Table III. Bond Lengths (Å) and Bond Angles (deg)

Rh-S(1)	2.462 (1)	Rh-S(2)	2.320 (1)
Rh-S(3)	2.482 (1)	Rh-C(1)	2.099 (6)
Rh-C(2)	2.098 (5)	Rh-C(5)	2.216 (6)
Rh-C(6)	2.197 (5)	S(1)-C(11)	1.822 (5)
S(1)-C(12)	1.834 (6)	S(2)-C(13)	1.819 (6)
S(2)-C(14)	1.828 (6)	S(3)-C(15)	1.821 (6)
S(3)-C(9a)	1.812 (5)	C(1)-C(2)	1.392 (8)
C(1)-C(8)	1.514 (9)	C(2)-C(3)	1.509 (11)
C(3)-C(4)	1.486 (11)	C(4)-C(5)	1.489 (11)
C(5)-C(6)	1.383 (9)	C(6)-C(7)	1.534 (10)
C(7)-C(8)	1.458 (11)	C(9)-C(10)	1.524 (8)
C(9)-S(3a)	1.811 (5)	C(10)-C(11)	1.512 (7)
C(12)-C(13)	1.507 (9)	C(14)-C(15)	1.485 (8)
S(1)-Rh-S(2)	86.0	S(1)-Rh-S(3)	95.3
S(2)-Rh-S(3)	86.5	S(1)-Rh-C(1)	154.7 (2)
S(2)-Rh-C(1)	88.4 (2)	S(3)-Rh-C(1)	109.0 (2)
S(1)-Rh-C(2)	116.1 (2)	S(2)-Rh-C(2)	85.9 (2)
S(3)-Rh-C(2)	147.0 (2)	S(2)-Rh-C(5)	159.7 (2)
S(1)-Rh-C(5)	87.1 (2)	C(1)-Rh-C(5)	89.7 (2)
S(3)-Rh-C(5)	113.2 (2)	S(1)-Rh-C(6)	110.4 (2)
C(2)-Rh-C(5)	80.0 (3)	S(3)-Rh-C(6)	82.8 (2)
S(2)-Rh-C(6)	161.2 (2)	Rh-S(1)-C(11)	114.5 (2)
Rh-S(1)-C(12)	103.6 (2)	C(11)-S(1)-C(12)	100.5 (3)
Rh-S(2)-C(13)	104.0 (2)	Rh-S(2)-C(14)	105.5 (2)
C(13)-S(2)-C(14)	101.8 (3)	Rh-S(3)-C(15)	99.6 (2)
Rh-S(3)-C(9a)	112.7 (2)	C(15)-S(3)-C(9a)	102.4 (2)
C(1)-C(2)-C(3)	125.1 (6)	C(2)-C(1)-C(8)	123.6 (5)
C(3)-C(4)-C(5)	114.6 (6)	C(2)-C(3)-C(4)	114.4 (6)
C(5)-C(6)-C(7)	127.1 (6)	C(4)-C(5)-C(6)	123.6 (6)
C(1)-C(8)-C(7)	113.7 (6)	C(6)-C(7)-C(8)	114.4 (6)
C(9)-C(10)-C(11)	111.6 (4)	C(10)-C(9)-S(3a)	110.3 (4)
S(1)-C(12)-C(13)	112.1 (4)	S(1)-C(11)-C(10)	109.8 (4)
S(2)-C(14)-C(15)	111.2 (4)	S(2)-C(13)-C(12)	113.3 (4)
		S(3)-C(15)-C(14)	113.7 (4)

labeled atoms of the ring, the pertinent values are −157, 80, 89, 52, 63, −147, 57, 73, and 154°. The torsion angles observed in the structure of the [18]aneS_6 free ligand[9] are different from these values, but both hexathia crown ethers are "inside out". Allowing for the flexibility of the [18]aneS_6 molecule, its coordination properties as a ligand should be similar to those of the [20]aneS_6 ligand. Such "noncrown", "inside-out" complexes may well be the rule for these large thioether macrocycles. As a consequence, these ligands may prefer to serve as bridging ligands between metal atoms rather than participating in the classical, encapsulating, "crownlike" bonding.

