Structural studies on diaryl selenide dihalides in solution: molecular complex formation of substituted diphenyl selenides with bromine

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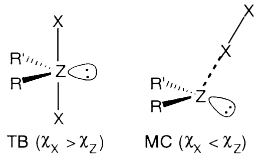
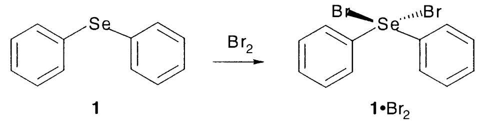
Diaryl selenides that yield molecular complexes (MC) with bromine are prepared by modulating the effective electronegativity of the selenium atom and the steric environment around the atom in diphenyl selenide (**1**) with various substituents at the 2-, 3- and/or 4-positions. Halogen induced ^{1}H and ^{13}C NMR chemical shifts of the diaryl selenides are examined. The chlorine and iodine adducts of the selenides are shown to be trigonal bipyramidal adducts (TB) and MC, respectively. In the case of bromine adducts, the structures of (3- and 4-$YC_6H_4)_2SeBr_2$ are demonstrated to be MC if Y is CN and NO_2, contrary to the general rule: they are TB if Y is less electron-withdrawing than the ethoxycarbonyl group. The CN and NO_2 groups increase the effective electronegativity of the Se atom in (3- and 4-$YC_6H_4)_2Se$ and do not give TB with bromine. The four chloro groups at all *meta*-positions in **1** are also effective for MC formation. However, 3,5-$(O_2N)_2C_6H_3SeBr_2Ph$ is TB. *Ab initio* MO calculations show that the structures of (3-$O_2NC_6H_4)_2Se$ and 3,5-$(O_2N)_2C_6H_3SePh$ are close to the C_2 and C_s symmetries, respectively, which reveals that the conformational change is also important when the structures of the bromine adducts are determined. The steric congestion must be more severe for TB formation than for MC formation. The structures of 2,6-$Cl_2C_6H_3SeBr_2C_6H_4Y$-*p* (Y = H and Br) are MC, which shows that the steric effect of 2,6-$Cl_2C_6H_3$ group is effective for MC formation. (2-$MeC_6H_4)_2SeBr_2$ and (2-$ClC_6H_4)_2SeBr_2$ are TB and MC, respectively: the electronic effect of the Cl group must play an additional role in the MC formation since the bulkiness of the Me and Cl groups are expected to be similar. The bromine adduct of (2,4,6-$Me_3C_6H_2)_2Se$ is also concluded to be MC: the steric effect of the four Me groups at the *ortho*-positions is large enough to give MC with bromine. The oxidation potentials (E_{ox}) of the diaryl selenides explain well the structures of the bromine adducts: the electronic effect is directly correlated with E_{ox} and the importance of the steric effect has been brought into sharp relief by E_{ox}. Results of MO calculations support the outline of the observations. The structural behavior of some halogen adducts such as 2,6-$Cl_2C_6H_3SeCl_2C_6H_4Y$-*p* (TB: Y = H and Br) is also discussed in some detail.

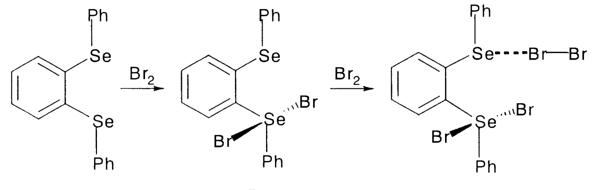
Introduction

It has been well established that diorganyl selenides such as diphenyl selenide (**1**) react with bromine, as well as chlorine and fluorine, to yield trigonal bipyramidal adducts (TB) with highly polar hypervalent bonds.[1,2] On the other hand, diorganyl selenides react with iodine to give molecular complexes (MC).[1,2] Mulliken has proposed a theory for MC based on quantum mechanics.[3] A theory for TB with hypervalent three center–four electron bonds (3c–4e) has also been proposed by Pimentel and Musher.[4a] The 3c–4e description of the X–Z–X bond in TB has been further developed by the preparation and characterization of a variety of compounds with the TB structure[1,2] and by theoretical calculations.[4] The structures of RZX$_2$R′, where Z = S, Se, Te and X = halogens *etc.*, are studied in some detail, in this line. Consequently, the character of the X–Z–X bond in TB is rather easily understood by the 3c–4e description.[1,2,4] Recently, the Z–X–X bond in RR′Z–X–X (MC) has also been proposed to be suitable for analysis by the 3c–4e model.[5] Although the examples of MC are growing, the numbers are not so many and the scope of the MC formation is not well established yet relative to the case of the TB formation.



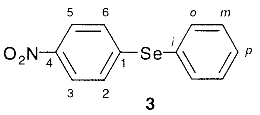


1 **1•Br$_2$**



2 **2•Br$_2$** **2•2Br$_2$**

The MC formation is the result of charge transfer (CT), within some limits, where electrons move from electron donors to acceptors in the complexes, $RSeX_2R'$. If CT from Se to X is large enough, TB adducts will form accompanied by the highly polar 3c–4e hypervalent X–Se–X bond.[2,4] The magnitude of CT from RSeR′ to X_2 is roughly estimated by the electronegativity[6] of Se (χ(Se)) and that of X (χ(X)). TB will form if χ(X) is larger than χ(Se), while the adducts will be MC when χ(X) is less than χ(Se) (general rule).[2] The bromine adducts of selenides are concluded to be TB based on the general rule. However, the adducts change from TB to MC if the effective electronegativity of Se (χ_{eff}(Se)) in RSeR′ increases sufficiently by modulating the electronic properties of the Se atom in the selenide. The adducts will be MC when χ_{eff}(Se) is larger than χ(X).[7] The steric congestion[8] is also important. It should be more severe for the TB formation than for the MC formation, since an Se atom in TB is four-coordinated whereas that in MC is three-coordinated. Indeed, the electronic and steric factors play an important role in stabilizing or destabilizing both TB and MC, but the magnitude must be larger for TB. This is our basic strategy to prepare diaryl selenides, especially variously substituted **1**, that yield MC with bromine.[9]



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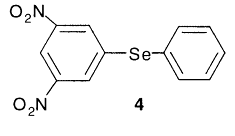

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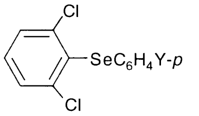
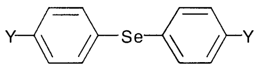
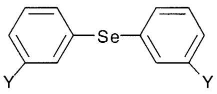


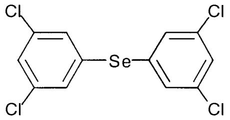
5 (Y = H), **6** (Y = Br)



7 (Y = Cl), **8** (Y = COOEt)
9 (Y = CN), **10** (Y = NO_2)



11 (Y = Cl), **12** (Y = CN)
13 (Y = NO_2)



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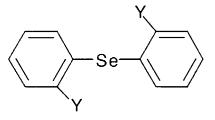
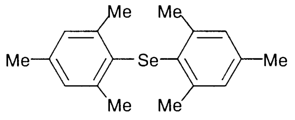


15 (Y = Me), **16** (Y = Cl)



17

The criteria distinguishing MC from TB adducts of the halogen adducts of aryl selenides in solutions based on the NMR chemical shifts are well established not only by the experimental results[2b,10] but also by theoretical calculations.[11] The MC formation of some bromine adducts of aryl selenides are reported based on the criteria; selenoxanthone,[7] selenanthrene[7] and 1-(phenylselanyl)-2-(phenyldibromoselanyl)benzene (**2**·Br_2).[11,12] The structure of **2**·Br_2 is TB. The tetrabromide, 1,2-($PhBr_2Se)_2C_6H_4$ (**2**·2Br_2), is obtained in the reaction of **2**·Br_2 with bromine. The structure of **2**·2Br_2 is TB for one of the $SeBr_2$ moieties and the other is MC, which is notated as (TB, MC).[11,12] Since **2**·Br_2 is a 2-phenyl(dibromo)selanyl derivative of **1**, it is recognized that a derivative of **1** reacts with bromine to give MC. The (TB, MC) formation of **2**·2Br_2 led us to the following working hypothesis: such substituted diphenyl selenides can be prepared[9] that yield MC with bromine if **1** is suitably modulated electronically[13] and/or sterically.[8] The phenyl(dibromo)selanyl group in **2**·Br_2 acts not only as a very strong electron-withdrawing group but also as a bulky group to the selanyl group at the 2-position of the diphenyl selenide. The electronic effect must increase the effective electronegativity of the selenium atom.

