product with the acetate anion being protonated by an endogenous proton source.

Subsequent workup afforded a 67% isolated yield of *N*-acetyl ethyl-L-alaninate. The measured specific rotation, $[\alpha]_D^{26°C}$, of +6.4° (*c* 0.933, Silanor-C) indicates that the L configuration of the amino acid has been maintained throughout the oxidation reaction. The fate of the rhenium is less certain although elemental analysis of the only Re-containing product suggests that a rhenium oxide having the empirical formula, ca. $HReO_4$, is formed.[18] The need for such an apparent excess of iodosobenzene is not obvious. Oxidation of the carbonyl ligands to CO_2 would nearly fit the observed reaction stoichiometry; however, this explanation is not very reasonable when considering the heterogeneous reaction conditions, and the rapid evolution of the gaseous product. Although the above oxidation reaction effectively cleaves the amino acid residue from the rhena moiety, the formation of the *N*-acetyl amino acid derivative is rather inconvenient if the free amino acid derivative is desired.

Future study of the synthesis and structures of rhena derivatives of amino acids and peptides is planned. The compatability and selectivity of rhena derivatization in the presence of more reactive functional groups will be examined, and the search for more convenient rhena cleavage reactions will be continued.

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Supplementary Material Available: Tables listing the atomic positional and thermal parameters and the observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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[18] Noddack, J.; Noddack, W. *Z. Anorg. Allg. Chem.* **1929**, *181*, 1.

Molecular Species Containing Persistent Voids. Template Synthesis and Characterization of a Series of *lacunar*-Nickel(II) Complexes and the Corresponding Free Ligands

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Abstract: A new family of lacunar ligands has been synthesized in the form of their nickel(II) complexes by a template process. The new species were designed to provide a protected void, or cavity, in the vicinity of a coordination site in order to facilitate the binding of small molecules to the metal ion. The nature of the ligand greatly limits collapse of the cavity, and the height and flexibility of the roof vary with the length of the homologous bridging group which varies from tetramethylene to octamethylene. The shorter dimethylene and trimethylene bridges are too short to span the cavity while longer bridges produce complicated systems containing isomers. The electron density at the metal ion is insensitive to bridge length so that the previously reported great change in O_2 affinity by the cobalt(II) complexes arises from steric effects.

Molecular structures containing sizable, noncollapsing voids are of significance for a variety of reasons, some fundamental and others associated with their applications in the study of other fundamental chemical processes. Macrocyclic ligands constitute one of the more primitive classes of such structures, being almost two dimensional. These substances are well-known because of their exceptional coordinating properties toward metal ions, even the larger alkali-metal ions.[1] Cram and associates[2] have pioneered the study of guest-host complexation between such host molecules and organic guest molecules. The cyclodextrins have long fascinated chemists because of the persistent void in their structures and the provocative interaction between the void and co-solutes.[3] With appropriate substituents, such structures have been studied as enzyme models.[4] Collman et al. appended four pivaloylamide groups on the same side of porphyrin and extended the void represented by the coordination site substantially in the third dimension, thereby producing highly effective reversible oxygen carriers of the iron and cobalt complexes.[5] An exemplary void-containing structure was created by Baldwin et al., who synthesized a "capped porphyrin" having a benzene ring suspended above the porphyrin.[6] A number of observations have suggested that conformational changes in the capped porphyrins may produce variations in the height of the cavity.[7] The simpler strapped

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[1] Melson, G. A. "Coordination Chemistry of Macrocyclic Compounds"; Plenum Press: New York, 1979.

[2] Peacock, S. S.; Walba, D. M.; Gaeta, F. C. A.; Helgeson, R. C.; Cram, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 2043-2052, and preceding papers in that series.

[3] Bender, M. L.; Komiyama, M. "Cyclodextrin Chemistry. Reactivity and Structure Concepts in Organic Chemistry"; Springer-Verlag: Berlin, 1978.

[4] Breslow, R.; Bovy, P.; Hersh, C. L. *J. Am. Chem. Soc.* **1980**, *102*, 2115-2116.

[5] Collman, J. P. *Acc. Chem. Res.* **1977**, *10*, 265-272.

[6] Almag, J.; Baldwin, J. E.; Huff, J. *J. Am. Chem. Soc.* **1975**, *97*, 227-228. Almag, J.; Baldwin, J. E.; Dyer, R. L.; Peters, M. *Ibid.* **1975**, *97*, 226-227.

[7] The O_2 binding constants do not increase as the chain length increases for the "roof-supports" (Linard, J. E.; Ellis, P. E., Jr.; Budge, J. R.; Jones, R. P.; Basolo, F. *J. Am. Chem. Soc.* **1980**, *102*, 1896-1904) despite the fact that the X-ray structure for the free ligand shows that the capped porphyrin with the short roof supports has a remarkably low roof (Jameson, G. B.; Ibers, J. A. *Ibid.* **1980**, *102*, 2823-2831).

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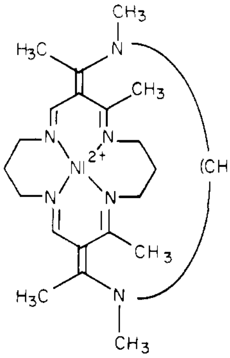
Table I. Analytical Data and Yields for the *lacunar*-Nickel(II) Complexes Having $CH_3\overline{N(CH_2)_nN}CH_3$ Homologous Bridges

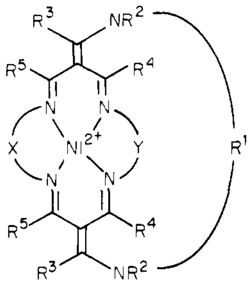
structure no.	bridge	ring size	calcd				found				yield, %
			C	H	N	Ni	C	H	N	Ni	
Ia	$(NCH_3)_2(CH_2)_4$	16	37.87	5.30	11.04	7.71	38.11	5.41	11.02	7.55	54
Ib	$(NCH_3)_2(CH_2)_5$	16	38.73	5.46	10.84		38.51	5.71	10.74		76
Ic	$(NCH_3)_2(CH_2)_6$	16	39.56	5.62	10.65		39.46	5.53	10.60		70
Id	$(NCH_3)_2(CH_2)_7$	16	40.37	5.77	10.46		40.07	6.10	10.52		59
Ie	$(NCH_3)_2(CH_2)_8$	16	41.15	5.92	10.28		41.08	5.98	10.19		54
II	$(NCH_3)_2(CH_2)_6$	15	38.78	5.34	10.85	7.58	38.91	5.19	10.81	7.30	18

porphyrins seem not to have effectively protected void regions,[8] though larger bridging groups clearly do provide sheltered cavities.[9]

The present report summarizes the template synthesis of a family of homologously bridged lacunar complexes[10] based on a synthetic tetraazamacrocycle that is neutral in charge. The substances described all have structure I, and the homologous bridge has the composition $CH_3N(CH_2)_nNCH_3$, where n = 4–8. These complexes are well-behaved examples of the much broader family of complexes of structure II. One example is given in which the basic chelating macrocycle has 15 members (X = $(CH_2)_2$, Y = $(CH_2)_3$, rather than X = Y = $(CH_2)_3$).



