Synthesis, Properties, and Multinuclear (^1H, ^{13}C, ^{77}Se) Magnetic Resonance Studies of the Hybrid Selenide Ligands o-$C_6H_4(SeMe)Y$ (Y = NMe_2, PMe_2, $AsMe_2$, $SbMe_2$, OMe, and SMe)

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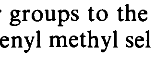
The reaction of *o*-bromophenyl methyl selenide with lithium dimethyl-phosphide, -arsenide, and -antimonide gave the seleno-phosphine o-$C_6H_4(SeMe)PMe_2$ (**2**), -arsine o-$C_6H_4(SeMe)AsMe_2$ (**3**), and -stibine o-$C_6H_4(SeMe)SbMe_2$ (**4**) respectively. The seleno-amine o-$C_6H_4(SeMe)(NMe_2)$ (**7**), -ether o-$C_6H_4(SeMe)OMe$ (**5**), and -sulphide o-$C_6H_4(SeMe)SMe$ (**6**) were obtained from methaneselenenyl bromide and RMgBr [R = o-$C_6H_4(OMe)$, o-$C_6H_4(NMe_2)$] or o-$C_6H_4(SMe)Li$. The bis-selenide o-$C_6H_4(SeMe)_2$ (**8**) is conveniently prepared from the polymeric selenide $-(o\text{-}SeC_6H_4Se)_n$, NaO_2SCH_2OH, and MeI. The *o*-substituted selenides have been characterised by mass spectrometry, ^1H, ^{13}C, and ^{77}Se n.m.r. spectroscopy, and for compounds (**2**), (**3**), (**4**), and (**8**) by the preparation of quaternary derivatives. The trends in the ^{77}Se n.m.r. chemical shifts and coupling constants are discussed.

We have recently shown that the ^{77}Se chemical shifts and one-bond coupling constants ($^1J_{M-Se}$) (M = Pt, Rh) of platinum metal bis-selenide complexes are sensitive parameters which respond in predictable ways to changes in the ligand geometry, substituents, chelate ring size, metal oxidation state, and *trans* ligand.[1-3] Bis-selenides are only moderate donors and this restricts the range of metal centres with which they produce stable complexes. In order to extend these studies to harder 3d metals, we report here the synthesis and detailed spectroscopic data on a series of hybrid bidentate ligands of general structure (**1**) in which the selenide group is combined with stronger σ-donors such as PMe_2 or $AsMe_2$.

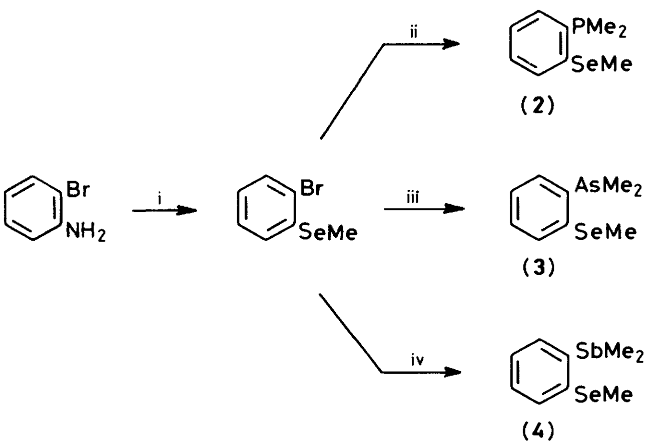


(**1**)

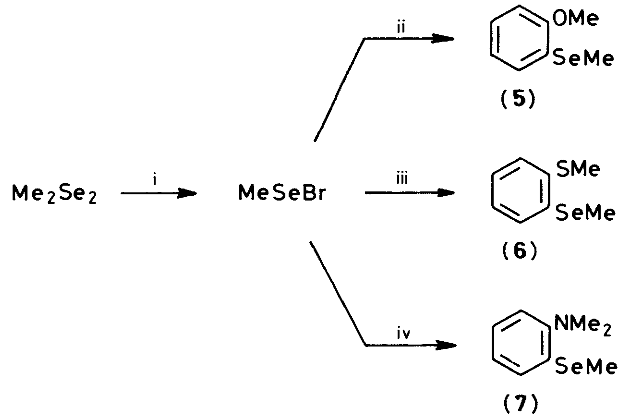
The phosphine–selenide hybrids o-$C_6H_4(PPh_2)(SeMe)$ and $P(o\text{-}C_6H_4SeMe)_3$ were reported some years ago.[4]

