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Substituent Effects on the Spectroscopic Properties and Reactivity of Hexacoordinate Silicon(IV) Porphyrin Complexes

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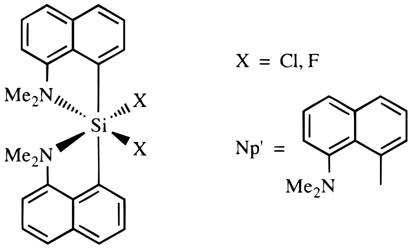
A general high-yield synthetic route to the hexacoordinate silicon porphyrin dichloride complexes *trans*-(Por)$SiCl_2$ {Por = the dianions of octaethylporphyrin (OEP), tetraphenylporphyrin (TPP), and tetrakis(*p*-(trifluoromethyl)phenyl)porphyrin (TTFP)} is reported. Reacting (Por)$SiCl_2$ with SbF_3 and AgOTf produces the corresponding difluoro *trans*-(Por)SiF_2 and bis(triflato) *trans*-(Por)Si$(OTf)_2$ complexes, respectively. The spectroscopic properties (^{1}H, ^{19}F, and ^{29}Si NMR and visible) of these hexacoordinate silicon compounds are surprisingly insensitive to the electron-donating ability of the porphyrin or the nature of the axial substituents. The nature of the porphyrin and the axial substituent do play a role in the reactivity of these silicon complexes. The strong Si−F bond makes the difluorides stable to hydrolysis and methanolysis. The dichlorides, on the other hand, do undergo hydrolysis and methanolysis, the extent of which is determined by the electronics of the porphyrin ring. The strong electron-donating ability of OEP stabilizes (OEP)$SiCl_2$ with respect to hydrolysis and methanolysis. (TTFP)$SiCl_2$, containing the least electron-donating porphyrin, reacts with MeOH to give a mixture of (TTFP)Si(OMe)Cl and (TTFP)Si$(OMe)_2$, whereas (TTP)$SiCl_2$ (TTP = the dianion of tetra-*p*-tolylporphyrin) reacts with MeOH to give only the monomethoxy derivative. The triflate groups on (OEP)Si$(OTf)_2$ are more labile than those in the corresponding tetraarylporphyrin complexes and can be displaced by THF to give the cationic species [(OEP)Si(OTf)(THF)]OTf or [(OEP)Si$(THF)_2$]$(OTf)_2$.

Introduction

Silicon, in sharp contrast to carbon, has a very rich and extensive hypercoordination chemistry.[1−7] Our interest in this area has centered on hexacoordinate complexes of silicon containing a porphyrin group. To date, most of the hexacoordinate silicon complexes have substituents arranged in a cis geometry as in $(Np')_2SiX_2$ ($Np' = C_{12}H_6NMe_2$; X = Cl, F).[8−10] On the other hand, since the silicon atom is small enough to fit into the central cavity of the porphyrin ring, the porphyrin moiety predisposes a trans geometry in hexacoordinate silicon complexes. A trans geometry has also been observed or proposed in hexacoordinate silicon complexes containing other tetradentate macrocyclic ligands. A trans geometry was proposed in (tmtaa)$SiCl_2$ (tmtaa = the dianion of dibenzotetramethyltetraaza[14]annulene) on the basis of spectroscopic similarities with the crystallographically characterized tin complexes *trans*-(tmtaa)SnX_2 (X = Cl, NO_3).[11,12] A trans geometry can also be obtained using the phthalocyanine group;[13−19] however, the resulting complexes exhibit poor solubility, which hampers their characterization and reactivity. The greater solubility imparted by the porphyrin moiety and the wide variety of ring substituents with differing electronic and steric properties make the porphyrin moiety a desirable ligand in hexacoordinate silicon chemistry.



