Communication

Sulfur-centered and nitrogen-centered radical substitution reactions of aromatic CpCo(dithiolene) complex with 2,2′-Dibenzothiazolyl disulfide

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ABSTRACT

Aromatic $[CpCo(S_2C_2(R)(H))]$ complexes (R = Me (**1**) and Ph (**5**)) reacted with 2,2′-dibenzothiazolyl disulfide (**2**, R′SSR′ (R′ = 2-benzothiazolyl)) as a sulfur-centered radical source to form some radical substitution products. 2-Benzothiazolylthiyl radical (R′S•) was substituted on the dithiolene ring or on the Me group of **1** to give $[CpCo(S_2C_2(Me)(SR'))]$ (**3**) or $[CpCo(S_2C_2(CH_2SR')(H))]$ (**4**), respectively. The reaction of **5** with **2** gave two different substitution products on the dithiolene ring but they were structural isomers. One was the substitution product $[CpCo(S_2C_2(Ph)(SR'))]$ (**6**) by the R′S• radical substitution (*S*-substituted product), and the other was *N*-substituted product (**7**). **7** was formed by a nitrogen-centered radical that is a resonant species of the 2-benzothiazolylthiyl radical. Conventional heating, photochemical and microwave-enhanced reactions were performed. The molecular structures of **3**, **4** and **7** were determined by X-ray diffraction studies.

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1. Introduction

Metalladithiolenes [1] and metallabenzenes [2] are pseudo aromatic metallacycles including conjugated π-electrons in the ring. Among them, π-extended metalladithiolene compounds are useful for molecular materials such as molecular conductors [3], magnetic materials [4] and optical materials [5]. On the other hand, one interesting chemical property is due to coexistence of aromaticity and unsaturation of the metallacycle [6]. Namely, they show not only electrophilic substitution reactions but also addition reactions on the ring. We have studied on the chemical reactivities of organometallic [CpM(dithiolene)] complexes (M = Co, Rh, Ir) so far [6,7]. Addition reactions involve alkylidene-, imido-, alkyne-, and norbornene-addition into the M–S bond due to unsaturation of the metallacycle [8]. On the basis of aromaticity of the metallacycle, the Friedel-Crafts acylation occurs on the dithiolene carbon of $[CpCo(S_2C_2(R)(H))]$ complex in the presence of Lewis acid [9]. Quite

recently, we reported the Suzuki-Miyaura cross-coupling reaction between the boronated $[CpCo(S_2C_2(Ph)(Bpin))]$ (Bpin = 4,4,5,5-tetramethyl-1,3,2-dioxaboronate) complex and aryl halides in the presence of Pd catalyst [10].

Furthermore, one remarkable result based on aromaticity has been carbon-centered radical substitution reactions to dithiolene complexes. For example, $[CpCo(S_2C_2(Ph)(H))]$ complex reacts with 1-cyano-1-ethylmethyl radical, which can be generated from thermolysis of 2,2′-azobis(isobutyronitrile) (AIBN) [11], to undergo radical substitutions on the dithiolene ring and on the Cp ring as well (Scheme 1) [9]. The former reaction has been the first case of radical substitution reaction to a pseudo aromatic metallacycle. In addition, this carbon-centered radical substitution could occur on the square-planar bisdithiolene complex $[Ni(S_2C_2(Ph)(H))_2]$ [12]. On the basis of these previous works, we focused on the reaction of a sulfur-centered radical with $[CpCo(S_2C_2(R)(H))]$ complexes (R = Me (**1**) and Ph (**5**)) under thermal, photochemical or microwaved (MW) condition. Recently, Horikoshi and Serpone et al. developed MW-enhanced organic radical reactions [13]. A sulfur-centered radical source used in this work is 2,2′-dibenzothiazolyl disulfide (**2**, (R′SSR′ (R′ = 2-benzothiazolyl))). This is one useful sulfur-centered radical source because its dissociation energy is 29 kcal, and it can generate the 2-benzothiazolylthiyl radical (R′S•) without any radical reaction initiators followed by a homolysis at
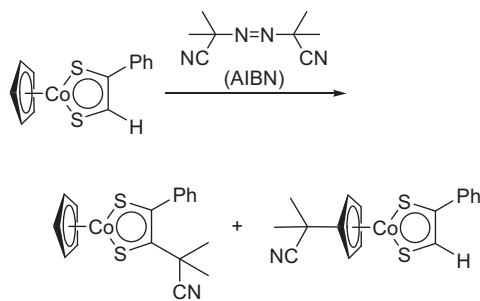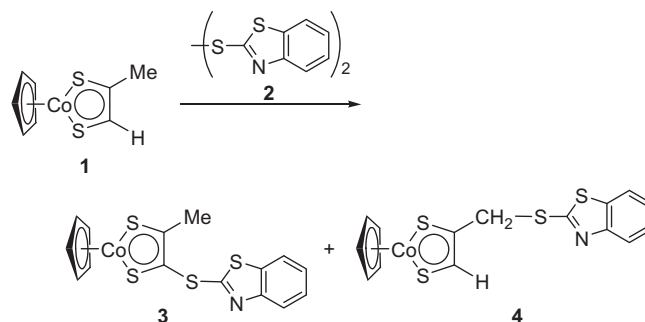

