

Preliminary communication

Cyclooctaselenadiazole: synthesis, decomposition pathway, and reaction with $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{L})_2$ ($\text{L} = \text{C}_2\text{H}_4, \text{PPh}_3$). Crystal and molecular structure of $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}]_2(\mu_2\text{-}\eta^3, \eta^2\text{-C}_8\text{H}_6\text{Se})$

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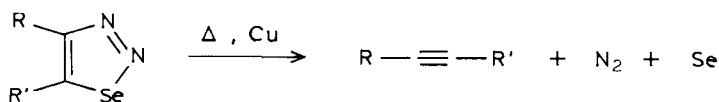
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Abstract

Thermolysis of cyclooctaselenadiazole (**2**) yields only selenium-containing products. Compound **2** reacts with CpCo sources to give $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}]_2(\mu_2\text{-}\eta^3, \eta^2\text{-C}_8\text{H}_6\text{Se})$, a fluxional compound whose structure has been determined by X-Ray crystallography.

Selenadiazoles have shown themselves to be useful intermediates in the synthesis of alkynes.

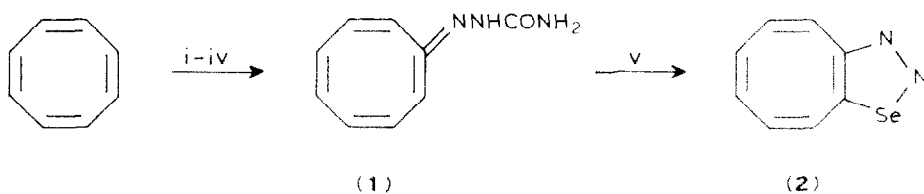


Ring-strained alkynes, inaccessible by other routes, such as cycloocta-1,5-diene-3-yne, have been prepared in this manner [1]. The reactions of selenadiazoles with transition metal complexes are also beginning to be explored [2]. We have now prepared cyclooctaselenadiazole (**2**) by an extension of an established procedure [3] (see Scheme 1).

Overnight reaction of the semicarbazone (**1**) (m.p. 185°C) with selenous acid in warm dioxane leads after chromatographic purification to 17% of **2**. Compound **2** may be crystallized from diethyl ether at -78°C as a light yellow solid (m.p. 30–32°C) ** that rapidly darkens on warming or exposure to light. We hoped that

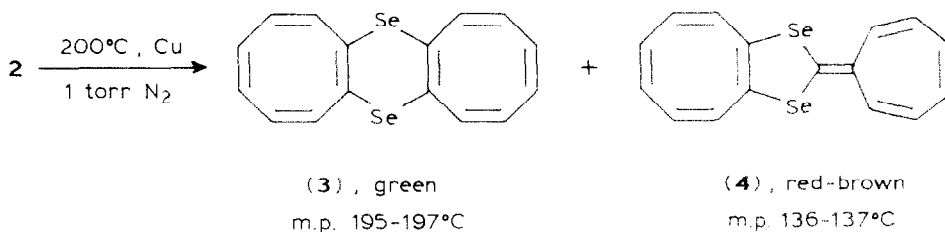
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** Satisfactory spectroscopic and microanalytical data were obtained for the new compounds 1–5.



Scheme 1. Reagents: (i) $\text{BR}_2, \text{CH}_2\text{Cl}_2, -78^\circ\text{C}$; (ii) $\text{NaOMe}, \text{DMSO}, -78^\circ\text{C}$ –room temperature [4]; (iii) $\text{H}_2\text{SO}_4(\text{aq}), \text{THF}, \text{room temperature}$ [5]; (iv) $\text{H}_2\text{NNHCONH}_2, \text{EtOH}, \text{reflux}$; (v) $\text{SeO}_2, \text{Dioxane}, 50^\circ\text{C}$.

