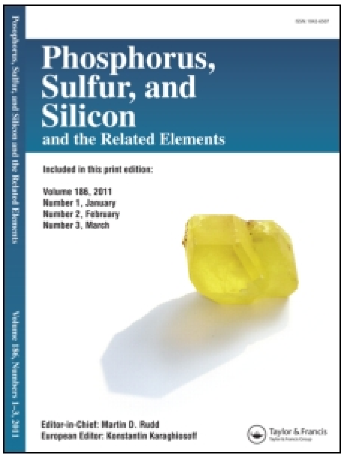

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THE REACTION OF $C_5H_5Co(CO)_2$ WITH $MeO_2CC{\equiv}CCO_2Me$ IN THE PRESENCE OF ELEMENTAL SELENIUM: MOLECULAR STRUCTURE OF 2,3,4,5,- TETRAKIS (METHOXYCARBONYL) SELENOPHENE

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THE REACTION OF $C_5H_5Co(CO)_2$ WITH $MeO_2CC{\equiv}CCO_2Me$ IN THE PRESENCE OF ELEMENTAL SELENIUM: MOLECULAR STRUCTURE OF 2,3,4,5,-TETRAKIS(METHOXYCARBONYL)SELENOPHENE

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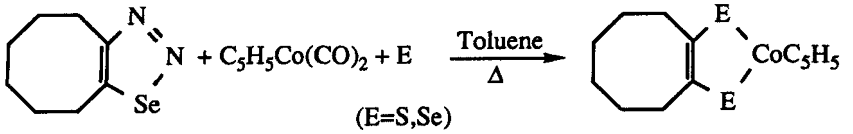
Cyclopentadienyldicarbonylcobalt reacts with dimethylacetylene dicarboxylate in the presence of selenium to yield cyclopentadienyl[1,2-bis(methoxycarbonyl)-1,2-diselenolato]cobalt (**1**), cyclopentadienyl[1-cyclopentadienyl-2,3,4,5-tetrakis(methoxycarbonyl)cobaltacyclopenta-2,4-diene]cobalt (**2**) and tetrakis(methoxycarbonyl)selenophene (**3**). These compounds have been characterized by spectroscopic and analytical techniques, and in the case of **3**, by a single crystal X-ray diffraction study.

Key words: Selenium; selenophenes; cobaltacyclopentadienes; diselenolenes.

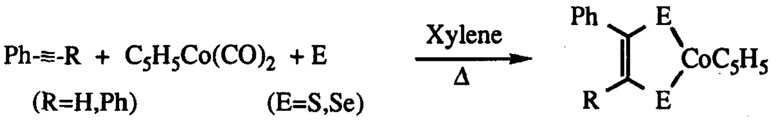
INTRODUCTION

We have previously demonstrated that 1,2,3-selenadiazoles may serve as precursors to cyclopentadienylcobalt diselenolenes[1] and dithiolenes[2] (Equation 1).



(1)

Kajitani *et al.* have demonstrated that phenyl alkynes react similarly[3] (Equation 2).



(2)

We now report the results of a study into the reactivity of the electron-deficient alkyne dimethylacetylene dicarboxylate (DMAD) in this system.

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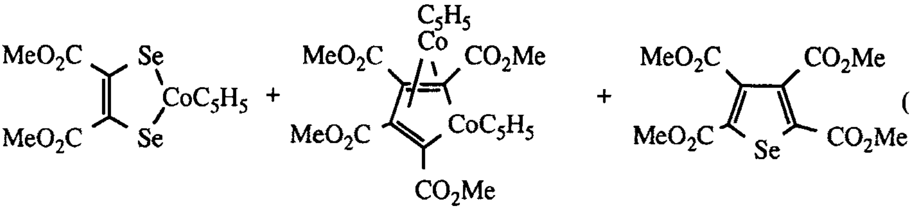
RESULTS AND DISCUSSION

Cyclopentadienyldicarbonylcobalt reacts with DMAD in refluxing toluene solution, in the presence of elemental selenium, to yield three products (**1**, **2** and **3**), which could be separated by column chromatography (Equation 3).

$$MeO_2CC{\equiv}CCO_2Me + C_5H_5Co(CO)_2 + Se \xrightarrow[\Delta]{\text{Toluene}}$$

