# Synthesis, Properties, and Multinuclear ($^1H$, $^{13}C$, $^{77}Se$) Nuclear Magnetic Resonance Studies of Selenoethers containing Two or More Selenium Atoms

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A convenient synthesis of MeSeLi from MeLi and $Se_8$ in tetrahydrofuran (THF) has been used to prepare the bis-selenoethers $MeSe[CH_2]_nSeMe$ ($n$ = 1,2,3,6, or 12) and *cis*-MeSeCH=CHSeMe. $PhSe[CH_2]_nSePh$ ($n$ = 1—3) and *cis*-PhSeCH=CHSePh have been prepared from $PhSe^-$, itself produced from $Ph_2Se_2$ and $LiAlH_4$–THF or sodium hydroxymethanesulphinate. The bis-selenoethers $o$-$C_6H_4(SeR)_2$ (R = Me or Ph) were obtained from $R_2Se_2$ and benzyne. The syntheses of $(RSeCH_2)_3CMe$ (R = Me or Ph), $(MeSeCH_2)_4C$, and $(MeSeCH_2CH_2CH_2)_2Se$ are also described. The $^1H$, $^{13}C$, and $^{77}Se$ n.m.r. spectra of these selenoethers have been recorded, and the chemical shifts and coupling constants ($^nJ_{Se-H}$, $^nJ_{Se-C}$) are discussed in terms of structures. Mass spectra of the selenoethers have been recorded and the principle fragmentation modes identified.

Selenoether ligands have been little used by organometallic and co-ordination chemists, owing to their relatively weak donor power, infamous reputation as malodorous compounds, and not least the lack of convenient syntheses for all but the simplest examples.[1] Recent developments in n.m.r. instrumentation have made possible the routine observation of $^{77}Se$ spectra ($I = \frac{1}{2}$, 7.5% natural abundance); this fact, coupled with the growing interest in selenium reagents in organic synthesis,[2] make a continuation of this neglect unlikely. At present only a few bis-selenoethers [3–9] and one tetradentate ligand [10] have been described, and several of the syntheses are lengthy. We required a range of structurally related bis- and poly-selenoethers, to extend our studies on high oxidation state co-ordination chemistry [11,12] to neutral selenium donors. Here we report convenient syntheses for a range of such ligands, from readily available materials, and their characterisation by $^1H$, $^{13}C$, and $^{77}Se$ n.m.r. and mass spectrometry.

## Results and Discussion

$MeSe[CH_2]_nSeMe$ ($n$ = 1, 2, 3, 6, *or* 12) *and* cis-MeSeCH=CHSeMe.—The usual route to diselena-alkanes is that of Aynsley *et al.*,[3] from $Me_2Se_2$ and Na–liquid ammonia [Scheme 1(a)]. The reaction is slow (*ca.* 2 days), but can be speeded up by replacement of the liquid ammonia with THF, before addition of the dihalogenoalkane.[10] Recalling that the most convenient syntheses of diphosphines and diarsines used $LiP(As)R_2$ in THF,[13] we have developed a route to bis-selenoethers *via* LiSeMe in THF, based upon the reaction of MeLi and $Se_8$ in THF and previously used by Drake [14] to make methylselenosilanes. The LiSeMe reacts *in situ* with α,ω-dichloroalkanes, giving $MeSe[CH_2]_nSeMe$ ($n$ = 1, 2, 3, 6, or 12) in good yield [Scheme 1(b)], the syntheses being complete in a few hours. The products are purified by fractionation ($n$ = 1, 2, 3, or 6) or crystallisation from methanol at low temperatures ($n$ = 12). This is also a more attractive route to $MeSeCH_2SeMe$ than the published synthesis [15] which requires the volatile and extremely malodorous MeSeH. The dimethyl selenide used as the $^{77}Se$ n.m.r. reference was obtained in >80% yield using LiSeMe and MeI.

*cis*-1,2-Dichloroethene did not react with LiSeMe in THF, even in the presence of added base (NaOMe), but after replacement of the THF with ethanol, and with an added equimolar amount of NaOEt, a moderate yield of *cis*-MeSeCH=CHSeMe (*ca.* 24%) was obtained. The substitution is stereospecific as are the corresponding reactions of NaSMe and NaSPh.[16,17]

$PhSe[CH_2]_nSePh$ ($n$ = 1—3) *and cis*-PhSeCH=CHSePh.—The reaction of PhLi with $Se_8$ is reported [18,19] to give only moderate yields of PhSeLi; we have used the commercially available † diphenyl diselenide, as a source of $PhSe^-$. The $Ph_2Se_2$ can be cleaved by sodium hydroxymethanesulphinate (Rongalite; $HOCH_2SO_2Na{\cdot}2H_2O$) in aqueous EtOH, by $NaBH_4$ in EtOH, or by $LiAlH_4$ in THF (Scheme 2). Although the $NaBH_4$ reduction is a good route to selenols, in our hands it has given variable yields of bis-selenoethers, often contaminated with $Ph_2Se_2$. This is probably due to the side-reaction of $NaBH_4$ with alcohols catalysed by organoselenium compounds.[22] The Rongalite and $LiAlH_4$ routes gave good yields of $PhSe[CH_2]_nSePh$ ($n$ = 1—3), and avoid the prior synthesis of PhSeH.[7,23] *cis*-PhSeCH=CHSePh was readily prepared by the Rongalite route in the presence of an excess of base (equimolar amount of NaOH).