Ia, n = 4
Ib, n = 5
Ic, n = 6
Id, n = 7
Ie, n = 8



II

In preliminary reports[11,12] we have summarized the results of three crystallographic studies on complexes containing ligands of this class. An outstanding feature is the permanence of the slightly variable void for any given example. The persistence of the void in the absence of accommodated groups arises from the saddle shape of the parent macrocyclic ring. The two unsaturated chelate rings rise on the same side of the NiN_4 plane, and the two unsaturated rings project on the opposite side. The consequencies of flexibility in different parts of the structures of a number of the known types of void-containing species can be judged from the simple diagrams of Figure 1 (smooth lines represent relatively inflexible structural components and wavy lines represent flexible components). The parent macrocycles in the new dry cave complexes have fixed conformations so long as the metal ion remains bound. This provides a substantial limit on the extent to which the void can collapse, despite the presence of a single-bridge span. In contrast, the strapped porphyrins seem to have relatively little constraint operating against collapse of the void. The capped porphyrin appears to be intermediate in this respect, while the pocket in the picket-fence porphyrin should be essentially invariant.

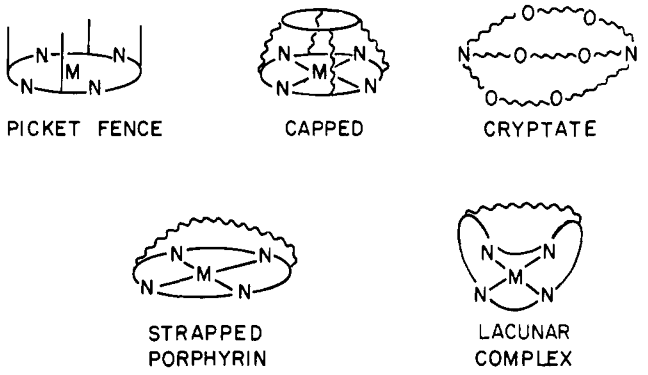


Figure 1. Diagramatic representation of the fixed (smooth lines) and flexible (wavy lines) components of molecular species having permanent voids.

The specific examples of the lacunar ligands reported here were used in an earlier communication to demonstrate how steric effects can be used to control the O_2 affinity of a metal ion in a reversible oxygen-carrying complex.[13] The success of those experiments is attributed to the change in the height of the cavity at the coordination site that accompanies the change in length of the homologous bridge. Closely related results have been found in studies of CO binding to iron(II) using the same ligands.[14] Here, the definitive synthesis and characterization of the nickel(II) complexes and the free ligands are presented.

Results and Discussion

Synthesis. The synthetic behavior and structural relationships associated with the group of lacunar ligands is particularly straightforward. The series includes nickel(II) complexes of structure I for which the bridging polymethylene chain varies from four to eight members. The lacunar complexes are isomerically simple and the only major product of the bicyclization reactions. The compounds can be prepared in good yield by either of two procedures. The first method extends the previously reported reaction of the methoxyethylidene-substituted precursor to cyclization reactions.[15]

It has previously been reported that the methoxy group of the precursor is readily replaced by primary or secondary amine groups in an addition–elimination process.[16] The reactivity of the precursor is similar to that of a carboxylate ester, a fact that may be rationalized by the electron-withdrawing effect of the metal ion acting through the conjugated ligand structure. The reaction is represented in eq 1. The second route involves initial formation of a bis(methylamine) derivative and reaction of this intermediate with a bridge-forming dinucleophile such as a ditosylate after deprotonation (Scheme I). Both processes involve template

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(8) Chang, C. K.; Traylor, T. G. *Prog. Natl. Acad. Sci. U.S.A.* **1973**, 2647–2650. Battersby, A. R.; Buckley, D. G.; Hartley, S. G.; Turnbull, M. D. *J. Chem. Soc., Chem. Commun.* **1976**, 879.

(9) (a) Traylor, T. G.; Campbell, D.; Tsuchiya, S.; Mitchell, M.; Stynes, D. V. *J. Am. Chem. Soc.* **1980**, *102*, 5939–5941. (b) Battersby, A. R.; Hamilton, A. N. *J. Chem. Soc., Chem. Commun.* **1980**, 117–119.

(10) The adjective lacunar is used in the context often applied in anatomy and biology to indicate the presence of a space or cavity where there would be none in the broader category of such systems. In biology one might mean a void or cavity in or among cells whereas here we mean a void or cavity among atoms.

(11) Schammel, W. P.; Mertes, K. S. B.; Christoph, G. G.; Busch, D. H. *J. Am. Chem. Soc.* **1979**, *101*, 1622–1623.

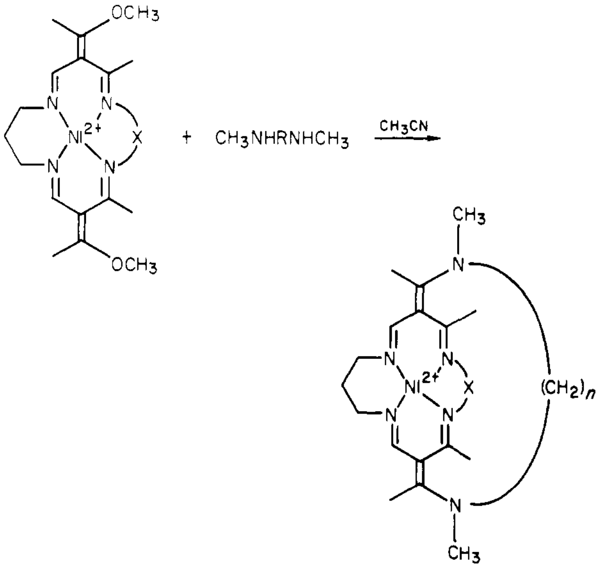
(12) Stevens, J. C.; Jackson, P. J.; Schammel, W. P.; Christoph, G. G.; Busch, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 3283–3285.

(13) Stevens, J. C.; Busch, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 3285–3287.

(14) Zimmer, L. L. Ph.D. Thesis, The Ohio State University, Columbus, OH, 1979.

(15) Schammel, W. P.; Zimmer, L. L.; Busch, D. H. *Inorg. Chem.* **1980**, *19*, 3159–3167.

(16) Corfield, P. W. R.; Mokren, J. D.; Hipp, C. J.; Busch, D. H. *J. Am. Chem. Soc.* **1973**, *95*, 4465–4466.



(1)

reactions in which Ni^{2+} maintains the favorable stereochemistry for the reaction. The reaction proceeds in good yield, giving the lacunar complexes as the predominant products. Analyses and yields are given in Table I.

