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1,2,3-Selenadiazoles as Precursors to Cyclopentadienylcobalt Dithiolenes and 1,4-Dithiins: Molecular Structures of Bis(cycloocteno)-1,4-dithiin and Bis(cycloocteno)-1,4-diselenin

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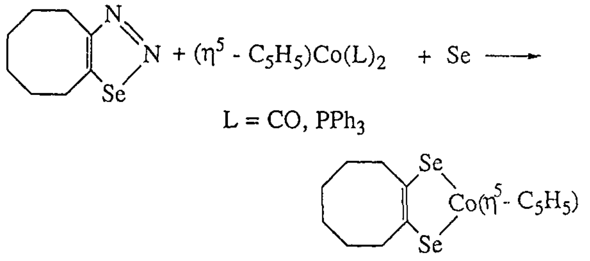
ABSTRACT

Cycloocteno-1,2,3-selenadiazole (**1**) *and cyclopentadienyldicarbonylcobalt* (**2**) *react in the presence of an excess of elemental sulfur to yield the dithiolene cyclopentadienyl(1,2-cyclooctenedithiolato)cobalt* (**3**). *Available evidence indicates that this reaction involves the intermediacy of a cobalt–alkyne complex. Compound* **3** *is the first example of a cyclopentadienylcobalt dithiolene bearing aliphatic substituents. Analogous reactions performed using only catalytic quantities of* **2** *provide high-yield syntheses of bis(cycloocteno)-1,4-dithiin* (**6**) *and bis(cycloocteno)-1,4-diselenin* (**7**), *whose structures have been determined by X-ray diffraction.*

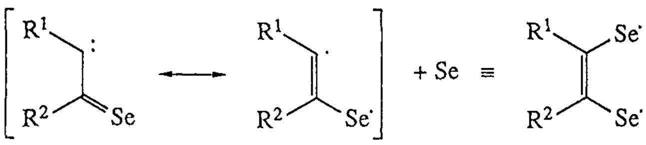
INTRODUCTION

In the course of our investigations into the reactions of 1,2,3-selenadiazoles with organotransition metal complexes [1], we have previously demonstrated that they may serve as precursors to cyclopentadienylcobalt diselenolenes [2] (Equation 1).



(1)

1,2,3-Selenadiazoles generally react via elimination of dinitrogen, and it is the fate of the selenaketocarbene intermediate thus produced that determines the outcome of their reactions. The formation of diselenolenes may be explained on the basis of the formal relationship shown in Equation 2: The selenaketocarbene already contains one carbon–selenium bond, and the second may be introduced by reaction with elemental selenium. If this view is correct, then it should be possible to prepare a thiaselenolene, a mixed sulfur/selenium system, by use of elemental sulfur in place of the selenium (Equation 3).



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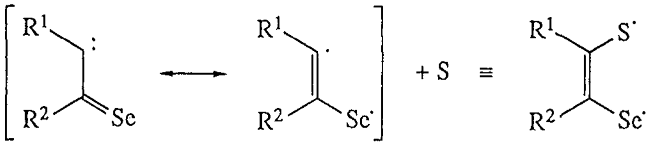


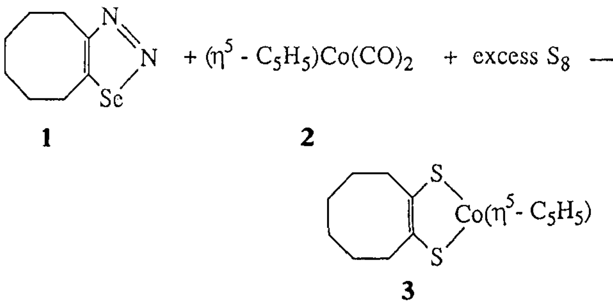
(3)

We have tested this hypothesis, and now report the results of our study.

