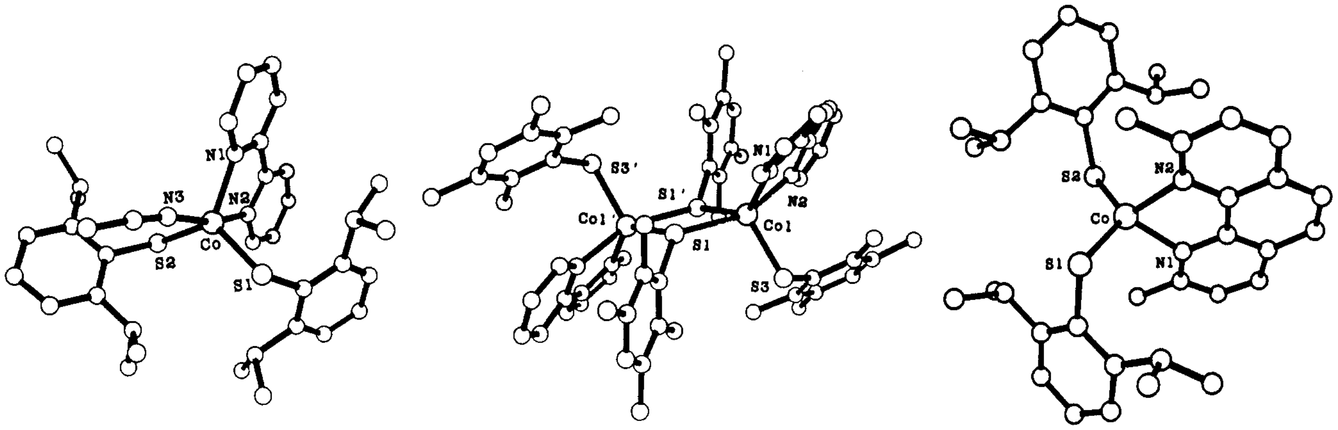


Figure 1. Structural diagrams (left to right) of $[Co(S\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2(bpy)(CH_3CN)]$, $[Co(S\text{-}2,3,5,6\text{-}Me_4C_6H)_2(bpy)]_2$, and $[Co(S\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2(2,9\text{-}Me_2phen)]$.

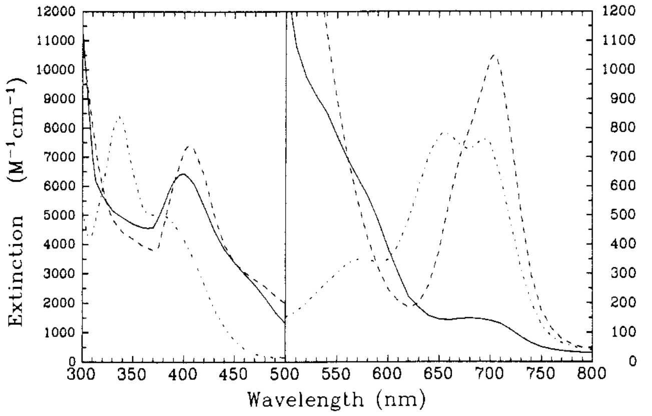


Figure 2. Electronic spectra (CH_3CN solutions) of $[Co(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2(1\text{-}Me\text{-}imid)_2]$ (···), $[Co(S\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2(phen)(CH_3CN)]$ (—), and $[Co(S\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2(2,9\text{-}Me_2phen)]$ (---).

coordination.[16] Moreover, the spectra are very similar to the spectrum of the $[(cys\text{-}S)_2Co(pyrazole)(his)]$ unit of the pyrazole-inhibited cobalt(II)-substituted catalytic center of LADH.[3b] The electronic spectra of **2** and its phen analogue in CH_3CN show markedly reduced extinctions for ligand field bands in the visible and in the near-infrared regions (Figure 2).[11] Reduced extinction for the ligand field bands in five- vs. four-coordinate Co(II) complexes is well established for complexes with nitrogen and oxygen donor ligands.[6,16] This result indicates that five-coordinate $[Co^{II}(S\text{-}cys)_2]$ centers should also be expected to have reduced extinction coefficients. The electronic spectrum of **2** in CH_3CN is very similar to that of the Co enzymes to which bpy has been added.[17] On the basis of the analogy of the structure of the phen-bound Zn enzyme,[18] the bpy-bound Co(LADH) is also five-coordinate.

