The Effect of the Porphyrin Macrocycle on the Spectroscopic Properties and Catalytic Activity of Electroreduced Nickel(II) Porphyrins

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The relationship between half-wave potential, the site of electron transfer, and the catalytic activity of a given [(P)Ni]⁻ complex toward CH₃I reduction was investigated for seven nickel(II) porphyrins. The investigated compounds are represented as (P)Ni^{II} where P = the dianions of *meso*-tetramethylporphyrin (TMeP), *meso*-tetraethylporphyrin (TEtP), *meso*-tetrapropylporphyrin (TPrP), *meso*-tetrakis(*p*-(diethylamino)phenyl)porphyrin (T(*p*-Et₂N)PP), *meso*-α,α,α,α-tetrakis(*o*-pivalamidophenyl)porphyrin (TpivPP), *meso*-tetrakis(*o,o,m,m*-tetrafluoro-*p*-(dimethylamino)-phenyl)porphyrin (T(*p*-Me₂N)F₄PP), or 5-(*N*-hexadec-4-ylpyridiniumyl)-10,15,20-triphenylporphyrin bromide (hTriP)⁺Br⁻. Each metalloporphyrin was reduced by controlled potential electrolysis in tetrahydrofuran containing 0.2 M TBAP, and the products were characterized by ESR and UV–visible spectroscopy. The electrogenerated room temperature ESR spectra of [(P)Ni]⁻ are characteristic of nickel(II) porphyrin π anion radicals and six of the seven reduced porphyrins also have UV–visible spectra typical of porphyrin π anion radicals. On the other hand, the reaction between electrogenerated [(P)Ni]⁻ and CH₃I is catalytic for five of the seven complexes under an applied potential, and this suggests the presence of Ni(I) in the singly reduced [(P)Ni]⁻ derivatives. [(hTriP)Ni]⁻ does not react with CH₃I while [(T(*p*-Me₂N)F₄PP)Ni]⁻ reacts to form one or more β-pyrrole methylated nickel chlorins.

Introduction

There has been considerable controversy in the literature over the site of reduction in nickel(II) porphyrins.[1–7] Nickel(I) porphyrin anions,[1,2] nickel(II) porphyrin π anion radicals,[1,3–6] and nickel(II) porphyrin π anion radicals with some Ni(I) character[1,5–7] have all been reported as electroreduction products of the neutral complex.

It was recently demonstrated that the site of electroreduction for two nickel(II) porphyrins, (T(*p*-Et₂N)PP)Ni and (T(*p*-Me₂N)F₄PP)Ni, was dependent on both experimental conditions and the coordination number of the neutral or singly reduced complex.[1] ESR spectra of nickel(II) porphyrin π anion radicals or nickel(II) porphyrin π anion radicals with some Ni(I) character were obtained in THF at room or low temperature under N₂ while ESR spectra of Ni(I) were obtained at low temperature in THF under a CO atmosphere as well as in dimethylformamide or pyridine under N₂.[1] The data suggests that Ni(I) is preferentially formed for 5-coordinate complexes while for 4- and 6-coordinate complexes, the π anion radical is favored as shown in Scheme I for [(T(*p*-Et₂N)PP)Ni]⁻ and [(T(*p*-Me₂N)F₄PP)Ni]⁻ where L and L′ = py, DMF, or CO.

The fact that Ni(I) can be generated from (T(*p*-Et₂N)PP)Ni at $E_{1/2}$ = −1.30 V and (T(*p*-Me₂N)F₄PP)Ni at $E_{1/2}$ = −0.91 V suggests that the half-wave potential for reduction of the Ni(II) complex is not a significant factor for the formation of nickel(I), and in order to confirm this, we have now electrochemically and spectrally investigated five additional (P)Ni complexes where P represents the porphyrin macrocycle. Each porphyrin was reduced by controlled potential electrolysis and the resulting product characterized by ESR and UV–visible spectroscopy in THF containing 0.2 M TBAP. The reaction between reduced [(P)Ni]⁻

Scheme I
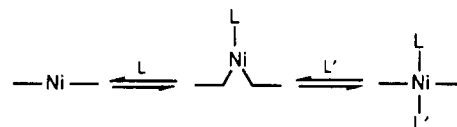
and CH₃I was also investigated in order to better understand any relationships which might exist between thermodynamic potentials, macrocycle structure, the site of electroreduction, and the catalytic reactivity of a reduced nickel porphyrin complex with a given alkyl halide.

