

The First [14]Cyclidene Complexes: Relationships between Macrocyclic Ring Size, Lacunar Cavity Shape, and Dioxygen Affinity of the Cobalt-Cyclidene Dioxygen Carriers

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The nickel(II) and cobalt(II) complexes have been synthesized and characterized as the first examples of metal complexes of a 14-membered cyclidene. [(2,3,16,17,19,25-Hexamethyl-3,16,20,23,26,29-hexaazabicyclo-[16.6.6]triaconta-1,17,19,23,25,29-hexaene-κ⁴N^{20,23,26,29})nickel(II)] hexafluorophosphate, NiC₃₀H₅₂N₆P₂F₁₂, crystallized in the orthorhombic space group *Pna*2₁, with *a* = 24.543(11) Å, *b* = 8.077(4) Å, *c* = 18.576(8) Å, and *Z* = 4. The structure revealed that the planar [14]cyclidene complex has a wide but very low cavity within which it might accommodate O₂, in sharp contrast to the deep-saddle shaped cavities of the 15- and 16-membered homologs. The cobalt(II) complex of the 14-membered cyclidene binds dioxygen reversibly at low temperatures with a reduced dioxygen affinity that has been ascribed to the cavity shape. Electrochemical data for the cobalt complex suggested that charge separation in the ligand system, which is caused by the twisting of the so-called vinyl groups, increases the electron density on the metal to some extent. Change in the parent macrocycle from a 16-membered ring to a 14-membered ring had little effect on the ESR spectra of the cobalt(II) complex and its dioxygen adduct. Autoxidation of the 14-membered cobalt(II) complex was found to be faster than that of its 16-membered analog, probably due to the more open cavity in the [14]cyclidene derivative and the more cathodic potential of its cobalt(III/II) couple.

Introduction

The lacunar cyclidenes constitute the first family of totally synthetic non-porphyrin ligands to form exceptionally efficacious O₂ carriers with both iron(II) and cobalt(II).¹⁻⁷ Favorable characteristics of the cyclidene based cobalt dioxygen carriers^{1,8} are (1) substantial dioxygen affinities at ambient and higher temperatures, (2) ability to function in a wide range of solvents, including water and various organic solvents, and (3) exceptional control over dioxygen affinity. The dioxygen binding properties depend markedly on the ligand substituents, as illustrated by the change in dioxygen affinity of the cobalt(II) [16]cyclidene complexes (see Figure 1B, Y = (CH₂)₃, R² = R³ = CH₃; or [Co(MeNMeC_n[16]cyclidene)]²⁺ in our simplified nomenclature⁹) by over four orders of magnitude on changing the polymethylene R¹ bridging group, -(CH₂)_n-, from *n* = 4 to *n* = 8.⁸ This strong dependence of the dioxygen binding characteristics on ligand substituents allows the influences of changes in ligand structure to be studied systematically. In addition, the cyclidene complexes have been modified in order to facilitate the formation of inclusion complexes with small organic molecules,¹⁰ making

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- (1) Stevens, J. C.; Busch, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 3285.
- (2) Herron, N.; Zimmer, L. L.; Grazybowski, T. T.; Olszanski, D. J.; Jackels, S. C.; Callahan, R. W.; Cameron, J. H.; Christoph, G. G.; Busch, D. H. *J. Am. Chem. Soc.* **1983**, *105*, 6585.
- (3) Herron, N.; Cameron, J. H.; Neer, G. L.; Busch, D. H. *J. Am. Chem. Soc.* **1983**, *105*, 298.
- (4) Herron, N.; Busch, D. H. *J. Am. Chem. Soc.* **1981**, *103*, 1236.
- (5) Schammel, W. P.; Mertes, K. S. B.; Christoph, G. G.; Busch, D. H. *J. Am. Chem. Soc.* **1979**, *101*, 1622.
- (6) Busch, D. H.; Olszanski, D. J.; Stevens, J. C.; Schammel, W. P.; Kijima, M.; Herron, N.; Zimmer, L. L.; Holter, K. S.; Mocak, J. *J. Am. Chem. Soc.* **1981**, *103*, 1472.
- (7) Busch, D. H.; Jackels, S. C.; Callahan, R. C.; Grazybowski, J. J.; Zimmer, L. L.; Kojima, M.; Olszanski, D. J.; Schammel, W. P.; Stevens, J. C.; Holter, K. A.; Mocak, K. *Inorg. Chem.* **1981**, *20*, 2834.
- (8) Busch, D. H. In *Oxygen Complexes And Oxygen Activation By Transition Metals*; A. E. Martell, D. T. Sawyer, Eds.; Plenum Publ. Corp.: New York, 1988.
- (9) For convenience, a simplified nomenclature has been developed for the cyclidene complexes. Following the labelling of substituents in Figure 1, a cyclidene complex may be identified as follows. [Metal-(R³NR²R¹[ring size]Cyclidene)]^{valence}. For example, for the cobalt complex of the 16-membered ring cyclidene complex with R¹ = (CH₂)₆, R² = R³ = CH₃, the nomenclature would be [Co(MeNMeC₆[16]cyclidene)]²⁺.

