J. Am. Chem. Soc. 1988, 110, 5397-5403

Reactions of the Nickel(I) Octaethylisobacteriochlorin Anion with Alkyl Halides

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Abstract: Reactions of Ni^{I}(OEiBC)$^-$ with alkyl halides were investigated in bulk solution and by electrochemical means. With the exception of factor F_{430}, the Ni hydrocorphinoid prosthetic group of methyl coenzyme M reductase, Ni(OEiBC) is the only tetrapyrrole to date that has been reduced to an isolable nickel(I) complex. Ni^{I}(OEiBC)$^-$ reacts with CH_3I in a 2:1 stoichiometry to afford neutral Ni^{II}(OEiBC) in quantitative yield and CH_4 and I^- in lesser yields. The nickel(I) complex also reacts with methyl *p*-toluenesulfonate to afford CH_4. Ni(OEiBC) mediates electrocatalytic reductions of alkyl halides and of methyl *p*-toluenesulfonate. Evidence is presented for a transient alkyl-Ni^{III}(OEiBC) intermediate, which is reducible at potentials positive of the Ni^{II}/Ni^{I} couple. The current/potential curves of the electrocatalytic reductions were analyzed to obtain relative rate constants for a series of alkyl halides. The reactivity trends I > Br > tosyl ≥ Cl and $CH_3 > n\text{-}C_4H_9 >$ *sec*-$C_4H_9 > t\text{-}C_4H_9$ are consistent with a nucleophilic, S_N2-like mechanism. Estimates of the second-order rate constant for reaction of Ni^{I}(OEiBC)$^-$ and CH_3I suggest that the nucleophilicity of the nickel(I) complex is comparable to that of the "supernucleophile" vitamin B_{12s}.

Nickel is an essential component of several key metabolic enzymes of acetogenic and methanogenic organisms.(1) Two of these enzymes, CO dehydrogenase and methyl coenzyme M reductase, catalyze reactions that may involve organonickel intermediates. These would represent the first organometallic species of biological importance since vitamin B_{12}.

The nickel site of CO dehydrogenase, which is more aptly named acetyl coenzyme A synthase,(2) binds CO as demonstrated by the ^{13}CO hyperfine broadening of the nickel EPR signal.(3,4) The enzyme catalyzes exchanges of label between free CO and the carboxyl carbon of acetyl CoA and between SCoA and acetyl CoA.(2) These observations suggest that CH_3, CO, and SCoA fragments are stored and assembled on the enzyme. Recent stereochemical evidence has led to a mechanistic hypothesis that the exchange and synthesis reactions proceed by reversible insertion of CO into the nickel–carbon bond of a methylnickel intermediate.(5)

Methyl coenzyme M reductase catalyzes the reductive cleavage of *S*-methyl coenzyme M, 2-(methylthio)ethanesulfonate, to methane.(6) The nickel(II) hydrocorphinoid complex factor F_{430}(7) is a prosthetic group of the enzyme.(8) F_{430}, the only known nickel-containing tetrapyrrole of biological significance, has been found in all methanogens.(1) An EPR signal detected in whole cells of *Methanobacterium thermoautotrophicum* was attributed to F_{430} in intact, active enzyme.(9) The *g* values and hyperfine coupling associated with this signal were consistent with a d^9 Ni(I) ion coordinated by four nitrogen atoms.(10) A similar EPR spectrum was obtained upon reduction of free F_{430} pentamethyl ester to its Ni(I) form.(11) Thus, the nickel in the enzyme would appear to be redox active. While little else is known about the role of nickel during catalysis, one suggestion was that activated (reduced?) F_{430} may react with methyl coenzyme M to afford a methylnickel form of F_{430}.(1)

We recently reported the characterization of Ni^{I}(OEiBC)$^-$,(12) the first nickel(I) complex of a porphyrin or hydroporphyrin ligand.(13,14) Aside from F_{430} itself, Ni(OEiBC) is the only tetrapyrrole to date that has been reduced quantitatively to an isolable nickel(I) complex. Solutions of Ni^{I}(OEiBC)$^-$ are stable for extended periods of time in the absence of oxidants but react immediately upon mixing with alkyl halides. Methane is a major product of the reaction with methyl iodide. Reactions with alkyl halides are sufficiently fast that Ni(OEiBC) can serve as an electrocatalyst. The spectroscopic and structural features and the reduction potentials of Ni(OEiBC) are different from those of F_{430}. Nonetheless, the observed reactivity and the accessibility and stability of the nickel(I) oxidation state suggested to us that Ni(OEiBC) might serve as a good *reactivity* model for F_{430}. Our interest in the chemistry of nickel hydroporphyrins(15) and the potential biological roles of organonickel species led us to investigate the reactivity of Ni^{I}(OEiBC)$^-$.

Reactions of low-valent metallotetrapyrroles with alkyl halides have been examined by several investigators. The metals and oxidation states represented in these studies include Co(II),(16) Co(I),(17,18) Fe(II),(19) Fe(I),(20) Fe("O"),(21) Rh(II),(22) and Rh(I).(23)

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(12) 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, 2,3,10-trihydro-2,3,7,8,12,13,17,18-octaethylporphyrin trianion (chlorin phlorin); OEPMe$_2$, 5,15-dimethyl-5,15-dihydro-2,3,7,8,12,13,17,18-octaethylporphyrin dianion (porphodimethene); PPDOBF$_2$, difluoro[2,2'-(1,3-propanediyldinitrilo)]bis[3-pentanone oximato]]borate anion; (dmgH)$_2$, bis[dimethylglyoximato]; tmc, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; TBAP, tetra-*n*-butylammonium perchlorate.

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0002-7863/88/1510-5397$01.50/0

Similarly, the reduction of alkyl halides by Ni(I) tetraaza macrocyclic complex has received considerable attention.[24,25] Intermediates with a metal–carbon bond were formed in many of these reactions. Mechanisms for the formation of this bond ran the gamut from halogen atom transfer or electron transfer to nucleophilic attack. Reactions of Ni(I) with alkyl halides generally appear to have radical mechanisms.[25,26]

In this paper we examine the reactivity of $Ni^I(OEiBC)^-$ with alkyl halides and other alkylating agents. Our results establish that Ni(I) in the OEiBC environment reacts by a two-electron, nucleophilic mechanism. The nucleophilicity of $Ni^I(OEiBC)^-$ appears to be comparable to that of vitamin B_{12s}.