The structures of the investigated complexes are shown in Figure 1 and are represented as (P)Ni^{II} where P = the dianions of *meso*-tetramethylporphyrin (TMeP), *meso*-tetraethylporphyrin (TEtP), *meso*-tetrapropylporphyrin (TPrP), *meso*-tetrakis(*p*-(diethylamino)phenyl)porphyrin (T(*p*-Et₂N)PP), *meso*-α,α,α,α-tetrakis(*o*-pivalamidophenyl)porphyrin (TpivPP), *meso*-tetrakis-(*o,o,m,m*-tetrafluoro-*p*-(dimethylamino)phenyl)porphyrin (T(*p*-Me₂N)F₄PP), and 5-(*N*-hexadec-4-ylpyridiniumyl)-10,15,20-triphenylporphyrin bromide (hTriP)⁺Br⁻.

Experimental Section

Chemicals. Tetrahydrofuran (THF), obtained from Mallinckrodt Inc., was distilled over CaH₂ and then over sodium benzophenone prior to use. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Fluka Chemical G. R. The salt was twice recrystallized from absolute ethyl alcohol and dried in a vacuum oven at 40 °C prior to use. Methyl iodide was purchased from Aldrich Chemical Co. and used directly.

(T(*p*-Et₂N)PP)H₂ was synthesized as described by Simonet[8a] using a modified method of Datta-Gupta.[8b] (T(*p*-Et₂N)PP)Ni was synthesized and purified by the method of Adler.[9] The free base (TpivPP)H₂ was synthesized by the method of Collman[10] and its Ni derivative, (TpivPP)-Ni, was synthesized as described in ref 5. The remaining compounds, (TRP)Ni,[11] where R is Me, Et, or Pr, (T(*p*-Me₂N)F₄PP)Ni,[12] and [(hTriP)Ni]⁺Br⁻ [13] were all synthesized by literature methods.

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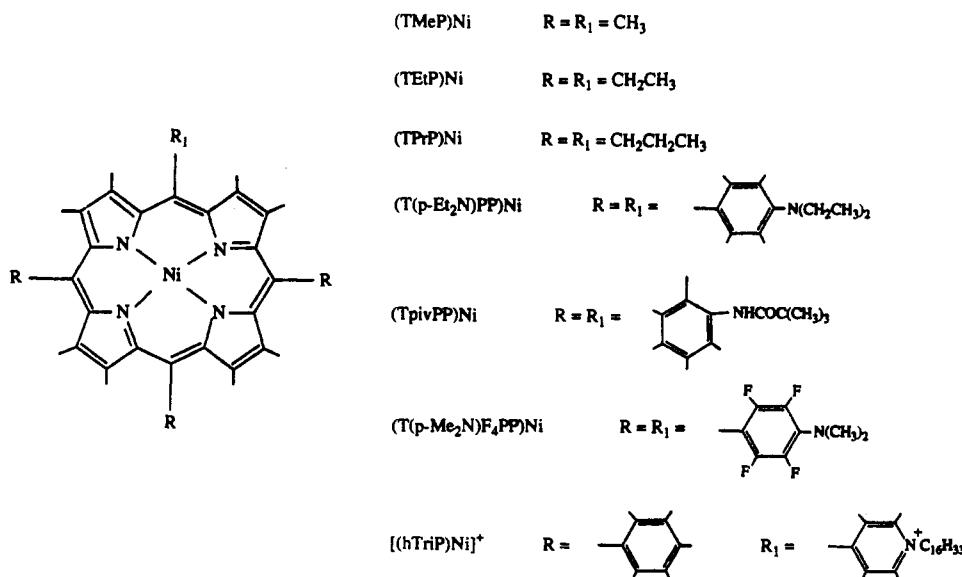(12) Kadish, K. M.; Araullo-McAdams, C.; Han, B. C.; Franzen, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 8364.

(TMeP)Ni   R = R₁ = CH₃

(TEtP)Ni   R = R₁ = CH₂CH₃

(TPrP)Ni   R = R₁ = CH₂CH₂CH₃

(T(p-Et₂N)PP)Ni   R = R₁ = ⟨benzene⟩—N(CH₂CH₃)₂

(TpivPP)Ni   R = R₁ = ⟨dimethylbenzene⟩—NHCOC(CH₃)₃

(T(p-Me₂N)F₄PP)Ni   R = R₁ = ⟨tetrafluorobenzene⟩—N(CH₃)₂

[(hTriP)Ni]⁺   R = ⟨benzene⟩   R₁ = ⟨pyridinium⟩—N⁺C₁₆H₃₃

Figure 1. Structures of the investigated porphyrins.

