Figure 2. Dispersion spectra of VFe protein at 2.0 K showing the effect of power. Conditions: protein concentration, 60 mg mL^{-1}; sp act., 230 nmol of C_2H_2 reduced min^{-1} (mg of protein)$^{-1}$; modulation amplitude, 2 G; 100-kHz field modulation ($H_{mod} \sim 8$ G); microwave power as indicated; microwave frequency, 9.53 GHz. Major absorption about 3500 G in top spectrum is due to S1 while signal at $H \geq 1100$ G originates from S2. Broad signal between $\sim$2800 G and $\sim$5500 G that grows with increasing power is due to S3. The symbol (*) indicates a cavity impurity.

extends from $\sim$2800 G to $\sim$5500 G, with a peak near $\sim$3500 G. No analogous signal is observed in the dispersion spectrum of the MoFe protein of conventional nitrogenase. Finally, with the power increased to 2 mW, all resonances are in passage. S1 still is present, but no longer is as evident because S3 has increased in strength and clearly has a larger integrated area. S2 now is fully absorption-like and underlies S1 and S3; it also has a large integrated area, although this is not so obvious since its spectrum is very broad, especially in the high-field region, possibly due to g-strain effects. It is interesting to note that the new signal, S3, is not present in the dispersion spectrum of Av1′ under all conditions. In particular, the spectrum of thionine oxidized Av1′, a state in which it has been shown that each of the protein's paramagnetic clusters is one-electron-oxidized,[8,9] no longer exhibits S3.

The past inability to detect S3 in the derivative absorption mode of Av1′ is due to its nonclassical line shape. Typically the absorption signal of the powder spectrum of a paramagnetic species exhibits well-defined high- and low-field shoulders easily detected in the derivative presentation. Although g-strain effects sometimes broaden the high-field shoulder beyond detection,[10,11] the low-field

shoulder normally remains observable (as in the case of S2). Figure 2 shows, however, that neither edge of the S3 signal has a well-defined shoulder. This situation is not unique to S3 and has been observed in the spectra of at least two other metalloproteins, both of which involve spin-coupled centers. Horseradish peroxidase compound 1 exhibits a spectrum[12] similar to that of S3 extending from $\sim$2400 G to $\sim$6000 G. This spectrum[12,13] arises from the spin coupling of a porphyrin free radical to an even spin ($S = 1$) Fe^{4+} ion; the broadening of the spectrum is hypothesized to originate from a normal distribution of J coupling constants.

A similar situation exists for the reduced primary electron acceptor in the reaction-center protein of photosynthetic bacteria.[14] Here a paramagnetic ubisemiquinone anion free radical is coupled to Fe^{2+} in an $S = 2$ state. The broadened spectrum of this center results from the overlap of ground- and excited-state signals, extends from $\sim$1200 G to $\sim$8000 G, and again, is best simulated by using a spread of J coupling constants.

Thus, the passage EPR technique demonstrates that the paramagnetism of the as-isolated VFe protein of vanadium nitrogenase from A. vinelandii comprises three components, not two, and the major components appear to be S2 and S3. Unfortunately, because S2 and S3 strongly overlap and we cannot observe the full S2 signal, the absolute integrated area of each cannot be determined. Although the origins of each of the three signals in the spectrum of the VFe protein are as yet unknown, it can be stated that S1 and S2 typify spectra of metalloprotein metal clusters, and the spectrum of S3 suggests that it may originate from a paramagnetic site coupled to a metal center.