In order to demonstrate the formation of MC in the reaction of substituted diphenyl selenides with bromine, **1** is chemically modified to increase the effective electronegativity of the selenium atom and/or to increase the bulkiness around the atom. Here, we present the results of our investigations.

Results

Substituted diphenyl selenides (**3**–**17**), bearing various substituents at the 2-, 3- and/or 4-positions of **1**, are prepared,[6] together with their chlorine, bromine and iodine adducts. The ^1H and ^{13}C NMR chemical shifts (δ(H) and δ(C), respectively) have been measured. Aromatic carbons are numbered 1, 2, . . and 6, except for the Ph groups in **1** and **3**–**5** and the *p*-BrC_6H_4 group in **6**, in which carbons are named *i*, *o*, *m* and *p*. Aromatic protons are numbered or named the same as the carbons with which they are directly bonded.

Table 1 shows the halogen induced δ(H) and δ(C) chemical shifts of chlorine, bromine and iodine for 4-nitrophenyl phenyl selenide (**3**), 3,5-dinitrophenyl phenyl selenide (**4**), 2,6-dichlorophenyl phenyl selenide (**5**) and 2,6-dichlorophenyl *p*-bromophenyl selenide (**6**), together with δ(H) and δ(C) values of the parent selenides. Table 2 collects the halogen induced chemical shifts for $(4\text{-}YC_6H_4)_2SeX_2$ (Y = Cl (**7**), COOEt (**8**), CN (**9**), NO_2 (**10**)), $(3\text{-}YC_6H_4)_2SeX_2$ (Y = Cl (**11**), CN (**12**), NO_2 (**13**)) and $(3,5\text{-}Cl_2C_6H_3)_2SeX_2$ (**14**). Table 3 exhibits the halogen induced chemical shift values for $(2\text{-}YC_6H_4)_2SeX_2$ (Y = Me (**15**), Cl (**16**)) and $(2,4,6\text{-}Me_3C_6H_2)_2SeX_2$ (**17**). Table 4 shows oxidation potentials (E_{ox}) of some diaryl selenides,[14] together with the structures of their halogen adducts. Results of MO calculations performed using Gaussian 94[15] and/or 98[16] programs with the B3LYP/6-311+G(2d,p) method are shown in Table 5. Optimized structures of some selenides and the chlorine adducts are shown in Fig. 1.

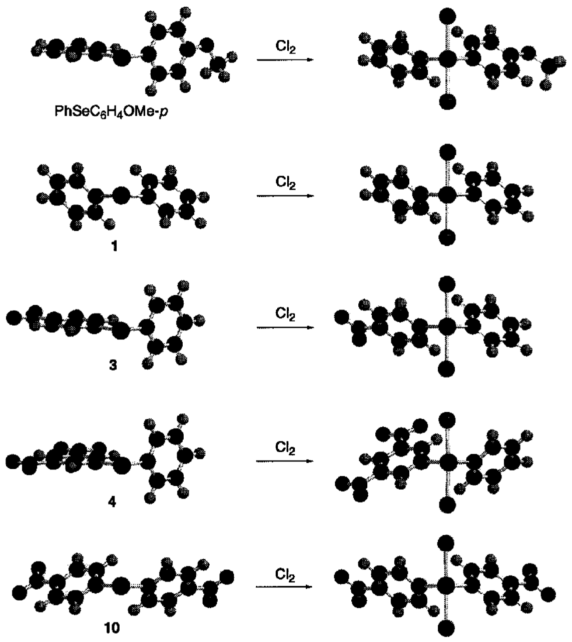


Fig. 1 Structures of some diaryl selenides and the chlorine adducts optimized with the B3LYP/6-311+G(2d,p) method.

Discussion

Structure of $ArSeX_2Ar'$ (X = Cl and I)

Before discussing the structures of diaryl selenide dibromides, it is worthwhile clarifying the structures of chlorine and iodine adducts of the selenides. The structures of the chlorine adducts of **3**–**17** in Tables 1–3 are concluded to be all TB. Large downfield shifts are observed for the C(1) (and C(*i*)) and C(4) (and C(*p*)) in the formation of the adducts. The shift values are *ca.* 10–12 and *ca.* 4–5 ppm, respectively, although the values are

Table 1 Halogen induced ^1H and ^{13}C NMR chemical shifts for **3**–**6** together with the chemical shifts of parent selenides[a,b]

Compd	H(2)	H(*o*)	C(1)	C(2) (C(6))	C(3) (C(5))	C(4)	C(*i*)	C(*o*)	C(*m*)	C(*p*)	Structure
3	7.35	7.60	143.1	129.6	123.8	146.1	127.1	135.8	129.9	129.3	Selenide
	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
3·Cl_2	0.85	0.37	5.7	1.7	0.6	3.0	14.6	−3.5	0.1	2.9	TB
3·Br_2	0.86	0.42	1.9	3.2	0.8	2.5	9.5	−2.7	0.4	2.6	TB
3·I_2	0.00	0.00	−0.8	0.2	0.1	0.2	−0.2	−0.3	0.1	0.2	MC
4	8.36	7.68	138.8	129.1	148.5	116.1	126.1	135.9	130.4	130.1	Selenide
	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
4·Cl_2	0.82	0.48	8.3	1.4	0.2	5.3	15.2	−4.8	0.6	2.8	TB
4·Br_2	0.88	0.47	5.0	3.1	−0.5	5.3	5.8	−3.7	0.3	2.6	TB
4·I_2	0.00	0.06	0.0	0.0	0.1	0.1	−0.1	−0.1	0.1	0.0	MC
5		7.36	130.4	141.7	128.3	130.5	131.2	130.8	129.1	126.8	Selenide
		0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
5·Cl_2		1.17	11.2	−6.5 (−6.6)	1.8 (3.3)	1.8	8.3	2.3	−0.2	5.1	TB
5·Br_2		0.01	[c]	−0.5	0.2	0.4	[c]	−0.1	0.2	0.7	MC
5·$2Br_2$[d]		0.02	−0.6	−1.4	0.6	1.2	−1.0	−0.6	0.5	1.5	MC
5·I_2		0.00	0.0	0.0	0.1	0.1	−0.1	−0.1	0.1	0.0	MC
6		7.34	130.2	141.8	128.5	130.9	132.1	132.6	132.3	121.2	Selenide
		0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
6·Cl_2		1.01	11.5	−6.6 (−6.8)	1.8 (3.2)	1.6	8.1	2.1	−0.3	6.0	TB
6·$2Br_2$		0.01	−0.2	−0.2	0.1	0.1	−0.3	0.0	0.1	0.2	MC
6·I_2		0.00	0.0	0.0	0.0	0.1	−0.1	0.0	0.0	0.0	MC

[a] Chemical shifts of selenides (δ) are given relative to TMS and the halogen induced chemical shifts ($\Delta\delta$) are measured with respect to their parent selenides. [b] In $CDCl_3$. [c] Not observed due to broadening. [d] At −30 °C.