In nondonor solvents, the spectra of **2** and its phen analogue show extinctions that indicate tetrahedral coordination. This result is consistent with the dissociation of the coordinated CH_3CN to give a four-coordinate complex. A further control experiment was done in which the phen ligand was replaced by 2,9-dimethyl-1,10-phenanthroline. It was anticipated that the steric effect of the two methyl groups ortho to the nitrogens would discourage five-coordination. X-ray crystallography established that $[Co(S\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2(2,9\text{-}Me_2phen)]$ (**4**) is indeed four-coordinate in the solid state even though it was crystallized from CH_3CN (Figure 1).[19,20] The electronic spectra of **4** in both CH_3CN (Figure 1) and in $CHCl_3$ are similar to the spectra of **2** in nondonor solvents with extinction coefficients that are in agreement with tetrahedral coordination.[19]

We have demonstrated that suitable modifications of the ligands can control the coordination geometry of bis(thiolate)cobalt(II) complexes. Our model studies support the view that the catalytic metal center in LADH remains four-coordinate during the enzymatic mechanism.

Acknowledgment is made to the National Institutes of Health for financial support (Grant GM-31849) and to Professor J. Lauher for use of the ROTOCHEM molecular graphics programs.

Supplementary Material Available: Tables of crystallographic data, fractional atomic coordinates, and isotropic and anisotropic thermal parameters and a plot of the electronic spectra in the near-infrared region (15 pages). Ordering information is given on any masthead page.

Department of Chemistry
State University of New York at Stony Brook
Stony Brook, New York 11794

Douglas T. Corwin, Jr.
Ronald Fikar
Stephen A. Koch*

Received March 27, 1987

---

(17) Syvertsen, C.; McKinley-McKee, J. S. *J. Inorg. Biochem.* **1984**, *22*, 43.

(18) Boiwe, T.; Brändén, C.-I. *Eur. J. Biochem.* **1977**, *77*, 173.

(19) $[Co(S\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2(2,9\text{-}Me_2phen)]$ (**4**). Crystal data: a = 12.548 (5) Å, b = 17.30 (1) Å, c = 16.82 (1) Å, β = 101.99 (6)°, V = 3573 (8) Å^3, Z = 4, monoclinic, $P2_1/n$, R (R_w) = 0.042 (0.047) for 1929 unique data. Electronic spectrum (CH_3CN):1710 (52), 1170 (63), 852 (35), 704 (1050), 674 (sh) (745), 475 (sh) (2680), 406 (7400), 315 (sh) (7330), 263 (27 800) nm.

(20) Bond distances (Å) and angles (deg) for **4**: Co–S1, 2.242 (2); Co–S2, 2.246 (2); Co–N1, 2.065 (5); Co–N2, 2.045 (5); S1–Co–S2, 124.80 (7); S1–Co–N1, 115.7 (2); S1–Co–N2, 104.0 (2); S2–Co–N1, 105.6 (2); S2–Co–N2, 117.3 (2); N1–Co–N2, 81.7 (2).

$(CH_3C_5H_4)_2TiS_2SiMe_2$: A Reactive Complex Containing an Si–S Ligand

Sir:

While the coordination chemistry of carbon–sulfur ligands is vast, very little is known about silicon–sulfur ligands.[1] Such species are of interest because they should prove as structurally variable as their carbon-based analogues but more reactive. Silanethiolates represent a bridge between organic thiolates and the thiometalates.[2] This paper summarizes our preliminary

---

(1) Ungurenasu, C.; Haiduc, I. *Rev. Roum. Chim.* **1968**, *13*, 657. Nametkin, N. S.; Tyurin, V. D.; Aleksandrov, G. G.; Kuźmin, O. V.; Nekhaev, A. I.; Andrianov, V. G.; Mavlonov, M.; Struchkov, Tu. T. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, 1353. Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125.

(2) Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 113. Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934.

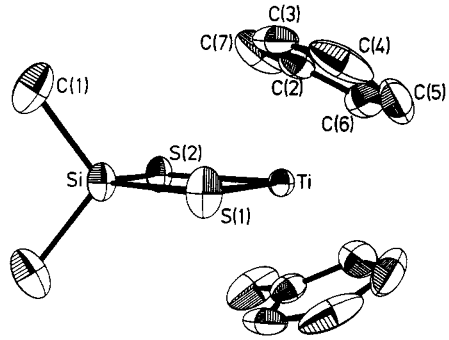


Figure 1. ORTEP of $(\mathrm{MeCp})_2\mathrm{TiS}_2\mathrm{SiMe}_2$ (**1**). Representative distances (Å) and angles (deg): Ti–S(1), 2.454 (1); Si–S(1), 2.110 (1); Si–C(1), 1.854 (4); S(1)–S(2), 3.26; S–Ti–S, 87.1; S–Si–S, 105.5; Ti–S(1)–Si, 83.4.