Scheme 1.

Scheme 2.

80 °C [14,15]. In addition, the R'S• radical can be stabilized by a conjugation effect of benzothiazolyl backbone. Here we report on the first case of sulfur-centered radical substitution to a pseudo aromatic metallacycle, on a radical substitution to a Me group combined with dithiolene ring, and an unexpected case of nitrogen-centered radical reaction as well.

2. Results and discussion

2.1. Reactions of [CpCo(S₂C₂(Me)(H))] (1) with 2,2'-dibenzothiazolyl disulfide (2)

1 reacted with 20 equiv of **2** (R'SSR') in refluxing benzene for 4 h to form two different substitution products. The ¹H NMR spectrum of one product exhibited absence of the hydrogen atom on the dithiolene ring, that usually appears around 9 ppm (vs TMS) [16]. The other product indicated absence of one hydrogen atom on the Me group ($\delta = 4.83$ ppm, singlet, 2H) but the signal of the dithiolene proton appeared at 8.76 ppm (singlet, 1H). Furthermore, both products showed the same molecular ion peaks by using those mass spectra ($m/z = 393$) to suggest the formation of a mono-substituted product by R'S• radical. These mass and ¹H NMR spectral data conform that the former species is the substitution product, which is formulated as [CpCo(S₂C₂(Me)(SR'))] (**3**) due to a substitution on the dithiolene carbon, and the latter is formulated as [CpCo(S₂C₂(CH₂SR')(H))] (**4**) due to a substitution on the Me group (Scheme 2). However, a disubstituted product was not obtained by this condition. Formation mechanisms for **3** and **4** are probably similar to those of typical organic radical reactions [17]; thus, addition of sulfur radical to the dithiolene carbon radical or to the CH₂• group followed by the radical hydrogen abstraction from the dithiolene ring or Me group. Probably, the transient CH₂• group could be stabilized by a π-conjugation effect of the aromatic cobaltadithiolene ring.

Results of the substitution reactions of **1** are summarized in Table 1. **3** and **4** were obtained in 10% and 12% yields by a conventional heating (CH) reaction in refluxing benzene (Entry 1). Yield of **3** relatively increased under refluxing MeCN (22% yield) but yield of **4** decreased (4% yield) (Entry 2). The reaction under refluxing xylene yielded **3** in 24% but did not give **4** at all and most of **1**

decomposed (Entry 3). On the basis of comparison between Entry 1 and 3, a thermal transformation of **4** to **3** is conceivable. However, the thermal reaction of **4** in refluxing xylene caused complicated decompositions and no product could be identified. The photochemical (*hν*) reaction of **1** with **2** for 24 h also gave **3** (6% yield) and **4** (10% yield) without any external heating (Entry 4). This result suggests the R'S• radical formation by the photolysis of **2**. The MW reaction of **1** with **2** gave **3** and **4** in 7% and 23% yields (Entry 5) during 40 min in refluxing diglyme (diethyleneglycol dimethyl ether, b.p. = 162 °C). This result clearly suggests that the MW reaction effects for this radical reaction with shorter reaction time and higher reaction selectivity for **4** than **3**, compared with the corresponding CH reaction or *hν* reaction.

