lation), a similar ligand environment may be inferred for our Cr(IV) complex, for incorporation of these ligands cannot occur after the formation of the (substitution-inert) Cr(III) center.

Note further that the two relatively straightforward bimolecular reactions described here involve complementary redox species. Both participants in the $(\mathrm{Mo^V})_2$–$\mathrm{Cr^{VI}}$ reaction undergo $2e^-$ transactions, whereas the partners in the $\mathrm{Cr^{IV}}$–$\mathrm{Cr^{VI}}$ reaction change by single units. The $(\mathrm{Mo^V})_2$–$\mathrm{Cr^{IV}}$ reaction, featuring a $1e^-$ oxidant and a $2e^-$ reductant, requires preliminary activation of the reductant, leading to the kinetic peculiarities observed for this step.

The ease with which the $\mathrm{Cr^{IV}}$–$\mathrm{Cr^{VI}}$ reaction, (10), proceeds is quite unexpected. Formal potentials for $\mathrm{Cr^{VI}}$–$\mathrm{Cr^{V}}$ and for

$$\mathrm{Cr^{IV}} + \mathrm{Cr^{VI}} \rightarrow 2\mathrm{Cr^{V}} \qquad (10)$$

$\mathrm{Cr^{V}}$–$\mathrm{Cr^{IV}}$ have been estimated[28] as 0.60 and 1.39 V, respectively, values that have been critically discussed by Linck.[29] Taken in combination, these lead to a highly unfavorable $\Delta E°$ of −0.79 V for (10). Possible variation of these potentials within the pH range 0–3 would be expected to alter the value of $\Delta E°$ but not its sign. The implication here is that chelation with the carboxylate anion employed has stabilized Cr(V) far more effectively than Cr(IV), with the ratio of the association constants of the two complexes exceeding 10^{12}.

Acknowledgment. We are grateful to Dr. R. N. Bose for valuable discussions and to Ms. Arla White for technical assistance.

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Contribution from the Department of Chemistry,
Rensselaer Polytechnic Institute, Troy, New York 12180-3590

Selective Cleavage of a Vinyl Ether Group from a Nickel(II) Macrocycle Complex and Synthesis of Derivatives

Colin P. Horwitz,* Ralph Navarro, and Gregory C. Dailey

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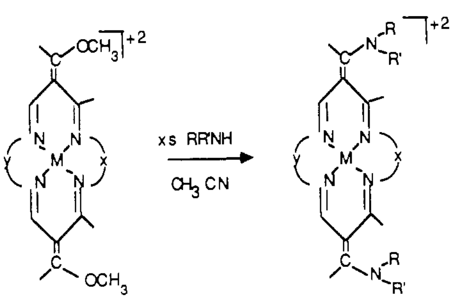
One of the two vinyl ether moieties is slowly cleaved from the macrocyclic compound $[\mathrm{Ni[(MeOEthi)_2Me_2[14]tetraeneN_4][PF_6]_2}$ (**1a**) by dissolving **1a** in methanol to form $[\mathrm{Ni[(MeOEthi)(H)Me_2[14]tetraeneN_4]][PF_6]}$ (**3**). The cleavage reaction can be accelerated by addition of aromatic amines, $\mathrm{C_6H_5NH(R)}$ (R = H, Me, Et), or sodium alkoxides, NaOR (R = Et, Me), to the methanol solution. Addition of NaOEt to a slurry containing $[\mathrm{Ni[(MeOEthi)_2Me_2[14]tetraeneN_4]][PF_6]_2}$ in $\mathrm{CH_3OD}$ yields $[\mathrm{Ni[(MeOEthi)(D)Me_2[14]tetraeneN_4]][PF_6]}$, as determined by ^{1}H NMR spectroscopy. Derivative compounds are prepared by the condensation of **3** with either propylamine ($\mathrm{PrNH_2}$) or 1-(6-aminohexyl)pyrrole ($\mathrm{PyrHexNH_2}$) in $\mathrm{CH_3CN}$ to form $[\mathrm{Ni[(PrNHEthi)(H)Me_2[14]tetraeneN_4]][PF_6]}$ (**5**) or $[\mathrm{Ni[(PyrHexNHEthi)(H)Me_2[14]tetraeneN_4]][PF_6]}$ (**6**), respectively. All compounds were characterized by UV–vis, ^{1}H NMR, and infrared spectroscopy as well as electrochemistry and elemental analysis.

Reaction of the alkylated Jager macrocycle **1** with a wide variety of primary and secondary amines to form complexes such as **2** (eq 1) has been elegantly demonstrated by Busch and co-workers.[1]



(1)

1 **2**

The excellent reversible dioxygen binding properties exhibited by some of the Fe and Co complexes[2] make them candidates for possible use as $\mathrm{O_2}$ sensors or $\mathrm{O_2/N_2}$ separators if they could be appropriately immobilized.[3] Recently, we have utilized the chemistry shown in eq 1 to append *N*-alkylpyrrole moieties onto the 14-membered Ni(II) macrocycle complex.[4] Polymer films containing the *N*-alkylpyrrole complexes were grown on platinum electrode surfaces through oxidative electropolymerization of the pyrrole groups. Electroactivity was maintained for the Ni center in these films, demonstrating successful immobilization of an intact macrocycle complex.

In order to avoid possible future complications that might arise from chemical and electrochemical properties associated with the polypyrrole backbone, an alternative method was sought for at-

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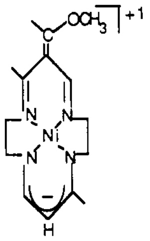
taching these modified Jager macrocycle complexes to electrode surfaces. Aromatic amines present as peripheral substituents on Schiff-base complexes,[5] porphyrins,[6] and ferrocene[7] have been electropolymerized by an oxidative coupling reaction.[8] Thus, an attempt was made to include aromatic amines such as aniline on the periphery of the macrocycle by using the chemistry described in eq 1. Presumably by having two aromatic amines on the complex, a polymer film could be formed in a manner analogous to that observed for the metal Schiff-base complexes.[5]

Reaction of **1a** with aniline according to eq 1 results in addition of the amine to the macrocycle framework, but no analogous reaction is observed when either *N*-methylaniline or *N*-ethylaniline is used. However, an unusual reaction ensues in the presence of any of the aromatic amines when the solvent is methanol. The product from reaction in methanol is [Ni[(MeOEthi)(H)Me$_2$[14]tetraeneN$_4$]][PF$_6$] (**3**). Cleavage of one vinyl ether group from the macrocycle **1a** is rather unusual behavior for the Jager compounds[1] and posed very interesting questions. This contribution seeks to address the formation of compound **3** and to explore some of its chemistry.



