



## Organometallic dithiolene complexes of benzenedithiolate analogues with $\pi$ -coordinating and $\pi$ -interacting Cp\* ligand

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### ABSTRACT

Organometallic dithiolene complexes, which were formulated as [Cp\*M(dcbdt)] and [Cp\*M(dcdmp)] (M = Co, Rh, Ir; Cp\* =  $\eta^5$ -pentamethylcyclopentadienyl, dcbdt = 4,5-dicyanobenzene-1,2-dithiolate, dcdmp = 2,3-dicyano-5,6-dimercaptopyrazine) were prepared from a low valent Cp\*Co<sup>I</sup> or high valent Cp\*M<sup>III</sup> species (M<sup>III</sup> = Co<sup>III</sup>, Rh<sup>III</sup>, Ir<sup>III</sup>). The UV–Vis absorption spectral and electrochemical data of them were obtained. The lowest absorption (HOMO–LUMO) energies of them became redshift in order of the Co > Rh > Ir complexes. The reduction potentials suggested that the central metal modifies their LUMO levels. The molecular and crystal structures of [Cp\*Co(dcbdt)] (**3a**), [Cp\*Co(dcdmp)] (**4a**) and [Cp\*Rh(dcdmp)] (**4b**) were determined by X-ray diffraction studies. The cobalt complexes **3a** and **4a** were monomeric, formally 16-electron complexes and have two-legged piano-stool geometries. The crystal structure of **3a** indicated some plane-to-plane intermolecular interactions such as benzene··benzene interaction on the dcbdt ligand and two Cp\*··benzene  $\pi$ - $\pi$  stackings. **4a** showed plane-to-plane interaction with a pseudo-4-fold-symmetry arrangement between the pyrazine moieties on the dcdmp ligand. The rhodium complex **4b** was dimeric in the crystal to form a criss-cross arrangement and had a three-legged piano-stool geometry, but it was monomerized in solution. The dimer of **3b** was observed in the oxidation process of the cyclic voltammogram.

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### 1. Introduction

Metal dithiolene complexes are widely investigated in chemistry, physics, optics and biology as well, because of their interesting  $\pi$ -electron system such as the  $\pi$ -electron delocalization [1],  $\pi$ -electron magnetic interaction [2],  $\pi$ -electron-induced electrical conductivity [3], and also biochemically reactive central metal [4]. Since the first dithiolene complex has been reported in '60s [5], enormous examples of them have been synthesized and developed.

To our knowledge, metal dithiolene complexes are classified into three main categories as follows. (1) Homoleptic dithiolene complex whose coordinating ligands are dithiolene only [6]. For example, bisdithiolene complexes with square-planar or tetrahedral geometry and trisdithiolene complexes with trigonal prismatic geometry are well known. (2) Heteroleptic dithiolene complex which has dithiolene and some other inorganic ligands [7]. In general, luminescent [(N<sup>N</sup>)M(dithiolene)] (N<sup>N</sup> = diimine) [8] and [(P<sup>P</sup>)M(dithiolene)] (P<sup>P</sup> = diphosphine) [9] complexes

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have been reported. (3) Organometallic dithiolene complex [10], which incorporates dithiolene ligand and some organic ligands to make metal–carbon bonds. Their typical examples are formulated as [CpM(dithiolene)] [10] (Cp =  $\eta^5$ -cyclopentadienyl) whose Cp/dithiolene ratio is often 1:1 (M = Co, Rh, Ir, Ni) [11,12], 1:2 (M = Mo) [13], or 2:1 (M = Ti, Mo, W) [14,15]. Among them, the Cp/dithiolene 1:1 complexes have been relatively classical, but recently the preparation and properties of new organometallic radical complexes [CpNi<sup>III</sup>(dithiolene)]<sup>•</sup> (S = 1/2) have been intensively studied [12]. These studies have really indicated that the Cp ligand is not only a  $\pi$ -coordinating ligand but also a  $\pi$ -interacting ligand to make intermolecular magnetic interactions through Cp··dithiolene [16], Cp··S=C [12,17], and Cp··Cp as well [16,18].

On the other hand, Cp/dithiolene 1:1 complexes of Co<sup>III</sup> have been developed since '60s [19]. Interestingly, some recent papers have described that the paramagnetic [CpNi<sup>III</sup>(dithiolene)]<sup>•</sup> complexes are isostructural to the diamagnetic [CpCo<sup>III</sup>(dithiolene)] with the same dithiolene ligand [18,20]. Namely, the isostructural CpCo complexes most probably have the similar intermolecular interaction based on the Cp ligand. Needless to say, Cp\* ligand (Cp\* =  $\eta^5$ -pentamethylcyclopentadienyl) is also supposed to be an attractive  $\pi$ -interacting ligand. Recently, [Cp\*Co(dithiolene)] incorporating benzene-1,2-dithiolate (bdt) [21], benzene-1,2,4,5-tetrathiolate [21], benzene-hexathiolate complexes [22] have been structurally characterized. Those crystal structures have

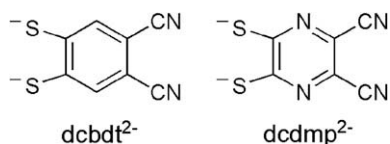


Chart 1.

commonly resulted in the intermolecular  $\text{Cp}^* \cdots$  benzene plane-to-plane interactions [21,22]. As noted above, probably a dithiolene ligand incorporating the benzene core is one of important keys to make those plane-to-plane interactions.

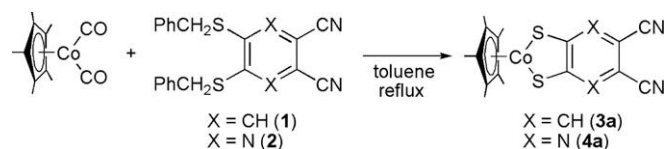
In this work, we focused on the  $[\text{Cp}^*\text{M}(\text{dithiolene})]$  ( $\text{M} = \text{Co}, \text{Rh}, \text{Ir}$ ) bearing slightly modified benzenedithiolate (bdt) ligand such as 4,5-dicyanobenzene-1,2-dithiolate (dcbdt, Chart 1). In addition, the  $\text{Cp}^*\text{M}$  complexes of 2,3-dicyano-5,6-dimercaptopyrazine (dcdmp, Chart 1) ligand whose six-membered core contains two nitrogen atoms (pyrazine core), were prepared for sake of comparison. A family of  $[\text{Cp}^*\text{Ni}^{\text{III}}(\text{bdt})]$  may be also interesting because of its magnetic behavior. However, there is a synthetic difficulty using the precursor  $[\text{Cp}^*_2\text{Ni}]$ . Almeida et al. have reported a rich family of square-planar or tetrahedral bisdithiolene complexes ( $\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{Pd}, \text{Pt}, \text{Cu}, \text{Au}$  and  $\text{Zn}$ ) based on the dcbdt [23,24] and the dcdmp ligands [25,26] and their structural, magnetic and electrical conductive properties have been studied as well [23–26]. Furthermore, Ueda et al. have reported the oxo-vanadium bisdithiolene complex of the dcbdt,  $[\text{O}=\text{V}(\text{dcbdt})_2]$  [27]. Although the dithiolene complexes of dcbdt and dcdmp have been intensively reported as introduced above, no organometallic dithiolene complexes of them, which are classified into the third category, have been known yet. Here we report on the synthetic procedure of  $[\text{Cp}^*\text{M}(\text{dcbdt})]$  (or dcdmp), their spectral, electrochemical characterizations, and crystal structure determinations, considering plane-to-plane interactions as well.

