K. pneumoniae.[6] (2) The metal ion composition is unchanged in the V⁻ protein.[6a,7a] (3) EPR spectroscopy shows that the WT and V⁻ cofactors are not distinguished by a major conformational rearrangement. (4) EXAFS shows that the local S and Fe environment of molybdenum is similar, if not identical. (5) ENDOR measurements show the molybdenum site is perturbed in the mutant cofactor. We conclude that the mutant cofactor cluster is not an isomer of the WT, which indicates that it differs by the addition, subtraction, or replacement of a metal–ligand(s). Points (4) and (5) suggest that this difference is most likely due to a change in non-sulfur ligands weakly bound at or near molybdenum, but it could be due to sulfur ligands distant from molybdenum. These possibilities can be tested chemically and spectroscopically. For example, chemical analysis can show whether the sulfur content of mutant cofactor differs from that of WT, and ⁵⁷Fe ENDOR and Mössbauer studies provide a probe of the iron sites in the cluster.

Coordinatively Unsaturated Tris(trimethylsilyl)silyl Complexes of Chromium, Manganese, and Iron

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Transition-metal silyl complexes exhibit a limited array of reactivity patterns compared to analogous compounds containing M–C or M–H σ-bonds. The majority of transition-metal silyls are coordinatively saturated and contain carbon monoxide, phosphines, or cyclopentadienyl ancillary ligands.[1] One approach to the design of more reactive silyl complexes is to place the metal in an electron-deficient, low coordination number environment. Use of sterically demanding silyl ligands should allow isolation of low-coordinate silyl complexes which may function as more reactive silylating reagents. Such species may also serve as precursors to conductive metal silicide thin films, which are not easily prepared by direct metal–silicon reactions.[2] Here we report use of the Si(SiMe₃)₃ (TTSS) ligand in preparing low coordination number silyl complexes of chromium, manganese, and iron.

First-row transition-metal dichlorides react with 2 equiv of (THF)₃Li(TTSS)[3] in ether solvents to afford air- and moisture-sensitive, anionic silyl complexes (eq 1 and 2). Compounds 1–3 are isolated following crystallization from diethyl ether/pentane.

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Table I. Data for Silyl Compounds 1–9

compd	color	yield, %	μ_{eff}, μ_B[a]	dec temp, °C[b]
Li(THF)₃[(TTSS)₂CrCl], **1**	orange	80	6.2[c]	
Li(DME)₂[(TTSS)₂MnCl], **2**	lt yellow	85	5.1[c]	143
Li(DME)₂[(TTSS)₂FeCl], **3**	purple	76	6.3[c]	142
NEt₄[(TTSS)₂FeCl], **4**	purple	62	5.8[d]	148
NEt₄[(TTSS)FeCl₂(pyr)], **5**	orange	62	5.3[d]	119
NEt₄[(TTSS)₂FeOSO₂CF₃], **6**	purple	74	6.1	139
(TTSS)₂Fe(DME), **7**	purple	79	5.7	160
(TTSS)₂Fe(Et₂O), **8**	blue-green	55	5.8	86
(TTSS)₂Mn(DME), **9**	lt yellow	76	5.4	161

[a] Magnetic moments were determined by the Evans Method[9] in benzene, unless otherwise noted. Diamagnetic corrections were not applied. [b] When heated in a sealed capillary, all compounds began to decompose at the temperatures given. [c] Diethyl ether solvent. [d] 1,2-Dimethoxyethane solvent.
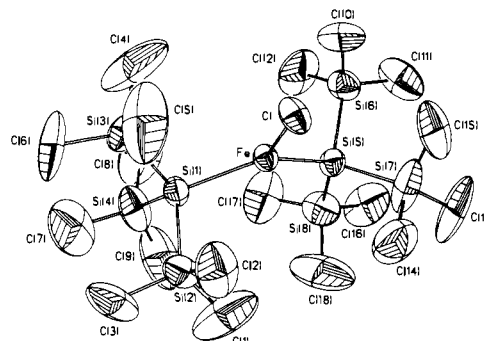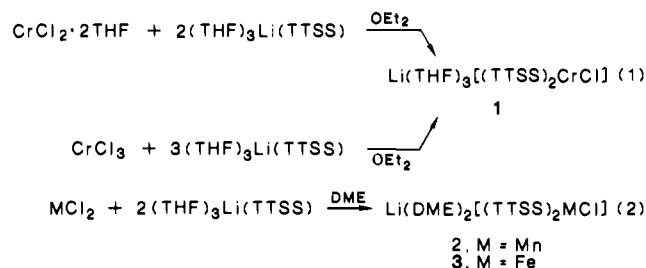

Figure 1. ORTEP view of the anion of **4**. Selected bond distances (Å) and angles (deg): Fe–Cl 2.284 (6), Fe–Si(1) 2.488 (6), Fe–Si(5) 2.491 (6), Si(1)–Si(2) 2.353 (8), Si(1)–Si(3) 2.331 (10), Si(1)–Si(4) 2.303 (10), Si(5)–Si(6) 2.370 (8), Si(5)–Si(7) 2.311 (9), Si(5)–Si(8) 2.331 (11), Cl–Fe–Si(1) 111.7 (2), Cl–Fe–Si(5) 111.1 (2), Si(1)–Fe–Si(5) 136.9 (2), Fe–Si(1)–Si(2) 105.2 (3), Fe–Si(1)–Si(3) 108.4 (3), Fe–Si(1)–Si(4) 121.2 (3), Fe–Si(5)–Si(6) 108.5 (3), Fe–Si(5)–Si(7) 106.0 (3), Fe–Si-(5)–Si(8) 120.5 (3).