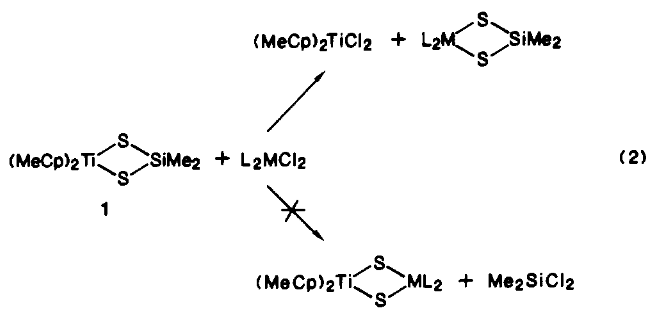
findings on the synthesis and, in particular, the reactivity of metal complexes of dimethylsilanedithiolate.

The centerpiece for our work in this project is $(\mathrm{MeCp})_2\mathrm{TiS}_2\mathrm{SiMe}_2$ (**1**, MeCp = η^5-$\mathrm{CH_3C_5H_4}$). This compound is conveniently prepared by treating THF solutions of $\mathrm{Me_2SiCl_2}$ with 2 equiv of $\mathrm{Li_2S}$[3] followed by $(\mathrm{MeCp})_2\mathrm{TiCl}_2$.[4] After 3 days, the olive brown solution was evaporated to dryness and extracted into $\mathrm{CH_2Cl_2}$; the filtered extract was diluted with hexanes and concentrated, giving dark green microcrystals of **1** (30% yield). The known $(\mathrm{Me_2SiS})_3$[5] may be an intermediate in this synthesis, and separate experiments show that treatment of this heterocycle with $\mathrm{Li_2S}$ for a few minutes followed by $(\mathrm{MeCp})_2\mathrm{TiCl}_2$ also gives **1** in 71% yield (eq 1).

$$(\mathrm{MeCp})_2\mathrm{TiCl}_2 + \mathrm{Li_2S_2SiMe_2} \xrightarrow[-2\mathrm{LiCl}]{} \underset{\mathbf{1}}{(\mathrm{MeCp})_2\mathrm{TiS_2SiMe_2}} \qquad (1)$$

We were unable to prepare **1** from $(\mathrm{MeCp})_2\mathrm{Ti(SH)}_2$ and $\mathrm{Me_2SiCl_2}$. Samples of **1** are air stable for extended periods although solutions must be handled anaerobically (the syntheses and properties of both **1** and its $\mathrm{C_5H_5}$ analogue are similar). A structural study[6] showed that **1** contains a (crystallographically imposed) planar $\mathrm{TiS_2Si}$ ring with tetrahedral titanium and silicon centers (Figure 1). Structurally, **1** is related to Petersens's $\mathrm{Cp_2Ti(CH_2)_2SiMe_2}$.[7]

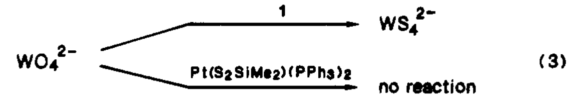
Both Ti–S[8] and Si–S[9] bonds are well-known to be reactive entities, and compound **1** provides an opportunity to determine the relative reactivity of these moieties in the same molecule. To this end, the reactions of **1** with $(\mathrm{MeCp})_2\mathrm{VCl}_2$ and *cis*-$\mathrm{PtCl_2(PPh_3)_2}$ were studied. These reactions are complete in 6 h at room temperature; the exclusive products are $(\mathrm{MeCp})_2\mathrm{TiCl}_2$ and the $\mathrm{S_2SiMe_2}$ chelate of the second metal[4] (eq 2). The platinum and vanadium $\mathrm{S_2SiMe_2}$ complexes were prepared independently by the direct reactions of $\mathrm{Li_2S_2SiMe_2}$ and the respective dichlorides. The salient finding here is that *the Ti–S bonds in **1** are substantially more labile than the Si–S bonds.* The relative reactivity of the Ti–S and Si–S bonds in **1** may be an example of frontier orbital control. There is a large body of evidence[10] for a low-lying acceptor orbital in compounds of the type $\mathrm{Cp_2TiX_2}$. The acceptor property of **1** is indicated by the fact that it undergoes reversible 1e reduction at −957 mV vs. Ag/AgCl.[11]



