

Synthesis and Downstream Reactions of 2-(Triphenylphosphino)-4,5-dicarbomethoxy-1,3-diselenole Tetrafluoroborate: X-ray Crystal Structure of a Nitroso Derivative of a 2-Ylidene-1,3-diselenole Stabilized by an Intramolecular O···Se Interaction

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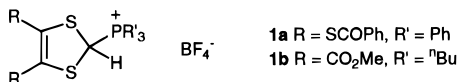
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The title 1,3-diselenole Wittig reagent **9** has been synthesised by a new, efficient route from readily-available starting materials and reacted with a variety of functionalized aldehydes to form the corresponding 2-ylidene-1,3-diselenones **12** in respectable yields. X-ray analysis of a nitrosated derivative **14e**, prepared by the reaction of **12e** with isoamyl nitrite, has provided the first direct evidence for the stabilization of such systems by intramolecular oxygen–selenium interactions.

The chemistry of the 1,3-dithiole ring system has been extensively studied primarily due to the many important properties which make it an attractive building block for the synthesis of new materials.¹ Some of these features are as follows: (i) the ring system is readily accessible from simple starting materials, and a large number of functionalities (including fused rings) can be incorporated into the 4- and 5-positions; (ii) the system is readily oxidized to the stable 6π 1,3-dithiolium cation; (iii) the presence of sulfur atoms and the planarity of the 1,3-dithiolium cation aids the formation of close intermolecular interactions in the solid state due to increased π – π overlaps. These factors have resulted in the 1,3-dithiole-2-ylidene unit acting as a key building block in areas as widespread as conducting polymers,² new π -electron donors,³ Langmuir–Blodgett films,⁴ and possible ferromagnetic⁵ and nonlinear optical materials.⁶ A principal source of many substituted 1,3-dithiole units are the substituted Wittig reagents typified by **1**.



Reagent **1a** has previously been employed in the synthesis of unsymmetrical tetrathiafulvalenes (TTF) and 1,3-dithiole-2-ylidene systems,⁷ while compound **1b** is widely documented as a basic component in many TTF

syntheses.⁸ We recently investigated the application of 1,3-dithiole Wittig reagents including **1b** in the synthesis of highly functionalized 1,3-dithiole-2-ylidene systems **2**⁹ which were subsequently transformed into nitroso-alkene species **3** (Scheme 1) following the precedent of Cava *et al.*¹⁰ The effect of five-membered S···O interactions in stabilizing nitrosoalkenes **3** was proved by X-ray analysis of three derivatives.^{9,11} With a view to extending our knowledge of such interactions, we sought to prepare 1,3-diselenole-2-ylidene systems *via* reactions of a 1,3-diselenole Wittig reagent. The synthetic sequence to reagent **4** from carbon diselenide, tributylphosphine, and dimethyl acetylenedicarboxylate has previously been reported (Scheme 2).¹² However, due to the extreme

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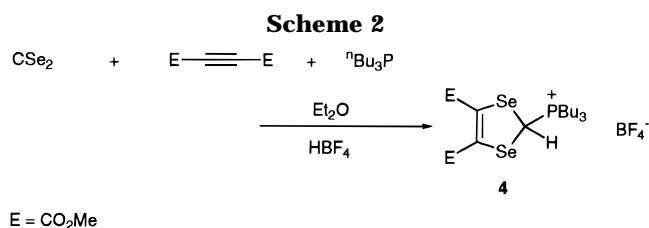
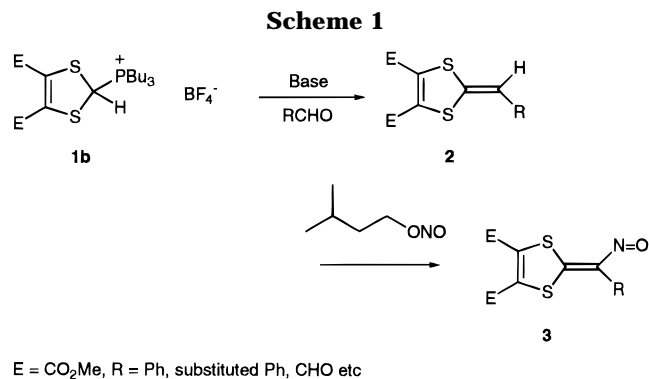
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toxicity of carbon diselenide, its lack of commercial availability, and difficulty of preparation,^{13a,b} a new route to this versatile synthetic reagent was sought which involved a more readily accessible source of selenium.