RESULTS AND DISCUSSION

Dithiolenes from Selenadiazoles

Equimolar quantities of cycloocteno-1,2,3-selenadiazole (**1**) and cyclopentadienyldicarbonylcobalt (**2**) react in the presence of an excess of elemental sulfur to yield the dithiolene, cyclopentadienyl(1,2-cyclooctenedithiolato)cobalt (**3**), in good yield (Equation 4). The product is an intensely colored purplish-blue crystalline solid, resembling the analogous diselenolene in its chemical and physical properties. There is no evidence for the formation of compounds containing both selenium and sulfur.



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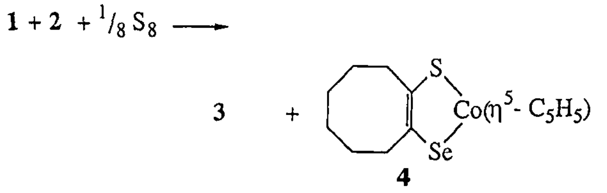
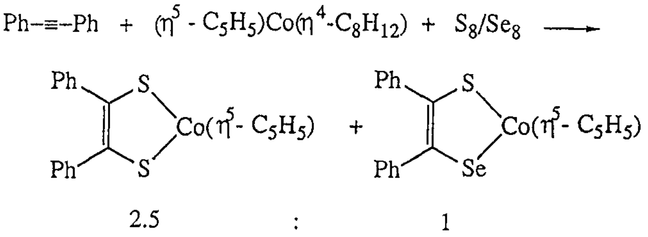


(5)

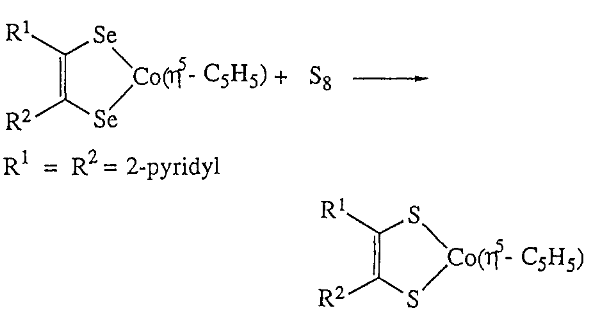
The same reagents, in the presence of an equimolar amount of sulfur, give rise to two products, which could not be separated by chromatographic techniques. ^{1}H NMR and mass spectroscopy reveal that these products are **3** and cyclopentadienyl(2-selenolatocyclooctenethiolato)cobalt (**4**) (Equation 5). Compounds **3** and **4** are formed in an approximate molar ratio of 1.5 : 1, suggesting an overall 4 : 1 preference for the incorporation of sulfur rather than selenium. The combined yield is rather poor, reflecting the limited availability of free chalcogen.

If **1** and **2** are reacted in the presence of an excess of both elemental sulfur and elemental selenium, then a similar result is obtained: No diselenolene is produced, and **3** predominates over **4** in the product mixture. In related experiments Kajitani et al. [3] have made comparable observations: The reaction of cyclopentadienylcobalt precursors with an activated acetylene in the presence of a selenium/sulfur mixture leads predominantly to the formation of the dithiolene (Equation 6).



(6)

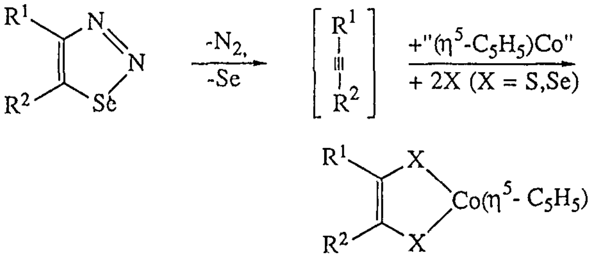
There are two potential explanations for the unexpected formation of dithiolenes from 1,2,3-selenadiazoles. One requires the possibility of chalcogen exchange in diselenolenes and related systems. This has been shown to occur in one case (Equation 7) [4].



