (rel. intensity) 349 ($[M^+]$, 100), 291 ($[M^+–Me_2CO]$(**9**$^+$), 79), 227 ($[M^+–Me_2CO–S_2]$, 30), 188 ($[CpCoS_2^+]$, 12), 124 ($[CpCo^+]$, 22). $^1H$ NMR ($CDCl_3$, 500 MHz, vs. TMS) δ = 8.44 (m, 1H, Py), 8.08 (d, *J* = 8.3 Hz, 1H, Py), 7.77 (dt, *J* = 8.3, 5.9 Hz, 1H, Py), 7.28 (t, *J* = 5.9 Hz, 1H, Py), 5.35 (s, 5H, Cp), 1.56 (s, 6H, Me). $^{13}C$ NMR ($CDCl_3$, 125 MHz, vs. TMS) δ = 182.2, 164.6 (dithiolene-C), 159.8, 146.6, 137.5, 125.7, 122.0 (Py), 80.1 (Cp), 74.4 ($Me_2COH$), 30.9 ($Me_2COH$). UV–Vis ($CH_2Cl_2$) $\lambda_{max}$/nm (ε) 406 (1600), 574 (10300). Anal. Calcd. For $C_{15}H_{16}CoNOS_2$: C, 51.57; H, 4.62; N, 4.01. Found: C, 51.53; H, 4.66; N, 4.01%.

**Complex 9.** Mass ($EI^+$, 70 eV) *m/z* (rel. intensity) 291 ($[M^+]$, 100), 227 ($[M^+–S_2]$, 27), 188 ($[CpCoS_2^+]$, 46), 124 ($[CpCo^+]$, 17). $^1H$ NMR ($CDCl_3$, 500 MHz, vs. TMS) δ = 9.66 (s, 1H, dithiolene-H), 8.55 (d, *J* = 3.6 Hz, 1H, Py), 8.05 (d, *J* = 7.9 Hz, 1H, Py), 7.64 (dt, *J* = 7.9, 3.6 Hz, 1H, Py), 7.22 (t, *J* = 3.6 Hz, 1H, Py), 5.28 (s, 5H, Cp). $^{13}C$ NMR ($CDCl_3$, 125 MHz, vs. TMS) δ = 169.6, 156.3 (dithiolene-C), 159.0, 149.5, 136.8, 121.8, 119.9 (Py), 79.4 (Cp). UV–Vis ($CH_2Cl_2$) $\lambda_{max}$/nm (ε) 294 (19600), 356 (3700), 589 (7200). Anal. Calcd. For $C_{12}H_{10}CoNS_2$: C, 49.48; H, 3.46; N, 4.81. Found: C, 49.34; H, 3.46; N, 4.76%.

### *4.7. Synthesis of complex **9** from **8** under heating condition*

Complex **8** (70 mg, 0.20 mmol) was reacted in refluxing *trans*-decahydronaphthalene (50 ml) for 18 h. An initial purple solution was changed to dark blue. After the reaction, solvent was removed under reduced pressure. The residue was separated by column chromatography on aluminum oxide (eluent = dichloromethane). The dark blue product 9 was obtained in 39% (23 mg, 0.079 mmol) yield.

Refluxing xylene solution (50 ml) of **8** (70 mg, 0.20 mmol) was stirred for 18 h in the presence of $H_2SO_4$ (3 μl). No reaction was confirmed and **8** was recovered in 99%.

### *4.8. Reaction of [CpCo(CO)$_2$], elemental sulfur with 2-methyl-4-(pyridin-4-yl)but-3-yn-2-ol (**10**)*

[$CpCo(CO)_2$] (2.63 ml, 18.6 mmol), elemental sulfur (1.91 g, 37.2 mmol) and 2-methyl-4-(pyridin-4-yl)but-3-yn-2-ol (**10**) (3.0 g, 18.6 mmol) were reacted in refluxing xylene (50 ml) for 17 h. Solvent was removed under reduced pressure, and the residue was separated by column chromatography on aluminum oxide. Two different fractions were separated with *n*-hexane/dichloromethane = 2:5(v/v). Both products were further purified by recrystallization from *n*-hexane/dichloromethane = 1:1(v/v). Complexes **11** and **12** were obtained in 22% (purple solid, 1.43 g, 4.10 mmol) and 4% (dark blue solid, 0.242 g, 0.73 mmol) yields, respectively.