$o$-$C_6H_4(SeR)_2$ (R = Me *or* Ph).—The $RSe^-$ ions are insufficiently nucleophilic to react directly with $o$-dichloro- (or dibromo-)benzene.[24] 1,2-Bis(methylseleno)benzene was obtained by addition of $Me_2Se_2$ to benzyne in $o$-$C_6H_4Cl_2$ solution. The main impurity is biphenylene, most of which crystallised on storing the crude product at −5 °C for several days. $o$-$C_6H_4(SePh)_2$ was made similarly from $Ph_2Se_2$, and the crude product converted into $o$-$C_6H_4(SePhCl_2)_2$ by $SO_2Cl_2$. This was subsequently reduced with zinc dust–ethanol to give the pure compound, although the overall yield is poor (*ca.* 5%). The reaction of benzyne with $Ph_2Se_2$ has been briefly reported before,[25] but the pure product was not isolated.

*Tris-selenoethers*.—The 1,1,1-tris-(R-selenomethyl)ethanes, $(RSeCH_2)_3CMe$ (R = Me or Ph), were obtained straight-

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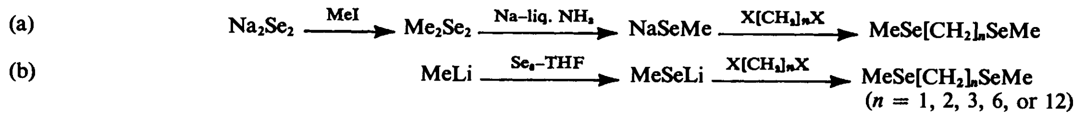
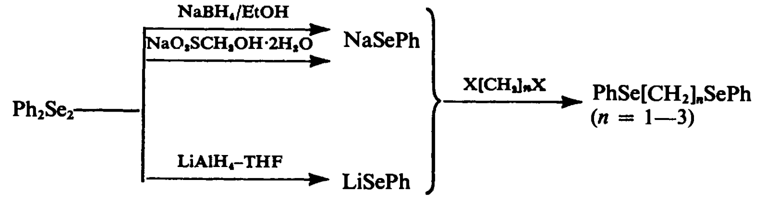
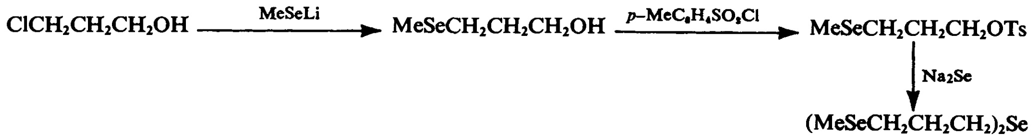
† $Ph_2Se_2$ can be made from PhSeH [20] or PhSeCN [21] if preferred.



Scheme 1.



Scheme 2.

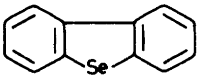


Scheme 3.

forwardly from $(BrCH_2)_3CMe$ and the appropriate $RSe^-$. MeSeLi and $C(CH_2Br)_4$ gave a relatively poor yield of the spirocyclic tetrakis-selenoether $C(CH_2SeMe)_4$. The synthesis of the linear tris-selenoether $\{MeSe(CH_2)_3\}_2Se$ is outlined in Scheme 3.

*Properties of Selenoethers.*—The methyl-substituted selenoethers are colourless or pale yellow oils (orange products result from contamination with diselenides) which have a characteristic, persistent odour. The phenyl-substituted compounds are viscous oils or low-melting solids with a mild odour. It appears that the ' reputation ' of selenoethers has arisen from contamination with selenols; of the ligands prepared in this study, only $MeSeCH_2SeMe$ and *cis*-MeSeCH=CHSeMe have a penetrating odour when pure.

Mass spectra were recorded to confirm the constitution of the products; prominent peaks are listed in the Experimental section. The presence of six natural isotopes of selenium ($^{74}$Se = 0.87%, $^{76}$Se = 9.02%, $^{77}$Se = 7.58%, $^{78}$Se = 23.52%, $^{80}$Se = 49.82%, $^{82}$Se = 9.19%)[26] leads to highly characteristic groups of peaks for selenium-containing fragments, but renders analysis of overlapping peaks difficult. The experimental section lists the peaks arising from the $^{80}$Se isotope only. All the compounds showed molecular ions, and the fragmentation patterns as expected showed considerable resemblance to those of the corresponding thioethers,[27,28] although for comparable species the selenium-containing ions often had lower relative intensities than those of sulphur fragments, consistent with the weaker C–Se bonds. The mass spectrum of $PhSeCH_2SePh$, shows a molecular ion at $m/z$ 328 (10.5%), and major peaks at 171 (63% $M$ – PhSe) and 93 (24%, CHSe), with $[C_7H_7]$ as the base peak. For $PhSe[CH_2]_2SePh$ and $PhSe[CH_2]_3SePh$ the base peak is $m/z$ 157 (PhSe), prominent peaks resulting from [$M$ – PhSe], and in the case of the propane-backbone material from β-cleavage, $m/z$ 171 (41% $PhSeCH_2$). For *cis*-PhSeCH=CHSePh, the base peak was again [PhSe] with $[PhSeC_2H_2]$, 183 (68%) as the other major selenium fragment. The fragmentation pattern of $o$-$C_6H_4(SePh)_2$ is quite different, but strongly resembles that[28] of $o$-$C_6H_4(SPh)_2$, exhibiting a complex overlapping pattern at $m/z$ 390 ($M^+$) and 388 ($M$ – 2H), with 234 (34%, $C_{12}H_{10}Se$), 233 (74%, $C_{12}H_9Se$), and 232 (100%, $C_{12}H_8Se$), as major ions, the base peak corresponding to the heterocycle (I).