The chosen route, which we have successfully executed, is outlined in Scheme 3. The known compound ethylene-triselenocarbonate, **5**,^{13c} was prepared as reported in the literature¹⁴ in high yield from commercially available hydrogen selenide (which can be safely handled from a cylinder) in five steps using 1,2-dibromoethane as the alkylating reagent and converted to the diester **6**¹⁵ in excellent yield (89%). Methylation of selone **6** proceeded smoothly with a slight excess of methyl trifluoromethanesulfonate in dry dichloromethane, to afford the diselenonium cation salt **7** (93%) which is stable for several days at 0 °C. Reduction of **7** with sodium cyanoborohydride in anhydrous propan-2-ol afforded the seleno ether **8** (91%) with no reduction of the ester functionalities. Seleno ether **8** was obtained as an orange oil which decomposed on standing and was, therefore, immediately dissolved in acetonitrile and treated sequentially with

Table 1. Products Obtained from the Reaction of Wittig Reagent **9 with a Variety of Aldehydes **11****

11 , R =	% yield of 12 ^a	% yield of 13 ^a
a 2-CF ₃ -C ₆ H ₄	31	24
b 2-pyridyl	21	42 ^b
c 2,4-di-NO ₂ -C ₆ H ₄	30	20
d C(O)Me	34	16
e CHO	36	32 ^b

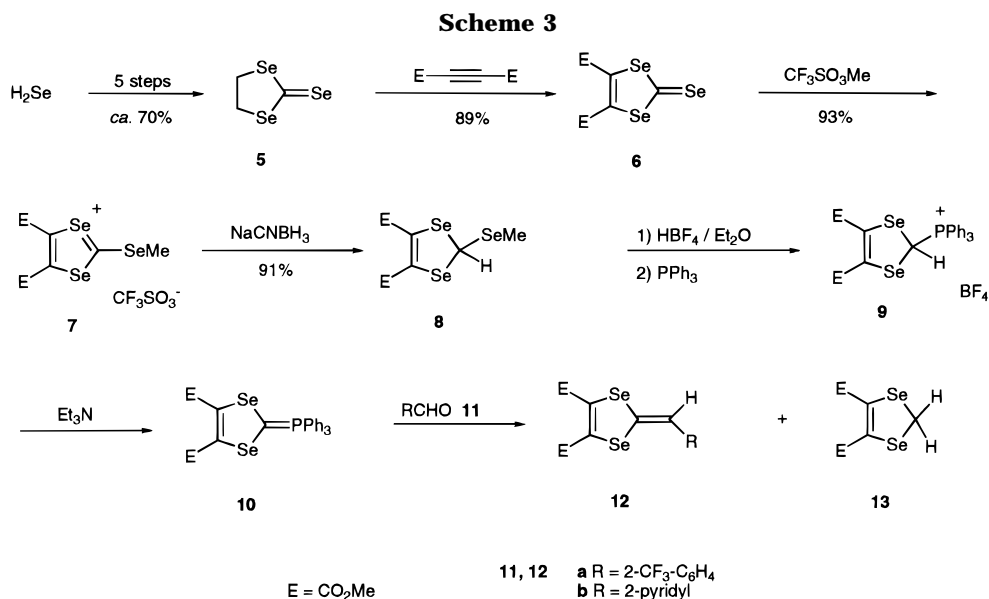
^a Yields quoted are of isolated products after purification by column chromatography. ^b Yields are based on ¹H NMR analysis of the crude reaction mixture.

tetrafluoroboric acid and triphenylphosphine; the Wittig reagent **9** thereby formed was used without isolation (attempts were made to isolate **9** without success).