Results and Discussion

The syntheses of hybrid bidentate ligands involve the sequential attachment of the donor groups to the ligand backbone.[5] The intermediate *o*-bromophenyl methyl selenide o-$C_6H_4Br(SeMe)$ is readily prepared from o-$C_6H_4Br(NH_2)$, KSeCN, and iodomethane (Scheme 1). Heavy group VB donor groups are most readily introduced *via* the anions ER_2^- (E = P, As, Sb)[6] and the reaction of o-$C_6H_4Br(SeMe)$ with PMe_2^- or $AsMe_2^-$ in tetrahydrofuran (THF), or $SbMe_2^-$ in liquid ammonia, produced compounds (**2**), (**3**), and (**4**), respectively (Scheme 1) as air-sensitive colourless liquids. The amino selenide (**7**) was prepared by two routes from o-$C_6H_4Br(NMe_2)$.[6] Successive treatment of the latter with BuLi, Se, and MeI gave a poor yield (8%); other workers have observed only moderate yields of ArSeLi from ArLi and Se.[7,8] A better yield was obtained from the reaction between o-$C_6H_4(NMe_2)MgBr$ and methaneselenenyl bromide MeSeBr (40%) (Scheme 2). Carbanions (R^-) react directly with R'_2Se_2 to give RSeR′ and $R'Se^-$,[9,10] but this route incorporates a maximum of 50% of the selenium into the product and it also produces highly unpleasant selenols upon hydrolysis of the reaction mixture. As an alternative we used MeSeBr, prepared *in situ* in hexane from stoicheiometric amounts of Me_2Se_2 and Br_2, which was treated directly with the carbanion. Similar routes using o-$C_6H_4(OMe)MgBr$ and o-$C_6H_4(SMe)Li$[11] and MeSeBr gave compounds (**5**) and (**6**).

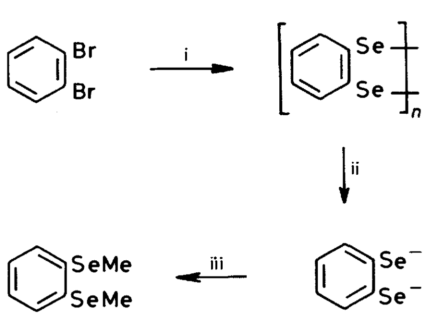


Scheme 1. *Reagents:* i, KSeCN–MeI; ii, $LiPMe_2$–THF; iii, $NaAsMe_2$–THF; iv, $NaSbMe_2$–liquid NH_3



Scheme 2. *Reagents:* i, Br_2; ii, o-$C_6H_4(MgBr)OMe$; iii, o-$C_6H_4(SMe)Li$; iv, o-$C_6H_4(NMe_2)MgBr$

The bis-selenide (**8**) has been prepared previously by the addition of Me_2Se_2 to benzyne,[12] although much biphenylene is also obtained. An alternative preparation is shown in Scheme 3. The poly-*o*-phenylenediselenide -(*o*-SeC_6H_4Se)-$_n$, obtained[13,14] from *o*-$C_6H_4Br_2$ and Na_2Se_2 in dimethylformamide, is cleaved by hydroxymethanesulphinic acid sodium salt (Rongalite, NaO_2SCH_2OH) to the dianion *o*-$C_6H_4(Se)_2^{2-}$ and this is alkylated with MeI. This reaction constitutes a convenient route for compounds of the type *o*-$C_6H_4(SeR)_2$ (R = alkyl). Attempts to cleave the polymer with $NaBH_4$–EtOH or $LiAlH_4$–THF followed by alkylation with MeI were unsatisfactory for reasons which are unclear.



