

A novel metallacycle, 1,2,5,3-cobaltadithiazole. Formation, structure, and properties of (η^5 -cyclopentadienyl or η^5 -pentamethylcyclopentadienyl)(1-phenylmethanimine-*N*,1-dithiolato)-cobalt(III)

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Abstract

(η^5 -Cyclopentadienyl)(1-phenylmethanimine-*N*,1-dithiolato)cobalt(III), [Co(η^5 -C₅R₅)(SNC(Ph)S)] (**1a**: R = H or **1b**: R = CH₃), which contain a 1,2,5,3-cobaltadithiazole ring were synthesized in the reactions of [Co(η^5 -C₅R₅)Ln] (Ln = (CO)₂ or 1,5-cyclooctadiene) with two types of heterocyclic compounds: (1) compounds with a partial structure of –S–N=C(Ph)–S– or with similar structures; and (2) compounds which give benzonitrile sulfide on thermolysis or photolysis. The crystals of **1b** are orthorhombic of space group *P*_{2,2,2} with *a* = 14.936 Å, *b* = 14.262 Å, *c* = 8.078 Å and *Z* = 4. The structure was solved and refined to *R* = 0.038 and *R*_w = 0.040 by using 3981 independent reflections. The structure of 1,2,5,3-cobaltadithiazole is similar to that of 1,2,5-cobaltadithiolenes. The 1,2,5,3-cobaltadithiazole ring is almost planar and perpendicular to cp*. The cobaltadithiolenes undergo a reversible one electron reduction which is ascribed to the process from Co^{III} to Co^{II}. The halfwave potential of –1.34 V versus Ag|0.1 mol dm^{–3} AgClO₄ for the reduction of **1b** is less negative than that of the cobaltadithiolene with a similar structure. This shows that the nitrogen atom in the ring attracts electrons and causes the cobaltadithiazole ring to be electron-deficient.

Key words: 1,2,5,3-Cobaltadithiazole; Metallacycle; Cobalt; Dithiolate

1. Introduction

A metalladithiolene ring consisting of one transition metal atom, two coordinated sulfur atoms, and two unsaturated carbon atoms is a very unique metallacycle [1]. Schrauzer pointed out that the dithiolene ring is a conjugated aromatic ring system with 6 π electrons [1a]. An NMR study which shows the existence of ring current in the metalladithiolene ring supports its aromaticity [2,3].

In an earlier stage of the research, the [M(1,2-ethylenedithiolato)_n]-type dithiolenes, which consist of only metal and dithiolato ligand, had been extensively studied. Another type of metalladithiolenes, [M(cp)_m(1,2-ethylenedithiolato)] (M = metal), which have another

ligand, cyclopentadienyl, were first synthesized by King [4]. A convenient one-pot synthesis of this type of metalladithiolenes from elemental sulfur, alkyne, and [M(cp)] species developed by Bönnemann *et al.* [5] allowed the preparation of metalladithiolenes of the type [M(cp)(1,2-ethylenedithiolato)] with a variety of substituents. We have extensively studied the chemistry of the cobaltadithiolenes and rhodiadithiolenes of this type and have reported their syntheses and unique physical and chemical properties [1e,6–14].

The metalladithiolene rings have aromatic character on one side; they also show unique reactivities due to unsaturation on the other side. The latter character gives rise to a variety of interesting physical and chemical properties in the metalladithiolene rings.

Many types of metalladithiolene rings containing various metal atoms and substituents have been synthesized. But an analogous metallacycle, metalladithia-

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zole, which contains an unsaturated nitrogen atom instead of an unsaturated carbon atom has not yet been reported.

As an extension of such studies, we developed the chemistry of a novel metallacycle, 1,2,5,3-cobaltadithiazole (**1**) and have studied its synthesis, structure and properties. In a preliminary report [15], we described the formation of $(\eta^5\text{-pentamethylcyclopentadienyl})(1\text{-phenylmethanimine-}N,1\text{-dithiolato})\text{cobalt(III)}$ in the reactions of $[\text{Co}(\text{cp}^*)\text{Ln}]$ ($\text{cp}^* = \text{pentamethylcyclopentadienyl}$, $\text{Ln} = (\text{CO})_2$ or 1,5-cyclooctadiene) with several types of heterocyclic compounds.