Table 2 Halogen induced ^1H and ^{13}C NMR chemical shifts for **7**–**14** together with the parent selenides[a,b]

Compd	H(2)	H(3)	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	Structure
7	7.34	7.26	128.9	134.2	129.5	133.8			Selenide
	0.00	0.00	0.0	0.0	0.0	0.0			
7·Cl_2	0.60	0.25	11.5	−1.6	0.4	4.7			TB
7·Br_2	0.61	0.22	7.8	−0.7	0.8	4.5			TB
7·I_2	0.02	0.03	−0.6	−0.2	0.2	0.6			MC
8	7.49	7.94	136.6	132.4	130.3	129.6			Selenide
	0.00	0.00	0.0	0.0	0.0	0.0			
8·Cl_2	0.60	0.23	10.1	−1.2	0.3	3.9			TB
8·Br_2	0.62	0.17	6.1	−0.1	0.5	3.6			TB
8·I_2	0.02	0.00	−0.5	−0.1	0.1	0.5			MC
9	7.56	7.56	136.5	133.1	132.8	111.6			Selenide
	0.00	0.00	0.0	0.0	0.0	0.0			
9·Cl_2	0.60	0.28	10.6	−1.1	0.4	4.5			TB
9·Br_2	0.00	0.00	−0.1	0.0	0.0	0.2			MC
9·I_2	0.01	0.01	−0.1	0.0	0.0	0.1			MC
10	7.61	8.16	138.8	133.2	124.5	147.6			Selenide
	0.00	0.00	0.0	0.0	0.0	0.0			
10·Cl_2	0.64	0.26	9.8	−0.6	0.4	2.0			TB
10·Br_2	0.00	0.00	−0.1	0.0	0.0	0.0			MC
10·I_2	0.00	0.00	−0.1	−0.1	0.0	0.0			MC
11	7.44		131.9	132.6	135.0	127.9	130.4	131.0	Selenide
	0.00		0.0	0.0	0.0	0.0	0.0	0.0	
11·Cl_2	0.53		11.3	−1.6	0.4	4.3	0.2	−1.7	TB
11·Br_2	0.55		6.8	−0.9	0.7	4.2	0.4	−0.5	TB
11·I_2	0.01		−0.5	−0.1	0.1	0.4	0.1	−0.1	MC
12	7.72		131.5	136.0	113.9	131.5	130.2	137.2	Selenide
	0.00		0.0	0.0	0.0	0.0	0.0	0.0	
12·Cl_2	0.60		12.3	−1.4	0.6	3.9	0.4	−2.1	TB
12·Br_2	0.01		−0.2	0.0	0.1	0.1	0.0	−0.1	MC
12·I_2	0.00		−0.2	0.0	0.0	0.1	0.0	0.0	MC
13	8.34		131.6	127.6	148.6	123.0	130.3	138.8	Selenide
	0.00		0.0	0.0	0.0	0.0	0.0	0.0	
13·Cl_2	0.57		12.5	−1.2	−0.2	3.9	0.6	−2.4	TB
13·Br_2	−0.01		0.0	0.1	0.1	0.1	0.1	−0.1	MC
13·I_2	−0.01		−0.1	0.0	0.0	0.1	0.1	−0.1	MC
14	7.32		132.2	130.9	135.7	128.3			Selenide
	0.00		0.0	0.0	0.0	0.0			
14·Cl_2	0.60		11.6	−1.7	0.5	4.2			TB
14·Br_2	0.61		−0.2	−0.1	0.1	0.7			MC
14·I_2	0.02		−0.1	0.0	0.0	0.1			MC

[a] Chemical shifts of selenides (δ) are given relative to TMS and the halogen induced chemical shifts ($\Delta\delta$) are measured with respect to their parent selenides. [b] In $CDCl_3$.

out of the ranges if the selenides are unsymmetrical such as **3**–**6** or if Y is strongly electron-withdrawing, such as **10**. The iodine adducts are all MC. The signals due to C(1) (and C(*i*)) and C(4) (and C(*p*)) are shifted downfield and upfield, respectively. The upfield shifts of *ipso*-carbons are characteristic of MC formation. Since the MC adducts are in equilibrium with the

Table 3 Halogen induced ^{1}H and ^{13}C NMR chemical shifts for **15**–**17** together with the parent selenides[a, b]

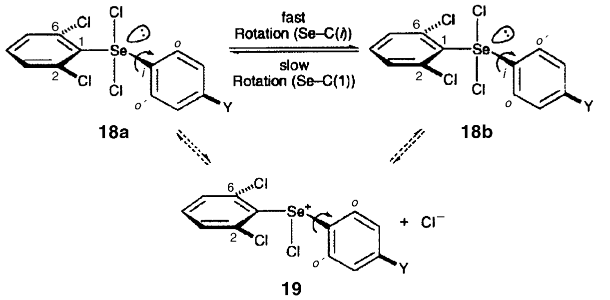
Compd	H(2)	H(3)	H(6)	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	Structure
15	2.39[c]	7.17	7.23	131.2	139.7	130.1	127.4	126.6	133.0	Selenide
	0.00[c]	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0	
15·Cl_2	0.46[c]	0.23	0.56	11.1	−1.8	1.0	5.0	0.6	−1.5	TB
15·Br_2	0.30[c, d]	0.22	0.55	3.5	−1.6	1.7	4.9	1.1	−1.2	TB
15·I_2	0.01[c]	0.03	0.02	−1.0	−0.2	0.4	0.8	0.4	0.0	MC
16		7.18	7.39	131.9	132.6	135.0	127.9	130.4	131.0	Selenide
		0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0	
16·Cl_2		0.28	0.64	11.8	−2.8	1.8	3.7	0.5	−2.3	TB
16·Br_2		0.05	0.05	−0.9	−0.1	0.4	1.1	0.4	−0.2	MC
16·I_2		0.00	0.04	−0.3	0.0	0.1	0.2	0.0	0.0	MC
17	2.24[c]	6.82		129.3	141.2	128.8	136.8			Selenide
	0.00[c]	0.00		0.0	0.0	0.0	0.0			
17·Cl_2	0.45[c]	0.18		10.3	−1.2	−0.2	3.9			TB
17·Br_2	−0.01[c, e]	0.00		−0.5	−0.1	0.1	0.4			MC
				0.7	−0.2	0.2	0.7			
17·I_2	−0.01[c]	0.00		0.0	0.1	0.1	0.2			MC

[a] Chemical shifts of selenides (δ) are given relative to TMS and the halogen induced chemical shifts ($\Delta\delta$) are measured with respect to their parent selenides. [b] In $CDCl_3$. [c] Methyl group. [d] At −30 °C. [e] At −20 °C.