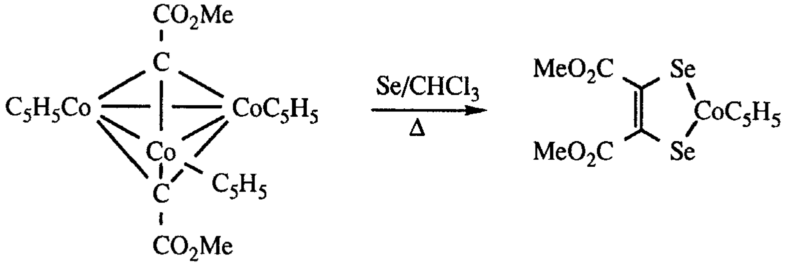


1 **2** **3**

(3)

The diselenolene (**1**) was only isolated in trace quantities, but was identified by its characteristic mass spectrum (m/z = 426, M^+). **1** has previously been prepared by Vollhardt *et al.*[4] via a biscarbyne cluster[5] (Equation 4).

$$MeO_2CC{\equiv}CCO_2Me + C_5H_5Co(CO)_2 \xrightarrow[\Delta]{\text{Decalin}}$$

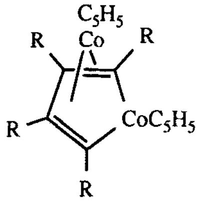


(4)

It seems probable that **1** arises in our reaction mixture by an equivalent *in situ* process. It is however also feasible that the cyclopentadienyldicarbonylcobalt reacts first with the selenium, perhaps to yield a cubane-like cluster $(C_5H_5)_4Co_4Se_4$, and that this intermediate is then cleaved by the alkyne.[3]

The dicobalt compound (**2**) has been characterized on the basis of spectroscopic and analytical data. Compounds of this type containing tricarbonyliron units ("ferroles") have been known for many years,[6] but cyclopentadienylcobalt analogues (Figure 1) are relatively rare.

Rosenblum *et al.*[7] reported the formation of a cobaltacyclopentadiene complex (R=H) in the photolytic reaction of photo-α-pyrone with $C_5H_5Co(CO)_2$; Brintzinger *et al.* prepared a similar compound (R=Me) by the reduction of $C_5H_5Co(CO)I_2$ in the presence of 2-butyne.[8] Both these compounds are found to exhibit fluxional behaviour, with the cyclopentadienylcobalt groups becoming equivalent at high temperature. **2** is however static on the NMR timescale: there is no change in the



2 : R=CO_2Me

FIGURE 1 Generalised structure of cobaltacyclopentadiene complexes.

^1H spectrum between room temperature and 100°C. This may be a result of the presence of four relatively large methoxycarbonyl substituents.

In ferroles there is a significant interaction between the two iron atoms. The mass spectrum of **2** provides evidence for an analogous cobalt-cobalt interaction: in addition to the molecular ion, other dicobalt fragments are also prominent.

We have studied the redox properties of **2** using cyclic voltammetry (see Figure 2). In acetonitrile solution this compound exhibits three reversible electrochemical processes. Two oxidations are practically superimposed on each other ($E = +210$, $+70$ mV with respect to an external $(C_5H_5)_2Fe/(C_5H_5)_2Fe^+$ couple), and there is also a reduction at more negative potentials ($E = -1.7V$). The observation of two separate oxidations at very similar potentials, presumably localized on different cobalt atoms, correlates with the absence of fluxionality in this molecule.

The selenophene derivative **3** has been characterized on the basis of spectroscopic and analytical data, and also by a single crystal X-ray diffraction study (*vide infra*).