The conformation of the precursor is especially favorable for closure of the second ring, and this is considered to be a major factor in the ease of formation of these structures. Figure 2 shows an edge-on view of the precursor structure.[16,17] The viewer is looking at the edge of the macrocycle and it is seen that the two methyl vinyl ether groups rise sharply above the NiN_4 plane. Because of this proximity of the two methoxyethylidene groups, ring closure is facilitated.

Characterization. The infrared spectra of these lacunar complexes are unremarkable and most useful for simple qualitative identification of the compounds.[18] The presence of only tertiary amines is clear from the absence of NH stretching modes. The principal absorptions due to the C=N and C=C linkages are centered at 1610 and 1550 cm^{-1} for most compounds of this class. The complexes have been characterized as their PF_6^- salts, and the anions show a broad strong IR band at 840 cm^{-1} and a medium intensity band at 560 cm^{-1}. Molar conductances measured at 25 °C on 10^{-3} M acetonitrile solutions give values from 240 to 290 Ω^{-1} mol^{-1} cm^2, which is in the usual range for 2:1 electrolytes.[19]

Proton NMR spectra (Table II) show that the *lacunar*-nickel(II) complexes possess a mirror plane. Figure 3A shows the proton NMR for the complex containing a hexamethylene bridging group. All of the complexes show two sharp methyl resonances in the range 1.89–2.45 ppm which correspond to the two kinds of methyl groups present in the parent macrocycle; the NCH_3 group appears as a third sharp methyl resonance in the range 3.23–3.30 ppm from Me_4Si. The presence of a total of three rather than six methyl resonances establishes the symmetry plane for the complexes. Broad, complex absorptions in the range 1.4–1.9 and 3.3–3.5 ppm are due to the methylene protons of the saturated side chains and polymethylene bridge. In addition, the vinyl proton of the parent macrocycle appears as a sharp singlet at 7.40–7.60 ppm.

^{13}C NMR spectra were obtained for the series of *lacunar*-nickel(II) complexes, and the chemical shifts are given in Table III. The ^{13}C NMR spectrum for the hexamethylene-bridged complex is given in Figure 3B. As in the case for the proton NMR, the results are consistent with the complexes possessing C_s symmetry. Spectra were recorded with broad-band proton decoupling in order to determine the number of unique carbon atoms and the chemical shift of each. Spectra were also obtained with the proton decoupler set at a discrete frequency (CW mode) just outside the usual proton frequency range in order to obtain ^{13}C spectra with residual proton coupling. With use of this "off-resonance" technique, the number of protons bound to each unique carbon atom could be easily determined without much loss of the nuclear Overhauser enhancement.

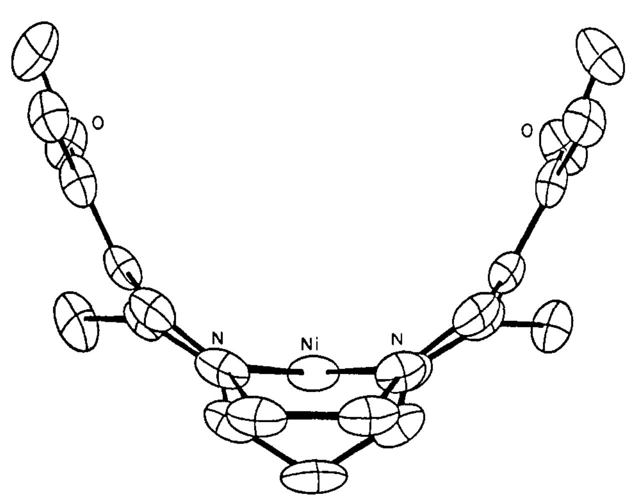
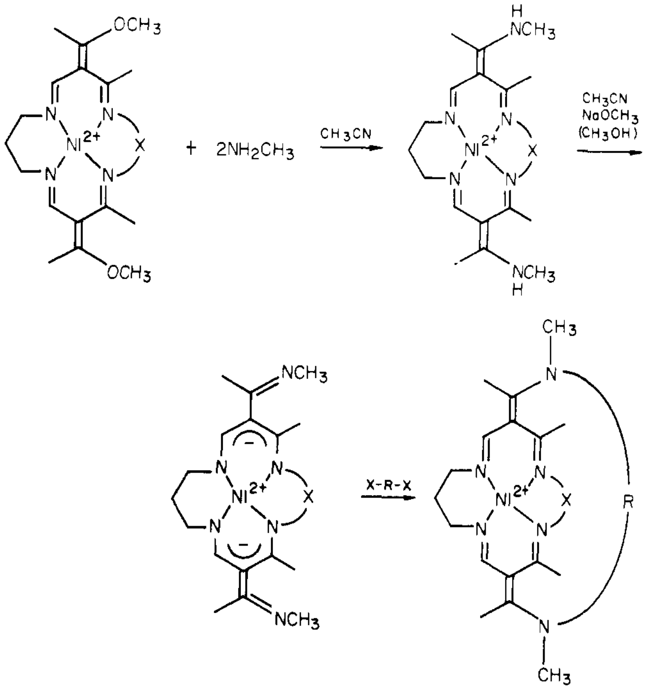


Figure 2. Crystal structure of the precursor complex $[Ni((MeOEthi)_2Me_2[15]tetraeneN_4)](ClO_4)_2$.

Scheme I



The interpretation of the ^{13}C spectra so obtained is extremely straightforward. All of the complexes show two resonances in the region 167.2–176.2 ppm that are assigned to the vinyl or imine carbons (a or b in Figure 3) due to the fact that these resonances remain singlets in the off-resonance experiments. A resonance in the range 161.0–159.0 ppm which becomes a doublet in the off-resonance spectrum is assigned to the imine carbon (c of Figure 3). The resonance for this carbon is of higher intensity than those for carbons a or b due to the enhancement of the signal by the Overhauser effect. All of the lacunar complexes show this very characteristic pattern in the downfield region of the spectrum, that is, two relatively low intensity peaks with one higher intensity peak slightly upfield.

The resonance assigned to the γ-carbon of the macrocycle (d in Figure 3) is found in the region 113.0–109.7 ppm. As expected, this peak remains a singlet in the off-resonance spectrum. Carbons e, f, and g fall in the range 57.9–45.9 ppm. These peaks are

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(17) Mokren, J. D. Ph.D. Thesis, The Ohio State University, Columbus, OH, 1974.

(18) Stevens, J. C. Ph.D. Thesis, The Ohio State University, Columbus, OH, 1979.

(19) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81–122.