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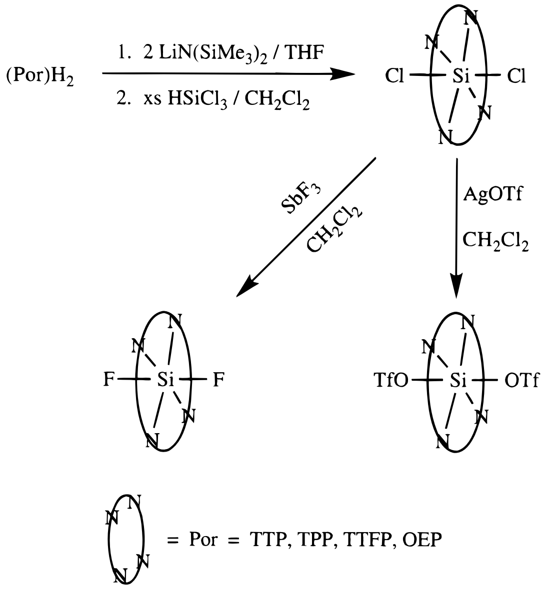
In group 14, a large number of germanium and tin porphyrin complexes have been reported.[11,20−50] However, prior to our work, *trans*-(OEP)SiX_2 (OEP = dianion of octaethylporphyrin; X = Cl, Me, Ph, OMe, OPh, OH, ClO_4) were the only known silicon porphyrin complexes.[28,51,52] We recently reported the preparation of (TTP)SiX_2 (TTP = dianion of tetra-*p*-tolylporphyrin; X = Cl, F, O_3SCF_3 {OTf}),[53] and showed that the chloro derivative is highly moisture sensitive. This reactivity is in sharp contrast to that of (OEP)$SiCl_2$, which is insensitive to moisture and, in fact, survives an acidic aqueous workup in its preparation. Octaalkylporphyrins have been reported to be better donor ligands compared to tetraarylporphyrins.[49,54,55] Therefore, we attributed the striking difference in reactivity between(TTP)$SiCl_2$ and (OEP)$SiCl_2$ to the TTP moiety being a weaker electron donor to the silicon, thus making the silicon more electrophilic.

Scheme 1



This observed difference indicates that the reactivity of silicon porphyrin complexes can be controlled to some extent by the substituents on the porphyrin ring. We sought to evaluate the effect of the ring substituents by examining the spectroscopic properties and reactivity of several silicon porphyrin complexes. Herein we report the synthesis and characterization for a series of new silicon porphyrin complexes (Por)SiX_2 (Por = OEP and the dianions of tetraphenylporphyrin (TPP) and tetrakis(*p*-(trifluoromethyl)phenyl)porphyrin (TTFP); X = Cl, F, OTf). The trends in reactivity for this series of silicon porphyrin complexes and the corresponding TTP derivatives are also reported.

Results and Discussion

Preparation of (Por)SiX_2. We have developed and reported a high-yield, single-pot preparative route for (TTP)$SiCl_2$, the first isolable (tetraarylporphyrinato)silicon(IV) complex.[53] This method has allowed us to extend our study of hexacoordinate silicon complexes to other tetraarylporphyrins and octaethylporphyrin. The generation of the porphyrin dianions followed by their reaction with excess $HSiCl_3$ under anhydrous conditions is general for a variety of porphyrins (Scheme 1) and permits the isolation of (Por)$SiCl_2$ in high yields (ca. >85%). This sequence of reactions represents an improved synthesis for silicon porphyrin complexes over conventional methods. For example, (OEP)$SiCl_2$ was obtained in 86% yield by the reactions described in Scheme 1 compared to a 52% yield using more conventional methods.[56] Also, attempts to adapt the preparation of (OEP)$SiCl_2$ to prepare the tetraarylporphyrin derivatives (TArP)$SiCl_2$ (TArP = TTP, TPP) were unsuccessful, producing the protonated porphyrins [(TArP)H_4]Cl_2 instead.[19,53,57]

The dichloro complexes (Por)$SiCl_2$ have good solubility in organic solvents such as CH_2Cl_2, THF, and toluene, although

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Table 1. ^{1}H, ^{19}F{^{1}H}, and ^{29}Si NMR Data (ppm) for (Por)SiX$_2$ Complexes

