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Electrophilic cleavage reactions of carbon–silicon bonds in neutral hexacoordinate silicon compounds: diorgano(phthalocyaninato)silicon *

Kohei Tamao, Munetaka Akita, Hidehito Kato, and Makoto Kumada

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606 (Japan)

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Abstract

Preparations of diorgano(phthalocyaninato)silicon [(Pc)Si(R^1)(R^2)] and their reactions with *N*-bromosuccinimide (NBS), halogens, copper(II) halides, and 3-chloroperbenzoic acid (MCPBA) are reported. The alkyl–silicon bonds are readily cleaved by NBS, halogens, and CuX_2 to give the corresponding alkyl halides. The reactivity of aryl–silicon bonds toward NBS and halogen depends greatly on the electronic effect of the substituent on the benzene ring, but these bonds are almost inert to CuX_2. The reactivity of the carbon–silicon bond towards NBS cleavage decreases in the order $4\text{-MeOC}_6H_4 > n\text{-C}_8H_{17} > 4\text{-MeC}_6H_4 > Ph \gg 3\text{-CF}_3C_6H_4$. Cleavage of alkyl–silicon bonds may involve one-electron transfer from substrate to reagent and alkyl radical intermediates, while the electrophilic aromatic substitution mechanism may operate in the cleavage of aryl–silicon bonds. [(Pc)SiR_2] are stable to MCPBA.

Introduction

Hexacoordinate silicon compounds have received much attention in recent years [1]. Examples include organopentafluorosilicates as synthetic reagents [2], silicon-catecholates as synthetic intermediates [3], benzoxasiloles in stereochemical studies [4], phthalocyaninatosilicon derivatives as one-dimensional conductors [5], and reaction intermediates proposed in many types of reactions at silicon [6].

We have been interested in the reactivity of carbon–silicon bonds in silicon compounds with coordination numbers > 4 (i.e. extracoordinate compounds). We have studied the reactions of anionic organopentafluorosilicates (**1**) with a variety of

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* Dedicated to Professor Colin Eaborn in recognition of his important contributions to organometallic chemistry.

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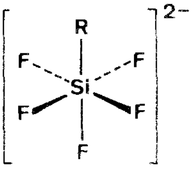
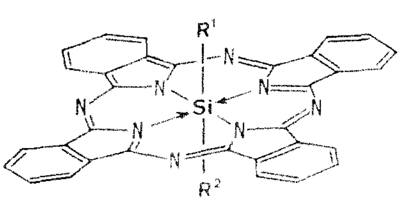
electrophiles which hardly affect carbon–silicon bonds in neutral tetracoordinate organosilicon compounds [2c–f]. Through those studies, we have demonstrated two new reaction mechanisms for cleavage of the carbon–silicon bond characteristic of anionic organopentafluorosilicates [2c,7]: (a) an electron-transfer mechanism (extracoordination effect) in reactions with halogens [2d], copper(II) halides [2e], tetracyanoethene [8], etc. and (b) an associative mechanism (template effect) in oxidative cleavage with 3-chloroperbenzoic acid (MCPBA) [6e].

In connection with this chemistry, we have been interested also in the reactivity of carbon–silicon bonds in neutral extracoordinate silicon compounds. We have now found that carbon–silicon bonds in diorgano(phthalocyaninato)silicon (**2**) are also readily cleaved by certain electrophiles.



(1)



[(Pc)Si(R^1)(R^2)] (**2**)

2a, R^1 = R^2 = Cl;
2b, R^1 = C$_8$H$_{17}$, R^2 = Cl;
2c, R^1 = Ph, R^2 = Cl;
2d, R^1 = R^2 = C$_8$H$_{17}$;
2e, R^1 = R^2 = Ph;
2f, R^1 = R^2 = 4-MeOC$_6$H$_4$;
2g, R^1 = R^2 = 4-MeC$_6$H$_4$;
2h, R^1 = R^2 = 3-CF$_3$C$_6$H$_4$;
2i, R^1 = C$_8$H$_{17}$, R^2 = Ph;
2j, R^1 = C$_8$H$_{17}$, R^2 = 4-Me$_6$H$_4$;
2k, R^1 = C$_8$H$_{17}$, R^2 = 4-MeC$_6$H$_4$;
2l, R^1 = C$_8$H$_{17}$, R^2 = 3-CF$_3$C$_6$H$_4$;
2m, R^1 = Ph, R^2 = 4-MeOC$_6$H$_4$;
2n, R^1 = Ph, R^2 = 4-MeC$_6$H$_4$;
2o, R^1 = Ph, R^2 = 3-CF$_3$C$_6$H$_4$;

The chemistry of phthalocyaninatosilicon [9] was initiated in 1960 [10] and studied extensively by Kenney and his coworkers [11], and has been extended to a new field of one-dimensional conducting polymers [5]. Although the first alkylsilicon phthalocyanin derivatives were reported in 1966 [12], less than twenty organo(phthalocyaninato)silicons have been reported so far [13] and little is known about the reactivity of the carbon–silicon bonds therein. We report here cleavage reactions of carbon–silicon bonds in diorgano(phthalocyaninato)silicon with electrophiles such as *N*-bromosuccinimide (NBS), halogens, and copper(II) halides.

Results and discussion

Synthesis of diorgano(phthalocyaninato)silicon

Symmetrical diorgano(phthalocyaninato)silicon compounds (**2d**–**2h**) were prepared from the dichloride **2a** [14] by treatment with Grignard reagents in the dark (eq. 1). Secondary alkyl groups could not be introduced, possibly owing to steric hindrance.

$$\underset{(\mathbf{2a})}{[(\mathrm{Pc})\mathrm{SiCl}_2]} + 2\ \mathrm{RMgX} \rightarrow \underset{(\mathbf{2d}\text{–}\mathbf{2h})}{[(\mathrm{Pc})\mathrm{SiR}_2]} \quad (1)$$

Unsymmetrical derivatives (**2i**–**2o**) were also prepared by a similar Grignard method from the corresponding monoorgano-monochloro precursors [(Pc)Si(R^1)Cl], (**2b** and **2c**) [12], which were prepared by a slight modification [14b] of Kenney's method [12] (eq. 2).