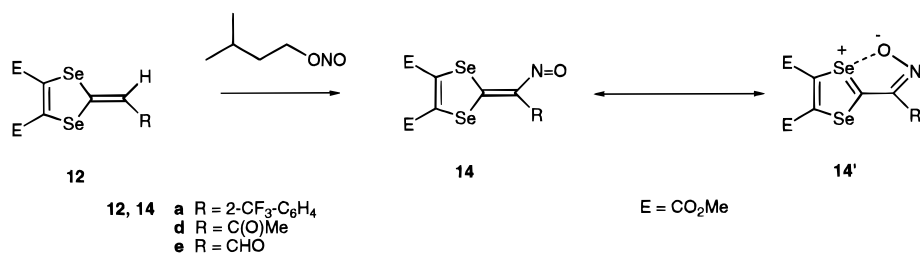
The transient phosphorus ylide **10** was conveniently prepared from **9** by treatment of the reaction mixture with an excess of triethylamine at room temperature. Trapping the ylide **10** with a variety of aldehydes **11** led to the desired 2-ylidene-1,3-diselenones **12** in moderate yields, along with a significant amount of the dihydro compound **13** which in some cases was isolated cleanly. The yields of the respective products from each aldehyde are recorded in Table 1.

The substitution of tributylphosphine for triphenylphosphine in the reactions to form **12a** and **12d**, however, led to neither of these products, and an increased yield of **13** was obtained (greater than 50% in one case). The purity of the tetrafluoroboric acid also appears to effect the amount of **13** produced, since older samples of the acid produced more of this unwanted product. The use of trifluoromethanesulfonic acid did not lead to any improvement in the yields of alkenes **12**.

The appearance of 1,3-diselenole derivative **13** alongside **12** is surprising, since no trace of **13** was observed in the ¹H NMR spectra of seleno ether **8**. Analogous 2-hydro-1,3-dithiole derivatives have been prepared by hydride reduction of the corresponding 1,3-dithiole cations similar to those obtained from **8** on treatment with tetrafluoroboric acid.¹⁶ A possible source of hydride for the formation of **13** was thought to be that employed to transform diselenonium cation salt **7** to seleno ether **8**; however, the use of only a slight excess of sodium cyanoborohydride and the high yields of the reduction



Scheme 4



step to form **8**, coupled with an exhaustive aqueous workup, make this scenario improbable. A definitive explanation for the production of **13** has not yet been found. However, investigations into possible reaction pathways with a view to optimizing the yields of the desired adducts **12** are in progress. In preliminary experiments the analogous reaction sequence to that in Scheme 3 using a 1,3-dithiole system yielded a large amount of a dihydro derivative, and the use of hydroquinone as a radical trap during the conversion of **8** to **9** did not reduce the amount of **13** present. To test the possibility (suggested by a referee) that fluoride ion was inducing the deselenomethylation of **8**, a solution of compound **8** in acetonitrile was stirred for 3 days in the presence of caesium fluoride, followed by addition of hydrochloric acid. However, no evidence for the formation of compound **13** was obtained (TLC analysis); gradual decomposition of compound **8** into unidentified products took place.

With a range of 1,3-diselenole-2-ylidene systems **12a–e** in hand, the formation of nitroso-alkene species derived from **12a,d,e** was investigated (Scheme 4). Nitroso alkenes are normally unstable;¹⁷ however, compounds **14** could be isolated in moderate yields by reaction of the alkenes **12** with isoamyl nitrite in dichloromethane at room temperature and were assumed to be stable due to an interaction between the selenium atoms and the nitroso-oxygen as depicted by the resonance stabilised structure **14'**. Such an intramolecular interaction, where π -delocalization and additional heteroaromatic stability can result, has previously been reported for related sulfur systems.^{9,18} The involvement of a selenium atom in such a stabilization is, however, less well documented. A solitary example of a nitroso group attached to a 2-ylidene-1,3-diselenone **15** has been reported,^{10b,c} and resonance form **15'** was proposed on the basis of NMR spectra; no crystallographic data were presented. Nitroso-alkene **14e** was obtained as bright green crystals which were characterized by an X-ray single crystal diffraction study.

