Structural and Nuclear Magnetic Resonance Studies of short Selenium–Nitrogen Bonds†

Herbert W. Roesky,* Karl-Ludwig Weber, Ulrich Seseke, Waltraud Pinkert, Mathias Noltemeyer, William Clegg, and George M. Sheldrick*
Institut für Anorganische Chemie der Universität, Tammannstrasse 4, D-3400 Göttingen, Federal Republic of Germany

$SeCl_4$ reacts with $Ph_3P{=}NSiMe_3$ (**2**) by elimination of $SiMe_3Cl$ to form $Ph_3P{=}NSeCl_3$ (**3**), which is converted to $(Ph_3P{=}N)_2SeCl_2$ (**4**) by a further mole of (**2**). Compound (**4**) may also be prepared from (**2**) and $SeOCl_2$ or Se_2Cl_2; (**4**) reacts with $SbCl_5$ to form $[(Ph_3P{=}N)_2SeCl]^+[SbCl_6]^-$ (**5**). 2,4,6-Tri-t-butylaniline and $SeOCl_2$ give chloro-*N*-(4,6-di-t-butyl-2-oxocyclohexa-3,5-dien-1-ylidene)selenamide, (**7**). Compounds (**3**), (**4**), (**5**), and (**7**), the previously reported diphenyl-*N*-(*p*-toluenesulphonyl)selenimide, (**1**), and 5,6-dimethyl-2,1,3-benzoselenadiazole, (**8**), have been studied by ^{77}Se n.m.r.; the crystal structures of (**1**), (**3**), (**4**), and (**7**) have been determined by *X*-ray diffraction. The Se–N bond lengths of 1.787(6), 1.680(4), 1.735(4), and 1.766(4) Å all indicate significant Se–N multiple bonding when compared with Se–N bonds from the literature, but curiously the longest of the four is in (**1**), the only structure containing a formal double bond. Although bond length alternation indicates that the quinone type resonance extreme predominates for (**7**), the Se–N and Se–O distances are shorter than in an analogous compound, *N*-(3,5-dimethyl-2-oxocyclohexa-3,5-dien-1-ylidene)phenylselenamide, the Se–O distance being reduced by 0.5 Å to 2.079(3) Å.

To our knowledge only 18 chemically distinct Se–N bond lengths have been determined crystallographically. In those cyclic and acyclic compounds[1–4] for which all uncharged resonance extremes involve nominally single Se–N bonds, the lengths fall in the range 1.824—1.846 Å, not much shorter than the sum of the covalent radii (1.86 Å).[5] When the selenium atom is bonded to one or two nitrogens in a potentially aromatic five- or six-membered ring the bond is within experimental error of 1.815 Å,[6–10] indicating very limited multiple-bonding character when compared with the prediction[5] of 1.64 Å for a double bond. Significantly shorter bonds (1.753—1.785 Å) are found in N_4Se_4,[5] $[N_4Se_4S_2]^{2+}$,[11] and $[N_3Se_3O_6]^{3-}$;[12] since the nitrogen atoms in these species make only two bonds, some degree of Se–N multiple bonding (with perhaps a bond order of *ca.* 1.5) is intuitively necessary. Structural evidence for an Se=N double (or triple) bond was totally lacking, in contrast to the extensive literature on S–N multiple bonds. Acyclic compounds of composition $R{-}N{=}Se{=}O$,[13] $RN{=}SeR'_2$, or $R{-}N{=}Se{=}N{-}R'$ are unknown where R or R′ are alkyl or aryl groups, though a few acyl and sulphonyl derivatives have been reported.[14–19] I.r. evidence for Se–N multiple bonds in these compounds is inconclusive.[14–20]

In order to characterise structurally the elusive Se=N bond we prepared $p\text{-}MeC_6H_4SO_2NSePh_2$ (**1**), which formally contains the double bond, according to a literature method[20] from chloramine-T and diphenyl selenide. Compound (**1**) is a colourless solid, with strong i.r. absorptions at 952 and 572 cm^{-1}. A suitable crystal of (**1**) for *X*-ray analysis was obtained from a solution in tetrahydrofuran (thf).

Since the kinetically and thermodynamically unstable Se–N bond can be stabilised by bulky substituents[4] or by groups which are suitable for forming resonance structures,[21] we allowed $Ph_3P{=}N{-}SiMe_3$ (**2**) to react with $SeCl_4$, Se_2Cl_2, and $SeOCl_2$. The reactions are summarised below. For (**3**) and (**4**) it proved possible to obtain crystals. An attempt to prepare a –N=Se=O derivative stabilised by a bulky substituent led to an unexpected product (**7**) (see above), which was also investigated crystallographically.

