Evidence for the Equilibrium and Estimation of the Equilibrium Constants between Molecular Complexes and Trigonal Bipyramidal Adducts of Diaryl Selenide Dibromides in Solution

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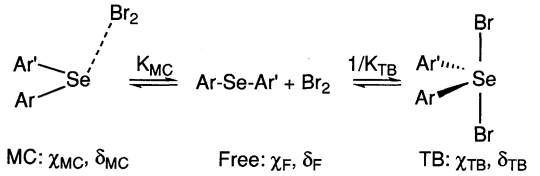
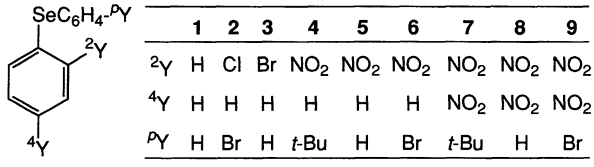
The equilibrium is clearly shown between molecular complexes (MC's) and trigonal bipyramidal adducts (TB's) in 2-$O_2NC_6H_4SeBr_2C_6H_4Y$-*p* in solution. The equilibrium constants are also estimated. Both TB's and MC's become unstable when the effective electronegativity of the selenium atom and the bulkiness around the atom in a selenide are increased, however, the magnitude is larger for TB's than for MC's.

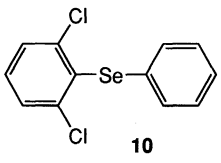
Although trigonal bipyramidal adducts (TB's) of selenides with bromine,[1a,b] as well as the molecular complexes (MC's) with iodine,[1b,c,2] have been established to equilibrate with the components in solution, the equilibrium of TB's with MC's has scarcely been mentioned. We have recently reported the typical examples of the MC formation of some diaryl selenides with bromine.[3] During the course of the investigations, we wondered, there must exist the equilibrium between an MC and a TB in a selenide dibromide, together with the components (eq. 1), if the selenide in question is suitably modulated.



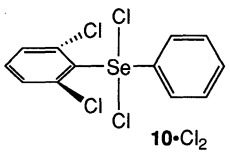
$$K = [MC] / [TB] = K_{TB} / K_{MC} \quad (2)$$



	1	2	3	4	5	6	7	8	9
^{2}Y	H	Cl	Br	NO_2	NO_2	NO_2	NO_2	NO_2	NO_2
^{4}Y	H	H	H	H	H	H	NO_2	NO_2	NO_2
^{p}Y	H	Br	H	*t*-Bu	H	Br	*t*-Bu	H	Br



10



10•Cl_2

A new method was devised to prove the equilibrium clearly. The chemical shifts of the *ipso* carbons of diaryl selenides were employed, since they changed dramatically on the structures of the adducts: the TB formation causes large downfield shifts for the *ipso* carbons, whereas the upfield shifts for the carbons are characteristic in the MC formation.[2] Therefore the equilibrium can be clearly proved, if one prepares such a diaryl selenide of which one of the *ipso* carbons shifts upfield whereas the other goes downfield, when bromine is added to the solution. The chemical shifts of *para* carbons were also employed to estimate the equilibrium constants.

Various diaryl selenides (**1** - **9**) were examined.[4] Table 1

Table 1. ^{13}C and ^{77}Se NMR Chemical Shifts of $ArSeX_2Ar'$ (X = null, Cl, Br, I) and the Calculated Shifts, together with the Intrinsic Shifts for "**4**•Br_2 (TB)" and "**4**•Br_2 (MC)"[a]

