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Inter-element linkage in 1,2- and 1,4-bis(arylselanyl)benzenes with halogens

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Abstract

The criteria to distinguish the structure of halogen adducts of aryl chalcogenides in solutions based on the NMR chemical shifts are confirmed by ab initio molecular orbitals (MO) calculations based on the gauge-including atomic orbitals (GIAO) theory. The criteria are applied to determine the structure of halogen adducts of 1,2-bis(phenylselanyl)benzene (**1**), 1,4-bis(phenylselanyl)benzene (**2**), and 1,4-bis(*p-tert*-butylphenylselanyl)benzene (**3**) (**1**·nX$_2$, **2**·nX$_2$, and **3**·nX$_2$, respectively: $n = 1$ and 2 and X = Cl, Br, and I) in CDCl$_3$. The structure of **1**·Br$_2$ is demonstrated to be trigonal bipyramidal (TB) not only in the solution but also in crystals. The TB formation of **1**·Br$_2$ is just the opposite of the MC (molecular complexes) formation of selenanthrene with bromine in the solution. The driving force for the TB and MC formation is discussed based on the structure of the parent selenides. The structure of **2**·2X$_2$ and **3**·2X$_2$ is (TB, TB) for X = Cl and Br and (MC, MC) for X = I. On the other hand, the structure of **1**·2Br$_2$ is revealed to be TB at one SeBr$_2$ moiety but MC for the other SeBr$_2$ group, which is described as (TB, MC). The bromine exchange is observed in **1**·2Br$_2$ in the conditions of NMR measurements. The rate of bromine exchange becomes sharp as excess bromine is added to the **1**·2Br$_2$ solution, which shows that the structural (TB, MC) $\rightleftarrows$ (MC, TB) site exchange in **1**·2Br$_2$ is accelerated by the excess bromine and/or its derivatives. Ab initio MO calculations are performed on the adducts to understand their structural features and on the proposed intermediate to confirm the mechanism.

Keywords: Bis(arylselanyl)benzene; Halogen adducts; X-ray crystallographic analysis; Ab initio MO calculations; TB, MC

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1. Introduction

Organic chalcogen compounds are well known to show versatile reactivities, and afford many structurally interesting compounds [1]. Among such chalcogen compounds, we have been interested in halogen adducts of aryl selenides, especially in bromine adducts of aryl selenides bearing plural selenium atoms closely placed in space [2]. If two or more selenium atoms are forced to be located at distances less than the sum of van der Waals radii in organic compounds, nonbonded interactions will take place between the selenium atoms. The interactions between their lone pairs are usually repulsive since they are characterized by the two center–four electron interactions (2c–4e) with severe exchange repulsion [2a]. However, some interactions containing those of lone pairs with σ*(Se–C) orbitals with the 3c–4e character can be attractive [2b]. This type of interaction works in the inter-element linkage of chalcogenides with halogens. Namely, novel structures, properties, and new types of chemical bonds are to be found in multi-element organic compounds such as bromine adducts of selenides [2c] (Plate 1).

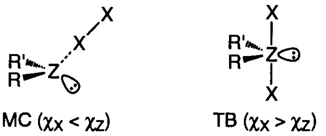

Plate 1.

The σ*-orbitals of halogens have been well established to accept n-electrons of chalcogenides such as selenides [3–5]. Molecular compounds [3] or molecular complexes (MC) will be formed, when the electron

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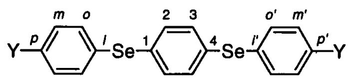


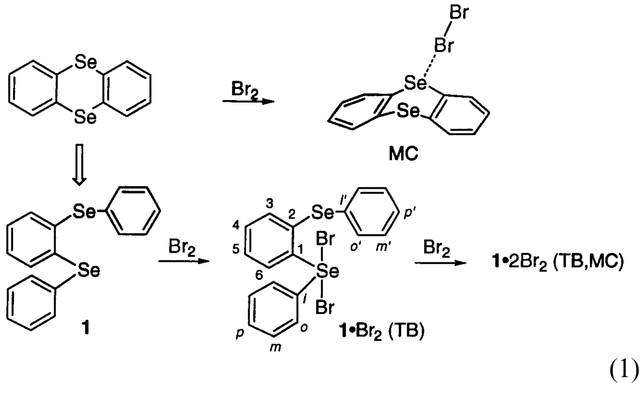
2 (Y = H), **3** (Y = *t*-Bu)

Plate 2.

transfer from a chalcogenide to a halogen is small. If the electron transfer becomes larger, the halogen molecule can no longer exist as a halogen molecule, resulting in the formation of trigonal bipyramidal (TB) adducts with the highly polar 3c–4e hypervalent bond, $X^{\delta-}-Z^{\delta+}-X^{\delta-}$ [6]. The Z–X–X bonds in MC are shown to be analyzed with the 3c–4e model [7]. The magnitude of the electron transfer can be estimated by the electronegativity [8] of elements: TB are formed if the electronegativity of halogens (χ_X) is larger than that of chalcogens (χ_Z), while MC are formed when χ_X is less than χ_Z (general rule) [1c,1d,9,10].

We have proposed criteria of the experimental rule distinguishing MC from TB for halogen adducts of aryl chalcogenides based on the NMR chemical shifts (δ) [9–11]. It is more useful if the criteria are demonstrated based on the theoretical background. Recently the magnetic shielding tensor calculated with the gauge-including atomic orbitals (GIAO) theory for the carbon nucleus [12–14], together with ^{77}Se nucleus [15–18], is shown to be reliable. This encouraged us to calculate the GIAO magnetic shielding tensor for ^{1}H, ^{13}C, and ^{77}Se nucleus (σ(X): X = H, C, and Se) to confirm the criteria based on the theoretical background. After establishment of the criteria not only experimentally but also theoretically (see Appendix A), the criteria are applied to determine the structure of halogen adducts of aryl selenides bearing plural selenium atoms closely placed in space.

1,2-Bis(phenylselanyl)benzene (**1**) is chosen as a model compound, which corresponds to a bis-selenide where one of the Se–C bonds in selenanthrene is cleaved [19]. Selenanthrene itself is demonstrated to give MC with bromine in solutions [20]: its rigid roof structure prevents the formation of TB with bromine. Therefore, the structure of $\mathbf{1}\cdot\mathrm{Br}_2$ is also of interest. If the reason for the MC formation of selenanthrene with bromine is really its rigid roof structure, **1** should give TB with bromine since **1** is free from the rigidity.