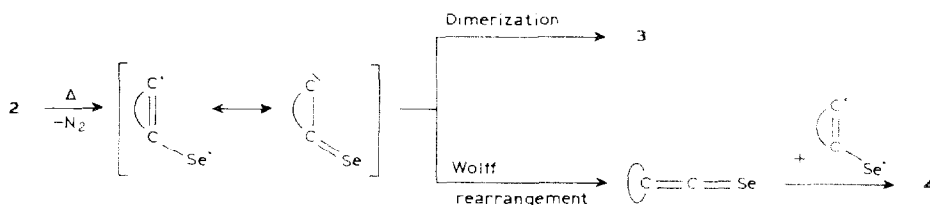
thermolysis of **2** would lead to cycloocta-1,3,5-triene-7-yne, as yet only identified as a transient intermediate [6]. After vacuum pyrolysis of **2** in the presence of copper powder, followed by column chromatography and HPLC, two compounds of identical molecular weight, **3** and **4**, were isolated. These were identified as bicyclooctatetraene-1,4-diselenine (**3**) and 2-cycloheptatrienidene-cycloocta[*d*]-1,3-diselenole (**4**).



Alternative structures for **4**, such as that of the still unknown dicycloocta-1,2-diselenine, have been excluded by detailed analysis of the ^1H NMR spectrum. The observed spectrum can only be reproduced by assuming the existence of two non-interacting three-spin systems, a situation that pertains only in the assigned structure.

Compounds **3** and **4** are formed in combined yield of 88%, in a ratio of approximately 1/1.

The formation of **4** presumably involves a Wolff rearrangement of the initially formed selenaketocarbene [7]:



The same products are formed when the reaction is performed in the presence of tetracyclone, which is known to react rapidly with strained alkynes; this, together with the high yield of the selenium-containing products, suggests that no elimination of selenium from the selenaketocarbene occurs under these conditions.

Similar results were obtained upon photolysis of ether solutions of **2** at low temperature, with or without added tetracyclone.

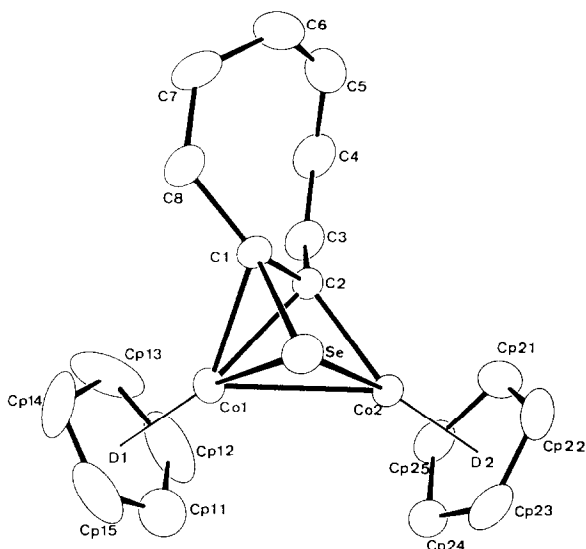
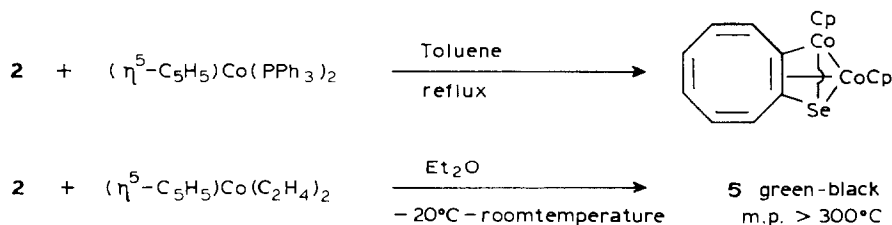