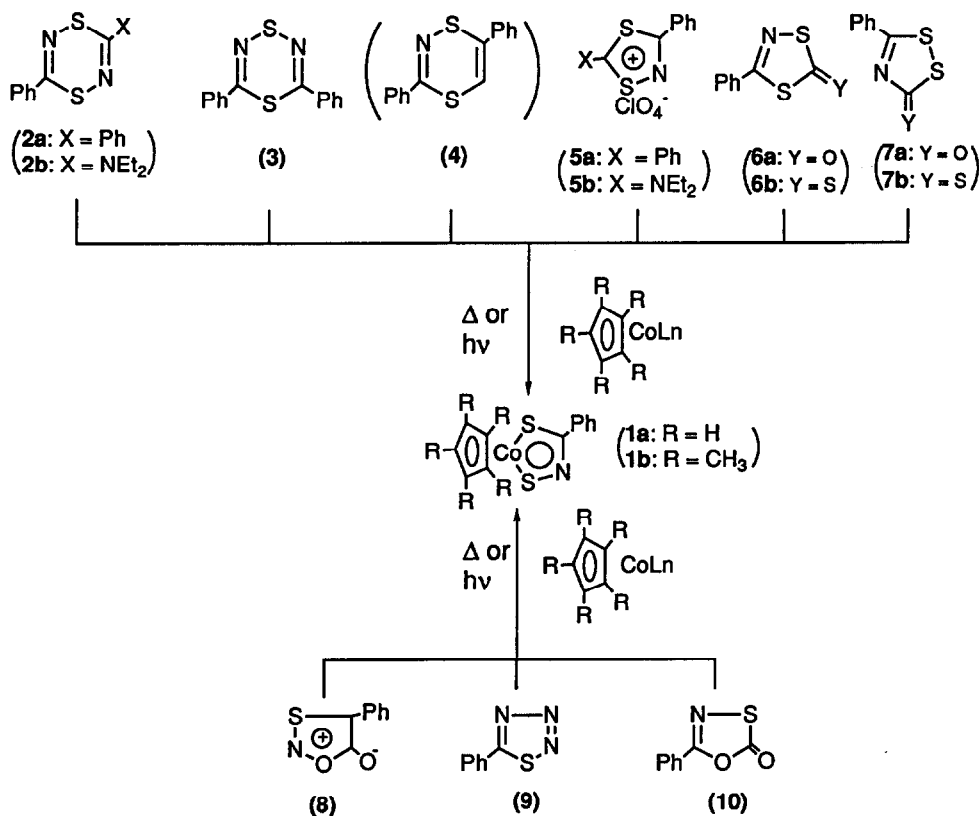
In this paper we report several routes for the formation of the 1,2,5,3-cobaltadithiazole ring in the reactions of $[\text{Co}(\text{cp})]$ species with heterocyclic compounds containing sulfur and nitrogen. We also describe its X-ray structure and some spectroscopic and electrochemical properties.

2. Results and discussion

2.1. Formation of the cobaltadithiazole ring

$(\eta^5\text{-Cyclopentadienyl}$ or $\eta^5\text{-pentamethylcyclopentadienyl})(1\text{-phenylmethanimine-}N,1\text{-dithiolato})\text{cobalt(III)}$

complexes (**1a** and **1b**) containing a novel metallacycle, 1,2,5,3-cobaltadithiazole, are formed in the reactions of $[\text{Co}(\text{cp})\text{Ln}]$ or $[\text{Co}(\text{cp}^*)\text{Ln}]$ ($\text{Ln} = (\text{CO})_2$ or 1,5-cyclooctadiene = cod) with two types of heterocyclic compounds. One class is the heterocyclic compounds which have the $-\text{S}-\text{CPh}=\text{N}-\text{S}-$ sequences. This category includes 3,6-diphenyl-1,4,2,5-dithiadiazine (**2a**), 3-dimethylamino-6-phenyl-1,4,2,5-dithiadiazine (**2b**), 3,5-diphenyl-1,4,2,6-dithiadiazine (**3**), 2-diethylamino-5-phenyl-1,3,4-dithiazolylum perchlorate (**5a**), 2,5-diphenyl-1,3,4-dithiazolylum perchlorate (**5b**), 5-phenyl-1,3,4-dithiazol-2-one (**6a**) and 5-phenyl-1,3,4-dithiazole-2-thione (**6b**). 4-Phenyl-1,2,3-dithiazol-5-one (**7a**) and 4-phenyl-1,2,3-dithiazole-5-thione (**7b**) which are the isomers of **6a** and **6b**, respectively, can also be used as the precursors for 1,2,5,3-cobaltadithiazole. The second class of materials which gives 1,2,5,3-cobaltadithiazole in the reaction with $[\text{Co}(\text{cp})]$ species includes the heterocycles which give nitrile sulfide in thermolysis or in photolysis [16]. This category consists of 4-phenyl-1,3,2-oxathiazolylum-5-olate (**8**), 5-phenyl-1,2,3,4-thiatriazole (**9**), (each a photochemical precursor for benzonitrile sulfide [17,18]), and 5-phenyl-1,3,4-oxathiazol-2-one (**10**) (a thermal precursor for benzonitrile sulfide [19]) (Scheme 1).



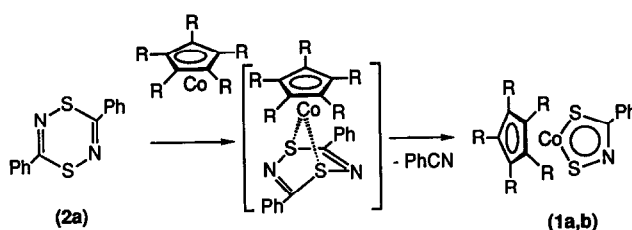
Scheme 1.

The first class heterocyclic compounds with an $-S-N=CPh-S-$ sequence react with $[Co(cp \text{ or } cp^*)(CO)_2]$ or $[Co(cp \text{ or } cp^*)(cod)]$ thermally and photochemically to give 1,2,5,3-cobaltadithiazoles, **1a** and **1b**, although the yields are not so high. The results are summarized in Table 1.

Although we could not find any systematic tendencies in the relationship between the yields of the cobaltadithiazole and the types of heterocyclic compounds or reaction conditions (photochemical or thermal), the reactions under milder conditions are apt to give higher yields. The lower yields under higher temperature or prolonged reaction time may cause the decomposition of the cobaltadithiazoles, because of their thermal instability.

The reactions between the heterocyclic compounds of this type would proceed *via* the attack of a thermally or photochemically formed coordinatively unsaturated cobalt species to the sulfur atoms of the heterocyclic compounds, as exemplified by the case of **2a** (Scheme 2).

When we used 3,5-diphenyl-1,4,2-dithiazine (**4**) as a source of ligand, we obtained only 3-phenyl-1,2,5-



Scheme 2.

cobaltadithiolenes (**11a** and **11b**) as the products. This suggests that benzonitrile is eliminated preferentially to phenylacetylene.