The molecule of **14e** (Figure 1) comprises a planar diselenole ring with three planar substituents at C(1), C(2), and C(3), inclined to the ring plane by 3.5°, 2°, and 83°, respectively. Such conformation and *cisoid* configu-

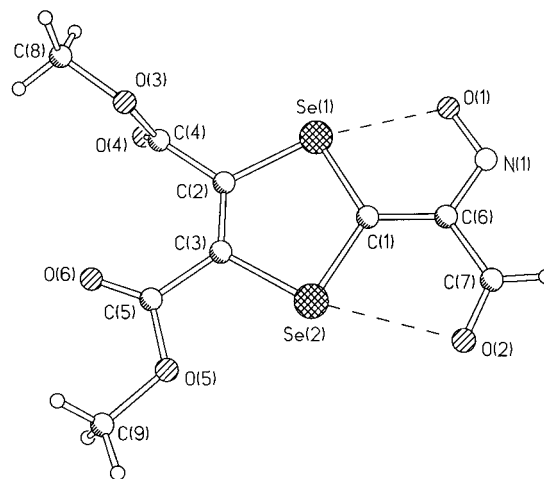


Figure 1. Molecular structure of **14e**. Bond distances (Å): Se(1)–C(1) 1.857(10), Se(2)–C(1) 1.852(10), Se(1)–C(2) 1.886(10), Se(2)–C(3) 1.887(10), C(2)–C(3) 1.33(2), C(1)–C(6) 1.39(1), C(6)–N(1) 1.37(1), N(1)–O(1) 1.244(13), C(6)–C(7) 1.44(2), C(7)–O(2) 1.21(2); bond angles (deg): C(2)Se(1)O(1) 165.7(4), C(6)N(1)O(1) 116(1), N(1)O(1)Se(1) 107.2(6).

rations of the nitroso and carbonyl groups result in short intramolecular contacts Se(1)···O(1) 2.513(8) and Se(2)···O(2) 2.733(8) Å, well below the sum of their Van der Waals radii (3.4 Å).¹⁹ These distances exceed similar S···O distances in **3** (2.35–2.43 Å for the nitroso group and 2.61 Å for the carbonyl one) in proportion to the difference in the chalcogen atom size, both the covalent and the Van der Waals radii of Se exceeding those of S by 0.15 Å.¹⁹ Thus the structure of **14e** implies substantial interactions between the nitroso oxygen and the selenium atom. Such interactions, similar to the hypervalent²⁰ or donor-acceptor S···O interactions, are much less studied for selenium than for sulfur. A few known examples include four supposedly hypervalent Se–O bonds with carbonyl,²¹ carboxyl,²² and nitro²³ groups, ranging from 2.30 to 2.38 Å, and two much shorter interactions in compounds **16** (2.04 Å)²⁴ and **17a** (2.08 Å)²⁵ which are closer to a single covalent Se–O bond