**Complex 11.** Mass ($EI^+$, 70 eV) *m/z* (rel. intensity) 349 ($[M^+]$, 100), 331 ($[M^+–H_2O]$, 65), 188 ($[CpCoS_2^+]$, 12), 124 ($[CpCo^+]$, 20). $^1H$ NMR ($CDCl_3$, 500 MHz, vs. TMS) δ = 8.54 (d, *J* = 6.0 Hz, 2H, Py), 7.20 (d, *J* = 6.0 Hz, 2H, Py), 5.37 (s, 5H, Cp), 1.55 (s, 6H, Me). $^{13}C$ NMR ($CDCl_3$, 125 MHz, vs. TMS) δ = 176.9, 163.1 (dithiolene-C), 152.6, 148.9, 123.9 (Py), 80.0 (Cp), 70.7 ($Me_2COH$), 32.9 ($Me_2COH$). UV–Vis ($CH_2Cl_2$) $\lambda_{max}$/nm (ε) 413 (1600), 562 (9200). Anal. Calcd. For $C_{15}H_{16}CoNOS_2$: C, 51.57; H, 4.62; N, 4.01. Found: C, 51.75; H, 4.62; N, 3.99%.

**Complex 12.** Mass ($EI^+$, 70 eV) *m/z* (rel. intensity) 331 ($[M^+]$, 100), 188 ($[CpCoS_2^+]$, 14), 124 ($[CpCo^+]$, 34). $^1H$ NMR ($CDCl_3$, 500 MHz, vs. TMS) δ = 8.55 (d, *J* = 7.6 Hz, 2H, Py), 7.43 (d, *J* = 7.6 Hz, 2H, Py), 5.39 (s, 5H, Cp), 5.05 (s, 2H, $CH_2$), 1.88 (s, 3H, Me). $^{13}C$ NMR ($CDCl_3$, 125 MHz, vs. TMS) δ = 173.1, 163.0 (dithiolene-C), 149.6, 149.4, 146.0 (Py), 122.8 ($C{=}CH_2$), 118.2 ($C{=}CH_2$), 77.3 (Cp), 23.6 (Me) UV–Vis ($CH_2Cl_2$) $\lambda_{max}$/nm (ε) 417 (1500), 587 (9900). Anal. Calcd. For $C_{15}H_{14}CoNS_2$: C, 54.37; H, 4.26; N, 4.23. Found: C, 54.25; H, 4.25; N, 4.41%.

### *4.9. Synthesis of complex **12** from **11** under heating condition*

Complex **11** (70 mg, 0.20 mmol) was reacted in refluxing *trans*-decahydronaphthalene (50 ml) for 18 h. An initial purple solution was changed to dark blue. After the reaction, solvent was removed under reduced pressure. The residue was separated by column chromatography on aluminum oxide (eluent = dichloromethane). The dark blue product **12** was obtained in 79% (52 mg, 0.157 mmol) yield.

Xylene solution (50 ml) of **11** (150 mg, 0.42 mmol) in the presence of $H_2SO_4$ (3 μl) was refluxed for 18 h. The product **12** was separated by the same way noted above, and was isolated in 89% yield (124 mg, 0.274 mmol).

### *4.10. Reaction of [CpCo(CO)$_2$], elemental sulfur with 4-ethynylpyridine*

[$CpCo(CO)_2$] (0.14 ml, 1.02 mmol), elemental sulfur (0.066 g, 2.02 mmol) and 4-ethynylpyridine (0.11 g, 1.02 mmol) were reacted in refluxing xylene (45 ml) for 4 h. Solvent was removed under reduced pressure, and the residue was separated by column chromatography on aluminum oxide (eluent: *n*-hexane/dichloromethane = 1:2(v/v)). Resulted dark blue product was further purified by recrystallization from *n*-hexane/dichloromethane. Complex **13** was obtained in 30% (dark blue solid, 0.089 g, 0.306 mmol) yield.