Experimental Section

Materials. Ni(OEiBC),[14] *trans*-Ni(OEC),[15] and Ni(OEP)[28] were prepared by literature methods. Acetonitrile (HPLC grade) and thioanisole were distilled from CaH_2. THF was distilled from sodium benzophenone ketyl. Bromomethane was obtained from Aldrich in the form of an anhydrous, 2.0 M solution in diethyl ether. Alkyl halides of the highest grade commercially available were used from freshly received bottles. (Further purification of alkyl halides did not alter the reactivity.) Tetrabutylammonium perchlorate, TBAP, was recrystallized three times from ethyl acetate and thoroughly dried in vacuo at 100 °C. All other reagents and solvents were reagent or HPLC grade and were used without further purification.

Physical Measurements. Owing to the extreme air sensitivity of the reduced nickel complexes, all experiments and manipulations were carried out under a nitrogen or argon atmosphere. Schlenk techniques or a Vacuum Atmospheres Co. drybox were employed. Absorption spectra were recorded on a Perkin-Elmer Lamda 4C spectrophotometer. NMR spectra were determined on a Varian XL-300 spectrometer.

Cyclic voltammetric measurements were made under an argon atmosphere using a conventional three-electrode cell. Solutions were 0.1 M in TBAP. The working electrode was a platinum disk. A platinum wire served as the counterelectrode. Electrodes were cleaned with concentrated nitric acid prior to use. The saturated calomel reference electrode (SCE) was separated from the bulk solution by a porous vycor disk. The instrumentation used included a Princeton Applied Research Model 173 potentiostat–galvanostat, a Model 176 current to voltage converter, and a Model 175 universal programmer. Data were recorded on a Bascom-Turner Model 3120T digital recorder. The digitization rate was sufficient to record data points at intervals of 2 mV or less.

Head-space gases and organic products were analyzed by gas chromatography and in some cases by GC/MS on Hewlett-Packard Model 5990A. The gas chromatographic analyses of organic products were conducted on a GOW-MAC Series 350 with a DC710 column. Head-space gases were analyzed on a Shimadzu GC-9A (thermal conductivity detector) with a 2.4-m Poropak Q column. Peak integrations were performed with a Shimadzu CR-1B integrator.

Bulk Reactions. Solutions of $Ni^I(OEiBC)^-$ were prepared by reduction with 1% sodium/mercury amalgam. The reduction and subsequent reaction were carried out in the drybox. In a typical experiment, 10 mg of Ni(OEiBC) was dissolved in 50 mL of THF and was reduced over an excess of the amalgam. Aliquots were removed periodically to permit the progress of the reduction to be monitored by UV–vis spectroscopy. When complete, the solution was decanted off of the amalgam and, in most cases, was reacted with an excess of the desired reagent. The nickel complex was recovered by a standard workup after removal of the solvent.

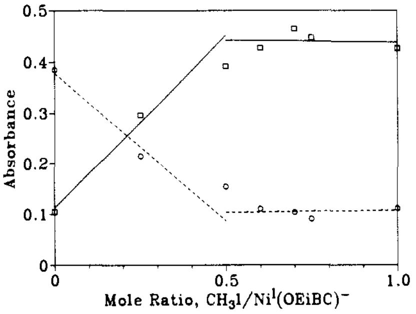

Figure 1. Spectrophotometric titration of $Ni^I(OEiBC)^-$ with CH_3I in THF: 592 nm, visible band of $Ni^{II}(OEiBC)$ (—); 570 nm, visible band of $Ni^I(OEiBC)^-$ (---).

In other experiments, the decanted nickel(I) solution was first concentrated to a volume of 1–2 mL and then reacted with the desired reagent. Aliquots of the resulting solution were analyzed for organic products by GC. Analogous procedures were used for experiments with Ni(OEP) and Ni(OEC).

Methane Quantification. A solution of 10 mg of reduced nickel complex in 50 mL of THF was prepared as above. Aliquots of 5 mL of this solution were placed in 15-mL serum bottles that had been thoroughly cleaned and dried. Each bottle was capped with a septum, and an excess (>100 equiv) of the methylating agent was added by syringe. The bottles were removed from the drybox. A 200-μL sample of the head-space gases was taken and analyzed by GC. The contents of each bottle were analyzed three times. A minimum of three reactions were run for each combination of reduced complex and alkylating agent. Standards were prepared by addition of a known quantity of pure methane to a 15-mL bottle that contained 5 mL of THF, which had been pretreated with amalgam.

Electrochemical Titrations. Solutions were prepared under an argon atmosphere from freshly distilled, degassed acetonitrile. A total of 15 mL of a solution 1.7 mM in Ni(OEiBC) and 0.1 M in TBAP was placed in the electrochemical cell. Titrations were conducted with 1.275 M solutions of alkyl halide or alkylating agent (1 equiv = 20 μL), which contained no electrolyte. The required volume of solution was added by microliter syringe. The flow of the argon gas blanket over the cell was adjusted to minimize evaporation of the solvent. The total volume of the solution in the cell was kept constant within 5%, the maximum dilution by added alkyl halide solution.

Results

A. Bulk Reactions. Ni(OEiBC). Addition of excess CH_3I to a solution of $Ni^I(OEiBC)^-$ resulted in an immediate color change. UV–vis spectra established that $Ni^I(OEiBC)^-$ had been quantitatively oxidized to Ni(OEiBC). The shapes and intensities of the bands in the spectrum of the Ni(OEiBC) formed by this reaction were inconsistent with the presence of any other chromophore. NMR spectra provided further confirmation that the oxidation was quantitative. The ^1H and ^{13}C NMR spectra of recovered Ni(OEiBC) were identical with those of authentic Ni(OEiBC). No additional peaks were observed.