Table II. Proton NMR and ^{13}C NMR Data[a] for the Monomeric *lacunar*-Nickel(II) Complexes

		proton NMR data				
structure no.	bridge	parent ring size	methyl	methylene	vinyl	^{13}C NMR data
Ia	$CH_3N(CH_2)_4NCH_3$	16	1.89, 2.34, 3.23	1.77,[b] 2.14, 3.3[c]	7.50	171.8, 169.0, 160.6, 112.7, 57.2, 55.2, 50.2, 39.4, 31.4, 30.1, 24.1, 20.5, 19.1
Ib	$CH_3N(CH_2)_5NCH_3$	16	1.91, 2.34, 3.29	1.80,[b] 2.17, 3.2[c]	7.40	173.7, 167.2, 159.1, 112.0, 57.9, 56.1, 51.2, 41.2, 30.7, 30.4, 27.1, 23.5, 20.3, 20.0
Ic	$CH_3N(CH_2)_6NCH_3$	16	1.92, 2.37, 3.26	1.98,[b] 3.3[c]	7.48	173.3, 167.5, 160.1, 110.9, 57.5, 56.1, 51.3, 40.2, 30.7, 30.3, 25.0, 24.0, 20.7, 19.7
II	$CH_3N(CH_2)_6NCH_3$	15	1.96, 2.38, 3.30	1.47,[b] 2.19, 3.3[c]	7.38	176.2, 167.5, 159.0, 111.2, 57.9, 56.0, 51.8, 41.3, 31.4, 26.5, 25.7, 22.1, 20.8
Ie	$CH_3N(CH_2)_7NCH_3$	16	2.00,[d] 2.50, 3.40	1.39, 3.23[c]	7.55	175.7, 166.9, 159.7, 110.8, 57.1, 56.1, 51.8, 39.0, 30.9, 29.9, 27.1, 26.4, 25.4, 20.5, 20.4
Id	$CH_3(N(CH_2)_8NCH_3$	16	1.90, 2.38, 3.23	1.44,[b] 2.19, 3.4	7.44	174.4, 167.3, 160.4, 110.5, 57.9, 56.6, 51.8, 39.6, 30.9, 29.9, 25.8, 24.9, 22.1, 21.0, 20.0

[a] CD_3CN solution; ppm relative to Me_4Si. [b] Broad. [c] Multiplit. [d] CD_3NO_2 solution.

Table III. $E_{1/2}$ Values[a] for the First Oxidation of the Polymethylene-Bridged Nickel(II) Complexes

structure no.	bridge	$E_{1/2}$, V	ΔE, mV[b]
Ia	$CH_3\overline{N(CH_2)_4N}CH_3$	+0.790	70
Ib	$CH_3\overline{N(CH_2)_5N}CH_3$	+0.780	65
Ic	$CH_3\overline{N(CH_2)_6N}CH_3$	+0.775	65
Id	$CH_3\overline{N(CH_2)_7N}CH_3$	+0.740	70
Ie	$CH_3\overline{N(CH_2)_8N}CH_3$	+0.770	60
II	$CH_3\overline{N(CH_2)_6N}CH_3$[c]	+0.690	60

[a] Rotating platinum electrode; CH_3CN solution with Bu_4NBF_4 supporting electrolyte and Ag/Ag^+ (0.1 N) reference electrode. [b] $|E_{3/4} - E_{1/4}|$. [c] Complex containing 15-membered parent macrocycle.

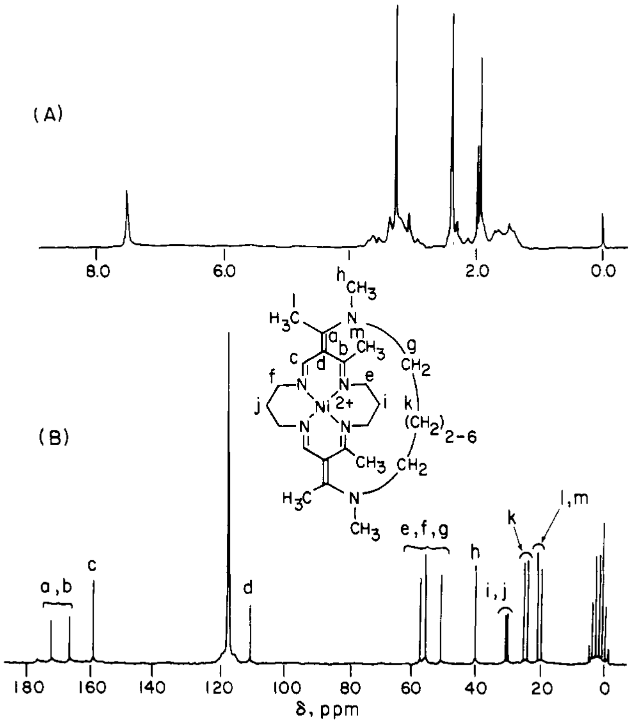


Figure 3. (A) Proton NMR spectrum of $[Ni((CH_2)_6(MeNEthi)_2Me_2[16]tetraeneN_4)](PF_6)_2$. (B) Carbon-13 NMR spectrum of $[Ni((CH_2)_6(MeNEthi)_2Me_2[16]tetraneneN_4)](PF_6)_2$.

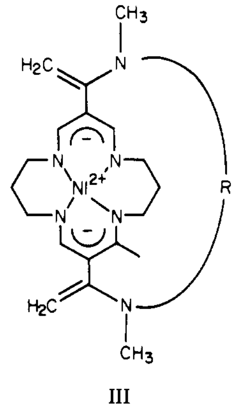
assigned on the basis of the off-resonance spectra, which show them to be methylene carbon atoms, and the relatively large methylene chemical shifts resulting from their positions α to a nitrogen atom.

The *N*-methyl of the bridge h appears as a peak in the range 41.3–39.4 ppm that splits into a quartet when the protons are allowed to couple to the carbon atoms in the CW experiment.

All of the complexes of ligands derived from the 16-membered macrocycle show two lower intensity peaks around 31 ppm due to carbons i and j. The 15-membered ring derivative shows only one peak in this region, as expected. The lower intensities of these peaks are due to the fact that these carbon atoms are unique and lie on the mirror symmetry element; thus they are expected to be approximately half the intensity of the other methylene peaks. The remainder of the methylene peaks in the region 29.9–21.5 ppm are due to the carbon atoms of the bridge.

On the basis of chemical shift and multiplicity in the off-resonance spectrum, two more peaks in the region around 21–22 ppm are assigned to the two methyl groups (l and m) of the parent macrocycle.