Table 4 Oxidation potentials of ArSeAr′[a] together with the structures of $ArSeX_2Ar'$ (X = Cl, Br and I)

	Structure of adduct				
Selenide	X = Cl	Br	I	E_{ox}/V	
Di-4-anisyl selenide	TB	TB	MC	1.65	(1.22)[b]
Di-4-tolyl selenide	TB	TB	MC	1.81	(1.32)[b]
1	TB	TB	MC	1.86	(1.38)[b]
7	TB	TB	MC	2.00	(1.44)[b]
8	TB	TB	MC	2.00	(1.54)[b, c]
3	TB	TB	MC	2.08	
4	TB	TB	MC	2.18	
12	TB	MC	MC	2.19	
9	TB	MC	MC	2.22	
13	TB	MC	MC	2.23	
10	TB	MC	MC	2.27	(1.76)[b]
15	TB	TB	MC	1.89	
17	TB	MC	MC	1.92	
5	TB	MC	MC	2.09	
16	TB	MC	MC	2.13	

[a] Oxidation potentials are given *versus* an Ag/AgI reference electrode with the ferrocene redox pair as a standard, measured in MeCN containing 0.1 M Et_4NClO_4 as a supporting electrolyte with a Pt electrode. [b] Ref. 14. [c] The value for $Se(C_6H_4COOH)_2$.



Scheme 1 Mechanism for the site exchange of the 2,6-dichlorophenyl plane in **5**·Cl_2 and **6**·Cl_2. The conformers are shown by **18a** and **18b** and an ionic species by **19**.

components, the magnitude of the observed shift values are governed not only by the intrinsic chemical shifts of the MC but also by the equilibrium (dissociation) constants of the adducts ($ArSeI_2Ar'$).[7,17]

The NMR signals revealed some structural features of the chlorine adducts. Both C(2) and C(3) (or C(6) and C(5)) signals of **5**·Cl_2 are observed as two types. Their chemical shifts, half-width values and integrations do not change with excess chlorine. The results show that the rotation of the 2,6-dichlorophenyl plane in **5**·Cl_2 around the Se–C(1) bond is restricted relative to the NMR time scale, as shown by **18a** and **18b** in Scheme 1. The plane must be locked almost perpendicular to the hypervalent Cl–Se–Cl bond due to the bulkiness of the chlorine atoms at the 2,6-positions. Consequently, the phenyl ring is placed nearly parallel to the hyprvalent bond, and it can rotate essentially freely under the conditions. The structure around the Se atom in **6**·Cl_2 is similar to that in **5**·Cl_2: the C(2) and C(3) (or C(6) and C(5)) signals of the 2,6-dichlorophenyl group in **6**·Cl_2 also gave two sets of data.

Although the ^{13}C NMR spectra gave little information on the dynamic behaviour of **5**·Cl_2 and **6**·Cl_2, δ(H) values shed light on this behaviour of the adducts. The δ(H(3)) and δ(H(5)) signals in **5**·Cl_2 are observed as a very broad singlet at an ambient NMR probe temperature of *ca.* 23 °C when measured at 300 MHz. The signals show a B_2 pattern in AB_2 at 45 °C. The behaviour of **6**·Cl_2 is very close to that of **5**·Cl_2. No noticeable differences are observed in the temperature and solvent dependences (C_6D_6 *vs.* $CDCl_3$) between **5**·Cl_2 and **6**·Cl_2. The results are in accordance with a mechanism involving rotation around the Se–C(1) bond. Rotation in an ionic species, such as **19**, formed by Se–Cl bond scission, is unlikely (Scheme 1). The contribution from the dissociation of **5**·Cl_2 and **6**·Cl_2 to the components would also be negligible under these conditions.[18]

The rotation around the Se–C(1) bonds in **17**·Cl_2 is also expected to be restricted due to the steric hindrance of the four methyl groups at all *ortho*-positions. However, only one set of signals is observed for C(2) and C(3) (or C(6) and C(5)) as shown in Table 3. These results show that the activation energy of the rotation around the Se–C(1) bond in **17**·Cl_2 is smaller relative to that in **5**·Cl_2. There are two posibilities for the smaller activation energy in **17**·Cl_2: one is the stabilization of the transition state and the other is the destabilization of the ground state. The latter is often observed in the rotational barrier of very crowded molecules.[19] While the Cl–Se–Cl bond in **17**·Cl_2 could have greater stability than that of **5**·Cl_2 due to the electron-donating six methyl groups, the steric hindrance in **17**·Cl_2 must be greater than that in **5**·Cl_2. Therefore, it is more plausible that the methyl groups at all *ortho*-positions in **17**·Cl_2 destabilize the ground state.

Next, we discuss the magnitude of the chlorine induced chemical shifts. The downfield shifts of C(1) and C(*i*) in **5**·Cl_2 and **6**·Cl_2 were 11.2–11.5 and 8.1–8.3 ppm, respectively, and those of C(4) and C(*p*) were 1.6–1.8 and 5.1–6.0 ppm, respectively. These results show that the downfield shifts of C(1) and C(*i*) of aryl rings perpendicular to and parallel to the Cl–Se–Cl

Table 5 Energies of ArSeAr′, $ArSeCl_2Ar'$ (TB) and $ArSeBr_2Ar'$ (TB) together with Cl_2, Br_2 and **1**·Cl_2 (MC), calculated with the B3LYP/6-311+G(2d,p) method[a]

	X	Cl		Br	
$ArSeX_2Ar'$	Null *E*(au)	*E*(au)	Δ*E*/kJ mol^{-1} [b]	*E*(au)	Δ*E*/kJ mol^{-1} [b]
1·X_2	−2864.9713	−3785.4266	96.3	−8013.2666	50.3
4-$MeOC_6H_4SeX_2Ph$	−2979.5316	−3899.9880	99.2	−8127.8283	53.6
3-$O_2NC_6H_4SeX_2Ph$	−3069.5407	−3989.9919	85.8	−8217.8317	40.8
3·X_2	−3069.5428	−3989.9919	74.8	[c]	
4·X_2	−3274.1050	−4194.5522	74.8	−8422.3917	27.8
10·X_2	−3274.1090	−4194.5558	74.1	−8422.3954	27.2
5·X_2	−3784.2108	−4704.6527	61.2	−8932.4924	14.6
(2,6-$Me_2C_6H_3)_2SeX_2$	−3022.2764	−3942.7143	50.7	−8170.5535	2.6
1·X_2 (MC)	−2864.9713	−3785.4031	34.7	[c]	

[a] $E(Cl_2) = -920.4186$ au and $E(Br_2) = -5148.2761$ au. 1 au (atomic unit) = 1 hartree = 4.360×10^{-18} J. [b] $\Delta E = [E(ArSeAr') + E(X_2)] - E(ArSeX_2Ar')$. [c] Not optimized due to convergence failure in the SCF.

bond are *ca.* 11 and 8 ppm, respectively, while those of C(4) and C(*p*) are less than 2 and 5–6 ppm, respectively. The chlorine induced chemical shifts of the aryl C(1) and C(4) carbons become larger and smaller when the π-orbitals of the aryl ring are parallel to the Cl–Se–Cl bond, respectively. The average values for carbons at the 1- and *ipso*-positions and 4- and *para*-positions are estimated to be 9.7–9.8 and 3.4–3.8 ppm, respectively. The observed chlorine induced chemical shifts for the corresponding carbons in Tables 1–3 are close to or slightly larger than the average values, except for C(4) of **10**·Cl_2. The smaller chlorine induced chemical shifts observed in **10**·Cl_2 is the result of the saturation effect by the strong electron-withdrawing nitro groups in the formation of the highly polar $Cl^{\delta-}$–$Se^{\delta+}$–$Cl^{\delta-}$ bond.

The chemical shift values of the *ortho*-carbons of aryl rings perpendicular and parallel to the Cl–Se–Cl bond are −6.5 to −6.8 and 2.1–3.2 ppm, respectively, whereas those of the *meta*-carbons are 1.8–3.3 and −0.2 to −0.3 ppm, respectively, as observed in **5**·Cl_2 and **6**·Cl_2. The average values for *ortho*- and *meta*-carbons are estimated to be −1.6 to −2.4 and 0.7–1.6 ppm, respectively. Most of the chlorine induced chemical shifts of the *ortho*- and *meta*-carbons are observed in these ranges.