$$\underset{(\mathbf{2b}\text{ or }\mathbf{2c})}{\left[(\mathrm{Pc})\mathrm{Si}(\mathrm{R}^1)\mathrm{Cl}\right]} + \mathrm{R}^2\mathrm{MgX} \rightarrow \underset{(\mathbf{2i}\text{–}\mathbf{2o})}{\left[(\mathrm{Pc})\mathrm{Si}(\mathrm{R}^1)(\mathrm{R}^2)\right]} \qquad (2)$$

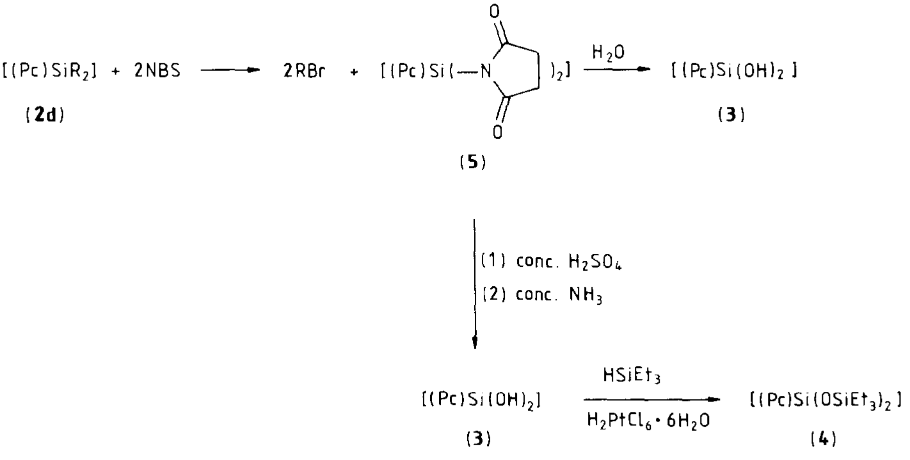
Of these organo(phthalocyaninato)silicon compounds, only three (**2c**–**2e**) were previously known. The dioctyl derivative **2d**, cited in a review as thesis work [13a], is fully characterized herein (see Experimental). All other new diorgano derivatives were obtained as deep green powders which were almost insoluble in organic solvents, and characterized mainly by mass spectra which showed diagnostic intense peaks, M^+ and $M^+ - \mathrm{R}$. It should be noted that the fragment peak from unsymmetrical [(Pc)Si(Ar)(n-C_8H_{17})] was only $[(\mathrm{Pc})\mathrm{SiAr}]^+$, no $[(\mathrm{Pc})\mathrm{Si}(\text{n-}C_8H_{17})]^+$ being observed, indicative of the selective cleavage of the alkyl-silicon bond in the parent $[(\mathrm{Pc})\mathrm{SiArR}]^{+\cdot}$. While the dioctyl derivative was light- and heat-sensitive, diaryl analogues were not.

Cleavage reactions

With NBS. The reaction of the dioctyl derivative **2d** with NBS was studied in detail: the whole reaction sequence is summarized in Scheme 1.

When **2d** was allowed to react with 2.4 molar equivalents of NBS in benzene in the dark at room temperature, the colour changed gradually from deep green to deep blue-violet. GLC analysis of the mixture showed that the reaction was almost complete in 2 h, to form bromooctane in about 60% yield (based on the two octyl groups). Thus, the reaction proceeded to cleave both of the alkyl–silicon bonds. The blue-violet precipitates were characterized to be [(Pc)Si$(OH)_2$] (**3**) [15], after filtration, washing with water, MeOH and diethyl ether.

Alternatively, the residue was treated successively with concentrated H_2SO_4, concentrated aqueous ammonia, and then Et_3SiH in the presence of a catalytic amount



Scheme 1.

Table 1

Cleavage reactions of [(Pc)SiR$_2$] with *N*-bromosuccinimide [a]

Entry	[(Pc)SiR$_2$]	NBS (equiv.)	Solvent	Conditions [b]	Product	Yield (%) [c]
				Temp., Time (h)		
1	[(Pc)Si(C_8H_{17})$_2$]	6.0	C_6H_6	rt, 2	$C_8H_{17}Br$	57
2		2.4	C_6H_6	rt, 2		61
3		2.4 [d]	C_6H_6	rt, 4.5		53
4		2.4 [e]	C_6H_6	rt, 3.5		36
5		1.2	C_6H_6	rt, 5		43
6		2.4	C_6H_6	rfx, 0.5		60
7		2.4	C_6H_6	rfx, 4		61
8		2.4 [f]	C_6H_6	rfx, 3		69
9		2.4	MeCN	rt, 4		62
10		2.4	diethyl ether	rt, 8		58
11		2.3	diglyme	rt, 3		57
12		1.4	CCl_4	rt, on		26
13		1.3	EtOH	rt, on		4
14		1.4	MeOH	rt, on		0
15	[(Pc)Si(C_6H_4OMe)$_2$]	2.4	C_6H_6	rt, 5	BrC_6H_4OMe	56
16		2.4	C_6H_6	rfx, 2		88
17		2.4	Et_2O	rt, 5		56
18	[(Pc)Si(C_6H_4Me)$_2$]	2.4	C_6H_6	rt, 4.5	BrC_6H_4Me	13
19		2.4	C_6H_6	rfx, 3.5		28
20	[(Pc)SiPh$_2$]	2.4	C_6H_6	rt, 7.5	PhBr	17
21		2.4	C_6H_6	rfx, 5		16
22		2.4 [f]	C_6H_6	rfx, 5		15
23		2.4	Et_2O	rt, 5		8
24	[(Pc)Si($C_6H_4CF_3$)$_2$]	2.4	C_6H_6	rt, 20	$BrC_6H_4CF_3$	trace
25		2.4	C_6H_6	rfx, 9		trace

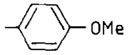
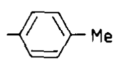
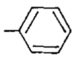
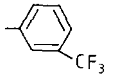
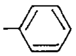
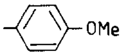
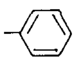
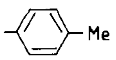
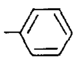
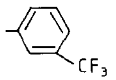
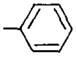
[a] Carried out on a 0.5 mmol scale in a given solvent (5 ml) in the dark. [b] rt = room temperature, rfx = reflux, on = overnight. [c] Determined by GLC, based on the stoicheiometry [(Pc)SiR$_2$] → 2RBr (100%). [d] In the ambient light. [e] In the presence of PhNO (2.2 equiv.). [f] In the presence of BPO (0.01 equiv.).

of $H_2PtCl_6 \cdot 6H_2O$ to give [(Pc)Si(OSiEt$_3$)$_2$] (**4**) [16]. These results were consistent with the formation of a hydrolyzable silicon species as the initial reaction product, possibly **5**, as shown in Scheme 1.