So that the monomeric structures of the dry cave complexes could be demonstrated, a neutral derivative was prepared from the hexamethylene-bridged species by deprotonation with use of an alkoxide. Reasonably good analytical data were obtained; the species is a nonelectrolyte on the basis of conductance measurements, and reprotonation produces the cationic starting material (exact ^{13}C NMR). The mass spectrum shows a parent ion at *m/e* 496 as expected for the monomeric species containing ^{58}Ni. This rather remarkable species is probably best described by structure III, in analogy to the previously described deprotonation product of the methoxyethylidene-precursor complex.[15,16]

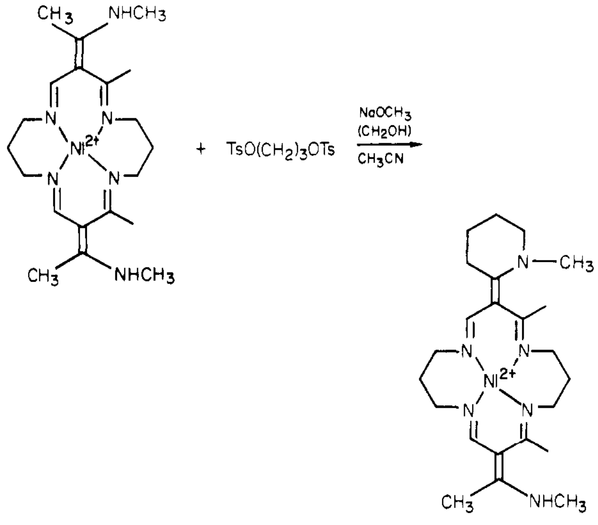


III

Definitive resolution of the question of the structures of these $CH_3\overline{N(CH_2)_nN}CH_3$-bridged derivatives has been accomplished by two X-ray crystal structure determinations on related cobalt complexes.[18] The ligand was first prepared on the nickel(II) ion, as described here, then removed and coordinated to cobalt.

Limits to the length of the homologous bridge have been indicated by the results of synthetic studies. Bridges shorter than four members, i.e., ethylene or trimethylene chains, seem unable to span the bridge position in the lacunar structure. Instead they produce *dimeric* ligands which are the subject of a separate publication. Similarly, complications occur for chains longer than those reported here. In this case mixtures of the *lacunar* and *dimeric* complexes are formed.

Dramatic illustration of the reluctance of the $(CH_2)_3$ linkage to span the bridging position for a dry cave structure comes from attempts to synthesize the corresponding *lacunar*-nickel(II) complex by the process described in Scheme I. As shown in eq 2, the bridging reaction is confined to one functional group, producing a piperidine. This cyclization strongly suggests that the vinyl methyl ionizes (as shown by the synthesis of the neutral complex of structure III) and acts as a nucleophile. The orange crystals analyzed well for structure IV (or for the isomeric lacunar complex). The compound was converted to its neutral derivative as described above for other complexes (structures III), and molecular weight studies both in solution (441 daltons by vapor-pressure osmometry) and in the gas phase (*m*/*e* parent ion 454 daltons) agreed with a monomeric stoichiometry (calcd mol wt 455.3 daltons). Spectral data completed the structure proof; the infrared spectra showed an amine NH stretch at 3358 cm^{-1} while proton NMR showed a broad amine proton resonance at 6.90 ppm. Both the proton and ^{13}C NMR spectra indicated the absence of mirror symmetry, each of the carbons being magnetically unique. Significantly, both proton and ^{13}C NMR spectra showed that the molecule possessed only five methyl groups, and the ^{13}C NMR spectrum also indicated the occurrence of some dynamic conformational process within the molecule at probe temperature. This motion was found to involve one *N*-methyl group, two vinyl carbons, and at least two methylene carbons. This data is best interpreted in terms of structure IV, the conformational dynamics being associated with the piperidine ring.



(2)

IV

Electrochemical Properties. Electrochemical measurements were obtained for the series of homologous $CH_3\overline{N(CH_2)_nN}CH_3$ bridged *lacunar*-nickel(II) complexes in acetonitrile. Data are given in Table III. The first oxidation step is believed to correspond to the nickel(II)-nickel(III) couple,[20] and therefore gives a measure of the electron density at the metal ion site. In addition to the first oxidation process, two more oxidations and one or two reductions are usually observed (Figure 4). The second oxidation occurs around +1.2 V and is usually reversible, while the third oxidation (1.7-2.0 V) often shows no counter peak in cyclic voltammetry. These two processes are probably due to ligand oxidations.

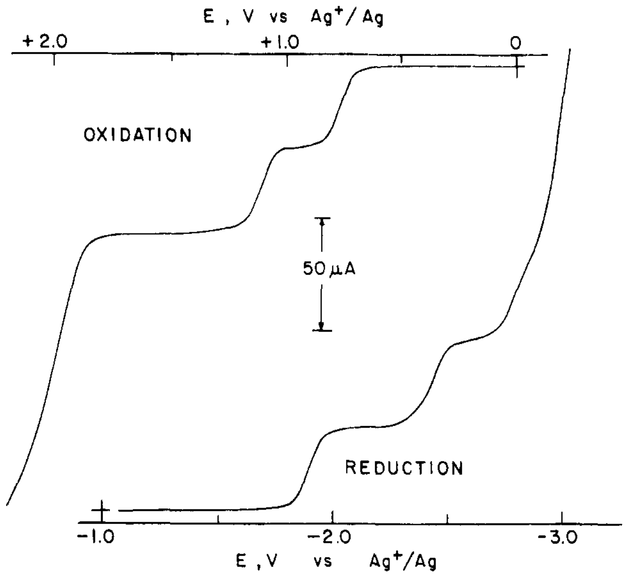


Figure 4. Voltammagram for $[Ni((CH_2)_6(MeNEthi)_2Me_2[16]tetraeneN_4)](PF_6)_2$ in 0.1 N *n*-Bu_4NBF_4 in CH_3CN; $Ag/AgNO_3$(0.1 N) as the reference electrode.

Examination of the potentials for the nickel(II)-nickel(III) couple reveals several interesting features. The value of $E_{1/2}$ is strictly *independent* of bridge length. Its value remains almost constant through the series at 0.771 ± 0.013 V. The small deviation is well inside the combined uncertainties of the quantities being compared. This is a matter of considerable significance since it has been found that the O_2 affinities of the corresponding cobalt(II) complexes vary across the series by some 5 orders of magnitude.[13] The constancy of the $E_{1/2}$ values for the nickel(II) complexes clearly show that the variation in the bridging chain does not force an obligatory alteration in electron density at the metal ion. It follows that the behavior of the cobalt-based oxygen carriers may be traced to steric effects and possibly to other geometric relationships. The change in length of the polymethylene chain alters the size of the cavity at the O_2 coordination site.

Removal of Ligand from Nickel(II) and Preparation of Ligand Salts. The role of nickel(II) is as a template in the synthesis of these bicyclic ligands. It must be replaced by metal ions appropriate to the function that is of immediate interest. In order to do this, it is necessary to remove the ligand from the Ni^{2+} ion. The special inertness of macrocyclic complexes[21] suggested that the ligand removal might be difficult. Also, the presence of C=N linkages in the ligand offered the possibility that ligand solvolysis might occur as has been observed often for free Schiff base ligands. Under conditions not conductive to C=N hydrolysis, other rearrangements have been noted for related ligand systems.[22,23]

The lacunar ligands can be removed from nickel(II) in good yield by the action of dry HCl in CH_3CN solution (eq 3). The progress of the reaction is indicated by the color change from the yellow of the *lacunar*-Ni^{2+} complex to the blue of $NiCl_4^{2-}$. The protonated ligand may be precipitated as the $ZnCl_4^{2-}$ or the PF_6^- salt. All of the ligands described here are completely removed from Ni^{2+} by a saturated HCl solution in ≤1 h at room temperature. The ligands are readily isolated as $ZnCl_4^{2-}$ salts; however these products often have undesirable physical properties and are difficult to purify. Consequently, it is convenient to metathesize the $ZnCl_4^{2-}$ salt to the PF_6^- salt. The preparation procedure is presented in the experimental section for the hexamethylene-