Fig. 1. Molecular structure of $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}]_2(\mu_2\text{-}\eta^3, \eta^2\text{-C}_8\text{H}_6\text{Se})$ (**5**). Some relevant bond distances (Å) and angles ($^\circ$): Se–Co(1) 2.316(1), Se–Co(2) 2.323(1), Se–C(1) 1.954(4), Co(1)–Co(2) 2.439(1), Co(1)–C(1) 1.975(3), Co(1)–C(2) 2.016(3), Co(2)–C(2) 1.908(3), C(1)–C(2) 1.402(5), C(1)–Se–Co(2) 76.4(1), C(1)–Se–Co(1) 54.3(1), Co(2)–Se–Co(1) 63.4(1), Co(2)–Co(1)–Se 58.4(1), Co(1)–Co(2)–Se 58.1(1), C(2)–C(1)–Se 101.6(2), Co(1)–C(1)–Se 72.2(1), C(2)–C(1)–Co(1) 71.0(2), C(1)–C(2)–Co(2) 106.1(2), C(1)–C(2)–Co(1) 67.9(2), Co(2)–C(2)–Co(1) 76.8(1).

Transition metals have been found in some cases to induce the elimination of selenium from selenadiazoles. The reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{PPh}_3)_2$ [8] with **2** in refluxing toluene led after chromatography to the isolation of **5** in 13% yield, together with some intractable material. The same compound was formed by reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{C}_2\text{H}_4)_2$ [9] with **2** in diethyl ether at or below room temperature.

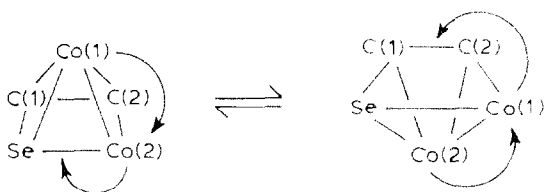
The structure of **5** was determined by standard spectroscopic means and confirmed by a single-crystal X-ray diffraction study*.



* Crystal data: $\text{C}_{18}\text{H}_{16}\text{Co}_2\text{Se}$, $M = 429.2$, monoclinic, space group $P2_1/a$, a 9.193(1), b 13.179(2), c 12.969(1) Å, β 92.67(1) $^\circ$, V 1569.5 Å³, $Z = 4$, D_c 1.82 g cm⁻³, $F(000) = 848$, $\mu(\text{Mo-K}\alpha)$ 43.97 cm⁻¹. The structure was solved by Patterson and Fourier methods and refined by least-squares techniques to $R = 0.035$ for 3000 observed reflections with $I > 2\sigma(I)$. Hydrogen atom positions were calculated and not refined. Atomic parameters for this work are available on request on the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The molecular structure of **5** is shown in Fig. 1. The structure shows some similarities to that of $[\text{Fe}(\text{CO})_3]_2(\mu_2\text{-}\eta^2,\eta^3\text{-C}_8\text{H}_{12}\text{Se})$ [10], and contains the novel $\mu_2\text{-}\eta^3,\eta^2\text{-C}_8\text{H}_6\text{Se}$ ligand. The four atoms C(1), C(2), Co(2) and Se atoms lie approximately in a plane; this unit bonds in cyclobutadiene-like fashion to Co(1). The three further double bonds of the cyclooctatetraene ring are not involved in bonding to the transition metal atoms.

Species **5** is a fluxional. At -30°C in $\text{THF-}d_8$ the cyclopentadienyl groups give rise to two distinct signals in the ^1H NMR spectrum at δ 4.63 and 5.18 ppm. At room temperature these signals coalesce to a single broad resonance at δ 4.85 ppm. This process could possibly involve a rotation of the $\text{C}_8\text{H}_6\text{Se}$ ligand about the Co–Co bond, but is more likely to involve a rocking of the Co_2 unit as depicted below, with C(1) first bonded to Co(1) and then to Co(2):



Cyclooctaselenadiazole (**2**), while failing to provide a route to cycloocta-1,3,5-triene-7-yne, does give rise to a novel ligand system in its reactions with transition metal complexes. Further studies are in progress to develop the chemistry of this and related selenium-containing ligands.

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