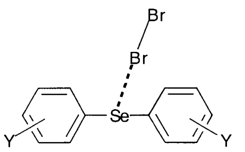
The chlorine induced chemical shifts for the *ortho*-protons of the phenyl and the *p*-bromophenyl groups in **5**·Cl_2 and **6**·Cl_2 are *ca.* 1.2 ppm when they are nearly parallel to the Cl–Se–Cl bond. Since the values for **5**·Br_2 are equal to those for **6**·Br_2, it is evident that they are mainly governed by the anisotropic effect of the hypervalent X–Se–X bonds, although the large electron-withdrawing ability of the group cannot be ignored. Those for the phenyl groups in $ArSeX_2Ar$ (X = Cl, Br) are 0.6–0.8 ppm as shown in Tables 1–3, and are 0.5–0.7 times larger than those of **5**·X_2 and **6**·X_2 (X = Cl, Br).

The chlorine induced δ(C(1)) and δ(C(*i*)) chemical shift values also change dramatically in TB formation depending on the substituents Y in the substituted diphenyl selenides: the values for **3**·Cl_2 are 5.7 and 14.6 ppm, respectively, for example. The importance of the conformational change from a selenide to its adduct is supported by *ab initio* MO calculations performed with the B3LYP/6-311+G(2d,p) method. The optimized structures of some selenides and their chlorine adducts are shown in Fig. 1 (for details, see MO Calculations section, below). The conformation of selenides is affected greatly by the electronic effect of Y. Although the conformation of symmetrical selenides is expected to be of C_2 symmetry, that of the unsymmetrical ones will be close to the C_s symmetry. The filled p-type lone pair orbital of Se in ArSePh is parallel to the π-orbitals of the Ar group, if Ar has an electron-withdrawing Y substituent, but the lone pair orbital is parallel to the π-orbitals of the Ph group if Y is electron-donating. The interactions between the lone pair orbital and the π-orbitals will stabilize the selenides in the predicted cases more than the inverse cases. However, the structures will be close to C_2 symmetry when TB adducts are formed mainly by steric constraints. The conformational change in the formation of TB must be responsible for the unique Y dependence of the chlorine induced chemical shifts.

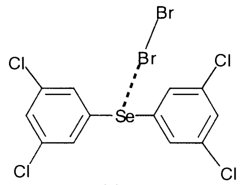
The iodine induced δ(C(1)) and δ(C(*i*)) values in MC formation also dramatically change depending on Y: the values for **3**·I_2 are −0.8 and −0.2 ppm, respectively, for example. It is worthwhile commenting that the halogen induced chemical shifts by chlorine and iodine are just the opposite in both sign and magnitude. The conformational change that occurs in MC formation is responsible for the phenomena. The position of the Se atom in the sequence of the X–Y–Z 3c–4e bond must also be important:[5] the Se atom is located at the center of the Cl–Se–Cl bond in **3**·Cl_2 but is at the terminal position of the Se–I–I bond in **3**·I_2.

Structure of $ArSeBr_2Ar'$

Electronic requirements for MC formation. The C(1) (and C(*i*)) signals of the bromine adducts of **3**, **4**, **7**, **8**, **11** and **15**, among **3**–**17**, are shifted downfield relative to those of the parent selenides. The structures of these bromine adducts must be TB. The electron-withdrawing ability of the two ethoxycarbonyl groups in **8** is not large enough for MC formation with bromine: disubstituted diphenyl selenides[13] at the 3,3′- or 4,4′-positions give TB adducts with bromine, if the electron-withdrawing ability of the substituent is less than that of the ethoxycarbonyl group.



9•Br_2 (Y = 4-CN), **10**•Br_2 (Y = 4-NO_2)
12•Br_2 (Y = 3-CN), **13**•Br_2 (Y = 3-NO_2)

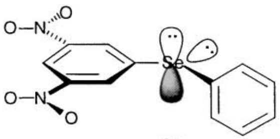


14•Br_2

On the other hand, upfield shifts were observed for C(1) (and C(*i*)) in **5**·Br_2, **6**·Br_2, **9**·Br_2, **10**·Br_2, **12**·Br_2, **14**·Br_2, **16**·Br_2 and **17**·Br_2: The structures must be MC. That of **13**·Br_2 must also be MC, although the upfield shifts are not explicitly recorded. Diaryl selenides with cyano or nitro groups at the 3,3′- or 4,4′-positions yield MC with bromine: the groups are sufficiently electron-withdrawing for MC formation. The four chloro groups at all the *meta*-positions in **14** are also effective for MC formation with bromine.

Why are **10**·Br_2 and **13**·Br_2 MC, while **4**·Br_2 being TB? The energy difference between the TB adduct and the components, Δ*E*, defined in the MO Calculations section, is evaluated to be only slightly larger for **4**·Br_2 than for **10**·Br_2 by MO calculations. A similar trend is also predicted for the chlorine adducts (see Table 5). Although the observed ΔE values are too small to be supported by calculations, the two nitro groups in **4** do not give MC with bromine under the experimental conditions. Since the two nitro groups in **4** are substituents of the same phenyl ring, the electron-withdrawing effect of the nitro groups would be saturated more strongly in **4** than in **10** and **13**.

The conformation of **4** must also play an important role for MC not to be given with bromine. The conformation of **4** is very close to C_s symmetry but that of **4**·Cl_2 is close to C_2 symmetry (Fig. 1). That of **4**·Br_2 must also be close to C_2 symmetry. The electron-withdrawing ability of the 3,5-dinitrophenyl group is a maximum in the C_s symmetry, as shown in **20**, since



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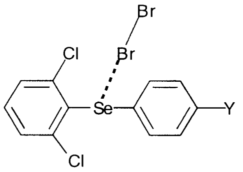
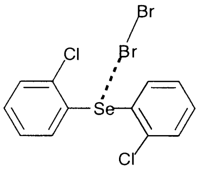
the p-type orbitals of the nitro groups are parallel to the p-type lone pair orbital of the Se atom. However, the effect is reduced in the C_2 symmetry. If the phenyl group can supply electrons to the bromine atoms through the Se atom, the hypervalent Br–Se–Br bond will be formed. The effect of the electron donation in **4**·Br_2 (TB) will be larger for the C_2 symmetry relative to the C_s symmetry (see **20** for the selenide part in **4**·Br_2). On the other hand, the conformations of **10** and **10**·Cl_2 (TB) are predicted to be of C_2 symmetry. Those of **13** and **13**·Cl_2 (TB) are also of C_2 symmetry, although these are not shown in Fig. 1. Indeed, the conformational changes around the Se atom between **4** and **4**·Cl_2 (TB) are large, but they are very small for **10** and **13**. Such a delicate change in the conformation of **4** relative to **10** and **13** in the reaction with bromine makes **4**·Br_2 TB.

The steric effect on the structures of **5**·Br_2, **6**·Br_2, **15**·Br_2, **16**·Br_2 and **17**·Br_2 will be discussed in the next section.