(1)

The structure of halogen adducts of **1** ($\mathbf{1}\cdot n\mathrm{X}_2$) is determined in solutions based on the criteria. The TB and MC notation is used for 1-($\mathrm{Ar}^{\mathrm{A}}\mathrm{SeX}_2$)$\mathrm{C}_6\mathrm{H}_4$($^{\mathrm{B}}$SeAr)-2, if the structure around $^{\mathrm{A}}\mathrm{SeX}_2$ is TB and MC, respectively. The (TB, TB) and (MC, MC) notation is adopted for 1-($\mathrm{Ar}^{\mathrm{A}}\mathrm{SeX}_2$)$\mathrm{C}_6\mathrm{H}_4$($^{\mathrm{B}}\mathrm{SeX}_2$Ar)-2, if the structures around $^{\mathrm{A}}\mathrm{SeX}_2$ and $^{\mathrm{B}}\mathrm{SeX}_2$ are both TB and both MC, respectively. The (TB, MC) notation is used when one of $^{\mathrm{A}}\mathrm{SeX}_2$ and $^{\mathrm{B}}\mathrm{SeX}_2$ moieties is TB but the other is MC (Plate 2).

After establishment of the structure of $\mathbf{1}\cdot\mathrm{Br}_2$ (Eq. (1)), the structure for the 1:2 adduct with bromine, $\mathbf{1}\cdot 2\mathrm{Br}_2$, is examined. That of 1:2 adducts of 1,4-bis(phenylselanyl)benzene (**2**) and 1,4-bis(*p-tert*-butylphenylselanyl)benzene (**3**) with halogens is also investigated as the reference compounds. The structural (TB, MC) $\leftrightarrows$ (MC, TB) site exchange is observed in $\mathbf{1}\cdot 2\mathrm{Br}_2$, together with the bromine migration in $\mathbf{1}\cdot\mathrm{Br}_2$. We present the results of investigations containing the molecular orbitals (MO) calculations performed on the adducts to understand the structural feature and on the proposed intermediate to confirm the mechanism.

2. Results and discussion

2.1. Structure of halogen adducts of 1–3 in solution

Table 1 shows the halogen induced δ(H), δ(C), and δ(Se) values (δ_i(H), δ_i(C), and δ_i(Se), respectively) of 1,2-bis(phenylselanyl)benzene (**1**), together with the δ values of **1**. Table 2 exhibits the values for 1,4-bis(phenylselanyl)benzene (**2**) and 1,4-bis(*p-tert*-butylphenylselanyl)benzene (**3**), together with δ for the parent selenides. The δ(C) values are not determined for $\mathbf{2}\cdot 2\mathrm{Br}_2$ due to its low solubility in CDCl_3.

Before discussion of the structure of $\mathbf{1}\cdot n\mathrm{X}_2$ (X = Cl, Br, I), we first examine the structure of $\mathbf{2}\cdot 2\mathrm{X}_2$ and $\mathbf{3}\cdot 2\mathrm{X}_2$. The δ_i(H), δ_i(C), and/or δ_i(Se) values of the phenyl and *p-tert*-butylphenyl groups are very close to those in $\mathrm{PhSeX}_2\mathrm{Ph}$ (X = Cl, Br, I) (see also Table 6). The additivity of the values in the central benzene ring is very good: $\delta_i(\mathrm{H}_2)$ and $\delta_i(\mathrm{C}_1)$ in $\mathbf{2}\cdot 2\mathrm{X}_2$ and $\mathbf{3}\cdot 2\mathrm{X}_2$ (X = Cl, Br) are well evaluated by ($\delta_i(\mathrm{H}_o)$ and $\delta_i(\mathrm{H}_m)$) and ($\delta_i(\mathrm{C}_i)$ and $\delta_i(\mathrm{C}_p)$), respectively. The results clearly show that the structure of $\mathbf{2}\cdot 2\mathrm{X}_2$ and $\mathbf{3}\cdot 2\mathrm{X}_2$ (X = Cl, Br) is (TB, TB) in the solution. The structure of $\mathbf{3}\cdot\mathrm{Cl}_2$ must be TB with a selenide Se atom at its *p*-position. That of $\mathbf{2}\cdot 2\mathrm{I}_2$ and $\mathbf{3}\cdot 2\mathrm{I}_2$ is (MC, MC) since $\delta_i(\mathrm{C}_i)$ are negative, although the equilibrium with the components must be considered (Plate 3).

After establishment of the (TB, TB) structure for $\mathbf{2}\cdot 2\mathrm{X}_2$ and $\mathbf{3}\cdot 2\mathrm{X}_2$ (X = Cl, Br), the next extension of our study is to examine the structure of $\mathbf{1}\cdot\mathrm{X}_2$ and $\mathbf{1}\cdot 2\mathrm{X}_2$ (X = Cl, Br, I). The ^{1}H- and ^{13}C-NMR signals of $\mathbf{1}\cdot\mathrm{Cl}_2$

Table 1
The δ_i(H), δ_i(C), and δ_i(Se) values of **1**, together with the δ values [a,b]

Compound [c]	H-3 H-6	H-4 H-5	H-*o* H-*o*′	H-*m* H-*m*′	H-*p* H-*p*′	C-1 C-2	C-3 C-6	C-4 C-5	C-*i* C-*i*′	C-*o* C-*o*′	C-*m* C-*m*′	C-*p* C-*p*′	Se Se	Structure
1	7.07	7.20	7.52	7.32	7.32	135.9	133.0	127.9	130.7	134.0	129.5	127.9	424.1	Selenide
	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
1·Cl_2 [d]	0.59	0.35	0.84	0.30	0.29	15.7	4.7	4.0	8.2	−0.4	0.2	4.2	160.6	TB
	0.31	0.19	0.14	−0.01	−0.03	−3.3	−3.3	0.3	1.2	−0.4	0.1	0.1	8.5	Selenide
1·2Cl_2	0.85	0.40	0.70	0.26	0.24	11.0	2.0	4.1	12.7	−1.5	0.2	4.2	173.4	(TB,TB)
1·Br_2 [e]	0.54	0.17	0.50	0.12	0.11	[f]	0.7	2.1	3.4	0.3	0.2	3.0	150, 13	TB
1·2Br_2 [g]	0.56	0.20	0.50	0.12	0.14	4.4	0.6	2.3	3.0	0.2	0.3	3.3	[h]	(TB,MC)
1·3Br_2 [i]	0.58	0.23	0.49	0.12	0.14	4.2	0.7	2.4	2.9	0.1	0.4	3.5	75	(TB,MC)
1·I_2	0.06	0.05	0.02	0.03	0.02	−0.5	0.3	0.5	−0.6	−0.3	0.2	0.9	6.3	MC
1·2I_2	0.10	0.09	0.03	0.05	0.04	−0.9	0.5	0.8	−1.0	−0.4	0.4	1.3	10.1	(MC,MC)

[a] The δ(H) and δ(C) values (ppm) are given from TMS and δ(Se) from MeSeMe.