Instrumentation and Methods. Cyclic voltammograms were obtained with an IBM Model EC 225 voltammetric analyzer and an Omnigraphic 2000 X-Y recorder using a three-electrode system. The working electrode was a 0.80 mm² platinum button. A platinum wire served as the counter electrode and a homemade saturated calomel electrode (SCE) was used as the reference electrode which was separated from the bulk solution by a glassy diaphragm connected to a bridge filled with the electrolyte solution. All potentials were measured vs SCE. Controlled-potential electrolysis was carried out with an EG&G Princeton Applied Research Model 174A potentiostat/model 179 coulometer system which was coupled with an EG&G Princeton Applied Research Model RE-0074 time-base X-Y recorder. All electrochemical measurements were carried out at 22 ± 1 °C unless otherwise specified.

Thin-layer spectroelectrochemical measurements were taken with a Tracor Northern 6500 multichannel analyzer/controller using an optically transparent platinum-gauze working electrode. UV-visible spectra of the neutral complexes were also recorded on an IBM 9430 spectrophotometer.

ESR spectra were taken with a Bruker Model ER 100D spectrometer equipped with an ER 040-X microwave bridge and an ER 080 power supply. The g values were measured relative to diphenylpicrylhydrazide (DPPH) ($g = 2.0037 ± 0.0002$).[14] The ESR spectrum of [(TPrP)Ni]⁻ was simulated using an ESR Version 1.01 software program by Calleo Scientific Software Publishers on a Macintosh SE. The simulation parameters were as follows: $g = 2.00$; $ã = 3.2$ G; $n = 9.39$ GHz; abundance cutoff = 0.01; line width = 1.9 G; spectral resolution = low. The line width used in the simulation was derived from an equation found elsewhere[15] and utilized the experimental value obtained for ΔH_{pp} (1.6 G). A Gaussian line shape best simulated the spectrum.

Results and Discussion

Electroreduction of (P)Ni. Room temperature cyclic voltammograms of the seven investigated nickel(II) porphyrins in THF containing 0.1 M TBAP are shown in Figure 2. Six of the seven complexes are reduced in two one-electron transfer steps, consistent with reports in the literature for these and other nickel porphyrins in nonaqueous media.[1,2,4,5] [(hTriP)Ni]⁺ differs from the other investigated complexes in that it is reduced in two steps via an overall three-electron transfer process. The first reduction occurs at $E_{1/2} = -0.74$ V and involves the addition of two electrons, one of which is transferred to the single positively charged pyridinium group. The product of this two-electron reduction has a single negative charge and, like the other singly reduced nickel porphyrins in this study, can be written as [(P)Ni]⁻.

The second reduction of each (P)Ni derivative, including [(hTriP)Ni]⁺, involves one electron and occurs at $E_{1/2}$ values between -1.39 and -1.85 V in THF containing 0.1 M TBAP. This reaction is reversible for all of the porphyrins except for (TpivPP)Ni. This complex, as well as (TRP)Ni, where R = Me, Et, or Pr, shows additional anodic peaks after scanning past potentials corresponding to the second reduction. These processes can be assigned to the oxidation of an electrogenerated phlorin[5] but may also be due to reactions involving one or more decomposition products. Neither the second reduction of (P)Ni nor any coupled reactions associated with this reduction were of concern in this study and these were not examined in further detail.

Table I summarizes half-wave potentials for the two reductions of (P)Ni in THF containing 0.1 M TBAP. The absolute potential difference between the first and second reduction, $\Delta E_{1/2}$, is equal to 1.00 V for [(hTriP)Ni]⁺ but ranges between 0.47 and 0.51 V for the other five complexes. These latter values of $\Delta E_{1/2}$ may be compared to a $0.42 ± 0.05$ V separation generally observed for porphyrins which undergo electron addition at the conjugated ring system to give porphyrin π anion radicals and dianions.[16,17] A $\Delta E_{1/2}$ value of 0.92 V has been reported for [(hTriP)M]⁺ in CH_2Cl_2 or DMF where M is Cu or VO and this larger separation is due, in part, to the facile first reduction of the positively charged complex.[18]

Spectral Characterization of [(P)Ni]⁻. A summary of room temperature ESR spectral data is given in Table II. Six of the seven reduced complexes have isotropic ESR signals with g_{iso} = 2.00 or 2.01, consistent with data in the literature for other singly reduced nickel porphyrins at room temperature.[1,3,5,6] These spectra are unambiguously assigned as nickel(II) porphyrin π anion radicals. [(TPrP)Ni]⁻ differs from the other investigated complexes in that it has a radical signal that is split into nine lines of different intensities with ΔH_{pp} = 2 G and g_{iso} = 2.00 (see Figure 3a). Computer simulation of this spectrum supports an interaction between the single unpaired electron and either the four nitrogens of the porphyrin ring (Figure 3b) or the eight β-pyrrole hydrogens of the porphyrin macrocycle (Figure 3c). To our knowledge, [(TPrP)Ni]⁻ is the only porphyrin radical which shows hyperfine splitting at room temperature.