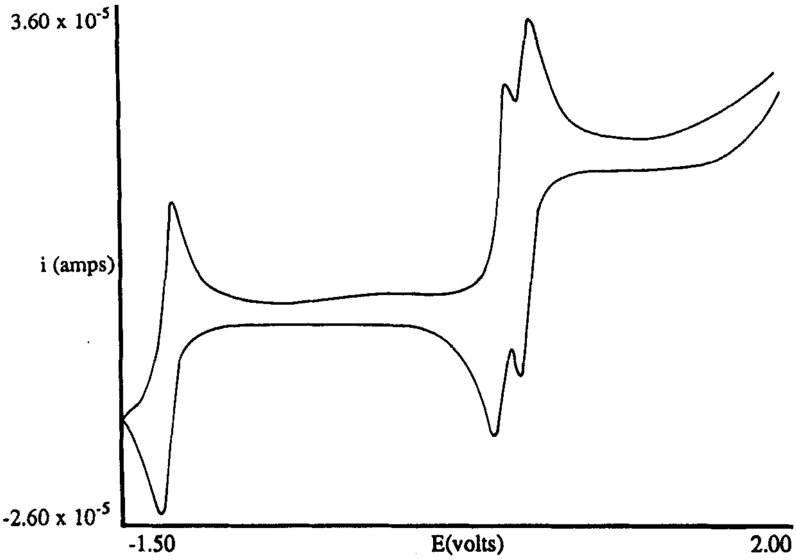


FIGURE 2 Cyclic Voltammogram of **2** (10^{-3}mol dm^{-3} in CH_3CN, Pt working and auxiliary electrodes, Bu_4NClO_4 supporting electrolyte, Ag/AgCl reference electrode).

Producing selenophenes from alkyne precursors was first reported over sixty years ago[9] by Briscoe *et al.*, who passed acetylene over selenium at 400°C to give the parent compound in low yield. This method has recently been developed into an efficient synthesis by Mohmand *et al.* [10]

3 has previously been prepared from DMAD and elemental selenium in refluxing *ortho*-dichlorobenzene (b.p. 179°C).[11] In our own studies we also investigated the possibility of producing the selenophene in the absence of $C_5H_5Co(CO)_2$, but in refluxing toluene (b.p. 111°C) DMAD and selenium do not appear to react.

Formation of the analogous thiophene by the cobalt-catalysed reaction of DMAD with sulphur has been studied by Bönnemann *et al.*[12] It appears that the sulphur

TABLE I

Bond lengths (Å) in **3**

Se1 -C1	1.866(7)	Se1 -C4	1.880(7)
O1 -C5	1.204(8)	O2 -C5	1.342(8)
O2 -C6	1.444(9)	O3 -C7	1.195(8)
O4 -C7	1.326(9)	O4 -C8	1.462(9)
O5 -C9	1.184(8)	O6 -C9	1.319(9)
O6 -C10	1.463(9)	O7 -C11	1.191(9)
O8 -C11	1.354(9)	O8 -C12	1.451(9)
C1 -C2	1.385(9)	C1 -C5	1.451(10)
C2 -C3	1.417(9)	C2 -C7	1.497(9)
C3 -C4	1.374(9)	C3 -C9	1.518(9)
C4 -C11	1.450(10)		

TABLE II

Bond angles (°) in **3**

C4 -Se1 -C1	87.7(3)	C6 -O2 -C5	116.7(7)
C8 -O4 -C7	115.4(6)	C10 -O6 -C9	115.0(6)
C12 -O8 -C11	115.9(7)	C2 -C1 -Se1	111.2(6)
C5 -C1 -Se1	120.5(5)	C5 -C1 -C2	128.4(7)
C3 -C2 -C1	114.6(7)	C7 -C2 -C1	124.2(7)
C7 -C2 -C3	120.5(6)	C4 -C3 -C2	115.9(6)
C9 -C3 -C2	121.3(6)	C9 -C3 -C4	122.4(7)
C3 -C4 -Se1	110.5(5)	C11 -C4 -Se1	121.6(6)
C11 -C4 -C3	127.8(7)	O2 -C5 -O1	123.7(7)
C1 -C5 -O1	125.8(7)	C1 -C5 -O2	110.4(7)
O4 -C7 -O3	125.2(7)	C2 -C7 -O3	122.8(8)
C2 -C7 -O4	111.9(7)	O6 -C9 -O5	126.1(7)
C3 -C9 -O5	122.1(7)	C3 -C9 -O6	111.6(7)
C8 -C11 -O7	124.5(8)	C4 -C11 -O7	123.3(8)
C4 -C11 -O8	109.6(3)		