Orange **1**, which is also obtained from reaction of CrCl₃ with 3 equiv of (THF)₃Li(TTSS) (eq 1), is thermally unstable at room temperature but may be stored indefinitely as a solid at –20 °C. Complexes **2** and **3** are stable at room temperature under nitrogen.
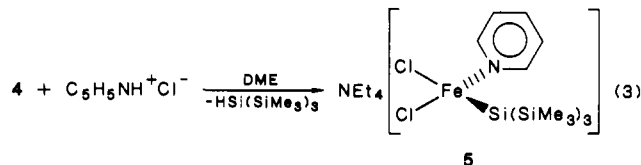
$$\text{CrCl}_2\cdot2\text{THF} + 2(\text{THF})_3\text{Li}(\text{TTSS}) \xrightarrow{\text{OEt}_2}$$
$$\text{Li}(\text{THF})_3[(\text{TTSS})_2\text{CrCl}] \quad (1)$$
$$\mathbf{1}$$
$$\text{CrCl}_3 + 3(\text{THF})_3\text{Li}(\text{TTSS}) \xrightarrow{\text{OEt}_2}$$

$$\text{MCl}_2 + 2(\text{THF})_3\text{Li}(\text{TTSS}) \xrightarrow{\text{DME}} \text{Li}(\text{DME})_2[(\text{TTSS})_2\text{MCl}] \quad (2)$$
$$\mathbf{2}, \text{M} = \text{Mn}$$
$$\mathbf{3}, \text{M} = \text{Fe}$$

Paramagnetic silyl complexes are quite rare[1] and to our knowledge do not exist for Cr, Mn, or Fe. These low-coordinate complexes possess large magnetic moments consistent with high-spin electron configurations (see Table I). In toluene at room temperature, the ESR spectrum of **2** exhibits a broad signal with $g = 2.003$ and $a = 1.87 \times 10^{-3}$ cm⁻¹. The compounds in Table I were characterized by infrared spectroscopy and elemental analyses. In some cases, carbon analyses were consistently low and variable;[4] therefore product stoichiometries were confirmed by hydrolysis and ¹H NMR integration of the released HSi-(SiMe₃)₃ and ether against an internal ferrocene standard. Additional characterization is by X-ray crystal structure determination and high-resolution mass spectrometry of related derivatives (vide infra).
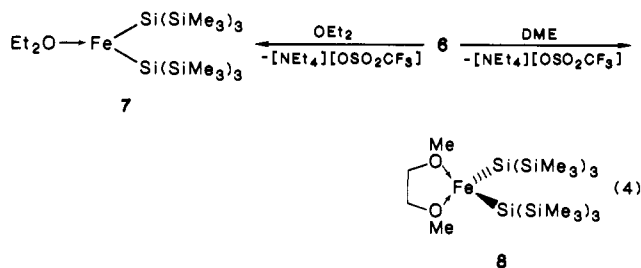
(4) We ascribe the difficulty in obtaining good carbon analyses to metal-catalyzed formation of silicon carbide, which does not burn completely during the combustion analysis.

Treatment of **3** with NEt_4Cl in 1,2-dimethoxyethane results in cation exchange to give $NEt_4[(TTSS)_2FeCl]$ (**4**), which has been structurally characterized.[5] An ORTEP view of the anion in **4** (Figure 1) shows the unusual three-coordinate geometry for the d^6 Fe(II) center. The steric bulk of the TTSS ligands results in a Si(1)–Fe–Si(5) angle of 136.9 (2)°, significantly larger than the Si–Fe–Cl angles (av 111.4 (4)°). These differences in bonding angles about iron are probably responsible for the observed deviations from tetrahedral environments about Si(1) and Si(5). Other metrical parameters associated with the TTSS ligation in **4** do not differ markedly from those found in $(CO)_5Mn(TTSS)$[6] and $(CO)_5Re(TTSS)$.[7] The Fe–Si bond distances (av 2.490 (6) Å) appear to be the longest yet observed for an iron silyl complex. Other reported Fe–Si distances range from 2.22 to 2.46 Å.[8]

The reaction chemistry of compounds **1–4** has been briefly surveyed. Acidolysis of **4** with 1 equiv of pyridinium hydrochloride gives the anionic pyridine complex **5** (eq 3), which may be

$$4 \ + \ C_5H_5NH^+Cl^- \xrightarrow[-HSi(SiMe_3)_3]{DME} NEt_4 \left[\begin{array}{c} Cl \\ Cl \end{array} Fe \begin{array}{c} N\text{—}\bigcirc \\ Si(SiMe_3)_3 \end{array} \right] \quad (3)$$

