

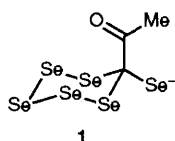
Preparation and X-Ray Structure of $[(\text{Ph}_3\text{P})_2\text{N}][\text{Se}_5\text{C}(\text{Se})\text{COMe}]$: an Anionic Derivative of the Se_5C RingTristram Chivers,*^a Masood Parvez,^a Michael Peach^b and Rainer Vollmerhaus^a^a Department of Chemistry, The University of Calgary, Calgary, Alberta T2N 1N4, Canada^b Department of Chemistry, Acadia University, Wolfville, Nova Scotia BOP 1X0, Canada

The reaction of potassium carbonate with red selenium in acetone, in the presence of $[\text{PPN}]\text{Cl}$ [$\text{PPN} = (\text{Ph}_3\text{P})_2\text{N}$], at 23 °C produces $[\text{PPN}][\text{Se}_5\text{C}(\text{Se})\text{COMe}]$ in which the anion is shown by X-ray crystallography to consist of a six-membered Se_5C ring in a chair conformation with significant endocyclic–exocyclic Se–Se interactions.

There is currently considerable interest in the chemistry of polyselenides, which is significantly different from that of polysulfides.¹ For example, there are no sulfur analogues of the bicyclic Se_{10}^{2-} , the spirocyclic Se_{11}^{2-} nor the Se_{16}^{2-} anions,^{2–4} all of which involve Se_6 rings and three- or four-coordinate selenium. Conversely, there is a report of the preparation of S_{12}^{2-} (of unknown structure)⁵ for which there is no known selenium analogue.

Since the Se_{12}^{2-} ion is a member of the series Se_x^{2-} ($x \geq 10$), we were prompted to investigate the synthesis of this polyselenide by the procedure used for S_{12}^{2-} , *i.e.* the reaction of potassium carbonate with selenium in acetone in the presence of $[\text{PPN}]\text{Cl}$.⁵ Surprisingly, we discovered that this reaction produces the novel $\text{Se}_5\text{C}(\text{Se})\text{COCH}_3^-$ anion **1** as its PPN^+ salt, which has been structurally characterized by X-ray crystallography. This anion represents the first example of the Se_5C ring system.

A mixture of red selenium (9.50 mg atoms), an excess of potassium carbonate (14.5 mmol) and $[\text{PPN}]\text{Cl}$ (2.44 mmol) in dry acetone (50 ml) was stirred at 23 °C under N_2 for 16 h. A green solid was separated by filtration and the volume of the dark-green filtrate was reduced to *ca.* 20 ml. This solution produced red crystals, identified as $[\text{PPN}][\text{Se}_5\text{C}(\text{Se})\text{COMe}]^\ddagger$ by X-ray crystallography (see below), after several days at –20 °C. A second crop was obtained by extraction of the green solid with hot acetone. The total yield was 26% (based on Se). The IR spectrum of $[\text{PPN}]\cdot\mathbf{1}$ (Nujol) exhibited a medium-strong band at 1676 cm^{-1} , which may be attributable to $\nu(\text{CO})$ in addition to the bands for the PPN cation. The ^1H NMR spectrum in CD_2Cl_2 gives a singlet at δ 2.43 (CH_3CO) and a multiplet at δ 7.3–7.7 for the aromatic protons of the PPN cation. The low stability of solutions of $[\text{PPN}]\cdot\mathbf{1}$ precluded the measurement of a ^{77}Se NMR spectrum.



Dark-red, rectangular crystals of $[\text{PPN}]\cdot\mathbf{1}$ were obtained from an acetone solution at –20 °C.‡ The molecular geometry and atomic numbering scheme for **1** are shown in Fig. 1. The anion consists of a six-membered Se_5C ring in a chair conformation with an exocyclic Se atom and a MeCO group attached to the carbon atom. The endocyclic Se–Se distances fall within the narrow range 2.327(2)–2.389(2) Å (*cf.* 2.34 Å for a Se–Se single bond in Se_8).⁶ The most interesting feature of the structure is the close contact between the exocyclic selenium atom, Se(1), and the geminal endocyclic selenium atoms, Se(2) and Se(6), which is reflected in the distances Se(1)–Se(2) = 2.942(2) and Se(1)–Se(6) = 2.955(2) Å [*cf.* Se(2)–Se(6) = 3.240(2) Å] and the bond angles Se(1)–C(37)–Se(2) = 99.5(4) and Se(1)–C(37)–Se(6) = 100.0(4)°. The endocyclic bond angles at selenium are in the range 100.46(6)–105.7(2)° while the Se(2)–C(37)–Se(6) bite angle is 113.9(4)° [*cf.* 95.4(1)° for Se–Ti–Se in $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiSe}_5$].⁷ The bond angle of 139.6(5)° at nitrogen in the PPN cation is not unusual.⁸

The transformation of acetone into the anion **1** by the reaction with selenium in the presence of a base formally involves the replacement of three hydrogen atoms of one methyl group by three Se atoms and thus it resembles the well known haloform reaction.⁹ In this reaction methylketones, *via* enolization, are converted into trihalomethylketones upon treatment with halogens in the presence of base. We propose