(I)

The methyl-substituted compounds generally show loss of Me, MeSe, and MeSeH in the major fragmentations. Those with long backbones ($C_6$ or $C_{12}$) show the expected[28] long series of alkylseleno and hydrocarbon fragments, whilst $MeSeCH_2CH_2SeMe$ and *cis*-MeSeCH=CHSeMe show evidence for elimination of the backbone, an unimportant or absent process in compounds with other than $C_2$ backbones. The mass spectra of the tris- and tetrakis-selenoethers are more complex, but are consistent with the expected fragmentations.

*N.m.r. Spectra.*—The $^1$H n.m.r. spectra (Table 1) are unexceptional with δ ($CH_3SeCH_2$) *ca.* 2.0, δ ($CH_3SeCHCH$) and δ ($CH_3SeC_6H_4$) *ca.* 2.3, and $^2J_{Se-H}$ 10—12 Hz. For $SeCH_2$ $^2J_{Se-H}$ is *ca.* 8—10 Hz, except for $RSeCH_2SeR$ (*ca.* 12—15 Hz), the larger values possibly reflecting a wide Se–C–Se angle leading to greater *s*-character in the C–Se bonds. For the alkene-backboned ligands *cis*-RSeCH=CHSeR, $^2J_{Se-H}$ and $^3J_{Se-H}$ are readily identified.

The $^{77}$Se n.m.r. spectra (Table 1) demonstrate both the wide range of $^{77}$Se chemical shifts and the sensitivity of these shifts to small changes in structure.[29-31] As shown by others[31,32] using unsymmetrical selenides ($RR^1Se$), the $^{77}$Se chemical shifts can be predicted with reasonable accuracy since the shift changes with R and $R^1$ are additive. Starting with δ (MeSe) = 0 from the $Me_2Se$ reference and δ (PhSe) *ca.* 208 p.p.m. from $Ph_2Se$, the shift for $o$-$C_6H_4SeMe$ should be *ca.* 208 p.p.m. *cf.* 202 [$o$-$C_6H_4(SeMe)_2$] and 228 [$o$-$C_6H_4Br(SeMe)$] found. The shift of 411 p.p.m. found for $o$-$C_6H_4(SePh)_2$ is close to that of $Ph_2Se$. For *cis*-MeSeCH=CHSeMe a 172 p.p.m. shift can be assigned to the *cis*-alkene linkage; added to 208 p.p.m. for PhSe this predicts 380 p.p.m. for *cis*-

**Table 1.** $^1$H and $^{77}$Se N.m.r. data

| | $^1$H (δ values; $J_{Se-H}$ in Hz) | | | |
|---|---|---|---|---|
| | MeSe | $CH_2Se$ | Others | $^{77}$Se (δ) |
| $Me_2Se$ | 2.0 (s) (10.5) | | | 0 |
| $MeSeCH_2SeMe$ | 2.08 (s) (11.0) | 3.63 (s) (15.5) | | 117 |
| $MeSe[CH_2]_2SeMe$ | 2.06 (s) (11.0) | 2.83 (s) (8.75) | | 121 |
| $MeSe[CH_2]_3SeMe$ | 2.05 (s) (10.8) | 2.64 (t) [a] | 1.98 (m) | 74 |
| $MeSe[CH_2]_6SeMe$ | 1.98 (s) (10.1) | 2.56 (t) [a] | 1.2—1.9 (br, m) | 77 |
| $MeSe[CH_2]_{12}SeMe$ | 1.98 (s) (10.0) | 2.56 (t) [a] | 1.1—1.8 (br, m) | 79 |
| MeSeCH=CHSeMe | 2.2 (s) (10.8) | | 6.82 (s) $^2J_{Se-H}$ 9.6, $^3J_{Se-H}$ 12.8 | 172 |
| *o*-$C_6H_4(SeMe)_2$ | 2.26 (s) (11.7) | | 7.0—7.5 (m) | 202 |
| *o*-$C_6H_4Br(SeMe)$ | 2.3 (s) (12.3) | | 6.9—7.6 (m) | 228 |
| $(MeSeCH_2CH_2CH_2)_2Se$ | 1.98 (s) (10.7) | 2.68 (t) [a]<br>2.65 (t) [a] | 2.0 (quint) | 73, 154 |
| $(MeSeCH_2)_3CCH_3$ | 2.0 (s) (10.7) | 2.75 (s) (8.7) | 1.15 (s) | 23 |
| $(PhSeCH_2)_3CCH_3$ | | 3.18 (s) (9.5) | 1.12 (s), 7.1—7.7 (m) | 240 |
| $(MeSeCH_2)_4C$ | 2.08 (s) (12.0) | 2.86 (s) (8.0) | | 25 |
| $Ph_2Se$ | | | | 416 [b] |
| $PhSeCH_2SePh$ | | 4.22 (s) (12.7) | 7.1—7.7 (m) | 346 |
| $PhSe[CH_2]_2SePh$ | | 3.14 (s) (9.5) | 7.1—7.7 (m) | 340 |
| $PhSe[CH_2]_3SePh$ | | 2.95 (t) [a] 2.1 (q) | 7.1—7.7 (m) | 289 |
| PhSeCH=CHSePh | | | 7.12 (s), $^2J_{Se-H}$ 10.5, $^3J_{Se-H}$ 13.3<br>7.1—7.7 (m) | 380 |
| *o*-$C_6H_4(SePh)_2$ | | | | 411 |