	^{1}H NMR[a]			
(Por)SiX$_2$	CH	Et or Ar	^{19}F{^{1}H} NMR[b]	^{29}Si NMR[c]
(OEP)SiCl$_2$	9.90 (s)	4.10 (q, $J = 7.6$ Hz, CH$_2$) 1.96 (t, $J = 7.6$ Hz, CH$_3$)		−220.1 (s)
(OEP)SiF$_2$	9.95 (s)	4.09 (q, $J = 7.7$ Hz, CH$_2$) 1.94 (t, $J = 7.7$ Hz, CH$_3$)	−44.3 (s, $J = 208.5$ Hz, SiF$_2$)	*d*
(OEP)Si(OTf)$_2$	9.88 (s)	4.08 (q, $J = 7.6$ Hz, CH$_2$) 1.94 (t, $J = 7.7$ Hz, CH$_3$)	−4.4 (s, OTf)	*d*
(TTP)SiCl$_2$[e]	9.03 (s)	7.98 (d, $J = 8.0$ Hz, C$_6$H$_4$) 7.56 (d, $J = 8.0$ Hz, C$_6$H$_4$) 2.65 (s, CH$_3$)		−217.9 (s)
(TTP)SiF$_2$[e]	8.99 (s)	7.99 (d, $J = 8.4$ Hz, C$_6$H$_4$) 7.56 (d, $J = 8.4$ Hz, C$_6$H$_4$) 2.66 (s, CH$_3$)	−45.1 (s, $J = 203.0$ Hz, SiF$_2$)	*d*
(TTP)Si(OTf)$_2$[e]	9.14 (s)	8.00 (d, $J = 8.0$ Hz, C$_6$H$_4$) 7.57 (d, $J = 8.0$ Hz, C$_6$H$_4$) 2.65 (s, CH$_3$)	−4.2 (s, OTf)	*d*
(TPP)SiCl$_2$	9.03 (s)	8.10 (m, *o*-C$_6$H$_5$) 7.76 (m, *m*, *p*-C$_6$H$_5$)		−218.0 (s)
(TPP)SiF$_2$	8.98 (s)	8.11 (m, *o*-C$_6$H$_5$) 7.76 (m, *m*, *p*-C$_6$H$_5$)	−44.5 (s, $J = 203.5$ Hz, SiF$_2$)	*d*
(TPP)Si(OTf)$_2$	9.16 (s)	8.14 (m, *o*-C$_6$H$_5$) 7.77 (m, *m*, *p*-C$_6$H$_5$)	−4.2 (s, OTf)	*d*
(TTFP)SiCl$_2$	9.01 (s)	8.25 (d, $J = 8.0$ Hz, C$_6$H$_4$) 8.04 (d, $J = 8.0$ Hz, C$_6$H$_4$)	13.4 (s, CF$_3$)	−218.5 (s)
(TTFP)SiF$_2$	8.97 (s)	8.27 (d, $J = 7.9$ Hz, C$_6$H$_4$) 8.04 (d, $J = 7.9$ Hz, C$_6$H$_4$)	13.5 (s, CF$_3$) −46.1 (s, $J = 205.0$ Hz, SiF$_2$)	*d*
(TTFP)Si(OTf)$_2$	9.14 (s)	8.28 (d, $J = 7.9$ Hz, C$_6$H$_4$) 8.06 (d, $J = 7.9$ Hz, C$_6$H$_4$)	13.3 (s, CF$_3$) −4.2 (s, OTf)	*d*

[a] At 250 MHz and ambient probe temperature in CD$_2$Cl$_2$; referenced to residual proton peak (5.32 ppm). The CH resonances are for the methine protons in OEP or the pyrrolic protons in TArP, and all couplings are $^{3}J_{\mathrm{HH}}$. [b] At 235 MHz and ambient probe temperature in CD$_2$Cl$_2$; referenced to external CF$_3$CO$_2$H (0.00 ppm). All couplings are $^{1}J_{\mathrm{SiF}}$ and are observed as satellites. [c] At 79.5 MHz and ambient probe temperature in CD$_2$Cl$_2$; referenced to external SiMe$_4$ (0.00 ppm). [d] Not observed. [e] From ref 53.

(OEP)SiCl$_2$ is significantly less soluble than the tetraaryl derivatives (TArP)SiCl$_2$ (TArP = TTP, TPP, TTFP). Reacting (Por)SiCl$_2$ with SbF$_3$ or AgOTf in CH$_2$Cl$_2$ (Scheme 1) produces the corresponding difluoro (Por)SiF$_2$ and bis(triflato) (Por)Si(OTf)$_2$ complexes, respectively. The difluoro and bis(triflato) complexes were obtained in >70% yields under unoptimized conditions and exhibit solubility properties similar to those of the dichloro complexes. Notable exceptions are (OEP)SiF$_2$, which exhibits poor solubility in most solvents (CHCl$_3$, CH$_2$Cl$_2$, MeOH, THF, and toluene), and (OEP)Si(OTf)$_2$, which is very soluble in THF due to a reaction with the solvent (vide infra).