[b] In $CDCl_3$.

[c] Carbons adjacent to the selenium atom without halogens are numbered as C-2 and C-*i*′ for **1**·Cl_2.

[d] Assignments are partly tentative even after SEL mode measurements.

[e] Although the signals separation was not complete, two sets of broad signals were observed at low temperature.

[f] Not observed due to broadening.

[g] The signals were broad ($\delta_{1/2} = 1$–4 Hz) at −60°C in CD_2Cl_2.

[h] Very broad.

[i] Three molar bromine was added to the solution of **1**.

Table 2
The δ_i(H), δ_i(C), and δ_i(Se) values of **2** and **3**, together with their δ values [a,b]

Compound	H-2 H-3	H-*o* H-*o′*	H-*m* H-*m′*	H-*p* H-*p′*	C-*t* C-*t′*	C-Me C-Me′	C-1 C-4	C-2 C-3	C-*i* C-*i′*	C-*o* C-*o′*	C-*m* C-*m′*	C-*p* C-*p′*	Se Se′	Structure
2	7.31	7.48	7.28	7.29			130.6	133.4	130.5	133.3	129.4	127.6		Selenide
	0.00	0.00	0.00	0.00			0.0	0.0	0.0	0.0	0.0	0.0		
2·2Cl_2	0.87	0.58	0.33	0.30			16.0	−1.0	11.6	−2.0	0.7	4.6		(TB,TB)
2·2Br_2	0.84 [c]	0.57 [c]	0.25 [c]	0.24 [c]			[d]	[d]	[d]	[d]	[d]	[d]		(TB,TB)
2·2I_2	0.01	0.04	0.04	0.02			0.5	0.1	−1.5	−0.6	0.5	1.3		(MC,MC)
3	7.28	7.42	7.31	1.30 [e]	34.6	31.3	130.8	133.5	126.6	132.8	126.5	151.2	410.2	Selenide
	0.00	0.00	0.00	0.00 [e]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
3·Cl_2	0.52	0.48	0.27	0.04 [e]	0.5	−0.2	9.5	−3.4	12.8	−1.7	0.6	4.4	181.9	(TB)
	0.13	0.10	0.05	0.04 [e]	0.2	−0.1	7.8	2.4	−3.0	−1.1	0.4	1.5	18.5	Selenide
3·2Cl_2	0.88	0.55	0.28	0.07 [e]	0.6	−0.3	15.8	−1.3	11.5	−1.6	0.7	4.9	166.3	(TB,TB)
3·2Br_2	0.82	0.56	0.24	0.07 [e]	0.7	−0.2	11.9	−0.3	6.6	−0.2	1.0	4.8	133.1	(TB,TB)
3·2I_2	0.05	0.07	0.06	0.02 [e]	0.2	−0.1	0.5	0.0	−1.6	−0.5	0.5	1.4	14.5	(MC,MC)

[a] The δ(H) and δ(C) values (ppm) are given from TMS and δ(Se) from MeSeMe.

[b] In $CDCl_3$.

[c] Broad due to equilibrium with the components.

[d] Not observed due to low solubility and low sensitivity.

[e] Values for *p*-*t*-butyl protons.

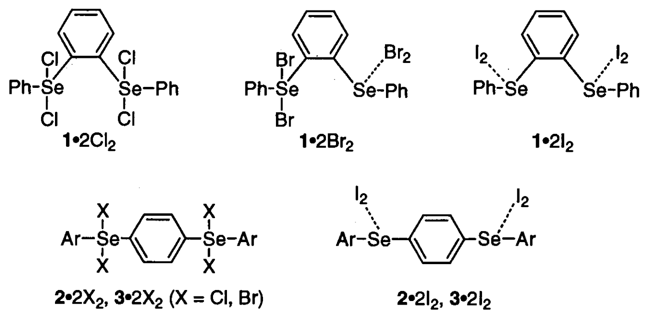


Plate 3.

consist of two sets: one corresponds to those of $\mathrm{PhSeCl_2}$ groups in $\mathrm{PhSeCl_2Ph}$ and the other appears close to those of PhSe groups in PhSePh. The appearance of the two sets of signals show that the chlorine migration in **1**·$\mathrm{Cl_2}$ must be much slower relative to the NMR time scale under the conditions of measurements. Therefore, the structure of **1**·$\mathrm{Cl_2}$ is concluded to be TB for the $\mathrm{SeCl_2}$ moiety. The $\delta_i(\mathrm{C_1})$ and $\delta_i(\mathrm{C}_i)$ values of **1**·$\mathrm{Cl_2}$ were larger and smaller compared with those observed in $\mathrm{PhSeCl_2Ph}$, respectively. This may be due to the through-bond and through-space interactions between the two selanyl groups, together with the conformational change before and after the formation of **1**·$\mathrm{Cl_2}$. Since the δ_i values of the two $\mathrm{PhSeCl_2}$ groups in **1**·$\mathrm{2Cl_2}$ are very close to those in $\mathrm{PhSeCl_2Ph}$, the structure of **1**·$\mathrm{2Cl_2}$ is concluded to be (TB, TB).

The $\delta_i(\mathrm{C_1})$, $\delta_i(\mathrm{C_2})$, $\delta_i(\mathrm{C}_i)$, and $\delta_i(\mathrm{C}_{i'})$ values are all negative, whereas $\delta_i(\mathrm{C_4})$, $\delta_i(\mathrm{C_5})$, $\delta_i(\mathrm{C}_p)$, and $\delta_i(\mathrm{C}_{p'})$ are all positive for **1**·$\mathrm{I_2}$ and **1**·$\mathrm{2I_2}$. The magnitudes become larger when **1**·$\mathrm{I_2}$ goes to **1**·$\mathrm{2I_2}$. These results show that the structure of **1**·$\mathrm{I_2}$ and **1**·$\mathrm{2I_2}$ are MC and (MC, MC), respectively, although the rapid equilibrium with the components must also be considered.