The formation of the cobaltadithiazole from $[Co(cp)]$ species and 5-phenyl-1,3,4-dithiazol-2-one (**6a**) and its thione (**6b**) can be explained by a similar mechanism (the attack of a coordinatively unsaturated Co species to the two sulfur atoms of the heterocyclic compounds and the succeeding elimination of CO or CS). In the reaction between **6a** and $[Co(cp)(cod)]$, the formation of CO was detected.

5-Phenyl-1,2,4-dithiazol-3-one (**7a**) and 5-phenyl-

TABLE 1. Formation of 1,2,5,3-cobaltadithiazoles in the reactions of $[Co(cp \text{ or } cp^*)Ln]$ with heterocyclic compounds having a partial structure of $-S-N=CPh-S-$

Heterocycle		$[Co(cp \text{ or } cp^*)Ln]$			Reaction			Yield of product (%)		Recovery heterocycle (%)
No.	Quantity (μmol)	cp or cp*	Ln	Quantity (μmol)	Solvent	Δ or $h\nu$	Time (h)	1	Other product	
2a	222	cp	cod	222	CH_2Cl_2	Δ (40°C)	23	5.9	—	—
2a	176	cp	cod	176	MeCN	$h\nu$ (r.t.)	18	8.0	—	31
2a	150	cp*	$(CO)_2$	150	CH_2Cl_2	Δ (40°C)	14	8.8	—	9.4
2b	204	cp	cod	203	Benzene	Δ (80°C)	5.5	6.4	—	—
2b	240	cp	cod	240	Benzene	$h\nu$ (r.t.)	19	4.7	—	—
2b	205	cp*	$(CO)_2$	205	Xylene	Δ (140°C)	18	9.2	—	39
3	152	cp	cod	152	Benzene	Δ (80°C)	18	8.1	—	33
3	151	cp	cod	151	MeCN	$h\nu$ (r.t.)	18	8.9	—	Trace
3	150	cp*	cod	150	CH_2Cl_2	Δ (40°C)	23	24	—	—
4	174	cp	cod	174	CH_2Cl_2	Δ (40°C)	18	0	37 ^a	—
4	163	cp	cod	163	MeCN	$h\nu$ (r.t.)	18	0	58 ^a	—
5a	201	cp	cod	203	MeCN	Δ (82°C)	4	7.6	—	—
5a	300	cp	cod	300	MeCN	$h\nu$ (r.t.)	22	Trace	—	—
5a	200	cp*	$(CO)_2$	200	MeCN	Δ (82°C)	4	8.3	—	—
5b	300	cp	cod	300	MeCN	Δ (82°C)	18	1.8	—	—
5b	300	cp	cod	300	MeCN	$h\nu$ (r.t.)	18	4.7	—	—
6a	355	cp	$(CO)_2$	355	Xylene	Δ (140°C)	6	7.3	—	—
6a	100	cp	cod	100	Benzene	$h\nu$ (r.t.)	18	21	—	—
6b	355	cp	$(CO)_2$	355	Benzene	Δ (80°C)	6	9.3	—	—
6b	100	cp	cod	100	Benzene	$h\nu$ (r.t.)	18	8.6	—	—
7a	355	cp	$(CO)_2$	355	Xylene	Δ (140°C)	4	19	Trace ^a	—
7a	178	cp	cod	178	Benzene	$h\nu$ (r.t.)	18	28	Trace ^a	—
7a	355	cp*	$(CO)_2$	355	Xylene	Δ (140°C)	4	6.6	Trace ^a	—
7b	355	cp	$(CO)_2$	355	Xylene	Δ (140°C)	4	Trace	9.6 ^a	—
7b	178	cp	cod	178	Benzene	$h\nu$ (r.t.)	18	19	7.7 ^a	—
7b	355	cp*	$(CO)_2$	355	Xylene	Δ (140°C)	4	Trace	Trace ^a	—

^a (η^5 -Cyclopentadienyl or η^5 -pentamethylcyclopentadienyl)(1,2-diphenyl-1,2-ethylenedithiolato)cobalt(III).

TABLE 2. Formation of 1,2,5,3-cobaltadithiazoles in the reactions of [Co(cp or cp*)Ln] with heterocyclic compounds to give benzonitrile sulfide

Heterocycle No.	Quantity (μ mol)	[Co(cp or cp*)Ln]			Reaction			Yield of product (%)		Recovery heterocycle (%)
		cp or cp*	Ln	Quantity (μ mol)	Solvent	Δ or $h\nu$	Time (h)	1	Other product	
8	710	cp	(CO) ₂	355	Xylene	Δ (140°C)	3	3.5	2.0 ^a	—
8	360	cp	(CO) ₂	180	Benzene	$h\nu$ (r.t.)	1.5	11	2.6 ^a	—
8	583	cp*	(CO) ₂	312	Xylene	Δ (140°C)	3	9.1	8.6 ^a	—
8	305	cp*	(CO) ₂	149	Benzene	$h\nu$ (r.t.)	3	16	11 ^a	—
9	300	cp	cod	150	Xylene	Δ (140°C)	23	0	—	5
9	300	cp	cod	150	Benzene	$h\nu$ (r.t.)	23	3.4	—	—
9	300	cp*	cod	150	Benzene	$h\nu$ (r.t.)	23	2.0	—	44
10	710	cp	(CO) ₂	355	Xylene	Δ (140°C)	4	8.2	—	—
10	306	cp*	(CO) ₂	152	Xylene	Δ (140°C)	22	8.4	—	—

^a (η^5 -Cyclopentadienyl or η^5 -pentamethylcyclopentadienyl)(1,2-diphenyl-1,2-ethylenedithiolato)cobalt(III).