3

Experimental Section

Physical Measurements. Infrared spectra were obtained as KBr pellets on a Perkin-Elmer 283B infrared spectrometer. UV–vis spectra were obtained by using a Hewlett-Packard HP8452A diode-array spectrophotometer controlled with a Zenith 159 personal computer. The ^{1}H NMR spectra were recorded by using either a Varian XL-200 or IBM WP-100 spectrometer. Mass spectral data were obtained on a Hewlett-Packard 5987 GC-MS by using electron-impact ionization, 70 eV, with a direct insertion probe. All deuterated solvents CD$_2$Cl$_2$, CH$_3$OD, CD$_3$OD, and CD$_3$CN (Cambridge Isotopes) were used as received. Elemental analyses were performed by Robertson Laboratory, Madison, NJ. All reactions were carried out with standard Schlenk techniques under a N$_2$ atmosphere. No precautions were taken to exclude air when ^{1}H NMR and UV–vis spectral data were obtained.

Electrochemistry. Electrochemical measurements were obtained with either an EG&G PAR Model 273 potentiostat/galvanostat or a Cypress Systems CYSY-1H electroanalytical system. Voltammograms were obtained in a three-compartment cell using the three-electrode mode with a glassy-carbon-disk electrode as the working electrode ($A \sim 7.5$ mm^2) (polished with 1-μm alumina (Buehler) prior to use), a Pt wire as counter electrode, and a SSCE (sodium chloride saturated calomel electrode) as reference electrode. The supporting electrolyte was either Bu$_4$NClO$_4$ or Bu$_4$NSO$_3$CF$_3$ with CH$_3$CN (Burdick and Jackson) as solvent.

Materials. All chemicals were of reagent grade and used without further purification. The macrocyclic complexes, and Ni[Ac$_2$Me$_2$[14]-tetraeneN$_4$] and [Ni[(MeOEthi)$_2$Me$_2$[14]tetraeneN$_4$]][PF$_6$]$_2$ (**1a**) were prepared according to procedures detailed in the literature,[1,9] and purity was checked by ^{1}H NMR spectroscopy. Methanol was distilled over Mg under a N$_2$ atmosphere. *N*-Methylaniline (Aldrich) was distilled prior to use. 1-(6-Aminohexyl)pyrrole and 1-(2-aminopropyl)pyrrole were prepared as described previously.[4,10]

Synthesis of [2,9-Dimethyl-3-(1-methoxyethylidene)-1,5,8,12-tetraazacyclotetradeca-1,4,9,11-tetraenato]nickel(II) Hexafluorophosphate ([Ni[(MeOEthi)(H)Me$_2$[14]tetraeneN$_4$]][PF$_6$] (3)). Procedure 1. A slurry was prepared containing [Ni[(MeOEthi)$_2$Me$_2$[14]tetraeneN$_4$]][PF$_6$]$_2$ (0.250 g, 0.37 mmol) in methanol (40 mL). To this solution was added 159 μL (1.47 mmol) of *N*-methylaniline. The solution was stirred at room temperature for 3 h. Unreacted starting material, a yellow solid, was filtered from the resulting dark red solution, and volatiles were removed under reduced pressure until a red precipitate began to form (approximately 5 mL of methanol remained in the flask). Petroleum ether (30–40 mL) was added to further precipitate the powdery product, which was recovered by filtration and dried in vacuo. The final solid product is stable for several hours in the presence of oxygen, but solutions rapidly decompose in air. A typical yield was 65% based on the starting macrocycle. Anal. Calcd (found) for C$_{15}$H$_{23}$N$_4$ONiPF$_6$: C, 37.61 (36.92); H, 4.84 (4.77); N, 11.7 (11.88); P, 6.47 (6.49).

Synthesis of [Ni[(MeOEthi)(H)Me$_2$[14]tetraeneN$_4$]][PF$_6$] (3). Procedure 2. A slurry was prepared containing [Ni[(MeOEthi)$_2$Me$_2$[14]tetraeneN$_4$]][PF$_6$]$_2$ (0.100 g, 0.147 mmol) in methanol (15 mL). To this mixture was added 1.2 equiv of NaOEt (12 mg, 0.176 mmol). Reaction was complete and a dark red solution resulted within 1 min of alkoxide addition. The product was isolated as in procedure 1. The yield was not determined.

Synthesis of [2,9-Dimethyl-3-[1-(propylamino)ethylidene]-1,5,8,12-tetraazacyclotetradeca-1,4,9,11-tetraenato]nickel(II) Hexafluorophosphate ([Ni[(PrNHEthi)(H)Me$_2$[14]tetraeneN$_4$]][PF$_6$] (5)). [Ni[(MeOEthi)(H)Me$_2$[14]tetraeneN$_4$]][PF$_6$] (15 mg, 0.03 mmol) was dissolved in acetonitrile (20 mL), and then *N*-propylamine (8 μL, 0.12 mmol) was added. The solution, which appeared to become a deeper red immediately following addition of the amine, was stirred for 5 h (reaction is probably over in less than 1 h) at room temperature, after which time volatiles were removed in vacuo. The resulting red solid residue was dissolved in methanol (10–15 mL), the solution volume reduced under vacuum until precipitation of a red-orange solid powder began (<5 mL methanol remaining), and petroleum ether added to further precipitate the red-orange product. The precipitate was recovered by filtration and dried in vacuo, yield 44%. Anal. Calcd (found) for C$_{17}$H$_{28}$N$_5$NiPF$_6$: C, 40.35 (38.87); H, 5.58 (5.28); N, 13.84 (13.30); P, 6.12 (6.14).

Synthesis of [2,9-Dimethyl-3-[1-((6-(1-pyrrolyl)hexyl)amino)-ethylidene]-1,5,8,12-tetraazacyclotetradeca-1,4,9,11-tetraenato]nickel(II) Hexafluorophosphate ([Ni[(PyrHexNHEthi)(H)Me$_2$[14]tetraeneN$_4$]][PF$_6$] (6)). To a CH$_3$CN solution (5 mL) of [Ni[(MeOEthi)(H)Me$_2$[14]tetraeneN$_4$]][PF$_6$] (54 mg, 0.13 mmol) was added 1-(6-aminohexyl)pyrrole (27 mg, 0.16 mmol). The solution became darker red upon addition of the amine. This solution was stirred under N$_2$ for 1 h at room temperature (no additional color changes occurring during this time), following which the solution volume was reduced to approximately 1 mL in vacuo and then Et$_2$O was added slowly to precipitate a red powder. The solid was recovered by filtration, washed with Et$_2$O, and dried in vacuo, yield 34 mg (34%). Anal. Calcd (found) for C$_{24}$H$_{37}$N$_6$NiPF$_6$: C, 47.06 (47.34); H, 6.08 (6.09); N, 13.70 (13.57); P, 5.05 (5.21).