The first reduction of (P)Ni is electrochemically and spectrally

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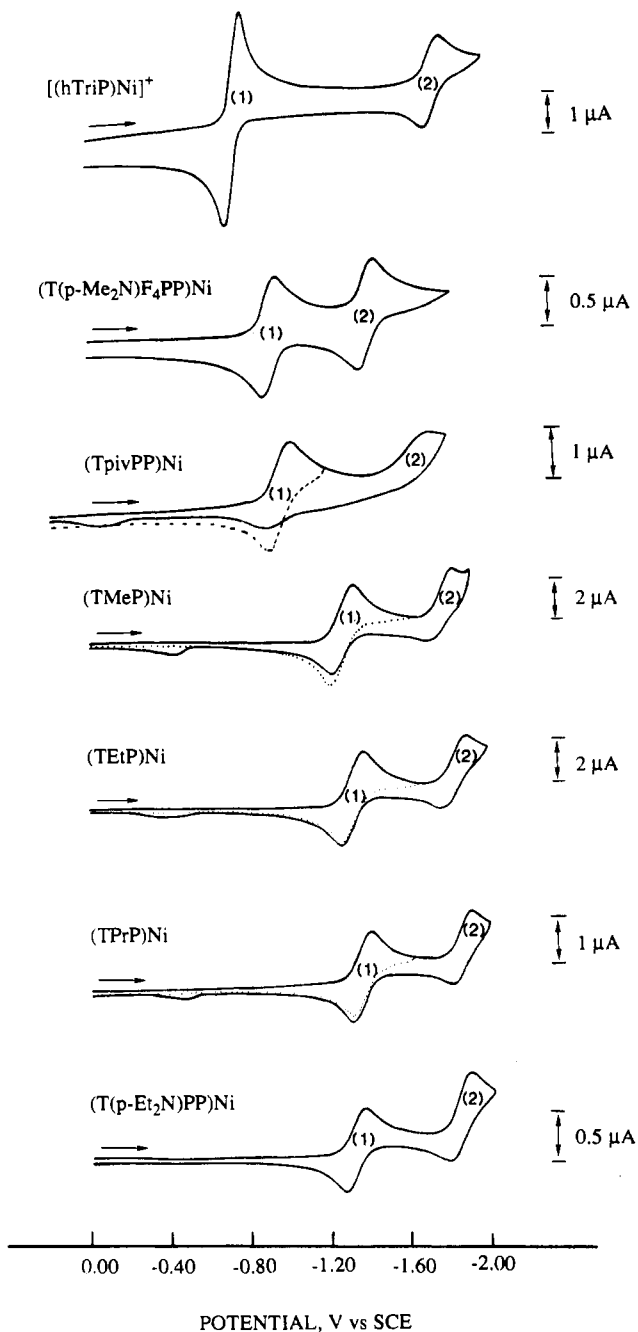(18) Kadish, K. M.; Liu, Y. H.; Sazou, D.; Senglet, N.; Guilard, R. *Anal. Chim. Acta* **1991**, *251*, 47.

POTENTIAL, V vs SCE

Figure 2. Cyclic voltammograms of (P)Ni in THF containing 0.1 M TBAP at 23 °C at v = 100 mV/s.

Table I. Half-Wave Potentials (V vs SCE) for Electroreduction of (P)Ni in THF containing 0.1 M TBAP

porphyrin	1st redn	2nd redn	$\Delta E_{1/2}$,[a] V	ref
[(hTriP)Ni]⁺	−0.74[b]	−1.74	1.00	d
(T(p-Me₂N)F₄PP)Ni	−0.91	−1.39	0.48	1
(TpivPP)Ni	−0.96	c		5
(TMeP)Ni	−1.27	−1.76	0.49	d
(TEtP)Ni	−1.32	−1.83	0.51	d
(TPrP)Ni	−1.34	−1.85	0.51	d
(T(p-Et₂N)PP)Ni	−1.30	−1.77	0.47	1

[a] $\Delta E_{1/2}$ = absolute potential difference between first and second reduction. [b] Two-electron reduction (see text). [c] Irreversible reduction at room temperature. [d] This work.

reversible in a thin-layer cell and the initial UV–visible spectrum of each (P)Ni^{II} complex could be quantitatively recovered upon reoxidation of the reduced species. UV–visible data of each (P)-Ni and electrogenerated [(P)Ni]⁻ complex are summarized in Table III and spectral changes obtained upon electroreduction of (TPrP)Ni and (TMeP)Ni are shown in Figure 4.