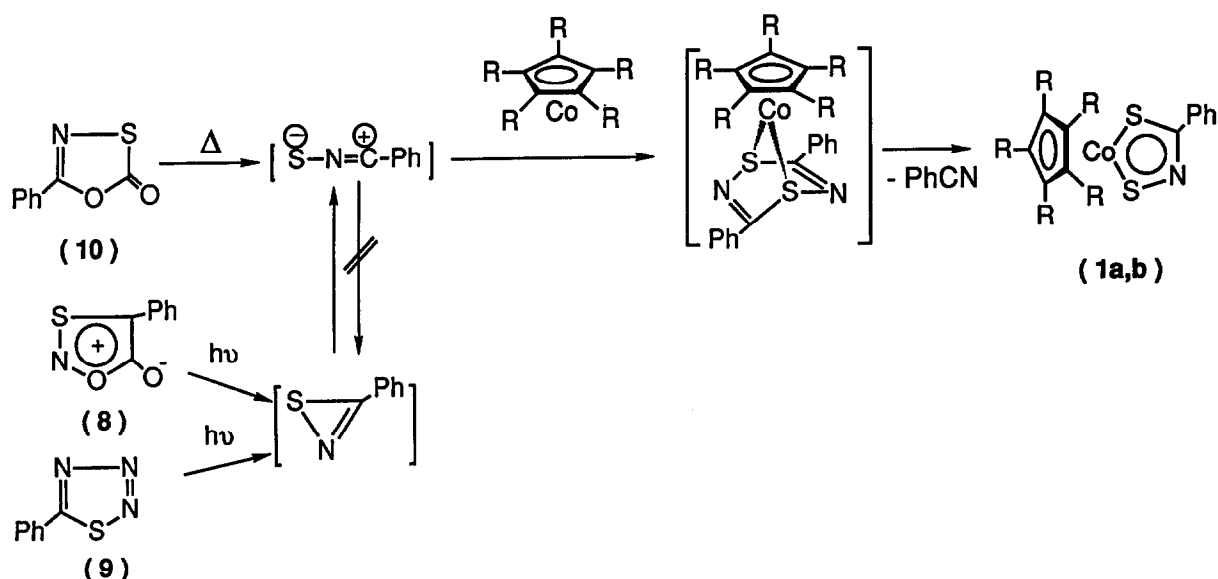
1,2,4-dithiazole-3-thione (7b), the isomers of 6a and 6b, respectively, were found to react with [Co(cp)] species to give 1. The compounds have no $-\text{S}-\text{N}=\text{C}(\text{Ph})-\text{S}-$ sequence but an $-\text{S}-\text{S}-\text{N}=\text{C}(\text{Ph})-$ sequence. The formation of the 1,2,5,3-cobaltadithiazole should involve the insertion of the coordinatively unsaturated cobalt species between the S-S bond and the extrusion of CO or CS in the reaction mechanisms.

The second class of compounds to give cobaltadithiazole in the reaction with [Co(cp)] species are the compounds which produce nitrile sulfide in thermolysis or photolysis. This category includes 4-phenyl-1,3,2-oxathiazolylum-5-olate (8), 5-phenyl-1,2,3,4-thiatriazole (9) and 5-phenyl-1,3,4-oxathiazol-2-one (10). The

former two compounds give photochemically benzonitrile sulfide.

The results are shown in Table 2. The compound 9 gives 1 in the reaction with [Co(cp)(cod)] under irradiation but gives no 1 even at elevated temperatures without irradiation. Both the thermal and photochemical reactions of compound 8 with [Co(cp)(CO)₂] give 1a. However, the photoreaction in which benzonitrile sulfide is formed gives a higher yield of cobaltadithiazole than the thermal reaction.

The mechanism for the formation of cobaltadithiazole in the reaction between [Co(cp)] species and benzonitrile sulfide is not yet clarified. A tentative mechanism *via* benzonitrile sulfide is shown in Scheme 3.



Scheme 3.

The two benzonitrile sulfides react with $[\text{Co}(\text{cp}^*)]$ species to form cobaltadithiazole **1b**.

2.2. Description of the structure of **1b**

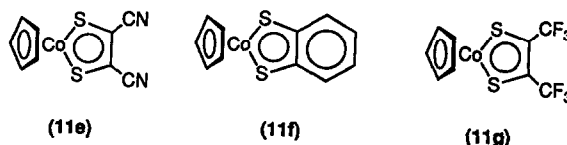
The unit cell consists of four molecules packed in a head-to-tail arrangement as shown in Fig. 1. The molecular structure and atom labeling for **1b** is shown in Fig. 2. Selected bond distances and angles are given in Table 3.

The coordination sphere of the cobalt atom can be viewed as trigonal with the center of a $\eta^5\text{-C}_5\text{Me}_5$ ligand occupying one coordination site and a dithiazole ligand coordinated through atoms S(1) and S(2) occupying the other two sites.

The five-membered ring (1,2,5,3-cobaltadithiazole ring), which consists of one atom each of Co, N and C and two atoms of S, is planar (average displacement of an atom from the least-square plane of the ring being 0.0171 Å), and is essentially perpendicular to the $\eta^5\text{-C}_5\text{Me}_5$ ligand. The dihedral angle between the two planes is 87.01°.

This structure is similar to that of cobaltadithiolenes in ($\eta^5\text{-cyclopentadienyl}$)(1,2-dicyano-1,2-ethylenedithiolato)cobalt(III) (**11e**) [20], ($\eta^5\text{-cyclopentadienyl}$)(1,2-benzenedithiolato)cobalt(III) (**11f**) [21], and ($\eta^5\text{-cyclopentadienyl}$)(1,2-bis(trifluoromethyl)-1,2-ethylenedithiolato)cobalt(III) (**11g**) [22]. In particular, the struc-

tures of cobaltadithiolenes, **11e** and **11f**, are very similar to the structure of the cobaltadithiazole **1b**.