Synthesis of [2,11-Dimethyl-3,10-bis(1-anilinoethylidene)-1,5,8,12-tetraazacyclotetradeca-1,4,8,11-tetraene]nickel(II) Hexafluorophosphate ([Ni(PhNHEthi)$_2$Me$_2$[14]tetraeneN$_4$]][PF$_6$]$_2$ (7)). [Ni[(MeOEthi)$_2$Me$_2$[14]tetraeneN$_4$]][PF$_6$]$_2$ (75 mg, 0.11 mmol) was dissolved in CH$_3$CN (5 mL). Upon addition of aniline (40 μL, 0.44 mmol) an immediate color change from yellow to amber was observed. The solution was stirred for 30 min and then the CH$_3$CN removed in vacuo. The resulting amber solid was dissolved in a minimum amount of warm methanol, and the soution was cooled to −20 °C overnight. An orange-brown solid was recovered from the methanol by filtration, washed with Et$_2$O, and dried in vacuo, yielding 52 mg of product, 59% yield. Anal. Calcd (found) for C$_{28}$H$_{34}$N$_6$NiP$_2$F$_{12}$: C, 41.86 (41.82); H, 4.24 (4.16), N, 10.46 (10.31).

Reaction of [Ni[(MeOEthi)$_2$Me$_2$[14]tetraeneN$_4$]][PF$_6$]$_2$ with NaOCH$_3$ for Mass Spectroscopy. A sample of **1a** (100 mg) was placed in a Schlenk flask along with 1 equiv of NaOCH$_3$. The flask was evacuated on a vacuum line, and then 5 mL of degassed methanol (three freeze–pump–thaw cycles) was vacuum-transferred to the reaction vessel. After distillation was complete, the reaction flask was closed off to the vacuum line and the methanol allowed to thaw. Reaction was allowed to proceed with stirring for 30 min, and then the volatiles were vacuum-distilled from the reaction vessel back into the original solvent flask. An aliquot of the recovered volatiles was taken for mass spectral analysis by electron impact by using the direct insertion probe. For the detuerium labeling

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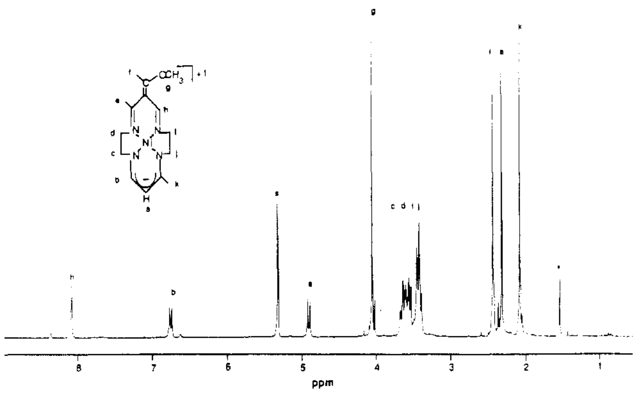


Figure 1. ^{1}H NMR spectrum of [Ni[(MeOEthi)(H)Me_2[14]tetraeneN_4]][PF_6] in CD_2Cl_2. The peak marked s is the solvent, and an asterisk denotes H_2O in the solvent.

Table I. Crystallographic Data for [Ni[(MeOEthi)(H)Me_2[14]tetraeneN_4][PF_6]

formula $C_{15}H_{23}N_4ONiPF_6$	fw 479.02
$a = 7.775\ (2)$ Å	space group $P\bar{1}$ (No. 2)
$b = 10.404\ (2)$ Å	$T = 258$ °C
$c = 13.466\ (3)$ Å	λ(Cu Kα) = 1.54178 Å
$\alpha = 67.63\ (3)°$	$\rho_{calcd} = 1.637$ g cm^{-3}
$\beta = 81.82\ (3)°$	$\mu = 28.79$ cm^{-1}
$\gamma = 75.00\ (3)°$	transm coeff = 0.6291–0.9150
$V = 971.8\ (4)$ Å^3	$R = 10.17$
$Z = 2$	$R_w = 13.10$

experiment 99% CH_3OD replaced CH_3OH.

Results

Synthesis of [Ni[(MeOEthi)(H)Me_2[14]tetraeneN_4]][PF_6]. (a) Reaction with Aromatic Amines. It has been stated that the [Ni[(MeOEthi)$_2Me_2$[X]tetraeneN_4]]$^{2+}$ (X = 14–16) complexes are unreactive toward aromatic amines,[1b] but we find for X = 14 that aniline does react with the macrocycle according to eq 1 to form **7**. The UV-vis spectrum is similar to those of other exchange products (Table II), the IR spectrum (KBr pellet) shows a sharp N-H stretch at 3355 cm^{-1}, and the elemental analysis is consistent with an addition product. Attempts to react *N*-methylaniline with [Ni[(MeOEthi)$_2Me_2$[14]tetraeneN_4]]$^{2+}$ under analogous conditions proved unsuccessful. Even upon refluxing of the mixture for 4 h in acetonitrile no reaction is observed by UV-vis spectroscopy. However, when *N*-methylaniline is added in excess to a slurry of [Ni[(MeOEthi)$_2Me_2$[14]tetraeneN_4]$^{2+}$ in *methanol*, a reaction does occur. After approximately 2–3 h of stirring the slurry at room temperature, the yellow solid starting material dissolves and a dark red solution forms. A red crystalline material is isolated by concentrating the solution followed by petroleum ether addition.