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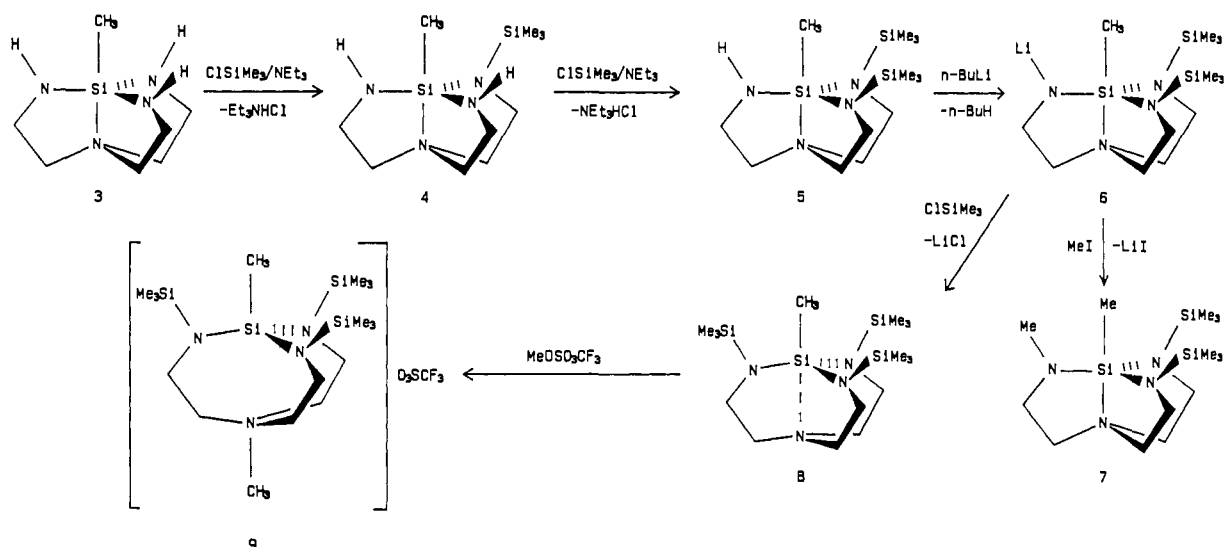
New Azasilatranes: Sterically Induced Transannular Bond Weakening and Cleavage

Dietrich Gudat, Lee M. Daniels, and John G. Verkade*

*Gilman Hall, Iowa State University
Ames, Iowa 50011*

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Recently we reported that azasilatranes **1** and **2** retain their structural integrity after undergoing di- or trisubstitution reactions on the equatorial NH functionalities with silyl groups of varying bulk (reaction 1).[1] Here we report that the greatly augmented

$$\text{1}\quad X = H$$
$$\text{2}\quad X = OEt$$
$$R' = H \text{ or } SiR_3$$
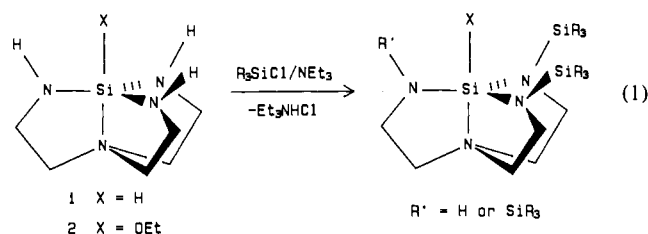
steric encumbrances resulting from the stepwise substitution of

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Scheme I

Table I. Selected NMR Data for 3–9

	R	R'	R″	δ ^{29}Si^a (ppm)		$^1J_{Si,C}$ (Hz)	$^2J_{Si,H}$ (Hz)
				SiCH$_3$	Si(CH$_3$)$_3$		
3^b	H	H	H	−68.3		66.2	5.87
4	SiMe$_3$	H	H	−56.7	4.00	c	5.8
5	SiMe$_3$	SiMe$_3$	H	−36.2^d	3.20	70.0	6.05
6^e	SiMe$_3$	SiMe$_3$	Li	−35.9	1.76	67	5.1
7	SiMe$_3$	SiMe$_3$	Me	−25.8	3.15	74.9	6.4
8	SiMe$_3$	SiMe$_3$	SiMe$_3$	−25.7	3.16	72.4	6.50
9^f	SiMe$_3$	SiMe$_3$	SiMe$_3$	−10.4	6.81	76.8	6.90

^{a} In CDCl$_3$ unless stated otherwise. ^{b} See ref 7. ^{c} Not determined in this intermediate. ^{d} −35.6 in benzene. ^{e} In benzene. ^{f} In CD$_2$Cl$_2$.