(8)

Scheme 3. *Reagents:* i, Na_2Se_2–DMF; ii, Rongalite; iii, MeI

Properties.—The selenides (**2**)—(**8**) are colourless or very pale yellow liquids; compounds (**5**), (**6**), (**7**), and (**8**) are air stable, but (**2**), (**3**), and (**4**) oxidise rapidly at the group VB atom on exposure to air. Mass spectra were recorded to confirm the identity and 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%) leads to highly characteristic groups of peaks for the selenium-containing ions, but complicates analysis of overlapping peaks. The fragmentation patterns of the selenides (**2**)—(**8**) were generally as expected for 1,2-disubstituted benzenes containing groups VB or VIB groups.[6,12,15–17] Thus (**2**), (**3**), and (**4**) show prominent parent ions (M^+) and ions resulting from successive losses of three methyl groups, with (M^+ – Me) as the base peak in each case. The fragmentation of compound (**7**) is similar, but also shows that the ions corresponding to (M^+ – Me) lose one and then two further hydrogen atoms; a feature also observed in the spectra of *o*-$C_6H_4(NMe_2)_2$[15] and $PhNMe_2$,[18] attributable to the formation of ions containing $(\text{-N=CH})_2^+$ and $(\text{-N}\equiv\text{CH})^+$ units. The mass spectrum of *o*-diphenylphosphinophenyl methyl selenide has (M^+ – Me) as the base peak and prominent ions at *m*/*z* 356 (M^+), 183 ($C_{12}H_8P$), 152 ($C_{12}H_8$), 107 (C_6H_4P), and 91 (C_7H_7) – again similar to *o*-$C_6H_4(PPh_2)Y$ molecules.[16]

For *o*-C_6H_4(OMe)(SeMe), the parent ion is also the base peak, and (P – Me)$^+$ and $(C_6H_4OMe)^+$ are the major fragments. The mass spectra of *o*-$C_6H_4(SeMe)_2$ (**8**)[12] and *o*-$C_6H_4(SMe)_2$[17] have been reported and that of *o*-C_6H_4(SMe)(SeMe) (**6**) is much as expected, and in particular the presence of an ion at *m*/*z* 123 corresponding to cleavage of SeMe from the parent ion, and the absence of a similar (M^+ – SMe) ion reflects the relative C–Se and C–S bond strengths.

Compounds (**2**), (**3**), (**4**), and (**8**) were also characterised by the preparation of quaternary derivatives (see the Table). Compounds (**2**), (**3**), and (**4**) formed monomethiodide derivatives on heating with an excess of MeI in ethanol or acetone, the ^1H n.m.r. spectra confirming the group VB atom as the site of quaternisation. Aryl(alkyl)selenides generally do not react with MeI under these conditions,[19] but upon heating compound (**8**) with dimethyl sulphate under more forcing conditions, the diselenonium salt was obtained.

N.m.r. Spectra.—The ^1H n.m.r. spectra (see the Table) were unexceptional with δ_{MeSe} *ca.* 2.3 and $^2J_{Se\text{-}H}$ *ca.* 12 Hz. Quaternisation of the heteroatom *ortho* to the SeMe group has little or no effect on the δ_{MeSe} resonance, but in the selenonium salt of (**8**) δ_{Me_2Se} lies at 3.0, $^2J_{Se\text{-}H}$9.5 Hz. For compounds (**2**), (**3**), (**4**), (**6**), and (**8**) the $^{13}C\{^1H\}$ spectra show δ_{MeSe} at 7.0—8.5, $^1J_{Se\text{-}C}$ *ca.* 65—70 Hz, but in compounds (**7**) and (**5**) the resonance occurs at *ca.* 4.4—4.6 p.p.m., while $^1J_{Se\text{-}C}$ is not significantly changed.