Compound[b]	C(1)	C(*i*)	C(4)	C(*p*)	^{77}Se
1	131.1	131.1	127.2	127.2	423.0
1•Cl_2 (TB)	+11.4	+11.4	+4.4	+4.4	+160.7
1•Br_2 (TB)	+7.9	+7.9	+4.4	+4.4	+120.0
"**1**•I_2 (MC)"[c]	-1.9	-1.9	+2.1	+2.1	(+17.0)[d]
4	136.2	124.5	125.5	153.2	481.2
4•Cl_2	+4.5	+9.1	+6.6	+3.1	+105.4
4•Br_2	-0.1	+2.0	+3.1	+1.4	----[e]
4•Br_2	-0.2	+1.9	+3.1	+1.4	
4•2Br_2	-0.2	+3.1	+4.6	+2.2	+49.4
4•2Br_2	-0.3	+3.0	+4.6	+2.2	
4•3Br2	-0.3	+3.5	+5.3	+2.6	+58.4
4•3Br_2	-0.4	+3.5	+5.4	+2.6	
"**4**•nBr_2"[c]	-0.5	+4.0	+6.1	+2.9	(+65.1)[d]
4•nBr_2	-0.6	+3.9	+6.2	+2.9	
4•I_2	-0.8	-0.3	+0.4	+0.2	+0.3
5	135.8	128.0	125.6	129.8	
5•2Br_2	-0.5	+2.3	+3.6	+1.4	
5•2Br_2	-0.6	+2.2	+3.6	+1.4	
6	135.1	126.9	126.0	124.8	
6•2Br_2	-0.5	+1.1	+2.0	+0.9	
6•2Br_2	-0.4	+1.0	+2.0	+0.9	
7	145.9	123.4	144.9	154.3	
7•2Br_2	-0.6	-0.1	0.0	+0.1	
7•2Br_2	-0.5	-0.2	+0.1	+0.1	
10	130.4	130.8	130.5	126.8	407.1
10•Cl_2 (TB)[f]	+11.2	+8.3	+1.8	+5.1	+160.3
10•8Br_2 (MC)[g,h]	-1.3	-1.6	+1.7	+2.4	----[e]
10•I_2 (MC)	0.0	0.0	0.0	+0.1	+0.6
"**4**•Br_2 (TB)"[i]	+0.7	+5.1	+6.6	+3.1	
"**4**•Br_2 (MC)"[i]	-8.0	-2.9	+4.0	+1.9	

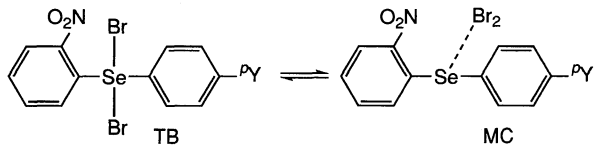
[a] Chemical shifts of halogen adducts are given from the parent selenides and the calculated shifts are shown by underlined. [b] [S] = 0.1 mol/l in $CDCl_3$. [c] Extrapolated chemical shifts. [d] Estimeted values based on the ^{13}C chemical shifts. [e] Not determined due to broadening and/or bromination. [f] See refs. 3b and 6. [g] At -30 °C. [h] See ref. 7. [i] Estimated intrinsic chemical shifts for the structures: the preliminary rules (ref. 8) predicted +0.8 and -7.2 ppm for C-I's of the "TB" and the "MC", respectively, which were improved as shown here. The values for other carbons were the same as predicted.

Table 2. Calculated Molar Fractions and Equilibrium Constants[a]

Compound	χ_F	χ_{MC}	χ_{TB}	K[b]
4•Br_2	0.51	0.07	0.42	0.17
4•2Br_2	0.26	0.10	0.64	0.16
4•3Br_2	0.13	0.12	0.75	0.16
"**4**•nBr_2"[c]	0.00	0.14	0.86	0.16
5•2Br_2	0.39	0.15	0.46	0.33
6•2Br_2	0.62	0.16	0.22	0.73
7•2Br_2	0.95	0.05	0.00	d

[a] Values are calculated under given conditions. [b] See eq. 2. [c] Under extrapolated conditions. [d] Very large.

shows the halogen induced NMR chemical shifts of C-1, C-*i*, C-4, and C-*p* carbons and selenium of **1** and **4** - **7**, among the selenides, together with those of 2,6-dichlorophenyl phenyl selenide (**10**). The chemical shifts of chlorine and iodine adducts of **1** - **10** showed the characteristics of the TB and MC formation, respectively.[2] The C-1 and C-*i* carbon chemical shifts of **2** and **3**, as well as **1**, moved downfield monotonically as bromine was added to the solution, while those of **7** - **10** shifted upfield with bromine. Indeed these results show that the bromine adducts of **1** - **3** and **7** - **10** are TB's and MC's, respectively, equilibrating with the components, but the observations do not tell whether the adducts are in equilibrium between TB's and MC's or not, at the first glance. On the other hand, the C-1 carbon chemical shifts moved upfield monotonically in **4** - **6**, whereas their C-*i* carbon chemical shifts moved downfield, as bromine was added to the solution. The characteristic behavior of



the chemical shifts in **4** - **6** with bromine satisfies the requirements to prove the existence of the equilibrium between TB's and MC's, together with the components, in solution.