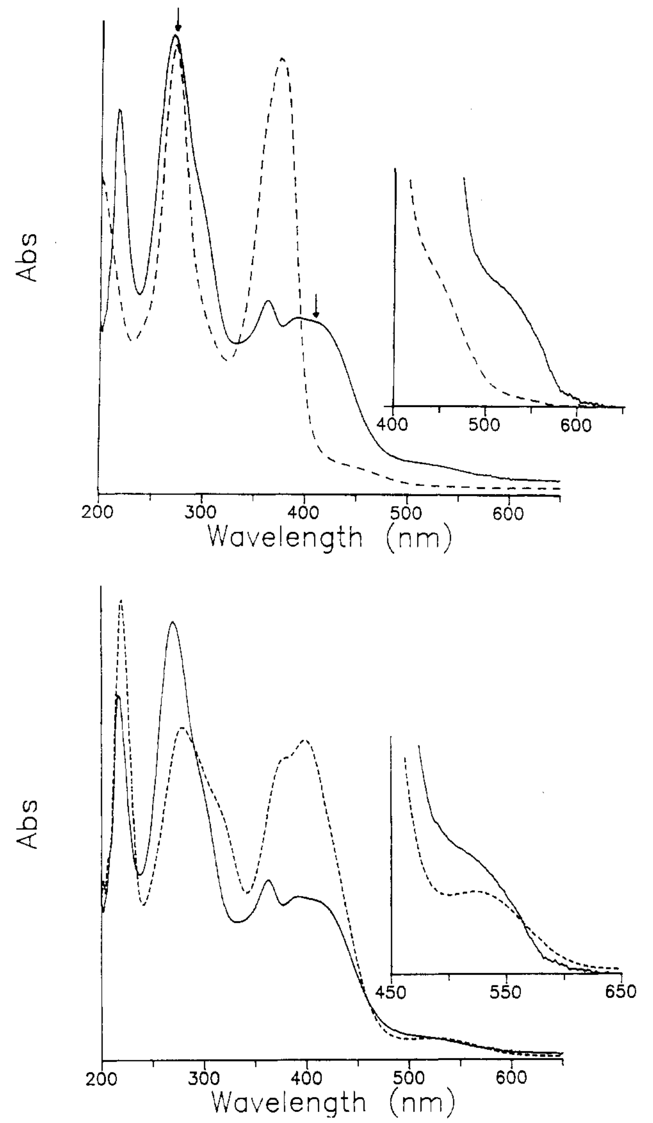


Figure 2. (a) Top: Electronic spectra of [Ni[(MeOEthi)$_2Me_2$[14]tetraeneN_4]][PF_6]$_2$ (---) and [Ni[(MeOEthi)(H)Me_2[14]tetraeneN_4]]-[PF_6] (—) in CH_3CN (arbitrary absorbance units). (b) Bottom: Electronic spectra of [Ni[(MeOEthi)(H)Me_2[14]tetraeneN_4]][PF_6] (—) and [Ni[(PrNHEthi)(H)Me_2[14]tetraeneN_4]][PF_6] (---) in CH_3CN (arbitrary absorbance units).

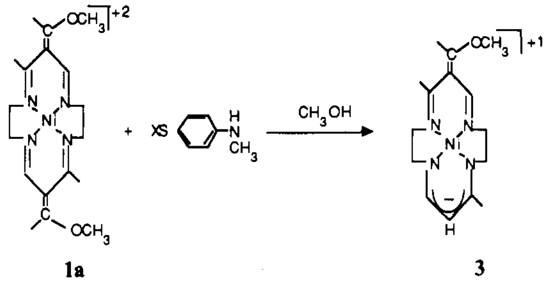
The ^{1}H NMR spectrum of the isolated material in CD_2Cl_2 is shown in Figure 1. Chemical shifts values are presented in Table II. The two doublets at δ 6.77 and 4.90 ppm ($J = 6.3$ Hz) are characteristic of a Jager type macrocycle possessing adjacent

Table II. ^{1}H NMR and UV–Vis Spectroscopic Data and Electrochemical Data

cmpd	chem shift, ppm[a–c]	λ_{max}, nm (10^3 ϵ, M^{-1} cm^{-1})[f]	$E_{p,ox}$-(Ni(II/III))[g]
1a[d]	8.12 (s, 2), 4.13 (s, 6), 3.56 (s, 6), 2.50 (s, 6), 2.36 (s, 6)	272, 376, 442	
3[e]	8.09 (s, 1), 6.77 (d, 1, $J = 6.3$), 4.90 (d, 1, $J = 6.3$), 4.05 (s, 3), 3.7–3.3 (m, 8), 2.43 (s, 3), 2.31 (s, 3), 2.07 (s, 3)	270 (38.2), 298 (sh), 364 (15.7), 402 (13.8), 520 (1.8)	1.02
5[e]	7.69 (s, 1), 6.72 (d, 1, $J = 6$), 4.78 (d, 1, $J = 6$), 3.5–3.2 (m, 10), 2.34 (s, 3), 2.26 (s, 3), 2.07 (s, 3), 1.75 (m, 2), 1.00 (tr, 3, $J = 3.8$)	280 (14.8), 314 (sh), 378 (12.4), 398 (13.1), 522 (0.75)	0.59
6[e]	7.68 (s, 1), 6.72 (d, 1, $J = 5.9$), 6.64 (tr, 2, $J = 2.1$), 6.06 (tr, 2, 2.1), 4.78 (d, 1, 5.9), 3.87 (tr, 2, $J = 7.0$), 3.6–3.2 (m, 10), 2.31 (s, 3), 2.25 (s, 3), 2.02 (s, 3), 1.8–1.6 (m, 4), 1.4–1.2 (m, 4)	278 (15.2), 314 (sh), 378 (13.6), 398 (14.5), 524 (0.9)	0.66
7[f]	7.9 (s, 1), 7.5–7.2 (m, 5), 3.44 (s, 4), 2.38 (s, 3), 2.18 (s, 3)	284 (15.1), 314 (13.5), 418 (36.3)	1.13[h]
8[d]	7.86 (br, 1), 7.0 (br, 2), 6.7 (br, 2), 4.5 (br, 2), 3.5 (br, 4), 2.4 (br, 3), 2.3 (br, 3)	248, 284, 310 sh, 422	

[a] Relative to external Me_4Si. [b] Values in parentheses are multiplicities, number of protons, and coupling constants (Hz). [c] Amine protons not observed. [d] CD_3CN. [e] CD_2Cl_2. [f] CH_3CN. [g] *E* (in V) vs Ag quasi-reference electrode, 0.1 M Bu_4NClO_4 or 0.1 M $Bu_4NSO_3CF_3$ in CH_3CN, glassy-carbon working electrode, Pt counter electrode. [h] *E*° for the quasi-reversible Ni(II/III) couple.

apical, a, and vinyl, b, protons.[11] Furthermore, the upfield shift for the methyl group denoted k also is observed in analogous systems. As indicated on the figure, resonances corresponding to a vinyl ether group on the macrocycle are still present. These data suggest formulation of the product as [Ni[(MeOEthi)(H)-Me_2[14]tetraeneN_4]][PF_6] (**3**, eq 2); the elemental analysis is consistent with this formulation.



(2)

1a **3**

The resonances assigned to the remaining vinyl ether group on **3** shift less than 0.1 ppm when compared to the starting material **1a** (Table II). The position of the vinyl proton resonance, h, which might be expected to be sensitive to changes in electron density within the macrocycle, is essentially unchanged. Thus the two halves of the macrocycle appear to be electronically isolated from each other.

A UV–vis spectrum of the product in acetonitrile is shown in Figure 2, and absorption maxima are presented in Table II. Modification of alkylated Jager molecules is known to affect the d → d transition of the metal center.[12] Removal of the one vinyl ether group causes a shift in the d → d transition from 442 nm in **1a** to 520 nm in the product. The d → d band is at 561 nm when both vinyl ether substituents are cleaved from the macrocycle.[12] The shift to lower energy for **3** thus is consistent with an observed trend for the d → d transition upon removal of electron-withdrawing substituents from the macrocycle.[12]

An attempt was made to obtain a single-crystal X-ray structure of this material. The structure could not be refined below approximately $R_w = 13$ (Table I), but the gross features of the molecule are as shown in eq 2 for **3**, in which one of the vinyl ether moieties is no longer present on the macrocycle framework. Furthermore, only one PF_6^- is required to balance the charge on the macrocycle and this counterion is well separated from the metal center in the solid state. A roughly square-planar arrangement of nitrogens exists about the nickel center. The macrocycle framework shows bent, vinyl ether remaining, and flat, vinyl ether removed, portions relative to the nitrogen square plane about the nickel. No comparisons with other structures are possible owing to the high refinement factor.