(7)

Our own work demonstrates, however, that such a reaction is not general. Treatment of cyclopentadienyl(1,2-cyclooctenediselenolato)cobalt (**5**) with sulfur leads to only minimal chalcogen exchange, even after prolonged reflux in toluene solution.

The second explanation suggests that the carbon–selenium bond of the 1,2,3-selenadiazole does not retain its integrity in reactions of this type. Our results clearly indicate that this interpretation is correct. It now seems likely that the key intermediate is not the selenaketocarbene, but the alkyne, probably formed within the coordination sphere of the transition metal atom (Equation 8).

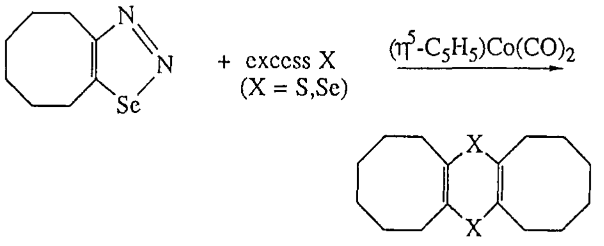


(8)

Alkynes possessing electron-withdrawing substituents are known to react with cyclopentadienylcobalt sources in the presence of sulfur to yield dithiolenes [5]. Our work, however, represents the first synthesis of a cyclopentadienylcobalt dithiolene bearing aliphatic substituents.

Dithiins from Selenadiazoles

As a minor byproduct of the synthesis of **3** we observed the formation of bis(cycloocteno)-1,4-dithiin (**6**). By reducing the amount of **2** used by a factor of 10, such that it effectively becomes a catalyst for the reaction, the yield of **6** can be increased substantially. The presence of **2** cannot be dispensed with altogether: It is necessary for reasonable yields to be obtained. We assume that the mechanism of this reaction involves the same intermediate cobalt alkyne complex as that implicated in the formation of **3**. This hypothesis is supported by the observation that only bis(cycloocteno)-1,4-diselenin (**7**) is produced under analogous conditions by the cobalt-catalyzed reaction of **1** with elemental selenium. There is no evidence in either case for the formation of other sulfur- or selenium-containing products (e.g., thiophenes or selenophenes), such as are formed in the absence of **2**.



6: X = S
7: X = Se (9)

Structures of **6** *and* **7**

The synthesis and spectroscopic characterization of **6** and **7** has previously been reported by Meier et al. [6, 7], but in view of continuing interest in 1,4-dithiins [8] and the apparent absence of structurally characterized 1,4-diselenins, we have now determined their structures by X-ray diffraction.

The structure of **6** is depicted in Figure 1, and selected bond lengths and angles for both compounds are listed in Tables 1, 2, and 3. Compound **6** adopts a boat conformation, in which the structural parameters resemble those found for other structurally characterized 1,4-dithiins. The mean boat angle of 148° and the flap angle of 131° are