2.2. Reactions of [CpCo(S₂C₂(Ph)(H))] (5) with 2,2'-dibenzothiazolyl disulfide (2)

The CH reaction of **5** with 20 equiv of **2** in refluxing benzene gave the substitution product that is formulated as [CpCo(S₂C₂(Ph)(SR'))] (**6**) in 19% yield and the recovery of **5** was obtained in 61% (Entry 6). No substitution product on the Ph group or on the Cp ligand was found. The thermal reaction of **5** with **2** in the presence of excess TEMPO (80 eq.) or O₂ (bubbled into solution) inhibited the formation of **6** with 80−90% recoveries of **5** (Entries 7 and 8), while compared with Entry 6. These results suggest that one reaction mechanism is a radical generation by the homolysis of **2**. The *hν* reaction of **5** with **2** formed **6** in 18% and the recovery of **5** in 61% yields (Entry 10). On the other hand, **5** reacted with **2** by CH in refluxing MeCN to afford two different substitution products (Scheme 3). One was **6** with molecular ion peak $m/z = 455$ by the mass spectrum. The other product (**7**) showed the same molecular ion peak ($m/z = 455$) to also suggest a monosubstituted product by the R'S group. Moreover, both of **6** and **7** exhibited absence of dithiolene protons in the ¹H NMR data. This fact suggests that the R'S unit is bound to the dithiolene carbon for both products, but they have two different substitution forms to the dithiolene ring. Therefore, both products are definitely structural isomers each other. Fortunately, **7** could be crystallized well and the X-ray structure was successfully obtained. Fig. 1(c) shows the molecular

Table 1
Reactions of [CpCo(S₂C₂(Me)(H))] (**1**) with 20 equiv of 2,2'-dibenzothiazolyl disulfide (**2**).

Entry	Conditionᵃ	Temp.	Time	Solvent	Vol./ml	Yield of **3**/%	Yield of **4**/%	Recovery of **1**/%
1	CH	reflux	4 h	benzene	30	10	12	17
2	CH	reflux	4 h	MeCN	30	22	4	60
3	CH	reflux	4 h	xylene	30	24	0	trace
4	*hν*	rt	24 h	benzene	50	6	10	56
5	MW	reflux	30 min	diglyme	30	7	23	44

ᵃ CH: conventional heating with oil bath, *hν*: photo irradiation from high pressure Hg lamp, MW: microwave irradiation with 150 W.
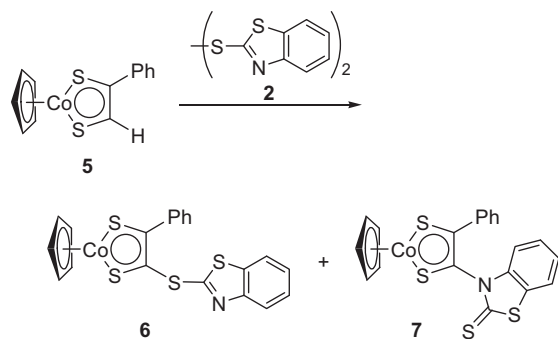
Scheme 3.

structure of **7** whose nitrogen atom of the R′S unit binds to the dithiolene carbon (N-substituted complex). Reaction mechanism can be explained by the similar radical reaction to those of **3** and **4**. Namely, the initial reaction is plausibly a hydrogen abstraction from **5** and then addition of sulfur-centered or nitrogen-centered radical provides **6** or **7**, respectively. Table 2 displayed that **6** and **7** were obtained under refluxing MeCN in 8% and 18% yields, respectively (Entry 9). However, no **7** was formed in refluxing benzene at all (Entry 6). Although the $h\nu$ reaction of **5** with **2** did not give **7** in benzene (Entry 10), both **6** (6%) and trace amount of **7** were obtained in mixed benzene/MeCN solution with $h\nu$ irradiation (Entry 11). The MW reaction of **5** with **2** during 40 min in refluxing diglyme gave **6** and **7** in 21% and 7% yields, respectively (Entry 12).