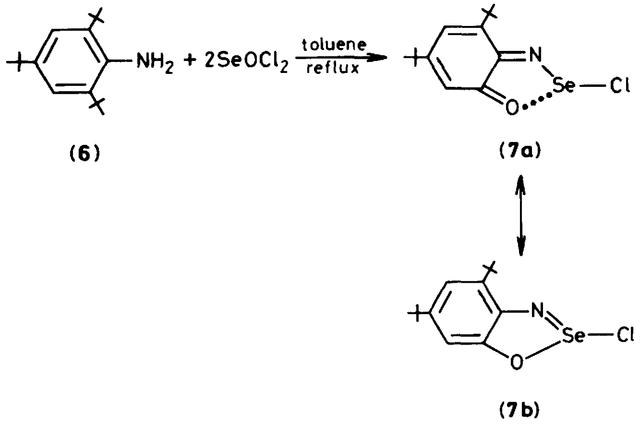
$$\underset{(2)}{Ph_3P{=}N{-}SiMe_3} + SeCl_4 \xrightarrow[\text{reflux}]{\text{toluene}} \underset{(3)}{Ph_3P{=}N{-}SeCl_3} + SiMe_3Cl$$

$$(2) + (3) \xrightarrow[\text{reflux}]{\text{toluene}} \underset{(4)}{(Ph_3P{=}N)_2SeCl_2} + SiMe_3Cl$$

$$(2) + \tfrac{1}{2}SeOCl_2 \xrightarrow[20\,^{\circ}\text{C}]{\text{toluene}} \tfrac{1}{2}(4) + \tfrac{1}{2}(Me_3Si)_2O$$

$$(2) + Se_2Cl_2 \xrightarrow[-78\,^{\circ}\text{C}]{\text{toluene}} \tfrac{1}{2}(4) + SiMe_3Cl + \tfrac{3}{16}Se_8$$

$$(4) + SbCl_5 \xrightarrow[-78\,^{\circ}\text{C}]{\text{toluene}} \underset{(5)}{[(Ph_3P{=}N)_2SeCl]^+[SbCl_6]^-}$$



(**6**) (**7a**) (**7b**)

Selenium-77 n.m.r. spectra of (**1**), (**3**), (**4**), (**5**), and (**7**) were recorded to establish whether the Se chemical shift is correlated

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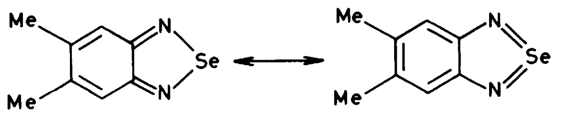
† *Supplementary data available* (No. SUP 56124, 13 pp.): H-atom co-ordinates, full bond lengths and angles, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.



(8a) (8b)

with the type of bonding; for this purpose the known 5,6-dimethyl-2,1,3-benzoselenadiazole, (**8**), was also prepared. An early *X*-ray analysis[10] of the corresponding desmethyl compound gave Se–N 1.83(2) Å with appreciable alternation of the C–C bond lengths, indicating that resonance extreme (**8a**) predominates.

Experimental

All reactions were carried out in an atmosphere of dry nitrogen, using solvents that had been dried and distilled under nitrogen.

Apparatus.—I.r. spectra were recorded on a Perkin-Elmer 180 spectrometer, using Nujol mulls and KBr plates; mass spectra on a Varian CH5 instrument. In the i.r. and mass spectra only predominant bands or peaks are reported. Hydrogen-1 n.m.r. spectra were run on a Bruker 60 E spectrometer with $SiMe_4$ internal standard; ^{77}Se and ^{31}P n.m.r. on a Bruker AM 50 instrument, with $SeOCl_2$ and 85% H_3PO_4 as external standards respectively. Elemental analysis were by Beller, Göttingen.

Diphenyl-N-(p-*toluenesulphonyl*)*selenimide* (**1**).—1.47 g (6.45 mmol) dry chloramine-T (dehydrated sodium *N*-chloro-*p*-toluenesulphonamide) were added at room temperature to a stirred solution of 1.5 g (6.43 mmol) diphenyl selenide in 10 cm^3 MeOH. After stirring for 24 h, decanting from NaCl and crystallising at −30 °C, the crude product was recrystallised from thf. The crystals contained thf of solvation. Yield 2.3 g (5.72 mmol, 89%), m.p. 113—114 °C. I.r.: 1 258vs, 1 332vs, 1 091vs, 952vs, 572vs, 553s cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 2.2 (s, 3 H, Me), 7.4 (m, 14 H, Ph). Mass spectrum, (field ionisation, 275 °C): *m*/*e* 403 (M^+).

Trichloro(*triphenylphosphoranylideneamino*)*selane* (**3**).—$SeCl_4$ (6.3 g, 28.6 mmol) was added slowly to a solution of (**2**) (10 g, 28.6 mmol) in toluene (250 cm^3) at room temperature. After 0.5 h of refluxing the white precipitate was filtered off, washed with toluene (100 cm^3) and dried *in vacuo*. The product was recrystallised from MeCN. Yield 9.5 g (20.6 mmol, 72%), colourless crystals, m.p. 159 °C (decomp.) [Found: C, 45.9; H, 3.1; Cl, 23.8; Se, 15.9. $C_{18}H_{15}Cl_3NPSe$ (M = 461.62) requires C, 46.8; H, 3.3; Cl, 23.0; Se, 17.1%]. I.r.: 1 115vs, 725vs, 540vs, 535vs cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 8.0 (m, 15 H, Ph). ^{31}P N.m.r. (CH_2Cl_2–$CDCl_3$): δ 33.2 [s, $^2J(^{31}P–^{77}Se)$ = 87 Hz for ^{77}Se satellites]. Crystals for the *X*-ray analysis were obtained from CH_2Cl_2, and contain solvent.

Dichlorobis(*triphenylphosphoranylideneamino*)*selane* (**4**).—(*a*) Compounds (**2**) (2.0 g, 5.72 mmol) and (**3**) (2.64 g, 5.72 mmol) were refluxed in toluene (80 cm^3) for 1 h. The white precipitate was filtered off, washed first with toluene and then with warm MeCN and dried *in vacuo*. Crystals were obtained from hot dimethylformamide (dmf). Yield 3.4 g (4.9 mmol, 86%).