the NH functions in **3** with bulky groups (Scheme I) leads to a significant weakening of the Si–N$_{ax}$ bond, facilitating what can be considered to be a retrograde S$_N$2 reaction. Trimethylsilylation of **3**[2] proceeds stepwise to give **4**[3] and **5**.[3] Deprotonation of **5** gives the isolable intermediate **6**[4] which further silylates to give novel **8** or alkylates to afford unsymmetrical **7**.[5]

Normally silatranes possess robust Si–N$_{ax}$ bonds, displaying upfield ^{29}Si chemical shifts and AA'MM' ^{1}H NMR spectra for their conformationally mobile CH$_2$CH$_2$ protons down to low temperatures.[6] However, increased substitution of the equatorial nitrogens in **3** is accompanied by ^{29}Si deshielding and general increases in $^1J_{SiC}$ and $^2J_{SiH}$ (Table I). Such changes in silatranes have been correlated with weakening of the N$_{ax}$–Si bond.[7–9] Unlike other symmetrically substituted azasilatranes, the CH$_2$CH$_2$ ^{1}H NMR resonances of **8** display an ABMX pattern at −60° with
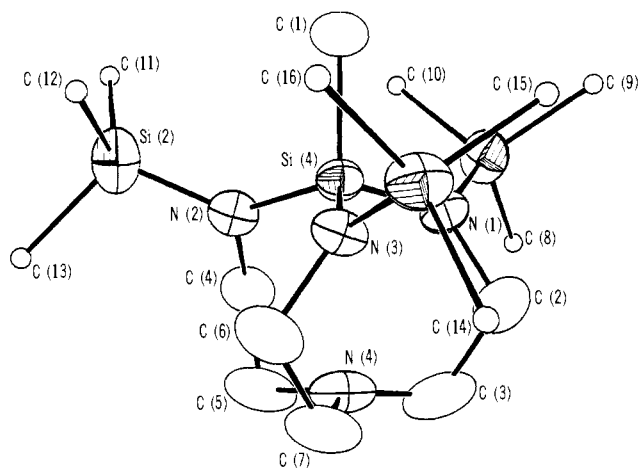
Figure 1. ORTEP drawing and atomic numbering scheme for **8**.

AA'MM' characteristics becoming fully evident at 100°.

From the structure of **8** (Figure 1) determined by X-ray means,[10] it is evident that the N$_{ax}$–C$_3$ geometry is nearly trigonal planar (angle sum = 356.2 (6)°). Although the Si–N$_{ax}$ distance, 2.775 (7) Å, is the longest ever recorded in an azasilatrane,[1] it is 24% shorter than the sum of the relevant van der Waals radii (3.65 Å).[11] This observation along with the slight *upward* protrusion of N$_{ax}$ (by 0.162 (6) Å above the plane of the adjacent carbons) and the larger than tetrahedral NSiN angles (av 112.1 (2)°) suggest the presence of a weak Si–N$_{ax}$ bond. This weak interaction renders N$_{ax}$ sufficiently basic for reaction with MeOSO$_2$CF$_3$ to give **9**.[12] The further deshielding of the ^{29}Si NMR signal of the bridgehead silicon in **9** with respect to **8** is consistent with the presence of essentially four-coordinate silicon.

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(3) A solution of 10 mmol of **3** in 25 mL of benzene was reacted with a mixture of 30 mmol each of Me$_3$SiCl and Et$_3$N for 12 h at room temperature to give **5** which was isolated by filtration of the Et$_3$NHCl formed followed by fractional distillation of the filtrate. Although monosubstituted **4** was detected spectroscopically, no evidence for trisilylated product was observed (**5**: bp 95–96 °C/0.1 Torr).

(4) Addition of 1.1 equiv of *n*-BuLi as a 0.2 M solution in hexane to 5.0 mmol of **5** in 20 mL of hexane at 50 °C for 20 min gave, after filtration and evaporation, **6** as a colorless, highly moisture-sensitive powder (mp 81–85 °C (dec)).