The stoichiometry of the reaction with respect to the reactants was investigated by means of a spectrophotometric titration. Figure 1 illustrates the changes in absorbance at 570 nm, the wavelength maximum of the major visible band of $Ni^I(OEiBC)^-$, and at 592 nm, the wavelength maximum of the major visible band of Ni(OEiBC). As is apparent, the error of the titration was relatively large. It was not possible to titrate a single solution by successive additions of CH_3I. Once the septum cap of a cell containing $Ni^I(OEiBC)^-$ is punctured, oxidation of unreacted $Ni^I(OEiBC)^-$ by air diffusing through the septum is relatively rapid. Each data point in Figure 1 was obtained with an independent solution prepared by reacting under anaerobic conditions (i.e. in a drybox) a fixed volume of a stock solution of $Ni^I(OEiBC)^-$ with an appropriate quantity of CH_3I. The UV–vis cell containing the resulting solution was capped with a stopper or an intact septum. Another source of error was the turbidity that was at times introduced by the sodium amalgam reduction. The extent of the turbidity and its attendant light scattering varied from aliquot to aliquot of the same solution. Given these difficulties, the variation in absorbance after a mole ratio of 0.6 is indistinguishable from experimental scatter. In agreement with this

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(26) The authors of ref 24 suggested that the mechanism was an oxidative addition (nucleophilic) of Ni(I) into the alkyl–halogen bond to afford an alkylnickel(III) halide complex. They ruled out simple electron transfer on the basis that Ni(I) complexes were not sufficiently strong reductants to affect the reduction of the alkyl halide. Unfortunately, the authors did not recognize that the contribution of overpotential to the reduction potentials of alkyl halides is on the order of 1.5 V.[27]

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conclusion, $Ni^I(OEiBC)^-$ bands were not observed in full wavelength range UV–vis spectra obtained for solutions with a mole ratio of 0.6 or greater. Thus, our data suggest a stoichiometry of roughly 2 nickel(I)/methyl iodide.

Other products of the reaction that were detected included I^- and CH_4. I^- was detected electrochemically (see below) but was not quantified. CH_4 was detected in the head-space gases by GC–MS. the yield of CH_4 (quantified by GC) was 50% of that expected for a 2:1 reaction stoichiometry, 0.25 mol of CH_4/mol of Ni^I. Ethane and other higher hydrocarbons were not detected. We did not find other products derived from the methyl group of methyl iodide in solution. However, this may reflect the small quantities of material used in these experiments rather than the absence of other products. (Alternatively, the recovery of methane is incomplete.) On the basis of the data presented above, the stoichiometry of the overall reaction is represented by unbalanced eq 1, where CHX represents an unknown product(s) containing methyl iodide derived carbon and $0 \leq x \leq 0.5$.

$$2Ni^I(OEiBC)^- + CH_3I \rightarrow 2Ni(OEiBC) + I^- + (1.0 - x)CH_4 + xCHX \quad (1)$$

$Ni^I(OEiBC)^-$ was also quantitatively reoxidized to Ni(OEiBC) by reaction with excess methyl *p*-toluenesulfonate or thioanisole. The former is a notoriously poor substrate in radical-based reactions. The latter has a methyl thioether group like *S*-methyl coenzyme M, the substrate of the methane-producing enzyme methyl coenzyme M reductase. Reaction with methyl *p*-toluenesulfonate was fast, but not as rapid as with CH_3I. The yield of methane was only about 12% of that expected for a 2:1 stoichiometry. The reaction with thioanisole was quite slow (minutes). Methane was not detected.

Ni(OEP) and Ni(OEC). In parallel sets of experiments, the products of the sodium amalgam reductions of Ni(OEP) and Ni(OEC) were reacted with CH_3I, methyl *p*-toluenesulfonate, and thioanisole. The experiments were performed before we determined that the products of the reductions were the phlorin complexes $Ni(OEPH)^-$ and $Ni(OECH)^-$, respectively.[14] Phlorins are reduced by two electrons relative to the neutral parent complex. However, the protonation of one of the meso carbons in these complexes stabilizes the phlorin anions sufficiently that they are weaker reductants than one-electron-reduced complexes (Ni(I) or Ni(II) anion-radical complexes).[14] Although the ground states of the phlorins and $Ni^I(OEiBC)^-$ are different, it is still informative to compare the reactivity.

$Ni(OEPH)^-$ and $Ni(OECH)^-$ both reacted rapidly with excess CH_3I. Roughly 0.05 mol of CH_4 was produced per 1 mol of complex. The UV–vis spectra of the complexes recovered from the reaction established that the phlorins had been oxidized to the neutral parent complexes Ni(OEP) and Ni(OEC), respectively. The oxidations were not quantitative, however. Excess absorbance near 435 nm (both) and 660 nm (OEC) suggested that other complexes were also present. Complexes methylated on the macrocycle are likely condidates. Precedent for this possibility is found in the reaction of sodium anthracenide-reduced Ni(OEP) with CH_3I, which was reported to afford $Ni(OEPMe_2)$, the nickel complex of the porphodimethene 5,15-dimethyl-5,15-dihydro-2,3,7,8,12,13,17,18-octaethylporphyrin, in 14% yield.[29]

$Ni(OEPH)^-$ and $Ni(OECH)^-$ reacted slowly with methyl *p*-toluenesulfonate. No CH_4 was detected. Unlike the case with $Ni^I(OEiBC)^-$, the reaction was not a simple oxidation that afforded the neutral parent complexes. The crude product of the $Ni(OEPH)^-$ reaction was a mixture of Ni(OEP) and $Ni(OEPMe_2)$. The latter, obtained in yields of approximately 50%, was identified on the basis of spectroscopic data.[29] Interestingly, our reaction sequence provides the shortest and highest yield route to this porphodimethene complex.[29,30] The UV–vis spectrum of the crude product of the $Ni(OECH)^-$ reaction exhibited bands characteristic of Ni(OEC). In addition, bands were observed at 312, 432, 460, and 663 nm. The optical density of these bands, which are presumably due to a porphodimethene-like complex, were comparable to the Ni(OEC) bands. The complex was not characterized further. Both $Ni(OEPH)^-$ and $Ni(OECH)^-$ were stable indefinitely in the presence of excess thioanisole.

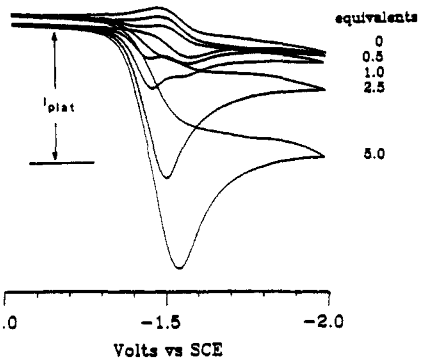

Figure 2. Cyclic voltammograms of the titration of Ni(OEiBC) with CH_3I, 0.0–5.0 equiv. Conditions: acetonitrile solution containing 0.1 M TBAP, recorded at 100 mV/s at a platinum electrode. Cathodic currents are plotted in a downward direction. i_{plat} is defined on the figure for the voltammogram with 5.0 equiv of CH_3I.