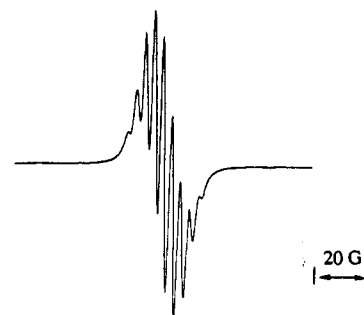**Table II.** ESR Data of [(P)Ni]⁻ in THF Containing 0.2 M TBAP at 298 K

porphyrin	g_{iso}	ΔH_{pp}, G
hTriP	2.00[a]	8
T(p-Me₂N)F₄PP	2.01	14
TpivPP	2.00	12
TMeP	2.01	14
TEtP	2.01	12
TPrP	2.00[b]	2
T(p-Et₂N)PP	2.01	11

[a] After the addition of two electrons. [b] Hyperfine splitting is present. $\tilde{a}$ = 3 G.

(a) [(TPrP)Ni]⁻ in THF, 0.2 M TBAP at 23 ˚C

g_{iso} = 2.00

20 G
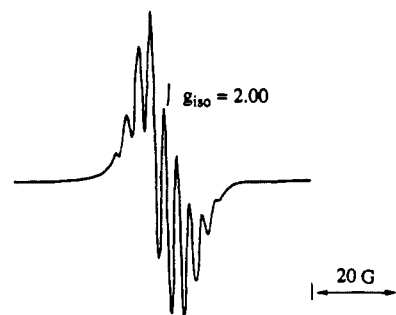
(b) Simulation- Interaction of e⁻ with 4 N

20 G
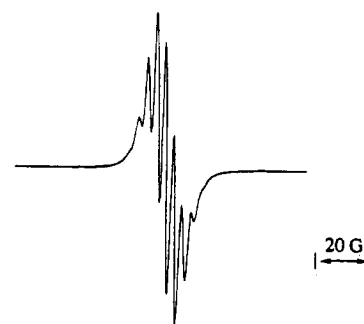
(c) Simulation- Interaction of e⁻ with 8 H

20 G

Figure 3. (a) Measured ESR spectrum of [(TPrP)Ni]⁻ in THF containing 0.2 M TBAP at 23 °C under N₂. (b) Computer ESR simulation of spectrum assuming interaction of one electron with four nitrogen atoms. (c) Computer ESR simulation of spectrum assuming interaction of one electron with eight hydrogen atoms.

The spectra of electrogenerated [(TPrP)Ni]⁻ and [(TMeP)Ni]⁻ have broad bands between 650 and 850 nm and this is also the case for the other [(P)Ni]⁻ complexes in THF (see Table III). These types of spectra are all characteristic of porphyrin π anion radicals.[19] In addition, six of the seven compounds show a red-shift of the Soret and visible bands upon generation of [(P)Ni]⁻

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Table III. UV–Visible Data for Neutral and Reduced (P)Ni in THF

porphyrin	λ, nm ($\epsilon \times 10^{-4}$, cm^{-1} M^{-1})	ref
(T(p-Et$_2$N)PP)Ni	442 (19.4), 539 (1.8), 582 (1.2)	1
[(T(p-Et$_2$N)PP)Ni]$^-$	437 (15.6), 530 (1.2), 573 (0.4), 680 (br)^a	
(T(p-Me$_2$N)F$_4$PP)Ni	412 (20.8), 527 (1.8), 557 (0.9)	1
[(T(p-Me$_2$N)F$_4$PP)Ni]$^-$	422 (13.3), 615 (1.2), 851 (0.2)	
(TpivPP)Ni	412 (10.7), 527 (1.0), 557 (0.4), 617 (0.1)	5
[(TpivPP)Ni]$^-$	421 (5.7), 527 (0.5), 557 (0.3), 617 (0.3), 860 (0.2)	
(TMeP)Ni	416 (19.5), 536 (1.2)	b
[(TMeP)Ni]$^-$	421 (6.0), 446 (6.5), 694 (1.4)	
(TEtP)Ni	416 (20.1), 536 (1.3)	b
[(TEtP)Ni]$^-$	424 (7.9), 446 (5.4), 525 (0.7), 680 (0.6)	
(TPrP)Ni	417 (23.8), 536 (1.5)	b
[(TPrP)Ni]$^-$	423 (9.3), 448 (5.8), 528 (1.0), 680 (0.9)	
[(hTriP)Ni]$^{+}$ ^{a}	417, 530	b
[(hTriP)Ni]$^-$	414, 490, 659	