Spectroscopic Properties of (Por)SiX$_2$. The multinuclear NMR data for the complexes (Por)SiX$_2$ (Por = OEP, TTP, TPP, TTFP; X = Cl, F, OTf) are presented in Table 1. The NMR spectroscopic data are in agreement with the trans geometry of these hexacoordinate silicon porphyrin complexes.[58,59] In the ^{1}H NMR spectra (CD$_2$Cl$_2$), (OEP)SiX$_2$ complexes exhibit a clean singlet at 9.91 ± 0.03 ppm for the four methine hydrogens, whereas (TArP)SiX$_2$ complexes exhibit sharp singlets at 9.05 ± 0.07 ppm for the eight pyrrolic hydrogens. Singlets are observed in the ^{29}Si NMR spectra (CD$_2$Cl$_2$) of the dichloro complexes (Por)SiCl$_2$ at −219 ± 1 ppm, consistent with a six-coordinate silicon in the presence of the strongly shielding magnetic field of a porphyrin ring. A ^{29}Si resonance was not observed for the other complexes (Por)SiX$_2$ (X = F, OTf), possibly due to the quadrupolar relaxation of the pyrrolic ^{14}N atoms which significantly broadens the ^{29}Si signal.[60,61] For the difluorides (Por)SiF$_2$, a singlet is observed at −45.0 ± 0.7 ppm with ^{29}Si satellites ($^{1}J_{\mathrm{SiF}} = 205 \pm 2$ Hz) in the ^{19}F NMR spectra (CD$_2$Cl$_2$). Changing the porphyrin causes remarkably small changes in the ^{19}F and ^{29}Si NMR chemical shifts and coupling constants, despite the varying electron-donating abilities of the porphyrin rings. Arnold and Bartley observed a similar insensitivity in ^{119}Sn chemical shifts for (Por)SnX$_2$ (Por = TPP, TTP, OEP; X = Cl, OH) complexes.[40]

The visible absorption data for the complexes (Por)SiX$_2$ (Por = OEP, TTP, TPP, TTFP; X = Cl, F, OTf) are presented in Table 2. These complexes exhibit normal-type visible spectra, as evidenced by the single, intense Soret band. Of the tetraarylporphyrins, the difluorides and bis(triflates) give purple solutions in CH$_2$Cl$_2$ whereas solutions of the dichlorides are dark green; this difference in the color of the CH$_2$Cl$_2$ solutions could be due to the slight blue-shifting of the visible absorbances for the dichloride complexes. The octaethylporphyrin complexes are partially soluble in CH$_2$Cl$_2$ and give magenta solutions. As observed in the NMR data, changing the substituents on the porphyrin ring has very little influence on the absorption properties of the porphyrin complexes; the greatest changes are observed upon substitution of the axial groups.

A significant dependence on the axial substituent X is observed in the mass spectra of the (Por)SiX$_2$ complexes. The parent molecular ions [(Por)SiF$_2$]$^{+}$ (Por = OEP, TPP, TTFP) are readily observed in the FAB mass spectra of the difluoro

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(58) The X-ray crystal structures of (TTP)SiX$_2$ (X = F, OTf) and (TTFP)SiF$_2$ confirm the trans configuration for these silicon porphyrin complexes.[53]

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(61) Independent ^{29}Si experiments on HSiCl$_3$ were hampered by quadrupolar relaxation of the ^{35}Cl atoms; a signal was not observed even using a DEPT pulse sequence until the sample had been cooled to −30 °C. Low-temperature ^{29}Si NMR experiments were not performed on (Por)SiX$_2$ (X = F, OTf) due to the considerable cryogen expense of an anticipated 24-h experiment (since polarization was not possible).

Table 2. Visible Absorption Data for (Por)SiX_2 Complexes in CH_2Cl_2

(Por)SiX_2[a]	λ_{max}, nm (log ϵ)	
	Soret band	Q bands
(OEP)$SiCl_2$	402 (5.27)	520 (4.07), 550 (4.15)
(OEP)SiF_2	388 (5.67)	508 (4.09), 542 (4.32)
(OEP)Si$(OTf)_2$	387 (5.29)	512 (3.75), 548 (4.14)
(TTP)$SiCl_2$	420 (5.53)	508 (3.46), 550 (4.04), 591 (3.66)
(TTP)SiF_2	412 (5.51)	447 (3.91), 546 (4.14), 587 (3.60)
(TTP)Si$(OTf)_2$	420 (5.74)	546 (4.32), 591 (3.82)
(TPP)$SiCl_2$	419 (5.58)	502 (3.48), 534 (4.13), 573 (3.70)
(TPP)SiF_2	406 (5.67)	430 (4.35), 521 (4.22), 556 (3.59)
(TPP)Si$(OTf)_2$	408 (5.69)	523 (4.27), 554 (3.57)
(TTFP)$SiCl_2$	429 (5.56)	492 (4.00), 535 (4.25), 571 (3.94)
(TTFP)SiF_2	407 (5.79)	489 (3.37), 523 (4.36), 554 (3.43)
(TTFP)Si$(OTf)_2$	407 (5.79)	490 (3.37), 523 (4.25), 556 (3.43)