The marked difference in product distributions for the reactions of $Ni(OEPH)^-$ and $Ni(OECH)^-$ with CH_3I and methyl *p*-toluenesulfonate suggests that the reaction mechanism depends upon the identity of the electrophilic reactant. Low-lying excited states of the reduced nickel complexes may be accessible. Different electrophiles may react with different electronic states. At any rate, our results make it clear that attempts to use reactivity as a probe of the dominant resonance form of a reduced metallotetrapyrrole complex[21] could be misleading.

B. Electrochemical Reactions. The reactions of the reduced complexes of Ni(OEP), Ni(OEC), and Ni(OEiBC) with alkyl halides are too rapid to investigate by conventional means. Although for sufficiently dilute solutions the reaction rates may be appropriate for stopped-flow methods, the extreme sensitivity of dilute solutions of the reduced complexes suggested that these experiments would be exceedingly difficult. We therefore turned to electrochemical methods to investigate kinetic aspects of these reaction systems.

Ni(OEP), Ni(OEC), and Ni(OEiBC) catalyze the electrochemical reduction of alkyl halides.[13,14] Although the reduction potentials of the three complexes are similar, the rates at which a particular substrate is reduced are quite different. Thus, factors other than those associated with simple outer-sphere electron transfer must be important in these reactions. Of the three, the Ni(OEiBC) complex is by far the most effective catalyst.[14]

We restrict our attention to the electrocatalytic reactivity of Ni(OEiBC) in the sections that follow. Ni(OEiBC) is the only complex of the three that affords a stable Ni(I) complex. It is also the only complex for which the product complex obtained by electrochemical reduction is the same as the product obtained by chemical reduction in bulk.

Titration of Ni(OEiBC) with Alkyl Halide. The initial portion of a cyclic voltammetric titration of Ni(OEiBC) with CH_3I in acetonitrile is illustrated in Figure 2. In the absence of the alkyl halide, the cyclic voltammogram of Ni(OEiBC) consisted of a single, reversible one-electron reduction at $E_{1/2} = -1.54$ V.[14] This process corresponds to the Ni^{II}/Ni^I couple. Upon addition of 0.5 equiv of CH_3I, a new cathodic wave appeared at a potential slightly positive of the Ni^{II}/Ni^I couple. The current at the peak of the Ni^{II}/Ni^I wave increased, and the wave became irreversible ($i_{p,a} < i_{p,c}$). No oxidation associated with the new cathodic wave was found upon scan reversal at a switching potential just beyond its peak, even at scan speeds as high as 2000 mV/s. Further addition of CH_3I led to a substantial increase in the cathodic current. The two distinct peaks merged to a single cathodic peak. At concentrations of CH_3I higher than those included in the figure, the cathodic peak became less pronounced, and the wave assumed

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the plateau shape characteristic of a diffusion-controlled electrocatalytic process.[31]

Evidence for the formation of I^- in this reaction was provided by the observation of an electrocatalytic oxidation at a potential corresponding to the first oxidation of Ni(OEiBC). The oxidations of Ni(OEiBC) appeared as the normal one-electron processes in the presence of CH_3I, provided that the potential was initially scanned to positive values. If, on the other hand, the potential initially was scanned past −1.5 V and then scanned to positive potentials, the first oxidation became electrocatalytic (for a brief period of time). Apparently, $Ni(OEiBC)^{\bullet +}$ catalyzes the oxidation of I^-, which was formed during the reduction of CH_3I.

The changes observed in the cyclic voltammogram of Ni(OEiBC) during titrations with other alkyl halides were similar to those observed with CH_3I. Generally, higher concentrations of the alkyl halide were necessary to achieve a comparable increase in current. One notable difference, for alkyl groups other than methyl, was the absence of a distinct, new cathodic wave at low concentrations of alkyl halide.

The interpretation of the new cathodic wave observed upon addition of 0.5 equiv of CH_3I is not clear. The wave does not appear to result from absorption phenomena. It was not observed unless both Ni(OEiBC) and CH_3I were present. In addition, it was unaffected by the identity of the working electrode (glassy carbon vs Pt). Neither ligand-binding equilibria nor an ECE process would be expected to result in a discrete new peak at the foot of the peak of the Ni(II)/Ni(I) process. The most probable explanation is that the new wave results from mass transport phenomena. Apparently, $Ni^I(OEiBC)^-$ is such as efficient catalyst that at low concentrations (i.e. at the foot of the Ni(II)/Ni(I) reduction peak) it quickly depletes CH_3I in the region near the electrode (diffusion layer). Other, larger alkyl halides reacts more slowly (see below) and are not depleted. Initially, the current increases rapidly as the potential becomes increasingly negative because the catalytic current is limited by the availability of $Ni^I(OEiBC)^-$. (This increases at more negative potentials.) Later, as CH_3I in the diffusion layer is depleted, the current reaches a maximum because it becomes limited by the rate at which CH_3I enters the diffusion layer from bulk solution. The normal peak for the Ni(II)/Ni(I) couple is still observed since most of the Ni(OEiBC) remains in the Ni(II) form. However, the total current at the Ni(II)/Ni(I) peak is larger than in the absence of CH_3I because of the continuing electrocatalytic reduction of the CH_3I that diffuses to the electrode continues.

Kinetic Analysis of Electrocatalysis. The minimal mechanism that will result in an electrocatalytic process, denoted EC_i', is given in eq 2 and 3. The reduction of OXID, the oxidized form of the catalyst, occurs at the electrode surface. Z is a strong oxidant, which is not itself reducible at the electrode in the potential range of interest. The substantial overpotential associated with the reduction of alkyl halides[27] makes them excellent substrates for electrocatalysis. Z oxidizes RED^{n-} to the oxidized member of the couple, OXID, which can be immediately rereduced at the electrode.

$$\text{OXID} + ne^- \rightarrow \text{RED}^{n-} \tag{2}$$

$$\text{RED}^{n-} + \text{Z} \xrightarrow{k} \text{OXID} + \text{products} \tag{3}$$

The shape of the current/potential curve depends upon the concentration of the substrate Z, the sweep rate, and the rate constant for eq 3. Rate constants can be obtained by analysis of the current/potential curve. Thus, a comparison of the electrocatalytic response of Ni(OEiBC) in the presence of a series of substrates can provide valuable information about the reaction mechanism.