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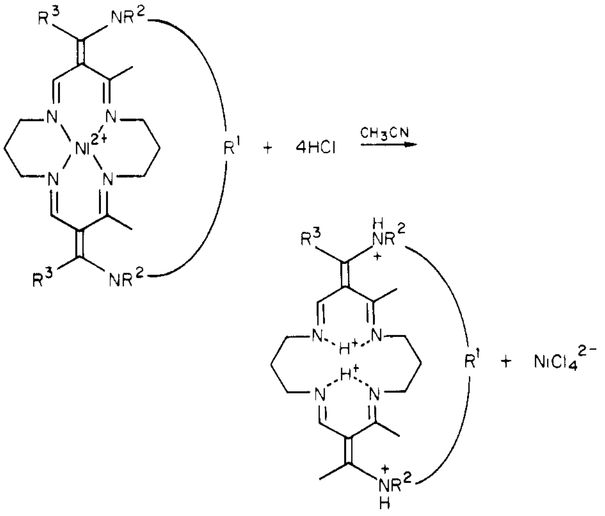
(20) Lovecchio, F. V.; Gore, E. S.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 3109-3118.

(21) Busch, D. H. *Acc. Chem. Res.* **1978**, *11*, 392-400.

(22) Tait, A. M.; Busch, D. H. *Inorg. Chem.* **1976**, *15*, 197-203.

(23) Skuratowicz, J. S.; Madden, I. L.; Busch, D. H. *Inorg. Chem.* **1977**, *16*, 1721-1725.



(3)

bridged ligand. The properties of the ligand salts will be detailed elsewhere.

Experimental Section

The solvents and reagents used in the synthesis of nickel(II) complexes were of reagent grade and were used without further purification unless otherwise noted.

Measurements. Elemental analyses were performed by Galbraith Laboratories, Inc. Infrared spectra were obtained as either Nujol mulls or KBr pellets. They were recorded on a Perkin-Elmer 457 grating infrared spectrometer. Mass spectra were run with an MS-9 mass spectrometer at 70 eV. Ultraviolet, visible, and near-infrared spectra were recorded on a Varian Instruments Carey Model 17D recording spectrophotometer.

Electrochemical measurements were performed with either an Indiana Instrument and Chemical Corp. controlled-potential and derivative voltmeter, Model ORN-1988A, with a Hewlett-Packard/Moseley Division XY recorder or a Princeton Applied Research Model 173 potentiostat/galvanostat and Model 175 universal programmer with a Houston Instrument Omnigraphic 2000 recorder. Measurements were made on CH_3CN solutions containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate as the supporting electrolyte. An H-type polarographic cell was employed. The working electrode was a platinum-disk electrode formed from the sealing of an 18-20-gauge platinum wire into soft glass. The reference electrode was a silver wire immersed in a 0.1 M CH_3CN solution of silver nitrate. All measurments were made in a Vacuum Atmospheres controlled-atmosphere chamber containing nitrogen. Proton NMR spectra were measured at 60 MHz on either a Varian A-60A or EM-360L spectrometer. ^{13}C NMR spectra were recorded on a Bruker WP-80 or HX90 spectrometer operating in the Fourier transform mode with the use of either broad band or off-resonance proton decoupling.

Conductance measurements were obtained with an Industrial Instruments, Inc., Model RC 16B, conductivity bridge on solutions of about 10^{-3} M. Molecular weight determination in chloroform solution used a Mechrolab Model 301A vapor phase osmometer at 37 °C.

(3,11-Diacetyl-4,10-dimethyl-1,5,9,13-tetraazacyclopentadeca-1,2,9,11-tetraeneato-*N*^{1},*N*^{5},*N*^{9},*N*^{13})nickel(II) [Ni(Ac_2Me_2[15]tetraeneatoN_4)] and (3,11-Diacetyl-4,10-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraeneato-*N*^{1},*N*^{5},*N*^{9},*N*^{13})nickel(II) [Ni(Ac_2Me_2[16]tetraeneatoN_4)]. These Jäger complexes were synthesized with use of previously published procedures.[24]

[2,11-Dimethyl-3,10-bis(1-methoxyethylidine)-1,5,8,12-tetraazacyclopentadeca-1,4,8,11-tetraene-*N*^{1},*N*^{4},*N*^{8},*N*^{11}]nickel(II) Hexafluorophosphate ([Ni($(MeOEthi)_2Me_2$[15]tetraeneN_4)]$(PF_6)_2$) and [2,12-Dimethyl-3,11-bis(1-methoxyethylidene)-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-*N*^{1},*N*^{5},*N*^{9},*N*^{13}]nickel(II) Hexafluorophosphate ([Ni($(MeOEthi)_2Me_2$[16]tetraeneN_4)]$(PF_6)_2$). These reagents were synthesized by published procedures.[15,16]

[2,12-Dimethyl-3,11-bis(1-(methylamino)ethylidene)-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-*N*^{1},*N*^{4},*N*^{9},*N*^{12}]nickel(II) Hexafluorophosphate ([Ni($(MeNHEthi)_2Me_2$[16]tetraeneN_4)]$(PF_6)_2$). This methylamine substitution product of methylated 16-membered ring Jäger complex was prepared according to the published procedure.[13]

(2,3,8,9,11,17-Hexamethyl-3,8,12,16,19,23-hexaazabicyclo[8.7.7]tetracosa-1,9,11,16,18,23-hexaene-κ^4*N*)nickel(II) Hexafluorophosphate ([Ni($(CH_2)_4(MeNEthi)_2$[16]tetraeneN_4)]$(PF_6)_2$). A 4.1-g sample (35.3 mmol) of *N*,*N'*-dimethyl-1,4-butanediamine dissolved in 1 L of acetonitrile was added slowly dropwise to solution of 25.0 g (35.3 mmol) of [Ni($(MeOEthi)_2Me_2$[16]tetraeneN_4)]$(PF_6)_2$ in 1 L of acetonitrile. The resultant deep red solution was rotary evaporated to dryness and the residue redissolved in 200 mL of acetonitrile. This solution was passed through a column (1.5-in. diameter, 15-in. length) of Woelm neutral alumina, eluting with acetonitrile. The broad yellow band was collected and rotary evaporated to about 50 mL whereupon the product began to precipitate. The slow addition of 100 mL of ethanol resulted in the formation of the yellow microcrystalline product which was collected by suction filtration and washed with ethanol and ether and dried in vacuo.

