Selective Si–C Bond Cleavage on a Diorganosilicon Porphyrin Complex Bearing Different Axial Ligands

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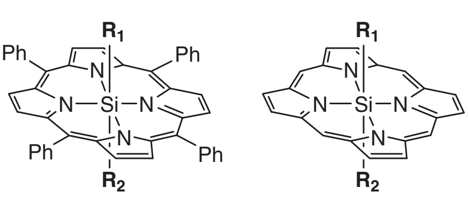
Tetraphenylporphyrinato methylphenylsilicon complex (abbreviated to Si(TPP)MePh) was synthesized and structurally characterized. Although the Si–Ph bond of Si(TPP)MePh is much longer than the Si–Me bond, photolysis and chemical oxidation of Si(TPP)MePh cleaved the Si–Me bond selectively and gave new phenyl-substituted silicon porphyrins. Theoretical studies of a model compound showed that significant σ–π orbital interaction raised the HOMO and is responsible for the silicon–carbon bond cleavage. The instability of phenyl radical to methyl radical caused selective bond cleavage.

Diorganosilicon porphyrin complexes are a unique class of neutral hexacoordinated silicon species having two axial organic ligands at the trans positions.[1] Although silicon porphyrins and their derivatives would be attractive materials for surface modification[2] and photodynamic therapy,[3,4] the number of organosilicon porphyrins is quite limited and only homoleptic axial ligands have been known. Kadish and co-workers have reported octaethylporphyrinato dimethylsilicon and diphenylsilicon complexes.[5] Aida and co-workers have reported several symmetrical diorganosilicon tetraphenylporphyrin complexes Si(TPP)R_2 (R = Et, *n*-Pr, CH_2SiMe_3, Ph, CH=CH_2, and C≡CPh) (Chart 1).[6] They found that axial alkyl ligands on silicon porphyrin complexes are highly photolabile and form the corresponding tetracoordinated silyl diradicals.[6c]

Since a key electronic characteristic of hexacoordinated silicon is three-center four-electron (3c-4e) bonding using a 3p orbital of silicon, axial ligands can interact with each other. Therefore, a diorganosilicon porphyrin complex bearing different axial ligands would be a good probe for their reactivity and selectivity. We report herein synthesis, structure, and electronic characteristics of a diorganosilicon porphyrin bearing different axial ligands, Si(TPP)MePh, and its selective Si–Me bond cleavage by photolysis and oxidation. Theoretical studies of porphyrinato methylphenylsilicon complex (abbreviated to Si(Por)MePh) as a model compound indicate that σ–π orbital interaction plays an important role in the properties of the silicon porphyrin.

The reaction of Si(TPP)ClMe[7] with phenylmagnesium chloride afforded Si(TPP)MePh as a green photosensitive solid in 39% isolated yield. The structure of Si(TPP)MePh was unequivocally determined by spectroscopic evidence[8] and X-ray structural analysis (Figure 1).[9]



Si(TPP)R_1R_2 Si(Por)R_1R_2

Chart 1.

$$\mathrm{Si(TPP)ClMe} \xrightarrow[\text{THF, rt}]{\text{PhMgCl}} \underset{39\%}{\mathrm{Si(TPP)MePh}} \qquad (1)$$

In the solid state, the geometry around hexacoordinated silicon is distorted, and the porphyrin ring is slightly ruffled. The average displacement for the meso carbon atoms from the least-squares plane of four nitrogen atoms (N4 plane) is 0.47 Å, similar to that of Si(TPP)Ph_2 (0.48 Å).[6a] Short contacts are found between ortho carbons of axial ligand and nitrogen atoms at 3.107–2.984 Å, within the sum of van der Waals radii (3.25 Å),[10] indicating severe steric repulsion exists in these positions and is responsible for the ruffled structure. Si–Me and Si–Ph bond lengths are 1.905(3) and 1.940(3) Å, which are much longer than standard tetravalent silicon–carbon bond lengths (1.87 Å),[10] showing typical 3c-4e hypervalent bonding. The remarkably long Si–Ph bond can be attributed to a weak 3c-4e bond, which is readily deformed by steric repulsion.