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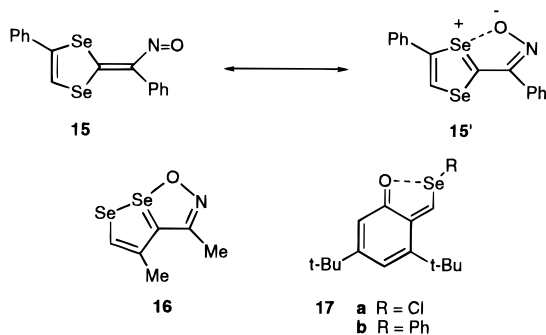
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length of 1.91 Å. In all these cases the hypervalent bonding is strongly aided by the formation of a five-membered pseudoaromatic ring and by the presence of a heteroatom (especially electronegative) linked to the Se atom in a *trans*-position to the oxygen. Selenium–oxygen interactions in a *trans*-position to a Se–C bond are much weaker (as is also the case for sulfur), the Se...O distance in **17b** being 2.48 Å.²⁶ For this molecule, *ab initio* calculations²⁶ indicated clearly the donation of an oxygen lone pair onto the Se atom, whose lone pairs are arranged perpendicular to the O...Se–C axis, in a trigonal–bipyramidal fashion. A similar picture can be expected in **14e**, where the Se...O distance is essentially the same, though no electronegative atom is bonded to Se. The interactions with chalcogens should affect the electron structure of a nitroso group by shifting it toward the oxime form (as in **15'**). In fact, the geometry of the CNO moieties in **14e**, **3**, and **16** is in reasonably good agreement with the structural correlation curve of nitroso–isonitroso–oxime transition²⁷ and corresponds to contributions of the C–N=O and C=N–O forms in *ca.* 0.6:0.4 (**14e**), 0.5:0.5 (**3**, *i.e.* close to the isonitroso structure) and 0.6:0.4 (**16**) ratios.

Although molecules of **14e** in the crystal are packed in parallel layers, the out-of-plane conformation of one methoxycarbonyl group prevents efficient overlap of the molecules. Each selenium atom participates in two short intermolecular contacts of Se(1)...Se(2) type, nearly perpendicular to the ring plane, of 3.72 and 3.77 Å, which is slightly less than twice the Van der Waals radius (4 Å).¹⁹



In conclusion, we have outlined an expedient route to the 1,3-diselenole Wittig reagent **9** avoiding the use of the noxious and fetid reagent CSe₂. Wittig reactions of **9** with a variety of aldehydes form the corresponding 2-ylidene-1,3-diselenoles **12**, three of which have been converted to the corresponding nitroso derivatives **14**. An X-ray crystallographic analysis of derivative **14e** has demonstrated that the stability of these compounds is due, at least in part, to an interaction between the nitroso oxygen and a selenium atom. An interaction of this type has rarely been confirmed by structural analysis. The availability of reagent **9** now paves the way for the synthesis of new 2-ylidene-1,3-diselenole derivatives, including tetraselenafulvalene systems.^{8b,28}

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Experimental Section

General Details. Solvents and reagents employed were standard reagent grade and were used as received unless otherwise stated. Anhydrous propan-2-ol was purchased from Aldrich; all other anhydrous solvents were obtained by standard techniques. Yields for compound **12a–e** are based on the initial amount of **6** employed when intermediates **8** and **9** were not isolated.

1,2-Dicarbomethoxyvinylene Triselenocarbonate (6). To a solution of 1,2-ethanedyltriselenocarbonate (**5**)¹⁴ (1.81 g, 6.5 mmol) in dry toluene (125 mL) was added dimethyl acetylenedicarboxylate (0.96 g, 6.8 mmol). The resulting solution was refluxed under argon for 1 h and the solvent removed *in vacuo* to afford **6** (2.26 g, 89%) as red needles (from methanol): mp 126–127 °C (lit.¹⁵ 127–129 °C).