Other results are summarized in Table 1: entry 2 represents the standard reaction conditions mentioned above. There are several significant features. (a) A large excess amount of NBS did not improve the yield of octyl bromide (entry 1), while the use of 1.2 equivalents of NBS resulted in the cleavage of higher than 80% of one Si–C bond (entry 5). Yields were not improved under reflux conditions (entries 6 and 7). (b) Although neiter daylight irradiation nor the presence of BPO (benzoyl peroxide) as a radical initiator improved the yields (entries 3 and 8), an appreciable decrease of the yield was observed in the presence of nitrosobenzene, a radical scavanger (entry 4). Thus, the NBS cleavage of the alkyl–silicon bond is not enhanced by radical initiators, but involves radical intermediates which may be quenched by a radical scavanger. (c) There is a notable solvent effect. Thus, comparable yields were obtained in all aprotic solvents examined (entries 9–12), but

Table 2

NBS cleavage of unsymmetrical [(Pc)Si(R^1)(R^2)] [a]

Entry	[(Pc)Si(R^1)(R^2)]		Conditions	Yield (%) [b]	
	R^1	R^2	Temp., Time (h)	R^{1}Br	R^{2}Br
26	C_8H_{17}		rt, 2 rfx, 1 [c]	20 20	81 96
27	C_8H_{17}		rt, 2 rfx, 1 [c]	72 72	17 17
28	C_8H_{17}		rt, 2 rfx, 1 [c]	65 65	4 14
29	C_8H_{17}		rt, 2 rfx, 1 [c]	31 70	0 14
30	C_8H_{17}	Cl [d]	rt, 2	11	–
31			rt, 2	4	88
32			rt, 2	3	9
33			rt, 2	0	0
34		Cl [d]	rt, 2	0	–

[a] Carried out on a 0.5 mmol scale in benzene with 2.4 equiv. of NBS in the dark, unless otherwise mentioned. [b] Determined by GLC. [c] Reactions at room temperature for 2 h followed by heating under reflux for 1 h. [d] With 1.2 equiv. of NBS.

almost no reaction occurred in alcoholic solvents (entries 13 and 14). (d) A significant electronic effect was observed with diaryl derivatives (entries 15–25). Thus, an electron-donating substituent facilitates the cleavage of the aryl–silicon bond, while an electron-withdrawing group almost completely inhibits cleavage. The reactivity of substituted phenyl–silicon bonds decreases in the order: 4-MeO > 4-Me > H ≫ 3-CF$_3$.

The following competitive reactions exhibit the electronic effect more clearly (eqs. 3 and 4).

$$\underset{(1/1)}{\mathbf{2f} + \mathbf{2g}} \xrightarrow[C_6H_6,\ rt,\ 17\ h]{2NBS} \underset{(75\%)}{4\text{-}MeOC_6H_4Br} + \underset{(trace)}{4\text{-}MeC_6H_4Br} \tag{3}$$

$$\underset{(1/1)}{\mathbf{2g} + \mathbf{2e}} \xrightarrow[C_6H_6,\ rt,\ 17\ h]{2NBS} \underset{(26\%)}{4\text{-}MeC_6H_4Br} + \underset{(4\%)}{C_6H_5Br} \tag{4}$$

Table 2 summarizes results observed with the unsymmetrical compounds [(Pc)Si(R^1)(R^2)], which reveal further interesting electronic effects, similar to the *trans* effect in transition metal chemistry. Entries 26–29 show the reactivity order of alkyl–silicon and aryl–silicon bonds. The 4-MeOC$_6$H$_4$–Si bond is much more

Table 3

Cleavage of [(Pc)SiR$_2$] with halogens and interhalogen [a]

Entry	[(Pc)SiR$_2$]	Halogen (equiv.)	Solvent	Time (h)	Product(s)	Yield [b] (%)
35	[(Pc)Si(C_8H_{17})$_2$]	Cl_2 (1.6)	CCl_4	6.5	$C_8H_{17}Cl$	10
36		Br_2 (4)	C_6H_6	6.5	C_8H_{17}-Br [c]	61
37		Br_2 (4)	CCl_4	6.5	C_8H_{17}-Br	51
38		I_2 (2.5)	CCl_4	53	C_8H_{17}-I	55
39		ICl (2.4)	C_6H_6	4	$C_8H_{17}Cl$	28
					$C_8H_{17}I$	58
40	[(Pc)Si(C_6H_4OMe)$_2$]	Br_2 (4)	Et_2O	1.5	$MeOC_6H_4Br$ [d]	74
41		ICl (2.4)	C_6H_6	4	$MeOC_6H_4I$ [e]	92
42	[(Pc)Si(C_6H_4Me)$_2$]	Br_2 (4)	Et_2O	5	MeC_6H_4Br	54
43	[(Pc)Si(C_6H_5)$_2$]	Br_2 (4)	Et_2O	5	C_6H_5Br	18
44	[(Pc)Si($C_6H_4CF_3$)$_2$]	Br_2 (4)	Et_2O	10	$CF_3C_6H_4Br$	trace

[a] Carried out on a 0.5 mmol scale at room temperature in the dark. [b] Determined by GLC. [c] Bromobenzene arising form the solvent was formed in substantial amounts. [d] 2,4-Dibromoanisole was also formed in substantial amounts, total yield being reported. [e] $MeOC_6H_4Cl$ was not formed at all. [(Pc)$SiCl_2$] was obtained in quantitative yield.

reactive than the alkyl–silicon bond (entry 26), while the alkyl–silicon bond is more reactive than all other aryl–silicon bonds examined (entries 27–29). It is noteworthy here that the reactivity of the alkyl–silicon bond (R^1) is influenced by the electronic effect of the aryl group (R^2) present in the *trans* position, an electron-withdrawing *trans* group lowering the reactivity of the alkyl–silicon bond (compare yields of R^1Br in entries 27–29), the extreme case being presented in entry 30 where the *trans* group is chlorine. The unsymmetrical diaryl series (entries 31–33) shows no such clear electronic effect, but emphasizes only the extremely high reactivity of the 4-$MeOC_6H_4$–Si bond. It is apparent, however, that electronegative groups also diminish the reactivity of the *trans* aryl–silicon bonds (entries 32–34).