In sharp contrast to simple prediction of the bond lengths, when a C_6D_6 solution of Si(TPP)MePh was irradiated by a 100 W halogen lamp for 7 min at room temperature in the presence of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), selective Si–Me bond cleavage occurred to give Si(TPP)Ph(TEMPO) and MeTEMPO in quantitative yields (Scheme 1).[11,12] Si(TPP)-Me(TEMPO) was not observed in the resulting mixture. Since an intense broad ESR signal was observed after irradiation at room temperature without TEMPO, persistent pentacoordinated silyl radical might be formed by homolysis of a Si–C bond in Si(TPP)MePh.[13] Irradiation of Si(TPP)MePh in carbon tetrachloride formed only Si(TPP)ClPh[12] by chlorine abstraction from carbon tetrachloride, showing typical silyl radical charac-

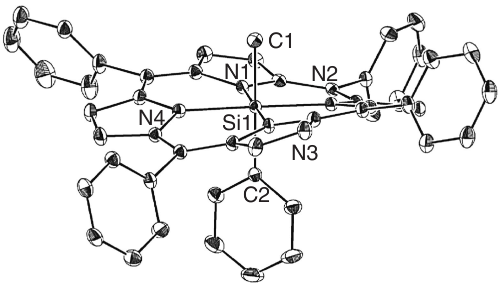
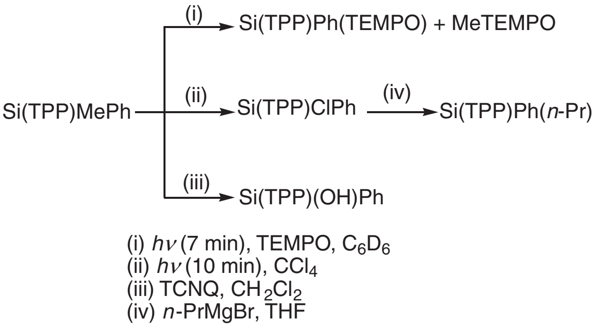


Figure 1. ORTEP drawing of Si(TPP)MePh (30% thermal ellipsoids; benzene molecules and hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Si1–N1 = 1.974(2), Si1–N2 = 1.996(2), Si1–N3 = 1.975(2), Si1–N4 = 1.982(2), Si1–C1 = 1.905(3), Si1–C2 = 1.940(3); C1–Si1–C2 = 178.8(1), C1–Si1–N1 = 89.6(1), N3–Si1–N4 = 90.6(1).



Scheme 1.

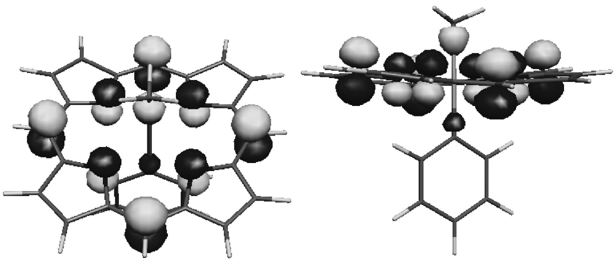


Figure 2. KS-HOMO of Si(Por)MePh.

ter.[14] No significant decomposition of Si(TPP)Ph(TEMPO) and Si(TPP)ClPh was observed even for thirty-minute irradiation.

Cyclic voltammetry of Si(TPP)MePh in dichloromethane showed an irreversible first oxidation wave at lower potential ($E_{\rm pa} = +0.73$ V vs. Ag/AgCl) than a reversible first oxidation wave ($E_{1/2} = +1.07$ V) of the corresponding free base $\mathrm{TPPH_2}$. Si(TPP)MePh was treated with one equivalent tetracyanoquinodimethane (TCNQ) as a one-electron oxidant in the dark to form Si(TPP)(OH)Ph in 91% yield after usual work-up.[15] One-electron oxidation of Si(TPP)MePh and a trace amount of water in the reaction vessel also caused selective Si–Me bond cleavage.