1,5-Bis(*p*-toluenesulfonato)pentane. A 26-g sample of 1,5-pentanediol (2.5 mol) was dissolved in 50 mL of pyridine and cooled in an ice bath. A 94.1-g sample (0.53 mol) of *p*-toluenesulfonyl chloride in 150 mL of pyridine was added dropwise over 1 h, during which time a white precipitate formed. The solution was stirred for 5 h and maintained at 0 °C throughout. Upon the slow addition of 1 L of H_2O, the white product precipitated and was isolated by suction filtration and washed with 1 L of cold water. The crude product was recrystallized by dissolving in 450 mL of hot methanol and cooling; yield 86.6 g (84%). The product was identified with ^{13}C NMR (relative to Me_4Si): 144.9, 133.2, 130.0, 127.8 (aromatic); 70.1, 28.2, 21.5 (methylene); 21.5 (methyl) ppm.

1,8-Bis(*p*-toluenesulfonato)octane. This compound was synthesized by using the same procedure as that for 1,5-bis(*p*-toluenesulfonato)pentane. 1,8-Octanediol (25 g) was allowed to react with 60.0 g of *p*-toluenesulfonyl chloride. The yield was 61 g (79%). ^{13}C NMR: 144.7, 133.4, 129.9, 127.8 (aromatic); 70.6, 28.7, 28.6, 25.1, 25.1 (methylene); 21.5 (methyl) ppm.

(2,3,9,10,19,25-Hexamethyl-3,9,13,17,20,24-hexaazabicyclo[9.7.7]pentacosa-1,10,12,17,19,24-hexaene-κ^4*N*)nickel(II) Hexafluorophosphate ([Ni($(CH_2)_5(MeNEthi)_2$[16]tetraeneN_4)]$(PF_6)_2$). A 10.9-g sample of [Ni($(MeNHEthi)_2Me_2$[16]tetraeneN_4)]$(PF_6)_2$ (15.4 mmol) was dissolved in 500 mL of acetonitrile under nitrogen in a 2-L three-neck round-bottomed flask equipped with a condenser, stir bar, and a 1-L dropping funnel.

A solution of 6.37 g of 1,5-bis(*p*-toluenesulfonato)pentane (15.4 mmol) dissolved in 500 mL of acetonitrile was placed in the dropping funnel. A solution prepared by reaction of 0.71 g of sodium metal (30.8 mmol) in 25 mL of methanol was added to the solution of the nickel complex, whereupon it turned deep red. The solution was brought to reflux under nitrogen, and the solution of the ditosylate was slowly added over a 4-h period, after which time the solution turned dark yellow-red and a white crystalline precipitate of sodium *p*-toluenesulfonate formed. The solution was concentrated on a rotary evaporator to about 100 mL and filtered through celite. A solution of 250 mL of methanol, saturated with ammonium hexafluorophosphate, was slowly added, and the solution was rotary evaporated to give the yellow microcrystalline product. Sometimes the product was dark brown and was chromatographed on alumina, eluting with acetonitrile.

(2,3,10,11,20,26-Hexamethyl-3,10,14,18,21,25-hexaazabicyclo[10.7.7]hexacosa-1,11,13,18,20,25-hexaene-κ^4*N*)nickel(II) Hexafluorophosphate ([Ni($(CH_2)_6(MeNEthi)_2$[16]tetraeneN_4)]$(PF_6)_2$). This bis(*N*-methyl), hexamethylene-bridged species could be synthesized by two routes: (1) by reacting *N*,*N'*-dimethyl-1,6-hexanediamine with [Ni($(MeOEthi)_2Me_2$[16]tetraeneN_4)]$(PF_6)_2$ or (2) in a manner analogous to the preceding synthesis by using 2.80 g (3.96 mmol) of [Ni($(MeNHEthi)_2Me_2$[16]tetraeneN_4)]$(PF_6)_2$, 0.54 g (7.94 mmol) of sodium, and 1.96 g (3.96 mmol) of 1,6-bis(*p*-toluenesulfonato)hexane. Yields: (1) 14.4–16.8 g (65–75%); (2) 2.25 g (72%).

(2,3,11,12,14,20-Hexamethyl-3,11,15,19,22,26-hexaazabicyclo[11.7.7]heptacosa-1,12,14,19,21,26-hexaene-κ^4*N*)nickel(II) Hexafluorophosphate ([Ni($(CH_2)_7(MeNEthi)_2Me_2$[16]tetraeneN_4)]$(PF_6)_2$). To a solution of 8.0 g (11.3 mmol) of [Ni($(MeNHEthi)_2Me_2$[16]tetraeneN_4)]$(PF_6)_2$ dissolved in 500 mL of acetonitrile was added a solution prepared by the reaction of 0.55 g (23.9 mmol) of sodium metal with 10 mL of methanol. The solution was brought to reflux, and 5.0 g (11.3 mmol) of 1,7-bis(*p*-toluenesulfonato)heptane dissolved in 250 mL of acetonitrile was added dropwise over a period of 6 h. When the addition was complete, the solution was evaporated to dryness and the residue was dissolved in 25 mL of acetonitrile. After filtrating through celite, the solution was applied to a column (2.5 cm × 25 cm) of neutral Woelm alumina and eluted with acetonitrile. The single yellow band was collected, and the volume of the solution was reduced. Addition of ethanol followed by further volume reduction resulted in formation of the yellow-orange product which was collected, washed with ethanol, and dried in vacuo.

(2,3,12,13,22,18-Hexamethyl-3,12,16,20,23,27-hexaazabicyclo[12.7.7]octacosa-1,13,15,20,22,27-hexaene-κ^4*N*)nickel(II) Hexafluorophosphate ([Ni($(CH_2)_8(MeNEthi)_2Me_2$[16]tetraeneN_4)]$(PF_6)_2$). This bis(*N*-methyl), octamethylene-bridged compound was synthesized in a

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(24) Riley, D. P.; Busch, D. H. *Inorg. Synth.* **1978**, *18*, 36–44.

J. Am. Chem. Soc. **1981**, *103*, 1478–1485

manner analogous to the preparation of the $(NMe)_2(CH_2)_5$ bridged derivative by using 5.6 g (7.9 mmol) of $[Ni((MeNHEthi)_2Me_2[16]tetraeneN_4)](PF_6)_2$ in 250 mL of acetonitrile, 0.36 g (15.8 mmol) of sodium in 25 mL of methanol, and 3.59 g (7.9 mmol) of 1,8-bis(*p*-toluenesulfonato)octane in 250 mL of acetonitrile. After the solution of the ditosylate was added, the mixture was refluxed for 18 under nitrogen. The dark solution was rotary evaporated to dryness, and the resulting product was dissolved in 25 mL of acetonitrile, and filtered through celite to remove sodium *p*-toluenesulfonate. The filtrate was chromatographed on a column of Woelm neutral alumina, eluting with acetonitrile. The orange-yellow band was collected and rotary evaporated to a small volume. The addition of methanol caused crystallization of the orange product.