2-(Triphenylphosphino)-4,5-dicarbomethoxy-1,3-diselenole Tetrafluoroborate (9). To a stirred solution of 1,2-dicarbomethoxyvinylene triselenocarbonate (**6**) (250 mg, 0.63 mmol) in dry dichloromethane (5 mL) was added methyl trifluoromethanesulfonate (110 mg, 0.66 mmol). The resultant mixture was stirred under an argon atmosphere for 2 h. Addition of a large excess of anhydrous ether led to the precipitation of a solid, which was filtered, washed with ether, and dried to give the salmon pink salt **7** (320 mg, 93%): mp 109–112 °C dec; δ_{H} (CDCl₃: 200 MHz) 4.05 (6H, s), 3.05 (3H, s). The salt was dissolved in anhydrous propan-2-ol (5 mL), and sodium cyanoborohydride (40 mg, 0.63 mmol) was added in one portion. Within 10 min the solution turned orange whereupon it was diluted with ether (100 mL) and washed with water (6 × 50 mL) and brine (50 mL). Drying (MgSO₄) and removal of the solvent *in vacuo* afforded the seleno ether **8** (235 mg, 91%) as an unstable orange oil [δ_{H} (CDCl₃: 200 MHz) 6.24 (1H, s), 3.78 (6H, s), 2.31 (3H, s)]. The essentially pure seleno ether was immediately dissolved in dry acetonitrile (15 mL) and cooled to 0 °C under argon, and tetrafluoroboric acid (0.5 mL of a 54% ethereal solution, 5 equiv) was added slowly with stirring. The mixture rapidly turned deep red and was maintained at 0 °C for 1 h, and then triphenylphosphine (180 mg, 0.68 mmol, 1.2 equiv) was added and the solution stirred at 20 °C overnight. The resultant solution containing Wittig reagent **9** was used in the subsequent reactions, without purification.

1-(4,5-Dicarbomethoxy-1,3-diselenol-2-ylidene)-1-[2-(trifluoromethyl)phenyl]methane (12a). To a solution of **9** in acetonitrile was added 2-(trifluoromethyl)benzaldehyde (120 mg, 0.69 mmol) and triethylamine (1 mL, excess). The mixture was stirred at room temperature for 3 h whereupon removal of the solvent *in vacuo* gave a dark brown oil. The residue was purified by column chromatography on silica gel using dichloromethane/hexane as eluant (1:1 v/v) to afford compound **12a** (92 mg, 31%) as orange crystals: mp 125.5–126.5 °C; δ_{H} (CDCl₃: 200 MHz) 7.70 (1H, m), 7.58 (1H, m), 7.40 (2H, m), 7.10 (1H, q, $J_{\text{HF}} = 3.8$ Hz), 3.83 (3H, s), 3.79 (3H, s). Anal. Calcd for C₁₅H₁₁F₃O₄Se₂: C, 38.32; H, 2.36. Found: C, 38.43; H, 2.33. ν_{max} (KBr)/cm⁻¹ 1727, 1584, 1433, 1310, 1244, 1168, 1120; m/z (⁸⁰Se, CI) (rel int) 473 (M⁺ + 1) (100).

1-(4,5-Dicarbomethoxy-1,3-diselenol-2-ylidene)-1-(2-pyridyl)methane (12b). To a solution of **9** in acetonitrile was added pyridine-2-carboxaldehyde (73 mg, 0.69 mmol) and triethylamine (1 mL, excess). The mixture was stirred at room temperature for 2 h and the product isolated as described for **12a** using dichloromethane/hexane as eluant (3:1 v/v) to afford **12b** (50 mg, 21%) a pale yellow solid: mp 127–129 °C; δ_{H} (CDCl₃: 200 MHz) 8.67 (1H, m), 7.65 (1H, td, $J = 4.5, 1.6$ Hz), 7.18 (1H, s), 7.05 (2H, m), 3.89 (3H, s), 3.84 (3H, s). Anal. Calcd for C₁₃H₁₁NO₄Se₂: C, 38.73; H, 2.75; N, 3.47. Found: C, 38.45; H, 2.66; N, 3.23; m/z (⁸⁰Se, CI) 406 (M⁺ + 1) (100).

1-(4,5-Dicarbomethoxy-1,3-diselenol-2-ylidene)-1-(2,4-dinitrophenyl)methane (12c). To a solution of **9** in aceto-