## 2. Results and discussion

### 2.1. Preparations and characterizations of $[\text{Cp}^*\text{M}(\text{dcbdt})]$ and $[\text{Cp}^*\text{M}(\text{dcdmp})]$ complexes ( $\text{M} = \text{Co}, \text{Rh}, \text{Ir}$ )

Almeida et al. have already reported the preparation of dithiolene precursor, which has been the  $\text{dcbdt}^{2-}$  ligand protected by two benzyl groups  $(\text{PhCH}_2)_2(\text{dcbdt})$  (**1**), and then **1** has treated with a strong base to isolate  $\text{H}_2\text{dcbdt}$  [24]. Furthermore, the  $\text{H}_2\text{dcbdt}$  has reacted with a metal source in the presence of a base again to give the corresponding  $\text{M}(\text{dcbdt})$  complexes [23,24]. For preparations of some dcdmp complexes, they have used a direct generation of the  $\text{dcdmp}^{2-}$  from 5,6-dichloropyrazine-2,3-dicarbonitrile and sodium sulfide [26]. The latter synthetic way is supposed to be better because isolation of an intermediate is not required.

On the other hand, we found more convenient way for  $[\text{Cp}^*\text{Co}(\text{dcbdt})]$  (**3a**) without generation of  $\text{dcbdt}^{2-}$ . One synthetic procedure was the direct reaction of  $[\text{Cp}^*\text{Co}(\text{CO})_2]$  with **1** in refluxing toluene without any other treatment to obtain **3a** in 74% yield (Scheme 1, described as method 1). One other procedure was the one-pot synthesis of **3a** without preparation of **1**, which is similar to the Almeida's method noted above [26]. Namely, 4,5-dichlorophthalonitrile treated with sodium sulfide in acetone to form  $\text{dcbdt}^{2-}$ , and successive addition of  $[\text{Cp}^*\text{Co}(\text{CO})_2]$  afforded **3a** in 50% yield (Scheme 2, method 2). The method 1 requires a low valent  $\text{Cp}^*\text{Co}^{\text{I}}$  species. In contrast, the method 2 requires a  $\text{Cp}^*\text{Co}^{\text{III}}$  species. Normally, there are two different synthetic methods to prepare  $[\text{Cp}^*\text{Co}^{\text{III}}(\text{dithiolene})]$  complexes. One is a simple ligand exchange reaction between  $\text{Cp}^*\text{Co}(\text{III})$  species and 1,2-dithiol-



Scheme 1. Method 1 for  $[\text{Cp}^*\text{Co}(\text{dcbdt})]$  ( $\text{X} = \text{CH}$ ) and  $[\text{Cp}^*\text{Co}(\text{dcdmp})]$  ( $\text{X} = \text{N}$ ) complexes.

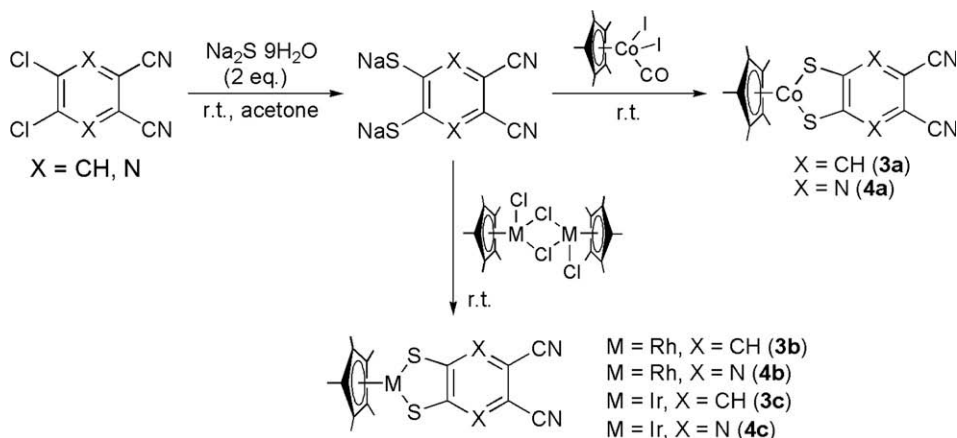
ate(2–) source, and the other is the reaction of  $\text{Cp}^*\text{Co}(\text{I})$  species with 1,2-dithioketone(0) or 1,2-dithiete(0). The latter reaction involves electron-transfer from  $\text{Cp}^*\text{Co}(\text{I})$  to  $\text{S}_2$  ligand, but eventually we can obtain the same product using both ways. In conclusion, the method 1 generates either 1,2-dithioketone(0) or 1,2-dithiete(0) as an intermediate from  $(\text{PhCH}_2)_2(\text{dcbdt})$  by homolysis of the C–S bond.

For preparations of  $[\text{Cp}^*\text{Rh}(\text{dcbdt})]$  (**3b**) and  $[\text{Cp}^*\text{Ir}(\text{dcbdt})]$  (**3c**) complexes, the method 2 is plausibly better way, because low valent  $\text{Cp}^*\text{Rh}^{\text{I}}$  and  $\text{Cp}^*\text{Ir}^{\text{I}}$  species are relatively difficult to prepare due to their air-sensitivity and multistep preparations [28]. On the other hand, probable  $\text{Cp}^*\text{Rh}^{\text{III}}$  and  $\text{Cp}^*\text{Ir}^{\text{III}}$  precursors are well known as the dimeric chloride-bridged  $[\text{Cp}^*\text{M}^{\text{III}}(\text{Cl})(\mu\text{-Cl})_2]$  complexes [29] and they are quantitatively obtained by the reaction of commercially available  $\text{MCl}_3 \cdot n\text{H}_2\text{O}$  with  $\text{Cp}^*\text{H}$  in MeOH [29]. Accordingly, **3b** and **3c** were obtained by the method 2 in 48% and 47% yields, respectively (Scheme 2). The method 1 for preparation of  $[\text{Cp}^*\text{Co}(\text{dcdmp})]$  (**4a**) resulted in 67% yield from  $(\text{PhCH}_2)_2(\text{dcdmp})$  (**2**) and  $[\text{Cp}^*\text{Co}(\text{CO})_2]$  (Scheme 1). In addition, the method 2 using 5,6-dichloropyrazine-2,3-dicarbonitrile resulted in 31% for **4a** ( $\text{M} = \text{Co}$ ) from  $[\text{Cp}^*\text{Co}(\text{CO})_2]$ , 34% for **4b** ( $\text{M} = \text{Rh}$ ), or 34% yield for **4c** ( $\text{M} = \text{Ir}$ ) from  $[\text{Cp}^*\text{M}(\text{Cl})(\mu\text{-Cl})_2]$ , respectively. The all products **3a–3c** and **4a–4c** were characterized by spectroscopies and elemental analyses.

The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of **3a–3c** and **4a–4c** in  $\text{CDCl}_3$  indicated that the all complexes were monomeric in their solutions. If complexes are dimeric as shown in Fig. 7, those  $^1\text{H}$  NMR signals on the dcbdt ligand or  $^{13}\text{C}$  NMR signals on the both dcbdt and dcdmp have to be inequivalent. However, only equivalent signals were commonly found (e.g.  $^1\text{H}$  NMR for **3b**,  $\delta = 8.14$  ppm (singlet, 2H, benzene)). As explained by X-ray data, **4b** was dimeric at solid state (Fig. 7), but the NMR result indicated the monomerization of **4b** while solubilized in a solvent. Accordingly, we had assumed that the following UV–Vis spectra and CV data had been obtained from monomeric species (Figs. 1–4).