(2,3,10,11,19,25-Hexamethyl-3,10,14,17,20,24-hexaazabicyclo[10.7.6]hexacosa-1,11,13,17,19,24-hexaene-κ^4N)nickel(II) Hexafluorophosphate ($[Ni((CH_2)_6(MeNEthi)_2[15]tetraeneN_4)](PF_6)_2$). This 15-membered macrocyclic dry cave complex was prepared by dissolving 5.0 g (7.19 mmol) of $[Ni((MeOEthi)_2Me_2[15]tetraeneN_4)](PF_6)_2$ in 500 mL of acetonitrile and slowly dripping in a solution of 1.04 g (7.19 mmol) of *N*,*N'*-dimethyl-1,6-hexanediamine in 500 mL of acetonitrile. The solution turned a dark brown-red and was rotary evaporated to give a viscous dark red oil which was dissolved in a minimum amount of acetone and chromatographed on an alumina column (3-in. diameter, 12–15-in. length) eluting slowly with a 1:1 mixture of acetone and dichloromethane. The light yellow band was collected, leaving numerous dark bands at the top of the column, and rotary evaporated to dryness, and the resulting product was slurried with absolute ethanol. The product was isolated, washed with ether, and dried in vacuo.

[3,10,13,19-Tetramethyl-2,11-dimethylene-3,10,14,18,21,25-hexaazabicyclo[10.7.7]hexacosa-12,19,20,25-hexaenato(2−)-κ^4N]nickel(II) [$Ni((CH_2)_6(1\text{-}MeN\text{-}vinyl)[16]hexaenatoN_4(2-))$]. All operations were carried out in a drybox. To a solution of 3.00 g of $[Ni((CH_2)_6(MeNEthi)_2[15]tetraeneN_4)](PF_6)_2$ in 25 mL of CH_3CN was added a solution of 1.00 g of potassium *tert*-butoxide in 20 mL of methanol. An immediate color change from yellow-orange to red-violet was observed. The solvent was removed under vacuum, and the residue was extracted with 75 mL of benzene. Inorganic salts were removed by filtration. The benzene was then removed under vacuum, and the purple solid was slurred in heptane or acetonitrile. The product was isolated by suction filtration and was dried in vacuo at room temperature. Anal. Calcd. for $NiC_{26}H_{42}N_6$: C, 62.79; H, 8.51; N, 16.90. Found: C, 63.37; H, 8.79; N, 16.28.

[3-(1-(Methylamino)ethylidene)-11-(1-methyl-2-piperidinylidene)-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-κ^4N]nickel(II) Hexafluorophosphate–Acetonitrile ($[Ni(Me_2(MAE)(MPip)[16]tetraeneN_4)](PF_6)_2\cdot CH_3CN$). A 1.51-g sample (0.0284 mol) of sodium methoxide in 10 mL of methanol was added to a 250-mL solution of 10 g (0.0142 mol) of (3,11-bis((1-methylamino)ethylidene)-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene)nickel(II) hexafluorophosphate in acetonitrile. The resulting red solution and another containing 5.44 g (0.0142 mol) of 1,3-ditosylpropane in 250 mL of acetonitrile were simultaneously dripped into 500 mL of refluxing acetonitrile, under an atmosphere of nitrogen, over a period of 5–6 h. The dark yellow solution was filtered to remove sodium tosylate and evaporated to a volume of 50 mL. Chromatography of this solution on a 25-cm Woelm neutral alumina column with acetonitrile eluent gave a single mobile yellow band which was collected and evaporated to dryness. The yellow-brown powder was recrystallized from acetonitrile saturated with ammonium hexafluorophosphate to yield large yellow-orange crystals containing one molecule of acetonitrile per complex, as solvent of crystallization; yield 4.8 g (45%). Anal. Calcd. for $Ni(C_{23}H_{38}N_6)(PF_6)_2\cdot CH_3N$: C, 38.09; H, 5.24; N, 12.44; Ni, 7.45. Found: C, 38.36; H, 5.24; N, 12.31; Ni, 7.27.

2,3,10,11,20,26-Hexamethyl-3,10,14,18,21,25-hexaazabicyclo[10.7.7]hexacosa-1,11,13,18,20,25-hexanene-N_4 Hexafluorophosphate ($[H_3((CH_2)_6(MeNEthi)_2Me_2[16]tetraeneN_4)](PF_6)_3$). Hydrogen chloride gas was bubbled through a solution of 5.00 g (6.33 mmol) of $[Ni((CH_2)_6(MeNEthi)_2Me_2[16]tetraeneN_4)](PF_6)_2$ in acetonitrile for approximately 10 min. The color of the solution did not turn deep blue as it did for most other dry cave complexes, but eventually it turned turquoise. The solvent was stripped by use of the rotary evaporator, and the residue was dissolved in 100 mL of water and 10 mL of absolute ethanol. To this solution was added a solution of 10.3 g of ammonium hexalfuorophosphate in 50 mL of water. Aliquots were added over a period of about 1 h. The cream colored solid formed was isolated by suction filtration, washed with ether, and dried in vacuo; yield 3.28 g (59%) of an off-white solid. The compound so isolated analyzed as a dihydrate. Anal. Calcd.: $C_{26}H_{51}N_6P_3F_{18}O_2$: C, 34.14; H, 5.62; N, 9.19. Found: C, 33.95; H, 5.40; N, 9.13. The water could be removed under vacuum at ~60 °C overnight, as evidenced by the disappearance of the band due to the O–H stretching mode from the infrared spectrum.

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Reaction of α,β-Unsaturated Acid Chlorides with Tris(triphenylphosphine)chlororhodium(I): Formation of Phosphonium Salts[1]

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Abstract: The reaction of (*E*)-cinnamoyl chloride and tris(triphenylphosphine)chlororhodium(I) in equivalent amounts in dichloroethane at 85 °C gives styryltriphenylphosphonium chloride and bis(triphenylphosphine)chlorocarbonylrhodium in good yields. (*E*)-2-Butenoyl chloride gives 1-propenyltriphenylphosphonium chloride, and (*E*)-2-heptenoyl chloride gives a mixture of 1- and 2-hexenyltriphenylphosphonium chlorides. 3-Methyl-2-butenoyl chloride gives only isobutylene. None of these α,β-unsaturated acid chlorides give the expected 1-chloro-1-alkene. Control experiments showed that the phosphonium salts are not formed by secondary reactions. Bis(triphenylphosphine)styryldichlorocarbonylrhodium was shown to be an intermediate in the formation of styryltriphenylphosphonium chloride. A study of the kinetics of decomposition of this intermediate showed that dissociation of chloride ion is the rate-determining step. The observed rate law is $-d[\text{intermediate}]/dt = k[\text{intermediate}]k'[PPh_3]/(k''[Cl^-] + k'[PPh_3])$. The significance of these observations for an understanding of the details of the "reductive elimination" reaction is discussed.

Wilkinson's catalyst (**1**) is known to be an effective stoichiometric reagent for the decarbonylation of acid chlorides under mild conditions and a catalyst for this process at elevated temperatures.[3,4] In the absence of a β-C–H bond in the substrate,

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