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Formation of (η^5-Pentamethylcyclopentadienyl)(1-phenylmethanimine-*N*,1-dithiolato)cobalt(III) Having a Novel Metallacycle, 1,2,5,3-Cobaltadithiazole, in Reactions of [Co(cp*)($CO)_2$] with Heterocyclic Compounds Containing S and N

Akihiro KATO, Masaki TONO,† Naoki HISAMATSU, Sho-hei NOZAWA,
Toru SUGIYAMA, Masatsugu KAJITANI, Takeo AKIYAMA, and Akira SUGIMORI*
Department of Chemistry, Faculty of Science and Technology,
Sophia University, Kioi-cho 7-1, Chiyoda-ku, Tokyo 102
†Advanced Polymer Research Laboratory, Sekisui Chemical Co.,
Hyakuyama 2-1, Shimamoto-cho, Mishima, Osaka 618

(η^5-Pentamethylcyclopentadienyl)(1-phenylmethanimine-*N*,1-dithiolato)cobalt(III) (**1**) containing 1,2,5,3-cobaltadithiazole ring (a novel metallacycle) is formed in the reactions of [Co(cp*)($CO)_2$] with several precursors of benzonitrile sulfide, 5-phenyl-1,3,4-oxathiazol-2-one (thermal precursor), 4-phenyl-1,3,2-oxathiazolylium-5-olate, and 5-phenyl-1,2,3,4-thiatriazole (photochemical precursors). Compound **1** is also formed in the thermal reactions of [Co(cp*)($CO)_2$] with 3,6-diphenyl-1,4,2,5-dithiadiazine, 3,5-diphenyl-1,4,2,6-dithiadiazine, 2-diethyl-amino-5-phenyl-1,3,4-dithiazolium perchlorate, 5-phenyl-1,2,4-dithiazol-3-one, or 5-phenyl-1,2,4-dithiazole-3-thione.

A metalladichalcogenolene ring consists of one metal atom, two coordinated chalcogen atoms, and two unsaturated carbon atoms. It is a pseudoaromatic metallacycle, has a unique valence state, and shows several characteristic physical and chemical properties.1)

Many types of metalladichalcogenolene rings containing various metal atoms and substituents have been synthesized.2) Cobaltadithiolene complexes having a cyclopentadienyl group (complex of the type **11**) can be synthesized in a one-pot reaction of [Co(cp)] species, alkyne, and sulfur.3) Recently, we reported a synthesis of selenium-containing cobaltadichalcogenolenes.4) But an analogous metalladichalcogenazole which contains an unsaturated nitrogen atom instead of an unsaturated carbon atom has not yet been reported. No cobaltadithiazole complex could be synthesized by a reaction analogous to the synthesis of cobaltadithiolenes (the reaction of [Co(cp)($CO)_2$] or [Co(cp)(cod)] with a nitrile and sulfur).

This report describes the formation of a novel metallacycle, 1,2,5,3-cobaltadithiazole, in the reactions of [Co(cp*)($CO)_2$] (**2**) (cp* = pentamethylcyclopentadienyl) with several sulfur-containing heterocyclic compounds: 4-phenyl-1,3,2-oxathiazolylium-5-olate (**3**), 5-phenyl-1,2,3,4-thiatriazole (**4**), 5-phenyl-1,3,4-oxathiazol-2-one (**5**), 3,6-diphenyl-1,4,2,5-dithiazine (**6**), 3,5-diphenyl-1,4,2,6-dithiazine (**7**), 2-diethylamino-5-phenyl-1,3,4-dithiazolium perchlorate (**8**), 5-phenyl-1,2,4-dithiazol-3-one (**9**), and 5-phenyl-1,2,4-dithiazole-3-thione (**10**). Among these organic compounds, **3**5) and **4**6) are photochemical precursors of benzonitrile sulfide.7) Compound **5** has been known to give benzonitrile sulfide in thermolysis.8) The formation of a cobaltadithiazole complex was accidentally discovered during the survey of the reactions of coordinatively unsaturated transition metal compounds with 1,3-dipolar organic compounds. When we treated $[Co(cp^*)(CO)_2]$ with **3**, **4**, or **5** under the conditions where benzonitrile sulfide is formed, we obtained a new type complex (η^5-pentamethylcyclopentadienyl)(1-phenylmethanimine-*N*,1-dithiolato)cobalt(III) having a novel metallacycle, 1,2,5,3-cobaltadithiazole. Thus, the reflux of xylene solutions of **5** and **2** or the UV-irradiation of benzene solutions of **3** or **4** and **2** in quartz tubes with a high pressure mercury lamp affords a cobalt complex, (η^5-pentamethylcyclopentadienyl)(1-phenylmethanimine-*N*,1-dithiolato)cobalt(III) (**1**). In the photoreaction between **3** and **2**, another cobalt complex, (η^5-pentamethylcyclopentadienyl)(1,2-diphenyl-1,2-ethylenedithiolato)cobalt(III) (**11**), was also obtained.