The distance of 2.129(1) Å between Co and S(1) bonded to C is nearly equal to that of 2.107(1) Å between Co and S(2) bonded to N in the cobaltadithiazole **1b**. These values are similar to the Co–S distances of 2.117(3) and 2.111(2) Å in **11e** and **11f**, respectively. The bond angle S–Co–S in **1b** is 89.20(5)°. This bond angle is somewhat smaller than the S–Co–S bond angles of 93.2 and 91.9° in **11e** and **11f**, respectively.

The S(1)–C(11) distance of 1.764(4) Å in **1b** is similar to those of 1.702(7) and 1.729(7) and 1.748(6) Å in **11e** and **11f**, respectively.

These facts suggest that the replacement of a carbon atom by a nitrogen atom of the cobaltadithiolenes ring causes only a small effect on its structure.

2.3. Spectroscopic properties of cobaltadithiazole

The ^1H and ^{13}C NMR spectra suggest the aromaticity of the ring. The appearance of the signals due to the hydrogen at the *ortho*-position of the benzene ring attached to the cobaltadithiazole ring in the lower magnetic field at δ 8.17–8.21 (for **1a**) and 8.13–8.09 (for **1b**) in the ^1H NMR spectra indicates the existence of the ring current in the cobaltadithiazole ring [3].

The characteristic absorptions of metalladithiolenes in the visible region are blue-shifted by the replacement of C by N. The cobaltadithiazoles have absorptions at 524 (for **1a**) and 527 nm (for **1b**), while the cobaltadithiolenes with two phenyl groups has absorption at 628 nm (for **11a**). The cobaltadithiolenes with a phenyl group $[\text{Co}(\text{cp})(\text{S}_2\text{C}_2\text{HPh})]$ and $[\text{Co}(\text{cp}^*)(\text{S}_2\text{C}_2\text{HPh})]$ have their absorption maxima at 592 and 610 nm, respectively.

2.4. Electrochemical properties

The cyclic voltammogram of **1b** is shown in Fig. 3. The electrochemical behavior of the cobaltadithiazoles is similar to that of cobaltadithiolenes [13]. Both cobaltadithiazole **1b** and the corresponding cobaltadithiolenes ($\eta^5\text{-pentamethylcyclopentadienyl}$)(1,2-diphenyl-1,2-ethylenedithiolato)cobalt(III) (**11b**) undergo a reversible one electron reduction which is ascribed to the process from Co^{III} to Co^{II} . The halfwave potential of -1.34 V versus $\text{Ag}|0.1 \text{ mol dm}^{-3} \text{ AgClO}_4$ for the reduction of **1b** is less negative than -1.55 V versus $\text{Ag}|0.1 \text{ mol dm}^{-3} \text{ AgClO}_4$ for that of **11b**. This shows that the nitrogen atom in the ring attracts electrons and causes the cobaltadithiazole ring to be electron-de-

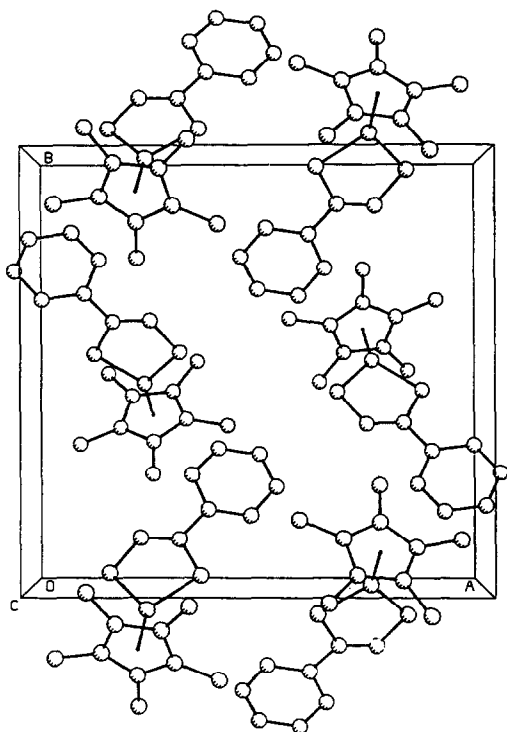


Fig. 1. Unit cell packing diagram of $[(\text{cp}^*)\text{CoSN}=\text{C}(\text{Ph})\text{S}]$ (**1b**).

m.p. 103°C (lit. 102–104°C). 3,5-Diphenyl-1,4,2,6-dithiazine (3) was synthesized by the method of Daley and Ress [24]; m.p. 81°C (lit. 78–80°C). 2-Diethylamino-5-phenyl-1,3,4-dithiazolium perchlorate (5a) and 2,5-diphenyl-1,3,4-dithiazolium perchlorate (5b) were synthesized according to Shibuya and Yonemoto [25,26]. 2,5-Diphenyl-1,3,4-dithiazolium perchlorate (5a); m.p. 215°C (lit. 215°C) and 2-diethylamino-5-phenyl-1,3,4-dithiazolium perchlorate (5b); m.p. 127°C

3.1. Materials

Heterocyclic compounds were synthesized according to the literature. 3,6-Diphenyl-1,4,2,5-dithiazine (2) was synthesized according to Lenz and Zwanenburg [23];