Interestingly, in the ^{13}C n.m.r. spectrum of *o*-C_6H_4(SeMe)PPh_2, the Se*Me* resonance is a doublet with $^4J_{P\text{-}C}$ 10.6 Hz, whereas in *o*-C_6H_4(SeMe)PMe_2 only a sharp singlet (line width < 2 Hz) is observed. The aromatic carbon resonances in the ^{13}C n.m.r. spectra are not readily assigned, and the *ipso* carbon resonance was often too weak to measure $^1J_{Se\text{-}C}$ (*cf.* ref 12). The $^{31}P\{^1H\}$ n.m.r. spectra of compound (**2**) and *o*-C_6H_4(SeMe)PPh_2 (see the Table) are very similar to those of the

Table. ^1H, ^{13}C, and ^{77}Se n.m.r. data

Compd.	^1H N.m.r./p.p.m.[a] δ_{MeSe}	^1H N.m.r./p.p.m.[a] δ_{MeE}	$^{13}C\{^1H\}$/p.p.m.[b] δ_{MeSe}	$^{13}C\{^1H\}$/p.p.m.[b] δ_{MeE}	$^{77}Se\{^1H\}$/p.p.m.[c]	$^{31}P\{^1H\}$/p.p.m.[d]
o-C_6H_4(SeMe)(NMe_2)	2.2 (12.9)	2.7(s)	4.6 (66)	44.6(s)	173	
o-C_6H_4(SeMe)(PMe_2)	2.21 (11.8)	1.18(d) (2.5)	7.9 (70)	14.5(d) ($^1J_{PC}$ 13.3)	201	−46.3
o-C_6H_4(SeMe)($AsMe_2$)	2.49 (11.6)	1.4(s)	8.2 (66.5)	10.6(s)	187	
o-C_6H_4(SeMe)($SbMe_2$)	2.3 (12.0)	0.95(s)	7.7 (66)	10.3(s)	221.5	
o-C_6H_4(SeMe)(OMe)	2.2 (11.7)	3.8(s)	4.4 (65)	55.5(s)	148.5	
o-C_6H_4(SeMe)(SMe)	2.25 (11.6)	2.4(s)	7.0 (66)	17.0(s)	185	
o-$C_6H_4(SeMe)_2$	2.26 (11.7)		8.0 (64.5)		200	
o-C_6H_4(SeMe)Br	2.3 (12.3)		7.1 (66.0)		228	
o-C_6H_4(SeMe)(PPh_2)	2.25 (12.0)		8.5(d) ($^4J_{PC}$ 10.6)		189(d) ($^3J_{PSe}$ 158)	−10.7
o-C_6H_4(SeMe)(PMe_3)I	2.3 (12.0)	2.0(d) (6)			205	+29.4
o-C_6H_4(SeMe)($AsMe_3$)I	2.4 (12.0)	2.2(s)			207	
o-C_6H_4(SeMe)($SbMe_3$)I	2.4 (11.0)	1.9(s)			240	
o-$C_6H_4(SeMe_2)_2(MeSO_4)_2$[e]	3.0 (9.5)		27.3 (55)		348.5	

[a] In $CDCl_3$ relative to internal $SiMe_4$; also aromatics δ 6.9—7.6 ($^2J_{SeH}$/Hz in parenthesis). [b] In $CDCl_3$ relative to internal $SiMe_4$; also aromatics δ 123—136; individual resonances not assigned. $^1J_{SeC}$/Hz in parentheses on δ_{MeSe} values. [c] In $CDCl_3$ relative to external Me_2Se, high frequency positive convention. [d] In $CDCl_3$ relative to external 85% H_3PO_4, high frequency position convention. [e] δ_H 3.25(s), δ_C 52.7 in $MeOSO_3^-$.

sulphide analogues o-$C_6H_4(SMe)PMe_2$ (δ −46.7)[6] and o-$C_6H_4(SMe)(PPh_2)$ (δ −13.8).