The signals of two phenyl groups in **1**·$\mathrm{Br_2}$ are observed as a set with some broad ones: $\delta(\mathrm{C_1})$ and $\delta(\mathrm{C_2})$ are not determined since the signals were very broad. The $\delta(\mathrm{C})$ values in **1**·$\mathrm{Br_2}$ were close to the averaged ones of the corresponding carbons in **1**·$\mathrm{Cl_2}$, except for C_i and C_o. The $\delta(\mathrm{C}_i)$ and $\delta(\mathrm{C}_o)$ are both halogen dependent (see Table 6). The $\delta_i(\mathrm{C}_i)$ and $\delta_i(\mathrm{C}_o)$ values of the phenyl groups in **1**·$\mathrm{Br_2}$ are very close to those of the half values in $\mathrm{PhSeBr_2Ph}$. The observations strongly suggest that the structure of **1**·$\mathrm{Br_2}$ is TB with the relatively fast bromine migration between the two Se atoms. While the $\delta_i(\mathrm{C_4})$, $\delta_i(\mathrm{C_5})$, $\delta_i(\mathrm{C}_p)$, and $\delta_i(\mathrm{C}_{p'})$ values of **1**·$n\mathrm{Br_2}$ increase in the order $n = 1$, 2, and 3, the $\delta_i(\mathrm{C_1})$, $\delta_i(\mathrm{C_2})$, $\delta_i(\mathrm{C}_i)$, and $\delta_i(\mathrm{C}_{i'})$ values become smaller in this order, although $\delta_i(\mathrm{C_1})$ and $\delta_i(\mathrm{C_2})$ are not determined for $n = 1$. These results are in accordance with the (TB, MC) structure for **1**·$\mathrm{2Br_2}$ accompanied by the substantial equilibrium with **1**·$\mathrm{Br_2}$ (TB) and bromine.

In order to examine the structure of **1**·$\mathrm{Br_2}$ and **1**·$\mathrm{2Br_2}$ in solutions more clearly, we propose a total $\delta_i(\mathrm{C})$ value for a Ph group ($\Sigma\, \delta_i(\mathrm{C})$) in $\mathrm{ArSeX_2Ph}$: $\Sigma\, \delta_i(\mathrm{C}) = \delta_i(\mathrm{C}_i) + 2\delta_i(\mathrm{C}_o) + 2\delta_i(\mathrm{C}_m) + \delta_i(\mathrm{C}_p)$. The $2\Sigma\, \delta_i(\mathrm{C})$ values for ArSePh (**1**–**3** and PhSePh) are collected in Table 3. The values clearly show that the (TB, TB) formation causes 25–30 ppm irrespective of halogens, where TB of $\mathrm{PhSeX_2Ph}$ is regarded as (TB, TB). Those for the MC formation are negligible.

The $2\Sigma\, \delta_i(\mathrm{C})$ values for **1**·$\mathrm{Cl_2}$, **1**·$\mathrm{Br_2}$, and **1**·$\mathrm{I_2}$ are 12.7, 14.8, and 0.2 ppm, respectively. The value for **1**·$\mathrm{Br_2}$ is very close to that for **1**·$\mathrm{Cl_2}$ and to a half value for the (TB, TB) formation, which is taken as evidence for the TB structure of **1**·$\mathrm{Cl_2}$ and **1**·$\mathrm{Br_2}$. The TB structure of **1**·$\mathrm{Br_2}$ reveals the reason for selenanthrene reacting with bromine to give an MC in solutions: the rigid roof structure of the selenanthrene prevents the formation of the planar structure necessary for the TB formation. The $2\Sigma\, \delta_i(\mathrm{C})$ values for **1**·$\mathrm{2Cl_2}$, **1**·$\mathrm{2Br_2}$, and **1**·$\mathrm{2I_2}$ are 28.6, 14.6, and 0.6 ppm, respectively. The (TB, TB) and (MC, MC) structure is well demonstrated for **1**·$\mathrm{2Cl_2}$ and **1**·$\mathrm{2I_2}$, respectively. The $2\Sigma\, \delta_i(\mathrm{C})$ value of 14.6 ppm for **1**·$\mathrm{2Br_2}$, together with that of 14.4 ppm for **1**·$\mathrm{3Br_2}$, is clear evidence for the (TB, MC) structure of **1**·$\mathrm{2Br_2}$ equilibrating with the components.

The (TB, MC) structure of **1**·$\mathrm{2Br_2}$ is the first observation of the MC structure for the bromine adduct of a substituted diphenyl selenide, to the best of our knowledge. The electron withdrawing ability of the $\mathrm{PhSeBr_2}$

Table 3
The $2\Sigma\, \delta_i(\mathrm{C})$ values in **1**·$n\mathrm{X_2}$, **2**·$n\mathrm{X_2}$, **3**·$n\mathrm{X_2}$, and $\mathrm{PhSeX_2Ph}$ [a,b]

	1·$n\mathrm{X_2}$			**2**·$n\mathrm{X_2}$			**3**·$n\mathrm{X_2}$			$\mathrm{PhSeX_2Ph}$ [c]		
n	Cl	Br [d]	I	Cl	Br	I	Cl	Br	I	Cl	Br	I
1	12.7	14.8	0.2				12.1	12 [e f]	−0.4 [e]			
2	28.6	14.6	0.6	27.2		−0.8	29.2	26.0	−0.4	26.8	25.0	0.2

[a] $\Sigma\, \delta_i(\mathrm{C}) = \delta_i(\mathrm{C}_i) + 2\delta_i(\mathrm{C}_o) + 2\delta_i(\mathrm{C}_m) + \delta_i(\mathrm{C}_p)$.
[b] In ppm.
[c] Classified as $n = 2$.
[d] 14.4 for $n = 3$.
[e] Not shown in Table 2.
[f] Based on broad signals.

Table 4
Selected crystal data and structure analysis results for **1**·Br_2

Formula	$C_{19}H_{16}Br_2Se_2Cl_2$
Formula weight	632.97
Crystal system	Triclinic
Space group	*P*-1(# 2)
a (Å)	11.326(2)
b (Å)	11.525(2)
c (Å)	9.863(2)
α (°)	113.04(1)
β (°)	105.16(1)
γ (°)	63.831(8)
V (Å^3)	1057.2(4)
Z	2
D_{calc} (g cm^{-3})	1.988
No. of observations	3198
No. of variables	226
F_{000}	604.00
μ(Cu–K$_\alpha$) (cm^{-1})	111.22
R	0.066
R_w	0.099
Goodness-of-fit	1.13

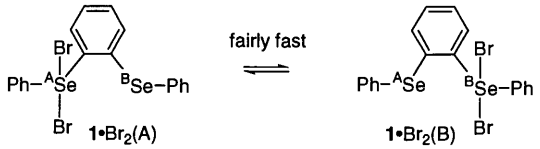
(TB) group must be very large and the bulkiness of the group toward the group at the 2-position must be very severe. Both electronic and steric effects of the $PhSeBr_2$ (TB) group should operate to prevent the formation of TB in the reaction of 1-$PhSeBr_2$(TB)C_6H_4SePh-2 (**1**·Br_2) with bromine. The results show that reactivities of organoselenium compounds can be controlled by chemically modulating the effective electronegativity of the selenium atom in a given selenide and/or by changing bulkiness around the selenium atom of the compound [10,20,21].