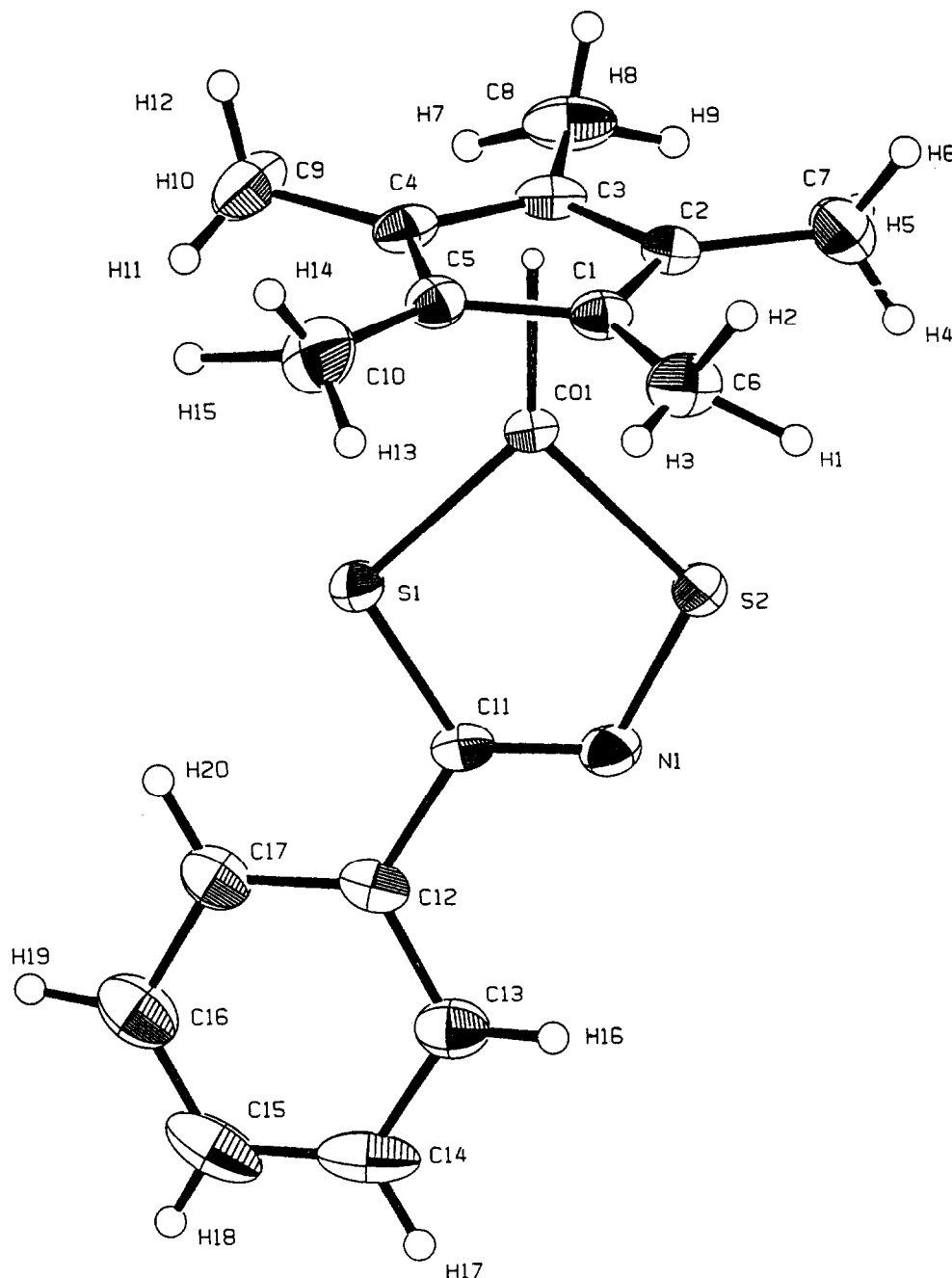


Fig. 2. Molecular structure of $[(\text{cp}^*)\text{CoSN}=\text{C}(\text{Ph})\text{S}]$ (**1b**) showing the atom labeling.

TABLE 3. Selected bond lengths (Å) and angles (°) for (η^5 -pentamethylcyclopentadienyl)(1-phenylmethanimine-*N*,1-dithiolato)cobalt(III) (**1b**) with estimated standard deviations (e.s.d.s) in parentheses

Co-S(1)	2.129(1)	Co-S(2)	2.107(1)
Co-C(1)	2.051(4)	Co-C(2)	2.054(5)
Co-C(3)	2.652(4)	Co-C(4)	2.079(5)
Co-C(5)	2.079(5)	S(1)-C(11)	1.764(4)
S(2)-N(1)	1.697(4)	N(1)-C(11)	1.284(6)
C(1)-C(2)	1.430(7)	C(2)-C(3)	1.425(6)
C(3)-C(4)	1.441(7)	C(4)-C(5)	1.443(6)
C(11)-C(12)	1.499(6)	C(12)-C(13)	1.413(7)
C(13)-C(14)	1.400(8)	C(14)-C(15)	1.37(1)
C(15)-C(16)	1.36(1)	C(16)-C(17)	1.405(8)
S(1)-Co-S(2)	89.20(5)	Co-S(1)-C(11)	103.4(2)
Co-S(2)-N	108.8(1)	S(2)-N-C(11)	116.3(3)
S(1)-C(11)-N	122.2(3)	C(1)-C(2)-C(3)	108.5(4)
C(2)-C(3)-C(4)	108.4(4)	C(3)-C(4)-C(5)	108.0(4)
C(4)-C(5)-C(1)	107.0(4)	C(5)-C(1)-C(2)	108.5(4)
C(11)-C(12)-C(13)	119.4(5)	C(11)-C(12)-C(17)	121.8(5)
C(12)-C(13)-C(14)	119.1(5)	C(13)-C(14)-C(15)	120.9(6)
C(14)-C(15)-C(16)	120.8(7)	C(15)-C(16)-C(17)	120.3(7)
C(16)-C(17)-C(12)	120.0(6)		

(lit. 129°C). 5-Phenyl-1,3,4-dithiazol-2-one (**6a**) and its thione (**6b**) were synthesized according to Greig and Paton; **6a**: m.p. 76.5–77°C (lit. [27] 76°C); **6b**: m.p. 118–119°C (lit. [28] 118°C).