^{a} Values of ϵ could not be determined. ^{b} This work.
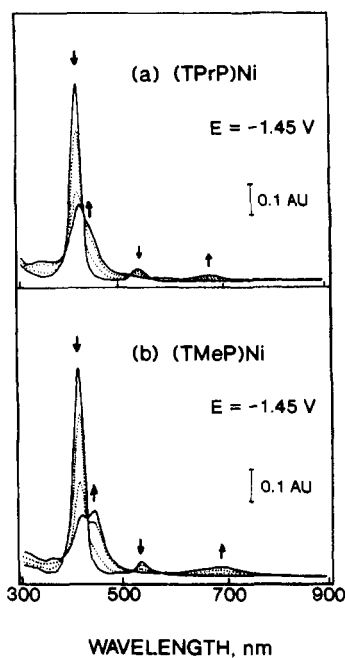

WAVELENGTH, nm

Figure 4. Thin-layer spectral changes obtained upon controlled potential reduction of (a) (TPrP)Ni and (b) (TMeP)Ni at $E = -1.45$ V in THF containing 0.2 M TBAP.

from (P)Ni, and this is also accompanied by a significant drop in the molar absorptivity. This is not the case for (T(p-Et$_2$N)-PP)Ni where the Soret band shifts from 442 to 437 nm upon electroreduction while the visible bands shift from 539 to 530 and from 582 to 573 nm. A very broad π anion radical marker band is observed at ≈680 nm in the UV–visible spectrum of [(T(p-Et$_2$N)PP)Ni]$^-$, but this band is very weak in intensity compared to the bands in this region for the other electrogenerated [(P)Ni]$^-$ complexes. Similar spectral changes have also been observed upon reduction of (OEC)Ni in CH$_3$CN containing 0.1 M TBAP, and it was suggested that the site of electron addition involved both the metal center and the porphyrin π ring system.[20]

Reactions of [(P)Ni]$^-$ with Methyl Iodide. Each (P)Ni complex except for [(hTriP)Ni]$^+$ shows an irreversible first reduction in solutions containing CH$_3$I, indicating a chemical reaction between the alkyl halide and the singly reduced [(P)Ni]$^-$ complex. [(hTriP)Ni]$^-$ does not react with CH$_3$I while [(T(p-Me$_2$N)F$_4$PP)Ni]$^-$ reacts noncatalytically to form one or more β-pyrrole methylated nickel chlorins as final, stable products.[1] Cyclic voltammograms for (TEtP)Ni in THF con-
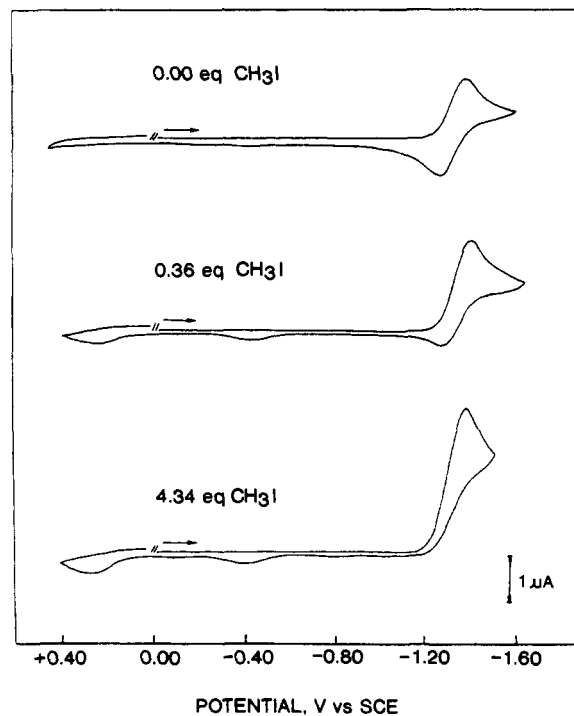

POTENTIAL, V vs SCE

Figure 5. Cyclic voltammograms of 2.1 × 10^{-3} M (TEtP)Ni in THF containing 0.1 M TBAP and various concentrations of CH$_3$I at $v = 100$ mV/s.

taining various concentrations of CH$_3$I are shown in Figure 5, and these are similar to voltammograms reported in the literature for (T(p-Et$_2$N)PP)Ni,[1] (TpivPP)Ni,[5] and (T(p-Me$_2$N)F$_4$PP)-Ni[1] in THF containing CH$_3$I.