2.2. Structure of **1**·Br_2 studied by X-ray crystallographic analysis

The structure of **1**·Br_2 is determined by X-ray crystallographic analysis. Tables 4 and 5 display the crystal data and selected bond lengths, angles, and torsional angles, respectively. Fig. 1 shows the structure of **1**·Br_2, which demonstrates its TB structure also in crystals. The Se(1)–C(7) bond is almost on the plane of the central benzene ring ($\angle$C(2)C(1)Se(1)C(7) = 169.4(5)°) and the two Se–Br bonds are almost perpendicular to the plane ($\angle$C(2)C(1)Se(1)Br(1) = − 77.5(4)° and $\angle$C(2)C(1)Se(1)Br(2) = 97.8(4)°). The torsional angle for C(1)C(2)Se(2)C(13) is 130.5(5)°. The feature of the structure is discussed in the forthcoming section.

2.3. Bromine migration and site exchange in **1**·Br_2 and **1**·2Br_2

We next discuss the bromine migration in **1**·Br_2 and the site exchange in **1**·2Br_2. The NMR signals of **1** are of course very sharp in $CDCl_3$ due to its quick molecular motion relative to the NMR time scale. The signals become broad as bromine is added to the solution until *n* in **1**·*n*Br_2 is about unity. However, the ^1H and ^{13}C signals become sharp again if more bromine is added to the **1**·Br_2 solution: the signals are substantially sharp when *n* = ca. 3 [22]. The bromine migration and the site exchange are shown in Eqs. (2) and (3), respectively.



(2)

Table 5
Selected interatomic distances, angles, and torsional angles of **1**·Br_2

Interatomic distances (Å)			
Se(1)–C(1)	1.944(6)	Se(2)–C(2)	1.920(7)
Se(1)–C(7)	1.959(7)	Se(2)–C(13)	1.940(7)
Se(1)–Br(1)	2.5193(9)	Se(2)–Br(1)	3.613(1)
Se(1)–Br(2)	2.6084(9)	Se(2)–Br(2)	4.382(1)
Se(1)–Se(2)	3.240(1)	C(1)–C(2)	1.40(1)
Bond angles (°)			
C(1)–Se(1)–C(7)	102.9(3)	C(2)–Se(2)–C(13)	96.7(3)
Br(1)–Se(1)–Br(2)	172.91(4)	Br(2)–Se(2)–C(13)	91.7(2)
C(1)–Se(1)–Br(1)	89.9(2)	Se(2)–C(2)–C(1)	121.8(5)
C(1)–Se(1)–Br(2)	87.8(2)	C(7)–Se(1)–Se(2)	162.2(2)
C(2)–C(1)–Se(1)	115.1(4)		
Torsional angles (°)			
C(1)–Se(1)–C(7)–C(8)	−47.4(6)	C(2)–Se(2)–C(13)–C(14)	−59.5(6)
C(2)–C(1)–Se(1)–C(7)	169.4(5)	C(1)–C(2)–Se(2)–C(13)	130.5(5)
C(2)–C(1)–Se(1)–Br(1)	−75.5(4)	Se(1)–C(1)–C(2)–Se(2)	−1.1(6)
C(2)–C(1)–Se(1)–Br(2)	97.8(4)		

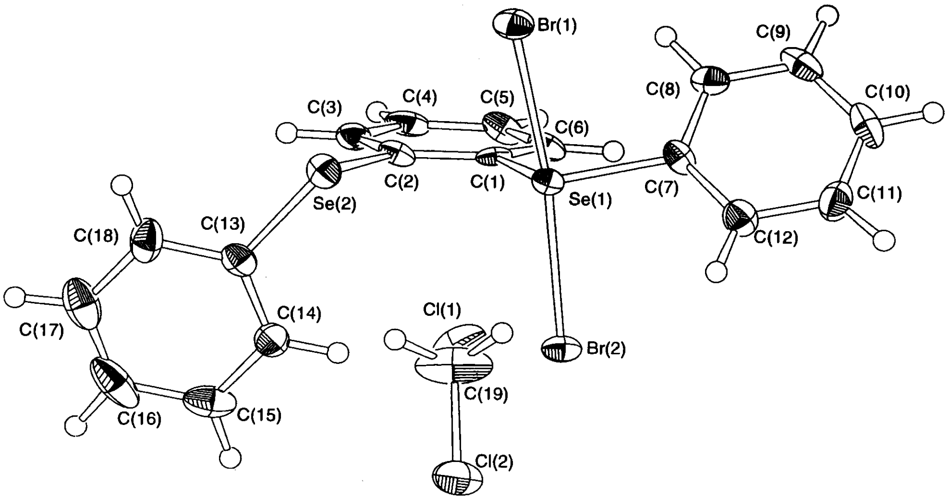
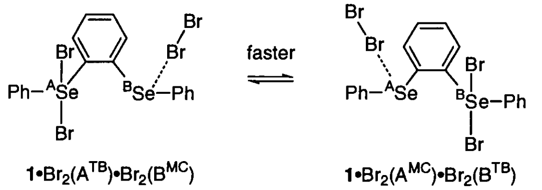
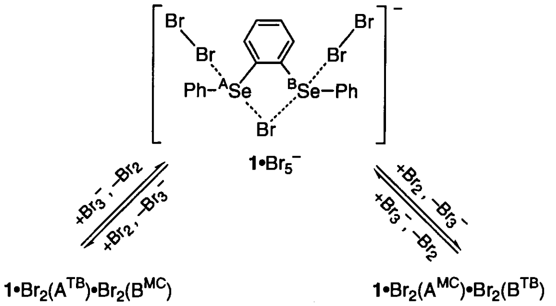


Fig. 1. Structure of $1{\cdot}Br_2$.



(3)

The bromine migration will occur between the two Se atoms intramolecularly in $1{\cdot}Br_2$ (Eq. (2)), but the intermolecular process may also be via dissociation–recombination process of the components. The intramolecular process seems only marginally faster than the intermolecular one: the bromine migration in $1{\cdot}Br_2$ is not significantly faster than that in $2{\cdot}Br_2$ and $3{\cdot}Br_2$ [23]. The signals of the former become sharper as $1{\cdot}2Br_2$ (TB, MC) is formed with the addition of bromine to the $1{\cdot}Br_2$ solution. The site exchange would be facilitated by free bromine in the solvent. It is natural to assume that the intramolecular exchange process is accelerated by adding bromine.