The UV–Vis spectra of them in dichloromethane solution showed electronic absorption at 546 (**3a**), 520 (**4a**), 468 (**3b**), 448 (**4b**), 405 (**3c**), and 407 nm (**4c**) as lowest energy absorption maxima (Figs. 1 and 2). Early works have described that these absorption are attributed to LMCT [30]. These results indicate that the absorption energy becomes lower in order of the  $\text{Co} > \text{Rh} > \text{Ir}$  complexes. This fact is consistent while compared with early data (e.g.  $[\text{Cp}^*\text{Co}(\text{dmit})]$  (677 nm) [21],  $[\text{Cp}^*\text{Rh}(\text{dmit})]$  (600 nm) [31],  $[\text{Cp}^*\text{Ir}(\text{dmit})]$  (477 nm) [32],  $\text{dmit} = 1,3$ -dithiol-2-thione-4,5-dithiolate). The reduction potentials taken from CV measurement well explain difference of these LUMO levels between Co, Rh and Ir complexes (Figs. 3 and 4). There are large differences of reduction potentials as follows:  $-1.19$  V (**3a**,  $\text{M} = \text{Co}$ ),  $-1.48$  V (**3b**,  $\text{M} = \text{Rh}$ ), and  $-1.97$  V (**3c**,  $\text{M} = \text{Ir}$ ) for the dcbdt complexes, and  $-0.97$  V (**4a**,  $\text{M} = \text{Co}$ ),  $-1.31$  V (**4b**,  $\text{M} = \text{Rh}$ ), and  $-1.63$  V (**4c**,  $\text{M} = \text{Ir}$ ) for the dcdmp complexes. However, no remarkable difference of the oxidation potential was found in the all complexes except for the oxidation process of **3b** (Table 1).

**3b** showed two oxidation waves at  $+0.39$  and  $+0.92$  V (Fig. 3). The first oxidation potential is quite lower than those of the other complexes ( $+0.68$  V –  $+0.89$  V, Table 1). This result probably



Scheme 2. Method 2 for  $[\text{Cp}^*\text{M}(\text{dcbdt})]$  ( $\text{X} = \text{CH}$ ) and  $[\text{Cp}^*\text{M}(\text{dcdmp})]$  ( $\text{X} = \text{N}$ ) complexes.

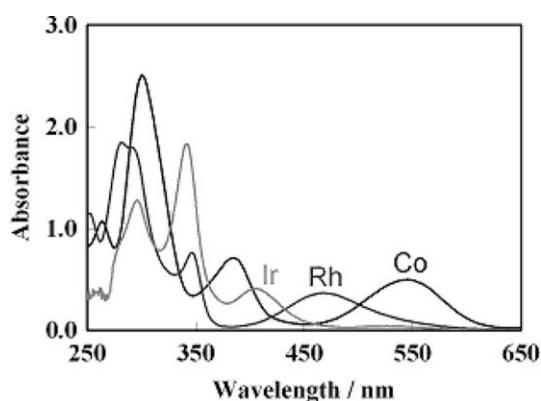


Fig. 1. UV-Vis spectra of  $[\text{Cp}^*\text{M}(\text{dcbdt})]$  ( $\text{M} = \text{Co}$  (3a), Rh (3b), Ir (3c)) in dichloromethane solution ( $c = \text{c.a. } 5.0 \times 10^{-5} \text{ mol dm}^{-3}$ ).

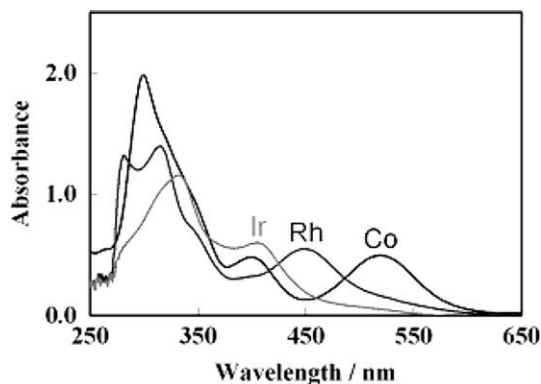


Fig. 2. UV-Vis spectra of  $[\text{Cp}^*\text{M}(\text{dcdmp})]$  ( $\text{M} = \text{Co}$  (4a), Rh (4b), Ir (4c)) in dichloromethane solution ( $c = \text{c.a. } 5.0 \times 10^{-5} \text{ mol dm}^{-3}$ ).

explains an existence of equilibrium between the monomer and dimer of **3b** in solution. The dimer can be precedently oxidized at a lower potential compared with the monomer, because the formal 18-electron dimer is more electron-rich than the 16-electron monomer. Namely, the second oxidation wave at +0.92 V corresponds to the oxidation of the monomer. In contrast, the monomer can be precedently reduced than the dimer. After that, the monomer–dimer equilibrium rapidly shifts and then the dimer becomes very poor amount. In fact, the reduction wave of the dimer couldn't be found. A previous work have already evidenced the dimer–

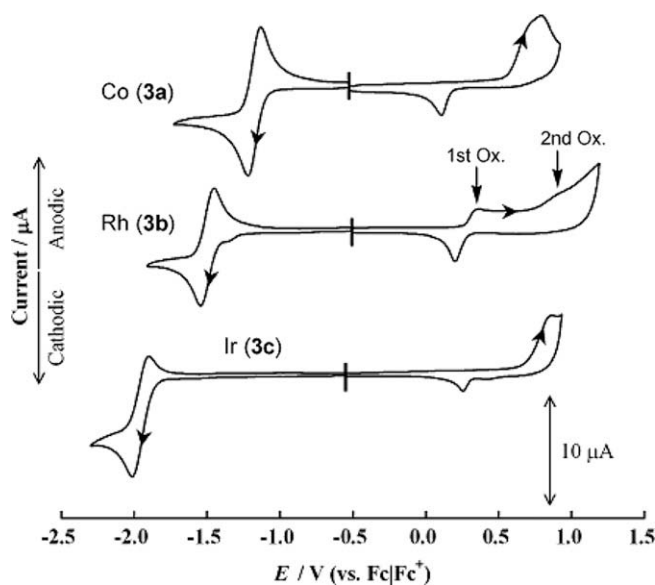


Fig. 3. Cyclic voltammograms of  $[\text{Cp}^*\text{M}(\text{dcbdt})]$  ( $\text{M} = \text{Co}$  (3a), Rh (3b), Ir (3c)) series in dichloromethane solution containing 0.1 M TBAP.

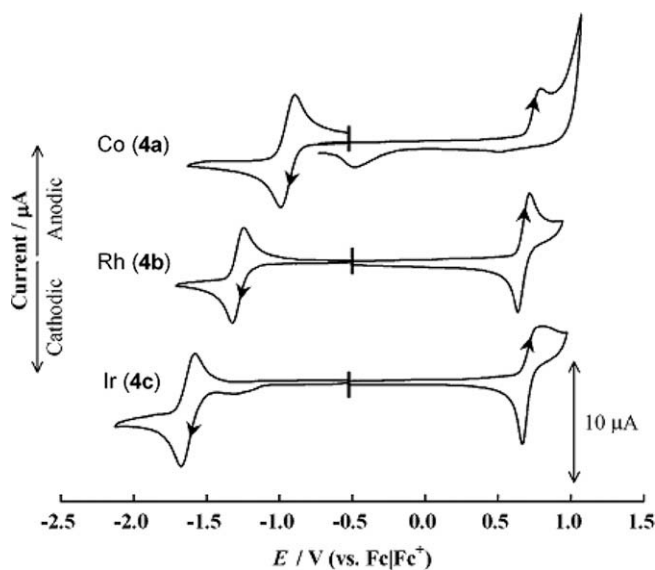


Fig. 4. Cyclic voltammograms of  $[\text{Cp}^*\text{M}(\text{dcdmp})]$  ( $\text{M} = \text{Co}$  (4a), Rh (4b), Ir (4c)) series in dichloromethane solution containing 0.1 M TBAP.