(*b*) $SeOCl_2$ (0.71 g, 4.2 mmol) in toluene (10 cm^3) was added dropwise to (**2**) (2.93 g, 8.4 mmol) in toluene (30 cm^3) at 0 °C; the reaction started immediately. After 2 h stirring at room temperature the precipitate was filtered off, washed three times with toluene (20 cm^3), and dried *in vacuo*. Yield 2.6 g (3.7 mmol, 88%).

(*c*) At −78 °C, Se_2Cl_2 (1.64 g, 7.16 mmol) in toluene (20 cm^3) was added dropwise to (**2**) (2.50 g, 7.15 mmol) in toluene (60 cm^3). The pale orange suspension was allowed to warm up to room temperature and stirred for an additional 2 h. The precipitate was dissolved in hot dmf (100 cm^3) and this solution decanted from elemental selenium. After cooling to room temperature the product crystallised. Yield 1.8 g (2.5 mmol, 71%), colourless crystals, m.p. 234—237 °C (decomp.) [Found: C, 60.3; H, 4.4; Cl, 10.1; N, 4.0; Se, 11.1. $C_{36}H_{30}Cl_2N_2P_2Se$ (M = 702.07) requires C, 61.6; H, 4.3; Cl, 10.1; N, 4.0; Se, 11.25%]. I.r.: 1 114vs, 729vs, 543vs, 530vs cm^{-1}. The ^{1}H and ^{31}P n.m.r. spectra in dmf indicated only decomposition products.

Chlorobis(*triphenylphosphoranylideneamino*)*selenonium Hexachloroantimonate* (**5**).—At −78 °C, $SbCl_5$ (0.31 g, 1.04 mmol) in CH_2Cl_2 (10 cm^3) was added dropwise to a suspension of (**4**) (0.73 g, 1.04 mmol) in CH_2Cl_2(30 cm^3). The precipitate disappeared at once and after stirring at room temperature for a further 1 h the solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 (5 cm^3) and after treating with toluene (100 cm^3) the colourless precipitate was filtered off. This crude product was recrystallised from a mixture of CH_2Cl_2 (5 cm^3) and toluene (50 cm^3). Yield 0.76 g (0.76 mmol, 73%), colourless powder, m.p. 154 °C (decomp.) [Found: C, 42.7; H, 3.0; Cl, 24.9; Se, 7.8. $C_{36}H_{30}Cl_7N_2SbSe$ (M = 1 001.08) requires C, 43.2; H, 3.0; Cl, 24.8; Se, 7.9%]. I.r.: 1 119vs, 725vs, 530vs, 345vs cm^{-1}. ^{1}H N.m.r. (CH_2Cl_2): δ 7.7 (m, 30 H, Ph). Mass spectrum (field desorption, CH_2Cl_2, 15 mA): *m*/*e* 667 [$(Ph_3PN)_2SeCl$, 90%], 276 (Ph_3PN, 100%). ^{31}P N.m.r. (CH_2Cl_2, $CDCl_3$): δ 28.3 [s, $^2J(^{31}P–^{77}Se)$ = 28 Hz for ^{77}Se satellites].

Chloro-N-(4,6-*di*-*t*-*butyl*-2-*oxocyclohexa*-3,5-*dien*-1-*ylidene*)-*selenamide* (**7**).—At room temperature, a solution of $SeOCl_2$ (6.34 g, 38.2 mmol) in toluene (20 cm^3) was added to a solution of (**6**) (5 g, 19.1 mmol) in toluene (80 cm^3). The red mixture was refluxed for 3 h and HCl evolution observed. After cooling, the precipitate, which consisted of 1.4 g (17 mmol) selenium and 0.7 g (0.2 mmol) of 2,4,6-tri-t-butylaniline hydrochloride, was filtered off and the solvent removed *in vacuo*. The residue was dissolved in warm MeOH (10 cm^3), filtered, and crystallised at −30 °C. The crude product was recrystallised three times from methanol (10 cm^3). Yield 0.7 g (2.1 mmol, 11%), orange-red needles, m.p. 133 °C [Found: C, 49.1; H, 5.8; Cl, 10.1. $C_{14}H_{20}ClNOSe$ (M = 332.73) requires C, 50.5; H, 6.05; Cl, 10.65%]. I.r.: 1 600vs, 1 502vs, 1 090s, 1 030s, 862vs, 729vs cm^{-1}. Mass spectrum (electron impact): *m*/*e* 333 (M^+, 10%), 298 (M − Cl, 97%), 218 (M − SeCl, 35%), 57 (C_4H_9, 100%). ^{1}H N.m.r. (CH_2Cl_2): δ 1.4 (s, 9 H, Me), 1.6 (s, 9 H, Me), 7.2 (d, J = 2 Hz, 1 H, Ph), 7.4 (d, J = 2 Hz, 1 H, Ph).

