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# Ligand exchange in cyclopentadienylcobalt diselenolenes. Isolation and characterization of the $Se_3$-chelate, $C_5H_5Co[(SeC_8H_{12})_2Se]$

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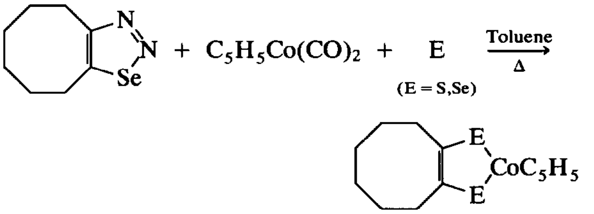
**Abstract**

The reactions of a range of cyclopentadienylcobalt diselenolenes with cycloocteno-1,2,3-selenadiazole involve ligand exchange and formation of cyclopentadienyl(1,2-cyclooctenediselenolato)cobalt. An example of a proposed intermediate in this process, the novel $Se_3$-chelate cyclopentadienyl[bis(2-selenolatocyclooct-1-enyl)-selenide]cobalt, has been prepared and characterised.

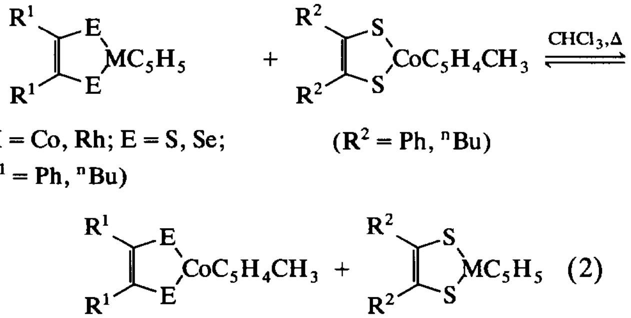
## 1. Introduction

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



(1)

Cyclopentadienylcobalt dichalcogenes are of interest in terms of both their physical and chemical properties [4]. Their ligand exchange reactions have been studied by Vollhardt and Walborsky [5]. Transfer of intact dithiolate/diselenolate ligands was shown to occur in a number of cases (eqn. (2)), and is assumed to take place through the intermediacy of a bridging cobaltadichalcogene dimer, such as that found in one form of cyclopentadienyl(*o*-dithiobenzene)cobalt [6].



(2)

We have now examined an alternative approach to the conversion of one cyclopentadienylcobalt diselenolene into another, *viz.* the reaction of the diselenolene with a 1,2,3-selenadiazole. The results of this work are presented below.

## 2. Results and discussion

Treatment of a range of cyclopentadienylcobalt diselenolenes with an excess of cycloocteno-1,2,3-selenadiazole (**1**) in toluene under reflux in all cases gives cyclopentadienyl(1,2-cyclooctenediselenolato)cobalt (**2**) (eqn. (3)). After 5 h, $^1H$ NMR and mass spectroscopy indicate that ligand exchange is essentially quantitative.

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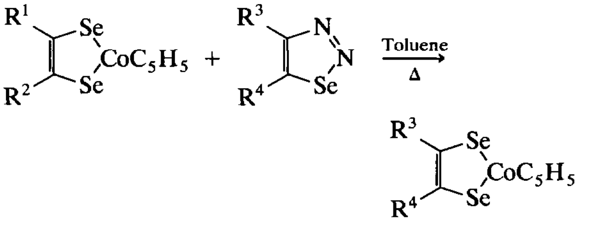
The product may be isolated by column chromatography, as previously described [2]. Compound **2** is itself inert towards ligand exchange under these conditions; no reaction was observed between **2** and 4-phenyl-1,2,3-selenadiazole.