$\mathrm{ML_2} = (\mathrm{MeCp})_2\mathrm{V}, \mathrm{Pt(PPh_3)_2}$

The kinetics of the reaction between **1** and *cis*-$\mathrm{PtCl_2(PPh_3)_2}$ were briefly examined spectrophotometrically. In $\mathrm{CH_2Cl_2}$ solution (25 °C), the rate of disappearance of **1** was found to be largely zero order in **1** and first order in *cis*-$\mathrm{PtCl_2(PPh_3)_2}$ ($k = 1.0 \times 10^{-4}$ $\mathrm{s^{-1}}$). Furthermore, this reaction was found to be 1.5 times faster in 1:10 $\mathrm{CH_3CN/CH_2Cl_2}$ than in pure $\mathrm{CH_2Cl_2}$.

The reactivity of **1** toward nucleophilic oxometalates provides further insight into the character of the $\mathrm{TiS_2Si}$ moiety. Intensely green acetonitrile solutions of **1** rapidly assume an orange color upon treatment with 1 equiv of $\mathrm{(PPh_4)_2WOS_3}$. Dilution of the reaction solution with toluene precipitated yellow crystals of $\mathrm{(PPh_4)_2WS_4}$ in 53% yield.[11] Similarly, solutions of **1** (2 mol) smoothly convert $\mathrm{(PPN)_2WO_4}$ into $\mathrm{(PPN)_2WS_4}$, which was isolated in 63% yield after two recrystallizations. The byproducts of these reactions, oligomeric siloxanes and oxotitanocenes, do not interefere with the isolation of the thiometalate products. The yields of these S for O exchange reactions were not optimized. The influence of the transition metal center on this S-transfer reaction is indicated by the complete *absence* of any reaction between $\mathrm{(PPN)_2WO_4}$ and $\mathrm{Pt(S_2SiMe_2)(PPh_3)_2}$ (eq 3). Clearly the *sulfur transfer ability of **1** arises from the combined effects of both the titanium and the silicon centers.*



An unusual property of **1** is its ability to effect S for O exchange without electron transfer. In contrast, $\mathrm{(Me_3Si)_2S}$ exhibits reductive tendencies.[13–15] For example, $\mathrm{(NBu_4)_2W_6O_{19}}$ is unreactive toward **1** but rapidly gives blue reduction products upon treatment with $\mathrm{(Me_3Si)_2S}$. Compound **1** (2.5 mol) quickly converts $\mathrm{(NBu_4)_3TaW_5O_{19}}$ into $\mathrm{(NBu_4)_3TaW_5O_{18}S}$ under anaerobic con-

---

(3) Gladysz, J. A.; Wong, Y. K.; Jick, B. S. *Tetrahedron* **1979**, *35*, 2329.

(4) For **1**: Anal. C, H, S, Si, Ti; ^{1}H NMR (δ; all ^{1}H and ^{13}C NMR data were recorded with a 200-MHz instrument on $\mathrm{CDCl_3}$ solutions): 6.32 (m, 4 H), 6.18 (m, 4 H), 2.16 (s, 6 H), 0.39 (s, 6 H). ^{13}C NMR: 130.9, 121.2, 117.2, 17.0, 5.45; FDMS m/z 328 ($\mathrm{M^+}$). For $\mathrm{Pt(S_2SiMe_2)(PPh_3)_2}$: Anal. C, H, P, S, Si; ^{1}H NMR 7.48–7.28 (m, 30 H), 0.52 (s, 6 H); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR 21.4 (J(Pt,P) = 3147 Hz); FDMS m/z 841 ($\mathrm{M^+}$). For $(\mathrm{MeCp})_2\mathrm{VS_2SiMe_2}$: Anal. C, H, S, Si, V. ^{1}H NMR 15.5 (v br), 6.2 (br), −1.0 (br); X-band EPR (toluene, 25 °C) $g = 2.00$, $a = 65$ G; FDMS m/z 331 ($\mathrm{M^+}$).

(5) Armitage, D. A.; Clark, M. J.; Sinden, A. W.; Wingfield, J. N.; Abel, E. W.; Louis, E. J. *Inorg. Synth.* **1969**, *6*, 207. For a recent discussion of $[(t\text{-BuO})_2\mathrm{SiS}]_2$ see; Wojnowski, W.; Peters, K.; Weber, D.; von Schnering, H. F. *Z. Anorg. Allg. Chem.* **1984**, *519*, 134.