[a] $J_{Se-H}$ not identified. [b] 402 for neat liquid (ref. 31).

PhSeCH=CHSePh, *cf.* the measured value 380 p.p.m. (the exact agreement is no doubt fortuitous). For the compounds $PhSe[CH_2]_nSePh$ and $MeSe[CH_2]_nSeMe$ similar calculations lead to δ *ca.* 130—120 p.p.m. for the backbones with $n = 1$ or 2 and then a decrease to *ca.* 70—80 p.p.m. for $n \geqslant 3$; the insensitivity of longer chains again is consistent with data for $R_2Se$, where changes more remote than the γ-carbon atom have a negligible effect on δ (Se).[32] The *ca.* 74 p.p.m. contribution for a $[CH_2]_3$ backbone predicts the shifts in the tris-selenoether $(MeSe[CH_2]_3)_2Se$ as 74 and 148 p.p.m. *cf.* 73 and 154 p.p.m. found experimentally. In $MeC(CH_2SeMe)_3$ (23 p.p.m.) and $C(CH_2SeMe)_4$ (25 p.p.m.), the effect of the extra SeMe group in the latter upon the $^{77}$Se shift appears negligible; hence a contribution of *ca.* 24 p.p.m. is assigned to the $CH_2C[CH_2]_3$ unit, leading to a predicted value for $MeC(CH_2SePh)_3$ of 232 p.p.m. (found 240 p.p.m.). The $R_2Se$ system most comparable would be dineopentyl selenide, for which a $^{77}$Se n.m.r. spectrum has not been reported, but extrapolation from the $^{125}$Te data on dineopentyl telluride using the approach of O'Brien *et al.*[32] suggests a contribution for a neopentyl group on $^{77}$Se of *ca.* 15 p.p.m., a reasonable agreement in view of the assumptions involved.

The $^{13}$C n.m.r. data are listed in Table 2. In $MeSe[CH_2]_nSeMe$ the δ (Me) value falls from 6.0 ($n = 1$) to 3.5 p.p.m. ($n = 12$), but $^2J_{Se-C}$ is invariant (63.3 Hz). The $CH_2$ resonances lie in the order C(1) < C(3)[C(4)] < C(2), this ordering resembling that of the $^{13}$C resonances in n-alkanes.[33] Except for $n = 1$, the $^1J_{Se-C}$ values are almost constant at *ca.* 60 Hz, and smaller $^2J_{Se-C}$ (*ca.* 6 Hz) have also been observed, the relative magnitude of the coupling being in agreement with other work.[34] A small $^3J_{Se-C}$ (4.4 Hz) was resolved in $MeSe[CH_2]_6SeMe$, but in $MeSe[CH_2]_{12}SeMe$ the overlapping resonances of the C(3)—C(6) methylene groups obscured any coupling to C(3). The δ ($CH_2$) value of 17.3 p.p.m. for $MeSeCH_2SeMe$ is lower than in the longer-backboned systems, and $^1J_{Se-C}$ is larger (83.9 Hz), effects paralleling those observed in the $^1$H n.m.r. spectra. For the tris-selenoether $(MeSeCH_2CH_2CH_2)_2Se$ the shifts and coupling constants are similar, although it is possible that the assignments of C(1) and C(3) in Table 2 should be reversed. The spectra of $(MeSeCH_2)_3CMe$ and $(MeSeCH_2)_4C$ are similar except that in the latter the methylene carbons appear to show two Se–C couplings (67.1 and 3.2 Hz). The former is readily assigned as $^1J_{Se-C}$, and the latter is probably a long-range coupling to a selenium three bonds away, observed as a result of the higher symmetry. The phenyl selenoethers show trends in shift positions and coupling constants for the backbone carbons similar to those for the methyl analogues. The aromatic carbon resonances were easily assigned, only the *ipso*- and *ortho*-carbon resonances showing Se–C coupling. The *ipso*-carbon resonance was sometimes weak, since this carbon carries no protons, and does not gain any nuclear Overhauser enhancement from proton noise decoupling. The $^1J_{Se-C}$ value is *ca.* 140 Hz, and $^2J_{Se-C}$ *ca.* 10 Hz. The $^{13}$C n.m.r. spectra of the aromatic regions for *o*-$C_6H_4(SeMe_2)_2$ and (especially) *o*-$C_6H_4(SePh)_2$ were complex, and have not been interpreted in detail. Thus for a series of compounds closely related in structure the $^{77}$Se n.m.r. chemical shifts and coupling constants are distinctive for individual species. This work also supports the use of the additive group effect for estimating chemical shift values.