The electronic effects obtained here may be summarized as follows:

(a) Reactivity of an R–Si bond toward NBS decreases in the order: 4-$MeOC_6H_4$ > n-C_8H_{17} > 4-MeC_6H_4 > Ph ≫ 3-$CF_3C_6H_4$.

(b) Reactivity of the alkyl–silicon bond is lowered by the *trans* group in the order (*trans* effect): 4-MeC_6H_4 > Ph > 3-$CF_3C_6H_4$ > Cl.

Of particular interest is that the alkyl–silicon bond is more reactive than 4-MeC_6H_4-Si or Ph–Si bonds toward NBS. This means that the NBS cleavage of the alkyl–silicon bond proceeds not by the traditional electrophilic mechanism, because, if so, these aryl–silicon bonds should be more reactive than the alkyl–silicon bond [17]. Plausible mechanisms will be discussed later.

With halogens. Diorgano(phthalocyaninato)silicon compounds were allowed to react with chlorine, bromine, iodine or iodine(I) chloride at room temperature in the dark; the results are listed in Table 3. Cleavage of the octyl–silicon bond by bromine proceeded smoothly, the chlorine or iodine cleavage was rather slow (entries 35–38). There was a significant electronic effect in the bromine cleavage of aryl–silicon bonds, the reactivity decreasing in the order 4-$MeOC_6H_4$ > 4-MeC_6H_4 > Ph ≫ 3-$CF_3C_6H_4$ (entries 40, 42–44). The reactivity of the 4-$MeOC_6H_4$–Si bond may be comparable with, or higher than, that of the alkyl–silicon bond (entries 36, 37 vs. 40).

Table 4

Cleavage of $[(Pc)SiR_2]$ with copper(II) halides [a]

Entry	$[(Pc)SiR_2]$	CuX_2 (equiv.)	Solvent	Conditions Temp. (°C), Time (h)	Product	Yield [b] (%)
45	$[(Pc)Si(C_8H_{17})_2]$	$CuCl_2$ (4)	thf	50, 5	$C_8H_{17}Cl$	65
46		$CuCl_2$ (2.2)	thf	50, 4	$C_8H_{17}Cl$	45
47		$CuBr_2$ (12)	thf	50, 5	$C_8H_{17}Br$	59
48		$CuBr_2$ (4)	thf	50, 5	$C_8H_{17}Br$	70
49		$CuBr_2$ (4) [c]	thf	50, 5	$C_8H_{17}Br$	50
50		$CuBr_2$ (4)	MeOH	60, 4	$C_8H_{17}Br$	26
51		$CuBr_2$ (4)	Et_2O	rt, 31	$C_8H_{17}Br$	20
52	$[(Pc)Si(C_6H_4OMe)_2]$	$CuBr_2$ (4)	thf	50, 7	$MeOC_6H_4Br$	23
53	$[(Pc)Si(C_6H_4Me)_2]$	$CuBr_2$ (4)	thf	50, 5	MeC_6H_4Br	12
54	$[(Pc)Si(C_6H_5)_2]$	$CuBr_2$ (4)	thf	50, 7	C_6H_5Br	18
55	$[(Pc)Si(C_6H_4CF_3)_2]$	$CuBr_2$ (4)	thf	50, 10	$CF_3C_6H_4Br$	0
56	$[(Pc)Si(C_8H_{17})(Ph)]$	$CuCl_2$ (4)	thf	50, 2	$C_8H_{17}Cl$ PhCl	60 0
57	$[(Pc)Si(C_8H_{17})(Ph)]$	$CuBr_2$ (4)	thf	50, 2	$C_8H_{17}Br$ PhBr	89 8

[a] Carried out on a 0.5 mmol scale. [b] Determined by GLC. [c] In the presence of PhNO (2 equiv.).

The iodine(I) chloride cleavage of the alkyl– and aryl–silicon bonds exhibited strikingly different tendencies. Thus, the alkyl–silicon bond was cleaved by iodine(I) chloride to form a mixture of chloroalkane and iodoalkane (entry 39), while the aryl–silicon system gave the iodoarene only, no chloroarene being formed at all (entry 41). These results suggest that the halogen cleavage of the alkyl–silicon bond may involve alkyl radicals, while a simple electrophilic mechanism may operate in the cleavage of the aryl–silicon bond.

Insoluble, deep blue-violet silicon moieties obtained in the halogen cleavage reactions were not readily characterized. For example, the bromine cleavage of **2d** was accompanied by partial destruction of the macrocyclic ligand, since treatment of the silicon residue with the octyl Grignard reagent did not reform the dioctyl compound **2d**, an uncharacterizable powder being formed. Only in entry 41, was $[(Pc)SiCl_2]$ formed quantitatively, indicative of a clean electrophilic cleavage of the two $4\text{-}MeOC_6H_4\text{–}Si$ bonds in **2f** (eq. 5).

$$\underset{(\mathbf{2f})}{[(Pc)SiAr_2]} + 2\ ICl \rightarrow 2\ ArI + [(Pc)SiCl_2] \qquad (5)$$

With copper(II) halides. The results of the reactions with CuX_2 are summarized in Table 4. Reactions with $CuCl_2$ or $CuBr_2$ were usually carried out in thf at 50 °C. Although the stoicheiometry could not be determined exactly, comparison of the yields of octyl halides with the variation in amounts of CuX_2 showed that 4 molar equivalents may be suitable for cleavage of both of the alkyl–silicon bonds (entries 45–48), consistent with the standard stoicheiometry established for CuX_2 cleavage of other metal–carbon bonds [18]. The stoicheiometry may be written as in eq. 6:

$$[(Pc)SiR_2] + 4\ CuX_2 \rightarrow 2\ RX + 4\ CuX + [(Pc)SiX_2] \qquad (6)$$

The silicon moiety obtained from the reaction with $CuBr_2$ was characterized after conversion to $[(Pc)Si(OSiEt_3)_2]$ (**4**) by a workup similar to that described for the NBS cleavage.