5-Phenyl-1,2,4-dithiazol-3-one (**7a**) and 5-phenyl-1,2,4-dithiazole-3-thione (**7b**) were prepared according to Goerdeler and Nandi [29] and MacDonald and McKinnon [30], respectively. **7a**: m.p. 90°C (lit. 89°C). **7b**: m.p. 134–137°C (lit. 136°C). 4-Phenyl-1,3,2-oxathiazolylum-5-olate (**8**) was prepared according to Gotthardt [17]; m.p. 125°C (lit. 125–127°C). 5-Phenyl-1,2,3,4-thiatriazole (**9**) and 5-phenyl-1,3,4-oxathiazol-2-one (**10**) were prepared according to Jensen *et al.* and How *et al.*, respectively [18,19]; **9**: m.p. 96.5–97°C (lit. 95–96°C) and **10**: m.p. 69°C (lit. 69–71°C).

The complex $[\text{Co}(\text{cp})(\text{CO})_2]$ was prepared in the reaction of $\text{Co}_2(\text{CO})_8$ with cyclopentadiene under reflux in dichloromethane and was purified by vacuum distillation. The complex $[\text{Co}(\text{cp})\text{cod}]$ was prepared by refluxing $[\text{Co}(\text{cp})(\text{CO})_2]$ with 1,5-cyclooctadiene in xylene.

The complex $[\text{Co}(\text{cp}^*)(\text{CO})_2]$ was prepared in the reaction of $\text{Co}_2(\text{CO})_8$ with pentamethylcyclopentadiene under reflux in dichloromethane. The complex was purified by alumina column chromatography. The complex $[\text{Co}(\text{cp}^*)\text{cod}]$ was prepared by refluxing $[\text{Co}(\text{cp}^*)(\text{CO})_2]$ with 1,5-cyclooctadiene in xylene.

3.2. Thermal reactions of heterocyclic compounds with $[\text{Co}(\text{cp})]$ species

The solutions of $[\text{Co}(\text{cp})\text{Ln}]$ and heterocyclic compounds in xylene, benzene, acetonitrile, or dichloromethane were refluxed under Ar.

3.3. Photoreactions of heterocyclic compounds with $[\text{Co}(\text{cp})]$ species

The benzene solutions of $[\text{Co}(\text{cp})\text{Ln}]$ and heterocyclic compounds were irradiated with a 400-W medium pressure mercury lamp under an Ar atmosphere at room temperature.

3.4. Isolation and identification of metalladithiazoles and metalladithiolenes

After the thermal or photochemical reaction, the solvent was evaporated *in vacuo*. The residue was separated by means of flush silica gel column chromatography (column, Wako gel C-300; eluent, CH_2Cl_2).

3.5. (η^5 -Cyclopentadienyl)(1-phenylmethanimine-*N*,1-dithiolato)cobalt(III) (**1a**)

Black crystals: UV (CHCl_3): 286 (ϵ , 25700 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$), 524 (ϵ , 4490 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) and 764 nm (ϵ , 778 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$). ^1H NMR (270 MHz, CDCl_3) δ 8.17–8.21 (m, 2H, Ph); 7.36–7.42 (m, 3H, Ph); 5.46 (s, 5H, cp). ^{13}C NMR (67.9 MHz, CDCl_3) δ 129.5 (Ph); 128.4 (Ph); 128.3 (Ph); 128.2 (Ph); 80.3 (cp ring). MS (70 eV): m/z (relative intensity) 291 (92, M^+), 190 (10), 188 (100, $[\text{M} - \text{PhCN}]^+$), 124 (67, CpCo), 103 (29, PhCN^+) and 59 (9, Co^+). Anal. Found: C, 48.52; H, 4.93; N, 3.51. $\text{C}_{12}\text{H}_{10}\text{CoNS}_2$ calcd.: C, 49.48; H, 4.81; N, 3.46%. Found: m/z 290.9588. $\text{C}_{12}\text{H}_{10}\text{CoNS}_2$ calcd.: M, 290.9586.

In ^{13}C NMR, the signal for the C in the cobaltadithiazole ring was not observed. The reason for this is not clear.

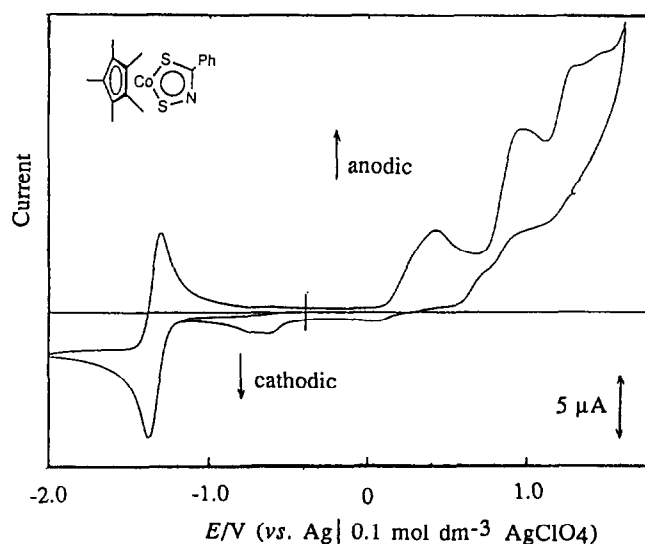


Fig. 3. Cyclic voltammogram of $[(\text{cp}^*)\text{CoSN}=\text{C}(\text{Ph})\text{S}]$ (**1b**) in acetonitrile. Scan rate, 100 mV s^{-1} ; temperature, 25°C.