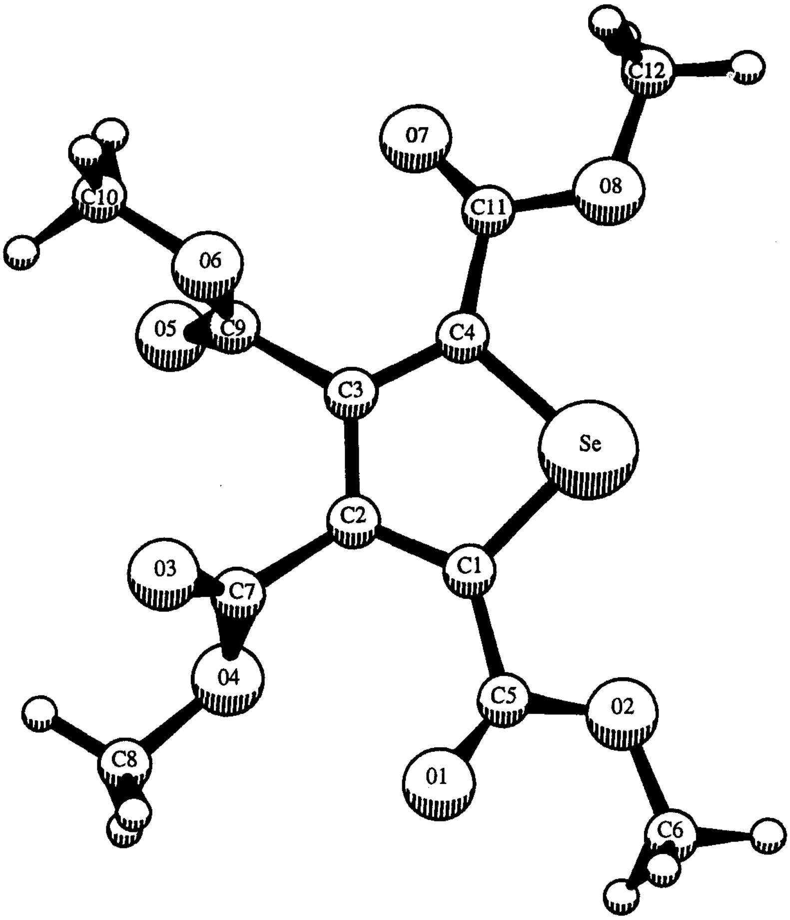


FIGURE 3 Perspective drawing of selenophene 3.

analogue of **1** is an intermediate in this process. However, cobaltacyclopentadiene complexes also react with sulphur or selenium to yield thiophenes or selenophenes,[13] so that in our system it is not clear whether **1** or **2** is involved in the formation of **3**.

The results of the single crystal X-ray diffraction study of **3** are summarized in Tables I and II, and the molecular structure is depicted in Figure 3. The molecular dimensions of selenophene have been determined in the gas phase by microwave spectroscopy[14]; those of dibenzoselenophene have been established by X-ray diffraction.[15]

Table III compares bond lengths and angles in the five-membered heterocyclic ring for these three symmetrically substituted compounds. It can be seen that the data are broadly similar, although the bonds in dibenzoselenophene are consistently longer. Note that although the substitution pattern for **3** is symmetric, there is in fact no plane of symmetry in the solid state structure of the molecule. This arises because of the interlocking arrangements of the four methoxycarbonyl substituents,

TABLE III

Bond lengths and bond angles in symmetrically substituted selenophenes

	C_4H_4Se	$C_{12}H_8Se$	$C_4(CO_2Me)_4Se$ (3)
Se-C1	1.855 Å	1.899 Å	1.873 Å (av.)
C1-C2	1.369 Å	1.398 Å	1.379 Å (av.)
C2-C3	1.433 Å	1.453 Å	1.417 Å
C4-Se-C1	87.75°	86.6°	87.7°
Se-C1-C2	111.56°	112.4°	110.8° (av.)
C1-C2-C3	114.55°	114.3°	115.3° (av.)

i.e., the carbonyl oxygen atoms of the substituents on C3 and C2 are on opposite sides of the plane of the heterocycle. Hence differing Se—C1 and Se—C4 bond lengths, etc. are observed, and the values for these parameters in Table III are averages.

The effect of a carboxyl substituent on the Se—C bond length is demonstrated by the structure of selenophene-2-carboxylic acid.[16] In this molecule the two Se—C distances are as follows: Se—C(H) = 1.850 A; Se—$C(CO_2H)$ = 1.872 A. It can be seen from the data in Table III that this lengthening of the bond between selenium and a carbon bearing a carbonyl function is also evident in the structure of **3**.

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. ^1H NMR spectra: Nicolet AM300; 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. Microanalyses: Perkin-Elmer PE240.