5,6-*Dimethyl*-2,1,3-*benzoselenadiazole*, (**8**).—4,5-Dimethyl-1,2-phenylenediamine (3.66 g, 26.8 mmol) and $SeOCl_2$ (4.45 g, 26.8 mmol) were refluxed in toluene (80 cm^3) for 10 h. The solvent was removed *in vacuo*, and the residue was recrystallised from EtOH three times. Yield 3.5 g (16.5 mmol, 61%), colourless

Table 1. Selenium-77 n.m.r. data

Compound	Solvent	$\delta(^{77}Se)^a$/p.p.m.	$^2J(^{77}Se–^{31}P)$/Hz
$SePh_2$[b]	neat	−1 077	—
(**1**)	$CDCl_3$	−827	—
$SeEtCl_3$[b]	CH_2Cl_2	−484	—
(**3**)[c]	CH_3CN–$CDCl_3$	−335	87
(**5**)[c]	CH_2Cl_2–$CDCl_3$	−145	28
(**7**)[c]	CH_2Cl_2–$CDCl_3$	+77	—
(**8**)[c]	CH_2Cl_2–$CDCl_3$	+157	—

[a] Negative values are to high field from external $SeOCl_2$. [b] Both from refs. 22 and 23. [c] Solvent ratio 5:1.

Table 2. Crystal data and structure refinement details

Compound	**(1)**	**(3)**	**(4)**	**(7)**
Formula	$MeC_6H_4SO_2NSePh_2{\cdot}0.5thf$	$Ph_3PNSeCl_3{\cdot}CH_2Cl_2$	$(Ph_3PN)_2SeCl_2$	$Bu^t{}_2C_6H_2ONSeCl$
M	483.43	546.55	702.47	332.67
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$Pna2_1$	$C2/c$
a/Å	19.423(4)	9.771(3)	21.646(3)	15.059(2)
b/Å	10.935(2)	10.452(3)	8.898(2)	13.777(3)
c/Å	21.211(4)	11.919(3)	16.737(6)	15.522(3)
α/°	90	91.91(3)	90	90
β/°	114.62(2)	92.83(3)	90	100.63(2)
γ/°	90	110.71(3)	90	90
U/Å^3	4 095.5	1 135.5	3 223.7	3 164.8
Z	8	2	4	8
D_c/Mg m^{-3}	1.42	1.60	1.45	1.40
F(000)	1 792	544	1 432	1 360
Measured reflections	8 358	3 130	6 211	2 281
Unique reflections	7 185	2 957	2 966	2 058
Observed reflections [$F > 4\sigma(F)$]	4 485	2 696	2 746	1 616
$2\theta_{max.}$/°	50	45	45	45
μ(Mo-K_α)/mm^{-1}	1.93	2.31	1.45	2.51
R [$= \Sigma\Delta/\Sigma\lvert F_o\rvert$]	0.062	0.050	0.031	0.041
R' [$= \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}\lvert F_o\rvert$]	0.054	0.055	0.031	0.040
g [$w^{-1} = \sigma^2(F) + gF_o{}^2$]	0.0002	0.001	0.0002	0.0001
Maximum residual electron density (Å^{-3})	0.6	0.8	0.4	0.2

Table 3. Atomic co-ordinates ($\times 10^4$) for (**1**) with estimated standard deviations in parentheses

Atom	x	y	z
Se	4 515(1)	6 304(1)	6 963(1)
S	4 935(1)	7 548(1)	8 243(1)
O(1)	4 590(2)	8 444(4)	8 519(2)
O(2)	4 960(2)	6 307(4)	8 482(2)
N	4 523(3)	7 681(5)	7 418(2)
C(11)	5 884(3)	8 018(6)	8 498(3)
C(12)	6 063(4)	8 918(7)	8 150(4)
C(13)	6 805(4)	9 318(7)	8 388(4)
C(14)	7 376(4)	8 806(8)	8 958(4)
C(17)	8 191(4)	9 232(10)	9 197(5)
C(15)	7 187(4)	7 911(9)	9 285(4)
C(16)	6 435(4)	7 512(8)	9 060(4)
C(21)	3 433(3)	6 077(6)	6 453(3)
C(22)	2 940(4)	6 949(8)	6 495(4)
C(23)	2 162(5)	6 749(10)	6 122(5)
C(24)	1 911(5)	5 749(10)	5 730(5)
C(25)	2 394(4)	4 918(8)	5 689(4)
C(26)	3 178(4)	5 077(7)	6 058(4)
C(31)	4 716(3)	6 998(6)	6 213(3)
C(32)	5 031(3)	6 243(6)	5 889(3)
C(33)	5 194(4)	6 719(6)	5 363(3)
C(34)	5 036(4)	7 913(7)	5 170(4)
C(35)	4 724(4)	8 650(6)	5 503(4)
C(36)	4 549(4)	8 197(6)	6 035(3)
Se′	444(1)	6 329(1)	7 311(1)
S′	136(1)	7 380(2)	8 376(1)
O(1′)	283(3)	8 477(4)	8 771(2)
O(2′)	500(2)	6 281(4)	8 717(2)
N′	322(3)	7 690(4)	7 719(3)
C(11′)	−848(4)	7 086(6)	8 066(3)
C(12′)	−1 111(4)	6 163(8)	8 339(4)
C(13′)	−1 877(4)	5 994(9)	8 128(5)
C(14′)	−2 397(4)	6 727(9)	7 639(5)
C(17′)	−3 248(4)	6 482(11)	7 385(6)
C(15′)	−2 134(6)	7 574(9)	7 369(6)
C(16′)	−1 358(5)	7 780(9)	7 563(5)
C(21′)	1 534(3)	6 231(6)	7 668(3)
C(22′)	1 974(4)	7 207(6)	7 987(4)
C(23′)	2 758(4)	7 085(7)	8 245(4)
C(24′)	3 078(4)	5 997(6)	8 182(4)
C(25′)	2 634(4)	5 037(8)	7 877(4)
C(26′)	1 847(4)	5 150(7)	7 598(4)
C(31′)	242(3)	7 032(6)	6 421(3)
C(32′)	10(4)	6 272(6)	5 858(3)
C(33′)	−129(4)	6 734(6)	5 214(3)
C(34′)	−27(4)	7 945(6)	5 135(4)
C(35′)	205(4)	8 712(7)	5 698(4)
C(36′)	345(4)	8 277(6)	6 359(3)
C(41)	3 138(9)	5 822(16)	39(11)
C(42)	3 294	6 247	728
C(43)	2 605	6 156	826
C(44)	2 024	5 676	197
C(45)	2 353	5 469	−289
C(51)	3 284(9)	5 961(24)	724(12)
C(52)	3 007	7 068	331
C(53)	2 227	7 219	214
C(54)	2 021	6 207	534
C(55)	2 674	5 429	849