3.6. (η^5 -Pentamethylcyclopentadienyl)(1-phenylmethanimine-*N*,1-dithiolato)cobalt(III) (**1b**)

Black crystals: m.p. 224–227°C (decomp). UV (CH_2Cl_2): 298 (ϵ , 26300 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$), 527 (ϵ , 5000 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) and 731 nm (ϵ , 900 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$). IR (KBr disk): 2980, 2960, 2920, 1490, 1454, 1423, 1022, 946, 777 and 700 cm^{-1} . ^1H NMR (270 MHz, CDCl_3): δ 8.13–8.09 (m, 2H, Ph); 7.32–7.29 (m, 3H, Ph); 1.95 (s, 15H, CH_3). ^{13}C NMR (67.9 MHz, CDCl_3): δ 183.4 (C in the cobaltadithiazole ring); 138.2 (Ph); 128.8 (Ph); 128.1 (Ph); 127.8 (Ph); 92.7 (cp ring); 10.9 (CH_3). MS (70 eV): m/z (relative intensity) 361 (25, M^+), 258 (66, $[\text{M} - \text{PhCN}]^+$), 133 (77), 119 (83), 103 (100, PhCN^+), 91 (31), 77(26), 76 (40) and 59 (6, Co^+). Anal. Found: C, 56.66; H, 5.73; N, 3.73. $\text{C}_{17}\text{H}_{20}\text{CoNS}_2$ calcd.: C, 56.50; H, 5.58; N, 3.88%.

The complex **1a** is less stable in the solid state than its pentamethyl analog **1b**; the complex **1a** gradually decomposes in the solid state at room temperature.

3.7. Collection and reduction of X-ray data

3.7.1. Preparation of a single crystal

A crystal of **1** was obtained by slow evaporation of 5:1 acetonitrile/hexane (v/v) in the dark.

3.7.2. Data collection

The X-ray data were collected using an AFC5 diffractometer and supplied to Rigaku Corporation on magnetic tape. The unit cell is orthorhombic with dimensions: $a = 14.936 \text{ \AA}$, $b = 14.262 \text{ \AA}$, $c = 8.078 \text{ \AA}$ and $V = 1720.8 \text{ \AA}^3$. For $Z = 4$ and F.W. = 361.40, the calculated density is 1.395 g cm^{-3} . Based on the systematic absences of $h00$: $h \ 2n$, $0k0$: $k \ 2n$ and the successful solution and refinement of the structure, the space group was determined to be $P_{2,2,2}$. The data were collected at ambient temperature using the ω - 2θ scan technique to a maximum 2θ value of 55.1.

3.7.3. Data reduction

Of the 4407 reflections which were collected, 3981 were unique ($R_{\text{int}} = 0.024$). The intensities of three representative reflections, which were measured after each block of 100 reflections, remained constant throughout data collection indicating crystal and electronic stability.

The linear absorption coefficient for Mo- $K\alpha$ was 12.2 cm^{-1} . The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = $0.56345\text{E} - 06$).

3.8. Structure solution and refinement

The structure was solved by using the automatic Patterson analysis option of SAPI91 which revealed the

positions of all but one of the non-hydrogen atoms. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined with fixed isotropic temperature factors. The final cycle of full-matrix least-squares refinement was based on 2706 observed reflections ($I > 3.00\sigma(I)$) and 251 variable parameters and converged (largest parameter shift was 0.18 times its e.s.d.) with unweighted and weighed agreement factors of $R = \sum w \| F_o \| - \| F_c \| / \sum \| F_o \| = 0.038$ and $R_w = [\sum w (\| F_o \| - \| F_c \|^2) / \sum w \| F_o \|^2]^{1/2} = 0.040$.

The standard deviation of an observation of unit weight was 1.24. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. Plots of $\sum w (\| F_o \| - \| F_c \|^2)$ versus $\| F_c \|$, reflection order in data collection, $\sin \theta / \lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.50 and $-0.39 \text{ e}^{-1} \text{ \AA}^{-3}$, respectively. The space group was non-centrosymmetric so a test for the determination of absolute configuration was determined. Refinement of the other enantiomer yielded significantly higher R -values ($R = 0.048$ and $R_w = 0.050$). All the results reported here refer to the enantiomer that yielded the lower R -values.

Neutral atom scattering factors were taken from Cromer and Waber. Anomalous dispersion effects were included in F_{calc} ; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation.

3.9. Cyclic voltammetry

Cyclic voltammograms were taken with a Huso polarograph Model 312 equipped with a Riken Denshi X-Y recorder Model F-42DG and a Huso potential scanning unit Model 321. The electrochemical measurements were carried out in $0.1 \text{ mol dm}^{-3} (\text{C}_2\text{H}_5)_4\text{-NClO}_4$ containing acetonitrile solutions at 25°C under an argon atmosphere by a three electrode system consisting of a test electrode (stationary or rotating platinum disk, 2 mm in diameter), a coiled platinum wire counter electrode, and $\text{Ag} | 0.1 \text{ mol dm}^{-3} \text{AgClO}_4$ in acetonitrile as a reference electrode.

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