The reaction with *N*-methylaniline, which forms **3**, has been studied by using 2–10 equiv of the amine, all other reaction parameters, e.g. temperature, solvent volume, etc., held constant. Best results are obtained with a 4:1 *N*-methylaniline/[Ni-[$(MeOEthi)_2Me_2$[14]tetraeneN_4]]$^{2+}$ stoichiometry. The 2:1 stoichiometry reacts too sluggishly to be of practical use, and poor yields are obtained. The 10:1 stoichiometry results in more rapid product formation (approximately 40 min by UV–vis spectroscopy), but the isolated material is tacky and less crystalline in nature.

The relative rate of formation of [Ni[(MeOEthi)(H)Me_2-[14]tetraeneN_4]]$^+$ decreases in the order aniline > *N*-methylaniline > *N*-ethylaniline. These relative rates were determined by reacting a constant concentration of compound **1a** in methanol with the appropriate amine (4 molar excess) for 45 min, removing the solvent, washing the solid with ether to remove unreacted amine, and then obtaining the UV–vis spectrum in CH_3CN. The absorbance value at 272 nm was ratioed to the absorption at 424 nm for a given reaction, see the arrows on Figure 2a, and this ratio compared for each reaction. Even after prolonged reaction times the final product made from *N*-ethylaniline was not free of impurities as determined by UV–vis spectroscopy; possibly unreacted starting material remained. Therefore, the *N*-methylaniline product was used in all subsequent studies as it provided the most reproducible product yield in terms of purity as determined by ^1H NMR spectroscopy.

The aromatic diamine *p*-phenylenediamine does not produce **3** in methanol under identical reaction conditions used to prepare **3** from *N*-methylaniline. Rather the starting material **1a** dissolves into the methanol in less than 5 min, following which an orange powder precipitates, **8**. UV–vis and ^1H NMR spectra (Table II) for the precipitate are characteristic of a product in which the amine has added onto the macrocycle as in eq 1.[1,4] Limited solubility in acetonitrile and acetone as well as broad resonances in the proton NMR spectrum suggest a material that is polymeric in nature. The IR spectrum (KBr pellet) has two relatively broad absorptions in the N–H stretching region (3425 and 3390 cm^{-1}), which likely arise from both primary and secondary amine functionalities in the complex, the symmetric stretch for the primary amine being obscured by the broad N–H stretch from the secondary amine. Presumably, the polymer comprises a linear chain of macrocycles attached to each other through the aromatic diamine. No molecular weight distribution has been determined nor have we attempted to alter the ratio of diamine to metal complex to control the degree of polymerization.

In order to gain additional insight into the reaction that forms [Ni[(MeOEthi)(H)Me_2[14]tetraeneN_4]]$^+$, an attempt was made to quantitatively determine the kinetics of eq 2. A stock solution (0.10 mM) of the macrocycle **1a** was prepared in methanol. The UV–vis spectrum of this stock solution taken after it was allowed to stand 7 h at room temperature revealed formation of [Ni-[(MeOEthi)(H)Me_2[14]tetraeneN_4]]$^+$ even though no aromatic amine had been added. Thus, methanol reacted directly with the starting macrocycle to form **3** but more slowly than in the presence of the amine. These observations suggested that the aromatic amines function to increase the methoxide ion concentration in the methanol solution. We sought to determine if alkoxide ion was responsible for the observed reactivity by deliberately adding NaOR (R = Me, Et) to the methanol solution. Although vinyl ether groups generally are stable to base hydrolysis,[13] the electronic properties of macrocycles are known to modify the reactivity of peripheral substituents.[14]

(b) Reaction with NaOR (R = Me, Et). Approximately 1 min after 1 equiv of either sodium methoxide or ethoxide was added to a methanol slurry containing **1a**, all of the solid starting material had dissolved, producing a red solution. The UV–vis spectrum of the solution indicated the presence of [Ni[(MeOEthi)(H)-Me_2[14]tetraeneN_4]]$^+$, and the ^1H NMR spectrum confirmed its formation. When CH_3OD (99% D) was used as the solvent, no resonance was detected at 3.90 ppm and the doublet at 6.77 ppm collapsed into a singlet. Thus, the apical proton in **3** comes from the solvent.

Reaction of **1a** with NaOMe in an NMR tube, CD_3OD solvent, was performed, and resonances in the proton NMR spectrum for the deuterated analogue of **3** were observed. However, a number of other resonances also were detected in the spectrum, suggesting formation of decomposition products. No definitive assignments could be made to these resonances.

Mass spectral analysis of the volatile components from reaction of **1a** with NaOMe in methanol (see Experimental Section for details) revealed major peaks at $m/e = 44$ and 43 u. Use of deuterated solvent, CH_3OD, shifted the $m/e = 44$ u peak to 45

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[11] (a) Riley, D.; Stone, J. A.; Busch, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 767. (b) Herron, N.; Grzybowski, J. J.; Matsumoto, N.; Zimmer, L. L.; Christoph, G. G.; Busch, D. H. *J. Am. Chem. Soc.* **1982**, *104*, 1999. (c) Caste, M. L.; Carins, C. J.; Church, J.; Lin, W. K.; Gallucci, J. C.; Busch, D. H. *Inorg. Chem.* **1987**, *26*, 78.

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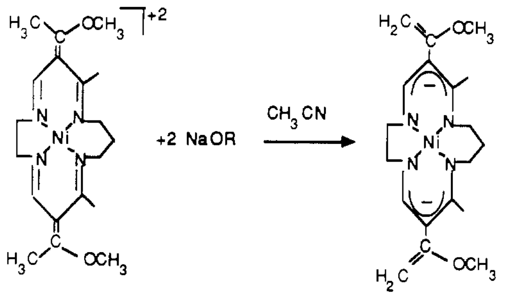
[14] Endicott, J. E.; Durham, B. In *Coordination Chemistry of Macrocyclic Compounds*; Melson, G. A., Ed.; Plenum Press: New York, 1985; p 393.

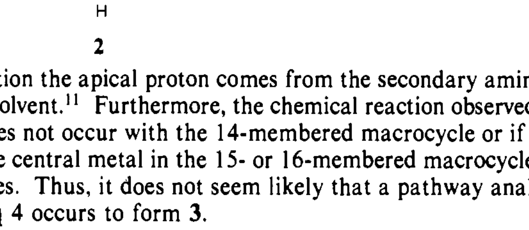
u, strongly indicating the product to be acetaldehyde. The 43 u peak is too large to arise solely from acetaldehyde and likely contains a significant contribution from trimethyl orthoacetate (parent peak 43 u), a logical reaction product.[15] However, owing to the overall low concentrations of all fragments detected in the mass spectrum a detailed analysis of the relative amounts of materials produced in the reaction is not reasonable. Furthermore, the proton NMR spectrum, which also shows multiple peaks, suggests that complicated reaction pathways may exist for the cleavage reaction.