Since **7** was obtained in polar solvents, we assumed a formation mechanism for **7** via an ionic reaction of **5** with 2-benzothiazole-thiol (R′SH), which can be formed from a hydrogen abstraction by

the R′S• radical. However, no reaction was found in refluxing MeCN with the complete recovery of **5**. Another possibility for the formation of **7** is an isomerization of **6** to **7** by a 1,3-shift, but **6** itself did not react in refluxing MeCN solution as well. Therefore, both S-substituted (**6**) and N-substituted (**7**) complexes were plausibly formed by the substitution reactions of sulfur-centered radical and nitrogen-centered radical intermediates, respectively. Both radical species are drawn in the resonance structures as proposed previously [18] (Scheme 4). In fact, an early work has already developed that the thermal reaction of **2** with cyclohexene has occurred both S-substitution and N-substitution reactions on the allylic position of cyclohexene [18a].

2.3. Molecular structures of substitution products

Fig. 1(a–c) exhibit the molecular structures of **3**, **4** and **7** together with those bond lengths of the R′S moieties. Fig. 1(a) and (b) definitely prove the sulfur-centered radical substitutions on the dithiolene carbon for **3** and on the Me group for **4**. Again Fig. 1(c) confirms the nitrogen-centered radical substitution on the dithiolene carbon for **7**. The all structures of them have typical two-legged piano-stool geometries with formal 16-electron unsaturated metal centers. The S3−C4 bond lengths of **3** and **4** are 1.749(7) Å and 1.752 (12) Å, respectively. These facts almost support single bond characters for them, and are similar to the single S4−C4 bonds of 1.751 (8) Å for **3** and 1.752(21) Å for **4** in the thiazole cycles. In addition, the double bonds of N1−C4 of **3** and **4** are found with 1.299(8) Å and 1.286(19) Å, respectively. Therefore, there are typical thiazole sulfide moieties in **3** and **4** (Fig. 1(a–b)). On the other hand, the S3−C9 bond lengths of **7** is 1.605(28) Å, and this is clearly shorter than the single bond of C9−S4 (1.793(21) Å) in the five-membered
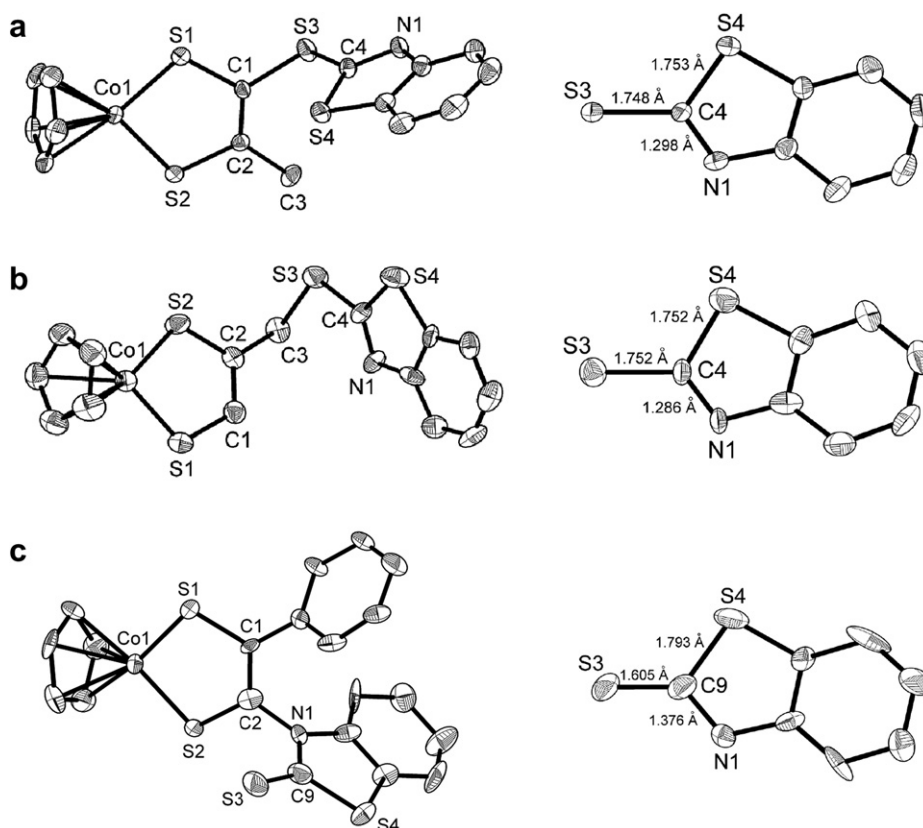

Fig. 1. ORTEP drawings of (a) **3**, (b) **4** and (c) **7**. Thermal ellipsoids are drawn at 30% probability level. All hydrogen atoms are omitted for simplicity.