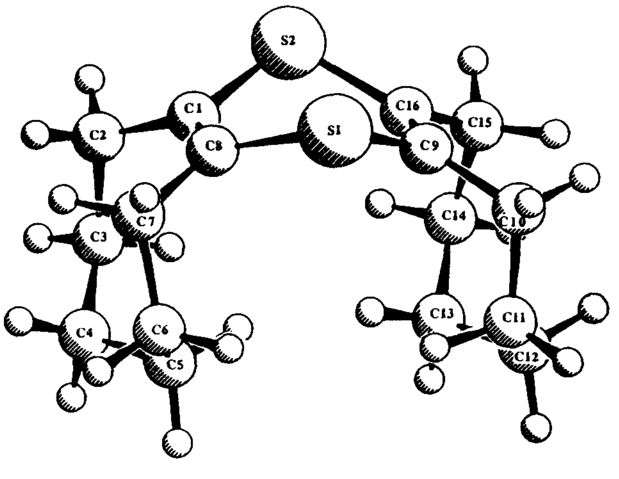


FIGURE 1 Perspective drawing of dithiin **6**

TABLE 1 Bond Lengths (Å) for **6** and **7**

	6		7
S1–C8	1.793(5)	Se1–C8	1.855(7)
S2–C1	1.796(4)	Se2–C1	1.869(7)
C1–C2	1.518(6)	C1–C2	1.513(10)
C2–C3	1.539(6)	C2–C3	1.545(10)
C4–C5	1.529(7)	C4–C5	1.506(12)
C6–C7	1.534(7)	C6–C7	1.541(11)
C9–C10	1.504(6)	C9–C10	1.501(11)
C10–C11	1.534(7)	C10–C11	1.527(11)
C12–C13	1.524(7)	C12–C13	1.499(14)
C14–C15	1.525(8)	C14–C15	1.548(14)
S1–C9	1.784(5)	Se1–C9	1.869(7)
S2–C16	1.795(5)	Se2–C16	1.864(8)
C1–C8	1.321(6)	C1–C8	1.327(11)
C3–C4	1.544(7)	C3–C4	1.551(12)
C5–C6	1.533(7)	C5–C6	1.561(12)
C7–C8	1.512(6)	C7–C8	1.520(11)
C9–C16	1.332(6)	C9–C16	1.347(11)
C11–C12	1.535(7)	C11–C12	1.576(13)
C13–C14	1.554(7)	C13–C14	1.545(14)
C15–C16	1.501(6)	C15–C16	1.484(11)

TABLE 2 Bond Angles (°) for **6** and **7**

	6		7
C9–S1–C8	102.5(2)	C9–Se1–C8	101.4(3)
C2–C1–S2	113.2(3)	C2–C1–Se2	112.8(6)
C8–C1–C2	124.0(4)	C8–C1–C2	124.8(7)
C4–C3–C2	116.1(4)	C4–C3–C2	116.5(7)
C6–C5–C4	116.6(4)	C6–C5–C4	116.4(7)
C8–C7–C6	112.1(4)	C8–C7–C6	112.7(6)
C7–C8–S1	114.4(3)	C7–C8–Se1	114.7(6)
C10–C9–S1	113.9(3)	C10–C9–Se1	113.2(6)
C16–C9–C10	124.0(4)	C16–C9–C10	124.9(7)
C12–C11–C10	115.1(4)	C12–C11–C10	115.1(7)
C14–C13–C12	116.4(5)	C14–C13–C12	116.6(8)
C16–C15–C14	114.0(4)	C16–C15–C14	112.4(7)
C15–C16–S2	114.5(4)	C15–C16–Se2	114.9(6)
C16–S2–C1	102.2(2)	C16–Se2–C1	100.9(3)
C8–C1–S2	122.6(4)	C8–C1–Se2	122.3(6)
C3–C2–C1	113.4(4)	C3–C2–C1	113.7(6)
C5–C4–C3	116.6(4)	C5–C4–C3	117.4(7)
C7–C6–C5	114.1(4)	C7–C6–C5	113.7(7)
C1–C8–S1	121.7(4)	C1–C8–Se1	112.3(6)
C7–C8–C1	123.8(4)	C7–C8–C1	122.8(7)
C16–C9–S1	122.1(4)	C16–C9–Se1	121.9(6)
C11–C10–C9	114.8(4)	C11–C10–C9	113.9(6)
C13–C12–C11	116.1(4)	C13–C12–C11	116.7(7)
C15–C14–C13	114.7(4)	C15–C14–C13	115.3(8)
C9–C16–S2	122.0(4)	C9–C16–Se2	121.8(6)
C15–C16–C9	123.4(4)	C15–C16–C9	123.2(7)