Reaction of the 15-membered macrocycle **1b** (M = Ni) with sodium alkoxide in acetonitrile has been investigated, and the reaction product is **4** (eq 3).[1b] When this reaction is carried out in methanol, a complex mixture of products results, which we have been unable to separate. Upon reaction of the 14-membered macrocycle **1a** in acetonitrile with NaOMe decomposition of the macrocycle occurs and no **3** is observed by UV-vis spectroscopy. In addition, no evidence for the 14-membered analogue of **4** is seen in the ^{1}H NMR spectrum. The reasons for the differences in reactivity observed for the two macrocycles are not obvious, but size effects on reactivity of Jager compounds have been noted previously.[11a]



1b **4** (3)

Amine complexes like **2** (X = 15, 16; M = Fe) react with base in methanol to form rearrangement products (eq 4).[11] In this reaction the apical proton comes from the secondary amine, not the solvent.[11] Furthermore, the chemical reaction observed in eq 4 does not occur with the 14-membered macrocycle or if nickel is the central metal in the 15- or 16-membered macrocycle complexes. Thus, it does not seem likely that a pathway analogous to eq 4 occurs to form **3**.



2 (4)

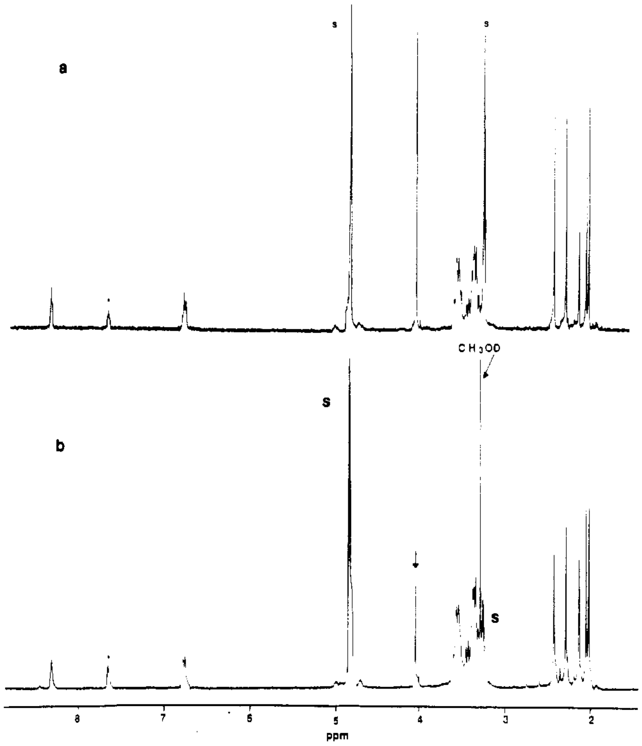


Figure 3. ^{1}H NMR spectra of $[Ni[(MeOEthi)(H)Me_2[14]tetraeneN_4]][PF_6]$ in CD_3OD taken (a) immediately upon dissolution and (b) after 18 h. Note that the peak for the apical proton a (Figure 1) lies under the solvent peak (s) at 4.8 ppm. Peaks marked with asterisks are due to a solvent impurity.

Electrochemistry of $[Ni[(MeOEthi)(H)Me_2[14]tetraeneN_4]][PF_6]$. The electrochemical properties of **3** were investigated with cyclic voltammetry in CH_3CN solution with $(n\text{-Bu})_4NClO_4$ or $(n\text{-Bu})_4NSO_3CF_3$ as supporting electrolyte and a glassy-carbon working electrode under an inert atmosphere of N_2. At all scan rates investigated, 10 mV/s to 1 V/s, an electrochemically irreversible Ni(II/III) oxidation process (Table II) was recorded. This electrochemical irreversibility contrasts most Jager type macrocycles, which exhibit a reversible Ni(II/III) redox process.[1,4] A linear plot of $i_{p,ox}$ vs $v^{1/2}$ was obtained, and the $E_{p,ox}$ shifted to less positive potentials with decreasing scan rate ($E_{p,ox}$ = 748 mV at 1 V/s and $E_{p,ox}$ = 690 mV at 5 mV/s). Both effects were expected for an irreversible electrochemical reaction.[16] At fast scan rates (20 mV/s to 1 V/s) a new quasi-reversible couple, which may be either ligand or metal based, appeared at $E°$ = 0.35 V. At 10 mV/s the redox process at 0.35 V was replaced by a sharp cathodic current spike, characteristic of an adsorption phenomenon.[16,17] The details of the voltammetry are complicated and serve to show that removal of one vinyl ether group has profound effects on the stability of the oxidized form of the macrocycle.

Reativity of $[Ni[(MeOEthi)(H)Me_2[14]tetraeneN_4]][PF_6]$. A reactivity pattern which might parallel that for the alkylated Jager compounds was envisioned for the remaining vinyl ether group on **3**. Thus, a series of reactions were performed with species known to react with **1a**.

(a) Reaction with CD_3OD. The Jager macrocycles react with an excess of ethanol in acetonitrile to exchange the alkoxy groups.[18] Dissolution of $[Ni[(MeOEthi)(H)Me_2[14]tetraeneN_4]]^+$ in CD_3OD results in slow exchange of the alkoxy group. The ^{1}H NMR spectrum of the product in CD_3OD taken immediately following dissolution of **3** resembles that in CD_2Cl_2 although there appears to be a solvent effect on the resonances arising from the various methyl groups (Figure 3a). However, if the CD_3OD solution is allowed to stand for 18 h at room temperature, the resonance at 4.1 ppm corresponding to the methoxy group (Figure 3b) decreases in relative integrated intensity by 50% from its starting value. In addition, a new singlet appears in the spectrum at 3.6 ppm assignable to CH_3OD formation. The doublet at 6.8 ppm (J = 2 Hz) does not change in relative integrated intensity during the entire reaction time. Therefore, exchange of the apical proton a (Figure 1) and/or the vinyl proton with the solvent does not occur on the time scale of this experiment (the resonance arising from the apical proton a is masked by the solvent peak).

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(16) Bard, A. J.; Faulkner, L. F. *Electrochemical Methods*; Wiley: New York, 1980.

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(18) Corfield, P. W. R.; Mokren, J. D.; Hipp, C. J.; Busch, D. H. *J. Am. Chem. Soc.* **1973**, *95*, 4465.