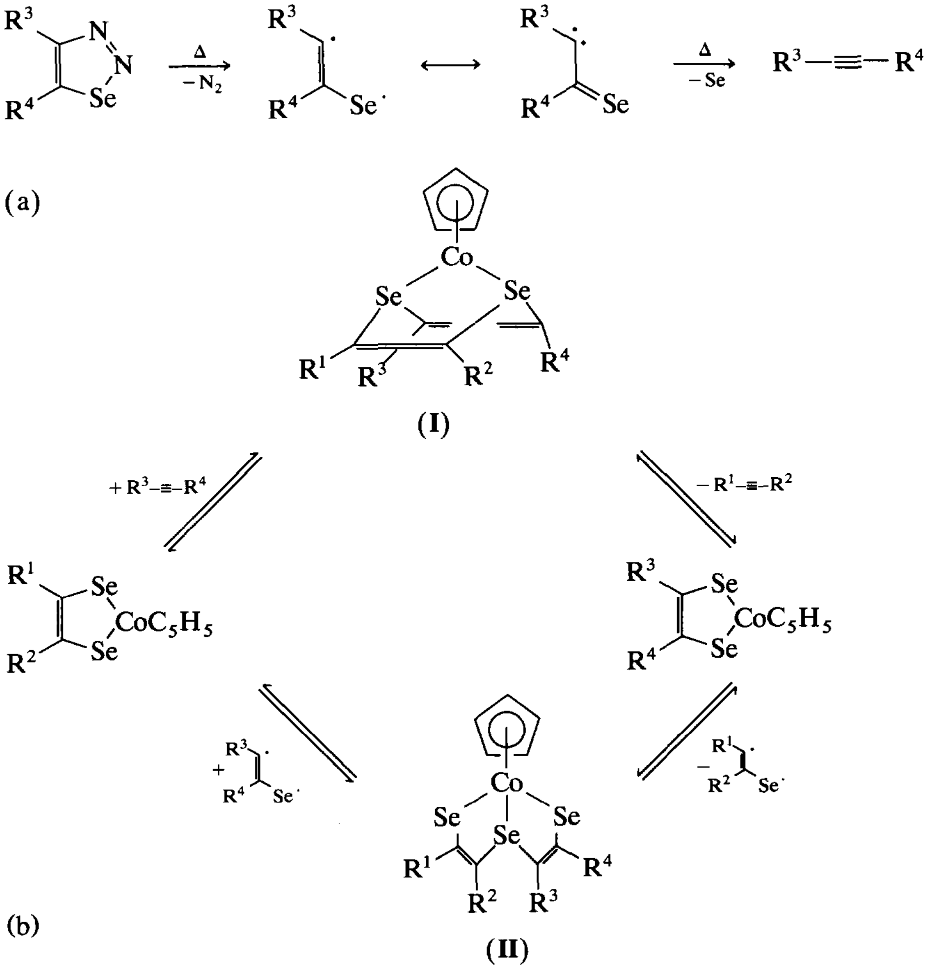


(3)

| $R^1$ | $R^2$ | $R^3$ | $R^4$ | % Yield |
|---|---|---|---|---|
| $-(CH_2)_6-$ | | Ph | H | 0 |
| Ph | H | $-(CH_2)_6-$ | | 100 |
| Ph | Ph | $-(CH_2)_6-$ | | 100 |
| $-CH{=}CH(CH_2)_2CH{=}CH-$ | | $-(CH_2)_6-$ | | 100 |

Two possible mechanisms for the exchange process may readily be envisaged (Scheme 1). Thermal decomposition of the 1,2,3-selenadiazole is assumed to be the first step in each case [7]. If both dinitrogen and selenium are lost, then an alkyne is produced. Under forcing conditions electron-deficient alkynes have been shown to react with dichalcogenes in some instances [8]. In mechanism (a), addition of alkyne to the cyclopentadienylcobalt diselenolene gives an intermediate, **I**, which may break down to yield either starting materials or ligand-exchanged product. A similar intermediate is involved in the reaction of cyclopentadienylcobalt precursors with 1,4-dithiins [9].

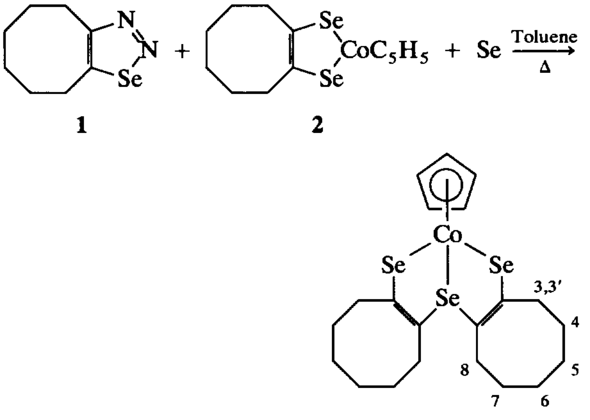
If only dinitrogen is lost from the 1,2,3-selenadiazole then a selenoketocarbene is produced. In mechanism (b) 1,3-dipolar cycloaddition of this species to the cyclopentadienylcobalt diselenolene forms a $Se_3$-chelate, **II**, which as before may break down to yield starting materials or product. Similar additions across the



Scheme 1.

cobalt–selenium partial double bond have been reported [10].