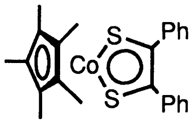
Table 1. Formation of 1,2,5,3-Cobaltadithiazole Compound (**1**) in the Reactions of $[Co(cp^*)(CO)_2]$ (**2**) with Several Heterocyclic Compounds

Org. compound		$[Co(cp^*)(CO)_2]$	Reaction conditions			Yield of **1**[a]
	Amount μmol	Amount μmol	Solvent	Δ or hν	Time h	%
3	305	149	benzene	hν (HP)[b]	3	16.2[c]
4	300	150	benzene	hν (HP)[b]	23	2
5	306	152	xylene	Δ (140 °C)	22	8.4
6	150	150	CH_2Cl_2	Δ (40 °C)	23	8.8[c]
7	150	150	CH_2Cl_2	Δ (40 °C)	23	24[c]
8	200	200	CH_3CN	Δ (82 °C)	4	8.3
9	355	355	xylene	Δ (140 °C)	4	6.6[c]
10	355	355	xylene	Δ (140 °C)	4	27[c]

a) The yield of **1** is calculated on the basis of $[Co(cp^*)(CO)_2]$.

b) Irradiated with a high pressure mercury lamp.

c) Compound (**11**) was obtained (in the reaction of **3**, 10.6%; in the reactions of **4**, **5**, **9**, and **10**, traces).



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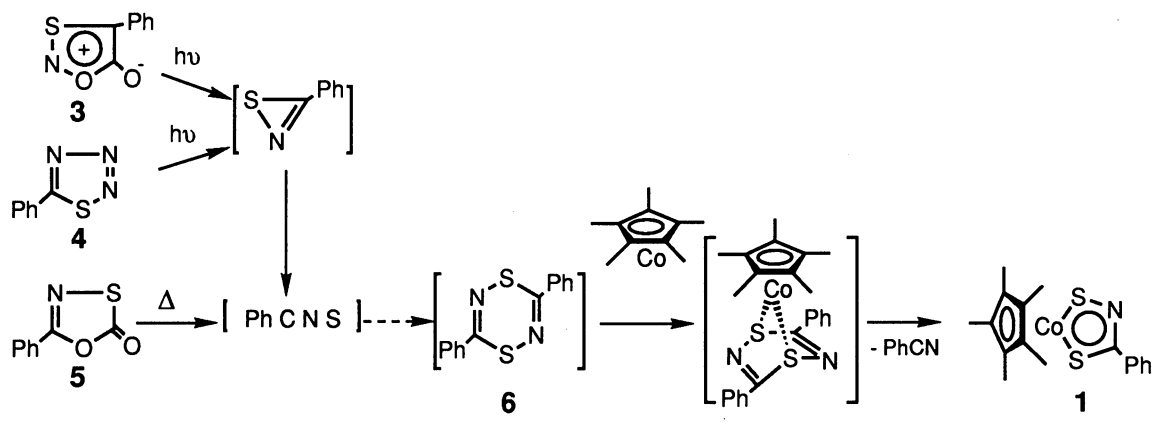
This novel complex **1** was identified on the basis of ^1H and ^{13}C NMR, MS and elemental analysis.[9] The results of elemental analysis agree satisfactorily with the calculated values. The spectroscopic properties of the cobaltadithiazole compound are similar to those of the corresponding cobaltadithiolene compounds. The fragmentation patterns of the cobaltadithiazole and cobaltadithiolene in a mass spectrometer are very similar: the main peaks of these compounds are M^+, $[Co(cp^*)S_2]^+$, $[PhC{\equiv}N]^+$ or $[PhC{\equiv}CPh]^+$, and Co^+. The ^1H and ^{13}C NMR signals can be reasonably assigned according to the postulated structure. The characteristic absorption of cobaltadithiolene at 617 nm in the visible region ($\varepsilon = 5600$ dm^3 mol^{-1}cm^{-1}) of cobaltadithiolene (**11**) shifts to 527 nm ($\varepsilon = 5000$ dm^3 mol^{-1}cm^{-1}) in cobaltadithiazole.