needles, m.p. 139 °C [Found: C, 45.2; H, 4.2; N, 11.1. $C_8H_8N_2Se$ (M = 211.12) requires C, 45.5; H, 3.8; N, 13.3%]. I.r.: 1 027w, 1 009m, 791vs, 752vs, 712s cm^{-1}. Mass spectrum (electron impact): m/e 212 (M^+, 100%). ^{1}H N.m.r. ($CDCl_3$): δ 2.3 (s, 6 H, Me), 7.6 (m, 2 H, Ph).

N.M.R. Investigations.—The ^{77}Se chemical shifts relative to $SeOCl_2$ are presented in Table 1, and compared with some literature data.[22,23] For (**4**) in dmf–$CDCl_3$, only a decomposition product with δ −60 p.p.m. could be observed.

Crystal Structure Determinations.—The crystal data and details of the four refinements are presented in Table 2. Data were collected at room temperature by a profile-fitting procedure[24] on a Stoe-Siemens four-circle diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å),

Table 4. Atomic co-ordinates ($\times 10^4$) for (**3**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Se	84(1)	6 755(1)	5 940(1)	C(23)	5 371(9)	10 354(7)	8 064(7)
Cl(1)	1 238(2)	8 998(1)	5 706(2)	C(24)	6 130(7)	10 569(7)	7 072(6)
Cl(2)	−1 784(2)	7 137(2)	6 814(1)	C(25)	5 741(7)	9 588(6)	6 268(5)
Cl(3)	1 785(1)	6 187(1)	4 509(1)	C(26)	4 660(6)	8 332(6)	6 393(4)
N	887(4)	6 456(4)	7 131(3)	C(31)	2 904(5)	5 080(5)	6 991(4)
P	2 478(1)	6 489(1)	7 558(1)	C(32)	1 743(5)	3 826(5)	6 793(4)
C(11)	2 324(5)	6 289(5)	9 043(4)	C(33)	2 036(7)	2 677(6)	6 427(5)
C(12)	3 140(7)	5 659(7)	9 635(5)	C(34)	3 461(8)	2 795(7)	6 274(6)
C(13)	2 998(10)	5 505(9)	10 771(5)	C(35)	4 588(7)	4 012(7)	6 477(6)
C(14)	2 092(8)	5 959(7)	11 327(5)	C(36)	4 322(6)	5 146(6)	6 835(5)
C(15)	1 262(7)	6 562(7)	10 769(5)	Cl(4)	816(33)	393(27)	10 238(39)
C(16)	1 361(6)	6 721(6)	9 600(4)	C(1)	1 483(77)	1 092(64)	9 143(44)
C(21)	3 937(5)	8 077(5)	7 369(4)	Cl(5)	2 657(27)	1 729(29)	9 817(29)
C(22)	4 294(7)	9 103(6)	8 202(5)				

Table 5. Atomic co-ordinates ($\times 10^4$) for (**4**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Se(1)	3 959(1)	4 487(1)	3 724(1)	C(35)	5 137	9 356	4 494
Cl(1)	5 156(1)	4 713(2)	3 868(1)	C(36)	4 685	8 323	4 719
Cl(2)	2 989(1)	2 860(2)	3 496(1)	C(31)	4 100	8 379	4 370
P(1)	3 546(1)	7 038(2)	4 737(1)	C(42)	4 541(1)	3 060(6)	1 771(2)
P(2)	3 935(1)	5 710(2)	2 088(1)	C(43)	4 574	1 543	1 567
N(1)	3 737(2)	5 319(5)	4 621(2)	C(44)	4 043	780	1 326
N(2)	3 823(2)	5 903(5)	3 037(2)	C(45)	3 479	1 536	1 289
C(12)	2 400(1)	6 247(3)	4 202(2)	C(46)	3 446	3 054	1 493
C(13)	1 792	6 485	3 955	C(41)	3 977	3 816	1 734
C(14)	1 565	7 945	3 881	C(52)	4 826(1)	6 571(4)	984(2)
C(15)	1 945	9 168	4 055	C(53)	5 351	7 364	746
C(16)	2 553	8 930	4 302	C(54)	5 685	8 200	1 303
C(11)	2 780	7 470	4 375	C(55)	5 494	8 244	2 099
C(22)	3 247(2)	8 504(4)	6 156(2)	C(56)	4 969	7 452	2 337
C(23)	3 243	8 670	6 985	C(51)	4 635	6 615	1 780
C(24)	3 520	7 585	7 468	C(62)	2 846(2)	7 321(5)	2 067(2)
C(25)	3 801	6 333	7 122	C(63)	2 356	8 065	1 698
C(26)	3 805	6 166	6 294	C(64)	2 321	8 119	867
C(21)	3 528	7 252	5 811	C(65)	2 776	7 429	404
C(32)	3 968(1)	9 468(4)	3 795(2)	C(66)	3 266	6 685	773
C(33)	4 420	10 501	3 570	C(61)	3 301	6 631	1 605
C(34)	5 005	10 445	3 919				