**Table 1**  
Redox potentials (vs Fc/Fc<sup>+</sup>) and electronic absorption maxima ( $\lambda_{\text{max}}$ /nm).

	$E_{1/2}(\text{red})/\text{V}$	$E_{1/2}(\text{ox})/\text{V}$	$\lambda_{\text{max}}/\text{nm}$
[Cp*Co(dcbdt)] ( <b>3a</b> )	-1.19(r)	+0.79(ir)	546
[Cp*Rh(dcbdt)] ( <b>3b</b> )	-1.48(r)	+0.39(r), +0.92(ir)	468
[Cp*Ir(dcbdt)] ( <b>3c</b> )	-1.97(r)	+0.89(ir)	405
[Cp*Co(dcdmp)] ( <b>4a</b> )	-0.97(r)	+0.81(ir)	520
[Cp*Rh(dcdmp)] ( <b>4b</b> )	-1.31(r)	+0.68(r)	448
[Cp*Ir(dcdmp)] ( <b>4c</b> )	-1.63(r)	+0.82(ir)	407

(r) Reversible wave. (ir) Irreversible wave.

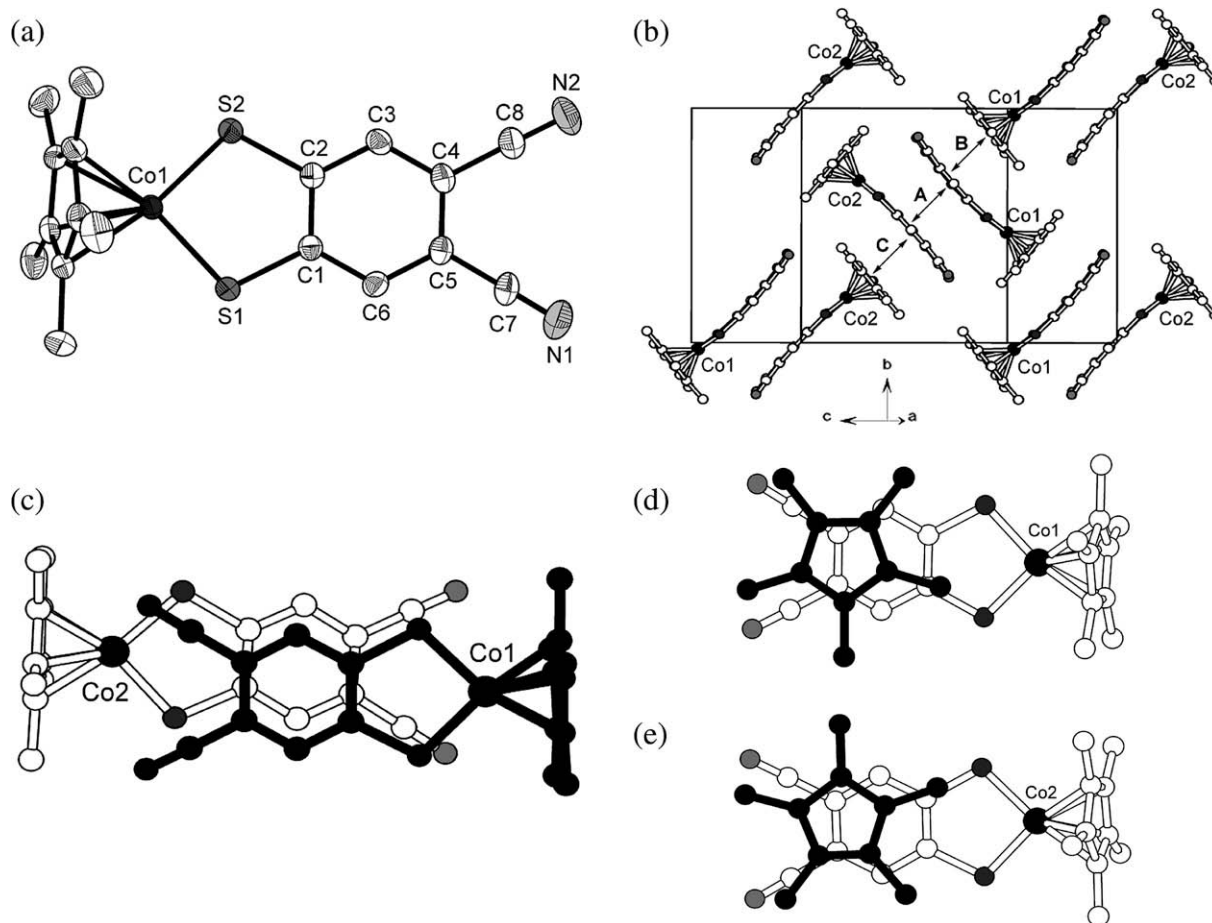
monomer equilibrium of [ $(\eta^6\text{-C}_6\text{R}_6)\text{Ru}(\text{dithiolene})$ ] complexes, and those electrochemical behavior have been investigated [33]. As noted above, no NMR signals attributed to the dimer were observed in solution, even if the solution was almost saturated. However, we assume that the dimer–monomer equilibrium rate is too fast to detect both species.

## 2.2. Crystal structure determination by X-ray diffraction study

The structures of the cobalt complexes **3a** and **4a**, and the rhodium complex **4b** were determined by single crystal X-ray structure analyses. The ORTEP drawings and crystal packing diagrams are displayed in Figs. 5–7. In addition, the selected bond lengths, bond angles and dihedral angles are summarized in Table 2. The both cobalt complexes **3a** and **4a** are monomeric and have two-legged piano-stool geometries (Figs. 5a and 6a). **3a** crystallized in the

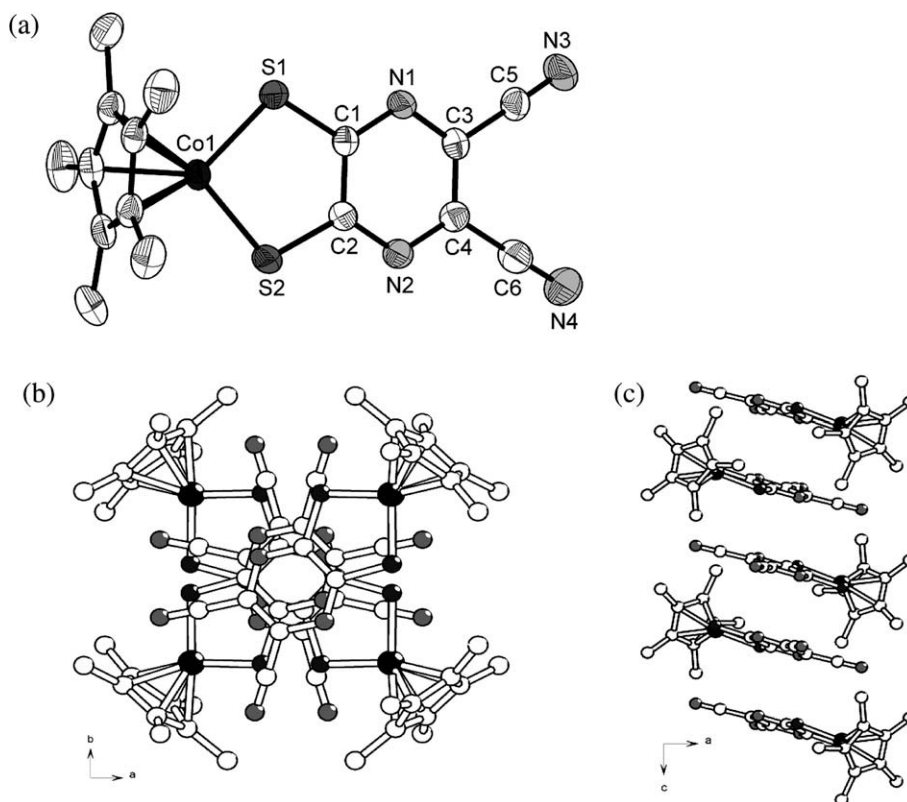
monoclinic, space group  $P2_1/n$  with two crystallographically independent molecules in general positions in the unit cell. **4a** crystallized in the orthorhombic, space group  $Pbcn$  with one independent molecule. On the other hand, **4b** is dimeric and has three-legged piano-stool geometry (Fig. 7). **4b** crystallized in the monoclinic, space group  $C2/c$ . The dimeric structure is perfectly symmetric and lies on a crystallographic inversion center. Namely, the half molecule of **4b** is crystallographically unique (Fig. 7b).