In the reaction of $[Co(cp^*)(CO)_2]$ (**2**) with **3**, **4**, or **5**, the cobaltadithiazole-forming reaction occurs under the condition where benzonitrile sulfide is produced. To explain the formation of cobaltadithiazole, the intermediacy of a dimer of the nitrile sulfide (3,6-diphenyl-1,4,2,5-dithiadiazine: **6**) would be postulated, because we have found that 1,4-dithiins react with [Co(cp)] species to give 1,2-ethylenedithiolatocobalt(III) complexes (complex of type **11**).[10] In fact, the reaction of **2** with **6**[11] gave **1** under mild conditions

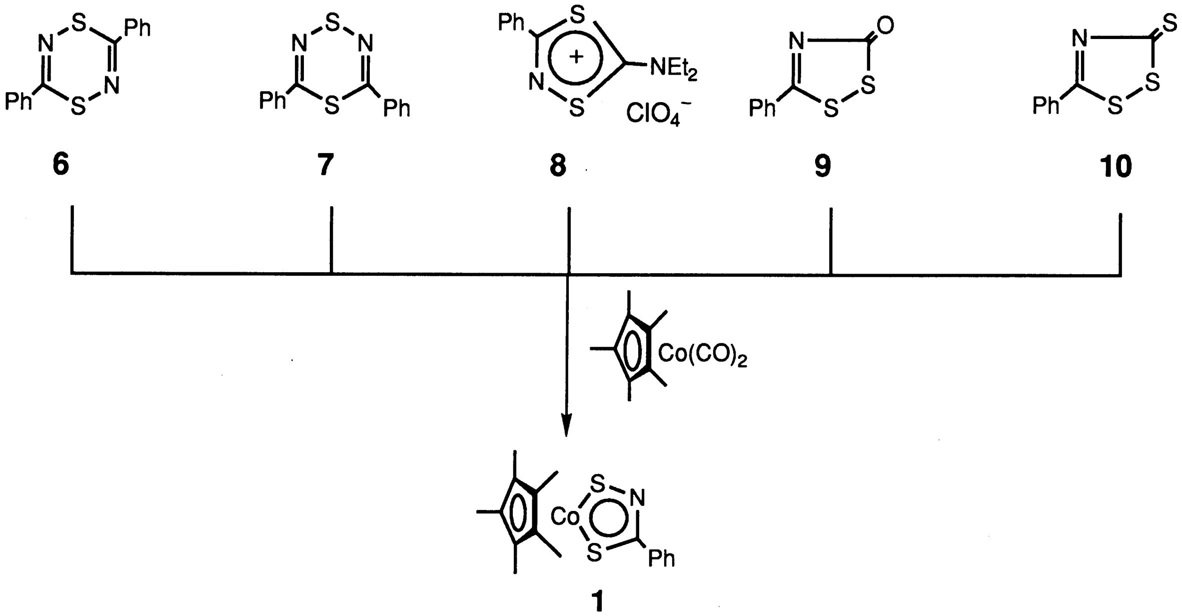
(Table 1). A tentative mechanism via benzonitrile sulfide for the formation of the cobaltadithiazole compound is shown in Scheme 1.



Scheme 1.

The thermal reactions of [Co(cp*)(CO)$_2$] (**2**) with 3,5-diphenyl-1,4,2,6-dithiadiazine (**7**)$^{11)}$ or 2-diethylamino-5-phenyl-1,3,4-dithiazolium perchlorate (**8**)$^{11)}$ also afforded **1**. These reactions support the structure of the cobaltadithiazole.

Other heterocyclic compounds, 5-phenyl-1,2,4-dithiazol-3-one (**9**)$^{12)}$ and 5-phenyl-1,2,4-dithiazole-3-thione (**10**)$^{13)}$ were found to react with [Co(cp*)(CO)$_2$] (**2**) to give **1** in 6.6 and 27% yields, respectively.



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9) (η^5-Pentamethylcyclopentadienyl)(1-phenylmethanimine-*N*,1-dithiolato)cobalt(III) (**1**) : Red crystals; mp 224-227 °C (decomp). UV (CH_2Cl_2) 298 (ε, 26300 $dm^3\ mol^{-1}\ cm^{-1}$), 527 (ε, 5000 $dm^3\ mol^{-1}\ cm^{-1}$) and 731 nm (ε, 900 $dm^3\ mol^{-1}\ cm^{-1}$) ; 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, 2 H, Ph), 7.32-7.29 (m, 3 H, Ph), and 1.95 (s, 15 H, CH_3); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ = 183.4 (C in the cobalta-dithiazole ring), 138.2 (Ph), 128.8 (Ph), 128.1 (Ph), 127.8 (Ph), 92.7 (cp ring), and 10.9 (CH_3); MS (70 eV) , *m/z* (relative intensity) 361 (25, M^+), 258 (66, $[M-PhCN]^+$), 133 (77), 119 (83), 103 (100, $PhCN^+$), 91 (31), 77(26), 76 (40), and 59 (6, Co^+). Found: C, 56.66; H, 5.73; N, 3.73%. Calcd for $C_{17}H_{20}CoNS_2$: C, 56.50; H, 5.58; N, 3.88%.

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