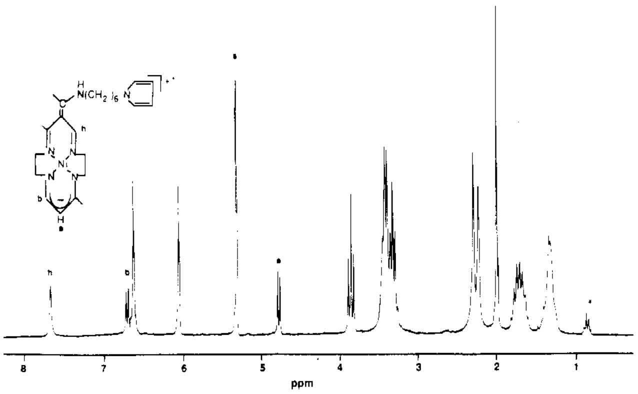
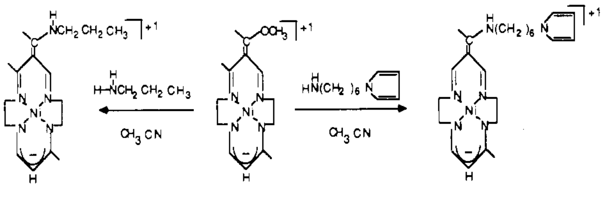


Figure 4. ^1H NMR spectrum of $[Ni[(PyrHexNHEthi)(H)Me_2[14]tetraeneN_4]][PF_6]$ in CD_2Cl_2 (s). The peak marked with an asterisk is an unidentified impurity.

After 40 h the OCH_3 resonance has decreased further but the vinyl proton remains unaffected.

(b) Reaction of $[Ni[(MeOEthi)(H)Me_2[14]tetraeneN_4]]$ with Amines. Both propylamine ($PrNH_2$) and 1-(6-aminohexyl)pyrrole ($PyrHexNH_2$)[4] react with **1a** according to eq 1 and also reasonably rapidly, less than 1 h, with **3** (eq 5). The ^1H NMR spectra in



(5)

5 **3** **6**

CD_2Cl_2 for these two derivatives show loss of the resonance assigned to the OCH_3 group in $[Ni[(MeOEthi)(H)Me_2[14]tetraeneN_4]]^+$, indicating reaction at this moiety (Table II). Shown in Figure 4 is the proton NMR spectrum of the 1-(6-aminohexyl)pyrrole derivative. Resonances arising from the pyrrole ring protons are readily observed as triplets at δ 6.64 and 6.06 ppm, confirming addition of this group to the macrocycle framework. The resonances assigned to the apical and vinyl protons in **3** shift about 0.1 ppm upon addition of either amine, further demonstrating the electronic isolation of the two halves of the macrocycle. The vinyl proton h in Figure 1 shifts nearly 0.5 ppm upfield upon incorporation of the amine.

The UV–vis spectra of the two derivative compounds are essentially identical (Table II). Substitution of the amine onto the macrocycle causes a shift to slightly lower energy for the d → d transition when compared to **3**, and the ligand bands also change intensity (Figure 2b). The IR spectra of **5** and **6** are similar to that of **3**, but a sharp absorption for the secondary amine at 3490 cm^{-1} is a new feature. No other significant differences are observed in the IR spectra for **3** and its derivatives, and no absorptions from the pyrrole ring were detected in the spectrum of **6**.

As mentioned above, **1a** reacts with *p*-phenylenediamine in methanol to substitute the aromatic amine onto the macrocycle (it also reacts to give a similar product in acetonitrile). No reaction is observed when **3** is dissolved in acetonitrile containing the aromatic diamine even upon prolonged refluxing of the mixture. 1-(2-Aminoethyl)pyrrole also does not react with **3**, as no change is observed in the UV–vis spectrum after 8 h at room temperature, but it does react rapidly with **1a**. Thus, modulation of the reactivity by a steric component appears to be imporant for $[Ni[(MeOEthi)(H)Me_2[14]tetraeneN_4]]^+$.

Electrochemistry of 5 and 6. The electrochemical properties for the two derivative macrocycles **5** and **6** are similar to those of **3**, but a shift to a more negative potential is recorded for the irreversible Ni(II/III) oxidation (Table II). Like the case for the starting material **3**, the oxidation shifts to less positive potentials upon decreasing the scan rate and $i_{p,ox}$ is linearly related to the square root of the scan rate. Furthermore, a new redox couple is observed at approximately $E° = 400$ mV as a result of the irreversible oxidation process. However, unlike the voltammetry for $[Ni[(MeOEthi)(H)Me_2[14]tetraeneN_4]]^+$, no adsorption waves are observed in the voltammogram for either derivative.

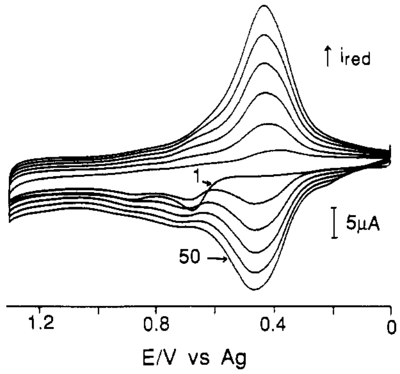


Figure 5. Cyclic voltammogram of $[Ni[(PyrHexNHEthi)(H)Me_2[14]tetraeneN_4]][PF_6]$ (0.5 mM, v = 100 mV/s, 0.1 M Bu_4NClO_4/CH_3CN, glassy-carbon electrode, E vs SSCE).

Polymer films could be grown for *both* the 1-(6-aminohexyl)pyrrole- and propylamine-containing macrocyclic complexes by scanning to potentials greater than 1.2 V vs SSCE. A monotonic increase in $i_{p,ox}$ and $i_{p,red}$ for the new redox couple at $E° = 430$ mV is observed upon continuous potential cycling, which is indicative of polymer film formation (Figure 5). Upon transfer of the electrode to a solution containing only supporting electrolyte, the wave at 430 mV retains electroactivity. At this time we do not know what portion of the macrocycle complex gives rise to this redox process. However, since the pyrrole moiety is not necessary for film growth to occur, the polymer film is most likely formed by some type of degradative coupling of the macrocycles. Other tetraaza macrocycles have been polymerized by direct oxidative coupling of the macrocyclic rings.[19]

The electrochemical behavior of compounds **3**, **5**, and **6** sharply contrasts with results obtained on the symmetrically substituted pyrrole-containing compounds we previously described.[4] Those polymer films exhibited distinct oxidation and reduction waves for the polypyrrole backbone as well as reversible voltammetry for the Ni(II/III) redox process. Note also that for the disubstituted aniline derivative, **7**, prepared under the conditions of eq 1, the Ni(II/III) couple is quasi-reversible (Table II).

Discussion

Reaction of compound **1a** with amines in acetonitrile appears to produce exchanged products of the general form shown in eq 2, or alternatively, no reaction may occur with some amines. However, changing to methanol solvent can drastically alter the reactivity pattern of the macrocycle. One of the vinyl ether moieties is slowly cleaved from the macrocycle by methanol. This was an unexpected result, as alcohols are known to undergo an exchange reaction in acetonitrile.[18] Addition of some aromatic amines to the methanol solution enhances the cleavage rate, and a further rate enhancement is observed when the strong base $NaOCH_3$ is added to the solution. The latter two observations suggest that a nucleophilic attack on a vinyl ether group is the first step in the reaction pathway to the cleavage product. Presumably, the aromatic amines that have been studied serve to increase the concentration of methoxide ion in solution rather than directly attacking the vinyl ether group. We have no direct proof for this assumption except that the *N*-alkylaniline derivatives do not undergo an exchange reaction with the vinyl ether groups in acetonitrile. The relative order of reactivity for the amines, aniline > *N*-methylaniline > *N*-ethylaniline, is opposite to the pK_a values measured in H_2O[20] for the amines but parallels their steric bulk.