[a] [(Por)SiX_2] = 1.5×10^{-6} M.

complexes (Por)SiF_2. For the bis(triflato) complexes (Por)Si$(OTf)_2$, the parent molecular ions were not observed in the FAB mass spectra. Instead, the highest-*m*/*z* species corresponded to the loss of one triflate group. Similarly, the parent molecular ions were not observed in the FAB mass spectra of the dichloro complexes (Por)$SiCl_2$. The highest *m*/*z* species observed corresponded to an ion which lost both chlorides and is associated with one or two molecules of the FAB matrix (3-nitrobenzaldehyde). The reactivities of these (Por)SiX_2 complexes in the mass spectrometer (i.e. F < OTf < Cl) reflect their observed chemical reactivities, as described in the next section.

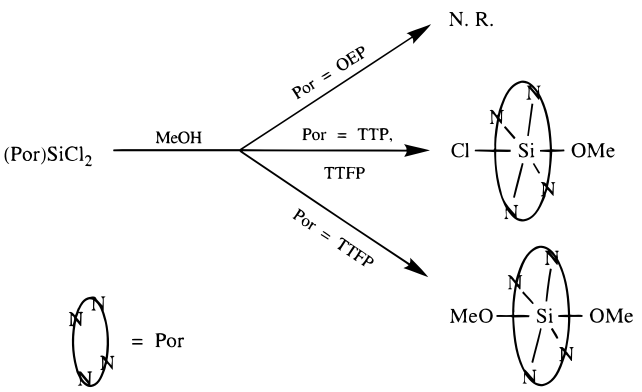
Reactivity of (Por)SiX_2. The effect of the axial substituents and varying electron-donating abilities of the porphyrins can be observed in the reactivity of these silicon porphyrin complexes. The difluorides (Por)SiF_2 are the most stable of the group and are unreactive with water and methanol. The Si−F bond is one of the strongest single bonds known (150−160 kcal/mol),[62,63] and the electron-donating ability of the porphyrins makes the silicon less electrophilic (vide supra). Both of these factors may account for the stability of the hexacoordinate silicon difluorides with respect to hydrolysis and methanolysis. Similarly, (OEP)$SiCl_2$ is also stable with respect to hydrolysis. On the other hand, tetraarylporphyrin derivatives (TArP)$SiCl_2$ are sensitive to hydrolysis. Hydrolysis of (TArP)$SiCl_2$ results in the demetalation and subsequent protonation of the porphyrin to give [(TArP)H_4]Cl_2 and presumably silica (eq 1).

$$\text{(TArP)SiCl}_2 \xrightarrow[\text{CDCl}_3]{\text{H}_2\text{O}} [\text{(TArP)H}_4]\text{Cl}_2 + \text{"silica"} \quad (1)$$

$$\text{TArP} = \text{TTP, TPP, TTFP}$$

The degree of methanolysis of (Por)$SiCl_2$ is inversely related to the electron-donating ability of the porphyrins (Scheme 2). (OEP)$SiCl_2$, which contains the most electron-donating porphyrin, does not react with neat MeOH, even with gentle heating (60 °C). (TTP)$SiCl_2$ reacts with MeOH at room temperature to give the monomethoxy complex (TPP)Si(OMe)Cl. The methoxy group in (TTP)Si(OMe)Cl is observed as a singlet at −2.13 ppm in the ^1H NMR ($CDCl_3$), indicating a close proximity of the methoxy group to the strongly shielding magnetic field of the porphyrin ring. (TTFP)$SiCl_2$, containing the least electron-donating porphyrin, is the most reactive with MeOH and gives a 1:1 mixture of mono- and disubstituted products (TTFP)Si(OMe)Cl and (TTFP)Si$(OMe)_2$. In the ^1H NMR spectrum ($CDCl_3$) of this mixture, two upfield resonances were observed at −2.15 and −2.30 ppm which were assigned to (TTFP)Si(OMe)Cl and (TTFP)Si$(OMe)_2$, respectively. From these results, it is clear that the electron-donating ability of the porphyrin affects the electrophilicity of the silicon atom. Thus, the reactivity toward methanolysis (and to some extent hydrolysis) of (Por)$SiCl_2$ increases in the order OEP < TTP < TTFP.

