

Formation and Photochemical and Thermal Reactions of
Adduct between 1,2,5,3-Cobaltadithiazole and Dimethyl Acetylenedicarboxylate

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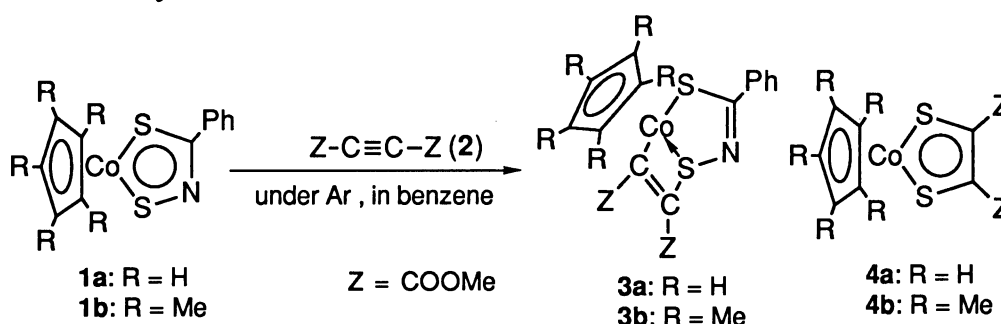
(η^5 -Cyclopentadienyl or η^5 -pentamethylcyclopentadienyl)(1-phenylmethanimine-*N*,1-dithiolato)cobalt(III) (**1**) reacts with dimethyl acetylenedicarboxylate (DMAD) to give the adducts in which Co and S of the 1,2,5,3-cobaltadithiazole ring in the cobalt complex are bridged by 1,2-dimethoxycarbonyl-ethylene-1,2-diyl groups (**3a**: the complex having Cp and **3b**: the complex having Cp*). The sulfur atom adjacent to N is preferentially reacted. Photolysis of **3** gives 3,4-dimethoxycarbonyl-1,2,5-cobaltadithiolene (**4**) with the elimination of benzonitrile. In thermolysis in benzene, **3a** undergoes selectively the elimination of benzonitrile to give **4a**, while **3b** undergoes the elimination of either DMAD or benzonitrile to give **1** or **4**.

We have reported unique reactivities of the 1,2,5-cobaltadithiolene ring, which consists of a cobalt atom, two coordinated sulfur atoms, and two unsaturated carbon atoms.¹⁾ The ring is a conjugated system with 6 π electrons and shows both aromaticity and unsaturation. Our studies on the reactivities of metalladithiolene ring in (η^5 -cyclopentadienyl)(1,2-ethylenedithiolato)metal(III) (metal = Co or Rh) have revealed a variety of interesting addition and dissociation reactions which occur in the metalladichalcogenolene rings.^{1d)} Insertion (addition) reactions between metal and sulfur are characteristic reactions for the metalladithiolene rings. Typical reactions are additions of alkylidenes by diazo compounds,²⁾ addition of alkyne,³⁾ and addition of quadicyclane.⁴⁾ Recently we succeeded in the synthesis of a nitrogen-containing analog of cobaltadithiolene, 1,2,5,3-cobaltadithiazole, which is a novel metallacycle.⁵⁾ The substitution of a nitrogen atom for a carbon atom may cause important changes in the physical and chemical properties of the metallacycle. In this paper we compare the reactivities of 1,2,5,3-cobaltadithiazole with those of 1,2,5-rhodiadithiolene in the reactions with dimethyl acetylenedicarboxylate.³⁾

(η^5 -Cyclopentadienyl or η^5 -pentamethylcyclopentadienyl)(1-phenylmethanimine-*N*,1-dithiolato)cobalt(III) (**1a** or **1b**) (0.1 mmol) reacts with dimethyl acetylenedicarboxylate (DMAD, **2**) (0.4 mmol) at room temperature for 24 h. The single 1:1 adduct between cobaltadithiazole and dimethyl acetylenedicarboxylate was obtained in high yield in each case (70% for **3a** with cp and 99% for **3b** with Cp*).⁶⁾ As byproducts, a small amount of (η^5 -cyclopentadienyl or -pentamethylcyclopentadienyl)(1,2-ethylenedithiolato)cobalt(III) (**4a**

or **4b**) (yield of **4a**, 2%; yield of **4b**, 1%) and a trace amount of tetramethyl thiophene-2,3,4,5-tetracarboxylate were obtained.