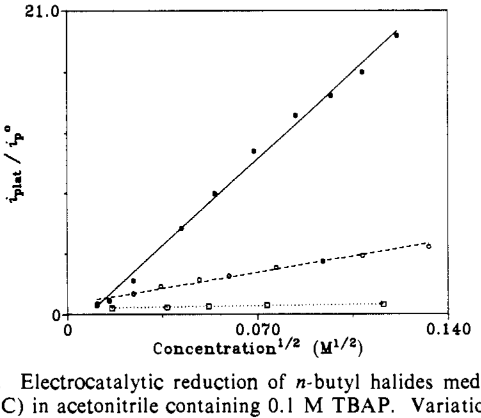

Figure 3. Electrocatalytic reduction of *n*-butyl halides mediated by Ni(OEiBC) in acetonitrile containing 0.1 M TBAP. Variation of the normalized plateau current $i_{plat}/i_p°$ with $(C_Z°)^{1/2}$ for butyl iodide (—), butyl bromide (- - -), and butyl chloride (···).

Table I. Relative Reaction Rates of $Ni^I(OEiBC)^-$ with RX

RX	rate
n-butyl chloride	1
methyl bromide	4500
n-butyl bromide	160
sec-butyl bromide	55
tert-butyl bromide	10
methyl iodide	4300
n-butyl iodide	4400
methyl *p*-toluenesulfonate	16

When reaction 3 is quantitative and occurs without intermediates and when the concentration of Z in bulk solution, $C_Z°$, is sufficiently large that reaction 3 is pseudo-first-order, it has been shown that the relationship in eq 4 holds.[31c] The definition of the

$$i_{plat}/i_p° = (1/0.447)[\sigma RTkC_z°/nFv]^{1/2} \tag{4}$$

symbols is as follows: i_{plat} is the plateau current of the catalytic reaction, the current at potentials well negative of the $E_{1/2}$ of the catalyst (see Figure 2), $i_p°$ is the peak current for the reversible reduction of the catalyst in the absence of Z, σ is a stoichiometric factor, k is the second-order rate constant for eq 3, and v is the rate at which the electrode potential is swept. The derivation of eq 4 implicitly assumed that the diffusion coefficients of OXID and RED^{n-} were identical. Analysis of the plateau current allows one to work in the regime where the current is affected by the kinetics of reaction 3 but is not affected by the kinetics of electron transfer to the catalyst. Inspection of eq 4 shows that a plot of $i_{plat}/i_p°$ vs $[C_Z°]^{1/2}$ will be linear at constant v and T. The slope of this plot is directly proportional to $k^{1/2}$.

The reaction scheme and analysis in eq 2–4 are too simple to be correct for electrochemical reductions catalyzed by Ni(OEiBC). We established above that the stoichiometry of the reaction of $Ni^I(OEiBC)^-$ with CH_3I is 2:1. Thus, the step corresponding to eq 3 is either a termolecular elementary process or else intermediates exist. A rigorous treatment of electrocatalysis by Ni(OEiBC) would require a detailed knowledge of the elementary processes that make up the reaction mechanism. This information is not available. Furthermore, a rigorous treatment is beyond our expertise and the scope of the investigation.

We recognized that eq 4 will be approximately correct if the initial reaction of $Ni^I(OEiBC)^-$ with substrate is second order and is rate limiting. Several observations suggested that the latter condition might be satisfied. Thus, we decided to apply the treatment derived for the simple case. Plots of $i_{plat}/i_p°$ vs $[C_Z]^{1/2}$ presented in the next section are nearly linear, as would be expected if eq 4 were applicable. This shows that our simplistic approach is reasonable. It also shows that the reaction of $Ni^I(OEiBC)^-$ with alkyl halides is second order overall. Given the degree of oversimplification, we do not expect to obtain accurate rate constants. The deficiencies of the model should not alter the relative magnitude of the rate constants for various substates, however.

Relative Reaction Rates. The variation of reaction rate with leaving group and alkyl group structure provides a means to distinguish between possible mechanisms for the reaction of

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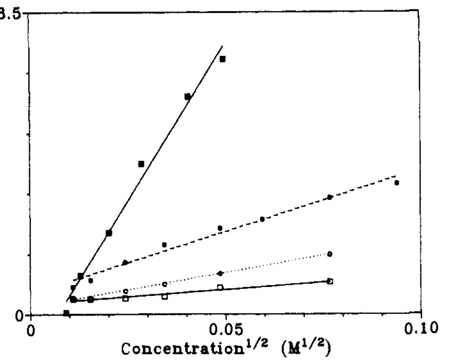

Figure 4. Electrocatalytic reduction of alkyl bromides mediated by Ni(OEiBC) in acetonitrile containing 0.1 M TBAP. Variation of the normalized plateau current $i_{plat}/i_p°$ with $(C_Z°)^{1/2}$ for methyl bromide (—, filled squares), *n*-butyl bromide (- - -), *sec*-butyl bromide (···), and *tert*-butyl bromide (—, open squares).

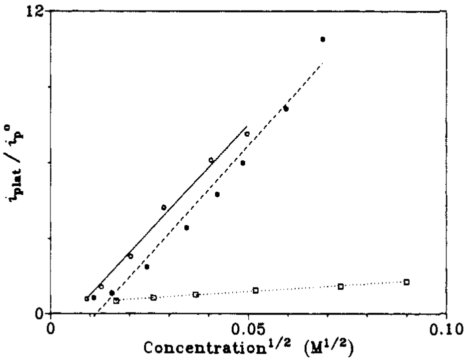

Figure 5. Electrocatalytic reduction of methyl halides and tosylate mediated by Ni(OEiBC) in acetonitrile containing 0.1 M TBAP. Variation of the normalized plateau current $i_{plat}/i_p°$ with $(C_Z°)^{1/2}$ for methyl bromide (—), methyl iodide (- - -), and methyl tosylate (···).

$\mathrm{Ni^{I}(OEiBC)^-}$ with alkyl halides. Accordingly, the cyclic voltammogram of Ni(OEiBC) in acetonitrile was monitored as the solution was titrated with a series of alkyl halides. The plots of $i_{plat}/i_p°$ vs $[C_Z°]^{1/2}$ that we obtained are presented in Figures 3–5. The relative rates for the various substrates are collected in Table I.[32]

Figure 3 shows the effect of the leaving group on the rate of reduction of *n*-butyl halides. As expected, the order is I > Br > Cl. This is consistent either with radical-based processes or with a nucleophilic attack of the d^9 nickel(I) on the carbon of the substrate.

The effect of the R group structure on the rate of reduction of a series of alkyl bromides is presented in Figure 4. The order is methyl ≫ primary > secondary > tertiary. These results clearly establish that $\mathrm{Ni^{I}(OEiBC)^-}$ reacts by a nucleophilic mechanism. The order is consistent with that expected on the basis of steric effects on the entering nucleophile. It is precisely the reverse of the order of rates expected for a radical-based process, which is dominated by the stability of the alkyl radical. For iodides, there is little difference between the rates of methyl and *n*-butyl.