The most remarkably feature of these reactions is that while the alkyl–silicon bond was readily cleaved by CuX_2, aryl–silicon bonds were very resistant to being cleaved (entries 45–48 vs. 52–55). In particular, it should be noted that the reactivity of the $4\text{-}MeOC_6H_4$–Si bond is much lower than the alkyl–silicon bond, making a sharp contrast to the reactivity order observed in the NBS and halogen cleavage reactions mentioned above. The reactivity order was further demonstrated by the selective cleavage of the alkyl–silicon bond in the unsymmetrical derivative **2i**, leaving the Ph–Si bond intact (entries 56 and 57).

A considerable drop in yields of bromooctane was observed in the presence of nitrosobenzene (entry 49). This strongly suggests the intermediacy of alkyl radical species.

Reaction mechanisms

The aforementioned results indicate that two distinct mechanisms may operate in the electrophilic cleavage reactions of diorgano(phthalocyaninato)silicon compounds: a radical mechanism for alkyl–silicon bonds and a traditional electrophilic cleavage mechanism for aryl–silicon bonds. These two possibilities are discussed separately.

Alkyl–silicon bonds. The most plausible mechanism for the cleavage of alkyl–silicon bonds in $[(Pc)SiR_2]$ by NBS and halogens may be visualized by eqs. 7–9, where XY stands for either NBS or halogen molecules.

$$[(Pc)SiR_2] + XY \xrightarrow{\text{electron transfer}} [\{(Pc)SiR_2\}^{+\cdot}, \{XY\}^{-\cdot}] \qquad (7)$$

$$[\{(Pc)SiR_2\}^{+\cdot}, \{XY\}^{-\cdot}] \xrightarrow{\text{in cage}} [\{(Pc)SiR\}^{+}, R^{\cdot}, X^{\cdot}, Y^{-}] \rightarrow [(Pc)SiRY] + RX \qquad (8)$$

$$\text{or} [\{(Pc)SiR\}^{\cdot}, Y^{\cdot}, RX] \rightarrow [(Pc)SiRY] + RX \qquad (8')$$

$$\xrightarrow{\text{diffusion}} \{(Pc)SiR\}^{+} + R^{\cdot} + X^{\cdot} + Y^{-} \rightarrow [(Pc)SiRY] + RX \qquad (9)$$

$$[(Pc)SiRY] + XY \rightarrow \rightarrow \rightarrow [(Pc)SiY_2] + RX \qquad (10)$$

Thus, in the first step, one-electron transfer may occur from $[(Pc)SiR_2]$ to an electrophile to form a pair of cation radical and anion radical (eq. 7). In the next step, there would be two processes. The main process may occur in the cage (eq. 8), while a partial diffusion of the alkyl radical may also take place (eq. 9); the latter process can be quenched by a radical trapping agent. In halogen cleavage, there would be a possibility for nucleophilic attack on the cation radical by the incipient halide ion (eq. 8′), but we cannot distinguish between these two processes at the present time because of the lack of stereochemcial discrimination. Cleavage of the second R–Si bond in $[(Pc)SiRY]$ may proceed by similar electron transfer processes, but might be slowed down by the introduction of an electronegative group (Y) on silicon (eq. 10).

The copper(II) halide cleavage may proceed by similar electron transfer, radical processes as shown in eqs. 11–15, the first three steps, eqs. 11–13, being described as if stepwise for clarity. The overall stoicheiometry has been presented in eq. 6.

$$[(\mathrm{Pc})\mathrm{SiR}_2] + \mathrm{CuX}_2 \rightarrow [(\mathrm{Pc})\mathrm{SiR}_2]^{+\cdot} + [\mathrm{CuX}_2]^- \tag{11}$$

$$[(\mathrm{Pc})\mathrm{SiR}_2]^{+\cdot} + [\mathrm{CuX}_2]^- \rightarrow [(\mathrm{Pc})\mathrm{SiR}]^+ + \mathrm{R}^\cdot + \mathrm{CuX} + \mathrm{X}^- \tag{12}$$

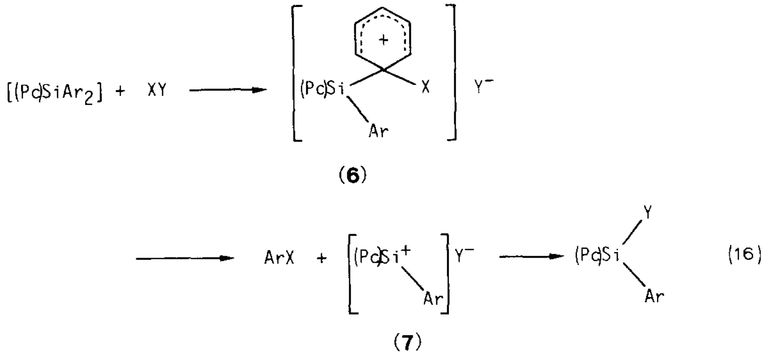
$$[(\mathrm{Pc})\mathrm{SiR}]^+ + \mathrm{X}^- \rightarrow [(\mathrm{Pc})\mathrm{SiRX}] \tag{13}$$

$$\mathrm{R}^\cdot + \mathrm{CuX}_2 \rightarrow \mathrm{RX} + \mathrm{CuX} \tag{14}$$

$$[(\mathrm{Pc})\mathrm{SiRX}] + 2\ \mathrm{CuX}_2 \rightarrow \mathrm{RX} + [(\mathrm{Pc})\mathrm{SiX}_2] + 2\ \mathrm{CuX} \tag{15}$$

It should be mentioned that the processes proposed here for the cleavage of the alkyl–silicon bonds in neutral hexacoordinate silicon compounds $[(\mathrm{Pc})\mathrm{SiR}_2]$ are similar to those for reactions of anionic hexacoordinate organopentafluorosilicates, $[\mathrm{RSiF}_5]^{2-}$ [2d,2e].