Acknowledgment is made to L. C. Strickland (of these laboratories) for his assistance with the crystal structure investigation. We also thank Dr. Steve Cooper for sending the atomic coordinates of the [18]aneS_6 molecule prior to publication of that structure.

Registry No. 1, 87156-15-8; **2**, 87156-17-0; $[Rh(COD)Cl]_2$, 12092-47-6; 1,4,7-trithiaheptane, 3570-55-6; 1,3-dibromopropane, 109-64-8.

Supplementary Material Available: Tables of structure factor amplitudes, hydrogen atom parameters, anisotropic thermal parameters, and bond lengths and bond angles (21 pages). Ordering information is given on any current masthead page.

Contribution from the Corporate Research Department,
Dow Corning Corporation, Midland, Michigan 48640

Exchange of Halogens between Tetrahalosilanes and Aryl Halides

Patricia M. Scaduto* and John L. Speier

Received February 14, 1983

Recently, we were studying reactions of bromobenzene with trichlorosilane in the vapor phase above 300 °C in small sealed Pyrex glass tubes and were surprised to find chlorobenzene among the products. The most likely source of chlorobenzene required an unknown exchange process, e.g.

$$\mathrm{SiCl + PhBr = SiBr + PhCl}$$

No example like this was found in published works. Exchanges of halogens between triethyliodosilane and alkyl halides[1] and between trimethyliodosilane and alkyl, benzyl, and allyl halides[2] were reported.

Results and Discussion

Mixtures of $SiCl_4$ and PhBr in a mole ratio of 1/1 underwent reversible exchange, which approached equilibrium at 310 °C in about 115 h. A constant value of about 0.07 was approached when the GLC area ratio of PhCl/PhBr was multiplied by the ratio of the Si–Br bonds/Si–Cl bonds. This latter ratio was calculated as the sum of the area percents of individual halosilanes multiplied by the number of Br or Cl atoms in each halosilane. Thus, in terms of individual bonds, not molecules

$$K = \frac{[\mathrm{C{-}Cl}]}{[\mathrm{C{-}Br}]}\,\frac{[\mathrm{Si{-}Br}]}{[\mathrm{Si{-}Cl}]} = 0.07 \qquad (1)$$

Various molar combinations of $SiCl_4$ and C_6Br_6 produced complex mixtures of compounds corresponding to the equation

$$n\mathrm{SiCl_4} + \mathrm{C_6Br_6} = n\mathrm{SiCl}_{4-m}\mathrm{Br}_m + \mathrm{C_6Br}_{6-nm}\mathrm{Cl}_{nm} \qquad (2)$$

$$m = 0, 1, 2, 3, 4$$

Equilibrium was approached in these systems in about 69 h at 310 °C and in about 1.5 h at 350 °C. The value of K calculated for this system by eq 1 was about 0.1.

To avoid the difficult task of quantitatively separating and identifying the compounds of the formula $C_6Br_{6-nm}Cl_{nm}$ when $nm = 0, 1, 2, 3, 4, 5$, and 6, values for m were approximated as the sum of the area percent of each halosilane multiplied by the number of Si–Br bonds each possessed. The identity of the halosilanes was established by GLC–mass spectrometry. Then $[\mathrm{Si{-}Br}] = nm$, $[\mathrm{Si{-}Cl}] = n(4 - m)$, $[\mathrm{C{-}Cl}] = nm$, and $[\mathrm{C{-}Br}] = 6 - nm$. $SiBr_4$ and C_6Cl_6 produced mixtures of products nearly identical with those from $SiCl_4$ and C_6Br_6, and equilibrium was reached in about the same time at the same temperatures. Values for K calculated by eq 1 ranged from 0.1 to 0.2.

A 1/1 molar mixture of $SiCl_4$ and EtBr was heated at 300 °C. Exchange occurred and approached equilibrium in about 17 h with the following area percents: EtCl, 11; $SiCl_4$, 41; EtBr, 30; $BrSiCl_3$, 15. These values in eq 1 give $K = 0.03$.