‡ Crystal data for $\text{C}_{39}\text{H}_{33}\text{NOP}_2\text{Se}_6$: $M = 1067.40$, triclinic, space group $P\bar{1}$; at 293 K, $a = 11.006(2)$, $b = 11.994(1)$, $c = 16.146(2)$ Å, $\alpha = 105.60(1)$, $\beta = 105.18(1)$, $\gamma = 92.32(1)^\circ$, $V = 1967.1(5)$ Å³, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 5.636$ mm^{-1} , $F(000) = 1032$, $D_c = 1.802$ g cm^{-3} . Intensity data were collected on an Enraf Nonius CAD-4 diffractometer operating in the ω – 2θ mode and using Mo-K α radiation (λ 0.71069 Å, graphite monochromator). Total number of unique reflections 11454, of which 3080 had $I > 3\sigma(I)$. Crystal dimensions 0.20 × 0.20 × 0.30 mm. The structure was solved by direct methods (SAPI) and was refined by full-matrix least-squares calculations with anisotropic thermal parameters for the non-hydrogen atoms to R 0.051 and R_w 0.035. An absorption correction (DIFABS) and allowance for anomalous dispersion were made. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

† Satisfactory C, H and N analyses were obtained.

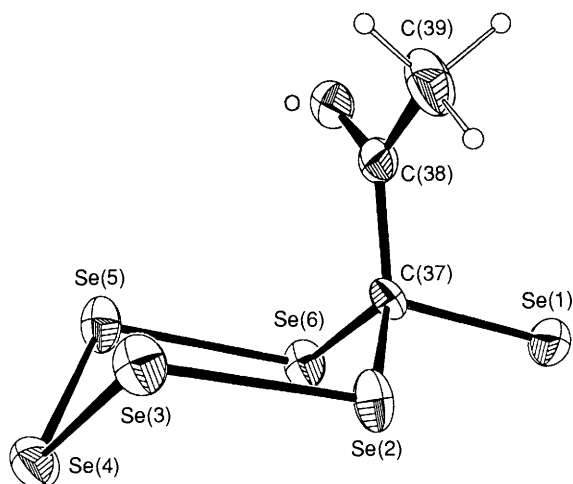
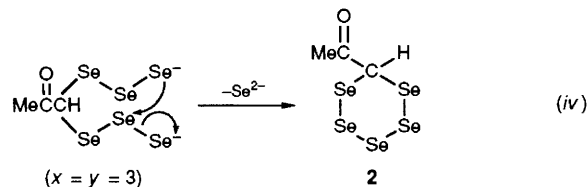
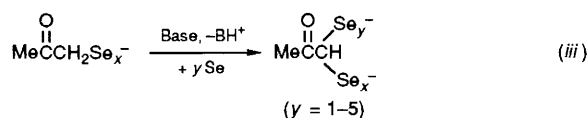
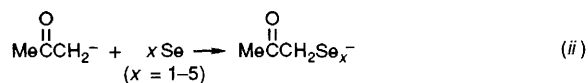
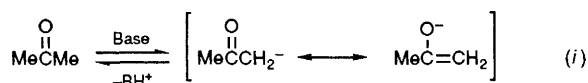


Fig. 1 ORTEP plot (50% probability ellipsoids) of the $\text{Se}_5\text{C}(\text{Se})\text{COMe}^-$ anion, **1**; selected bond lengths (Å) and bond angles ($^\circ$): Se(2)–Se(3) 2.389(2), Se(3)–Se(4) 2.327(2), Se(4)–Se(5) 2.339(2), Se(5)–Se(6) 2.375(2), Se(2)–C(37) 1.933(10), Se(6)–C(37) 1.935(8), Se(1)–C(37) 1.923(8), C(37)–C(38) 1.50(1), C(38)–C(39) 1.49(1), C(38)–O 1.23(1), Se(3)–Se(2)–C(37) 105.7(2), Se(2)–Se(3)–Se(4) 102.26(6); Se(3)–Se(4)–Se(5) 100.46(6), Se(4)–Se(5)–Se(6) 101.48(6), Se(5)–Se(6)–C(37) 105.3(3), Se(6)–C(37)–Se(2) 113.9(4), Se(1)–C(37)–Se(2) 99.5(4), Se(1)–C(37)–Se(6) 100.0(4), Se(1)–C(37)–C(38) 109.9(6), Se(2)–C(37)–C(38) 115.4(7), Se(6)–C(37)–C(38) 115.6(7), C(37)–C(38)–O 120.5(9), C(39)–C(38)–O 118.0(1), C(39)–C(38)–C(37) 121.7(9).

that the formation of **1** is mechanistically analogous to the haloform reaction. As indicated in Scheme 1, a sequence involving (i) enolization, (ii) formation of a polyselenide, (iii) enolization and creation of a second polyselenide chain, and (iv) intramolecular cyclization with elimination of Se^{2-} could account for the construction of the Se_5C ring, **1**. The conversion of **2** into **1** requires a third enolization followed by reaction with selenium. Investigations of the extension of this reaction to different methyl ketones and other chalcogens are in progress.

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Scheme 1 Formation of the $\text{Se}_5\text{C}(\text{Se})\text{COMe}^-$ anion from the reaction of acetone with selenium in the presence of base. The lengths of the polyselenide chains in step (iv) are arbitrarily taken as $x = 3$ and $y = 3$. If $x + y > 6$ the Se_z^{2-} (where $z = x + y - 5$) is eliminated.

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