Aryl–silicon bonds. No evidence for radical mechanisms has been obtained in the cleavage reactions of aryl–silicon bonds in $[(\mathrm{Pc})\mathrm{SiAr}_2]$. An electrophilic aromatic substitution mechanism may be most likely for the NBS and halogen cleavages, as shown in eq. 16. The mechanism involves cationic intermediates, (**6** and **7**), and is consistent with the observed acceleration of the cleavage by the electron-releasing 4-MeO group on the benzene ring.

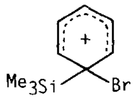


(**6**)

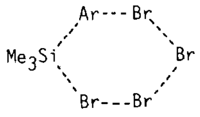
(**7**)

(16)

It is relevant to compare these intermediates with those proposed for the well-known classical halogen cleavage of aryl–silicon bonds in ordinary tetracoordinate silicon compounds [17]. An ionic intermediate (**A**) has been proposed for bromine cleavage in highly solvating media, such as aqueous ethanoic acid [19]: the subsequent nucleophilic attack on silicon results in loss of the SiMe_3 group. On the other hand, in nonpolar solvents, a six-centre intermediate (**B**) seems to be more likely, in which nucleophilic attack on silicon is achieved by the incipient bromide ion [20].

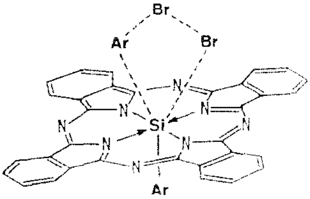


(**A**)

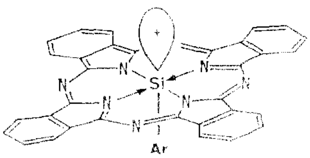


(**B**)

In the hexacoordinate silicon compounds, (**2**), coordination sites on silicon have already been occupied by nitrogen atoms on the macrocyclic ring. Therefore, such nucleophilic assistance by incipient bromide ion should be almost impossible because of the formation of an unfavourable seven-coordinate silicon intermediate, as exemplified by (**C**), which involves a front-side, four-centre interaction. Consequently, in hexacoordinate [(Pc)SiAr$_2$] compounds, it seems more likely that formation of the ionic intermediate (**6**) is followed by cleavage of the silicon–carbon bond prior to interaction of the silicon centre with Br$^-$, thus forming **7**. This pentacoordinate siliconium ion would be short-lived, but should have a lobe perpendicular to the Pc ring and might be stabilized by p_π–p_π interactions through the surrounding phthalocyanine π-electrons (**D**). It should be mentioned here that Krueger and Kenney have already proposed a similar siliconium cation intermediate [(Pc)Si(OH)]$^+$ in alcoholysis of [(Pc)Si(OH)$_2$] to [(Pc)Si(OR)$_2$] [21].



(**C**)



(**D**)

It should be further pointed out that intermediate **6** contains a tertiary carbon–silicon bond. This sequence (eq. 16), therefore should not be a favourable process, inherently, due to steric hindrance, in view of the lack of even secondary alkyl–silicon phthalocyanines, as mentioned above. This may account, in part, for the observed low reactivity of electronically less activated aryl groups.

In copper(II) halide cleavage, aryl–silicon bonds (including the 4-MeOC$_6$H$_4$–silicon bond) exhibited extremely low reactivity. The main reason may lie in the fact that copper(II) halide cleavage may be initiated by electron transfer rather than atom transfer. Thus, if one-electron transfer occurred, formation of an aryl radical from $[(Pc)SiAr_2]^{+\cdot}$ would be less favourable than in the case of the alkyl analogues (cf., eqs. 11–12). Further study, however, is required to elucidate the mechanisms fully.

Attempted reactions with MCPBA

In connection with the ready oxidative cleavage of the carbon–silicon bond in [RSiF$_5$]$^{2-}$ by MCPBA [6e], we applied similar reaction conditions to two diorgano(phthalocyaninato)silicon compounds, **2d** and **2f**, which exhibited the highest reactivity toward NBS and halogens. Both compounds, however, were inert to MCPBA in any solvent (diethyl ether, benzene or dmf) under conditions in which organopentafluorosilicates reacted. No alcohols were detected by GLC, and only the starting materials were recovered (by IR spectroscopy).

We have already shown that the intermediate formation of a pentacoordinate silicon species from a hexacoordinate silicon species via dissociation of a fluoride ion is essential for the MCPBA oxidation [6e]. Failure of the MCPBA oxidation of [(Pc)SiR$_2$] may thus be ascribed to the high stability of the hexacoordination due to the rigid macrocyclic ring. This result may thus support the idea that MCPBA oxidation of the carbon–silicon bond requires a vacant site on the silicon centre or, conversely, imply that [(Pc)SiR$_2$] has no room for coordination of MCPBA as a seventh ligand.

Conclusion

Alkyl–silicon bonds in neutral hexacoordinate silicon compounds, [(Pc)SiR$_2$], are highly activated towards electrophilic reagents such as NBS, halogen and CuX$_2$. These bonds seem to be cleaved by initial electron transfer from substrate to reagent, and subsequent homolytic scission to give alkyl radicals and siliconium cationic species, [(Pc)SiR]$^+$. Aryl–silicon bonds in [(Pc)SiAr$_2$] are cleaved by these reagents through an electrophilic aromatic substitution mechanism, with formation of aryl halides and the cationic species [(Pc)SiAr]$^+$. The possible intervention of pentacoordinate siliconium cation species, [(Pc)SiR]$^+$, is the most characteristic feature in the electrophilic cleavage of carbon–silicon bonds in [(Pc)SiR$_2$], making a sharp contrast to the classical electrophilic cleavage of carbon–silicon bonds in tetracoordinate silicon compounds.

Carbon–silicon bonds in [(Pc)SiR$_2$] seem not to be as reactive as those in [RSiF$_5$]$^{2-}$. For example, the reactivity of the aryl–silicon bonds in [(Pc)SiAr$_2$] is mainly governed by the electronic effect of substituents on the benzene ring, while such electronic effects in [RSiF$_5$]$^{2-}$ are masked by the high reactivity of the aryl–silicon bonds [22]. In both cases, activation of the carbon–silicon bond by high coordination may be ascribed to rehybridization from sp^3 to sp^3d^2; alternatively, the axial C–Si–C bond in [(Pc)SiR$_2$] or the F–Si–C bond in [RSiF$_5$]$^{2-}$ may be described in terms of a three-center four-electron bond [23]. The higher reactivity of [RSiF$_5$]$^{2-}$ should thus be attributable to the negative charge.