A compound of type **II**, cyclopentadienyl[bis(2-selenolatocyclooct-1-enyl)selenide]cobalt (**3**), was isolated from the reaction of **2** with **1** in the presence of selenium (eqn. (4)). Higher yields of **3** were obtained by the direct reaction of **1** with cyclopentadienyldicarbonylcobalt and selenium, without the intermediate isolation of **2**.



**1** **2** **3**

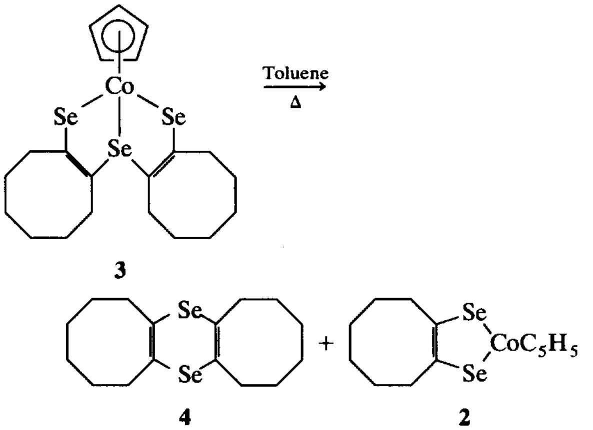
(4)

Compound **3** is a green crystalline solid, soluble in all common organic solvents, and was characterised on the basis of spectroscopic and analytical data. The $^1H$ NMR spectrum has seven groups of resonances. Five of these may be assigned to four pairs of $CH_2$ groups (labelled 4–7 in Equation 4) and the cyclopentadienyl ring. The remaining two signals have an integration ratio of 3 : 1. This pattern arises because the protons on C-3 (or C-8; we have not distinguished these possibilities) are inequivalent and give rise to two resonances, one of which overlaps with that due to the remaining pair of $CH_2$ groups.

Nine separate signals are observed in the $^{13}C$ NMR spectrum, the two at lowest field having $^{77}Se$ satellites. $^1J(^{13}C–^{77}Se)$ is smaller when an electron lone pair on selenium is blocked [11]. The resonance at 126.7 $\delta$ ($J = 82$ Hz) is thus assigned to C-1, that at 151.69 $\delta$ ($J = 126.5$ Hz) to C-2.

Compound **3** might have been thought of as a low-spin $d^6$ complex of the type *fac*-$CoX_3L_3$. However, such complexes usually exhibit only two *d–d* transitions in the visible region [12]. In the UV/VIS spectrum of **3** there are three visible bands, together with a charge transfer absorption in the ultraviolet. The similarity of this spectrum to that of **2** is notable, and suggests the presence of some delocalisation in the $Se_3$-chelate, analogous to that in the diselenolenes.

Compound **3** breaks down on heating under reflux in toluene solution to give **2** and bis(cycloocteno)-1,4-diselenin, **4** (eqn. (5)). This is the fragmentation required of a species of type **II** in order for ligand exchange to occur by mechanism (b); **4** results from the dimerisation of the expelled selenoketocarbene.



**3** **4** **2**

(5)

Our results therefore provide substantial evidence that the ligand exchange observed in reactions of cyclopentadienylcobalt diselenolenes with 1,2,3-selenadiazoles proceeds *via* a $Se_3$-chelate, such as **3**.

## 3. Experimental details

All reactions were performed by use of standard Schlenk techniques and pre-dried solvents under dinitrogen. Alumina used for column chromatography was pretreated with 2% $H_2O$. NMR spectra: $^1H$, Nicolet AM300; $^{13}C$, General Electric QE500; tetramethylsilane as internal standard. UV/VIS spectra: Perkin–Elmer Lambda 9. IR spectra: Perkin–Elmer 983G. Mass spectra: MS902 operating at 70 eV. Melting points (uncorrected): Electrothermal apparatus. Microanalysis: Perkin–Elmer PE240.

