bonding, such as $Fe(CO)_3$ or $Pt(PPh_3)_2$, will yield the predicted[14] *nido*-$Sn_9ML_x^{4-}$ structures. Main-group polyhedral clusters, such as the 22-electron *closo*-Bi_9^{5+} ion, clearly violate traditional cluster electron counting rules,[22] and distortions to alternate geometries are known to be low-energy processes.[23] Our attempts to isolate Rudolph's proposed *nido*-$Sn_9Pt(PPh_3)_2^{4-}$ have been unsuccessful thus far.[14]

Supplementary Material Available: Experimental data and tables of crystal data, atomic coordinates and isotropic thermal parameters, bond lengths and bond angles, and anisotropic thermal parameters (23 pages); table of observed and calculated structure factors (70 pages). Ordering information is given on any current masthead page.

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Synthesis and Reactivity of Silyliron Porphyrin Complexes

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Several alkyliron porphyrin complexes have been synthesized and well characterized,[1,2] but we are aware of no reported preparation of silyliron porphyrin species. Two possible reasons can be offered for the absence of silyliron porphyrin studies. The first is the lack of a general method for preparation of transition-metal silyl complexes. Each metal silyl complex requires a different synthetic route. Secondly, as is described here, the silyliron porphyrin products tend to be much less stable than their alkyl analogues.

The first silyliron porphyrin complexes, paramagnetic trimethylsilyliron(III) tetraphenylporphyrin, and the corresponding diamagnetic silyliron(II) porphyrin anion are reported. Interest in silyliron porphyrins is not limited to porphyrin chemistry, but the synthesis of these derivatives provides a new class of paramagnetic organometallic compounds. The highly reactive silyliron porphyrin complexes are generated in situ along with other products and are characterized by proton and deuterium NMR spectroscopy. It is also shown that propylene oxide is inserted into the iron–silicon bond of the silyliron(III) porphyrin derivative, as is the case with other transition-metal silyl complexes.[3]

The lithium silyl reagent was generated in hexamethylphosphoramide (HMPA) solution by cleavage of hexamethyldisilane by lithium methyl at 0 °C.[4] All reactions were performed in an inert argon atmosphere. The silyliron(III) tetraphenylporphyrin complex was prepared by combination at room temperature of a stoichiometric amount of the lithium silyl in HMPA with a toluene solution of chloroiron(III) tetraphenylporphyrin (TPPFeCl) at a concentration of 1.0–5.0 mM. In order to identify the various products, it was most convenient to utilize TPPFeCl deuteriated at the pyrrole position. Formation of the silyl complex was monitored by deuterium NMR spectroscopy, in which case the pyrrole deuterium signal at 79.5 ppm for high-spin TPPFeCl was converted to a unique new signal at −21.7 ppm. A relatively sharp pyrrole deuteron (proton) signal in this region is characteristic of a low spin iron(III) porphyrin complex.[5] Pyrrole deuteron signals for other byproducts and decomposition products could be associated with the following species: 43.0 ppm, high-spin iron(II) HMPA complex;[6] 13.5 ppm, oxoiron(III) porphyrin dimer; and −16.5 ppm, methyliron(III) porphyrin complex (from lithium methyl).[7] These additional products varied in quatity as a function of mixing procedure and time after mixing. The putative silyliron(III) pyrrole signal at −21.7 ppm was converted to the iron(II) HMPA signal with a half-life of approximately 30 min at 25 °C (The silyliron(III) porphyrin was not particularly stabilized at lower temperature.). An analogous proton NMR spectrum for a toluene-d_8 solution recorded shortly after generation of the trimethylsilyliron(III) porphyrin is shown in Figure 1.

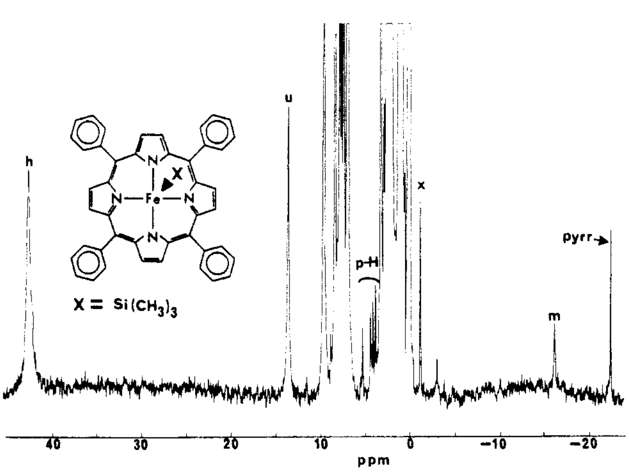

Figure 1. Proton NMR spectrum of trimethylsilyliron(III) tetraphenylporphyrin, 360 MHz, 24 °C, toluene solution, TMS reference. The pyrrole signals of silyliron(III) porphyrin are denoted "pyrr", silyl group "x", and phenyl ring hydrogens "p-H". Pyrrole signals of the high-spin iron(II) porphyrin HMPA complex are labeled "h", μ-oxo-dimeric iron(III) porphyrin "u", and methyliron(III) porphyrin complex "m".