These few examples show that reversible exchange occurred in these systems. Equilibrium concentrations of Si-halogen/C–Halogen bonds were approached which were affected very little by the structure of the halosilane or of the organic halide.

Experimental Section

$SiCl_4$ was Dow Corning semiconductor grade. $SiBr_4$ was prepared by passing Br_2 over semiconductor grade silicon at 400 °C (98% pure $SiBr_4$ was produced, as determined by GLC). The organic halides were purchased reagent grade chemicals. All experiments were carried out in sealed 8-mm-o.d., 4-mm-i.d. Pyrex tubes about 17 cm long. Reagents were added to the tubes in a dry ice bath and sealed in

---

[1] Nagai, Y.; Maramatsu, H.; Ohtsuki, M.; Matsumoto, H. *J. Organomet. Chem.* **1969**, *17*, 819.

[2] (a) Friedrich, E. C.; Abma, C. B.; Vartanian, P. F. *J. Organomet. Chem.* **1980**, *187*, 203. (b) Friedrich, E. C.; DeLucca, G. *Ibid.* **1982**, *226*, 143.

0020-1669/83/1322-3363$01.50/0

Table I. Results from Exchange Reactions between Halosilanes and Aryl Halides

			GLC area %							
n	temp, °C	time, h	$SiCl_4$	$BrSiCl_3$	Br_2SiCl_2	Br_3SiCl	$SiBr_4$	PhCl	PhBr	*K*
$n SiCl_4 + PhBr = BrSiCl_3 + PhCl$										
1.0	310	21	30	12				16	39	0.03
1.0	310	45	31	15				18	33	0.05
1.0	310	115	28	16				21	31	0.07
0.25	350	65	6	8	6	2		20	58	0.1
$n SiBr_4 + PhCl = Br_3SiCl + PhBr$										
0.25	350	65	5	7	5	1		20	62	0.1
$n SiCl_4 + C_6Br_6 = n SiCl_{4-m}Br_m + C_6Br_{6-nm}Cl_{nm}$										
1.0	310	21	34	36	23	6.8	0.5			0.07
1.5	310	21	40	39	17	3.9	0.2			0.07
2.0	310	21	49	35	13	2.1	0.06			0.06
4.0	310	21	64	28	5.8	0.4	0.03			0.04
1.0	310	7.5	42	37	16.5	4.2	0.3			0.04
1.0	310	69	28	39	25	7.7	0.5			0.1
1.0	350	1.5	29	38	24	8.2	0.4			0.09
1.0	350	7.5	24.5	39	26.6	9.5	0.6			0.1
$n SiBr_4 + C_6Cl_6 = n SiBr_{4-m}Cl_m + C_6Cl_{6-nm}Br_{nm}$										
1.0	310	45	47	37	13	2.5	0.3			1.1
1.0	310	65	54	35	9.2	1.3	0.3			0.1
1.5	350	1.5	0.8	7.6	26	41	25			5.6
1.5	350	7.5	22.6	38.5	28	10	1			0.2
2.0	310	45	5.1	21	35.4	29	9.3			0.7
2.0	310	69	12	30	35	19	4			0.2

quantities to develop about 30–50 atm of pressure if vaporized as perfect gases at 300 °C. After each tube was heated, it was chilled in dry ice, opened, and capped with a rubber septum, and its contents were analyzed by GLC. An F&M Scientific Model 810 interfaced with a Perkin-Elmer Sigma-10 data system and $^3/_{16}$ in. × 10 ft stainless-steel column packed with 16.7% OV-210 on Chromosorb P with a temperature program of 20 °C/min from 60 to 280 °C was used. Products were identified by coinjection with authentic samples or by GLC–mass spectrometry for compounds such as $BrSiCl_3$, Br_2SiCl_2, and Br_3SiCl for which no authentic samples were available.

In this manner data tabulated in Table I were gathered.

Registry No. PhBr, 108-86-1; PhCl, 108-90-7; C_6Br_6, 87-82-1; C_6Cl_6, 118-74-1; $(SiCl_4)_n$, 10026-04-7; $(SiBr_4)_n$, 7789-66-4.