In order to obtain insight into the electronic structure of diorganosilicon porphyrin complexes, DFT calculations were carried out using Si(Por)MePh as a model compound.[16] The highest occupied Kohn–Sham orbital (KS-HOMO) of Si(Por)MePh is shown in Figure 2, which is formed by significant interaction between the porphyrin π orbital and 3c-4e $\sigma_{\text{Si–C}}$ orbital. The 3c-4e bonding orbital and porphyrin π system can interact effectively with each other because of their favorable geometry and, therefore, raise their KS-HOMO. Consequently, one-electron removal from the KS-HOMO by irradiation or oxidation weakened the axial bond. Evaluation of the bond dissociation energies by DFT calculations supports the selective Si–Me bond cleavage. Cleavage of a Si–Me bond is by 38.1 kJ/mol more favorable than that of a Si–Ph bond probably owing to the instability of phenyl radical.

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8 Spectroscopic data for Si(TPP)MePh: green crystalline solid, ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 8.97 (s, 8H, pyrrole), 7.90 (d, 8H, $J = 6.7$ Hz, *o*-H in *meso*-Ph), 7.41–7.28 (m, 12H, *m*-H and *p*-H in *meso*-Ph), 5.46 (t, 1H, $J = 7.8$ Hz, axial *p*-Ph), 5.07 (t, 2H, $J = 7.8$ Hz, axial *m*-Ph), 1.11 (d, 2H, $J = 7.8$ Hz, axial *o*-Ph), -6.38 (s, 3H, axial SiMe); ^{13}C NMR (126 MHz, $\mathrm{CD_2Cl_2}$): δ 150.4, 143.6, 140.5, 133.8, 131.0, 127.4, 126.3, 126.2, 122.0, 121.7, 117.9, 10.8; ^{29}Si NMR (99 MHz, $\mathrm{CD_2Cl_2}$): δ -197.4; IR (KBr, cm^{-1}): 1600, 1490, 1440, 1350, 1260; UV–vis ($\mathrm{CH_2Cl_2}$): $\lambda_{\max}$/nm (log ε) 342 (4.53), 452 (5.49), 559 (3.44), 602 (4.00), 649 (4.40); Anal. Found: C, 82.55; H, 5.34; N, 7.32%. Calcd for $\mathrm{C_{51}H_{36}N_4Si}$: C, 83.57; H, 4.95; N, 7.64%.

9 Crystal data for Si(TPP)MePh•$\mathrm{C_6H_6}$: $M_{\rm r} = 811.04$, monoclinic, $P2_1/n$, $T = 173$ K, $a = 13.1694(9)$ Å, $b = 23.401(2)$ Å, $c = 14.416(1)$ Å, $\beta = 102.327(1)^\circ$, $V = 4340.1(5)$ Å^3, $Z = 4$, $R1 = 0.0826$ (all data), $wR2 = 0.1623$ (all data), GOF = 1.229. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-717651.

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12 Isolation of Si(TPP)Ph(TEMPO) and Si(TPP)ClPh was failed owing to their instability toward chromatography. Chemical trap of Si(TPP)ClPh using 1-propylmagnesium bromide gave Si(TPP)Ph(*n*-Pr) in 59% yield.

13 According to the reaction products, participation of tetracoordinated silyl biradical[6c] in the reaction of Si(TPP)MePh may be ruled out.

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15 Further oxidation of Si(TPP)MePh using an excess amount of TCNQ proceeded, and Si(TPP)(OH)$_2$[6b] was obtained in 75% yield. Structures of Si(TPP)(OH)Ph and Si(TPP)(OH)$_2$ were determined by NMR spectroscopy and X-ray structural analysis. The experimental details are described in Supporting Information.

16 All calculations were carried out at the B3LYP/6-31G(d) level with Gaussian 03 package programs. Details and full reference of Gaussian 03 are described in Supporting Information.

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