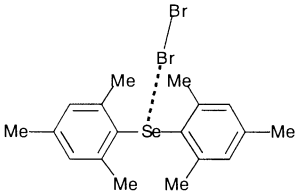
Steric requirements for MC formation. The structures of **5**·Br_2, **6**·Br_2 and **16**·Br_2 are demonstrated to be MC whereas those of **7**·Br_2, **11**·Br_2 and **15**·Br_2 are TB, judging from the bromine induced C(1) (and C(*i*)) chemical shifts. Although the two chloro groups at the 3,3′- and 4,4′-positions in **7** and **11** do not work effectively for the MC formation with bromine, the groups at the 2,2′-positions in **5**, **6** and **16** do effectively. These results show that the steric effect is also important for MC formation with bromine. Since the coordination number is four for TB but is three for MC, the steric congestion must be more severe for TB than for MC. On the other hand, **15**·Br_2 is TB: MC formation of **16**·Br_2 compared with TB formation of **15**·Br_2 must be due to the difference in the electronic ability of the two groups, since the bulkiness of the methyl and chloro groups are similar.



5•Br_2 (Y = H), **6**•Br_2 (Y = Br)



16•Br_2



17•Br_2

Two sets of signals are observed for the 2,4,6-$Me_3C_6H_2$ groups in **17**·Br_2. The chemical shifts of **17**·Br_2 are very different from those of **17**·Cl_2 (TB) but they are similar to **17**·I_2 (MC). One signal for C(1) is shifted upfield by 0.5 ppm but another (C(1′)) is shifted downfield by 0.7 ppm. The total halogen induced chemical shift ($\Sigma\delta_i$(C)) has been proposed to examine the structures of halogen adducts of aryl selenides in solutions:[11] $\Sigma\delta_i(C) = \delta_i(C(1)) + 2\delta_i(C(2)) + 2\delta_i(C(3)) + \delta_i(C(4))$. The $2\Sigma\delta_i$(C) values for **17**·X_2, where X = Cl, Br and I, are 22.8, 1.3 and 1.4 ppm, respectively. Therefore, it is concluded that **17**·Br_2, as well as **17**·I_2, is MC, while **17**·Cl_2 is TB, based on above discussion.

Oxidation potentials of parent selenides

The n(p_z)-orbital of the selenium atom in a diaryl selenide must play an important role in TB formation, but the electron transfer from HOMO to the σ*-orbital of a halogen occurs in the initial stage of the reaction.[20] The oxidation potentials (E_{ox}) of diaryl selenides correlate well with the energies of HOMO. The HOMO has both the π-character of the aryl groups and the n(p_z)-character of the selenium atom in ArSeAr′. Therefore, it is expected to serve as a good measure to predict the structure of the bromine adduct. The E_{ox} values of some parent selenides are given in Table 4. The E_{ox} values of the 3- and 4-substituted diphenyl selenides become larger as the electron-withdrawing ability of the substituent(s) increases.[14,21] As shown in Table 4, the bromine adduct of a 3- or 4-substituted diphenyl selenide will be MC when E_{ox} is larger than 2.2 V under the conditions. The borderline between the existence of the two structures occurs with **4**·Br_2 (TB) and **12**·Br_2 (MC). However, E_{ox} values for **4** and **12** are essentially the same (2.18 V and 2.19 V, respectively). This may be reflected in the conformational change of **4** in the reaction with bromine as discussed above.

The oxidation potentials of **1**, di-4-tolyl selenide, **15** and **17** are 1.86, 1.81, 1.89 and 1.92 V, respectively. The value for di-4-tolyl selenide is smaller than that of **1** due to the electron-releasing effect of the methyl groups. However, the values of **15** and **17** are larger than that of **1**, irrespective of the electron-releasing group(s) in **15** and **17**. This must come from the steric effect exerted by the methyl groups at the 2-positions,[8] which prevents the cations produced from stabilizing by effective solvation. A similar steric effect is also observed for the chloro groups at the 2-positions in **5** and **16**: the oxidation potentials of **5** and **16** are larger than that of **7**. Such steric effects must be greater in TB formation than in MC formation. Although the E_{ox} values of **5**, **16** and **17** are all less than 2.2 V, the structures of the bromine adducts are all MC. These results clearly show the importance of the steric effect of methyl and chloro groups at the *ortho*-positions on the reaction of the selenides with bromine.

MO Calculations

Table 5 shows the energies of **1**, **3**–**5**, **10**, *p*-$MeOC_6H_4SePh$, 3-$O_2NC_6H_4SePh$ and $(2,6\text{-}Me_2C_6H_3)_2Se$, a model of **17**, together with the chlorine and bromine adducts of TB structures, calculated by the B3LYP/6-311+G(2d,p) method. Table 5 also contains the results of MO calculations for **1**·Cl_2 (MC), and also for the Cl_2 and Br_2 adducts. The energy differences between the halogen adducts and the components are also given in the Table ($\Delta E = [(E(\text{ArSeAr}') + E(X_2)] - E(\text{ArSeX}_2\text{Ar}'$; X = Cl, Br)).

In the case of X = Cl, ΔE decreases in the order of *p*-$MeOC_6H_4SePh$ > **1** > 3-$O_2NC_6H_4SePh$ > **3**, which is a reflection of the electron-withdrawing ability of the substituent. The ΔE values are almost equal for **3**, **4** and **10**. The decrease in ΔE from **10** to $(2,6\text{-}Me_2C_6H_3)_2Se$ *via* **5** is just the opposite to the expectation based on the electron-withdrawing ability of the substituents. This must be due to the steric effects of the chloro and methyl groups at the *ortho*-positions. The trend in ΔE is more dramatic for X = Br. The ratios of $\Delta E(\mathrm{ArSeBr_2Ar'})$: $\Delta E(\mathrm{ArSeCl_2Ar'})$ are about 0.53 for $\mathbf{1}\cdot X_2$ and p-$\mathrm{MeOC_6H_4SeX_2Ph}$, 0.37 for $\mathbf{3}\cdot X_2$, $\mathbf{4}\cdot X_2$ and $\mathbf{10}\cdot X_2$, 0.24 for $\mathbf{5}\cdot X_2$ and 0.06 for $\mathrm{(2,6\text{-}Me_2C_6H_3)_2SeX_2}$. The decrease in the ratio from 0.53 to 0.37 is a reflection of the smaller electron-accepting ability of bromine relative to that of chlorine. The larger volume of bromine relative to that of chlorine must mainly contribute to the decrease from 0.37 to 0.06 *via* 0.24. The steric congestion must be more severe for TB formation with bromine.[22] The results of MO calculations support the outline of the observations.

Conclusion

Typical examples of MC formation in the reaction of substituted diphenyl selenides with bromine are reported. This has been clearly demonstrated by increasing the effective electronegativity of the Se atom and the steric hindrance around the atom in diphenyl selenide (**1**) with various substituents at the 2-, 3- and/or 4-positions of the phenyl groups. Oxidation potentials of diaryl selenides and *ab initio* MO calculations support these observations. Diaryl selenide dibromides are in equilibrium with their components.[23] They also equilibrate between the MC and TB structures if diaryl selenides are appropriately designed.[24] Studies on the halogen adducts of selenides bearing more complex structures are in progress in our laboratory.

Experimental

General

Chemicals were used without further purification unless otherwise noted. Solvents and reagents were purified by standard methods as necessary. Melting points are uncorrected. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a JEOL JNM-AL 300 spectrometer and ^{1}H (90 MHz) and ^{13}C (22.4 MHz) NMR spectra were recorded on a JEOL EX-90 spectrometer. The ^{1}H and ^{13}C chemical shifts are given in ppm relative to those of internal $CHCl_3$ slightly contaminated in solution and $CDCl_3$ as the solvent, respectively. Column chromatography was performed on silica gel (Fuji Silysia BW-300), acidic alumina and basic alumina (E. Merk). Flash column chromatography was performed with 300–400 mesh silica gel, acidic alumina and basic alumina and analytical thin layer chromatography was performed on precoated silica gel plates (60F-254) with the systems (v/v) indicated.