After establishment of the equilibrium between TB's and MC's, next extension of our study is to estimate the equilibrium constants. Intrinsic chemical shifts of "$ArSeBr_2Ar'$ (TB)" and "$ArSeBr_2Ar'$ (MC)" are necessary for the estimation. The values of "$ArSeBr_2Ar'$ (TB)" were estimated from the data of various $ArSeX_2Ar'$ (TB: X = Cl, Br).[5] The intrinsic values of "$ArSeBr_2Ar'$ (MC)" were roughly estimated based on the extrapolated chemical shifts of the bromine adduct of **10** ("**10**•Br_2 (MC)")[6,7] and those of "$PhSeI_2Ph$ (MC)", together with those for "$PhSeI_2Me$ (MC)".[2]

The values enabled to set up the empirical rules,[8] from which the molar fractions for TB's, MC's, and free selenides and the equilibrium constants (K's in eq. 2) were calculated. The preliminary intrinsic chemical shifts were improved with a trial and error method until the difference between predicted and observed chemical shifts was less than 0.1 ppm. The results are summarized in Table 2. Both TB's and MC's do exist and they are in equilibrium with the components in **4** - **6**. The K value becomes larger as the substituent at the *p*-position of **4** - **6** changes from the *t*-butyl group to the bromo group. While **1**•Br_2 itself exists as a TB in solution, the substitution at the *o*-position with a nitro group or a halogen, as in **2** - **6**, promotes the dissociation to the components, which equilibrate with an MC. Only MC's are formed in 2,4-dinitro derivatives **7** - **9** and in **10**. The ^{77}Se chemical shifts of the adducts also supported the existence of the equilibrium.

These results exhibit that 1) diaryl selenides yield both TB's and MC's with bromine, which equilibrate each other, together with the components, if the selenides are suitably modulated, 2) both TB's and MC's become unstable when the effective electronegativity of the selenium atom and the bulkiness around the atom in a selenide are increased: the magnitude of the effects is larger for TB's than for MC's,[9] and 3) the stability of the Se-Br-Br bond in MC's would not be different from that of the Br-Se-Br bond in TB's, if the conditions are suitable.

References and Notes

1 a) J. D. McCullough and B. A. Eckerson, *J. Am. Chem. Soc.*, **67**, 707 (1945); b) J. D. McCullough, *J. Am. Chem. Soc.*, **64**, 2672 (1942); N. W. Tideswell and J. D. McCullough, *J. Am. Chem. Soc.*, **79**, 1031 (1957); c) J. D. McCullough and B. A. Eckerson, *J. Am. Chem. Soc.*, **73**, 2954 (1951).

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3 a) W. Nakanishi, Y. Yamamoto, S. Hayashi, H. Tukada, and H. Iwamura, *J. Phys. Org. Chem.*, **3**, 369 (1990); W. Nakanishi, Y. Okumura, and S. Hayashi, *J. Phys. Org. Chem.*, **4**, 523 (1991); b) W. Nakanishi, S. Hayashi, Y. Nakamura, and H. Iwamura, *Chem. Lett.*, **1992**, 735.

4 Elementary analyses were satisfactory for the new selenides.

5 Halogen induced chemical shifts of various diaryl selenides were averaged and/or simplified, if necessary.

6 There would be no room for the TB formation with bromine around the selenium atom of **10**: the TB could be negligible in **10**•Br_2. The 2,6-$Cl_2C_6H_3$ plane in **10**•Cl_2 (TB) has been demonstrated to be locked perpendicularly to the hypervalent Cl-Se-Cl bond[3b] and the chemical shifts of **10** were little affected by the addition of iodine (Table 1), exhibiting the difficult approach of iodine to the selenium atom of **10**.

7 The chemical shifts of **10** + 8Br_2 measured at -30 °C were recognized to be intrinsic for "**10**•Br_2".

8 Preliminary rules are as follows (SeX_2 denotes $ArSeX_2Ar'$): 1) the dissociation of $SeCl_2$ (TB) is negligible, 2) $\Delta\delta$(C-*p*)'s of "$SeBr_2$ (TB)" are equal to those of $SeCl_2$ (TB), 3) $\Delta\delta$(C-*p*)'s of "$SeBr_2$ (MC)" are 60 % of those of "$SeBr_2$ (TB)", 4) $\Delta\delta$(C-*i*)'s of "$SeBr_2$ (TB)" are estimated by eqs. 4a and 4b,

$\Delta\delta$(C-*i*)'s of "$SeBr_2$ (TB)" = ($\Delta\delta$(C-*i*)'s of $SeCl_2$) - 4.0, if $\Delta\delta$(C-*i*)'s of the latter $\geq$ 5 ppm (4a)

$\Delta\delta$(C-*i*)'s of "$SeBr_2$ (TB)" = 0.04 x ($\Delta\delta$(C-*i*)'s of $SeCl_2$)^2, if $\Delta\delta$(C-*i*)'s of the latter < 5 ppm (4b)

5) $\Delta\delta$(C-*i*)'s of "$SeBr_2$ (MC)" are smaller than those of "$SeBr_2$ (TB)" by 8.0 ppm.

9 This supports our strategy to prepare MC's of selenides with bromine. See ref. 3.