Scheme 2



(OEP)Si$(OTf)_2$, which is sparingly soluble in CH_2Cl_2, can readily be dissolved in CD_2Cl_2 upon the addition of THF (4 equiv). The ^1H NMR spectrum showed the expected resonances for the OEP group and THF, but after the solution was heated at 50 °C for ca. 2 h, the resonances for THF were broadened and shifted slightly upfield. This was interpreted as displacement of the triflates with THF to yield a base-stabilized cationic species, [(OEP)Si(OTf)(THF)](OTf) or [(OEP)Si$(THF)_2$]$(OTf)_2$, in rapid equilibrium with free THF. Displacement of the triflate groups by THF in the tetraarylporphyrin derivatives (TArP)Si$(OTf)_2$ (TArP = TTP, TPP, TTFP) was not apparent by ^1H NMR spectroscopy. However, THF solutions of (TArP)Si$(OTf)_2$ solidify with time (<12 h) due to the formation of polytetrahydrofuran. This would suggest that THF does indeed displace triflate, and the resulting silyl cation initiates the ring-opening polymerization of THF. In contrast, more than a month is required for THF solutions of (OEP)Si$(OTf)_2$ to solidify at room temperature.

The electronic properties of the porphyrin groups play an important role in the reactivity of these triflate complexes. The electron-rich OEP group reduces the electrophilicity of silicon which in turn facilitates the dissociation of triflate. However, the resulting silyl cation is too poor a Lewis acid to promote rapid ring-opening polymerization of THF. With the less electron-rich TArP groups, the silicon atom is more electrophilic and binds the triflate groups more tightly. On the other hand, silyl cations containing TArP groups are stronger Lewis acids, compared to the OEP derivative, and more readily promote the ring-opening polymerization of THF. The properties and reactivities of porphyrin containing silyl cations are currently under investigation.

Experimental Section

General Procedures. All manipulations of oxygen- or water-sensitive compounds were carried out either under an atmosphere of argon using Schlenk or vacuum-line techniques or under a helium/argon atmosphere in a Vacuum Atmospheres drybox. ^1H NMR (400 and 250 MHz) and ^{19}F NMR (376 and 235 MHz) spectra were recorded on a Varian VXR 400S and a Bruker AC-250 spectrometer, respectively. ^{29}Si NMR (79.5 MHz) spectra were recorded on a Varian VXR

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400S spectrometer. The ^{1}H chemical shifts were referenced to the residual proton peak of the solvent: C_6D_5H, δ 7.15; $CDHCl_2$, δ 5.32. The ^{19}F chemical shifts were referenced to external CF_3CO_2H (δ 0.00). The ^{29}Si chemical shifts were referenced to external $SiMe_4$ (δ 0.00). UV−vis spectra were recorded using a Cary 16 spectrophotometer interfaced with a 486-based PC (OLIS and Grams 486 software). Elemental analyses were carried out by Oneida Research Services. Low- and high-resolution FAB mass spectral analyses, in a 3-nitrobenzaldehyde (NBA) matrix, were carried out by the Washington University Mass Spectrometry Resource.

Materials. The porphyrins (TTP)H$_2$, (TPP)H$_2$, and (TTFP)H$_2$ were prepared according to the literature methods,[64] and (OEP)H$_2$ was purchased from Strem. All of the porphyrins were treated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, Aldrich) to remove any chlorin impurities.[65] (TTP)SiX$_2$ (X = Cl, F, OTf) complexes were prepared as described in the literature.[53] Anhydrous diethyl ether was stored over $[Cp_2TiCl]_2ZnCl_2$[66] and vacuum-transferred immediately prior to use. Dichloromethane was distilled from and stored over CaH_2, and vacuum-transferred immediately prior to use. Methanol was dried over Mg and vacuum-transferred immediately prior to use. Benzene-d_6 was dried over NaK and stored over $[Cp_2TiCl]_2ZnCl_2$.[66] Dichloromethane-d_2 was dried over P_2O_5 and stored over CaH_2. Tetrahydrofuran (THF) and toluene were distilled from potassium/benzophenone under argon. Chlorosilanes were purchased from Aldrich or Strem and stored under vacuum over CaH_2. All other reagents were used as received.