The Cp\*/CoS<sub>2</sub> dihedral angles in **3a** and **4a** are almost 90° as shown in Table 2, but the Cp\*/RhS<sub>2</sub> dihedral angle is 55.933° for **4b**. These results evidence the difference of those piano-stool geometries. Although the Co-dithiolene rings of **3a** and **4a** are almost planar, the Rh-dithiolene ring for **4b** is folded at the S··S hinge, whose dithiolene folding angle is 13.585°. Formally, the 16-electron CpM<sup>III</sup> (or Cp\*M<sup>III</sup>) dithiolene complexes are coordinatively unsaturated [34]. However, a strong  $\pi$ -electron donation from the sulfur to metal can stabilize the electron poor metal center [35]. In fact, the only dimeric CpCo dithiolene complex has been reported for the formal 18-electron dimer, [CpCo(bdt)]<sub>2</sub> in the crystal at room temperature, with a single crystal-to-single crystal phase transition at 150 °C to the monomeric form [36]. The isostructural selenium complex [CpCo(bds)]<sub>2</sub> (bds = benzene-1,2-diselenolate) has been dimeric as well [37]. Those dimers can be monomerized in solution, or monomer/dimer equilibria have been observed [30a,33,37]. In contrast, the [Cp\*Rh(dithiolene)] complexes are relatively easy to dimerize. Actually, the dimeric Rh complexes have been well known as follows: [Cp\*Rh(bdt)]<sub>2</sub> [38],

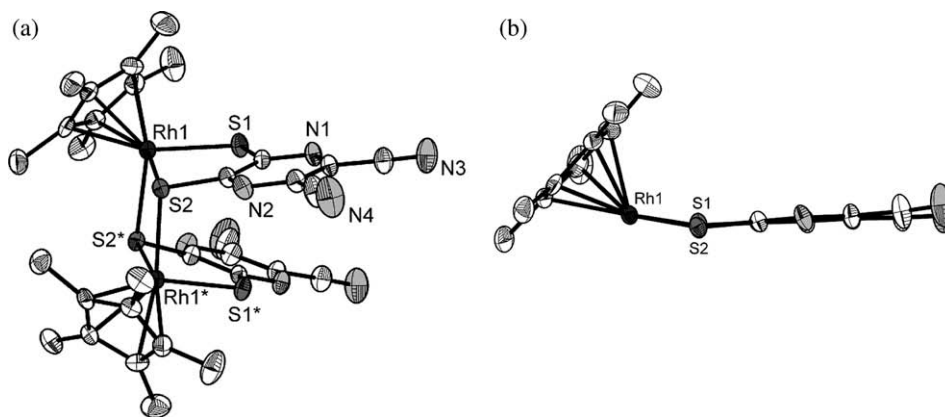


**Fig. 5.** (a) ORTEP drawing of **3a**. One of two independent molecules is shown. The thermal ellipsoid is drawn at 30% probability level. All hydrogen atoms are omitted for simplicity. (b) Packing diagram of **3a** showing benzene···benzene (A) and Cp\*···benzene interactions (B and C). (c) Overlap pattern of A interaction. (d,e) Overlap patterns of B and C interactions.





**Fig. 6.** (a) ORTEP drawing of **4a**. The thermal ellipsoid is drawn at 30% probability level. (b) Projection view along the *c* axis of **4a** showing intermolecular pyrazine...pyrazine interaction, giving rise to a pseudo-4-fold symmetry arrangement within the *c* axis column. (c) Projection view along the *b* axis of **4a**.



**Fig. 7.** (a) ORTEP drawing of **4b**. The thermal ellipsoid is drawn at 30% probability level. (b) Side view of **4b** showing the folded dithiolene ring. The half molecule of **4b** is shown.

[Cp\*Rh(dmit)]<sub>2</sub> [31], and [Cp\*Rh(mnt)]<sub>2</sub> (mnt = maleonitrile-1,2-dithiolate) [39]. According to our literature survey, there are two geometrically different [Cp(or Cp\*)M(dithiolene)] dimers (M = Co, Rh). One is an *inversion-centered dimer* (Fig. 8a), which has been observed in the dimeric [CpM(dichalcogenolene)]<sub>2</sub> complexes, and the other is a *criss-cross dimer* (Fig. 8b) whose two molecules are shifted at almost 90°. The latter example involves the dimeric [Cp\*M(dichalcogenolene)]<sub>2</sub> complexes and also **4b** in this work as well.

The Co–S bond lengths in the monomeric **3a** and **4a** are c.a. 2.12–2.14 Å (Table 2). These results are similar to those of typical monomeric [CpCo(dithiolene)] complexes [40], but shorter than those of the dimeric [CpCo(bdt)]<sub>2</sub> complex (Co–S = 2.230, 2.246 Å) [36]. Similarly, the Rh–S (2.347, 2.359 Å) bond lengths

in the dimeric **4b** are longer than those of the monomeric [CpRh(dmit)] (Rh–S = 2.241, 2.242 Å) [31]. These facts explain a strong  $\pi$ -electron donation from the sulfur to metal center to shorten the M–S bond in these electron poor monomeric complexes. In the dimer **4b**, the S2 atom is tripodal, because it is coordinating to another rhodium atom (Rh1\*). The Rh1\*–S2 bond length is 2.423 Å, which is slightly longer than those of the Rh1–S1 and Rh1–S2 in the dithiolene ring (Table 2). Accordingly, the Rh1\*–S2 is supposed to be a weaker bond compared with the others. In fact, such dimeric species monomerize again in solution, followed by the Rh1\*–S2 bond cleavage.