1 2 3 3 2 1
$RSeCH_2CH_2CH_2CH_2CH_2CH_2SeR$

$CH_2$ positions in $RSe[CH_2]_6SeR$

## Experimental

Mass spectra were obtained with an A.E.I. MS 30 instrument at 70 eV using the direct insertion probe. The *m*/*z* values refer to $^{80}$Se peaks, and the intensities are not corrected for the other Se isotopes. $^1$H N.m.r. spectra were recorded for *ca.* 40% solutions in $CDCl_3$, relative to internal $Me_4Si$, with Perkin-Elmer R12 and R32 and Varian XL-100 spectrometers. $^{13}$C N.m.r. spectra were obtained at 22.5 MHz in $CDCl_3$ [except

**Table 2.** $^{13}$C N.m.r. data (δ values; $J_{Se-C}$ in Hz)

| | Me | C(1) [a] | C(2) | C(3—*n*) |
|---|---|---|---|---|
| $Me_2Se$ | 5.7 (61.0) | | | |
| $MeSeCH_2SeMe$ | 6.0 (63.3) | 17.3 (83.9) | | |
| $MeSe[CH_2]_2SeMe$ | 4.0 (63.3) | 24.9 (60.5) | | |
| $MeSe[CH_2]_3SeMe$ | 4.0 (63.3) | 24.8 (60.4) | 30.2 (5.9) | |
| $MeSe[CH_2]_6SeMe$ | 3.7 (63.3) | 25.1 (59.1) | 29.8 (6.2) | 29.4 (4.4) |
| $MeSe[CH_2]_{12}SeMe$ | 3.5 (63.3) | 25.1 (59.6) | 29.9 (6.2) | 29.5, 29.2, 28.9 |
| $MeSeCH{=}CHSeMe$ | 7.0 (59.1) | 123.9, $^1J_{Se-C}$ 103, $^2J_{Se-C}$ 16.3 | | |
| $(MeSeCH_2CH_2CH_2)_2Se$ | 4.1 (63.3) | 25.1 (61.9) [b] | 30.7 (7.4) | 23.7 (62.7) [b] |
| $(MeSeCH_2)_3CCH_3$ | 6.5 (63.3) | 38.0 (66.0) | 40.6 (4.5) | 25.3 |
| $(MeSeCH_2)_4C$ | 6.3 (61.9) | 35.1 (67.1, 3.2) | 43.6 (4.5) | |

| | Aromatic | | | | | | |
|---|---|---|---|---|---|---|---|
| | *ipso* | *ortho* | *meta* | *para* | C(1) [a] | C(2) | C(3) |
| $Ph_2Se$ | 131.4 (144.1) | 132.9 (11.3) | 129.3 | 127.0 | | | |
| $PhSeCH_2SePh$ | 130.9 (144.0) | 132.9 (10.4) | 129.1 | 127.6 | 21.1 (86.6) | | |
| $PhSe[CH_2]_2SePh$ | 132.5 [c] | 133.2 (10.1) | 129.3 | 127.3 | 27.3 (66.0) | | |
| $PhSe[CH_2]_3SePh$ | 131.4 (123.0) | 132.6 (10.4) | 129.0 | 126.8 | 27.4 (63.3) | 30.1 (6.6) | |
| $PhSeCH{=}CHSePh$ | 130.4 (141.5) | 132.1 (11.3) | 129.3 | 127.4 | 126.0, $^1J$ 104.0, $^2J$ 15.5 | | |
| $(PhSeCH_2)_3CCH_3$ | 131.0 [c] | 133.0 (10.9) | 129.1 | 127.1 | 40.2 (64.3) | 40.1 (5.0) | 25.6 |
| *o*-$C_6H_4Br(SeCH_3)$ | 135.1 (111.9) | 123.8 (25.2) [d] | *e* | *e* | 7.1 (66.0) [f] | | |
| *o*-$C_6H_4(SeCH_3)_2$ | 135.0 [c] | 133.0 (10.5) | 127.3 | | 8.0 (64.6) [f] | | |
| *o*-$C_6H_4(SePh)_2$ | ((128.2, 128.6, 129.8, 129.9, 132.9, 133.5, 135.0) [g] | | | | | | |

[a] C(1), C(2), C(3) refer to backbone carbon atoms, the numerals indicating position in relation to the selenium atom. [b] The assignments of the C(1) and C(3) signals are not unambiguous and may possibly be reversed. [c] *ipso*-Resonance too weak for $J_{Se-C}$ to be measured. [d] C–Br resonance. [e] Other ring carbon resonances not assigned. [f] Methyl signal. [g] Ring carbon resonances not assigned; $J_{Se-C}$ not identified.