In order to assign the proton NMR signal for the coordinated trimethylsilyl group, deuterium labeling of hexamethyldisilane was carried out by the reaction of hexachlorodisilane and methyl-d_3 magnesium iodide which was prepared from methyl-d_3 iodide and magnesium in ether solution. The trimethylsilyliron(III) porphyrin product prepared from this deuteriated material exhibited a deuterium NMR signal at −1.2 ppm. This resonance is also seen in the proton NMR spectrum in Figure 1, and integration with the −21.7 ppm pyrrole signal yields the expected 9:8 proton intensity pattern. The −1.2 ppm coordinated trimethylsilyl signal vanishes in concert with the disappearance of the −21.7 ppm signal from homolytic decomposition. The coordinated trimethylsilyl proton signal at −1.2 ppm shows a surprisingly small paramagnetic shift when compared to the corresponding β-CH_2-butyliron(III) porphyrin resonance at −64 ppm. Hence, unpaired spin transfer through the silicon atom is much less efficient as compared with the carbon analogue.

The deuterium spectrum of pyrrole-deuteriated trimethylsilyliron(III) tetraphenylporphyrin was recorded from 218 to 313 K. A plot of chemical shift vs $1/T$ was linear with an intercept of 12.4 ± 1.5 ppm and a slope of −10 400 ± 390 ppm (K). This result confirms that the −21.7 ppm signal represents a single species

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(6) Assignment of the 43.0-ppm resonance to the high-spin iron(II) HMPA complex was verified by examination of the deuterium NMR spectrum of $TPPFe^{II}$-d_8(HMPA), which was generated by addition of HMPA to TPPFe(II)-d_8 in toluene. The position of the pyrrole deuteron resonance for the TPPFe-d_8(HMPA) complex is consistent with the presence of iron(II) on the basis of comparision with the known value for $TPPFe^{II}$ (2-methylimidazole) at 43.4 ppm; Goff, H. M.; La Mar, G. N. *J. Am. Chem. Soc.* **1977**, *99*, 6599.

(7) Reaction of the toluene solution of TPPFeCl-d_8 with lithium methyl in HMPA yielded a low-spin methyliron(III) porphyrin complex which had only one pyrrole deuterium resonance at −16.5 ppm.

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and not a dynamically averaged resonance. The phenyl resonances were observed in the range of 3.89–5.34 ppm. This group of signals was assigned by comparison of the proton NMR spectra of Figure 1 and of TPPFeSi(CH$_3$)$_3$-d_{20} deuteriated at all phenyl positions.

The homolytic cleavage decomposition of the silyliron(III) porphyrin yields the iron(II) porphyrin coordinated by HMPA (pyrrole hydrogens at 43.0 ppm). Addition of 1 equiv of lithium silyl to this species produces a low-spin silyliron(II) porphyrin anionic complex. This species can be generated from pure iron(II) porphyrin in toluene solution by addition of lithium trimethylsilyl. The complex is concluded to be diamagnetic by virtue of its sharp pyrrole deuteron NMR signal at 8.2 ppm.[5] A proton signal at −1.8 ppm is assigned to the coordinated trimethylsilyl group by comparison with the deuterium NMR spectrum of the deuteriosilyl derivative. The silyliron(II) anion was oxidized to the silyliron(III) derivative by addition of 0.5 equiv of iodine in benzene solution.

Addition of 1 equiv of propylene oxide to trimethylsilyliron(III) porphyrin led to the formation of a new low-spin iron(III) porphyrin species. After 30 min the deuterium NMR spectrum showed two signals of approximately equal intensity at −18.8 and −21.7 ppm. On the basis of comparision with the alkyl analogues,[2] the new signal at −18.8 ppm is tentatively assigned to a siloxyalkyliron(III) porphyrin from the ring-opening and insertion reaction of cyclic ether into the iron–silicon bond.

A synthetic route via the reaction of low valent iron(I) porphyrin anion and trimethylchlorosilane in tetrahydrofuran was not successful. The THF solvent underwent ring opening and insertion into the silicon–iron bond with the formation of a siloxyalkyliron(III) derivative. This chemistry finds precedence with other transition-metal silyl complexes.[8]

Synthesis of the first silyliron porphyrin derivatives provides possibilities for the formation of other silylmetalloporphyrins. The demonstrated reactivity with cyclic ether insertion can be used as a synthetic route for various organosilanes. This work also provides new examples of paramagnetic coordination compounds and opportunities for the investigation of new reaction types.

Acknowledgment. This work was supported by National Science Foundation Grant CHE-8705703.