In the crystal structure of **3a**, some plane-to-plane interactions were observed within one layer. One is an intermolecular benzene...benzene interaction at the dcbdt ligand (**A** = c.a. 3.7 Å)

**Table 2**  
Selected bond lengths (Å), bond angles (°) and dihedral angles (°).

	<b>3a</b> <sup>a</sup>	<b>4a</b>	<b>4b</b>
<i>Bond length</i>			
M1–S1	2.1362(7)	2.1299(11)	2.359(2)
M1–S2	2.1214(10)	2.1463(13)	2.347(2)
S1–C1	1.737(3)	1.722(3)	1.715(9)
S2–C2	1.734(2)	1.727(3)	1.760(8)
C1–C2	1.407(4)	1.419(5)	1.444(11)
M1*–S2	–	–	2.423(2)
<i>Bond angles</i>			
S1–M1–S2	93.04(3)	93.68(4)	86.85(7)
M1–S1–C1	104.21(8)	103.71(12)	104.8(2)
M1–S2–C2	104.22(12)	103.50(14)	104.2(2)
S1–C1–C2	118.5(2)	119.9(2)	121.8(6)
S2–C2–C1	119.5(2)	119.2(3)	120.2(6)
<i>Dihedral angles</i>			
Cp*/MS <sub>2</sub>	92.888	92.861	55.933
MS <sub>2</sub> /S <sub>2</sub> C <sub>2</sub> <sup>b</sup>	7.113	1.949	13.585

<sup>a</sup> Data taken from one of two independent molecules.

<sup>b</sup> Dithiolene folding angles at the S···S hinge.

between two independent molecules shown as the Co1 and Co2 molecules (Fig. 5b). The others are intermolecular Cp\*···benzene interactions in the two Co1 molecules (**B** = c.a. 3.6 Å) and the two Co2 molecules (**C** = c.a. 3.6 Å). These face-to-face dihedral angles ( $\theta$ ) are very small to indicate their parallels ( $\theta_A = 1.868^\circ$ ,  $\theta_B = 3.244^\circ$ , and  $\theta_C = 2.263^\circ$ ). Fig. 5c displays the overlap pattern of **A**, and Fig. 5d and e exhibit the overlap patterns of **B** and **C**, respectively. **A–C** lie on two dimensional columns along the ( $b + c$ ) axis in the crystal (Fig. 5b). In the crystal structure of **4a**, the molecules interact at the pyrazine moiety each other (c.a. 3.5 Å). The face-to-face dihedral angle is  $11.658^\circ$ . This intermolecular interaction lies on one dimensional column along the  $c$  axis. Fig. 6b and c indicated that the pyrazine moieties interacted at van der Waals contact to afford this one dimensional chain structure, with a pseudo-4-fold-symmetry arrangement. However, no plane-to-plane interaction based on Cp\* ligand was observed in **4a**. One reason might be due to an introduction of some nitrogen atoms at the benzene core.

### 3. Conclusion

In this work, we studied on the organometallic Co, Rh and Ir complexes of mixed Cp\*/dcbdt and Cp\*/dcdmp ligands. Among them, the Co complex of the dcdmp (**4a**) showed one dimensional  $\pi$ – $\pi$  interaction based on its pyrazine moiety, but no Cp\*···pyrazine interaction was observed. On the other hand, the Co complex

of the dcbdt (**3a**) had both benzene···benzene and Cp\*···benzene interactions within one plane (two dimensional). However, the dimeric [Cp\*Rh(dcbdt)]<sub>2</sub> complex did not result in no remarkable plane-to-plane interactions, because probably one side of the dithiolene ligand was hidden by dimerization. As described in the introduction of this paper, the complexes of non-substituted  $\eta^5$ -cyclopentadienyl ligand (Cp) have shown the intermolecular Cp···Cp [16,18] and Cp···dithiolene interactions [16]. Especially, while the complex has paramagnetic Ni<sup>III</sup> ( $S = 1/2$ ), those  $\pi$ – $\pi$  interactions make strong magnetic interactions [16–18], because there are some spin densities on the Cp ligand. We believe that the Cp\*/bdt complexes of Ni<sup>III</sup> will be interesting compounds because the Ni<sup>III</sup> complexes could be *isostructural* to the complexes of Co<sup>III</sup> as previously reported [20], although there is a synthetic difficulty for [Cp\*Ni<sup>III</sup>(dithiolene)]<sup>+</sup> complexes. Therefore, two dimensionally magnetic interaction based on plane-to-plane interactions such as benzene···benzene and Cp\*···benzene, will be expected by using the  $\pi$ -interacting Cp\* ligand.

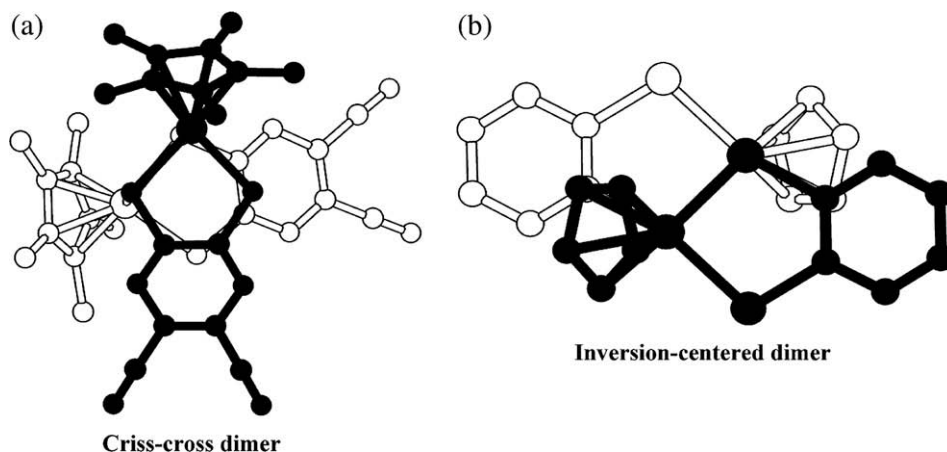
## 4. Experimental

### 4.1. Materials and instrumentation

All reactions were carried out under an argon atmosphere by means of standard Schlenk techniques. All solvents were dried and distilled by Na-benzophenone (for benzene and toluene), molecular sieve (for acetone) or CaH<sub>2</sub> (for methanol) before use. Cp\*H (1,2,3,4,5-pentamethylcyclopentadiene), 4,5-dichlorophthalonitrile, and 5,6-dichloropyrazine-2,3-dicarbonitrile were obtained from Wako Pure Chemicals Industries, Ltd. RhCl<sub>3</sub>·3H<sub>2</sub>O and IrCl<sub>3</sub>· $n$ H<sub>2</sub>O were obtained from STREAM Chemicals. [Cp\*Co(CO)<sub>2</sub>] [41], [Cp\*Co(CO)I<sub>2</sub>] [42], [Cp\*M(Cl)( $\mu$ -Cl)]<sub>2</sub> (M = Rh, Ir) [29], (PhCH<sub>2</sub>)<sub>2</sub>(dcbdt) (**1**) [24], and (PhCH<sub>2</sub>)<sub>2</sub>(dcdmp) (**2**) [43] were prepared by literature methods. 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. CV measurements

All electrochemical measurements were performed under an argon atmosphere. Solvents for electrochemical measurements were dried by molecular sieve 4A before use. A platinum wire served as a counter electrode, and the reference electrode Ag/AgCl was corrected for junction potentials by being referenced internally to the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) couple. A stationary



**Fig. 8.** (a) Criss-cross dimeric structure of **4b** from the top view. (b) Inversion-centered dimer of [CpCo(bds)]<sub>2</sub>. [37]

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 mmol dm<sup>-3</sup> dichloromethane solutions of complexes containing 0.1 mol dm<sup>-3</sup> tetra-*n*-butylammonium perchlorate (TBAP) at 25 °C.

#### 4.3. X-ray diffraction study

Single crystals of complexes **3a**, **4a** and **4b** 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. The measurement was made on a Rigaku MERCURY diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Each structure was solved by direct methods and expanded Fourier techniques [44]. 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 of complexes were used for the Crystal Structure crystallographic software package of Molecular Structure Corp [45]. Crystallographic data of complex **3a**, **4a** and **4b** are summarized in Table 3.