The first reduction of (TEtP)Ni is reversible in THF alone and occurs at $E_{1/2} = -1.32$ V. However, the addition of 0.25–0.45 equiv of CH$_3$I to this solution results in both an irreversible first reduction and a 30% increase in the cathodic peak current. The peak current continues to increase with further additions of CH$_3$I (see Figure 5), and in the presence of 10.8 equiv, the i_{pc} value is enhanced by a factor of 2.7 compared to that for the reduction of (TEtP)Ni in THF alone. This increase in peak current could suggest an overall reduction of (P)Ni by three electrons but is more appropriately accounted for by a catalytic reduction of CH$_3$I. An anodic peak appears at $E_p = 0.30$ V after scanning past potentials corresponding to the first reduction of (TEtP)Ni, and this is also the case for (T(p-Et$_2$N)PP)Ni, (TpivPP)Ni, (TPrP)Ni, (TMeP)Ni, and (T(p-Me$_2$N)F$_4$PP)Ni. This anodic peak is attributed to an oxidation of free I$^-$. It is also consistent with a catalytic reduction of CH$_3$I, whose direct reduction does not occur in THF up to potentials of at least -1.60 V.[1]

Ratios of the peak current for reduction of (P)Ni in the presence and absence of CH$_3$I (i_p/i_{p0}) have previously been used to study the catalytic reduction of alkyl halides by reduced Ni(II) complexes,[21-24] and this method was also utilized in the present study. The i_p/i_{p0} ratio is a measure of the rate at which the Ni(II) complex is regenerated during the catalytic cycle[23] and also gives qualitative information on the relative strength of any transient Ni–C bond formed as an organonickel intermediate.[24] In general, an increase in the i_p/i_{p0} ratio corresponds to a faster regeneration rate of the initial Ni(II) complex and also implies a weaker Ni–C bond in the organonickel intermediate.

Figure 6 shows diagnostic plots of i_p/i_{p0} vs [CH$_3$I]/[(P)Ni] for each complex where i_p and i_{p0} are the cathodic peak currents

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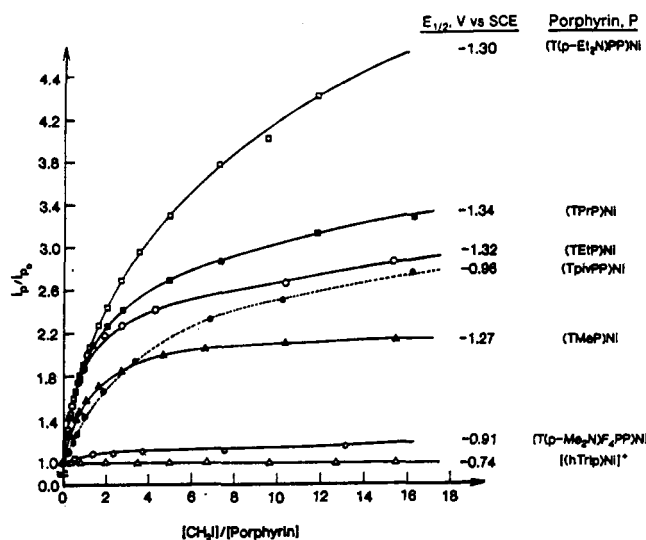(24) Gosden, C.; Pletcher, D. *J. Organomet. Chem.* **1980**, *186*, 401.

Figure 6. Plot of i_p/i_{p0} vs [CH_3I]/[(P)Ni] ratio where i_p and i_{p0} are the measured cathodic peak currents for the first reduction of (P)Ni in the presence and absence of CH_3I.

for the reduction of (P)Ni in the presence and absence of CH_3I. The catalytic current is different for each metalloporphyrin, and this indicates different regeneration rates of the original (P)Ni derivatives. The data in this figure also suggests a relationship between half-wave potentials for conversion of (P)Ni to [(P)Ni]$^-$, the catalytic reactivity of a reduced [(P)Ni]$^-$ complex, and the site of electron transfer. Nickel porphyrins which show the highest catalytic activity toward CH_3I reduction also have the most negative half-wave potentials, and these results suggest greater Ni(I) character in the reactive [(P)Ni]$^-$ species. As the half-wave potential for reduction of (P)Ni becomes more positive, the catalytic activity of [(P)Ni]$^-$ decreases, perhaps indicating an increase in the π anion radical character and a corresponding decrease in the Ni(I) character of the singly reduced species. The porphyrin with the most positive half-wave potential for reduction, [(hTriP)Ni]$^-$, does not react with CH_3I while the porphyrin with the next most positive half-wave potential for reduction, [(T(p-Me$_2$N)F$_4$PP)Ni]$^-$, reacts non-catalytically to form one or more β-pyrrole methylated chlorins.[1] This suggests a high degree of π anion radical character in both singly reduced species.