Table 2
Reactions of [CpCo(S$_2$C$_2$(Ph)(H))] (**5**) with 2,2′-dibenzothiazolyl disulfide (**2**).

Entry	Condition	Temp.	Time	Solvent	Vol./ml	Additive	Yield of **6**/%	Yield of **7**/%	Recovery of **5**/%
6	CH	reflux	4 h	benzene	30		19	0	61
7	CH	reflux	4 h	benzene	30	TEMPO[a]	2	0	90
8	CH	reflux	4 h	benzene	30	O$_2$[b]	9	0	80
9	CH	reflux	4 h	MeCN	30		8	18	54
10	$h\nu$	rt	24 h	benzene	50		18	0	61
11	$h\nu$	rt	24 h	benzene/MeCN	50		6	trace	75
12	MW	reflux	40 min	diglyme	30		21	7	24

[a] 80 equiv were used.
[b] O$_2$ gas was introduced with bubbling into the solution.

heterocycle. The C9−N1 of **7** is 1.376(36) Å that are longer than the N1−C4 double bonds in **3** and **4**. Namely, there is a thiazol thione (C=S) moiety in **7** (Fig. 1(c)).

3. Conclusion

In this work, the reactions of **2** as a sulfur-centered radical source with [CpCo(S$_2$C$_2$(R)(H))] (R = Me (**1**), Ph (**5**)) were studied. No substitution product on the Cp ligand or on the Ph group in **5** was obtained. Although 1-cyano-1-ethylmethyl radical (carbon-centered radical) has been reactive for both dithiolene ring and Cp ligand [11], 2-benzothiazolylthiyl radical (sulfur-centered radical) shows selective reactivity for dithiolene ring and for Me group on the dithiolene ligand. We conclude that the former reaction is the first observation of a sulfur-centered radical substitution to a pseudo aromatic metallacycle. In this subject, we focused on the reactivity of a sulfur-centered radical generated from **2**, but a nitrogen-centered radical substitution product was obtained as well.

4. Experimental

4.1. Materials and instrumentation

All reactions were carried out under argon atmosphere by means of standard Schlenk techniques. Solvents were purified by Na-benzophenone for benzene and xylene (Wako Chemical) or by CaH$_2$ for MeCN (Wako Chemical) before use. TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl) and diglyme were provided from Tokyo Chemical Industry Co., Ltd and used after degassed treatment. **1** [19] and **5** [20] were prepared by literature method. 2,2′-dibenzothiazolyl disulfide and 2-benzothiazolethiol were purchased from Wako Pure Chemical Industries, Ltd. Silica gel TLC plate (20 cm^2 glass plate) was provided from MERCK. Mass spectrum was recorded on a JEOL JMS-D300. NMR spectra were measured with a JEOL LA500 spectrometer. UV–Vis spectra were recorded on a Hitachi model UV-2500PC. Elemental analyses were determined by using a Shimazdu PE2400-II instrument.

4.2. Thermal reactions of [CpCo(dithiolene)] complexes with 2,2′-dibenzothiazolyl disulfide

[CpCo(dithiolene)] complex (**1** or **5**, 0.1 mmol) and 2,2′-dibenzothiazolyl disulfide (**2**, 2.0 mmol) were reacted for 4 h in refluxing

S-centered radical   N-centered radical
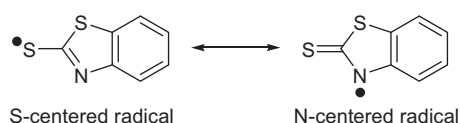
Scheme 4.

benzene or MeCN (30 ml). After the reaction, solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel, and then the starting material (**1** or **5**) was separated from the mixture of substitution products (**3/4** or **6/7**). The mixture (**3/4** or **6/7**) was further placed on the silica gel TLC (20 cm^2 glass plate) and precisely separated with dichloromethane as an eluent. The products were scratched off by iron spatula and they were individually extracted from the silica gel with dichloromethane. Isolated yields of **3**, **4**, **6** and **7** are summarized in Tables 1 and 2.