5

crystallized from diethyl ether/1,2-dimethoxyethane. The chloride ligand in **4** may be abstracted by $Me_3SiOSO_2CF_3$ in toluene giving Me_3SiCl and $NEt_4[(TTSS)_2FeOSO_2CF_3]$ (**6**), isolated as purple crystals from pentane/toluene. The triflate ligand in **6** is weakly coordinated and is readily displaced by ethers (eq 4). Neutral

$$Et_2O \longrightarrow Fe \begin{array}{c} Si(SiMe_3)_3 \\ Si(SiMe_3)_3 \end{array} \xleftarrow[-[NEt_4][OSO_2CF_3]]{OEt_2} \mathbf{6} \xrightarrow[-[NEt_4][OSO_2CF_3]]{DME} \begin{array}{c} Me \\ O \\ O \\ Me \end{array} Fe \begin{array}{c} Si(SiMe_3)_3 \\ Si(SiMe_3)_3 \end{array} \quad (4)$$

7   **8**

complexes **7** and **8** are crystallized from pentane. Manganese silyl complex $(TTSS)_2Mn(DME)$ (**9**), obtained similarly from the lithium salt **2** and $Me_3SiOSO_2CF_3$, presumably has a four-coordinate structure analogous to **8**. Mass spectra of **8** and **9** contain no parent ions but feature strong peaks due to $M(TTSS)_2^+$. Exact

mass measurements gave values of 550.1724 for **8** (calcd: 550.1729) and 549.1764 for **9** (calcd: 549.1760) for the $M(TTSS)_2^+$ ions.

We are presently examining the chemistry of these and related low-coordinate transition-metal silyl complexes. Initial results indicate that coordinative unsaturation in these systems provides a high degree of reactivity toward unsaturated substrates.

Synthetically and Biologically Interesting *N*-Acylquinone Imine Ketals and *N*-Acylquinol Imine Ethers from Anodic Oxidation of Anilides

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The electrochemistry of aromatic amines has been extensively studied;[1] however, less is known about the electrochemical oxidation of the corresponding amides.[2–4] Several types of reactions have been reported, but most involved poor yields and/or material balances and no synthetic use has been made of this chemistry. Thus, the anodic oxidation of simple anilides in acetonitrile/pyridine gives pyridination products,[2b,3a,b] while amide derivatives of *p*-anisidine in nucleophilic solvents (water, methanol) afford mixtures of benzoquinone, benzamide, or methyl benzoate, depending on the reaction conditions.[2a,3a,c] Unstable intermediates have been detected in the anodic oxidations[3c] of *N*-aryl amides by cyclic voltammetry and ultraviolet spectroscopy, but these compounds were not isolated or characterized. Finally, anodic oxidation of the anilide of *N*-methyl-*p*-anisidine affords the corresponding *N*-methylbenzoxazolium perchlorate,[3c] and various dimeric products are formed under other reaction conditions.[3d,4]

The extensive biological interest in the oxidation products derived from acylated aromatic amines[5,6] and the synthetic po-

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(5) $C_{26}H_{74}ClNFeSi_8$: monoclinic, $P2_1/c$, $a = 14.943$ (3) Å, $b = 21.198$ (3) Å, $c = 15.291$ (4) Å, $\beta = 99.16$ (2)°, $V = 4782$ (2) Å^3, $Z = 4$, $\mu = 5.83$ cm^{-1}, Mo Kα ($\lambda = 0.71073$ Å), 23 °C, Nicolet R3 diffractometer, graphite monochromator, purple crystal (0.35 × 0.30 × 0.25 mm) from 1,2-dimethoxyethane/diethyl ether, sealed in glass capillary. Of 5425 reflections collected ($4° \leq 2\theta \leq 42°$), 5181 were unique ($R_{int} = 1.77\%$), and 1957 with $F_o \geq 5\sigma(F_o)$ were considered observed. No absorption correction was needed. A model for disorder found in NEt_4^+ was constructed by constraining the NC_4 fragment to tetrahedral symmetry and refining the C–C distances as a common variable. The overall temperature factor, $U_{iso} = 0.068$, obtained from a Wilson plot is large and reveals that the structure is unusually thermally active. Absence of diffraction data beyond $2\theta = 42°$, the disordered NEt_4^+ ion, and the low density (D(calcd) = 1.00 g cm^{-3}) are in keeping with a very loose lattice packing. Solution by direct methods (SOLV), blocked cascade refinement, non-hydrogen atoms anisotropic, hydrogen atoms (except for those of NEt_4^+ which were ignored) isotropic (fixed and idealized positions): $R_F = 9.6\%$, $R_{wF} = 10.3\%$, data/parameter = 6.7, GOF = 1.58, highest peak = 0.61 e$^-$/Å^3 (within NEt_4^+).

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