### *3.1. Cyclopentadienyl(1,2-cyclooctenediselenolato)cobalt (2)*

#### *3.1.2. via ligand exchange*

A mixture of cyclopentadienyl(1-phenylethene-1,2-diselenolato)cobalt, **5** (0.08 g, 0.21 mmol) [13] and cycloocteno-1,2,3-selenadiazole, **1** (0.43 g, 2.00 mmol) [7] in toluene (20 ml) was heated for 5 h under reflux. The solvent was removed by distillation under reduced pressure, and the residue examined by $^1H$ NMR and mass spectroscopy. The product was identified as **2** by comparison of the spectra with those of an authentic sample [2]. Purification was effected by chromatography (25 × 2 cm column) with a 3 : 1 mixture of petroleum ether (b.p. 40–60°C) and toluene as eluent. A single blue band was eluted, and after removal of the solvent, left a residue that was crystallised from pentane at −30°C. Yield: 0.05 g (61%).

Experiments involving cyclopentadienyl(1,2-diphenylethene-1,2-diselenolato)cobalt (0.09 g, 0.19 mmol) [13] or cyclopentadienyl(cycloocta-1,3,5-triene-3,4-diselenolato)cobalt (0.08 g, 0.21 mmol) [2] in place of **5** yielded similar results.

### *3.1.2. From 3*

A solution of compound **3** (0.20 g, 0.35 mmol) in toluene (20 ml) was heated for 4 h under reflux. The colour changed from green to blue. The solvent was distilled off under reduced pressure and the residue purified by chromatography (25 × 2 cm column). Elution with a 5:1 mixture of petroleum ether (b.p. 40–60°C) and toluene yielded two bands. The first, yellow, band contained bis(cycloocteno)-1,4-diselenin (**4**) [7]. Removal of the solvent from the second, blue, band yielded **2** (0.10 g, 73%).

## *3.2. Cyclopentadienyl[bis(2-selenolatocyclooct-1-enyl)selenide]cobalt (3)*

### *3.2.1. From 2*

A mixture of **1** (0.03 g, 0.14 mmol), **2** (0.05 g, 0.13 mmol) and selenium (0.08 g, 1.00 mmol) in toluene (20 ml) was heated for 5 h under reflux. The solvent was distilled off under reduced pressure and the residue purified by chromatography (25 × 2 cm column). Elution with a 3:1 mixture of petroleum ether (b.p. 40–60°C) and toluene gave a blue band, which yielded a mixture of **2** and **5** as identified by $^1$H NMR spectroscopy. A second, green, band was eluted with diethyl ether. After removal of the solvent the residue was crystallised from pentane at −30°C, and identified as **3** by spectroscopic means (see below). Yield: 0.02 g (26%).

### *3.2.2. From $C_5H_5Co(CO)_2$*

A mixture of **1** (4.00 g, 18.6 mmol), cyclopentadienyldicarbonylcobalt (5.44 g, 30.2 mmol) [14] and selenium (9.80 g, 124 mmol) in toluene (250 ml) was heated for 4 h under reflux. The solvent was removed by distillation under reduced pressure and the residue purified by chromatography (25 × 6 cm column). Elution with toluene gave a single green band, and after removal of the solvent **3** crystallised from pentane at −30°C as dark needles. Yield: 3.50 g (65%).

$^1$H NMR (300 MHz, $CDCl_3$): $\delta = 1.35$ (m, 4H, H-5), 1.43 (m, 4H, H-6), 1.57 (m, 4H, H-7), 1.67 (m, 4H, H-4), 2.36 (m, 6H, H-3.8), 2.45 (m, 2H, H-3′), 5.06 (s, 5H, $C_5H_5$). $^{13}$C NMR (125.5 MHz, $CDCl_3$): $\delta = 26.04$ (C-5), 26.24 (C-6), 29.97 (C-7), 30.28 (C-4), 34.76 (C-8), 34.94 (C-3), 85.08 ($C_5H_5$), 126.76 ($J(^{13}C-^{77}Se) = 82$ Hz, C-1), 151.69 ($J(^{13}C-^{77}Se) = 126.5$ Hz, C-2). UV/VIS (hexane): $\lambda_{max}$ (lg $\epsilon$) = 305 nm (3.760), 427 (2.657), 582 (3.226), 761 (2.223). IR (KBr disc, selected bands): $\bar{\nu} = 3064$ cm$^{-1}$ (m), 2919 (s), 2843 (s), 1642 (w), 1585 (s), 1459 (s), 1442 (s), 1418 (s), 1350 (m), 1305 (m), 876 (m), 739 (w), 699 (w), 555 (w). MS: $m/z = 580$ ($M^+$). M.p. 190°C. Anal. Found: C, 43.85; H, 4.96. $C_{21}H_{29}CoSe_3$ (577.3) Calc.: C, 43.67; H, 5.03%.

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