for *o*-$C_6H_4(SePh)_2$, in $(CD_3)_2SO$], with a JEOL FX90 instrument, using a 30° pulse and a scan cycle time of 1 s, with proton decoupling throughout. $^{77}$Se N.m.r. spectra (also with $CDCl_3$ as solvent) were recorded with a JEOL FX90 instrument at 17.06 MHz, using external $Me_2Se$ as zero reference. A 45° pulse angle was used with the chemical shift range −150 to +1 000 p.p.m., with proton decoupling throughout (+ve δ values to high frequency of $Me_2Se$). Selenium powder, MeLi, and $Ph_2Se_2$ were obtained from Aldrich Chemical Co. Dimethyl diselenide was prepared from Se, $NaBH_4$, and MeI as described by Klayman,[22] and $Me_2Se$ from LiMeSe and MeI, in a similar manner to $MeSe[CH_2]_nSeMe$ (see later); *o*-$C_6H_4Br(SeMe)$ was prepared by the literature route,[35] as was $Ph_2Se$.[36]

Aqueous waste was treated with an excess of NaOCl solution before disposal; NaOCl solution is also useful for removing the odour of organoselenium materials from glass-ware.

All preparations were conducted under an atmosphere of nitrogen. Tetrahydrofuran was distilled from $LiAlH_4$ immediately before use, and ethanol distilled from magnesium ethoxide.

2,5-*Diselenahexane*.—Selenium powder (11.14 g, 0.142 mol) and THF (300 cm$^3$) were frozen (liquid nitrogen bath) and methyl-lithium in diethyl ether (Aldrich; 100 cm$^3$, 0.155 mol) was added. On warming to room temperature with stirring, the selenium dissolved to give a pale yellow solution. 1,2-Dichloroethane (6.97 g, 0.071 mol) was added and the mixture stirred for 1 h and refluxed for 15 min. After cooling to room temperature, the mixture was hydrolysed with water (200 cm$^3$), the organic phase separated, washed with $NaHCO_3$ and NaCl solutions, and dried ($Na_2SO_4$) overnight. The solvent was removed by distillation, and the residue fractionated *in vacuo*; yield 8.0 g (53%), b.p. 80 °C at 4.5 mmHg (lit.,[4] 88 °C at 8 mmHg); *m*/*z* 218 ($C_4H_{10}Se_2^+$, 29%), 190 (42), 175 (37), 123 (100), 109 (28), 107 (35), 95 (100), 94 (27), and 93 (70).

The other bis-selenoethers were prepared similarly: 2,4-diselenapentane (40%), b.p. 66 °C at 11 mmHg (lit.,[4] 76 °C at 12 mmHg), *m*/*z* 204 ($C_3H_8Se_2^+$, 52%), 189 (5), 109 (100), 94 (18), and 93 (40); 2,6-diselenaheptane (76%), b.p. 50 °C at 0.05 mmHg (lit.,[4] 102 °C at 8 mmHg), *m*/*z* 232 ($C_5H_{12}Se_2^+$, 29%), 217 (100), 202 (12), 190 (7), 175 (72), 137 (8), 121 (23), 109 (53), 95 (44), 94 (36), and 93 (53); 2,9-*diselenadecane* (50%), b.p. 112 °C at 0.3 mmHg (Found: C, 36.0; H, 6.8. $C_8H_{18}Se_2$ requires C, 35.3; H, 6.8%), *m*/*z* 274 ($C_8H_{18}Se_2^+$, 10%), 259 (3), 179 (13), 163 (16), 123 (6), 109 (20), 95 (7), and 55 (100); 2,15-*diselenahexadecane* (73%), recrystallised from methanol at low temperature (Found: C, 47.0; H, 8.6. $C_{14}H_{30}Se_2$ requires C, 47.2; H, 8.4%), *m*/*z* 358 ($C_{14}H_{30}Se_2^+$, 11%), 343 (17), 263 (10), 247 (13), 123 (9), 109 (15), and 55 (100).

1,1,1-*Tris*(*methylselenomethyl*)*ethane* was prepared from 1,1,1-tris(bromomethyl)ethane[38] (27%), b.p. 95 °C at 0.1 mmHg (Found: C, 27.2; H, 5.0. $C_8H_{18}Se_3$ requires C, 27.4; H, 5.1%), *m*/*z* 352 ($C_8H_{18}Se_3^+$, 13%) 337 (17), 163 (11), 149 (12), 109 (46), 93 (10), and 69 (100).

*Tetrakis*(*methylselenomethyl*)*methane* was prepared from tetrakis(bromomethyl)methane (Fluka) and isolated as a yellow viscous oil (10%) (Found: C, 24.5; H, 4.6. $C_9H_{20}Se_4$ requires C, 24.3; H, 4.5%), *m*/*z* 446 ($C_9H_{20}Se_4^+$, 10%), 431 (17) 163 (43), 147 (21), 109 (75), 95 (10), 93 (17), and 67 (100).