**Table 3**
Crystallographic data.

| Compound | **3** | **5** | **6** | **8** | **11** |
|---|---|---|---|---|---|
| Formula | $C_{12}H_{10}NOS_2Co$ | $C_{22}H_{22}CoNOS_2$ | $C_{15}H_{14}NOS_2Co$ | $C_{15}H_{16}CoNOS_2$ | $C_{15}H_{16}CoNOS_2$ |
| FW (g mol$^{-1}$) | 307.27 | 439.46 | 347.33 | 349.35 | 349.35 |
| Crystal color | green | darkblue | green | purple | purple |
| Crystal shape | cubic | platelet | prismatic | chunk | platelet |
| Crystal size (mm) | 0.30 × 0.23 × 0.10 | 0.35 × 0.225 × 0.025 | 0.30 × 0.17 × 0.03 | 0.30 × 0.30 × 0.13 | 0.30 × 0.17 × 0.01 |
| Crystal system | triclinic | monoclinic | monoclinic | monoclinic | orthorhombic |
| Space group | $P\bar{1}$ (No. 2) | $P2_1$ (No. 4) | $P2_1/n$ (No. 14) | $C2/c$ (No. 15) | $Pbca$ (No. 61) |
| $T$ (K) | 298 | 298 | 298 | 298 | 298 |
| $a$ (Å) | 8.859(1) | 10.8938(13) | 6.008(4) | 29.859(3) | 6.318(3) |
| $b$ (Å) | 9.400(2) | 6.2634(7) | 19.204(4) | 6.7005(4) | 18.303(9) |
| $c$ (Å) | 8.383(1) | 15.5231(17) | 12.947(3) | 18.4393(16) | 26.335(12) |
| $\alpha$ (°) | 111.553(10) | | | | |
| $\beta$ (°) | 101.99(1) | 103.553(5) | 98.24(3) | 124.6952(10) | |
| $\gamma$ (°) | 67.26(1) | | | | |
| $V$ (Å$^3$) | 597.1(2) | 1029.7(2) | 1478.3(9) | 3033.2(4) | 3045(3) |
| $Z$ | 2 | 2 | 4 | 8 | 8 |
| Diffractometer | four-circle | CCD | four-circle | CCD | CCD |
| $D_{calc}$ (g cm$^{-3}$) | 1.709 | 1.417 | 1.561 | 1.530 | 1.524 |
| μ (mm$^{-1}$) | 1.766 | 1.047 | 1.436 | 1.400 | 1.395 |
| Total reflections | 2920 | 8129 | 7428 | 11335 | 22048 |
| Unique reflections ($R_{int}$) | 2742 (0.015) | 4637 (0.0236) | 3394 (0.042) | 3400 (0.032) | 3487 (0.105) |
| Unique reflections ($I > 2\sigma(I)$) | 1596 | 3641 | 1480 | 2517 | 1478 |
| $R_1$, $wR_2$ ($I > 3\sigma(I)$) | 0.057, 0.080 | | 0.054, 0.089 | | |
| $R_1$, $wR_2$ ($I > 2\sigma(I)$) | | 0.0346, 0.0652 | | 0.0535, 0.1319 | 0.0541, 0.1338 |
| Goodness-of-fit | 1.500 | 1.004 | 1.230 | 1.038 | 1.073 |

**Complex 13.** Mass (EI$^+$, 70 eV) *m/z* (rel. intensity) 291 ([M$^+$], 100), 227 ([M$^+$–$S_2$], 35), 188 ([$CpCoS_2^+$], 45), 124 ([$CpCo^+$], 20). $^1$H NMR ($CDCl_3$, 500 MHz, vs. TMS) δ = 9.13 (s, 1H, dithiolene-H), 8.57 (d, $J$ = 7.0 Hz, 2H, Py), 7.69 (d, $J$ = 7.0 Hz, 2H, Py), 5.43 (s, 5H, Cp). $^{13}$C NMR ($CDCl_3$, 125 MHz, vs. TMS) δ = 160.4, 157.1 (dithiolene-C), 150.3, 146.1, 120.5, (Py), 79.7 (Cp). UV–Vis ($CH_2Cl_2$) $\lambda_{max}$/nm (ε) 364 (5200), 583 (9900). Anal. Calcd. For $C_{12}H_{10}CoNS_2$: C, 49.48; H, 3.46; N, 4.81. Found: C, 49.23; H, 3.70; N, 4.77%.

### 4.11. X-ray diffraction study

A single crystal of **3**, **5**, **6**, **8**, and **11** were obtained by recrystallization from the dichloromethane solutions and then vapor diffusion of *n*-hexane into those solutions. Crystals were mounted on the top of a thin glass fiber. Measurements for **3** and **6** were made on Rigaku AFC5S four-circle diffractometer, and for **5**, **8**, and **11** were made on Rigaku Mercury CCD diffractometer with graphite-monochromated MoKα radiation ($\lambda$ = 0.71073 Å). Each structure was solved by direct methods and expanded Fourier techniques [41]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations, and these were not refined. Absorption corrections were applied. For **3** and **6**, idealized positions were used for the TEXSAN crystallographic software package of Molecular Structure Corp [42]. All calculations for **8** and **11** were performed using the Crystal Structure software package [43], and for **5** was done using WinGX software package [44]. Crystallographic data are summarized in Table 3.

### 4.12. CV measurements

All electrochemical measurements were performed under an argon atmosphere. Solvents for electrochemical measurements were dried by 4 Å molecular sieve before use. A platinum wire served as a counter electrode, and the reference electrode is Ag/AgCl was corrected for junction potentials by being referenced internally to the ferrocene/ferrocenium (Fc/Fc$^+$) couple. A stationary platinum disk (1.6 mm in diameter) was used as a working electrode. The Model CV-50 W instrument from BAS Co. was used for cyclic voltammetry (CV) measurements. CVs were measured in 1.0 mmol dm$^{-3}$ dichloromethane solutions of complexes containing 0.1 mol dm$^{-3}$ tetra-*n*-butylammonium perchlorate (TBAP) at 25 °C.

## 5. Supplementary material

CCDC No. 723293 (for **3**), 723294 (for **5**), 723295 (for **6**), 723296 (for **8**), and 723297 (for **11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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