There is a level A alert in the CIF report for **4b**, because of a large void of 259 Å<sup>3</sup>. This result suggests an existence of cocrystallized solvent. The solvent was supposed to be CH<sub>2</sub>Cl<sub>2</sub>, because the elemental analysis revealed the (**4b**)<sub>2</sub>(CH<sub>2</sub>Cl<sub>2</sub>) formula. Unfortunately, we couldn't determine the positions of those atoms. However, structure of the main molecule [Cp\**Rh*(dcdmp)]<sub>2</sub> was nicely refined, and the fair *R*<sub>1</sub> and GOF values were obtained without the solvent (Table 3).

#### 4.4. Synthesis of [Cp\*Co(dcbdt)] (**3a**) by method 1

[Cp\*Co(CO)<sub>2</sub>] (40 mg, 0.16 mmol) and **1** (39 mg, 0.1 mmol) were reacted in refluxing toluene (15 ml) for 5 h. The solvent was removed under reduced pressure, and the residue was separated by column chromatography on silica gel (eluent: dichloromethane). A purple solid was isolated and the product was further purified by recrystallization from dichloromethane and hexanes. **3a**

was obtained as a purple solid in 74% (29.5 mg) yield. A benzene solution (80 ml) of [Cp\*Co(CO)<sub>2</sub>] and **1** was refluxed for 42 h to give **3a** in 67% yield.

#### 4.5. Synthesis of [Cp\*Co(dcbdt)] (**3a**) by method 2

An acetone solution (20 ml) of 4,5-dichlorophthalonitrile (60 mg, 0.3 mmol) was added to acetone solution (30 ml) of Na<sub>2</sub>S·9H<sub>2</sub>O (120 mg, 0.5 mmol) and stirred at room temperature for 4 h. An acetone solution (20 ml) of [Cp\*Co(CO)<sub>2</sub>] (190 mg, 0.39 mmol) was further added to the reaction mixture and reacted for 20 h. The solvent was removed under reduced pressure. Dichloromethane was added to dissolve a product and dried with MgSO<sub>4</sub>. Solid components were removed by filtration. The filtrate was concentrated and was moved to column chromatography on silica gel. A purple product was separated with dichloromethane. The purple product **3a** was further purified by recrystallization from dichloromethane and hexanes (50% yield).

##### 4.5.1. [Cp\*Co(dcbdt)] (**3a**)

Mass (EI<sup>+</sup>, 70 eV) *m/z* (rel. intensity) 384 (M<sup>+</sup>, 100), 135 (Cp<sup>+</sup>, 18), <sup>1</sup>H NMR (CDCl<sub>3</sub>, vs TMS, 500 MHz)  $\delta$  8.14 (s, 2H, benzene), 1.93 (s, 15H, Cp<sup>\*</sup>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, vs TMS, 125 MHz)  $\delta$  160.0 (CN), 134.3, 116.8, 106.4 (benzene), 93.4 (Cp<sup>\*</sup>), 10.9 (Me). UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\text{max}}$ /nm ( $\epsilon$ ) 546 (10 000), 385 (14 400), 300 (50 600), 264 (21 600). IR (KBr disk) 2222 cm<sup>-1</sup> ( $\nu_{\text{CN}}$ ). Elemental Anal. Calc. for C<sub>18</sub>H<sub>17</sub>CoN<sub>2</sub>S<sub>2</sub>: C, 56.24; H, 4.46; N, 7.29; S, 16.68. Found: C, 56.14; H, 4.37; N, 7.34; S, 16.94%.

#### 4.6. Synthesis of [Cp\*Co(dcdmp)] (**4a**) by method 1

[Cp\*Co(CO)<sub>2</sub>] (61 mg, 0.25 mmol) and (PhCH<sub>2</sub>)<sub>2</sub>(dcdmp) (75 mg, 0.2 mmol) were reacted in refluxing toluene (30 ml) for 28 h. The solvent was removed under reduced pressure, and the residue was separated by column chromatography on silica gel (eluent: dichloromethane). A dark red solid was isolated and the product was further purified by recrystallization from dichloromethane and hexanes. [Cp\*Co(dcbdt)] (**4a**) was obtained as a dark red solid in 67% yield.

#### 4.7. Synthesis of [Cp\*Co(dcdmp)] (**4a**) by method 2

An acetone solution (20 ml) of 5,6-dichloropyrazine-2,3-dicarbonitrile (60 mg, 0.3 mmol) was added to acetone solution (30 ml) of Na<sub>2</sub>S·9H<sub>2</sub>O (120 mg, 0.5 mmol) and stirred at room temperature for 2 h. An acetone solution (20 ml) of [Cp\*Co(CO)<sub>2</sub>] (58 mg, 0.12 mmol) was further added to the reaction mixture and reacted for 2 h. The solvent was removed under reduced pressure. The purple product **4a** (31% yield) was purified and was crystallized by the same procedure as method 2 for **3a**.

##### 4.7.1. [Cp\*Co(dcdmp)] (**4a**)

Mass (EI<sup>+</sup>, 70 eV) *m/z* (rel. intensity) 386 (M<sup>+</sup>, 100), 342 (M<sup>+</sup>-SC, 10), 135 (Cp<sup>+</sup>, 10). <sup>1</sup>H NMR (CDCl<sub>3</sub>, vs TMS, 500 MHz)  $\delta$  1.86 (s, 15H, Cp<sup>\*</sup>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, vs TMS, 125 MHz)  $\delta$  114.4 (benzene), 94.6 (Cp<sup>\*</sup>), 10.7 (Me) but other <sup>13</sup>C signals for CN group and benzene ring were very weak. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\text{max}}$ /nm ( $\epsilon$ ) 520 (10 000), 399 (9800), 300 (40 300). IR (KBr disk) 2233 cm<sup>-1</sup> ( $\nu_{\text{CN}}$ ). Elemental Anal. Calc. for C<sub>16</sub>H<sub>15</sub>CoN<sub>4</sub>S<sub>2</sub>: C, 49.74; H, 3.91; N, 14.50. Found: C, 49.58; H, 4.37; N, 14.47%.

#### 4.8. [Cp\*Rh(dcbdt)] (**3b**) and [Cp\*Rh(dcdmp)] (**4b**) by method 2

An acetone solution (40 ml) of 4,5-dichlorophthalonitrile (120 mg, 0.63 mmol) was added to acetone solution (40 ml) of Na<sub>2</sub>S·9H<sub>2</sub>O (350 mg, 1.44 mmol) and stirred at room temperature