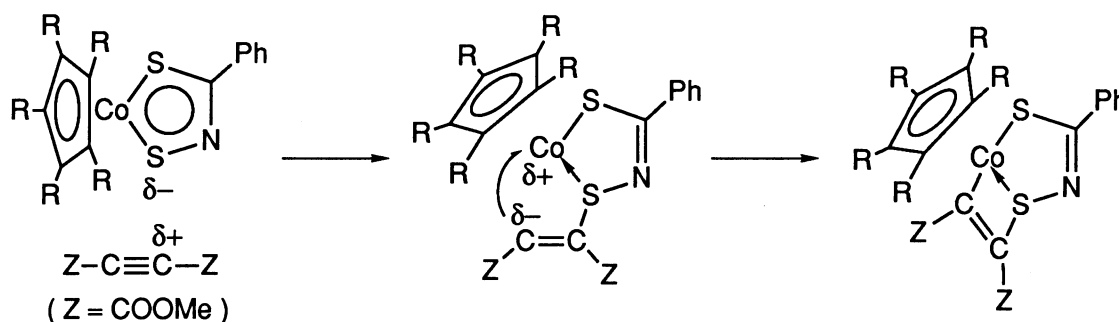
The comparison of their NMR and MS values with those of the adduct between rhodiadithiolene and DMAD shows that the alkyne bridges between cobalt and S which is adjacent to N. The ^{13}C NMR of the adduct between a rhodiadithiolene (η^5 -cyclopentadienyl)(1,2-dimethoxycarbonyl-1,2-ethylenedithiolato)-rhodium(III) and DMAD, the structure of which was determined by X-ray diffraction,^{3b)} showed that the signal of the C adjacent to the bridged S appears at $\delta = 107.4$ (up-shifted from $\delta = 134$ for that of the free dithiolene) and that of the other C appears at $\delta = 178.6$ (down-shifted). The signal of the C in the cobaltadithiazole ring in the adduct **3b** appears at $\delta = 203.4$. This value is greater than $\delta = 184.3$ of the free cobaltadithiazole. The down-shift indicates that the bridging occurs at the S atom away from the C atom, namely at the S atom adjacent to N.



The addition reaction between Co and S occurs in the reaction with diazo compounds (the bridging by methylene).²⁾ The addition of methylene is initiated by the attack of the negatively charged C of the 1,3-dipolar diazo compound to the positively charged central metal of the metalladithiolenes. The electron-rich diazo compounds react more easily.

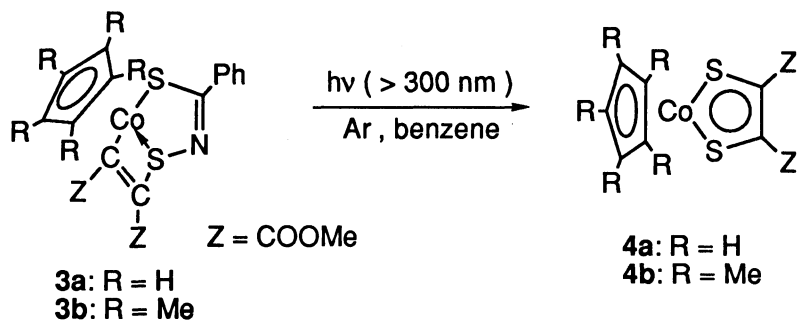
In contrast to the addition of methylene, the addition of alkyne occurs only with electron deficient alkynes, DMAD and methyl acetylenecarboxylate to **1**. The adducts of methyl acetylenecarboxylate are unstable and decompose gradually at room temperature. Diphenylacetylene does not react with **1**.

The initial step of the reaction would be the electrophilic attack of the electron-deficient alkyne to the lone pair-electrons at the S atom. Between the two sulfur atoms in the ring, the electron-rich one should be attacked selectively. The S atom adjacent to C is electron-poorer than the S atom adjacent to N, because the π -electron density at the former S is lowered by the conjugation with the electron-attracting N atom.



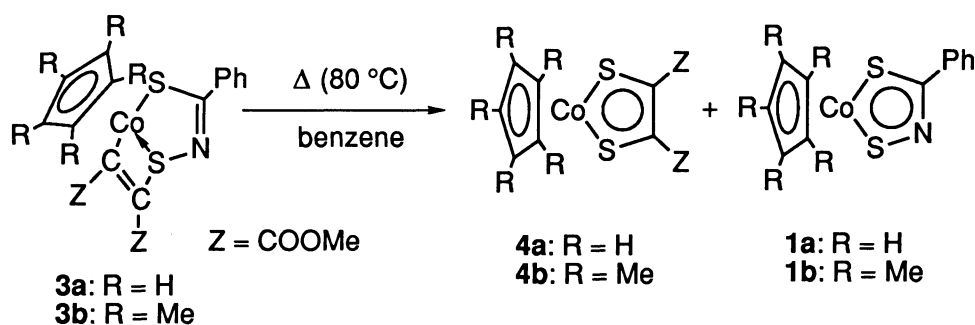
The alkyne adducts of 1,2,5,3-cobaltadithiazole **3** are less stable than the alkyne adducts of 1,2,5-cobaltadithiolene. The adducts **3a** and **3b** react thermally and photochemically. The irradiation of **3** in a

