Dioxygen Insertion into the Axial Si-C Bonds of Organosilicon Porphyrins

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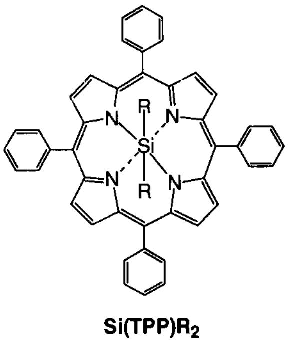
A dialkylsilicon porphyrin Si(TPP)(CH_2CH_3)$_2$ (1) (TPP = 5, 10, 15, 20-tetraphenylporphinato) reacted with dioxygen in the dark to give a bis(ethylperoxide) complex (5), from which a dihydroxysilicon porphyrin (Si(TPP)(OH)$_2$, 6) was obtained upon reduction and hydrolysis. In contrast with the phosphorous analogue [P(TPP)(OH)$_2$]OH, the crystal structure of 6 showed an almost planar conformation of the porphyrin ligand.

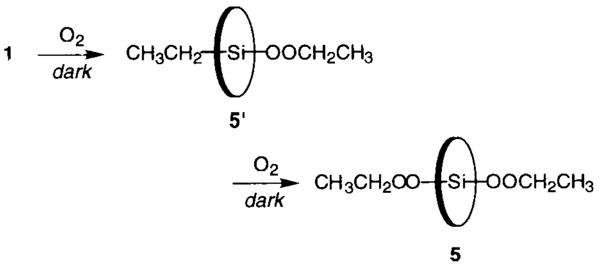
Hypervalent silicon compounds have attracted considerable attention from a fundamental interest in their unique structures and reactivities in contrast to tetracoordinate silicon compounds.[1] We have recently succeeded in the synthesis and structural determination of a series of hexacoordinate organosilicon porphyrins (**1** - **4**).[2] In the course of this study, we have also found that the axial Si-C bonds of the dialkylsilicon porphyrin (**1**) are cleaved upon excitation of the porphyrin ligand with visible light.[3,4] Herein we report the formation of a bis(alkylperoxide)silicon porphyrin (**5**) from the dialkyl complex and dioxygen without photoexcitation, together with the crystal structure of a dihydroxysilicon complex (**6**) derived from **5**.



1 R = CH_2CH_3
2 R = $CH{=}CH_2$
3 R = C_6H_5
4 R = $C{\equiv}CC_6H_5$
5 R = $OOCH_2CH_3$
6 R = OH

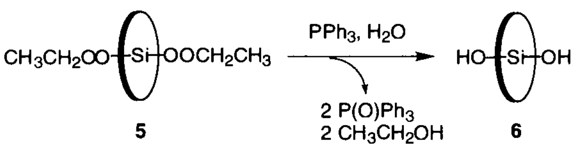
Si(TPP)R$_2$

A typical example of the dioxygen insertion (Scheme 1) is shown below: Into a NMR tube containing a C_6D_6 solution (0.5 mL) of Si(TPP)(CH_2CH_3)$_2$ (**1**) (7.0 mg, 10 μmol) was bubbled dioxygen for 5 min, and the tube was sealed, wrapped in aluminum foil, and allowed to stand at 25 °C in the dark. In the ^{1}H NMR spectrum of the reaction mixture, the intensities of the signals due to **1** (δ -7.43 [CH_2], δ -4.69 [CH_3]) gradually decreased with time (100 → 55 → 6 → 0 % in 0 → 5 → 11 → 25 days, respectively), while new signals assignable to the bis(ethylperoxide) complex (**5**) (δ -0.35 [CH_2], δ -1.09 [CH_3])[5] appeared (90 % yield in 25 days).[6] The reaction is likely to proceed in a stepwise fashion, since a mono-ethyl-mono-ethylperoxide complex (**5'**) (δ -4.50 [CH_2], δ -7.00 [CH_3], δ -0.37 [$OOCH_2$], δ -1.11 [$OOCH_2CH_3$]) was detected during the reaction period of 11 days. On the other hand, organosilicon porphyrins bearing axial Si-C (sp^2) and Si-C (sp) bonds such as **2** [R = $CH{=}CH_2$], **3** [C_6H_5], and **4** [$C{\equiv}CC_6H_5$] were inert to dioxygen under similar conditions.



Scheme 1.