2,5-*Diselenahex*-3-*ene* [cis-1,2-*Bis*(*methylseleno*)*ethene*].—Selenium powder (11.14 g, 0.142 mol) and THF (300 cm$^3$) were frozen (liquid nitrogen bath), methyl-lithium in diethyl ether (100 cm$^3$, 0.155 mol) was added, and the mixture was allowed to warm to room temperature with stirring. Removal of the solvent by distillation left a light brown oil, which was dissolved in dry ethanol (300 cm$^3$). Sodium (3.2 g, 0.14 mol) was dissolved in the mixture, *cis*-1,2-dichloroethene (Aldrich) (6.14 g, 0.06 mol) was added dropwise, and the mixture was refluxed with stirring for 16 h. After cooling to room temperature, the mixture was hydrolysed with water (200 cm$^3$) and extracted into diethyl ether (100 cm$^3$). The organic phase was separated, washed with $NaHCO_3$ and NaCl solutions and dried ($Na_2SO_4$) overnight. The solvent was removed by distillation and the residue fractionated *in vacuo* (yield 24%); b.p. 60 °C at 5 mmHg (lit.,[37] 93 °C at 10 mmHg), *m/z* 216 ($C_4H_8Se_2^+$, 100%), 201 (47), 190 (33), 175 (48), 121 (17), 106 (16), 95 (41), 94 (17), and 93 (54).

1,2-*Bis(methylseleno)benzene*.—To a solution of anthranilic acid (11.7 g, 0.087 mol) and trichloroacetic acid (0.1 g) in THF (100 cm$^3$) at 0 °C was added pentyl nitrite (16.3 g, 0.139 mol) over 1—2 min, and the solution was stirred at room temperature for 2 h. On cooling to 10 °C, the mixture was filtered and washed with THF and 1,2-dichlorobenzene until the washings were colourless (CARE should be taken not to let the solid dry out as it is explosive when dry). The solid was made into a slurry with 1,2-dichlorobenzene (150 cm$^3$) and added to dimethyl diselenide (10.7 g, 0.057 mol) in 1,2-dichlorobenzene (50 cm$^3$), and the mixture was heated to reflux with stirring. After cooling, the solvent was removed by distillation *in vacuo* and the *residue* fractionated (yield 2.1 g, 27.9%), b.p. 102 °C at 0.1 mmHg (Found: C, 36.6; H, 4.0. $C_8H_{10}Se_2$ requires C, 36.4; H, 3.8%), *m/z* 266 ($C_8H_{10}Se_2^+$, 69%), 264 (61), 251 (59), 249 (55), 236 (45), 156 (20), and 91 (100).

3-*Methylselenopropan*-1-*ol*.—This was prepared from 3-chloropropan-1-ol by the route used for 2,5-diselenahexane, and isolated as a pale yellow oil (54.8%), b.p. 100 °C at 8 mmHg, $\delta_H$ 1.95 (m), 2.0 (s), 2.63 (t), 3.04 (s), and 3.71 (t).

2,6,9-*Triselenadecane* [*Bis*-(3-*methylselenopropyl*) *Selenide*].—To 3-methylselenopropan-1-ol (11.7 g, 0.076 mol) in pyridine (10 cm$^3$) was added toluene-*p*-sulphonyl chloride (Aldrich; 14.5 g, 0.076 mol) at 0 °C, and the mixture was stirred for 16 h. After careful hydrolysis with iced water (70 cm$^3$) a yellow oil was separated for use in the next step.

Sodium hydroxymethanesulphinate (10.8 g, 0.07 mol) was added with stirring to selenium powder (3 g, 0.038 mol) followed by sodium hydroxide (8 g) in ethanol (150 cm$^3$), and the mixture was heated to 50 °C. The foregoing yellow oil was then added and the mixture stirred at 50 °C for 16 h. After cooling, it was hydrolysed with water (100 cm$^3$) and extracted into diethyl ether. The organic phase was washed with $NaHCO_3$ and NaCl solutions and dried ($MgSO_4$); 2 h. The solvent was removed by distillation, and the residue pumped at 120 °C and 0.5 mmHg for 72 h to yield an orange *oil* (3.1 g, 30%) (Found: C, 27.6; H, 5.2. $C_8H_{18}Se_3$ requires C, 27.4; H, 5.1%), *m/z* 352 ($C_8H_{18}Se_3^+$, 12%), 337 (7), 245 (25), 217 (64), 137 (100), 121 (22), 109 (46), 95 (23), and 93 (22).

1,2-*Bis(phenylseleno)ethane*.—(i) To diphenyl diselenide (10.0 g, 0.032 mol) in THF (50 cm$^3$) was added lithium aluminium hydride (2.4 g, 0.064 mol) in THF (15 cm$^3$) and the mixture was refluxed for 1 h. 1,2-Dibromethane (6.0 g, 0.032 mol) was added dropwise and the mixture refluxed for 5 h. After cooling to room temperature, it was hydrolysed with saturated sodium chloride solution (200 cm$^3$); the aqueous phase was separated and washed with diethyl ether (2 × 50 cm$^3$), and the combined ethereal phases were dried ($Na_2SO_4$) overnight. The solvent was removed under reduced pressure and the residue treated with ethanol; at 0 °C a white crystalline precipitate gradually appeared (1.9 g, 17.3%).