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nitrile, was added 2,4-dinitrobenzaldehyde (124 mg, 0.69 mmol) and triethylamine (1 mL, excess). The mixture was stirred at room temperature for 30 min and the product isolated as described for **12a** with dichloromethane/hexane as eluant (1:1 v/v) to give **12c** (93 mg, 30%) as orange crystals: mp 142 °C; δ_{H} (CDCl₃: 200 MHz) 8.82 (1H, d, $J = 3.0$ Hz), 8.45 (1H, dd, $J = 10, 3.0$ Hz), 7.7 (1H, d, $J = 10$ Hz), 7.2 (1H, s), 3.85 (3H, s), 3.81 (3H, s). Anal. Calcd for C₁₄H₁₀N₂O₈Se₂: C, 34.17; H, 2.05; N, 5.69. Found: C, 34.36; H, 2.03; N, 5.66. ν_{max} (KBr)/cm⁻¹ 1740, 1718, 1624, 1533, 1434, 1245. m/z (⁸⁰Se, CI) (rel int) 494 (M⁺+1) (15), 303 (60), 163 (100), 149 (80).

1-(4,5-Dicarbomethoxy-1,3-diselenol-2-ylidene)propan-2-one (12d). To a solution of **9** in acetonitrile, was added methylglyoxal (1 mL of an aqueous solution, excess) and triethylamine (1 mL, excess). The mixture was stirred at room temperature for 1 h, diluted with water (50 mL), and extracted with dichloromethane (2 × 50 mL), the organic portions were combined and dried (MgSO₄), and the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel with dichloromethane/hexane as eluant (1:1 v/v), followed by dichloromethane, to afford **12d** (80 mg, 34%) as a yellow solid: mp 117–119 °C; δ_{H} [(CD₃)₂CO: 200 MHz] 7.46 (1H, s), 3.73 (3H, s), 3.72 (3H, s), 2.10 (3H, s). Anal. Calcd for C₁₀H₁₀O₅Se₂: C, 32.63; H, 2.74. Found: C, 32.64; H, 3.01. ν_{max} (KBr)/cm⁻¹ 1734, 1701, 1625, 1577, 1475, 1431, 1231. m/z (⁸⁰Se, CI) (rel int) 371 (M⁺+1) (100).

1-(4,5-Dicarbomethoxy-1,3-diselenol-2-ylidene)ethanal 12e. To a solution of **9** in acetonitrile was added glyoxal (1 mL of a 40% aqueous solution, excess) and triethylamine (1 mL, excess). The solution was then stirred at room temperature for 1 h. Purification as described for **12d** afforded **12e** (67 mg, 36%) as a pale yellow solid: mp 108–110 °C (lit.¹² 108–109 °C).

4,5-Dicarbomethoxy-1,3-diselenole (13). This compound was isolated as a malodorous orange oil, in the yields stated in Table 1, as the first product to elute from the column during the purification of **12a–e**: δ_{H} (CDCl₃: 200 MHz) 4.52 (2H, s), 3.80 (6H, s); δ_{C} (CDCl₃: 100 MHz) 163.7, 134.6, 53.6, 14.0; ν_{max} (neat)/cm⁻¹ 1716, 1567, 1431, 1239; m/z (⁸⁰Se, CI) (rel int) 317 (M⁺+1) (100); HRMS calcd for C₇H₈O₄Se₂ 315.8753; found 315.8757.

Preparation of Nitrosated Derivatives 14: General Procedure. To a stirred solution of the appropriate 1,3-diselenol-2-ylidene derivative **12** (50 mg) in dichloromethane (5 mL) at 0 °C was added isoamyl nitrite (0.5 mL 3.75 mmol, excess). The mixture was maintained at 0 °C for 15 min before being stirred at room temperature for 12 h. The solvent was removed *in vacuo*, and cold methanol (2 mL) was added to the residue to induce precipitation. The resulting nitroso derivatives were isolated by filtration and further purified by crystallization from the appropriate solvent where stated.

1-(4,5-Dicarbomethoxy-1,3-diselenol-2-ylidene)-1-(2-trifluoromethylphenyl)-1-nitrosomethane (14a): green crystals (20 mg, 37%) (from hexane/dichloromethane) mp 148–150 °C; δ_{H} (CDCl₃: 200 MHz) 8.05 (1H, m), 7.80 (1H, m), 7.60–7.50 (2H, m), 3.99 (3H, s), 3.89 (3H, s); δ_{C} (CDCl₃: 100 MHz) 163.27, 162.95, 155.58, 134.63, 133.03, 132.19, 131.59, 129.93, 129.56, 129.37, 128.71, 127.31, 126.46, 54.71, 53.18; m/z (⁸⁰Se, CI) (rel int) 502 (M⁺+1) (30) 488 (10), 276 (25), 188 (100); HRMS Calcd for C₁₅H₁₀F₃NO₅Se₂ 500.8841; found 500.8840.