4.3. Photochemical reactions of [CpCo(dithiolene)] complexes with 2,2′-dibenzothiazolyl disulfide

[CpCo(dithiolene)] complex (**1** or **5**, 0.1 mmol) and **2** (2.0 mmol) were reacted for 24 h under high pressure Hg lamp in benzene or mixed benzene/MeCN solution (50 ml). All products and starting material were separated by the same manner as noted above.

4.4. Microwave reactions of [CpCo(dithiolene)] complexes with 2,2′-dibenzothiazolyl disulfide

A three-pronged microwave double cylindrical cooling reactor with a reflux condenser was located in the waveguide. The reaction mixtures were irradiated by continuous 2.45 GHz microwave radiation with an IDX Inc. green-motif I microwave-type apparatus with monomodal microwave radiation system [13]. All products and starting material were separated by the same manner as noted in the Section 4.2.

4.4.1. Spectroscopic data of **3**

Mass (EI$^+$, 70 eV) m/z (rel. intensity) 393 ([M$^+$], 74), 290 ([M$^+$ − S$_2$C$_2$Me], 100), 188 ([CpCoS$_2^+$], 13), 124 ([CpCo$^+$], 19). ^{1}H NMR (CDCl$_3$, 400 MHz, vs. TMS) δ 7.84 (d, J = 8.0 Hz, 1H, C$_6$H$_4$), 7.56 (d, J = 8.0 Hz, 1H, C$_6$H$_4$), 7.37 (t, J = 8.0 Hz, 1H, C$_6$H$_4$), 7.23 (t, J = 8.0 Hz, 1H, C$_6$H$_4$), 5.40 (s, 5H, Cp), 2.69 (s, 3H, Me). UV–vis (CH$_2$Cl$_2$) λ_{max}/nm (ϵ/M·cm^{-1}) 569 (8300), 408 (1500), 290 (36 800). Anal. Calcd. for C$_{15}$H$_{12}$CoNS$_4$: C, 45.79; H, 3.07; N, 3.56; S, 32.60. Found: C, 45.80; H, 2.96; N, 3.71; S, 32.43.

4.4.2. Spectroscopic data of **4**

Mass (EI$^+$, 70 eV) m/z (rel. intensity) 393 ([M$^+$], 33), 227 ([M$^+$ − SCNSC$_6$H$_4$], 100), 188 ([CpCoS$_2^+$], 27), 124 ([CpCo$^+$], 16). ^{1}H NMR (CDCl$_3$, 400 MHz, vs. TMS) δ 8.76 (s, 1H, dithiolene-H), 7.87 (d, J = 8.0 Hz, 1H, C$_6$H$_4$), 7.73 (d, J = 8.0 Hz, 1H, C$_6$H$_4$), 7.41 (t, J = 8.0 Hz, 1H, C$_6$H$_4$), 7.28 (t, J = 8.0 Hz, 1H, C$_6$H$_4$), 5.34 (s, 5H, Cp), 4.83 (s, 2H, CH$_2$). UV–vis (CH$_2$Cl$_2$) λ_{max}/nm (ϵ/M·cm^{-1}) 566 (8700), 414 (1600), 290 (35 300). HR-mass (EI$^+$, 70 eV): Calcd for C$_{15}$H$_{12}$CoNS$_4$ 392.9185, Found 392.9182.

Table 3
Summary of crystal data.