Experimental

General

^{1}H NMR, IR, UV, MS, and GLC facilities have been described in a previous paper [2d]. All mass spectra were measured at 70 eV in the region of m/z 200–850. n-Octyltrichlorosilane was prepared by the usual platinum-catalyzed hydrosilation of 1-octene with trichlorosilane [2d].

*Preparation of **2a–2c***

[(Pc)SiCl$_2$] (**2a**) was prepared from SiCl$_4$ and 1,3-diiminoisoindoline in 1,2,3,4-tetrahydronaphthalene and tri-n-butylamine (reflux, 2 h) in 80% yield according to the literature method [14b]. [(Pc)Si(Ph)Cl] (**2c**) [12] was obtained similarly, in 36% yield, from PhSiCl$_3$ after heating at 120 °C for 6 h followed by filtration, washing thoroughly with methanol, propanone and diethyl ether. [(Pc)Si(n-C$_8$H$_{17}$)Cl] (**2b**) was prepared similarly (150 °C, 6 h, 35% yield).

*Preparation of diorgano(phthalocyaninato)silicons **2d–2o***

A typical procedure: preparation of **2d**. The reaction was carried out under dinitrogen, and under protection from light by covering the reaction flask with aluminum foil. To a suspension of **2a** (3.05 g; 5 mmol) in dry diethyl ether (10 ml) was added a solution of n-octylmagnesium chloride prepared from n-octyl chloride (4.5 g; 30 mmol) and magnesium (0.6 g; 25 mg-atom) in diethyl ether (20 ml) at room temperature with stirring. After being stirred overnight, the mixture was hydrolyzed at 0 °C by addition of cold water and 6 *M* HCl. The green suspension was filtered (Whatman paper 541) with suction. The filter cake was washed successively with a saturated $NaHCO_3$ solution, water, methanol, and diethyl ether and dried in vacuo to leave 3.3 g (86% yield) of **2d** as a deep green powder. The powder was kept under dinitrogen in the dark. An analytically pure sample was obtained by the following procedure. The product obtained above (200 mg) was heated under reflux in benzene (50 ml) under dinitrogen in the dark, and the hot mixture was filtered quickly. The filtrate was kept in a closed flask in the dark overnight at room temperature. The deep green precipitate was collected by filtration, washed with pentane, methanol, propanone and pentane again, dried in vacuo, and weighed (64 mg). M.p. 160–165 °C (decomp. in a sealed tube); ^1H NMR ($CDCl_3$): δ −6.39 (m, 4H), −4.10 (m, 4H), −1.48 (m, 4H), −0.72 (m, 4H), −0.10 (m, 4H), 0.1–0.9 (m, 14H), 8.25–8.45 (m, 8H), 9.6–9.8 (m, 8H); IR (KBr): 2950w, 2915w, 2850m, 1612w, 1500m, 1460w, 1420m, 1340sh, 1334s, 1287m, 1185vw, 1163w, 1118s, 1076s, 953vw, 905m, 870vw, 800vw, 770vw, 740s, 730m, 698w, 642w, 568w, 523w, 513w cm^{-1}; UV (cyclohexane) λ_{max} ($\log \epsilon$): 783 (4.88), 653 (3.89), 617 (3.93), 325 (4.46), 243 nm (4.59); *m/z*: 766 (56%, M^+), 653 (100%, $M^+ - C_8H_{17}$). Anal. Found: C, 74.94; H, 6.66; N, 14.32. $C_{48}H_{50}N_8Si$ calc: C, 75.16, H, 6.57, N, 14.61%.

Other compounds were prepared by similar Grignard methods.

2e: 85% yield; IR (KBr): 3050vw, 1610m, 1560m, 1508m, 1480m, 1465s, 1422m, 1384w, 1334s, 1289m, 1167w, 1122s, 1080s, 908s, 760s, 735s, 700m, 570w, 532m, 505w, 428w cm^{-1}: *m/z*: 694 (99%, M^+), 617(100%, M^+ − Ph).

2f: 86% yield; IR (KBr): 1592m, 1500m, 1467w, 1424m, 1335s, 1290m, 1274m, 1246m, 1188m, 1163w, 1120s, 1077s, 1030w, 906m, 818w, 807w, 797w, 757m, 734s, 569w, 535w, 507w, 426w cm^{-1}; *m/z*: 754 (100%, M^+), 647 (92%, $M^+ - C_6H_4OMe$).

2g: 90% yield; IR (KBr): 1612m, 1508m, 1464w, 1422m, 1334s, 1289m, 1165m, 1119s, 1077s, 907m, 805w, 793w, 756m, 733s, 619w, 569w, 530w, 482w, 424w cm^{-1}; *m/z*: 722 (100%, M^+), 631 (89%, $M^+ - C_6H_4Me$).

2h: 86% yield; IR (KBr): 3050vw, 1610w, 1509m, 1478w, 1463w, 1422m, 1400w, 1333s, 1317s, 1289m, 1164m, 1116s, 1074s, 1063s, 904m, 753m, 730s, 698m, 650w, 525w, 503w, 424w cm^{-1}; *m/z*: 830 (61%, M^+), 685 (100%, $M^+ - C_6H_4CF_3$), 559 (8%, $PcSiF^+$).

2i: 88% yield; IR (KBr): 3070vw, 2925m, 2860w, 1618w, 1524m, 1470w, 1431m, 1340s, 1293m, 1167m, 1122s, 1080s, 910m, 760m, 735s, 696w, 645w, 571w, 525w, 420w cm^{-1}; *m/z*: 730 (24%, M^+), 617 (100%, $M^+ - C_8H_{17}$).

2j: 82% yield; IR (KBr): 3060vw, 2970w, 2925w, 2860w, 1615w, 1595w, 1504m, 1467w, 1425m, 1335s, 1290m, 1278w, 1248w, 1183w, 1162w, 1118s, 1075s, 902m, 820w, 753m, 731s, 565w cm^{-1}; *m/z*: 760 (24%, M^+), 647 (100%, $M^+ - C_8H_{17}$).