Previous studies[20,21] of *para*- and *meta*-substituted methyl phenyl selenides have found a correlation between the ^{77}Se chemical shift [δ_{Se}] and the Hammett σ constant of the aromatic substituent, but for *ortho*-substituted derivatives the δ_{Se} values are irregular and the range larger. Thus the δ_{Se} values given in the Table range from 148.5 [compound (**5**)] to 228 (*o*-bromophenyl methyl selenide) to which the literature values[19] for o-$C_6H_4(SeMe)Y$ [Y = H δ 202; Y = Cl δ 201; Y = Me δ 162] could be added. Three effects may influence the δ_{Se} values in these *ortho* substituted methyl phenyl selenides: (*i*) an electronic effect of the substituent transmitted through the aromatic ring, (*ii*) a steric effect in which the *o*-substituent influences the tendency of the SeMe group to lie in the plane of the ring and hence affects the π-interaction between the selenium lone pairs and the benzene π-system,[20] and (*iii*) direct interaction 'through space' between the mutually *ortho* groups which will depend both upon the size and electronegativity of the substituent. Only (*i*) will contribute to δ_{Se} in the *meta*- and *para*-substituted analogues, whilst the varying importance of (*i*)—(*iii*) could account for the lack of a clear pattern in δ_{Se} for the *ortho*-analogues. It is interesting to consider the ^{31}P chemical shifts in the series o-$C_6H_4(PMe_2)Y$ (Y = H, OMe, NMe_2, PMe_2, $AsMe_2$, $SbMe_2$, SMe, or SeMe) which all lie at *ca.* −50 ± 5 p.p.m.,[6] compared with *ca.* 80 p.p.m. range in the selenides described here. Allowing for the greater chemical shift range observed in ^{77}Se n.m.r. (*ca.* 3 000 p.p.m.) *versus* ^{31}P (*ca.* 700 p.p.m.), it is still apparent that the varying influence of the *o*-Y substituent is markedly greater in the ^{77}Se n.m.r. spectra. A more detailed rationalisation of these trends must await further data, especially on the *para*- and *meta*-substituted analogues of the ligands in the Table.

o-Diphenylphosphinophenyl methyl selenide shows a large $^3J_{P-Se}$ coupling (158 Hz) whilst no similar coupling was resolved for compound (**2**), effects paralleling those in the ^{13}C n.m.r. spectra above. Quaternisation of the group VB atom in compounds (**2**), (**3**), or (**4**) deshields the selenium nucleus, shifting the δ_{Se} resonance to higher frequency by 4—20 p.p.m. – again in an irregular manner.

Conversion of o-$C_6H_4(SeMe)_2$ into o-$C_6H_4(SeMe_2)_2^{2+}$ results in a larger high-frequency shift (148.5 p.p.m.). Co-ordination of these ligands to metal ions also results in large high frequency shifts in δ_{Se}; these studies will be reported elsewhere.

Experimental

Many organoselenium compounds have persistent repulsive odours and all synthetic work must be performed in a good fume cupboard. All syntheses were conducted under a dry nitrogen atmosphere. ^{1}H, ^{13}C, and ^{77}Se n.m.r. spectra were recorded in $CDCl_3$ solutions on a Bruker AM 360 spectrometer,[1,2] referenced to $SiMe_4$ (^{1}H, ^{13}C) and Me_2Se (^{77}Se), using the high frequency positive convention. Other physical measurements were made as described previously.[12] Mass spectra; ions refer to ^{80}Se fragments, and intensities are uncorrected.

The preparations of o-$C_6H_4Br(SeMe)$[4] and o-$C_6H_4(PPh_2)(SeMe)$[4] were conducted as described elsewhere.

Methaneselenenyl Bromide.—Bromine (4.0 g, 0.025 mmol) was dissolved in dry hexane (75 cm^3) and the solution was added dropwise to a stirred solution of Me_2Se_2 (4.7 g, 0.025 mol) in hexane (100 cm^3) at 0 °C. The reagent, stored at 0 °C, was used within 2 h of preparation.

o-*Dimethylaminophenyl Methyl Selenide* (**7**).—*Method 1*. (*o*-Bromophenyl)dimethylamine (10 g, 50 mmol) in a mixture of dry diethyl ether (50 cm^3) and dry hexane (50 cm^3) was treated with butyl-lithium (1.4M solution in hexane; 35.7 cm^3) with vigorous stirring at 0 °C. The mixture was stirred for an additional 30 min as elemental selenium (4 g, 50 mmol) was added in several aliquots after which the mixture was allowed to stir for a further hour. Iodomethane (7.1 g, 50 mmol) was then added dropwise, and the mixture briefly heated to reflux, cooled to room temperature, and hydrolysed with water (100 cm^3).