(4)

We propose a mechanism of the facile site exchange between (TB, MC) and (MC, TB) in $1{\cdot}2Br_2$, which is shown in Eq. (4). The reaction proceeds along with a key intermediate, $1{\cdot}Br_5^-$. The anion may be produced in the reaction of $1{\cdot}2Br_2$ with a tribromide ion, for example: Br^- is added to $1{\cdot}2Br_2$ in this reaction. The proposed intermediate contains a bridging bromine atom. Such a bridging bromine atom in organic chalcogen compounds is reported for $C_6H_{10}Br_6Te_2$ [24]. The intermediacy of $1{\cdot}Br_5^-$ is further examined based on the MO calculations.

2.4. Examination based on ab initio MO calculations

Ab initio MO calculations are performed on **1** and $1{\cdot}Br_2$ (TB) with the HF/6-311 + G(d,p) method using the Gaussian 94 program [25]. Fig. 2 shows the results. The observed structure of $1{\cdot}Br_2$ is well reproduced in the calculations. In order to clarify the structural and mechanistic future of $1{\cdot}nBr_2$, model calculations are also performed on 1,2-bis(methylselanyl)ethene (**4**), $4{\cdot}Br_2$ (TB), $4{\cdot}2Br_2$ (TB,MC), and $4{\cdot}Br_5^-$ with the B3LYP/6-311 + G(d,p) method [26]. Fig. 2 also contains the results. The nonbonded Se(2)···Se(1)–C 3c–4e interactions are strongly suggested in **1** and $1{\cdot}Br_2$, which are stabilized by the electron donor–acceptor interaction, since the atoms in the observed and/or the calculated structures are almost on the plane of central benzene. The torsional angle of $C_1C_2Se_2C_i$ of 108–130° also supports the interaction. The optimized structures of **4** and $4{\cdot}Br_2$ (TB) are close to those of **1** and $1{\cdot}Br_2$ (TB), respectively, except for the torsional angles between $C_1C_2Se_2C_i$ and $C_1C_2Se_2C_{Me}$. The angles of the former are substantially larger than those of the latter in magnitude.

The key intermediate $1{\cdot}Br_5^-$ is proposed to be produced in the reaction of $1{\cdot}2Br_2$ (TB, MC) with Br_3^-. A model anion $4{\cdot}Br_5^-$ is calculated to be the C_s symmetry and its frequencies are predicted to all be positive by the frequency analysis. The total energy of $4{\cdot}Br_5^-$ with Br_2 is evaluated to be not so different from that of $4{\cdot}2Br_2$ (TB, MC) with Br_3^-: $\Delta H = H(4{\cdot}Br_5^-) + H(Br_2) - H(4{\cdot}2Br_2) - H(Br_3^-) = 0.0117$ au (30.7 kJ mol^{-1}). The results are in accordance with the mechanism proposed in Eq. (4) and demonstrate that the anion is likely to exist in solutions.

3. Experimental

^{1}H (400 MHz), ^{13}C (100 MHz), and ^{77}Se (76 MHz) NMR spectra were recorded on a JEOL JNM-LA 400 spectrometer. The ^{1}H, ^{13}C, and ^{77}Se chemical shifts are given in ppm relative to those of internal $CHCl_3$ slightly contaminated in the solution, $CDCl_3$ as the solvent, and external MeSeMe, respectively. Chemicals were used without further purification unless otherwise noted. Solvents were purified by standard methods. Melting points were measured with a Yanako-MP apparatus and uncorrected. Column chromatography was performed on silica gel (Fuji Silysia BW-300), acidic alumina and basic alumina (E. Merck).

*3.1. Synthesis of 1,2-bis(phenylselanyl)benzene (**1**) [27]*

A mixture of diphenyliodonium-2-carbonylate [28] (6.0 g; 78.8 mmol) and diphenyl diselenide (4.1 g; 13.1 mmol) in *o*-dichlorobenzene (40 ml) was refluxed at 180°C for 2 h under an argon atmosphere. The removal of the solvent under reduced pressure was given the impure orange oil. The oil was purified by Silica Gel column chromatography containing basic alumina to give **1** (a colorless oil; 4.0 g; 78% yield); NMR is in Table 1.

*3.2. Synthesis of 1,4-bis(phenylselanyl)benzene (**2**)*

Diphenyldiselenide (5.0 g; 16.0 mmol) was reduced by $NaBH_4$ (1.33 g; 35.2 mmol) in ethanol (50 ml) under an argon atmosphere. After a few minutes, DMF (60 ml) was substituted forethanol. Then dibromobenzene (3.4 g; 14.4 mmol) and Cu_2O (5.0 g; 35.0 mmol) were added. After a usual workup, the solid was purified by Silica Gel column chromatography containing basic alumina to give **2** (colorless needles; 3.98 g; 64% yield): m.p. 100–101°C; NMR is in Table 2. Anal. Calc. for $C_{18}H_{14}Se_2$: C, 55.69; H, 3.64. Found: C, 55.62; H, 3.65%.

*3.3. Synthesis of 1,4-bis(p-tert-butylphenylselanyl)benzene (**3**)*

Bis(*p-tert*-butylphenyl)diselenide (3.0 g; 7.1 mmol) was reduced by $NaBH_4$ (0.59 g; 15.6 mmol) in ethanol (30 ml) under an argon atmosphere. After a few minutes, DMF (60 ml) was substituted for ethanol. Then dibromobenzene (1.33 g; 5.64 mmol) and Cu_2O (2.22 g; 15.5 mmol) were added. After a usual workup, the solid was purified by Silica Gel column chromatography containing basic alumina to give **3** (colorless needles; 1.75 g; 62% yield): m.p. 87–88°C; NMR is in Table 2. Anal. Calc. for $C_{26}H_{30}Se_2$: C, 62.40; H, 6.04. Found: C, 62.10; H, 6.03%.