Table 6. Atomic co-ordinates ($\times 10^4$) for (**7**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Se(1)	3 982(1)	5 349(1)	6 023(1)	C(6)	5 713(3)	4 611(3)	6 437(3)
Cl(1)	2 459(1)	5 069(1)	5 579(1)	C(7)	4 726(3)	2 039(3)	5 777(3)
O(1)	5 371(2)	5 464(2)	6 440(3)	C(8)	4 287(3)	2 225(4)	4 819(3)
N(1)	4 222(2)	4 104(3)	5 918(2)	C(9)	3 987(3)	1 980(4)	6 338(3)
C(1)	5 070(3)	3 843(3)	6 142(3)	C(10)	5 205(3)	1 055(3)	5 848(4)
C(2)	5 391(3)	2 860(3)	6 097(2)	C(11)	7 931(3)	3 217(3)	6 919(3)
C(3)	6 294(3)	2 735(3)	6 335(2)	C(12)	8 511(3)	4 079(4)	7 295(4)
C(4)	6 935(3)	3 495(3)	6 654(3)	C(13)	8 265(3)	2 852(4)	6 103(3)
C(5)	6 639(3)	4 413(3)	6 701(3)	C(14)	8 028(3)	2 396(4)	7 595(3)

and semi-empirical absorption corrections applied. The selenium atoms were found from the Patterson function, the remaining atoms from difference electron-density syntheses. The structures were refined with complex neutral-atom scattering factors, riding hydrogens (C–H 0.96 Å) with fixed isotropic thermal parameters, and all other atoms anisotropic to give the *R* indices quoted in Table 2. In (**4**) the phenyl rings were refined as rigid groups. The asymmetric unit of (**1**) contains two molecules of the compound, plus one molecule of thf which is disordered over two interpenetrating sites. An adequate model for the disordered thf was achieved with two overlapping pentagons (C–C 1.44 Å) which were refined as rigid groups with isotropic thermal parameters; the occupation factors refined to 0.58(1) and 0.42(1). The solvent dichloromethane molecule in (**3**) also exhibited high thermal motion. Inversion of the polar axis direction in (**4**) increased *R* from 0.031 to 0.059, and *R′* from 0.031 to 0.061, thus the alternative absolute structure may be confidently rejected.

A Data General mini-computer was used for all calculations, using programs written by G. M. S. Final atomic co-ordinates are given in Tables 3—6 and selected molecular dimensions in Tables 7—10.

Table 7. Selected mean bond lengths (Å) and angles (°) in (**1**)

Se–N	1.787(6)	N–Se–C	99.5(3)
Se–C	1.933(7)	C–Se–C	98.2(3)
N–S	1.598(6)	Se–N–S	112.5(3)
S–O	1.438(5)	N–S–C	107.9(3)
S–C	1.770(7)	O–S–O	117.1(3)

Table 8. Selected mean bond lengths (Å) and angles (°) in (**3**)

Se–N	1.680(4)	Se–N–P	137.1(3)
Se–Cl(1)	2.248(2)	N–Se–Cl(1)	104.6(1)
Se–Cl(2)	2.291(2)	N–Se–Cl(2)	94.6(2)
Se–Cl(3)	2.634(2)	N–Se–Cl(3)	98.1(2)
Se–Cl(3′)	2.983(2)	N–Se–Cl(3′)	93.4(1)
N–P	1.600(4)	N–P–C	103.0—114.3(2)
P–C	1.793(4)	Se–Cl(3)–Se′	96.1(1)

Table 9. Selected mean bond lengths (Å) and angles (°) in (**4**)

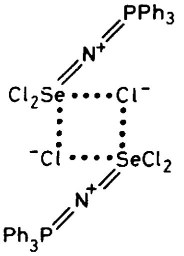
Se–N	1.735(4)	Se–N–P	124.5(3)
Se–Cl	2.595(2)	N–Se–Cl	99.4(1)
N–P	1.606(4)	N–Se–N	102.5(2)
P–C	1.798(4)	Cl–Se–Cl	149.9(1)
		N–P–C	103.1—115.7(2)

Table 10. Selected bond lengths (Å) and angles (°) in (**7**)

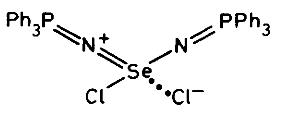
Se(1)–N(1)	1.766(4)	C(4)–C(5)	1.348(6)
Se(1)–Cl(1)	2.302(2)	C(5)–C(6)	1.407(6)
Se(1)–O(1)	2.079(3)	C(6)–C(1)	1.450(6)
N(1)–C(1)	1.310(5)	N(1)–Se(1)–Cl(1)	91.1(1)
C(6)–O(1)	1.283(5)	N(1)–Se(1)–O(1)	83.7(1)
C(1)–C(2)	1.445(6)	O(1)–Se(1)–Cl(1)	174.7(1)
C(2)–C(3)	1.352(5)	C(1)–N(1)–Se(1)	116.6(3)
C(3)–C(4)	1.448(5)	Se(1)–O(1)–C(6)	108.1(3)