Synthesis of compounds

Diphenyl diselenide[25] and bis(p-bromophenyl) diselenide[25] were prepared according to the methods in the literature or the improved method.

Selenide dichlorides were prepared in the reaction of selenides with chlorine or sulfuryl chloride in inert solvent such as carbon tetrachloride, hexane, or dichloromethane. NMR spectra of bromine and iodine adducts were measured for mixtures of selenides with halogens at the given ratios.

The physical properties, ^{1}H NMR data and the results of elementary analyses of **3**–**17** and their chlorine adducts are as follows. Their ^{13}C NMR data are shown in Tables 1–3.

4-Nitrophenyl phenyl selenide (3). Diphenyl diselenide (2.03 g, 6.50 mmol) was reduced by $NaBH_4$ (0.74 g, 19.51 mmol) in ethanol under argon atmosphere and the resulting selenate anion was allowed to react with p-nitrochlorobenzene (2.05 g, 13.00 mmol) at low temperature. The reaction mixture was refluxed for 2 h. After the usual work-up, the crude product was purified by flash chromatography on a silica gel column containing acidic and basic alumina eluted with hexane. Recrystallization from ethanol gave 2.83 g pure product as yellow needles. Yield 78%, mp 58 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, J = 9.0 Hz, 2H), 7.32–7.76 (m, 5H), 8.04 (d, J = 9.0 Hz, 2H). Anal. Calcd. for $C_{12}H_9NO_2Se$: C, 51.81; H, 3.26; N, 5.04%. Found: C, 51.71; H, 3.29; N, 5.12%.

λ^4-4-Nitrophenyl(phenyl)dichloroselane ($\mathbf{3}\cdot Cl_2$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.66 (m, 3H), 7.72–8.22 (m, 2H), 8.20 (d, J = 9.4 Hz, 2H), 8.37 (d, J = 9.4 Hz, 2H). Anal. Calcd. for $C_{12}H_9Cl_2NO_2Se$: C, 41.29; H, 2.60; N, 4.01%. Found: C, 41.25; H, 2.81; N, 3.91%.

3,5-Dinitrophenyl phenyl selenide (4). Diphenyl diselenide (1.50 g, 4.80 mmol) was reduced by $NaBH_4$ (0.55 g, 14.42 mmol) in an aqueous THF under argon atmosphere and the resulting selenolate anion was allowed to react with 3,5-dinitrobenzenediazonium chloride (2.66 g, 11.53 mmol) at low temperature. The reaction mixture was stirred at 4 °C for 1.5 h and at 40 °C for 2 h. After usual work-up, the crude product was purified by flush chromatography on a silica gel column containing acidic and basic alumina eluted with hexane. Recrystallization from ethanol gave 2.61 g of pure product as yellow needles. Yield 84%, mp 101–102 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.82 (m, 5H), 8.36 (d, J = 2.0 Hz, 2H), 8.78 (t, J = 2.1 Hz, 1H). Anal. Calcd. for $C_{12}H_8N_2O_4Se$: C, 44.60; H, 2.50; N, 8.67%. Found: C, 44.63; H, 2.53; N, 8.72%.

λ^4-3,5-Dinitrophenyl(phenyl)dichloroselane ($\mathbf{4}\cdot Cl_2$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62–7.83 (m, 3H), 7.88–8.24 (m, 2H), 9.18 (br s, 2H), 9.18 (t, J = 2.0 Hz, 1H). Anal. Calcd. for $C_{12}H_8Cl_2N_2O_4Se$: C, 35.57; H, 2.05; N, 7.11%. Found: C, 35.74; H, 2.06; N, 6.82%.

2,6-Dichlorophenyl phenyl selenide (5). The synthetic procedure was similar to that of **4**. Colorless prisms. Yield 68%, mp 53.5–54.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04–7.40 (m, 5H), 7.36 (br s, 2H), 7.50 (d, J = 4.8 Hz, 1H). Anal. Calcd. for $C_{12}H_8Cl_2Se$: C, 47.72; H, 2.67%. Found: C, 47.97; H, 2.72%.

λ^4-2,6-Dichlorophenyl(phenyl)dichloroselane ($\mathbf{5}\cdot Cl_2$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32–7.74 (m, 6H), 8.34–8.62 (m, 2H). Anal. Calcd. for $C_{12}H_8Cl_4Se$: C, 38.64; H, 2.16%. Found: C, 38.88; H, 2.22%.

2,6-Dichlorophenyl *p*-bromophenyl selenide (6). The synthetic procedure was similar to that of **4**. Colorless prisms. Yield 72%, mp 109–110 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, J = 8.5 Hz, 2H), 7.25 (t, J = 8.0 Hz, 1H), 7.34 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 7.7 Hz, 2H). Anal. Calcd. for $C_{12}H_7BrCl_2Se$: C, 37.83; H, 1.85%. Found: C, 37.67; H, 1.75%.

λ^4-2,6-Dichlorophenyl(*p*-bromophenyl)dichloroselane ($\mathbf{6}\cdot Cl_2$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.52 (m, 3H), 7.65 (d, J = 9.0 Hz, 2H), 8.35 (d, J = 9.2 Hz, 2H). Anal. Calcd. for $C_{12}H_7BrCl_4Se$: C, 31.90; H, 1.56%. Found: C, 31.74; H, 1.65%.

Bis(4-chlorophenyl) selenide (7)[26]. Selenium powder (1.00 g, 12.66 mmol) was reduced by $NaBH_4$ (1.44 g, 37.99 mmol) in H_2O under argon atmosphere and the resulting sodium diselenate was allowed to react with 4-chlorobenzenediazonium chloride (4.88 g, 27.86 mmol) at low temperature. The reaction mixture was stirred at 4 °C for 1.5 h and at 40 °C for 2 h. After the usual work-up, the crude product was purified by flash chromatography on a silica gel column containing acidic and basic alumina eluted with hexane. Recrystallization from hexane gave 2.37 g pure product as colorless prisms. Yield 62%, mp 96–97 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, J = 8.8 Hz, 4H), 7.34 (d, J = 8.8 Hz, 4H). Anal. Calcd. for $C_{12}H_8Cl_2Se$: C, 47.72; H, 2.67%. Found: C, 47.88; H, 2.81%.

λ^4-Bis(4-chlorophenyl)dichloroselane ($\mathbf{7}\cdot Cl_2$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, J = 9.0 Hz, 4H), 7.94 (d, J = 9.0 Hz, 4H). Anal. Calcd. for $C_{12}H_8Cl_4Se$: C, 38.64; H, 2.16%. Found: C, 38.58; H, 2.22%.

Bis(4-ethoxycarbonylphenyl) selenide (8). The synthetic procedure was similar to that for **7**. Colorless prisms. Yield 48%, mp 48–49 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (t, J = 8.7 Hz, 6H), 4.37 (q, J = 8.6 Hz, 4H), 7.49 (d, J = 7.1 Hz, 4H), 7.94 (d, J = 7.1 Hz, 4H). Anal. Calcd. for $C_{18}H_{18}O_4Se$: C, 57.30; H, 4.81%. Found: C, 57.11; H, 4.69%.

λ^4-Bis(4-ethoxycarbonylphenyl)dichloroselane ($8\cdot Cl_2$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.41 (t, J = 7.1 Hz, 6H), 4.43 (q, J = 7.2 Hz, 4H), 8.17 (d, J = 9.2 Hz, 4H), 8.09 (d, J = 9.2 Hz, 4H). Anal. Calcd. for $C_{18}H_{18}Cl_2O_4Se$: C, 48.24; H, 4.05%. Found: C, 48.06; H, 4.11%.