The organic layer was separated and dried ($MgSO_4$) for 16 h. The solvent was removed by distillation, the residue fractionated under reduced pressure to yield a yellow oil (0.9 g, 8.3%), b.p. 60 °C/0.3 Torr, *m/z* 215 [($C_9H_{13}NSe^+$) 16%], 200 (10), 199 (8), 198 (10), 185 (8), 184 (9), 183 (8), 120 (24), and 91 (100) (Found: C, 50.7; H, 6.0; N, 6.5. $C_9H_{13}NSe$ requires C, 50.5; H, 6.1; N, 6.5%).

Method 2. This was a similar route to that described for compound (**5**), using the Grignard reagent from (*o*-bromophenyl)dimethylamine and MeSeBr (40% yield).

Dimethyl-(o-*methylselenophenyl*)*phosphine* (**2**).—A solution of $LiPMe_2$ in tetrahydrofuran (100 cm^3) was made from lithium (1 g, 0.14 mol) and PMe_2Ph (6.5 g, 0.047 mol) as described.[6] The dark red solution was added dropwise to o-$C_6H_4Br(SeMe)$ (8.8 g, 0.035 mol) in THF (150 cm^3) until the red colour was no longer discharged. The resulting solution was stirred for 1 h, heated to reflux, cooled, and hydrolysed with aqueous ammonium chloride (100 cm^3). The organic phase was separated, dried (Na_2SO_4), and the solvent removed by distillation. Fractionation of the residue under reduced pressure, gave the product (**2**) (3 g, 30%), b.p. 115 °C/2 Torr, *m/z* 232 [($C_9H_{13}PSe^+$) 9%], 215 (100), 200 (60), 156 (33), and 91 (50).

The monomethiodide o-$C_6H_4(SeMe)(PMe_3)I$ was obtained by refluxing the phosphine (**2**) (0.23 g, 1 mmol) and MeI (0.71 g, 5 mmol) in acetone (50 cm^3) for 3 h. The solution was concentrated to *ca.* 10 cm^3 under reduced pressure, cooled, and the resulting white crystalline precipitate filtered off, rinsed with diethyl ether, and dried (0.34 g, 91%), m.p. 268 °C (Found: C, 32.2; H, 4.2. $C_{10}H_{16}IPSe$ requires C, 32.2; H, 4.3%).

Dimethyl-(o-*methylselenophenyl*)*arsine* (**3**).—Sodium dimethylarsenide in THF (200 cm^3) was prepared from sodium wire (3.2 g, 0.14 mol) and iododimethylarsine (27.4 g, 0.12 mol),[6] and was added dropwise to *o*-bromophenyl methyl selenide (30 g, 0.12 mol) in THF (100 cm^3). The mixture was stirred for 30 min, hydrolysed, and the organic phase separated and dried (Na_2SO_4). The solvent was distilled off, and the residue was fractionated under reduced pressure to give the *arsine* (**3**) (10.8 g, 33%), b.p. 100 °C/1 Torr, *m/z* 276 [($C_9H_{13}AsSe)^+$ 26%], 261 (100), 246 (24), 231 (28), 156 (30), and 91 (59).

The monomethiodide was prepared as described for compound (**2**) (67% yield) (Found: C, 29.1; H, 3.7. $C_{10}H_{16}AsISe$ requires C, 28.8; H, 3.8%).

Dimethyl-(o-*methylselenophenyl*)*antimonide* (**4**).—Sodium (3.45 g, 0.15 mol) was dissolved in liquid ammonia (300 cm^3) and Me_3SbBr_2 (14 g, 0.04 mol) was added in several aliquots over 30 min. The solution was stirred for 3 h during which time it turned deep red, and then treated with dry ammonium chloride (2.1 g, 0.04 mol).[6] The liquid ammonia solution was then added dropwise to a solution of o-$C_6H_4Br(SeMe)$ (9.3 g, 0.037 mol) in dry THF (150 cm^3) cooled to −78 °C. The mixture was stirred for a further 1 h, allowed to warm to room temperature, and then worked up as for compound (**3**). Fractionation gave *the antimonide* (**4**) as a colourless air-sensitive oil (1.3 g, 11%), b.p. 86 °C/0.3 Torr, *m/z* 322 [($C_9H_{13}SeSb)^+$ 12%], 307 (100), 292 (38), 277 (33), 201 (32), and 91 (88).