Results and Discussion

The structures of compounds (**1**), (**3**), (**4**), and (**7**) are shown in Figures 1—4. A surprising conclusion from the crystal structure analyses is that the Se–N bond [1.787(6) Å] in (**1**), although formally a double bond and about the same length as in N_4Se_4 [1.785(20) Å],[5] is actually the longest of the four Se–N bonds investigated. The short Se–N bonds in (**4**) [1.735(4) Å] and especially (**3**) [1.680(4) Å] appear to derive appreciable double bond character from resonance structures of the type (**3a**) and (**4a**), which is consistent with the long Se–Cl bonds [2.634(2) and 2.983(2) Å] involving the bridging chlorine in (**3**) and both chlorines [2.595(2) Å] in (**4**). These chlorines thus carry appreciable partial negative charges. A dimeric structure is also observed[25] for CF_3SeCl_3, but the Se–C bonds are *cis*, and the mean Se–Cl distance in the four-membered ring (2.64 Å) is shorter than the mean of 2.81 Å in (**3**).



(3a)



(4a)

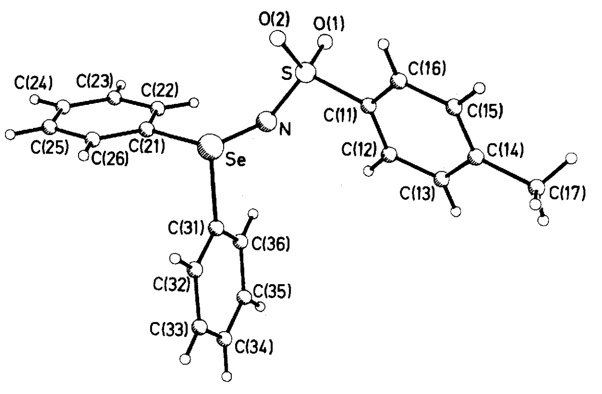
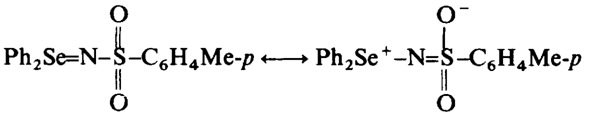


Figure 1. The structure of one molecule of (**1**); the other is very similar

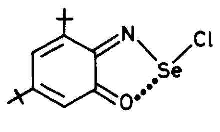
The loss of double bond character in (**1**) could be accounted for by a resonance structure (**1b**) involving a positive charge on selenium, in view of the electron-withdrawing nature of the *p*-toluenesulphonyl group. In the corresponding compound in which sulphur replaces selenium, which is not isostructural with (**1**), structure (**1a**) makes a larger contribution [S^{IV}–N 1.628, S^{VI}–N 1.598 Å].[26]



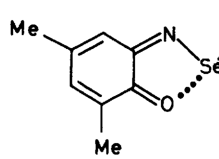
$$Ph_2Se{=}N{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{-}C_6H_4Me\text{-}p \longleftrightarrow Ph_2Se^{+}{-}N{=}\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{-}C_6H_4Me\text{-}p$$

(ylene) (**1a**) (ylide) (**1b**)

The structure of (**7**) may be compared with that of (**9**);[27] in both cases the alternating bond lengths in the ring indicate that

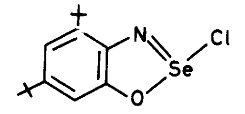


(7a)



(9a)

the quinone description (shown) predominates. However, the Se–N and especially Se ··· O distances are both much shorter in (**7**) [1.766(4) and 2.079(3) Å] than in (**9**) [1.805(3) and 2.575(3) Å]. The chlorine substituent clearly favours Se^{IV}, required for the alternative resonance extreme (**7b**).



(7b)

The above conclusions are consistent with the pyramidal co-ordination of Se in (**1**), and the somewhat reduced stereochemical influence of the lone pair(s) in (**3**) and (**4**).

Compounds (**3**) and (**4**) are surprisingly stable, being only slowly hydrolysed in the presence of moisture. Despite the short Se–N bonds they show no i.r. absorptions in the range 900—960 cm^{-1}, supporting a reassignment[20] of ν(Se=N) from 900—950 to 550—590 cm^{-1} in *N*-(*p*-toluenesulphonyl)selenimides such as (**1**). Compound (**3**) is slightly soluble in polar solvents, while