Bis(4-cyanophenyl) selenide (9). The synthetic procedure was similar to that of **7**. Colorless needles. Yield 72%, mp 142–143 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (br s, 8H). Anal. Calcd. for $C_{14}H_8N_2Se$: C, 59.38; H, 2.85; N, 9.89%. Found: C, 59.61; H, 2.95; N, 9.84%.

λ^4-Bis(4-cyanophenyl)dichloroselane ($9\cdot Cl_2$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, J = 8.9 Hz, 4H), 8.16 (d, J = 8.9 Hz, 4H). Anal. Calcd. for $C_{14}H_8Cl_2N_2Se$: C, 47.49; H, 2.28; N, 7.91%. Found: C, 47.62; H, 2.35; N, 8.11%.

λ^4-Bis(4-nitrophenyl) selenide (10). The synthetic procedure was similar to that of **7**. Yellow needles. Yield 78%, mp 172–173 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, J = 8.9 Hz, 4H), 8.16 (d, J = 8.9 Hz, 4H). Anal. Calcd. for $C_{12}H_8N_2O_4Se$: C, 44.60; H, 2.50; N, 8.67%. Found: C, 44.74; H, 2.47; N, 8.54%.

λ^4-Bis(4-nitrophenyl)dichloroselane ($10\cdot Cl_2$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (d, J = 9.5 Hz, 4H), 8.42 (d, J = 9.4 Hz, 4H). Calcd. for $C_{12}H_8Cl_2N_2O_4Se$: C, 36.57; H, 2.05; N, 7.11%. Found: C, 36.81; H, 2.17; N, 7.08%.

Bis(3-chlorophenyl) selenide (11). The synthetic procedure was similar to that of **7**. Colorless needless. Yield 69%, mp 108–109 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.9–7.6 (m, 8H). Anal. Calcd. for $C_{12}H_8Cl_2Se$: C, 47.72; H, 2.67. Found: C, 47.81; H, 2.61.

λ^4-Bis(3-chlorophenyl)dichloroselane ($11\cdot Cl_2$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25–7.72 (m, 4H), 7.90 (d, J = 8.2 Hz, 2H), 7.97 (br s, 2H). Anal. Calcd. for $C_{12}H_8Cl_4Se$: C, 38.64; H, 2.16%. Found: C, 38.71; H, 2.26%.

Bis(3-cyanophenyl) selenide (12). The synthetic procedure was similar to that of **7**. Colorless prisms. Yield 77%, mp 94.5–95.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (t, J = 8.8 Hz, 2H), 7.61 (d, J = 7.5 Hz, 2H), 7.69 (d, J = 7.5 Hz, 2H), 7.72 (s, 2H). Anal. Calcd. for $C_{14}H_8N_2Se$: C, 59.38; H, 2.85; N, 9.89%. Found: C, 59.08; H, 2.89; N, 9.74%.

λ^4-Bis(3-cyanophenyl)dichloroselane ($12\cdot Cl_2$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (t, J = 8.1 Hz, 2H), 7.89 (dt, J = 7.7 and 1.1 Hz, 2H), 8.26 (ddd, J = 1.1, 2.2 and 8.3 Hz, 2H), 8.32 (t, J = 1.3 Hz, 2H). Anal. Calcd. for $C_{14}H_8Cl_2N_2Se$: C, 47.49; H, 2.28; N, 7.91%. Found: C, 47.52; H, 2.25; N, 7.88%.

Bis(3-nitrophenyl) selenide (13). The synthetic procedure was similar to that of **7**. Yellow needles. Yield 77%, mp 112–113 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (t, J = 8.1 Hz, 2H), 7.79 (dt, J = 1.3 and 7.7 Hz, 2H), 8.18 (ddd, J = 0.9, 2.2 and 8.3 Hz, 2H), 8.34 (t, J = 1.9 Hz, 2H). Anal. Calcd. for $C_{12}H_8N_2O_4Se$: C, 44.60; H, 2.50; N, 8.67%. Found: C, 44.54; H, 2.57; N, 8.64%.

λ^4-Bis(3-nitrophenyl)dichloroselane ($13\cdot Cl_2$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (t, J = 8.4 Hz, 2H), 8.37 (ddd, J = 0.7, 1.1 and 8.1 Hz, 2H), 8.48 (ddd, J = 0.9, 1.7 and 8.1 Hz, 2H), 8.91 (t, J = 2.0 Hz, 2H). Anal. Calcd. for $C_{12}H_8Cl_2N_2O_4Se$: C, 36.57; H, 2.05; N, 7.11%. Found: C, 36.71; H, 2.27; N, 7.15%.

Bis(3,5-dichlorophenyl) selenide (14). The synthetic procedure was similar to that of **7**. Colorless prisms. Yield 81%, mp 74–75 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25–7.43 (br s, 6H). Anal. Calcd. for $C_{12}H_6Cl_4Se$: C, 38.85; H, 1.63%. Found: C, 38.68; H, 1.68%.

λ^4-Bis(3,5-dichlorophenyl)dichloroselane ($14\cdot Cl_2$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (t, J = 1.7 Hz, 2H), 7.92 (d, J = 1.7 Hz, 2H). Anal. Calcd. for $C_{12}H_6Cl_6Se$: C, 32.62; H, 1.37%. Found: C, 32.55; H, 1.19%.

Di-2-tolyl selenide (15). The synthetic procedure was similar to that of **7**. Colorless needles. Yield 59%, mp 61–62 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.39 (s, 6H), 7.00–7.31 (m, 8H). Anal. Calcd. for $C_{14}H_{14}Se$: C, 64.37; H, 5.40%. Found: C, 64.22; H, 5.55%.

λ^4-(Di-2-tolyl)dichloroselane ($15\cdot Cl_2$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.85 (s, 6H), 7.28–7.55 (m, 6H), 7.74–8.04 (m, 2H). Anal. Calcd. for $C_{14}H_{14}Cl_2Se$: C, 50.63; H, 4.25%. Found: C, 5.52; H, 4.33%.

Bis(2-chlorophenyl) selenide (16). The synthetic procedure was similar to that of **7**. Colorless needles. Yield 72%, mp 56–57 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01–7.41 (m, 6H), 7.41–7.62 (m, 2H). Anal. Calcd. for $C_{12}H_8Cl_2Se$: C, 47.72; H, 2.67%. Found: C, 47.65; H, 2.51%.

λ^4-Bis(2-chlorophenyl)dichloroselane ($16\cdot Cl_2$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.73 (m, 6H), 7.83–8.20 (m, 2H). Anal. Calcd. for $C_{12}H_8Cl_4Se$: C, 38.64; H, 2.16%. Found: C, 38.51; H, 2.16%.

λ^4-Bis(2,4,6-trimethylphenyl) selenide (17). The synthetic procedure was similar to that of **7**. Colorless needles. Yield 76%, mp 105.5–106.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.23 (s, 6H), 2.24 (s, 12H), 6.82 (s, 4H). Anal. Calcd. for $C_{18}H_{22}Se$: C, 68.13; H, 6.99%. Found: C, 67.94; H, 6.95%.

λ^4-Bis(2,4,6-trimethylphenyl)dichloroselane ($17\cdot Cl_2$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.32 (s, 6H), 2.69 (s, 12H), 7.00 (s, 4H). Anal. Calcd. for $C_{18}H_{22}Cl_2Se$: C, 55.69; H, 5.71%. Found: C, 55.88; H, 5.92%.

Ab initio calculations

Ab initio MO calculations were performed with the B3LYP/6-311+(2d,p) method, using the Gaussian 94[15] and 98[15] programs.

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