Compound	3	4	7
Formula	$C_{15}H_{12}NS_4Co$	$C_{15}H_{12}NS_4Co$	$C_{20}H_{14}NCoS_4$
FW (g mol^{-1})	393.44	393.44	455.51
Crystal color	Purple	Purple	Purple
Crystal shape	Prismatic	Prismatic	Prismatic
Crystal size (mm)	$0.37 \times 0.10 \times 0.07$	$0.27 \times 0.13 \times 0.05$	$0.30 \times 0.13 \times 0.03$
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/a$ (No. 14)	$P2_1/n$ (No. 14)
T (K)	298	298	298
a (Å)	14.308(3)	9.110(3)	7.906(6)
b (Å)	6.033(2)	18.177(3)	29.043(5)
c (Å)	18.476(2)	9.897(3)	9.116(6)
β (°)	92.08(1)	106.57(2)	110.71(5)
V (Å^3)	1593.8(7)	1570.7(7)	1957(2)
Z	4	4	4
D_{calc} (g cm^{-3})	1.640	1.664	1.545
μ (mm^{-1})	1.591	1.614	1.307
Total refls.	3994	3855	4565
Unique refls. (R_{int})	3652 (0.077)	3607 (0.112)	4336 (0.054)
Unique refls. ($I > 2\sigma(I)$)	1470	1922	1835
R_1 ($I > 2\sigma(I)$)	0.046	0.052	0.057
wR_2 ($I > 2\sigma(I)$)	0.097	0.091	0.091
Goodness-of-fit	1.37	1.59	1.30

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

4.4.3. Spectroscopic data of 6

Mass (EI$^+$, 70 eV) m/z (rel. intensity) 455 ([M$^+$], 100), 391 ([M$^+ - S_2$], 50), 290 ([M$^+ - S_2C_2$Ph], 94), 188 ([CpCoS$_2^+$], 10), 124 ([CpCo$^+$], 6). ^{1}H NMR (CDCl$_3$, 400 MHz, vs. TMS) δ 7.81 (d, $J = 8.2$ Hz, 1H, C$_6$H$_4$), 7.60 (d, $J = 7.9$ Hz, 1H, C$_6$H$_4$), 7.20–7.45 (m, 7H, Ph + C$_6$H$_4$), 5.46 (s, 5H, Cp). ^{13}C NMR (CDCl$_3$, 100 MHz, vs. TMS) δ 179.3 (dithiolene carbon), 169.5 (dithiolene carbon), 153.8, 147.5, 141.3, 135.8, 128.9, 128.4, 127.9, 126.0, 124.0, 121.9, 120.8 (Ph or 2-benzothiazolyl), 80.2 (Cp). UV–vis (CH$_2$Cl$_2$) λ_{max}/nm (ϵ/M·cm^{-1}) 575 (7400), 292 (40 500). Anal. Calcd. for C$_{20}$H$_{14}$CoNS$_4$: C, 52.73; H, 3.10; N, 3.07; S, 28.16. Found: C, 52.88; H, 2.94; N, 3.21; S, 28.10.

4.4.4. Spectroscopic data of 7

Mass (EI$^+$, 70 eV) m/z (rel. intensity) 455 ([M$^+$], 84), 391 ([M$^+ - S_2$], 47), 290 ([M$^+ - S_2C_2$Ph], 100), 188 ([CpCoS$_2^+$], 15), 124 ([CpCo$^+$], 10). ^{1}H NMR (CDCl$_3$, 400 MHz, vs. TMS) δ 7.34–7.36 (m, 2H, Ph), 7.32 (ddd, $J = 8.0$, 2.0, 1.0 Hz, 1H, C$_6$H$_4$), 7.11–7.20 (m, 4H, Ph + C$_6$H$_4$), 7.06 (ddd, $J = 8.0$, 8.0, 2.0 Hz, 1H, C$_6$H$_4$), 6.18 (dt, $J = 8.0$, 1.0 Hz, 1H, C$_6$H$_4$), 5.49 (s, 5H, Cp). UV–vis (CH$_2$Cl$_2$) λ_{max}/nm (ϵ/M·cm^{-1}) 577 (5100), 291 (30 500). HR-mass (EI$^+$, 70 eV): Calcd for C$_{15}$H$_{12}$CoNS$_4$ 454.9341, Found 454.9346.

4.5. X-ray diffraction study

Single crystals were obtained from recrystallization by vapor diffusion of hexane into those dichloromethane solutions. Crystals were mounted on the top of a thin glass fiber. Measurement was made on Rigaku AFC5S four-circle diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). Each structure was solved by direct methods and expanded Fourier techniques [21]. 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. Idealized

positions were used for the TEXSAN crystallographic software package of Molecular Structure Corp [22]. The all crystals included some alert A in the CIF check lists. Crystallographic data are summarized in Table 3.

Appendix. A Supplementary material

CCDC 767140–767 142 contain the supplementary crystallographic data for 3, 4 and 7. 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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