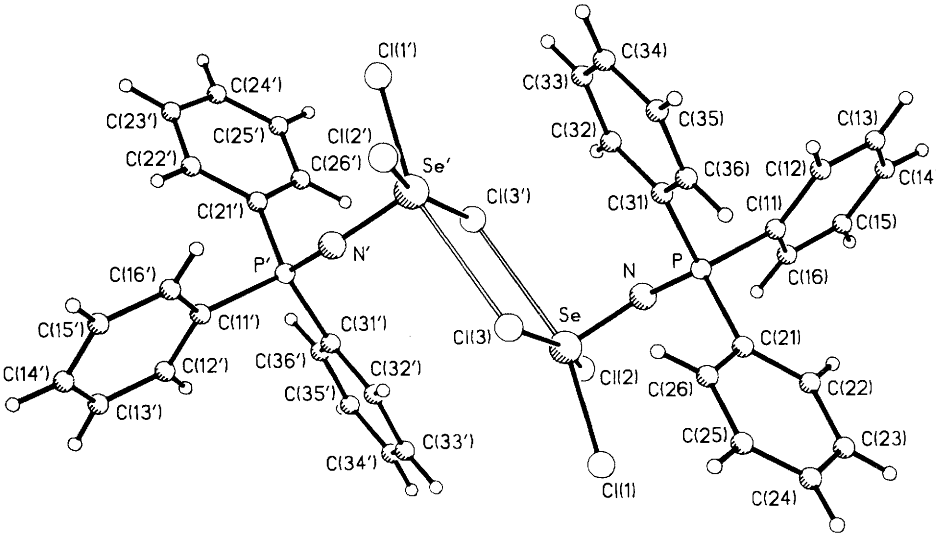


Figure 2. The structure of the dimer unit of (**3**); atoms generated by the crystallographic centre of symmetry are primed

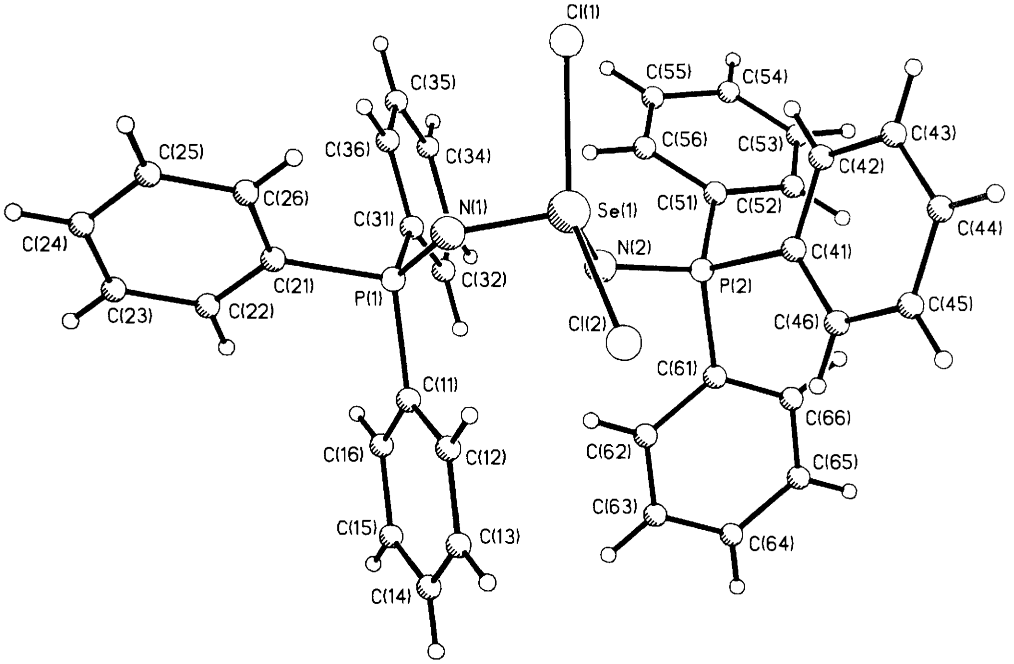


Figure 3. The molecule of (**4**)

(**4**) is only soluble in hot dmf with partial decomposition. Compound (**4**) reacts with $SbCl_5$ to give the selenonium salt (**5**) which is characterised by i.r., ^{77}Se n.m.r., and field desorption mass spectra. Compound (**5**) is soluble in CH_2Cl_2 or $CHCl_3$ and insoluble in non-polar solvents like toluene or hexane; it is very sensitive towards moisture and should be kept under an atmosphere of dry nitrogen.

Selenium-77 n.m.r. investigations of selenium–nitrogen compounds are rare, and it would be premature to generalise on the basis of the chemical shift data presented in Table 1. However, it appears that selenium atoms in conjugated cyclic systems [*e.g.* compounds (**7**) and (**8**)] and selenium atoms carrying a formal positive charge [*e.g.* compound (**5**)] are shifted strongly to low field, whereas the addition of chlorine substituents and concomitant change from Se^{II} to Se^{IV} produces a smaller irregular trend in the same direction.

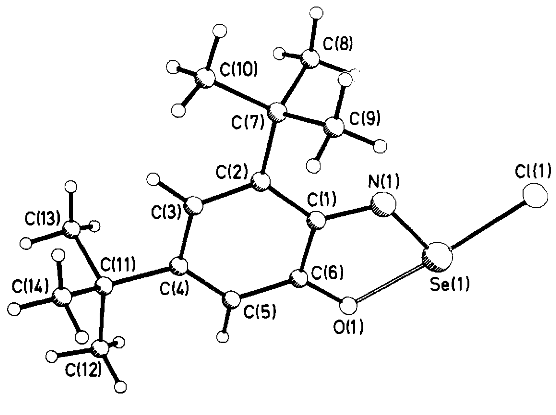


Figure 4. The molecule of (**7**)

In order to get n.m.r. data for (**4**) it was dissolved in hot dmf; but when this solution was cooled to room temperature, (**4**) crystallised immediately. From the suspension only one signal at -60 p.p.m. was observed, which we did not assign to (**4**) but to a soluble decomposition product. The coupling constants of (**3**) and (**5**) were confirmed by ^{31}P n.m.r. spectra, which showed the expected satellite peaks.

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