[Li$_2$(THF)$_2$](Por) (Por = TPP, TTFP, OEP). The lithium salts of the porphyrin dianions [Li$_2$(THF)$_2$](Por) (Por = TPP, TTFP, OEP) were prepared using a method similar to that reported by Arnold and co-workers.[67−69] In a typical procedure, THF (40 mL) was added to a flask containing (TTFP)H$_2$ (0.50 g, 0.56 mmol) and freshly sublimed $LiN(SiMe_3)_2$ (0.19 g, 1.16 mmol). The flask was sealed with a Teflon stopcock, and the reaction solution was heated at 60 °C for 4 h. The green solution was evaporated to dryness, and the solid was heated to 90 °C for 10 h under vacuum to remove $HN(SiMe_3)_2$ and any unreacted $LiN(SiMe_3)_2$. At this point, the [Li$_2$(THF)$_2$](TTFP) could be used as is for the preparation of (TTFP)SiCl$_2$, described below, or isolated as a purple solid (0.54 g, 92%). ^{1}H NMR (CD_2Cl_2): δ 8.79 (s, 8 H, pyrrole β), 8.34 (d, 8H, $J = 7.8$ Hz, $C_6H_4CF_3$), 8.02 (d, 8H, $J = 7.8$ Hz, $C_6H_4CF_3$), −0.06 (br s, 16H, C_4H_8O). [Li$_2$(THF)$_2$](Por) (Por = TPP, OEP) complexes were obtained in >90% yields, and ^{1}H NMR data were consistent with reported values.[67,69]

(Por)SiCl$_2$ (Por = TPP, TTFP, OEP). The dichloro(porphyrinato)silicon(IV) complexes (Por)SiCl$_2$ (Por = TPP, TTFP, OEP) were prepared by the reaction of $HSiCl_3$ with the corresponding porphyrin dianion [Li$_2$(THF)$_2$](Por) in CH_2Cl_2. In a typical procedure, CH_2Cl_2 (30 mL) was added to a flask containing [Li$_2$(THF)$_2$](TTFP) (250 mg, 0.24 mmol). The flask and contents were cooled to −78 °C, and $HSiCl_3$ (50 mg, 0.37 mmol) added by vacuum transfer. The flask was sealed with a Teflon stopcock, and the contents were stirred at −78 °C for 1 h. After the reaction mixture was warmed to room temperature and stirred for 2 h, the volatiles were removed under vacuum. The residue was extracted with CH_2Cl_2 (40 mL), and the extract was filtered through Celite. The filtrate was evaporated to dryness to give (TTFP)SiCl$_2$ as a green solid (234 mg, 96%). MS calcd (found), m/z: 1064.2 (1064.1) $[MH - 2Cl + NBA]^+$. (TPP)SiCl$_2$ was obtained in 91% yield. Anal. Calcd for $C_{44}H_{28}N_4Cl_2Si$: C, 74.25; H, 3.97; N, 7.87. Found: C, 74.55; H, 3.93; N, 7.89. MS calcd (found), m/z: 944.3 (943.9) $[MH_2 - 2Cl + 2NBA]^+$. (OEP)SiCl$_2$ was obtained in 86% yield, and spectroscopic properties were consistent with literature values.[28] The spectroscopic data for the (Por)SiCl$_2$ complexes can be found in Tables 1 and 2.

(Por)SiF$_2$ (Por = TPP, TTFP, OEP). The difluoro(porphyrinato)silicon(IV) complexes (Por)SiF$_2$ (Por = TPP, TTFP, OEP) were prepared by the reaction of SbF_3 with the corresponding (Por)SiCl$_2$ in CH_2Cl_2. In a typical procedure, CH_2Cl_2 (30 mL) was added to a flask containing (TTFP)SiCl$_2$ (100 mg, 0.10 mmol) and SbF_3 (20 mg, 0.11 mmol). The resultant slurry was stirred at room temperature for 14 h and then filtered through Celite. The filtrate was evaporated to dryness to give (TTFP)SiF$_2$ as a red-purple solid (82 mg, 81%). MS calcd (found), m/z: 950.16 (950.16) $[M]^+$. (TPP)SiF$_2$ was obtained in 74% yield. MS calcd (found), m/z: 678.21 (678.20) $[M]^+$. (OEP)SiF$_2$ was obtained in 86% yield. MS calcd (found), m/z: 598.3 (598.3) $[M]^+$. The spectroscopic data for the (Por)SiF$_2$ complexes can be found in Tables 1 and 2.