The monomethiodide was prepared as for compound (**3**) and was recrystallised from acetone, m.p. 160 °C (Found: C, 25.8; H, 3.5. $C_{10}H_{16}ISbSe$ requires C, 25.9; H, 3.5%).

o-Methoxyphenyl Methyl Selenide (**5**).—To magnesium turnings (1.32 g, 0.055 mol) in dry diethyl ether (150 cm^3) was added dropwise *o*-bromoanisole (8.35 g, 0.050 mol) in dry diethyl ether (50 cm^3), over 30 min, with vigorous stirring, to give a clear solution. This was added slowly by transfer tube to methaneselenenyl bromide (50 mmol) in hexane (175 cm^3), prepared and used *in situ* at 0 °C. The mixture was refluxed briefly, cooled to room temperature, and hydrolysed with water (100 cm^3). The organic layer was separated and dried ($MgSO_4$) for 16 h. The solvent was removed by distillation and the residue fractionated under reduced pressure to yield a pale yellow oil (2.5 g, 25%), b.p. 85 °C/0.3 Torr (lit.,[22] 78 °C/0.3 Torr) (Found: C, 47.6; H, 4.8. Calc. for $C_8H_{10}OSe$: C, 47.8; H, 5.0%); *m/z* 202 [$(C_8H_{10}OSe)^+$ 100%], 187 (15), 157 (21), 107 (96), and 91 (36).

Methyl o-Methylthiophenyl Selenide (**6**).—*o*-Bromothioanisole (10.2 g, 0.05 mol) in dry diethyl ether (50 cm^3) and dry hexane (50 cm^3) was treated dropwise at 0 °C with butyllithium (1.4M, 35.7 cm^3) in hexane. The mixture was stirred at 0 °C for 1 h and then added to MeSeBr (0.05 mol) prepared as above. The resulting mixture was heated briefly to reflux, cooled, and worked up in the usual way. Fractionation gave the *selenide* (3.5 g, 32%), b.p. 89 °C/0.3 Torr (lit.,[23] 78 °C/0.5 Torr) (Found: C, 44.0; H, 4.6. Calc. for $C_8H_{10}SSe$: C, 44.2; H, 4.6%); *m/z* 218 [$(C_8H_{10}SSe)^+$ 43%], 203 (22), 123 (13), 108 (24), and 91 (100).

1,2-*Bis(methylseleno)benzene* (**8**).—Sodium ethoxide [from Na (0.92 g, 0.04 mol], sodium hydroxymethanesulphinate (3.1 g, 0.02 mol), sodium hydroxide (2 g), and poly-(*o*-diselenobenzene)[14] (2.34 g, 0.01 mol) were added successively to ethanol (120 cm^3) and the mixture was heated at *ca.* 50 °C for 15 min, when a colourless solution was produced. Iodomethane (2.48 g, 0.02 mol) was added dropwise and the mixture refluxed overnight. After the reaction had been cooled to room temperature, the mixture was hydrolysed with saturated brine (100 cm^3) and extracted with diethyl ether (100 cm^3). The organic extract was washed with saturated aqueous $NaHCO_3$ and brine and dried (Na_2SO_4). The solvent was distilled off and fractionation of the residue under reduced pressure gave *bis-selenide* (**8**) (1.25 g, 53%) (Found: C, 36.3; H, 3.8. $C_8H_{10}Se_2$ requires C, 36.4; H, 3.8%).

The *bis(methylsulphonate)* was prepared by gentle heating of compound (**8**) with an excess of Me_2SO_4, and was recrystallised from acetone, m.p. 159 °C (Found: C, 27.6; H, 4.2. $C_{12}H_{22}O_8S_2Se_2$ requires C, 27.9; H, 4.3%).

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