ditions. The same transformation can be effected with $(Me_3Si)_2S$[15] but the process is slow (hours) and the procedure requires controlled, intermittent introduction of air.[15b]

To summarize, $(MeCp)_2TiS_2SiMe_2$ represents a rare example of a metal complex of a silicon sulfide ligand. Our Li_2SSiMe_2 reagent should permit the synthesis of a variety of $Me_2SiS_2^{2-}$ complexes. This class of compound may be useful since we have shown that **1** can function as an efficient, nonreductive atom- or chelate-transfer agent.[16]

Acknowledgment. This research was supported by the National Science Foundation. Platinum was loaned to us by Johnson Matthey Inc. We thank Catherine Jones for her assistance with the kinetic studies and Dr. Curtis Schwartz for the gift of $(NBu_4)_3TaW_5O_{19}$.

Supplementary Material Available: Description of the structure determination and tables of atomic coordinates, hydrogen atom coordinates, bond angles and distances, and thermal parameters (5 pages); a listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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Received May 27, 1987

Reductive Chemistry of Nickel Hydroporphyrins: The Nickel(I) Octaethylisobacteriochlorin Anion

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F_{430},[1] a Ni(II) hydrocorphinoid complex,[2] is a prosthetic group of methyl-coenzyme M reductase.[3] This enzyme catalyzes the reductive cleavage of *S*-methyl-coenzyme M, 2-(methylthio)ethanesulfonate, to methane. An EPR signal detected in whole cells of *Methanobacterium thermoautotrophicum* was attributed to a Ni(I) form of F_{430} in intact, active enzyme.[4] Although free F_{430} and F_{430} pentamethyl ester have been reduced to their Ni(I) forms,[4,5] Ni(I) tetrapyrrole complexes with more extensive π systems are unknown. We report here the synthesis and reactivity of the nickel(I) octaethylisobacteriochlorin anion, $Ni^{I}(OEiBC)^-$,[6] the first Ni(I) tetrapyrrole complex with a π system extending over the macrocycle. Our results demonstrate important and substantive differences in the reactivity of metalloporphyrins and metallohydroporphyrins.

Cyclic voltammograms of Ni(OEP), Ni(OEC),[7] and Ni(OEiBC)[8] in nitrile solvents[9] showed only a single reversible one-electron reduction near −1.5 V vs. SCE.[11,12] Bulk electrolyses of these complexes at −1.65 V did not appear to afford stable species. On the shorter time scale of electrolysis in an OTTLE[6] cell (1 min vs. about 1 h), Ni(OEiBC) underwent a reversible one-electron reduction.[9] The spectrum of $Ni(OEiBC)^-$ (Figure 1) is characterized by well-defined Soret and visible bands. Band maxima are blue-shifted and molar extinctions are slightly diminished compared with those of $Ni^{II}(OEiBC)$, suggesting that the metal ion is the site of reduction. Species with identical spectra were generated by reduction with dilute sodium amalgam in dry THF or acetonitrile. The EPR spectrum of these materials unequivocally confirmed the $Ni^{I}(OEiBC)^-$ formulation (Figure 2). The anisotropy and hyperfine coupling to the four nitrogens of OEiBC are consistent with an unpaired electron in the $d_{x^2-y^2}$ orbital of a square-planar nickel(I) complex.[13] Observed g values of 2.201 and 2.073 and hyperfine coupling of 9.8 G are similar to those of reduced F_{430} species[4,5] and Ni(I) macrocyclic complexes.[13-15]

Changes in the spectrum of Ni(OEC) upon reduction in the OTTLE[9] paralleled those observed for Ni(OEiBC), suggesting formation of $Ni^{I}(OEC)^-$. In contrast, $Ni(OEP)^-$ exhibited broadened, red-shifted bands of reduced extinction, typical of ring reduction. Stable, significant concentrations of $Ni^{I}(OEC)^-$ and of $Ni^{II}(OEP)^-$ were not obtained by sodium amalgam reduction in either THF or acetonitrile. Instead, reduction proceeded directly to the diamagnetic, two-electron-reduced phlorin complexes $Ni(OEPH)^-$ and $Ni(OECH)^-$, which were identified on the basis of UV-vis and ^1H NMR evidence.[16] EPR spectra of minor concentrations of $Ni(OEC)^-$ and $Ni(OEP)^-$ were obtained with rapidly frozen, partially reduced solutions. Signals observed at $g = 2.08$ and $g = 2.003$, respectively, confirmed the assignments of the sites of reduction suggested by UV-vis spectra.

Nickel(I) macrocyclic complexes catalyze the electrocatalytic reduction of alkyl halides.[15,17,18] The cyclic voltammetric reduction of Ni(OEiBC) in dichloromethane exhibited features characteristic of a diffusion-controlled electrocatalytic process,[19] the reduction of dichloromethane by $Ni^{I}(OEiBC)^-$. The *i*–*E* curve in this solvent

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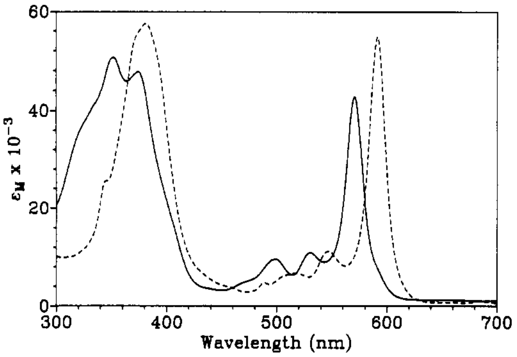

Figure 1. UV–vis spectra of 1 mM Ni^{I}(OEiBC)$^-$ (—) and Ni^{II}(OEiBC) (- - -) in acetonitrile containing 0.1 M TBAP recorded in an OTTLE cell. The Ni^{I} species was obtained by electrolysis at −1.70 V.

did not have the normal peak-shaped appearance. Instead, it looked like a polarographic wave (plateau shaped with an inflection point near −1.5 V) and had a limiting current 4.95 times that of a reversible one-electron process. The identical *i–E* curve was obtained when the scan direction was reversed.