(5) Solutions of 2.0 mmol of **6** in 20 mL of benzene with excess (10 mmol) of MeI and Me$_3$SiCl, respectively, were refluxed for 12 h. Cooling the reaction mixture to room temperature, followed by filtration of the lithium salt and fractional distillation of the filtrate afforded **7** and **8** as a colorless liquid and solid, respectively (**7**: bp 94–96 °C/0.1 Torr; **8**: mp 101–103 °C)).

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(10) Crystal data: space group *P*1̄ (no. 2) *a* = 9.382 (4) Å, *b* = 9.640 (4) Å, *c* = 14.856 (6) Å, α = 90.13 (3)°, β = 101.72 (2)°, γ = 106.05 (2)°, *V* = 1261.9 (9) Å^3, *Z* = 2, d_{calc} = 1.06 g/cm^3, μ(Mo Kα) = 2.36 cm^{-1}; 3287 unique reflections in the +h,±k,±l hemisphere, 1610 observed ($F_o^2 > 3\sigma(F_o^2)$). The choice of the centric space group was suggested by intensity statistics and was confirmed by successful refinement. The structure was solved by direct methods. The hydrogen atoms were used in idealized positions for structure factor calculations, and the methyl groups were refined rigidly with C–H distances of 1.08 Å. Refinement of 250 parameters converged with agreement factors of $R_1 = \sum|F_o - F_c|/\sum F_o$ = 0.0466 and R_2 = sqrt[$\sum w(F_o - F_c)^2/\sum w(F_o^2)$] = 0.0530. The refinement was carried out with the SHELX-76 package.

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(12) Addition of 2.5 mmol of MeO$_3$SCF$_3$ to 2 mmol of **8** dissolved in 20 mL of benzene at 30 °C produced a colorless precipitate of **9** which was recrystallized from CHCl$_3$ (mp 250–55 °C (dec)).

Some silatranes have beneficial biological actions, while others are toxic.[6] The biological properties of the new derivatives reported here are under investigation.

Registry No. 3 (CC entry), 63344-73-0; **3** (silane entry), 31701-36-7; **4** (CC entry), 122722-12-7; **4** (silane entry), 122699-00-7; **5** (CC entry), 122699-04-1; **5** (silane entry), 122699-01-8; **6** (CC entry), 122699-05-2; **6** (silane entry), 122699-10-9; **7** (CC entry), 122699-06-3; **7** (silane entry), 122699-02-9; **8** (CC entry), 122699-07-4; **8** (silane entry), 122699-03-0; **9**, 122699-09-6.

Supplementary Material Available: Tables of positional and anisotropic thermal parameters, bond lengths, torsion angles, general displacement expressions, and bond angles and a listing of ^{1}H and ^{13}C NMR data for 4–9, an elemental analysis for 5, and high resolution mass spectral data for 5 and 7–9 (9 pages); table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

Figure 1. ORTEP drawing of 1·1.5CH$_2$Cl$_2$ showing the 55% probability thermal ellipsoids and atom labels for all non-hydrogen atoms (excluding CH$_2$Cl$_2$ solvate molecules). The hydrogen atoms on the formate ligands are included as isotropic spheres (B_{eq} = 1.0). Selected interatomic distances (Å) and angles (deg) are as follows: Fe1–O1, 2.168 (8); Fe1–O2, 2.045 (8); Fe1–O4, 2.132 (8); Fe1–O6, 2.16 (1); Fe1–N11, 2.14 (1); Fe1–N21, 2.13 (1); Fe2–O1, 2.129 (9); Fe2–O3, 2.09 (1); Fe2–O5, 2.07 (1); Fe2–N31, 2.104 (9); Fe2–N41, 2.13 (1); Fe1···Fe2, 3.585 (4); O1–Fe2–O5, 107.9 (4); O1–Fe2–O3, 88.8 (3); O1–Fe2–N41, 90.8 (4); O1–Fe2–N31, 147.3 (5); O3–Fe2–N41, 173.8 (4); Fe1–O1–Fe2, 113.1 (4).
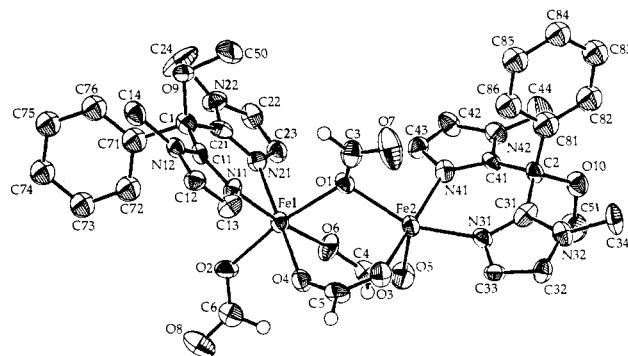
Self-Assembly and Dioxygen Reactivity of an Asymmetric, Triply Bridged Diiron(II) Complex with Imidazole Ligands and an Open Coordination Site