(ii) To sodium ethoxide [from sodium (3.5 g, 0.15 mol)] in ethanol (200 cm$^3$) were added sodium hydroxymethanesulphinate (10 g, 0.065 mol), sodium hydroxide (6 g), and diphenyl diselenide (10 g, 0.032 mol). The mixture was stirred and heated at 50 °C for 15 min giving a colourless solution and a white precipitate of sodium salts. 1,2-Dibromoethane (6 g, 0.032 mol) was added dropwise, and the mixture refluxed for 20 h. After cooling, the mixture was hydrolysed with water (200 cm$^3$), and extracted into diethyl ether (150 cm$^3$). The organic layer was washed with $NaHCO_3$ and NaCl solutions and dried ($Na_2SO_4$) overnight. The solvent was then removed and the residue recrystallized from ethanol to give white *crystals* (4.36 g, 40%), m.p. 46 °C (Found: C, 49.7; H, 4.3. $C_{14}H_{14}Se_2$ requires C, 49.4; H, 4.1%), *m/z* 342 ($C_{14}H_{14}Se_2^+$, 5%), 314 (11), 185 (90), 158 (10), 157 (100), and 77 (56).

The other bis(phenylseleno)alkanes were prepared by route (ii).

1,1-Bis(phenylseleno)methane gave (from 5% ether–hexane) bright yellow crystals (40%), m.p. 30 °C (lit.,[6] 30.0 °C) (Found: C, 47.6; H, 3.8. $C_{13}H_{12}Se_2$ requires C, 48.7; H, 3.7%), *m/z* 328 ($C_{13}H_{12}Se_2^+$, 11%), 171 (63), 158 (9), 157 (9), 93 (24), 91 (100), and 77 (21).

1,3-*Bis(phenylseleno)propane* was isolated as an orange oil (73.5%) (Found: C, 51.2; H, 4.8. $C_{15}H_{16}Se_2$ requires C, 50.8; H, 4.5%), *m/z* 356 ($C_{15}H_{16}Se_2^+$, 37%), 314 (27), 279 (12), 234 (16), 199 (84), 171 (41), 158 (18), 157 (100), 93 (20), 91 (75), and 77 (88).

1,1,1-*Tris(phenylselenomethyl)ethane* was isolated as a yellow viscous oil (36%) from 1,1,1-tris(bromomethyl)ethane (Found: C, 51.0; H, 4.6. $C_{23}H_{24}Se_3$ requires C, 51.4; H, 4.5%), *m/z* 538 ($C_{23}H_{24}Se_3^+$, 23%), 461 (2), 383 (2), 314 (5), 237 (7), 171 (27), 157 (24), 93 (15), and 91 (100).

cis-1,2-*Bis(phenylseleno)ethene* was isolated as a brown oil (40%) from *cis*-1,2-dichloroethene (Found: C, 49.9; H, 3.4. $C_{14}H_{12}Se_2$ requires C, 49.7; H, 3.6%), *m/z* 340 ($C_{14}H_{12}Se_2^+$, 24%), 314 (24), 234 (22), 183 (68), 158 (38), 157 (100), 154 (71), 103 (20), 91 (33), and 77 (60).

1,2-*Bis(phenylseleno)benzene*.—To a solution of anthranilic acid (6.85 g, 0.05 mol) and trichloroacetic acid (0.1 g) in THF (100 cm$^3$) at 0 °C was added pentyl nitrite (17.4 g, 0.15 mol) over 2 min, and the mixture was stirred for 2 h. It was then cooled, filtered, and washed with THF and 1,2-dichlorobenzene until the washings became colourless. (CARE: This solid is explosive if allowed to dry.) The precipitate was made into a slurry with 1,2-dichlorobenzene (150 cm$^3$) and added to diphenyl diselenide (5 g, 0.016 mol); the mixture was refluxed with stirring for 0.5 h. The solvent was removed by vacuum distillation, and the residue dissolved in hot toluene (100 cm$^3$). The solution was filtered hot, the filtrate cooled to 0 °C, and sulphuryl chloride (15 cm$^3$, 0.19 mol) added; the solution was then stirred for 0.5 h at 0 °C and 1 h at room temperature. The precipitate was filtered off, washed with toluene, dried *in vacuo*, and added to zinc powder (2.6 g, 0.04 mol) in dry ethanol (100 cm$^3$); the mixture was stirred under reflux for 1 h, then filtered hot, and the residue was washed with ethanol and dichloromethane. Evaporating the filtrate to dryness yielded a brown oil which was dissolved in the minimum amount of ethanol. A light brown *precipitate* appeared after 2 weeks at 0 °C (0.26 g, 4.2%) (Found: C, 55.2; H, 3.7. $C_{18}H_{14}Se_2$ requires C, 55.7; H, 3.6%), *m/z* 390 ($C_{18}H_{14}Se_2^+$, 96%), 388 (98), 313 (7), 312 (4), 234 (34), 233(74), 232 (100), 157 (12), 154 (26), 152 (77), 91 (20), and 77 (48).

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