The shape of cyclic voltammetric wave forms for electrocatalytic processes depends upon the concentration of substrate, magnitudes of the sweep rate and the rate constant for reaction of catalyst and substrate. Higher substrate concentrations, large rate constants, and slow sweep rates favor catalytic behavior. Reduction of Ni(OEiBC) in dichloromethane was electrocatalytic at sweep rates as high as 2000 mV/s. In contrast, the reduction of Ni(OEC) only became catalytic at scan rates of 20 mV/s. The reduction of Ni(OEP) was reversible ($E_{1/2}$ = 1.46 V) at scan rates greater than 20 mV/s. In nitrile solutions,[9] all three complexes catalyzed the reduction of added alkyl halide.[11,20] Preliminary data establish that the second-order rate constants for reaction of alkyl halides with Ni^{I}(OEiBC)$^-$ are at least 10 times and may be as much as 1000 times greater than those for Ni(OEP)$^-$.

Bulk solutions of Ni^{I}(OEiBC)$^-$ in THF reacted instantaneously with methyl iodide. Recovery of Ni^{II}(OEiBC) was quantitative, as judged by UV–vis and ^{1}H and ^{13}C NMR spectra. Analysis of head-space gases by GC–MS established the presence of significant quantities of methane. Ethane was not detected.

Two factors lead to accessibility of a stable nickel(I) complex for only the OEiBC macrocycle. The −1.70 V reduction potential of H$_2$(OEiBC)[21] (vs. 1.45 V for H$_2$(OEP) and H$_2$(OEC)[21]) helps ensure that the e_g π^* orbitals[22] of OEiBC lie higher in energy than the nickel d orbitals and therefore that nickel is the site of reduction. However, formation of the unstable Ni^{I}(OEC)$^-$ anion demonstrates that other factors must be operative here. The intrinsic hole sizes of planar free-base hydroporphyrins increase with increasing saturation of the macrocycle.[23,24a,26] Hole size affects the ligand field strength of the macrocycle and consequently the energy of the nickel σ^* $d_{x^2-y^2}$ LUMO orbital. A nickel(I) ion should be larger than a high-spin nickel(II) ion. Of the macrocycles considered here, only OEiBC accomodates high-spin nickel(II).[26,27] Even so, the reduction potential of the Ni^{II}(OEiBC)/Ni^{I}(OEiBC)$^-$ couple is considerably negative of that of F$_{430}$[5,30] and many nickel tetraazamacrocylic complexes,[14,31] suggesting that the OEiBC hole size is smaller than optimal for nickel(I).[32]

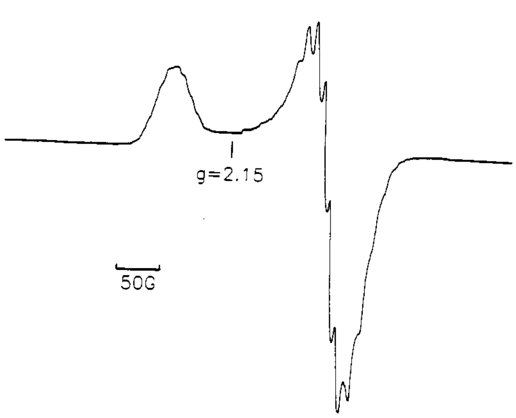

Figure 2. EPR spectrum of Ni^{I}(OEiBC)$^-$ in 2-MeTHF glass at 120 K. Conditions: frequency, 9122 MHz; power, 0.5 mW; modulation amplitude, 2.5 G.

An intriguing possibility suggested by our results is that the distinguishing difference between porphyrins, hydroporphyrins, corrins, and other tetrapyrroles is the range of hole sizes readily accessible in these complexes. Evidence of increased flexibility of hydroporphyrins was provided by the saddle-shaped conformations (S_4-ruffled) observed in structures of nickel(II) hydroporphyrins.[24,26] Ruffling stabilizes low-spin nickel(II) by reducing Ni–N distances.[23-26] The steepness of the saddle increases with saturation of the macrocycle π system[24a,26] since the macrocycle must ruffle to a greater degree to achieve the same Ni–N distance[23] typical for low-spin nickel(II) (about 1.92 Å). It is precisely the more saturated macrocycles that can flatten to accommodate the roughly 2.1 Å Ni–N distance required for nickel(I). The ability of the OEiBC macrocycle to provide near-optimal bond lengths for two members of a redox couple with radii that differ by about 0.2 Å is remarkable. Apparently, the hole sizes/ligand field strengths of hydroporphyrins can be adjusted over a wide range with only small changes in conformational energy.

Acknowledgment. We thank Dr. William H. Orme-Johnson and Neil Bastian for assistance in obtaining EPR spectra and the Camille and Henry Dreyfus Foundation (Young Faculty Grant to A.M.S), the Research Corp., and the National Institutes of Health (Grant No. GM33882) for support of this research.

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Received May 21, 1987

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