(6) Crystal data: orthorhombic, *Pnma* (no. 62), $a = 9.898$ (1) Å, $b = 13.906$ (2) Å, $c = 11.468$ (3) Å, $Z = 4$, $D_c = 1.382$ g cm^{-3}, $V = 1578.252$ Å^3, $F(000) = 668$, Mo Kα radiation ($\lambda = 0.7107$ Å), μ(Mo Kα) = 8.69 cm^{-1}, $T = 293$ K. 1563 reflections ($I > 2.56\sigma(I)$); the structure was solved by using MULTAN and SHELX to $R = 0.040$ and $R_w = 0.044$. Inspection of the thermal parameter list reveals no abnormalities perpendicular to the mirror plane.

(7) Tikkanen, W. R.; Liu, J. Z.; Egan, J. W., Jr.; Petersen, J. L. *Organometallics* **1984**, *3*, 825.

(8) Draganjac, M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 745.

(9) Abel, E. W.; Armitage, D. A. *Adv. Organomet. Chem.* **1967**, *5*, 1. Brandes, D. *J. Organomet. Chem. Libr.* **1979**, *7*, 257.

(10) Tikkanen, W. R.; Egan, J. W., Jr.; Petersen, J. L. *Organometallics* **1984**, *3*, 1646. Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(11) An attempt to generate a $\mathrm{Me_2SiS_2}$ complex from the reaction of $\mathrm{(PPh_4)_2WS_4}$ and $\mathrm{Me_2SiCl_2}$ gave good yields of $\mathrm{(PPh_4)_2[W_3S_9]}$[12] and $\mathrm{(Me_2SiS)_3}$. In this reaction the silicon halide assumes the somewhat incongruous role as a sulfur-abstracting reagent, inducing the condensation of the thiometalates.

(12) Pan, W.-H.; Leonowicz, M. E.; Stiefel, E. I. *Inorg. Chem.* **1983**, *22*, 652 and references therein.

(13) Do, Y.; Simhon, E. D.; Holm, R. E. *Inorg. Chem.* **1985**, *24*, 2827. We and others have found that the reaction of VO(salen) with $\mathrm{(Me_3Si)_2S}$ can give significant quantities of $\mathrm{V(OSiMe_3)(salen)}$, depending on the experimental details. Reductive silylation is the major reaction pathway for VO(salen) + $\mathrm{PhP(SiMe_3)_2}$: Amarasekera, J., unpublished results.

(14) Money, J. K.; Huffmann, J. C.; Christou, G. *Inorg. Chem.* **1985**, *24*, 3297.

(15) (a) Klemperer, W. G.; Schwartz, C. *Inorg. Chem.* **1985**, *24*, 4461. (b) Schwartz, C. Ph.D. Thesis, University of Illinois at Urbana—Champaign, 1986

ditions. The same transformation can be effected with (Me$_3$Si)$_2$S[15] but the process is slow (hours) and the procedure requires controlled, intermittent introduction of air.[15b]

To summarize, (MeCp)$_2$TiS$_2$SiMe$_2$ represents a rare example of a metal complex of a silicon sulfide ligand. Our Li$_2$SSiMe$_2$ reagent should permit the synthesis of a variety of Me$_2$SiS$_2^{2-}$ 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$_4$)$_3$TaW$_5$O$_{19}$.

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.

---

(16) We previously showed that Cp$_2$TiE$_2$C$_2$R$_2$ (E = S, Se) are good chelate-transfer agents: Bolinger, C. M.; Rauchfuss, T. B. *Inorg. Chem.* **1982**, *21*, 3947.

School of Chemical Sciences
University of Illinois
Urbana, Illinois 61801

Dean M. Giolando
Thomas B. Rauchfuss*

Department of Chemistry
University of Auckland
Auckland, New Zealand

George M. Clark

Received May 27, 1987

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

Sir:

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$^{\rm I}$(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$^{\rm II}$(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$^{\rm I}$(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$^{\rm I}$(OEC)$^-$. In contrast, Ni(OEP)$^-$ exhibited broadened, red-shifted bands of reduced extinction, typical of ring reduction. Stable, significant concentrations of Ni$^{\rm I}$(OEC)$^-$ and of Ni$^{\rm II}$(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 ^{1}H 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$^{\rm I}$(OEiBC)$^-$. The *i–E* curve in this solvent

---

(1) Gunsalus, R. P.; Wolfe, R. S. *FEMS Microbiol. Lett.* **1978**, *3*, 191.