TABLE 3 Torsion Angles

	6	7
C8–C1–C2–C3	−81.6	−82.3
C1–C2–C3–C4	75.1	73.4
C2–C3–C4–C5	−71.0	−70.0
C3–C4–C5–C6	79.8	80.2
C4–C5–C6–C7	−54.1	−54.1
C5–C6–C7–C8	−49.9	−50.5
C6–C7–C8–C1	85.9	86.8
C7–C8–C1–C2	−1.1	−0.8
C16–C9–C10–C11	−82.0	−81.6
C9–C10–C11–C12	77.3	75.9
C10–C11–C12–C13	−73.2	−73.4
C11–C12–C13–C14	80.0	80.5
C12–C13–C14–C15	−53.0	−52.0
C13–C14–C15–C16	−50.7	−51.4
C14–C15–C16–C9	87.8	87.2
C15–C16–C9–C10	−0.4	−1.2

almost identical to those found in 2,5-diphenyl-1.4-dithiin [8].

Compounds **6** and **7** are isostructural (see Tables 1, 2, and 3). Compound **7** thus resembles the selenanthrenes [9], although there are slight differences in the values of the boat and flat angles. For example, in octafluoroselenanthrene [10], these are 140° and 122°, compared with 147° and 129° in **7**. Notable in the crystal structure of **7** is the presence of short intermolecular Se–Se contacts (3.85 Å) between pairs of molecules. This is less than the sum of van der Waal's radii (4.0 Å). There is, however, no extended interaction encompassing more than two of the molecules within the crystal.

CONCLUSION

The reactions of **1** demonstrate that 1,2,3-selenadiazoles may serve as precursors not only to selenium-containing compounds (as is well established), but also to those containing sulfur. Indeed, in this system there seems to be a marked preference for incorporation of sulfur as opposed to retention of selenium, such that expected products containing both elements could not be isolated. This trend culminates in the apparent inability of tellurium to enter into reactions of this type [11].

EXPERIMENTAL

All reactions were performed using standard Schlenk techniques and pre-dried solvents under an atmosphere of dinitrogen. Alumina used for column chromatography was pretreated with 2% H_2O. ^{1}H NMR spectra: Nicolet AM300; tetramethylsilane as internal standard. VIS spectra: Perkin Elmer Lambda 9. IR spectra: Perkin Elmer 983G. Mass spectra: MS902 operating at 70 eV. Melting points (uncorrected): Electrothermal apparatus. Microanalyses: Perkin Elmer PE240.

Cyclopentadienyl(1,2-cyclooctenedithiolato)cobalt (**3**)

A mixture of **1** [6] (1.18 g, 5.5 mmol), **2** [12] (0.99 g, 5.5 mmol) and sulfur (0.08 g, 27.5 mmol) in toluene (50 mL) was heated for 3 h under reflux. During this time the color of the solution changed from red to deep purplish blue. The solvent was removed by distillation under reduced pressure and the residue purified by chromatography (25 × 4 cm column). Using a mixture of petroleum ether (bp 40–60°C) and toluene (2:3), a single purplish-blue band was eluted.

After removal of the solvent the residue was crystallized from pentane at −30°C as darkly-colored needles. Yield: 1.11 g (68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.14 (m, 4H, H-5,6), 1.64 (m, 4H, H-4,7), 2.92 (m, 4H, H-3,8), 5.25 (s, 5H, C_5H_5). VIS(hexane): $\lambda_{\max}$ (Lg ϵ) = 419 nm (2.585), 582 (3.226), 740 (2.090). IR (KBr disc, selected bands): $\bar{\nu} = 3089\ \text{cm}^{-1}$ (m), 2911(s), 2845(s), 1475(s), 1435(m), 1408(s), 1353(m), 1339(m), 1257(m), 1104(m), 1019(m), 998(vs), 833(s), 800(m), 410(s). MS: m/z = 296 (M^+). Mp 140°C. Anal. Calcd. for $C_{13}H_{17}CoS_2$ (296.3): C, 52.69; H, 5.78. Found: C, 52.11; H, 5.36.