Figure 5 shows the relative rates of reaction for three methylating agents. Methyl iodide and methyl bromide react at comparable rates. Methyl-*p*-toluenesulfonate reacts quite a bit more slowly. That the tosylate reacts rapidly enough to be electrocatalytic is strong evidence against a radical-based mechanism. The sluggishness of the tosylate reaction relative to the bromide is unusual for carbon-based nucleophiles but is typical of transition-metal-centered nucleophiles.[33,34] Transition-metal-centered nucleophiles are relatively soft and react more rapidly with the soft, polarizable bromides and iodides than the harder tosylates.

Crude calculations suggest that the second-order rate constant for the reaction of $\mathrm{Ni^{I}(OEiBC)^-}$ with $\mathrm{CH_3I}$ are on the order of 10^4–10^5 $\mathrm{M^{-1}\,s^{-1}}$. Thus, reaction rates for $\mathrm{Ni^{I}(OEiBC)^-}$ are as fast or faster than the rates for such "supernucleophiles"[35] as $\mathrm{Rh^{I}(P\text{-}PDOBF_2)}$,[33] $\mathrm{Co^{I}(dmgH)_2(PBu_3)^-}$,[35] or vitamin $\mathrm{B_{12s}}$.[35]

C. Radical Clock Probe. In addition to kinetic evidence, the existence of radical intermediates is frequently established by the use of substrates, which give rise to rearranged products when free radicals are formed.[36] 1-Bromo-5-hexene undergoes a one-electron reduction to afford the 1-hexenyl radical, which cyclizes to the cyclopentylmethyl radical[37] with a rate constant of 2.2×10^5 $\mathrm{s^{-1}}$.[38] Both 1-hexene and methylcyclopentane are produced if capture and reduction of the radicals are competitive with cyclization. Two-electron nucleophilic pathways should give 1-hexene as the sole product.

As a further probe of the reaction mechanism, a solution of $\mathrm{Ni^{I}(OEiBC)^-}$ was reached with an excess of 1-bromo-5-hexene. Analysis of the resulting hydrocarbon product established that the ratio of 1-hexene to methylcyclopentane was 6:4. Although these results appear to be consistent with fast trapping of radical intermediates, other scenarios can explain the formation of methylcyclopentane in a two-electron mechanism. These are discussed below.

Discussion

Reactivity of $\mathrm{Ni^{I}(OEiBC)^-}$. The reactivity of $\mathrm{Ni^{I}(OEiBC)^-}$ is truly remarkable. It has a standard reduction potential of −1.54 V vs SCE[14] and is a paramagnetic, 17-electron complex. Yet, our data unequivocally show that this complex reacts with alkyl halides via a two-electron nucleophilic pathway rather than by electron transfer. The reaction with methyl *p*-toluenesulfonate and the preference for smaller alkyl groups are particularly telling in this respect. Our crude estimates of the second-order rate constants suggest that $\mathrm{Ni^{I}(OEiBC)^-}$ ranks among the most reactive nucleophiles. It even reacts slowly with thioanisole.

The mechanism(s) that we propose for the reduction of alkyl halides and tosylates by $\mathrm{Ni^{I}(OEiBC)^-}$ consists of a sequence of reactions presented in eq 5–11. The equations are written for the specific case with $\mathrm{CH_3I}$ as substrate.

$$\mathrm{Ni^{II}(OEiBC)} + e^- \rightarrow \mathrm{Ni^{I}(OEiBC)^-} \tag{5}$$

$$\mathrm{Ni^{I}(OEiBC)^-} + \mathrm{CH_3I} \rightarrow \mathrm{CH_3Ni^{III}(OEiBC)} + \mathrm{I^-} \tag{6}$$

$$\mathrm{CH_3Ni^{III}(OEiBC)} + e^- \rightarrow \mathrm{CH_3Ni^{II}(OEiBC)^-} \tag{7}$$

$$\mathrm{CH_3Ni^{III}(OEiBC)} + \mathrm{Ni^{I}(OEiBC)^-} \rightarrow \mathrm{CH_3Ni^{II}(OEiBC)^-} + \mathrm{Ni^{II}(OEiBC)} \tag{8}$$

$$\mathrm{CH_3Ni^{II}(OEiBC)^-} + \text{“H”} \rightarrow \mathrm{Ni^{II}(OEiBC)} + \mathrm{CH_4} + \text{other products(?)} \tag{9}$$

$$\mathrm{CH_3Ni^{III}(OEiBC)} \rightarrow \mathrm{Ni^{II}(OEiBC)} + \mathrm{CH_3^{\bullet}} \tag{10}$$

$$\mathrm{CH_3^{\bullet}} \rightarrow \mathrm{CH_4} + \text{other products} \tag{11}$$

The reduction of Ni(OEiBC), eq. 5, occurs at the surface of an electrode poised at a potential near −1.5 V vs SCE. Our observations establish that the reaction of $\mathrm{Ni^{I}(OEiBC)^-}$ with $\mathrm{CH_3I}$, eq 6, is second order and rate limiting and proceeds by a nucleophilic mechanism. The neutral, paramagnetic methylnickel complex formed in this reaction, see below, can react via several different pathways. (By convention, we count the alkyl group as an anionic ligand and therefore formally consider this a Ni(III) complex.[39]) Electrocatalysis with Ni(OEiBC) occurs at the

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[32] Differences in the diffusion coefficients of the various substrates have been neglected in the relative rates given in Table I.