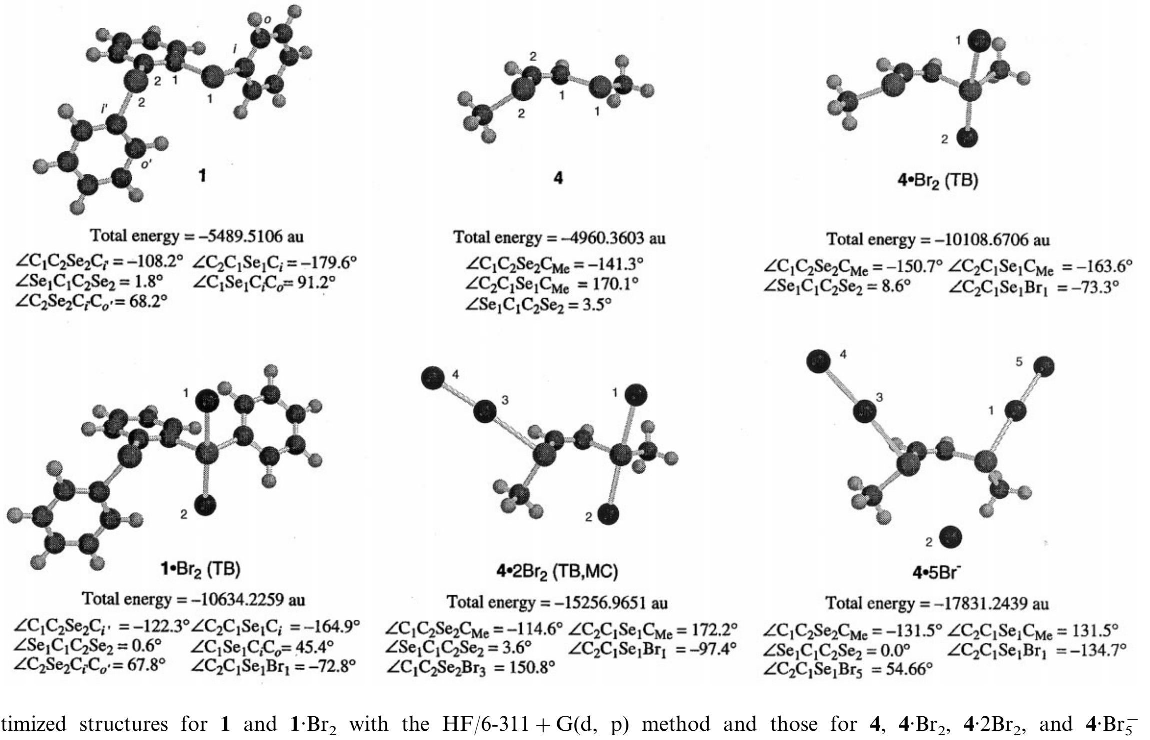


Fig. 2. Optimized structures for **1** and **1**·Br_2 with the HF/6-311 + G(d, p) method and those for **4**, **4**·Br_2, **4**·$2Br_2$, and **4**·Br_5^- with the B3LYP/6-311 + G(d,p) method. Total energies for Br_2 are − 5144.7265 and − 5148.2849 au with HF/6-311 + G(d, p) and B3LYP/6-311 + G(d, p) methods, respectively. The energy for Br_3^- is evaluated to be − 7722.5754 au with the latter method.

*3.4. Synthesis of 1,2-bis(phenylselanyl)benzene dichloride (**1**·Cl_2)*

Chlorine adducts were precipitated when sulfuranyl chloride was introduced to a selenide solution in usual solvents, hexane and chloroform (chloroform-*d*), after the concentration became substantially larger than the solubility. **1**·Cl_2 (colorless needles; 88% yield): m.p. 119°C; NMR is in Table 1. Anal. Calc. for $C_{18}H_{14}Cl_2Se_2$: C, 47.09; H, 3.07. Found: C, 47.22; H, 3.10%.

*3.5. Synthesis of 1,2-bis(phenylselanyl)benzene tetrachloride (**1**·2Cl_2)*

Pale yellow crystals: m.p. 198–200°C (Lit. m.p. 196–200°C) [27]; NMR is in Table 1.

*3.6. Synthesis of 1,2-bis(phenylselanyl)benzene dibromide (**1**·Br_2)*

Orange crystals: m.p. 107°C. NMR is in Table 1. Anal. Calc. for $C_{18}H_{14}Br_2Se_2$: C, 39.45; H, 2.58. Found: C, 39.51; H, 2.54%.

*3.7. Synthesis of 1,2-bis(phenylselanyl)benzene tetrabromide (**1**·2Br_2)*

Red crystals: m.p. 77°C. NMR is in Table 1. Anal. Calc. for $C_{36}H_{28}Br_{10}Se_4$: C, 27.44; H, 1.80. Found: C, 27.44; H, 1.78%.

*3.8. Synthesis of 1,4-bis(phenylselanyl)benzene dichloride (**2**·Cl_2)*

Colorless needles: NMR is in Table 2. Anal. Calc. for $C_{18}H_{14}Cl_2Se_2$: C, 47.09; H, 3.07. Found: C, 47.32; H, 3.15%.

*3.9. Synthesis of 1,4-bis(phenylselanyl)benzene tetrachloride (**2**·2Cl_2)*

Pale yellow crystals: NMR is in Table 2. Anal. Calc. for $C_{18}H_{14}Cl_2Se_2$: C, 47.09; H, 3.07. Found: C, 47.26; H, 3.11%.

*3.10. Synthesis of 1,4-bis(phenylselanyl)benzene dibromide (**2**·Br_2)*

Orange crystals: NMR is in Table 2. Anal. Calc. for $C_{18}H_{14}Br_2Se_2$: C, 39.45; H, 2.58. Found: C, 39.70; H, 2.60%.

*3.11. Synthesis of 1,4-bis(phenylselanyl)benzene tetrabromide (**2**·2Br_2)*

Red crystals: NMR is in Table 2. Anal. Calc. for $C_{18}H_{14}Br_4Se_2$: C, 30.54; H, 1.99. Found: C, 30.72; H, 1.98%.

*3.12. X-ray crystal structure analysis of **1**·Br_2*

The single crystals were obtained via slow evaporation of chloroform and dichloromethane solutions. One of the crystals which were suitable was subjected to X-ray crystallographic analysis. All measurements were made on a Rigaku RAXIS imaging plate with a detector with graphite monochromated Cu–K_α radiation ($\lambda = 1.54178$ Å).

The data were collected at a temperature of -70 ± 1°C to a maximum 2θ value of 136.5°. A total of 21 6.0° oscillation images were collected, each being exposed for 20 min. The crystal-to-detector distance was 105.00 mm. The detector swing angle was 0.00°. Readout was performed in the 0.100 mm pixel mode.

The structure of **1**·Br_2 was solved by direct methods, SIR92 [29], and expanded using Fourier techniques, DIRDIF94 [30]. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on a total of 6413 reflections with 3198 observed reflections ($I > 1.50\sigma(I)$). Crystallographic details are listed in Table 4.