**Table 3**  
Crystallographic data.

Compound	<b>3a</b>	<b>4a</b>	<b>4b</b>
Formula	C <sub>18</sub> H <sub>17</sub> CoN <sub>2</sub> S <sub>2</sub>	C <sub>16</sub> H <sub>15</sub> CoN <sub>4</sub> S <sub>2</sub>	C <sub>32</sub> H <sub>30</sub> N <sub>8</sub> Rh <sub>2</sub> S <sub>4</sub>
FW (g mol <sup>-1</sup> )	384.40	386.37	860.69
Crystal color	Purple	Purple	Dark brown
Crystal shape	Prism	Block	Block
Crystal size (mm)	0.23 × 0.13 × 0.07	0.13 × 0.13 × 0.10	0.30 × 0.05 × 0.05
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> (#14)	<i>P</i> <i>b</i> <i>c</i> <i>n</i> (#60)	<i>C</i> 2/ <i>c</i> (#15)
<i>T</i> (K)	298.1	298.1	298.1
<i>a</i> (Å)	16.1544(9)	19.803(5)	21.1256(15)
<i>b</i> (Å)	14.1443(5)	11.666(3)	9.3084(5)
<i>c</i> (Å)	17.4177(9)	15.319(3)	21.6226(15)
$\beta$ (°)	116.4909(5)		99.0146(10)
<i>V</i> (Å <sup>3</sup> )	3562.0(3)	3538.9(14)	4199.5(5)
<i>Z</i>	8	8	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.434	1.450	1.361
$\mu$ (mm <sup>-1</sup> )	1.198	1.209	1.013
Total refls.	25 769	20 306	16 010
Unique reflections	8071 (0.026)	3976 (0.031)	4797 (0.028)
( <i>R</i> <sub>int</sub> )			
Unique reflections	5552	2491	3856
( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))			
<i>R</i> <sub>1</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0387	0.0458	0.0586
<i>wR</i> <sub>2</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0987	0.1171	0.1003
Goodness-of-fit	0.981	1.047	1.194
(GOF)			

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

for 4 h. A dichloromethane solution (30 ml) of  $[\text{Cp}^*\text{Rh}(\text{Cl})(\mu\text{-Cl})_2]$  (190 mg, 0.31 mmol) was further added to the reaction mixture and reacted for 20 h. The solvent was removed under reduced pressure. The red product **3b** (48% yield) was purified and was crystallized by the same procedure as method 2 for **3a**. The red product **4b** was obtained in 34% yield by the same method 2 as **3b** from  $[\text{Cp}^*\text{Rh}(\text{Cl})(\mu\text{-Cl})_2]$  (200 mg, 0.32 mmol),  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  (370 mg, 1.56 mmol) and 5,6-dichloropyrazine-2,3-dicarbonitrile (120 mg, 0.61 mmol).

#### 4.8.1. $[\text{Cp}^*\text{Rh}(\text{dcbdt})]$ (**3b**)

Mass ( $\text{EI}^+$ , 70 eV)  $m/z$  (rel. intensity) 428 ( $\text{M}^+$ , 100), 316 ( $\text{Cp}^*\text{RhS}_2\text{CH}_2^+$ , 15).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , vs TMS, 500 MHz)  $\delta$  8.14 (s, 2H, benzene), 2.04 (s, 15H,  $\text{Cp}^*$ ). UV–Vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon$ ) 468 (6800), 347 (14 200), 282 (34 400), 253 (21 400). IR (KBr disk)  $2219\text{ cm}^{-1}$  ( $\nu_{\text{CN}}$ ). Elemental Anal. Calc. for  $\text{C}_{18}\text{H}_{17}\text{RhN}_2\text{S}_2(\text{CH}_2\text{Cl}_2)$ : C, 44.46; H, 3.73; N, 5.46. Found: C, 44.37; H, 3.41; N, 5.75%.

#### 4.8.2. $[\text{Cp}^*\text{Rh}(\text{dcdmp})]_2$ (**4b**)

Mass ( $\text{EI}^+$ , 70 eV)  $m/z$  (rel. intensity) 430 ( $\text{M}^+$ , 100), 386 ( $\text{M}^+ - \text{SC}$ , 32), 238 ( $\text{Cp}^*\text{Rh}^+$ , 22).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , vs TMS, 500 MHz)  $\delta$  1.93 (s, 15H,  $\text{Cp}^*$ ). UV–Vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon$ ) 448 (10 300), 316 (26 100), 282 (24 700). IR (KBr disk)  $2222\text{ cm}^{-1}$  ( $\nu_{\text{CN}}$ ). Elemental Anal. Calc. for  $\text{C}_{32}\text{H}_{30}\text{N}_8\text{Rh}_2\text{S}_4(\text{CH}_2\text{Cl}_2)$ : C, 41.91; H, 3.41; N, 11.85. Found: C, 41.67; H, 3.35; N, 11.95%.

#### 4.9. $[\text{Cp}^*\text{Ir}(\text{dcbdt})]$ (**3c**) and $[\text{Cp}^*\text{Ir}(\text{dcdmp})]$ (**4c**) by method 2

An acetone solution (30 ml) of 4,5-dichlorophthalonitrile (130 mg, 0.65 mmol) was added to acetone solution (50 ml) of  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  (430 mg, 1.77 mmol) and stirred at room temperature for 4 h. A dichloromethane solution (30 ml) of  $[\text{Cp}^*\text{Ir}(\text{Cl})(\mu\text{-Cl})_2]$  (280 mg, 0.35 mmol) was further added to the reaction mixture and reacted for 20 h. The solvent was removed under reduced pressure. The red product **3c** (47% yield) was purified and was crystallized by the same procedure as method 2 for **3a**. The red product **4c** was obtained in 34% yield by the same method 2 as **3c** from  $[\text{Cp}^*\text{Ir}(\text{Cl})(\mu\text{-Cl})_2]$  (560 mg, 0.70 mmol),  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  (790 mg, 3.30 mmol) and 5,6-dichloropyrazine-2,3-dicarbonitrile (240 mg, 1.22 mmol).

#### 4.9.1. $[\text{Cp}^*\text{Ir}(\text{dcbdt})]$ (**3c**)

Mass ( $\text{EI}^+$ , 70 eV)  $m/z$  (rel. intensity) 518 ( $\text{M}^+$ , 100).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , vs TMS, 500 MHz)  $\delta$  8.37 (s, 2H, benzene), 2.16 (s, 15H,  $\text{Cp}^*$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , vs TMS, 125 MHz)  $\delta$  159.9 (CN), 134.5, 116.5, 107.3 (benzene), 93.8 ( $\text{Cp}^*$ ), 10.5 (Me). UV–Vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon$ ) 405 (8100), 342 (36 500), 296 (25 400), 262 (8300). IR (KBr disk)  $2218\text{ cm}^{-1}$  ( $\nu_{\text{CN}}$ ). Elemental Anal. Calc. for  $\text{C}_{18}\text{H}_{17}\text{IrN}_2\text{S}_2$ : C, 41.76; H, 3.31; N, 5.41; S, 12.39. Found: C, 41.86; H, 3.59; N, 5.64; S, 12.61%.

#### 4.9.2. $[\text{Cp}^*\text{Ir}(\text{dcdmp})]$ (**4c**)

Mass ( $\text{EI}^+$ , 70 eV)  $m/z$  (rel. intensity) 520 ( $\text{M}^+$ , 100), 476 ( $\text{M}^+ - \text{SC}$ , 20).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , vs TMS, 500 MHz)  $\delta$  1.77 (s, 15H,  $\text{Cp}^*$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , vs TMS, 125 MHz)  $\delta$  114.1 (benzene), 94.6 ( $\text{Cp}^*$ ), 9.9 (Me) but other  $^{13}\text{C}$  signals for CN group and benzene ring were very weak. UV–Vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon$ ) 407 (9600), 334 (25 300). IR (KBr disk)  $2224\text{ cm}^{-1}$  ( $\nu_{\text{CN}}$ ). Elemental Anal. Calc. for  $\text{C}_{16}\text{H}_{15}\text{IrN}_4\text{S}_2$ : C, 36.98; H, 2.91; N, 10.78; S, 12.34. Found: C, 37.09; H, 2.82; N, 10.64; S, 12.50%.

### Appendix A. Supplementary material

CCDC 724140, 724141 and 724142 contains the supplementary crystallographic data for **3a**, **4b** and **4a**. These data can be obtained

free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.05.022](https://doi.org/10.1016/j.jorganchem.2009.05.022).

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