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potential of the $\mathrm{Ni^{II}(OEiBC)/Ni^{I}(OEiBC)^-}$ couple. Thus, the standard potential of the $\mathrm{CH_3Ni^{III}(OEiBC)/CH_3Ni^{II}(OEiBC)^-}$ couple (eq 7) must be equal to or positive of the $\mathrm{Ni^{II}(OEiBC)/Ni^{I}(OEiBC)^-}$ couple (eq 5). (If not, a separate reduction wave would be observed for the alkylnickel couple, and the onset of catalysis would only occur at a potential negative of this wave.[21]) Consequently, $\mathrm{CH_3Ni^{III}(OEiBC)}$ can either be reduced at the electrode poised near −1.5 V (overall, an ECE mechanism) or can be reduced by $\mathrm{Ni^{I}(OEiBC)^-}$ in bulk solution, eq 8 (a DISP[40] or disproportionation mechanism). The DISP mechanism readily explains the observed 2:1 stoichiometry for the reaction with $\mathrm{CH_3I}$ in bulk solution. In either event, $\mathrm{CH_3Ni^{\mathit{II}}(OEiBC)^-}$ reacts rapidly with an as yet unknown proton source to afford products, eq 9. The mechanism of this process may involve reaction with solvent, trace quantities of water and/or additional alkyl halide.[25b] Another possible mechanism for loss of $\mathrm{CH_3Ni^{III}(OEiBC)}$ is that the methyl–nickel bond homolyzes, eq 10, to afford a radical. To the extent that it occurs, homolysis will change the stoichiometry of the reaction. Although the observed 2:1 stoichiometry in bulk solution, eq 1, rules out eq 10 and 11 as the sole or main pathway for loss of $\mathrm{CH_3Ni^{III}(OEiBC)}$, the data is not of sufficient quality to rule it out as a minor pathway. This pathway could be more important in the case of other alkyl groups or leaving groups, whose reaction stoichiometries have not been investigated. Clearly, isotopic labeling studies and more precise studies of the reaction stoichiometry as a function of substrate will be necessary to characterize the reaction steps following eq 6.

Our evidence strongly implicates $\mathrm{CH_3Ni^{III}(OEiBC)}$ as the product of reaction 5. The two-electron nucleophilic mechanism established for this reaction requires that an intermediate complex derived from Ni(OEiBC) and $\mathrm{CH_3I}$ exist. Dealkylation of this intermediate must be an extremely facile process because the reaction of $\mathrm{Ni^{I}(OEiBC)^-}$ and $\mathrm{CH_3I}$ results in quantitative and nearly instantaneous reoxidation of the complex to Ni(OEiBC). The only reasonable site for alkylation of $\mathrm{Ni^{I}(OEiBC)^-}$ by $\mathrm{CH_3I}$ is the $\mathrm{d^9}$ Ni(I) atom. The increased electron density at the metal atom in this complex should lead to high reactivity with electrophiles at this site. Furthermore, reduction of the formally 17-electron $\mathrm{CH_3Ni^{III}(OEiBC)}$ complex would be expected to occur at nickel, which would weaken the carbon–nickel bond. The intermediacy of a C-alkylated complex, on the other hand, would require that facile cleavage of a carbon-carbon σ bond occurs and is triggered by addition of an electron to a macrocycle π or metal-based LUMO. This is not likely. Although the loss of the alkyl group from N-alkylated metalloporphyrin complexes can be facile in the presence of a nucleophile,[41] these complexes are rather less plausible intermediates than a nickel alkyl complex. We are unaware of a precedent for direct n-alkylation of a low-valent metallotetrapyrrole complex. Moreover, for Fe,[42] Co,[43,44] Rh,[23,45] and Ir[46] complexes of *N*-alkylporphyrins, migration of the *N*-alkyl group from N to the metal has been demonstrated under reducing conditions.[47]

Although no alkylnickel tetrapyrrole complex has been reported previously, ample precedent exists for formation of alkylmetallotetrapyrrole complexes.[16,20–23,43] Most of the latter have been synthesized by reaction of a low-valent metallotetrapyrrole complex with an alkyl halide. The apparent nonexistence of alkylnickel porphyrin complexes may simply reflect the inaccessibility of Ni(I) in the porphyrin environment. Alkylnickel complexes with analogous ligand donor sets are known, however. Methyl nickeltetramethylcyclam, $\mathrm{CH_3Ni^{II}(tmc)^+}$, has been prepared by several means, including the reaction of $\mathrm{Ni^{I}(tmc)^+}$ with $\mathrm{CH_3I}$.[25a,51] The complex is stable for minutes in water and for several hours in nonaqueous solvents. Presumably, the lesser stability of the $\mathrm{CH_3Ni^{\mathit{II}}(OEiBC)^-}$ complex reflects its anionic charge and the stronger ligand field provided by the OEiBC ligand. Additionally, the standard reduction potential of $\mathrm{Ni^{II}}$ in the OEiBC macrocycle is considerably negative of the $\mathrm{Ni^{II}}$ in the tmc macrocycle.[13,14,24d,52]

To date, we have not been able to prepare $\mathrm{CH_3Ni^{III}(OEiBC)}$ from $\mathrm{Ni^{I}(OEiBC)^-}$. Apparently, reaction 6 is also the rate-determining step under the conditions of reaction in bulk solution. Thus, the initially formed methylnickel complex reacts with $\mathrm{Ni^{I}(OEiBC)^-}$ before the latter can be completely consumed by $\mathrm{CH_3I}$.

The existence of an alkylnickel intermediate leads to equivocal interpretation of the results from the reaction of $\mathrm{Ni^{I}(OEiBC)^-}$ with 1-bromo-5-hexene. Three mechanisms could account for the mixture of products. The first is that reaction 6 proceeds by a one-electron mechanism (either outer-sphere electron transfer or inner-sphere halogen-atom abstraction). Capture and reduction by $\mathrm{Ni^{I}(OEiBC)^-}$ of the hexenyl radical formed in this reaction occurs competitively with cyclization. The second possibility is that reaction 6 proceeds by a two-electron nucleophilic mechanism. Homolysis of the resulting alkyl–nickel bond in a portion of the product leads to formation of free 1-hexenyl radical after the rate-determining step of the overall reaction. Finally, $\mathrm{CH_2CH(CH_2)_3CH_2Ni^{III}(OEiBC)}$ is formed by a two-electron nucleophilic mechanism and then undergoes intramolecular cyclization. The facile cyclizations of a valeronitrile group when bound to Ni(tmc)[53] and of 5-hexenyllithium[54] provide precedent for this possibility. The first scenario is inconsistent with the observed dependence of the reaction rate on the nature of the alkyl group. At present, we have no basis for distinguishing the second and third possibilties.