Pletcher[21,23,24] has studied the catalytic reactions of numerous electrogenerated Ni(I) complexes with alkyl halides and has demonstrated that the catalytic activity of a given reduced nickel complex is dependent on solution conditions as well as the structure and nature of both the nickel macrocycle and the alkyl halide. In this present study, the alkyl halide (CH_3I) and solution conditions (THF, 0.1 M TBAP) were invariant, and these factors can therefore be eliminated as sources to account for differences in the catalytic activities shown in Figure 6. This suggests that, in the present study, the differences in porphyrin basicity or structure will affect the thermodynamics and/or kinetics of processes leading to regeneration of (P)Ni^{II}. The macrocyclic basicity is related to the half-wave potentials for conversion of (P)Ni to [(P)Ni]$^-$, and these values vary between -0.74 and -1.34 V in THF containing 0.1 M TBAP. However, $E_{1/2}$ values alone cannot explain the different catalytic activities. For example, the half-wave potential for reduction of (TPrP)Ni ($E_{1/2} = -1.34$ V) is only slightly more negative than that for (T(p-Et$_2$N)PP)Ni ($E_{1/2} = -1.30$ V), but as seen in Figure 6, the catalytic activities of these two compounds are considerably different. A similar discrepancy also appears when comparing (TpivPP)Ni and (TMeP)Ni. The former compound is reduced at $E_{1/2} = -0.96$ V, but its catalytic activity is higher than that of (TMeP)Ni which is reduced at a much more negative potential ($E_{1/2} = -1.27$ V). These data imply the existance of other factors which might

stabilize or destabilize a proposed (P)Ni(CH$_3$) intermediate or, alternatively, might interfere or enhance the interaction of CH_3I with singly reduced [(P)Ni]$^-$.

Possible Mechanisms for the Catalytic Reduction of CH_3I. The electrocatalytic behavior of [(P)Ni]$^-$ can be explained by one of several different mechanisms. The catalytic reduction of alkyl halides by [(OEiBC)Ni^I]$^-$ is thought to proceed by an oxidative addition mechanism which involves formation of an unstable σ-bonded product, (OEiBC)Ni(CH$_3$). This proposed σ-bonded intermediate decomposes to regenerate the initial Ni(II) species, but it has never been isolated or detected.[25] The catalytic reduction of different alkyl halides by other reduced non-porphyrin nickel complexes is also thought to proceed by the same oxidative addition mechanism, but again, none of the intermediates have been isolated.[21-24,26]

All attempts to isolate (P)Ni(CH$_3$) complexes in the present study have, to date, been unsuccessful. The addition of excess CH_3I to electrogenerated [(T(p-Et$_2$N)PP)Ni]$^-$ or [(TpivPP)Ni]$^-$ under N_2 in the absence of an applied potential gives only the original Ni(II) species after purification.[1,5] This is consistent with the mechanism proposed for (OEiBC)Ni and other non-porphyrin nickel complexes.[21-26]

The catalytic reduction of CH_3I by [(P)Ni]$^-$ might also be explained by an outer-sphere mechanism in which [(P)Ni]$^-$ reacts with CH_3I to generate the initial nickel(II) porphyrin which is then further reduced at this potential. This type of mechanism should be independent of the porphyrin central metal ion and depend only on the half-wave potentials for formation of [(P)M]$^-$ from (P)M. If this mechanism were operative, (TPP)Zn whose $E_{1/2}$ for reduction (-1.33 V) is similar to the $E_{1/2}$ for reduction of (T(p-Et$_2$N)PP)Ni (-1.30 V), (TPrP)Ni (-1.34 V), and (TEtP)-Ni (-1.32 V) should also react with CH_3I in a catalytic fashion. This is not the case, and even in the presence of 400 equiv of CH_3I, there is no reaction between reduced (TPP)Zn and CH_3I.[1] Because of this result, an outer-sphere mechanism cannot explain the catalytic behavior of the [(P)Ni]$^-$ complexes and an oxidative addition mechanism appears to be operative.

In summary, the type of porphyrin macrocycle has a definite effect on the reaction between electrogenerated [(P)Ni]$^-$ and CH_3I. Plots of i_p/i_{p0} vs [CH_3I]/[(P)Ni] show a different catalytic current for each [(P)Ni]$^-$ complex, and this indicates a different regeneration rate of (P)Ni^{II}. The half-wave potential for reduction of the neutral complex seems to be a dominant factor in determining the catalytic activity of a given [(P)Ni]$^-$ species, but other factors may also be involved. In addition, a relationship may exist between half-wave potentials for conversion of (P)Ni to [(P)Ni]$^-$, the catalytic reactivity of a reduced [(P)Ni]$^-$ complex, and the site of electron transfer.

Studies of electrogenerated [(P)Ni]$^-$ with different alkyl and aryl halides as well as with other reagents are now in progress and should help to further clarify the conditions needed for formation of a given nickel(I) porphyrin. The formation of Ni(I) is associated with very specific reaction chemistry (such as the conversion of CO_2 to CH_4 in coenzyme F430[27]), and these types of reactions are now being investigated for a variety of porphyrin complexes.

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