2k: 49% yield; IR (KBr): 3060vw, 2960w, 2920w, 2850w, 1615w, 1504m, 1465w, 1421m, 1333s, 1289m, 1161w, 1117s, 1070s, 904m, 800w, 751m, 730s, 635w, 565w, 520w cm^{-1}; *m/z*: 744 (29%, M^+), 631 (100%, $M^+ - C_8H_{17}$).

2l: 67% yield; IR (KBr): 3060vw, 2960w, 2925w, 2850w, 1614w, 1508m, 1481w, 1465w, 1422m, 1333s, 1318m, 1290m, 1160m, 1116s, 1100m, 1072s, 1060s, 900m, 790w, 750m, 730s, 697w, 663w, 638w, 562w, 520w, 420w cm^{-1}; *m/z*: 798(26%, M^+), 684 (100%, $M^+ - C_8H_{17}$).

The following three compounds (**2m**–**2o**) were slightly impure, judging from the mass spectra which showed parent peaks (relative intensity 10–20%) due to the symmetrical diaryl derivatives **2f**–**2h**, respectively, in addition to the desired peaks. Since the diphenyl derivative **2e** was not detected, the observed contamination by the symmetrical diaryl derivatives was tentatively attributable to the possible contamination of the starting phenylchloro derivative **2c** by dichloro derivative **2a**. These impure compounds were used in the present suitable study, because no purification method was available.

2m: 85% yield; IR (KBr): 1637w, 1617w, 1597w, 1512sh, 1502m, 1469w, 1427m, 1338s, 1295m, 1277w, 1249w, 1087w, 1065w, 1120s, 1077s, 907m, 819w, 797w, 757m, 735s, 569w, 582w, 507w, 427w cm^{-1}; *m/z*: 756 (20%, ?), 724 (53%, M^+), 647 (100%, $\text{PcSiC}_6\text{H}_4\text{OMe}^+$), 617 (77%, PcSiPh^+).

2n: 64% yield; IR (KBr): 3070w, 1616w, 1510m, 1468w, 1426m, 1338s, 1293m, 1166w, 1122s, 1080s, 907m, 805w, 757m, 735s, 697w, 570w, 530m, 480w, 425w cm^{-1}; *m/z*: 723 (17%, ?), 708 (94%, M^+), 631 (100%, $\text{PcSiC}_6\text{H}_4\text{Me}^+$), 617 (56%, PcSiPh^+).

2o: 87% yield; IR (KBr): 3070w, 1617w, 1513m, 1486w, 1472w, 1430m, 1410w, 1340s, 1325s, 1297m, 1165m, 1123s, 1105sh, 1080s, 1064s, 906m, 795w, 757m, 734s, 700m, 665w, 643w, 570w, 530m, 506m, 426w cm^{-1}; *m/z*: 830 (23%), 762 (63%, M^+), 685 (100%, $\text{PcSiC}_6\text{H}_4\text{CF}_3{}^+$), 617 (53%, PcSiPh^+).

Reaction of $PcSiR_2$ with NBS, halogens or copper(II) halides

A typical procedure is given for cleavage of **2d** with NBS. The reaction was carried out in the dark. A mixture of **2d** (1.13 g; 1.48 mmol), NBS (660 mg; 3.71 mmol), and dry benzene (15 ml) was stirred at room temperature for 12 h. GLC analysis (Silicon DC550, 30% on Celite 545, 3 m) of the reaction mixture showed the formation of bromooctane in 55% yield. The insoluble residue was transformed into the known compound **4** by the following workup, similar to the literature procedure [12]. The mixture was filtered and the deep blue powder was washed with diethyl ether. The powder was mixed with conc. H_2SO_4 (20 ml) for 2 h and the mixture was poured into an ice-water mixture. After filtration, the blue powder was stirred with conc. aqueous ammonia for 3 h, filtered, and washed successively with water, methanol, and diethyl ether. A mixture of the resulting powder, triethylsilane (2 ml), $H_2PtCl_6 \cdot 6H_2O$ in propanone (0.08 *M*, 2 ml) and 1,2,4-trimethylbenzene (30 ml) was heated under reflux for 2 h. After evaporation of the solvent, the residue was subjected to column chromatography on basic alumina. Blue bands eluted by benzene and trichloromethane were collected and stripped of solvent to give deep blue microcrystals (230 mg) of $[(\text{Pc})\text{Si}(\text{OSiEt}_3)_2]$ (**4**) [16], which were further purified for analysis by washing with pentane, methanol, and propanone: ^{1}H NMR (CDCl_3): δ −2.54 (q, *J* 8 Hz, 12H), −1.34 (t, *J* 8 Hz, 18H), 8.14–8.35 (m, 8H), 9.43–9.70 (m, 8H); IR (KBr): 2945w, 2870w, 1612w, 1517m, 1427m, 1332s, 1290m, 1122s, 1080s, 1038s, 1005w, 910m, 760m, 730s, 573w, 530w, 420w cm^{-1}; *m/z*: 802 (52%, M^+), 671 (100%, $M^+ - \text{Et}_3\text{SiO}$). Anal. Found: C, 65.29; H, 5.77; N, 13.59. $\text{C}_{44}\text{H}_{46}\text{N}_8\text{O}_2\text{Si}_3$ calc: C, 65.80; H, 5.77; N, 13.95%.

Other reactions for determination of yields of organic halides were carried out on a 0.5 mmol scale in 5 ml of given solvent in the dark. NBS, I_2 (purified by sublimation), or CuX_2 was added to the reaction mixture as a solid. Bromine or iodine(I) chloride was added via microsyringe. Chlorine was used in solution in

CCl_4, the concentration of which was determined by iodometric titration. Procedures for isolation of organic products were as follows. In the case of NBS or CuX_2 cleavage, the mixture was filtered and the filtrate was washed with water, and dried over Na_2SO_4. In halogen cleavage, the filtrate was first washed with a $Na_2S_2O_3$ solution to remove the excess halogen and subjected to the same workup as above. In all cases, pure samples were obtained by bulb-to-bulb distillation and/or preparative GLC, and characterized by comparison with the authentic commercial samples.

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