Comparison with the Reactivity of Other Low-Valent Macrocyclic Complexes. The reactivity of $\mathrm{Ni^{I}(OEiBC)^-}$ is unique for nickel(I) in a square-planar tetraaza complex. $\mathrm{Ni(tmc)^+}$ has a

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(47) One reviewer suggested that the product of reaction 6 could be a N,Ni-bridged methylene $\mathrm{Ni^{II}(OEiBC)}$ complex. We consider this a rather remote possibility. Synthetic routes that start with metalloporphyrin complexes and are known to afford N, metal-bridged carbene complexes include deprotonation of $\mathrm{[(\mathit{N}\text{-}CH_2CO_2C_2H_5)Ni^{II}(TPP)]ClO_4}$,[48] one-electron oxidation of vinylidenecarbeneiron(II) porphyrins,[49] and reaction of Co(OEP) complexes with ethyl diazoacetate.[50] All involve the generation of carbenoid species or a carbanion. This would not be facile with methyl iodide or methyl *p*-toluenesulfonate. Another potential problem with the suggestion is that the bridging carbene can migrate to the periphery of the porphyrin ring. Thermolysis of N,Ni-bridged $\mathrm{(CH_2CO_2C_2H_5)Ni^{II}(TPP)}$ led to rearrangement to (homoporphinato)nickel derivatives (insertion of carbene into $\mathrm{C_\alpha}$–meso bond).[48a]

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similar reaction stoichiometry but reacts via a radical-based mechanism.[25] The effect of the substrate alkyl group structure on the reaction rates for this complex is the opposite of that observed for Ni^{I}(OEiBC)$^-$. Additionally, Ni(tmc)$^+$ does not react with tosylates.[25c] One might expect that the differences in mechanism arise from the different steric demands of tmc and OEiBC. The *N*-methyl groups adjacent to the metal in tmc could create too much steric congestion for nickel(I) to function effectively as a nucleophile. The nickel in OEiBC should be relatively unhindered. Pletcher has shown, however, that the reactivity order tertiary > secondary > primary still holds for a relatively unhindered nickel(I) tetraaza macrocyclic complex.[24a] (Strangely, this paper proposes a nucleophilic mechanism.[26]) Thus, it would appear that radical-based mechanisms are characteristic of nickel(I) tetraaza macrocyclic complexes.

The reactivity of Ni^{I}(OEiBC)$^-$ more closely resembles that of several low-valent tetrapyrrole complexes. Fe(I)[20] and Rh(II)[22b] porphyrins and Co(I)[35] corrins have been reported to react by nucleophilic mechanisms. The reactivity of the nickel complex still differs in several important respects. Ni(OEiBC)$^-$ is the only one of these complexes that does not form a stable, isolable alkyl complex. Aside from Co(I), the others react at rates several orders of magnitude lower than the nickel(I) complex. With the exception of RFe^{III}(P), the alkyl complexes obtained are reduced at potentials negative of the couple for the parent, nonalkylated metal complex. Apparently, paramagnetic alkylmetal complexes are reduced at potentials positive of the parent couple while diamagnetic alkylmetal complexes are reduced at more negative potentials. Effective electrocatalysis requires a potential negative of the alkylmetal complex couple.[21] Rhodium porphyrin and cobalt porphyrin mediated electrocatalysis must therefore be run at potentials negative of that required for formation of the intermediate alkyl complex.

It is clear from the above discussion that Ni^{I}(OEiBC)$^-$ is particularly well suited to mediate electrocatalysis. It reacts rapidly, is an effective mediator at the potential of the Ni^{II}/Ni^{I} couple, and does not have long-lived (inert) alkyl intermediates that tie up the catalyst and slow the reaction.

Biological Significance of the Reactivity of Ni^{I}(OEiBC)$^-$. Investigations of the mechanism of methyl coenzyme M reductase are at a relatively early stage. Some evidence suggests that the nickel in F$_{430}$ is redox active during the catalytic cycle.[9] Given what is known about the cofactors required for the reaction and the makeup of the enzyme, it is difficult to conceive a plausible mechanism for the reductive cleavage of *S*-methyl coenzyme M to methane that does not actively involve the nickel. Information about the reactivity of low-valent nickel complexes will be quite useful in defining the range of possible mechanisms for the enzyme. Therefore, the most important result of our investigation is the discovery that Ni^{I} can react by a two-electron nucleophilic pathway. Only radical-based mechanisms were established for nickel(I) prior to our study.

Nickel is not a particularly common element in biological systems. Its presence in these systems invites one to speculate about the reasons that it has been selected for this chemistry. Assuming that methylnickel F$_{430}$ is an important intermediate in methanogenesis, our results suggest that nickel combines several desirable properties for the chemistry of interest. We have shown that Ni^{I}(OEiBC)$^-$ (and presumably by extention the nickel(I) form of F$_{430}$) is an extremely reactive nucleophile. It may in fact be sufficiently reactive that *S*-methyl coenzyme M can alkylate it. This substrate is unlikely to be reactive in radical-based mechanisms. When the system is poised at the potential required for reduction to nickel(I), the alkylnickel complex, once formed, will be readily reduced and cleaved.[55] This will not occur with the other biologically significant low-valent metal complex of sufficient nucleophilicity that reaction with *S*-methyl coenzyme M is a possibility. The alkyl complexes of vitamin B$_{12}$ are too stable. In fact, the role of B$_{12}$ has been described as being a reversible radical carrier.[56] An overly stable intermediate is not a desirable feature for rapid catalysis. Finally, a potential disadvantage of strong nucleophiles is that they are often strong bases. Protonation of this key intermediate would not be desirable. The sluggishness of the methyl tosylate reaction with Ni^{I}(OEiBC)$^-$ suggests that the latter is a rather soft base. Thus, nickel(I) may combine the properties of being a very strong nucleophile with being a weak base toward the proton.

Acknowledgment. We thank 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. We also thank James Hoglen and Professor Thomas Hollocher for their assistance with GC and GC-MS analyses.

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(55) It has not yet been established that the reduction potential of alkylnickel(III) complexes is invariably positive of the Ni^{II}/Ni^{I} couple.

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Redox-Coupled Linkage Isomerizations with η^2-Coordinated Anilines

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Contribution from the Department of Chemistry, Stanford University,
Stanford, California 94305. *Received February 1, 1988*

Abstract: In solution, the complex [Os(NH$_3$)$_5$(PhNH$_2$)]$^{2+}$ undergoes a linkage isomerization from its nitrogen-bound form to one in which the metal center engages the aromatic ring. Upon one-electron oxidation this η^2-coordinated species reverts to the nitrogen isomer. Through the utilization of this facile redox change, isomerization rates and the related thermodynamic parameters were determined for both valences of osmium, and comparisons are made with the results obtained in a similar investigation of the sterically encumbered *N,N*-dimethylaniline derivative.

Our interest in the chemistry of electron-rich metal centers containing saturated auxiliary ligands[1] has recently focused on the reactivity of pentaammineosmium(II) with unsaturated organic molecules.[2] Because of the great tendency for osmium(II) to back-bond,[1] many of these complexes feature coordination modes that differ from the corresponding osmium(III) analogues. Thus, aldehydes and ketones, which coordinate through the oxygen to

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