When the bis(ethylperoxide) complex (**5**), thus obtained, was treated with PPh_3, a diethoxide complex and $P(O)Ph_3$ were quantitatively formed (by ^{1}H NMR), the former of which was hydrolyzed upon treatment with water to afford Si(TPP)(OH)$_2$ (**6**) (Scheme 2).[7] The crystal structure of **6** was successfully obtained as shown in Figure 1,[8] where the porphyrin ligand adopts an almost planar conformation: The average displacement for the *meso* carbon atoms from the four pyrrole nitrogen plane (Δr) and the Si(1)-N(3) bond distance (d_{Si-N}) are 0.06 and 1.977(6) Å, respectively. This is in sharp contrast with the crystal structure of the phosphorous analogue ([P(TPP)(OH)$_2$]OH),[9] in which the porphyrin ligand is significantly ruffled with Δr and d_{Si-N}, respectively, of 0.83 and 1.89 Å. The planar conformation of the porphyrin ligand in **6** is also interesting, since reported examples of silicon porphyrins with axial hetero atoms, such as Si(TTP)(OSO_2CF_3)$_2$[10] and Si(TTP)F_2[11] (TTP: 5, 10, 15, 20-tetrakis(4-methylphenyl)-porphinato), adopt a highly ruffled



Scheme 2.

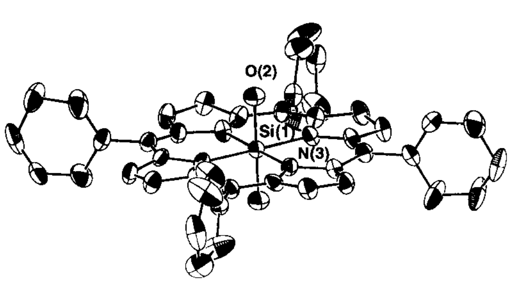


Figure 1. An ORTEP view (30% probability ellipsoids with hydrogen atoms omitted for clarity) of Si(TPP)(OH)$_2$ (**6**).

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conformation with respect to the porphyrin ligand. It should be also noted that the Si(1)-O(2) bond distance (1.671(8) Å) is considerably shorter than those reported for hexacoordinate silicon complexes (1.77 - 1.84 Å),[10,12] but is comparable to those of tetracoordinate silicon compounds.[13]

In conclusion, we have shown that dioxygen inserts into the Si-C bonds of dialkylsilicon porphyrins in the dark to give bis(alkylperoxide) complexes. Although a similar dioxygen insertion has been reported for a dialkylgermanium porphyrin, the reaction requires excitation of the porphyrin ligand with visible light.[14] This contrasting trends imply the uniqueness of organosilicon porphyrins in the reaction with radical species. Studies on possible application of organosilicon porphyrins to controlled radical reactions are the subjects worthy of further investigation.

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References and Notes

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5 Assignments were made by reference to those for the germanium analogue (Ref. 14). Another possible product, Si(TPP)(OCH$_2$CH$_3$)$_2$ (separately prepared from Si(TPP)(OH)$_2$ and ethanol) showed the axial ethoxy signals at δ -2.23 (OCH$_2$C*H*$_3$) and δ -2.67 (OC*H*$_2$CH$_3$).

6 Signals due to acetaldehyde (δ 9.83 [CHO], δ 2.23 [CH$_3$]) were also observed (10% yield based on the initial amount of **1**).

7 **6** was also obtained by hydrolysis of Si(TPP)Cl$_2$: Anal. Calcd for $C_{44}H_{30}N_4O_2Si$: C, 78.31; H, 4.48; N, 8.30%. Found: C, 77.55; H, 4.92; N, 8.14%. MALDI-TOF-MS: *m/z* 674 [M$^+$], 657 [M$^+$ - OH]. UV-vis (CH$_2$Cl$_2$): λmax 597, 555, 424 nm.

8 A crystal suitable for the X-ray crystallographic analysis was obtained by slow diffusion of a cyclohexane vapor into a concentrated CH$_2$Cl$_2$ solution of **6**. The crystal was mounted on the top of a glass capillary and placed on a Mac Science MXC 18 four-circle diffractometer, where the diffraction data were measured with a graphite-monochromated Cu Kα radiation (λ = 1.54178 Å) at room temperature. Lattice parameters were determined by least squares fitting of 20 reflections. The structure was solved by direct methods and refined on F_0 by full-matrix least squares using the CRYSTAN GM package. The non-hydrogen atoms were refined anisotropically, while the hydrogen atoms except for the OH hydrogen were included using a riding model with fixed C-H distances of 0.96 Å and isotropic temperature factors set equal to those of their adjacent carbon atoms. The OH hydrogen atom was found in the difference fourier map and was treated isotropically with a site occupation factor of 0.5. Crystal data: $C_{44}H_{30}N_4O_2Si$, M = 674.8, space group $I\bar{4}$, a = 13.520(5), c = 9,766(4) Å, V = 1785(2), Z = 2, Dc = 1.255 g cm^{-3}, R = 0.084, Rw = 0.105.

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