(2) (a) Pfalz, A.; Jaun, B.; Fassler, A.; Eschenmoser, A.; Jaenchen, R.; Gilles, H. H.; Diekert, G.; Thauer, R. K. *Helv. Chim. Acta* **1982**, *65*, 828. (b) Livingston, D. A.; Pfaltz, A.; Schreiber, J.; Eschenmoser, A.; Ankel-Fuchs, D.; Moll, J.; Jaenchen, R.; Thauer, R. K. *Helv. Chim. Acta* **1984**, *67*, 334. (c) Pfaltz, A.; Livingston, D. A.; Jaun, B.; Diekert, G.; Thauer, R. K.; Eschenmoser, A. *Helv. Chim. Acta* **1985**, *68*, 1338.

(3) Ellefson, W. L.; Whitman, W. B.; Wolfe, R. S. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 3707.

(4) Albract, S. P. J.; Ankel-Fuchs, D.; Van der Zwaan, J. W.; Fontijn, R. D.; Thauer, R. K. *Biochim. Biophys. Acta* **1986**, *870*, 50.

(5) Jaun, B.; Pfaltz, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1327.

(6) Abbreviations: OEP, 2,3,7,8,12,13,17,18-octaethylporphyrin dianion; OEC, *trans*-2,3-dihydro-2,3,7,8,12,13,17,18-octaethylporphyrin dianion (chlorin); OEiBC, mixture of *ttt*- and *tct*-2,3,7,8-tetrahydro-2,3,7,8,12,13,17,18-octaethylporphyrin dianion (isobacteriochlorin); OEPH, 5-hydro-2,3,7,8,12,13,17,18-octaethylporphyrin trianion (phlorin); OECH, 2,3,(5 or 10)-trihydro-2,3,7,8,12,13,17,18-octaethylporphyrin trianion (chlorin phlorin—the position of meso reduction has not been established); OTTLE, optically transparent thin-layer electrode; TBAP, tetra-*n*-butylammonium perchlorate.

(7) Stolzberg, A. M.; Stershic, M. T. *Inorg. Chem.* **1987**, *26*, 1970.

(8) Johansen, J. E.; Angst, C.; Kratky, C.; Eschenmoser, A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 141.

(9) Acetonitrile solution. Butyronitrile or benzonitrile was used for Ni(OEP) owing to its minimal solubility in acetonitrile.[10]

(10) Fuhrhop, J.-H.; Kadish, K. M.; Davis, D. G. *J. Am. Chem. Soc.* **1973**, *95*, 5140.

(11) Conditions: 25 °C, 100 mV/s sweep rate, 0.1 M in TBAP, Pt (cyclic voltammetry, bulk electrolysis) or Au-minigrid (OTTLE) working electrode, SCE reference electrode.

(12) $E_{1/2}$ vs. SCE: Ni(OEP), −1.5 V;[10] Ni(OEC), −1.46 V;[7] Ni(OEiBC), −1.52 V; and ferrocenium/ferrocene (Fc$^+$/Fc), +0.40 V.

(13) Lovecchio, F. V.; Gore, E. S.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 3109.

(14) (a) Gagne, R. R.; Ingle, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 1444. (b) Gagne, R. R.; Ingle, D. M. *Inorg. Chem.* **1981**, *20*, 420.

(15) Becker, J. Y.; Kerr, J. B.; Pletcher, D.; Rosas, R. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *117*, 87.

(16) (a) Woodward, R. B. *Ind. Chim. Belg.* **1962**, *27*, 1293. (b) Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1963**, *85*, 818. (c) Sugimoto, H. *J. Chem. Soc., Dalton Trans.* **1982**, 1169.

(17) (a) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 713. (b) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 719. (c) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 5353. (d) Ram, M. S.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1986**, *25*, 3267.

(18) (a) Gosden, C.; Healy, K. P.; Pletcher, D. *J. Chem. Soc., Dalton Trans.* **1978**, *972*. (b) Healy, K. P.; Pletcher, D. *J. Organomet. Chem.* **1978**, *161*, 109. (c) Gosden, C.; Pletcher, D. *J. Organomet. Chem.* **1980**, *186*, 401. (d) Gosden, C.; Kerr, J. B. Pletcher, D.; Rosas, R. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *117*, 101.

(19) (a) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; pp 455–461. (b) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706. (c) Saveant, J. M.; Vianello, E. *Electrochim. Acta* **1965**, *10*, 905.