William B. Tolman, Avi Bino, and Stephen J. Lippard*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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In the marine invertebrate respiratory protein hemerythrin (Hr), two dissimilar ferrous ions, one five- and the other six-coordinate, cooperate to bind dioxygen reversibly (eq 1).[1,2] An important

Deoxyhemerythrin   Oxyhemerythrin

(1)
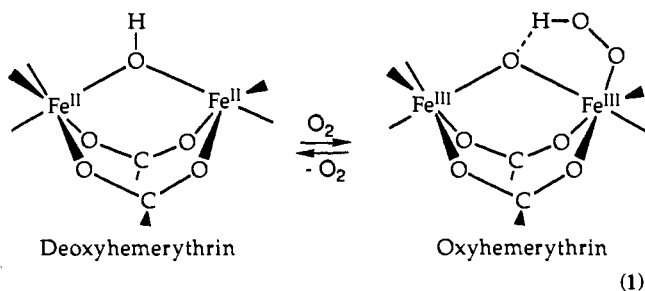
objective in the quest for model complexes that can mimic the biological activity of Hr, therefore, is the synthesis of an asymmetric diiron(II) complex[3] with an open terminal coordination position. Accurate spectroscopic and magnetic models of the diiron centers in the reduced and oxidized forms of Hr containing the {Fe$_2$(OR)(O$_2$CR')$_2$}$^+$ (R = H, Ph)[4] and {Fe$_2$O(O$_2$CR')$_2$}$^{2+}$ cores,[4b,5]

respectively, are currently available. None of the diiron(II) compounds can model the molecular oxygen binding function of the protein, however, because they are capped by tridentate N-donor ligands and thus lack an open coordination site. By using bidentate instead of tridentate groups as terminal ligands on the diiron core, one can gain access to such a site.[6] Here we report the preparation by self-assembly of an asymmetric, triply bridged diiron(II) complex, **1**, from ferrous ions and biomimetic carboxylate and bis imidazole ligands, together with its X-ray crystal structure and Mössbauer and ESR spectra. Air oxidation of **1** yields the diiron(III) complex **2**, the oxo bridge of which is shown by resonance Raman spectroscopic experiments to derive from dioxygen.

Stirring of a 1:1 mixture of Fe(O$_2$CH)$_2$·2H$_2$O[7] and bis(1-methylimidazol-2-yl)phenylmethoxymethane (BIPhMe)[8] in MeOH with strict exclusion of air for 0.5 h gave a colorless solution, which, upon workup, afforded [Fe$_2$(O$_2$CH)$_4$(BIPhMe)$_2$] (**1**) as a colorless powder (91%). This formula is supported by
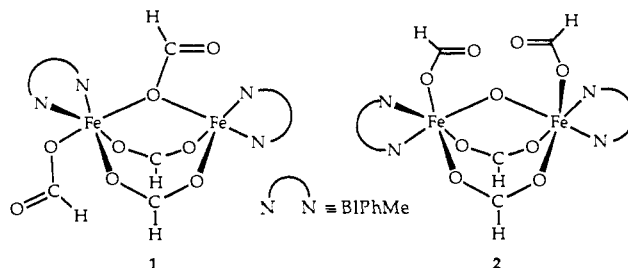
analytical data, the appearance of formate and BIPhMe vibrations in the FTIR spectrum, and an X-ray structure determination, performed on a crystal obtained from CH$_2$Cl$_2$/CH$_3$CN, which revealed an asymmetric molecule with an open coordination site

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