1-(4,5-Dicarbomethoxy-1,3-diselenol-2-ylidene)-1-nitrosoethanal (14e): green crystals (18 mg, 34%) (from hexane/dichloromethane) mp 132–133 °C; δ_{H} (CDCl₃: 200 MHz) 11.12 (1H, s), 3.99 (3H, s), 3.90 (3H, s). Anal. Calcd for C₉H₇NO₆Se₂: C, 28.22; H, 1.84; N, 3.66. Found: C, 28.35; H, 2.00; N, 3.45. ν_{max} (neat)/cm⁻¹ 1734, 1653, 1396, 1281, 1247, 1211; m/z (⁸⁰Se, CI) (rel int) 386 (M⁺+1) (100), 372 (90), 357 (30), 303 (50).

1-(4,5-Dicarbomethoxy-1,3-diselenol-2-ylidene)-1-nitrosopropan-2-one (14d): green crystals (29 mg, 55%) (from hexane/dichloromethane) mp 119–120 °C; δ_{H} (CDCl₃: 200 MHz) 4.00 (3H, s), 3.99 (3H, s), 3.10 (3H, s). Anal. Calcd for C₁₀H₉NO₆Se₂: C, 30.25; H, 2.28; N, 3.53. Found: C, 30.38; H, 2.39; N, 3.31. ν_{max} (neat)/cm⁻¹ 2958, 2926, 2854, 1741, 1703, 1641, 1400, 1283, 1223; m/z (⁸⁰Se, CI) (rel int) 400 (M⁺+1) (20), 386 (80), 145 (45), 86 (100).

Crystal Structure Determination. The X-ray single crystal diffraction experiment was performed at room temperature on a Siemens SMART CCD detector. Crystal data for **14e**: C₉H₇NO₆Se₂, $M = 383.08$, orthorhombic, space group $Pna2_1$ (No.33), $a = 9.270(1)$, $b = 24.337(3)$, $c = 5.3406(6)$ Å, $V = 1204.9(4)$ Å³ (from 424 reflections with $12 < \theta < 21^\circ$), $Z = 4$, $D_c = 2.11$ g cm⁻³, $F(000) = 736$, graphite-monochromated Mo K_{α} radiation, $\lambda = 0.71073$ Å, $\mu = 61.6$ cm⁻¹, dark green crystal of $0.18 \times 0.2 \times 0.4$ mm, ω scan mode, $2\theta \leq 51.5^\circ$, 4896 total data, 1667 unique data, $R_{\text{int}} = 0.076$, a semiempirical absorption correction²⁹ based on strongest equivalents (transmissions $T_{\text{min}} = 0.1866$, $T_{\text{max}} = 0.2684$) was applied. The structure was solved by direct methods (SHELXS-86 programs³⁰) and refined by full-matrix least squares (SHELXL-93 software³¹) against F^2 of all data with Chebyshev weighting scheme and empirical extinction correction. The refinement of 169 variables (all non-H atoms with anisotropic displacement parameters, methyl groups as rigid bodies, H(7) riding) converged at $wR(F^2) = 0.128$ and goodness-of-fit 1.104 for all data, and $R(F) = 0.046$ for 1593 "observed" data with $I \geq 2\sigma(I)$. The absolute structure (direction of the polar axis) was determined by refining the Flack parameter,³² which converged at $-0.02(3)$. Residual electron density features: $\Delta\rho_{\text{max}} = 0.58$, $\Delta\rho_{\text{min}} = -0.71$ eÅ⁻³.³³

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(33) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.