(Por)Si(OTf)$_2$ (Por = TPP, TTFP, OEP). The bis(trifluoromethanesulfonato)(porphyrinato)silicon(IV) complexes (Por)Si(OTf)$_2$ (Por = TPP, TTFP, OEP) were prepared by the reaction of AgO_3SCF_3 with the corresponding (Por)SiCl$_2$ in CH_2Cl_2. In a typical procedure, CH_2Cl_2 (20 mL) was added to a flask containing (TTFP)SiCl$_2$ (100 mg, 0.10 mmol) and AgO_3SCF_3 (78 mg, 0.30 mmol). The resultant slurry was stirred at room temperature for 10 h and then filtered through Celite. The red filtrate was evaporated to dryness to give (TTFP)Si(OTf)$_2$ as a red-purple solid (98 mg, 80%). MS calcd (found), m/z: 1065.1 (1065.1) $[MH_4 - OTf]^+$. (TPP)Si(OTf)$_2$ was obtained in 77% yield. Anal. Calcd for $C_{46}H_{28}N_4F_6O_6S_2Si$: C, 58.84; H, 3.01; N, 5.97. Found: C, 58.62; H, 2.69; N, 5.63. MS calcd (found), m/z: 792.18 (792.19) $[MH_3 - OTf]^+$. (OEP)Si(OTf)$_2$ was obtained in 92% yield. MS calcd (found), m/z: 858.2 (858.1) $[M]^+$, 709.3 (709.3) $[M - OTf]^+$. The spectroscopic data for the (Por)Si(OTf)$_2$ complexes can be found in Tables 1 and 2.

Hydrolysis of (Por)SiCl$_2$ (Por = OEP, TTP, TPP, TTFP). The hydrolytic sensitivity of (Por)SiCl$_2$ (Por = OEP, TTP, TPP, TTFP) was checked by adding a drop of water to a $CDCl_3$ or CD_2Cl_2 solution of the silicon porphyrin complex in an NMR tube. The reaction, which was instantaneous for the silicon tetraarylporphyrin complexes, was monitored by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra of the hydrolysis products [(TArP)H$_4$]Cl$_2$ (TArP = TTP, TPP, TTFP) were confirmed by comparison to spectra of authentic samples prepared from the reaction of (TArP)H$_2$ with anhydrous HCl(g) in CH_2Cl_2.

Methanolysis of (Por)SiCl$_2$ (Por = OEP, TTP, TTFP). The reactivity of (Por)SiCl$_2$ (Por = OEP, TTP, TTFP) with MeOH was determined by dissolving a sample of the silicon porphyrin complex in MeOH in an NMR tube equipped with a J. Young valve (Wilmad Glass). After 1 h, the reaction volatiles were removed in vacuo, and the residue was dissolved in $CDCl_3$. The extent of methanolysis was then determined by ^{1}H NMR spectroscopy. (OEP)SiCl$_2$ did not react with MeOH. (TTP)SiCl$_2$ reacted with MeOH to give the monomethoxy derivative (TTP)SiCl(OMe), which exhibited a methoxy resonance at −2.14 ppm. (TTFP)SiCl$_2$ reacted with MeOH to give a mixture of (TTFP)SiCl(OMe) and (TTFP)Si(OMe)$_2$ in approximately equal amounts, with methoxy resonances at −2.15 and −2.30 ppm, respectively.

(OEP)Si(OTf)$_2$ and THF. An NMR tube was charged with (OEP)Si(OTf)$_2$ (11 mg, 0.013 mmol), CD_2Cl_2 (0.5 mL), and THF (4 equiv) and heated to 50 °C for several hours. In the ^{1}H NMR spectrum, the THF was observed as two very broad slightly upfield resonances at 2.90 and 1.50 ppm, suggesting the formation of a THF adduct, either [(OEP)Si(OTf)(THF)]OTf or [(OEP)Si(THF)$_2$](OTf)$_2$, which is in equilibrium with free THF. Attempts to isolate the THF adduct were unsuccessful.

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