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Transient Formation of Hydrogen Tetraoxide [HOOOOH] from the Dimerization of Perhydroxyl (HOO•): Concerted Homolytic Dissociation to Singlet Oxygen ($^1O_2$) and Hydrogen Peroxide

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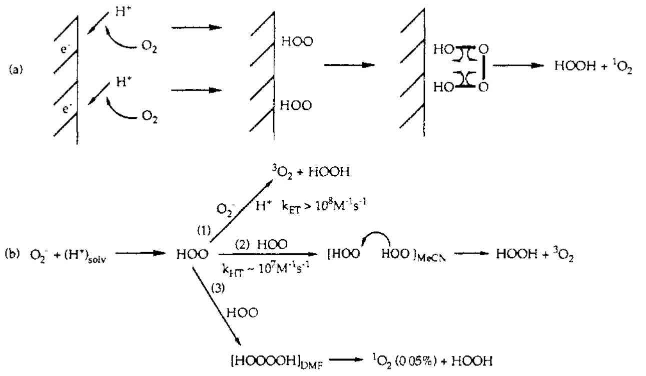
In a recent report,[1] we described the production of singlet oxygen ($^1O_2$) from the addition of superoxide ion ($O_2^{\bullet -}$) to excess halocarbon substrates (RX) in aprotic solvents. This appears to result from the dimerization of the primary product of the nucleophilic substitution reaction (ROO$^\bullet$) via radical–radical coupling to give a transient dialkyltetraoxygen (ROOOOR). The latter rapidly undergoes homolytic dissociation to $^1O_2$ and ROOR. These results have prompted us to investigate whether the perhydroxyl radical (HOO$^\bullet$) undergoes a similar reaction path.

Scheme I



Here we wish to report that electrolytic reduction of protons in the presence of oxygen in acetonitrile results in substantial photoemission at 1268 nm from $^1O_2$ production at a platinum electrode surface. A previous investigation[2] has demonstrated that such an electrolysis (~ +0.5 V vs SCE at Pt and −0.2 V at glassy carbon) yields hydrogen atoms (H$^\bullet$) that couple with $^\bullet O_2^\bullet$ to give HOO$^\bullet$, which is specifically adsorbed. The presence of excess protons precludes the electron-transfer reduction of O_2 (−0.9 V vs SCE). Table IA summarizes the yield of $^1O_2$ (estimated from the intensity of the 1268-nm emission) from the steady-state electrolysis at platinum of O_2 in acetonitrile.[3]

In order to test whether or not this $^1O_2$ results from the homolytic dissociation of a hydrogen tetraoxygen intermediate (formed via radical–radical coupling of two surface HOO$^\bullet$ groups), the electrolysis experiment has been conducted with a 50:50 mixture of $^{36}O_2/^{32}O_2$. This produces a 50:50 surface population of $H^{18}O^{18}O^\bullet$ and $H^{16}O^{16}O^\bullet$ molecules, which disproportionate to O_2 and HOOH. If this occurs via H-atom transfer (HOO$^\bullet$ + HOO$^\bullet$ → HOOH + $^3O_2$), there will be no change in the isotopic abundance of $^{36}O_2$ and $^{32}O_2$ nor formation of any $^{34}O_2$ (and no formation of $^1O_2$). In contrast, a radical–radical coupling pathway (with concerted homolytic dissociation of HOOOOH) will result

$$H^{18}O^{18}O^\bullet + {}^\bullet{}^{16}O^{16}OH \rightarrow [H^{18}O^{18}O^{16}O^{16}OH] \rightarrow H^{18}O^{16}OH + (^{18}O^{16}O) \quad (1)$$

in a fractional distribution of 0.5 $^{34}O_2$, 0.25 $^{36}O_2$, and 0.25 $^{32}O_2$ (each as $^1O_2$). Mass spectral analysis of such a mixture would give a molecular-ion current fraction $[I_{34}/(I_{34} + I_{36})]$ with a value of 0.67. The results from this experiment, which are summarized in Table IB, confirm that the dominant pathway is represented by eq 1 and is consistent with the substantial production of $^1O_2$ (Table IA).[4] An analogous pathway has been observed for alkylperoxy radicals (2ROO$^\bullet$ → ROOOOR → ROOR + O_2) with comparable isotopic mixing.[5,6]

Additional evidence for the production of $^1O_2$ from the electrolytic formation of HOO$^\bullet$ at an electrode surface is the positive result when diphenylisobenzofuran (DPBF, a $^1O_2$ trap) is present in the electrolysis solution (Table IC).

In contrast to the large yields of $^1O_2$ that are obtained in the electrolytic reduction experiments, the yield of $^1O_2$ in homogeneous

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[3] Singlet oxygen production was detected by measuring its characteristic 1268-nm chemiluminescence. The chemiluminescence spectrometer that was used for these measurements has been described (Kanofsky, J. R. *J. Biol. Chem.* **1983**, *258*, 5991–5993). Light emission was not observed with dimethylformamide as the solvent; the reasons for this difference are not known.

[4] The electrolysis was done in a sealed cell into which a known amount of a 50:50 $^{36}(O_2)$:$^{32}(O_2)$ had been introduced. After a measured number of coulombs had been passed, the head space was sampled with a gas syringe and analyzed with a Hewlett-Packard Model 5790A-5970A GC-MS mass spectrometer.

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