benzene solution with a medium pressure lamp brings about the migration of DMAD moiety and the elimination of benzonitrile to afford 3,4-dimethoxycarbonyl-1,2,5-cobaltadithiolenes (**4**) (yield of **4a**, 70% and recovery of **3a**, 30% ; yield of **4b**, 60% and recovery of **3b**, 40% for 3 h irradiation).



This photochemical behavior is different from that of the adduct between cobaltadithiolenes and DMAD. study of the photoreaction of the adduct between $(\eta^5\text{-cyclopentadienyl})(1,2\text{-dimethoxycarbonyl-1,2-ethylenedithiolato})\text{cobalt(III)}$ and deuterated DMAD revealed that the irradiation causes selectively the elimination of the alkyne moiety bridging between Co and S and no migration of the alkyne moiety.

In thermolysis in benzene under reflux, **3a** undergoes almost selectively the elimination of benzonitrile accompanied by the elimination of DMAD (yield of **4a**, 75%; yield of **1a**, trace; and recovery of **3a**, 26% for the thermolysis for 2 h), while **3b** undergoes the elimination of either DMAD or benzonitrile to give **1b** (56%) and **4b** (12%) in the thermolysis for 2 h (recovery of **3b**, 30%).



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- 6) Adduct **3a**: mp 67-70 °C; ^1H NMR (CDCl_3) δ = 3.67 (3H, s, COOCH_3), 3.90 (3H, s, COOCH_3), 5.23 (5H, s, Cp), 7.37 (3H, m, Ph), and 8.07 (2H, d, J = 7.4 Hz, Ph); ^{13}C NMR (CDCl_3) δ = 52.2 (OCH_3), 52.4 (OCH_3), 86.1 (Cp), 124.9 (S-C-COOMe), 128.2 (Ph), 128.7 (Ph), 131.4 (Ph), 136.7 (Ph), 154.6 (S-C-COOMe), 170.6 (Co-C-COOMe), 172.2 (Co-C-COOMe), and 204.3 (S-C-N); MS (70 eV) m/z (relative intensity) 330 (85, M^+ -PhCN), 291 (19, M^+ -DMAD), 277 (100), 246 (99), 188 (72, CpCoS_2), 124 (17, CpCo), 111 (11), 103 (78), and 59 (9).
 Found: C, 49.78; H, 3.94; N, 3.12%. Calcd for $\text{C}_{18}\text{H}_{16}\text{NO}_4\text{S}_2\text{Co}$: C, 49.89; H, 3.72; N, 3.23%.
 Adduct **3b**: mp 81-83 °C (dec); ^1H NMR (CDCl_3) δ = 1.68 (15H, s, Cp^*), 3.65 (3H, s, COOCH_3), 3.85 (3H, s, COOCH_3), 7.33 (3H, m, Ph), and 8.11 (2H, d, J = 6.9 Hz, Ph); ^{13}C NMR (CDCl_3) δ = 9.1 ($\text{C}_5(\text{CH}_3)_5$), 52.2 (OCH_3), 52.4 (OCH_3), 94.5 ($\text{C}_5(\text{CH}_3)_5$), 124.5 (S-C-COOMe), 127.7 (Ph), 128.4 (Ph), 130.9 (Ph), 137.1 (Ph), 155.3 (S-C-COOMe), 170.0 (Co-C-COOMe), 181.3 (Co-C-COOMe), and 203.4 (S-C-N); MS (70 eV) m/z (relative intensity) 400 (61, M^+ -PhCN), 361 (59, M^+ -DMAD), 258 (100, Cp^*CoS_2), 133 (39), 111 (72), 103 (68, PhCN), and 59 (88, Co); FAB-MS m/z 504 ($\text{M}+1$); Found: C, 54.86; H, 5.20; N, 2.79%. Calcd for $\text{C}_{23}\text{H}_{26}\text{NO}_4\text{S}_2\text{Co}$: C, 54.86; H, 5.21; N, 2.78%.

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