At least two sites are susceptible to nucleophilic attack by the methoxide ion, as shown in Scheme I. The first step in pathway

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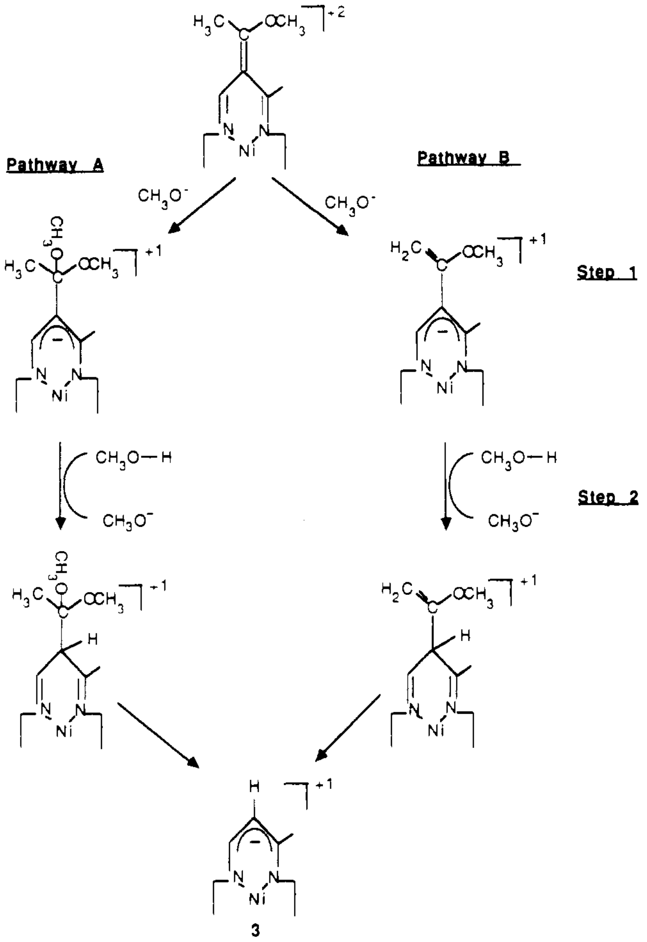
Scheme I



A is commonly observed for vinyl ether groups,[13] while the alternative pathway has the precedence shown in eq 3. Following deprotonation or addition of CH_3O^- to the vinyl ether carbon, the apical position of the macrocycle becomes more basic and deprotonation of methanol occurs (step 2, Scheme I). This reaction accounts for addition of the deuterium label to the apical position on the macrocycle. The basic nature of species like those formed in step 1 has been demonstrated. Loss of the organic fragments acetaldehyde and trimethyl orthoacetate to generate **3** must be a complicated pathway and may involve the methoxide ion produced in step 2. No convincing experimental evidence is available to suggest a pathway for loss of the organic fragments. We do suspect however that some decomposition of the macrocycle occurs that acts to reduce the vinyl ether carbon to an appropriate oxidation state for addition of a proton (deuteron) to form the acetaldehyde. Many extraneous peaks are observed in both the in situ NMR spectrum as well as the mass spectrum.

Since the ^1H NMR spectrum of the cleavage product **3** indicates electronic isolation of the two halves of the molecule, we can only suggest that cleavage of the second vinyl ether group is kinetically limited. The probable cause for this observation is a reduction in the overall electrophilic nature of the macrocyle when the positive charge is lowered from +2 to +1. No doubly cleaved product, which should have an absorption at 561 nm, has been observed spectrophotometrically in the isolated solid, although we cannot discount that some is formed but not detected.

Reactivity of the remaining vinyl ether moiety is evidenced by the metathesis reaction with propylamine and 1-(6-aminohexyl)pyrrole. However, reactivity of the vinyl ether group in **3** is more limited than in **1a**. Since we have as yet been unable to obtain a high-quality single-crystal X-ray structure of **3**, it is not possible to determine if steric effects are important in the reactions of this complex. The reactivity of compound **3** toward selected amines makes it is possible to prepare and evaluate the chemical properties of some interesting asymmetrically substituted macrocycle complexes.

Acknowledgment. We thank Profs. C. Breneman and L. Frye for helpful discussions.

Supplementary Material Available: Figures depicting the structure of **3** and tables of bond distances and angles, crystallographic data, data collection and refinement parameters, and positional parameters (11 pages); a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Yale University, New Haven, Connecticut 06511

Unusual Stereochemical Rigidity in Seven-Coordination. Synthesis and Structural Characterization of $ReH_2(EPh_3)(CO)(PMe_2Ph)_3$ (E = Si, Sn)

Xiao-Liang Luo,* Gayle K. Schulte, Peter Demou, and Robert H. Crabtree

Received March 16, 1990

Reaction of $ReH_3(CO)(PMe_2Ph)_3$ (**1**) with Ph_3SiH and Ph_3SnH in refluxing THF leads to the formation of $ReH_2(EPh_3)(CO)(PMe_2Ph)_3$ (E = Si (**2**), Sn (**3**)). The solution spectroscopic data are consistent with the formulation of **2** and **3** as seven-coordinate with no H···H or Si···H interactions, but they are stereochemically rigid on the NMR time scale even at elevated temperatures, which is unusual for seven-coordinate complexes containing only monodentate ligands. Compound **2** has been structurally characterized by single-crystal X-ray crystallography in solvated and unsolvated forms. Crystal data for **2**: monoclinic, space group $P2_1$, $a = 9.958$ (3) Å, $b = 18.268$ (6) Å, $c = 12.175$ (2) Å, $\beta = 112.47$ (2)°, $V = 2047$ (2) Å^3, and $Z = 2$. Crystal data for **2**·THF: monoclinic, space group $P2_1/c$, $a = 15.341$ (2) Å, $b = 15.178$ (2) Å, $c = 19.074$ (1) Å, $\beta = 93.055$ (8)°, $V = 4435.0$ (7) Å^3, and $Z = 4$. Unexpected distortions from standard seven-coordination polyhedra are present in both forms, and possible reasons are discussed.

Introduction

The structure and dynamic stereochemistry in seven-coordination has been considered as one of the most complicated subjects in coordination chemistry.[1] Much of the importance of seven-coordinate structures arises from their role as intermediates (or transition states) in the associative or dissociative reactions of six- or eight-coordinate complexes. In this context, synthesis and structural studies of seven-coordinate complexes are beneficial to a thorough understanding of the mechanisms and factors that control these reactions. Stereochemical nonrigidity has been a general observation in seven-coordinate complexes due to facile intramolecular rearrangements.[2]

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