Bis(cycloocteno)-1,4-dithiin (**6**)

A low yield synthesis of this compound has previously been published [7]. The preparation of **6** may be efficiently accomplished by a procedure analogous to that used for **3**, except for the difference in the quantity of **2** required. Combining 1.08 g **1** (5.0 mmol), 0.09 g **2** (0.5 mmol), and 0.80 g sulfur (25.0 mmol) yields, after purification, 0.50 g **6** (71%). For the crystal structure analysis **6** was recrystallized from pentane at −30°C.

Bis(cycloocteno)-1,4-diselenin (**7**)

This compound has previously been prepared by the thermolysis of **1** [6] in its pure state. Heating a toluene solution of **1** in the presence of excess elemental selenium and a small quantity of **2** also gives good yields of **7**. X-ray quality crystals were obtained by recrystallization from pentane at −30°C.

Crystal Structure Analyses

Details are given below.

Crystal Data for (**6**). $C_{16}H_{24}S_2$, M = 280.5, triclinic, a = 7.253(5), b = 9.647(7), c = 12.402(8)Å, α = 107.7(1), β = 92.7(1), γ = 111.1(1)°, U = 576.0(8)Å^3, Z = 2, D_x = 1.23 g cm^{-3}, $F(000)$ = 304, space group $P\bar{1}$ (No. 2), Mo-Kα radiation, λ =

0.71073 Å, μ(Mo-Kα) = 2.9 cm^{-1}. Blue plates, dimensions 0.15 × 0.40 × 0.85 mm; Siemens P3/V2000 diffractometer, θ-2θ scans, θ scan range 1.2°, $3 \leq 2\theta \leq 50°$; 3485 unique reflections measured, Lp corrections, direct methods solution (SHELXS86) and least squares refinement (SHELX76); nonhydrogen atoms anisotropic, hydrogen atoms included at calculated positions (C–H = 1.08 Å) with common isotropic temperature factor that refined to U = 0.089(4) Å^2. In the final cycles the 2233 data with $F > 6\sigma(F)$ gave R = 0.066, R_w = 0.073 with weighting scheme $w = 2.3/[\sigma^2(F) + 0.00177\,F^2]$, data/parameter ratio = 13.6. $\Delta\rho$ in final ΔF map ± 0.26 e Å ^{3}.

Crystal Data for (**7**) $C_{16}H_{24}Se_2$, M = 374.3, triclinic, a = 7.282(3), b = 9.647(4), c = 12.498(4)Å, α = 108.0(1), β = 93.2(1), γ = 110.7(1)°, U = 767.7(5)Å^3, Z = 2, D_x = 1.62 g cm^{-3}, $F(000)$ = 376, space group $P\bar{1}$ (No. 2), Mo-Kα radiation, λ = 0.71073 Å, μ(Mo-Kα) = 46.5 cm^{-1}. Blue plates; dimensions 0.17 × 0.43 × 1.0 mm. Siemens P3/V2000 diffractometer θ-2θ scans, θ scan range 1.2°, $3 \leq 2\theta \leq 50°$; 3555 unique reflections measured, Lp and absorption corrections, direct methods solution (SHELXS86), and least squares refinement (SHELX76); nonhydrogen atoms anisotropic, hydrogens included at calculated positions with common isotropic temperature factor that refined to U = 0.058(6) Å^2. In the final cycles the 2073 data with $F > 6\sigma(F)$ gave R = 0.068, R_w = 0.077 with $w = 1.581/[\sigma^2(F) + 0.000250\,F^2]$, data/parameter ratio 12.6. $\Delta\rho$ in final ΔF map ± 0.48 e Å^{-3}.

SUPPLEMENTARY MATERIAL AVAILABLE

Tables of fractional atomic coordinates, anisotropic thermal parameters, and hydrogen atom coordinates are available on request from the Cambridge Crystallographic Data Centre.

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