3.13. Ab initio MO calculations

Ab initio molecular orbital calculations were performed on Origin computer using Gaussian 94 program [25] with 6-311 + G(2d,p), 6-311 + G(d,p) and 3-21G* basis sets at the DFT (B3LYP level). The calculations at the HF level were also carried out.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 143534 for **1**·Br_2. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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Table 6

Calculated δ_i(H), δ_i(C), and δ_i(Se) values for PhSeH and PhSeMe and the observed values for PhSeMe and PhSePh, together with the δ values of the parent selenides

Compound	H(Me)	C(Me)	H-2	H-2′	H-3	H-3′	H-4	C-1	C-2	C-2′	C-3	C-3′	C-4	Se	Structure
Calculated values for PhSeH and PhSeMe with the B3LYP/6-311+G(2d,p) method [a]															
PhSeH	3.71		7.43	7.40	7.44	7.39	7.30	148.4	131.7	133.9	133.7	134.1	128.9	80.7	Selenide
	0.00		0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
PhSeCl$_2$H	4.81		0.31	0.47	0.30	0.37	0.51	6.1	−0.4	2.4	1.5	2.0	7.3	151.2	TB
PhSeBr$_2$H	3.54		0.30	0.47	0.32	0.39	0.52	4.5	0.7	3.6	1.8	2.2	7.4	36.7	TB
PhSeBr$_2$H	0.83		0.07	0.03	0.18	0.16	0.25	−4.4	1.0	1.0	1.1	1.0	3.6	97.8	MC [b]
PhSeBr$_2$H	1.20		0.29	0.76	0.15	0.32	0.39	−10.9	6.7	6.6	0.6	0.8	6.0	54.7	MC
PhSeMe	2.13	15.1	7.50	6.20	7.44	7.53	7.30	153.7	132.0	128.0	133.0	134.0	128.1	165.3	Selenide
	0.00	0.0	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
PhSeCl$_2$Me	1.33	36.6	0.37	1.65	0.32	0.25	0.50	3.7	1.5	−0.3	2.0	1.1	8.1	232.6	TB
PhSeBr$_2$Me	1.32	35.2	0.35	1.60	0.32	0.25	0.50	1.9	2.4	0.8	2.1	1.3	8.1	153.4	TB
PhSeCl$_2$Me	0.14	15.3	0.27	2.18	0.16	0.27	0.44	−7.6	6.3	10.9	0.5	1.4	7.3	169.3	MC
PhSeBr$_2$Me	0.17	16.1	0.29	2.20	0.17	0.27	0.45	−8.1	6.5	11.2	0.7	1.5	7.5	155.0	MC
Observed values															
PhSeMe	2.36	7.2	7.42		7.26		7.21	131.7	130.2		128.8		125.9	207.1	Selenide
	0.00	0.0	0.00		0.00		0.00	0.0	0.0		0.0		0.0	0.0	
PhSeCl$_2$Me	1.57	38.5	0.54		0.31		0.36	9.3	−1.7		1.1		5.8	284.5 [c]	TB
PhSeBr$_2$Me	1.56	36.4	0.50		0.31		0.33	6.4	−1.1		1.4		5.7	226.8 [c]	TB
PhSeI$_2$Me	0.27	5.0	0.10		0.09		0.14	−2.0	0.2		0.6		1.9	44.7 [d]	MC
[PhSeI$_2$Me]	0.42	9.1	0.15		0.13		0.21	−3.6	0.4		1.0		3.4	67	[MC]
PhSePh			7.47		7.26		7.27	131.1	132.9		129.9		127.2	423.0	Selenide
			0.00		0.00		0.00	0.0	0.0		0.0		0.0	0.0	
PhSeCl$_2$Ph			0.56		0.31		0.29	11.4	−1.7		0.5		4.4	160.7 [e]	TB
PhSeBr$_2$Ph			0.59		0.27		0.31	7.9	−0.5		0.6		4.4	120.0 [f]	TB
PhSeI$_2$Ph			0.03		0.05		0.03	−1.0	−0.3		0.3		1.1	6.8 [g]	MC
[PhSeI$_2$Ph]			0.08		0.13		0.08	−1.9	−0.6		0.6		2.1	17	[MC]

[a] The σ(Se) value for MeSeMe and σ(C) and σ(H) for TMS were 1952.3, 181.9, and 30.99, respectively.

[b] The torsional angle of C_oC_iSeH was assumed to be 0.00°.

[c] $\nu_{1/2} = 5$ Hz.

[d] $\nu_{1/2} = 8$ Hz.

[e] $\nu_{1/2} = 4$ Hz.

[f] $\nu_{1/2} = 80$ Hz.

[g] $\nu_{1/2} = 2$ Hz.

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Appendix A

The criteria of the experimental rule distinguishing MC from TB of $ArSeX_2R$ in solutions are confirmed by the ab initio MO calculations using the Gaussian 94 program [25] with the B3LYP/6-311G + (2d,p) method [31] based on the GIAO theory. The GIAO magnetic shielding tensors of ^1H, ^{13}C, and ^{77}Se nucleus (σ(X): X = H, C, and Se) are calculated on the TB and MC structure for $PhSeX_2H$ and $PhSeX_2Me$ (X = Cl, Br, or null). Calculations are also performed for $PhSeBr_2H$ (MC) assuming the planar structure for PhSeH. The results are collected in Table 6.

The criteria are well supported by the MO calculations especially for those of δ_i(C) [32]. One must be careful when the criteria concerning the δ_i(Se) are employed to determine the structure of halogen adducts aryl selenides, since the small positive δ_i(Se) values would not mean the formation of MC in some cases. It might be the reflection of the equilibrium between TB and its components. The upfield shifts of the *ipso* carbons of aryl groups are safely applied to determine the MC formation of the adducts.

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[11] The criteria are summarized as follows. (1) Large downfield shifts of *ipso* and *para* carbons of aryl groups are observed in the TB formation relative to those of the parent selenides: the former depends on the electronegativity of halogens, whereas the latter is almost independent of them. (2) The signal of *para* carbon shifts downfield, whereas the *ipso* carbon goes upfield in the formation of MC: the shift values are often small but the values must be moderate if the equilibrium between the MC and its components are taken into account. (3) Very large downfield shifts are observed for ^{77}Se-NMR signals in the TB formation, whereas the values are small in the formation of MC. (4) Large downfield shift of the *ortho* protons in the TB formation are also useful.

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[32] Although the MO calculations demonstrate that the criteria are effective for $ArSeX_2R$ (TB and MC) where R = H and Me and X = Cl and Br, the results must be applicable for various $ArSeX_2R$ (TB and MC). The experimental criteria are established on $ArZX_2R$ (TB) where (Z,X) = (Se,Cl), (Se, Br), (Te, F), (Te,Cl), (Te,Br), and (Te,I) and on $ArZX_2R$ (MC) where (Z,X) = (S,Br), (S, I), and (Se,I).