Cyclopentadienyl[(1-cyclopentadienyl-2,3,4,5-tetrakis(methoxycarbonyl)cobaltacyclopenta-2,4-diene)]cobalt (2) and tetrakis(methoxycarbonyl)selenophene (3). A mixture of cyclopentadienyldicarbonylcobalt[17] (1.80g, 10 mmol) dimethylacetylene dicarboxylate (1.38g, 10 mmol) and selenium (2.56g, 30 mmol) in toluene (100 ml) was heated for 3h under reflux. The solvent was removed by distillation under reduced pressure and the residue purified by chromatography (25 × 4 cm column). Using a 1:1:1 mixture of dichloromethane, diethyl ether and petroleum ether (b.p. 40–60°C) three fractions were eluted. These were identified (in their order of elution) as **3**, **1** and **2**.

1: After removal of the solvent from the second fraction (purple), only a trace of blue solid was obtained. MS: m/z = 426(M^+).

2: After removal of the solvent from the third fraction (khaki), the residue was crystallized from pentane at −30°C as dark green-brown needles. Yield: 0.29g (11%). ^1H NMR (300 MHz $CDCl_3$): δ = 3.76 (*s*, 6H, CH_3), 3.84 (*s*, 6H, CH_3), 4.82 (*s*, 5H, C_5H_5), 5.29 (*s*, 5H, C_5H_5). UV/Vis (hexane): λ_{max} (Lgε) = 535 nm (2.529), 400 (3.204), 375 (3.279), 292 (3.905). IR (KBr disc; selected bands) $\tilde{\nu}$ = 3116 cm^{-1} (w), 3088 (w), 2987 (w), 2946 (m), 2848 (w), 1715 (s), 1687 (s), 1435 (s), 1379 (m), 1364 (s), 1204 (vs), 1170 (s), 1078 (m), 996 (m), 825 (m). MS: m/z = 532 (M^+). M.p. 118°C.

$C_{22}H_{22}Co_2O_8$ (532.3) Calcd. C49.64 H4.17
Found C 48.84 H4.20

3: After removal of the solvent from the first fraction (yellow), the residue was crystallized from pentane at −30°C as colourless prisms. Yield: 0.07 g (4%). ^1H NMR (300 MHz, $CDCl_3$): δ = 3.92 (*s*, 12H, CH_3). IR (KBr disc, selected bands): $\tilde{\nu}$ = 3016 cm^{-1} (w), 2960 (w), 2851 (w), 1721 (vs), 1549 (m), 1474 (w), 1430 (m), 1380 (w), 1306 (m), 1256 (vs), 1220 (s), 1098 (m), 998 (m), 975 (m), 847 (m), 764 (m). MS: m/z = 364 (M^+). M.p. 126°C.

$C_{12}H_{12}O_8Se$ (363.2) Calcd. C39.69 H3.33
Found C40.00 H3.40

Crystal structure analysis: orthorhombic, $\underline{a}$ = 8.642 (10), $\underline{b}$ = 18.016 (16), $\underline{c}$ = 18.713 (20) Å, U = 2913.5 (5.1) Å^3, $Z = 8$, D_x = 1.66 gcm^{-3}, $F(000)$ = 1456, space group Pcab (No. 61, alt. Pbca), Mo-Kα radiation, λ = 0.71073 Å, μ(Mo-Kα) = 25.1 cm^{-1}.

Octagonal prisms; dimensions 0.3 × 0.5 × 1.0 mm. 3371 unique diffraction intensities were recorded on a Siemens P3/V2000 diffractometer using $\theta/2\theta$ scans, θ scan range 1.2°, $3 < 2\theta < 55°$. These were corrected for Lorentz, polarisation and absorption effects. The structure was determined by Patterson (SHELXS86) and difference Fourier (SHELX76) methods and refined by least squares. Non-hydrogen atoms were allowed anisotropic vibrations. All hydrogen atoms were located in a ΔF map but were included in the refinement at positions calculated from the geometry of the molecule, with a common isotropic vibration parameter which refined to U = 0.16(1)Å^2. In the final cycles the 1642 data with $F > 4\sigma(F)$ gave R = 0.065, R_w = 0.054 with weighting scheme $\underline{w} = 2.61/[\sigma^2(F) + 0.00043F^2]$. $\Delta\rho$ in the final ΔF map was ±0.19 eÅ^{-3}; data/parameter ratio = 8.6.

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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