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Preliminary communication

The preparation and properties of some cyclopentadienylcobalt 1,2-diselenolene complexes

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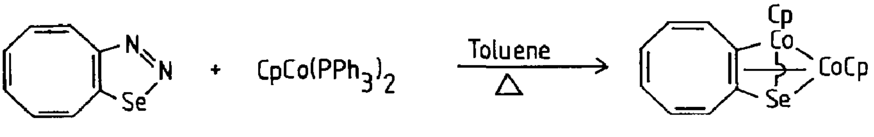
Abstract

The reaction of selected bicyclic 1,2,3-selenadiazoles with $(\eta^5\text{-}C_5H_5)Co(PPh_3)_2$ in the presence of an excess of elemental selenium leads to cyclopentadienylcobalt 1,2-diselenolene complexes. These bright blue compounds are the first to contain diselenolene ligands without electron-withdrawing substituents. They may be reversibly reduced electrochemically.

We are engaged in a study of the reactions of 1,2,3-selenadiazoles with organotransition metal complexes. We have previously reported that treatment of cyclooctaselenadiazole with cyclopentadienylcobalt sources yields the binuclear complex, **1**, whose crystal structure has been determined [1].



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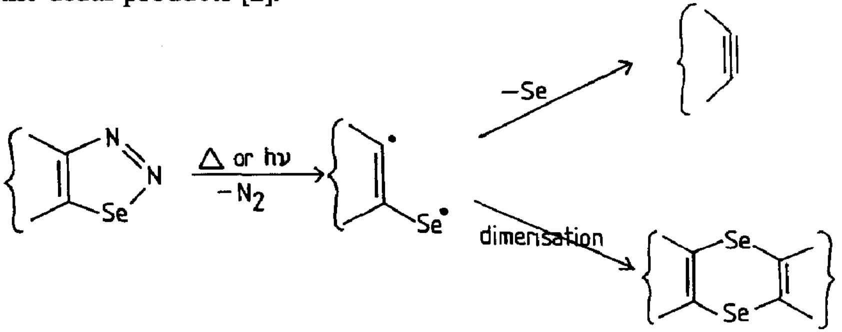
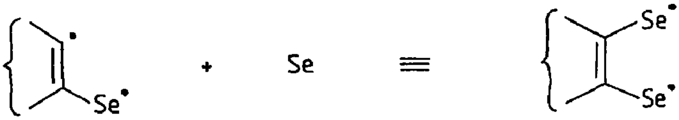
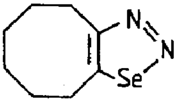
The synthetic utility of selenadiazoles arises from the ease with which dinitrogen is eliminated. The fate of the selenaketocarbene thus produced determines the outcome of the reaction. In the absence of other reagents, alkynes or diselenines are the usual products [2].



We have now examined the use of selenadiazoles as a potential source of diselenolene ligands, on the basis of the following formal relationship.



Treatment in refluxing toluene of one of the bicyclic selenadiazoles **2–4** with (η^5-C_5H_5)Co(PPh_3)$_2$ in the presence of an excess of elemental selenium led to a rapid darkening of the reaction mixture. Column chromatography led to the isolation in moderate yield of a single dark royal blue product. This was purified by low-temperature crystallization from pentane and characterized by standard spectroscopic means.



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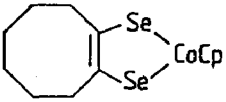

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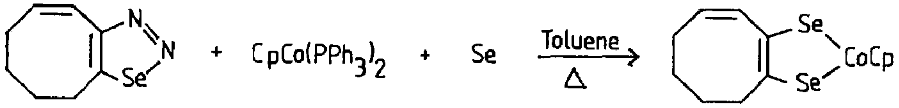

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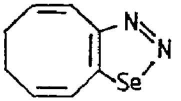

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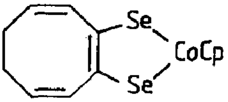

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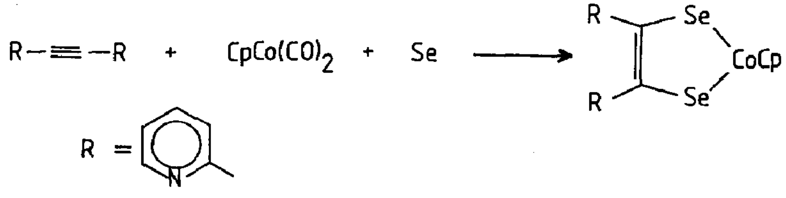
The precise mechanism of the transformation is unknown, but there are obvious similarities between this reaction and that recently reported by Kajitani et al. [3].



The synthesis of **5–7** however represents the first preparation of diselenolenes which do not contain electron withdrawing substituents.

The air-stable compounds **5–7** are at first glance most notable for their intense colour. Ultraviolet-visible spectroscopy has been used to investigate the dependence of the colour on the degree of unsaturation of the alicyclic ring. Relevant data are summarized in Table 1. Although the positions of the bands are similar for each compound, there are significant differences in the intensity pattern of absorption.

Table 1

UV-Vis spectroscopic and voltammetric data

Complex	λ_{max}(nm) [a]	ϵ(dm^3 mol^{-1} cm^{-1}) [a]	$E_{\frac{1}{2}}$ (mV) [b]
5	827	920	−652
	603	1960	
	494	410	
6	830	460	−830
	615	3410	
	495	810	
7	841	370	−815
	631	2560	
	495	610	

[a] Data obtained on 10^{-3} mol dm^{-3} solutions in hexane. [b] Data obtained on 10^{-3} mol dm^{-3} solutions in acetonitrile/methanol (3/1) using Et_4NClO_4 as supporting electrolyte, methanolic SCE as reference cell.

Absorption at ca. 830 nm is greatest for **5**, and it is this compound that is visibly the deepest blue.

We have also studied compounds **5**–**7** by cyclic voltammetry. Each compound undergoes a reversible one-electron reduction. The potential at which this occurs varies depending on the degree of unsaturation of the alicyclic ring. Compound **5** again differs more significantly from the other two than they do from each other: the reasons for this behaviour are still under study. Relevant data are summarized in Table 1, and may be compared with the results obtained by McCleverty on cyclopentadienylcobalt-dithiolene complexes [4].

We are currently investigating the extent to which the synthetic method used in the preparation of compounds **5**–**7** is of general applicability.

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