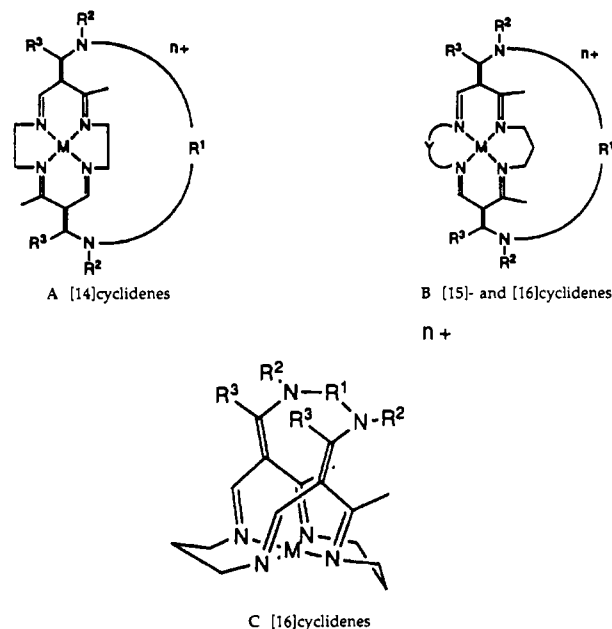


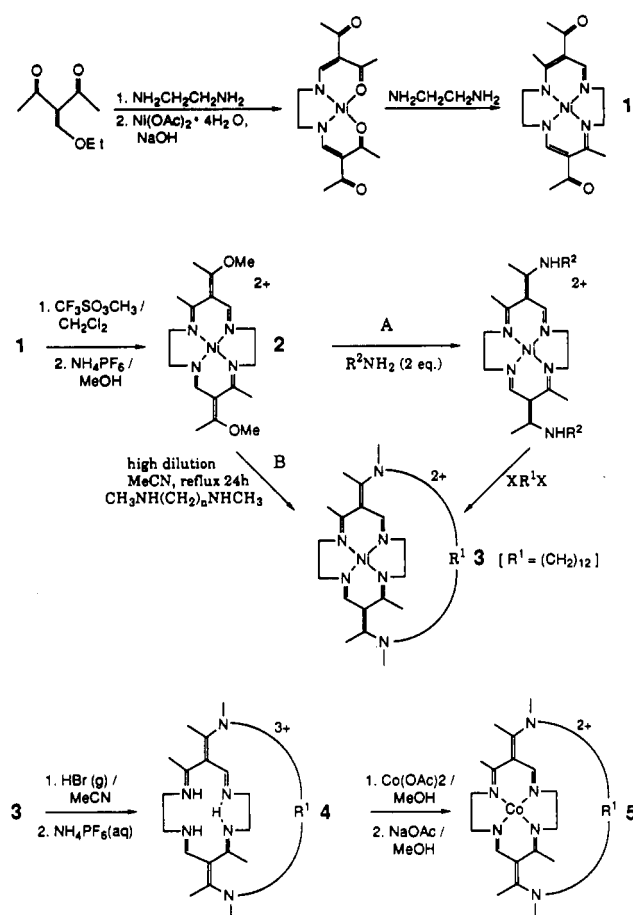
Figure 1. Structures of the [14]cyclidenes (A), and [15]- and [16]cyclidenes (B), and stereochemical view of [16]cyclidenes (C).

them realistic models for enzymes, such as cytochromes P450, which bind both dioxygen and substrates prior to the catalytic event. The broad range of cyclidene complexes is summarized in recent reviews and the literature cited therein.^{8,11-13}

In examining the effect on dioxygen binding properties, ligand substitution has received much attention, but variation of the parent cyclidene ring has not yet been explored extensively. Previous studies on the cyclidene complexes have concentrated

- (10) Meade, T. J.; Takeuchi, K. J.; Busch, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 725.
- (11) Busch, D. H. *La Trasfusione del Sangue* **1988**, *33*, 57.
- (12) Busch, D. H.; Cairns, C. In *Synthesis of Macrocycles: The Design of Selective Complexing Agents*; R. M. Izatt, J. J. Christensen, Eds.; J. Wiley & Sons: New York, 1987.
- (13) Busch, D. H.; Stephenson, N. A. In *Inclusion Compounds, Volume 5: Inorganic & Physical Aspects of Inclusion*; J. Atwood, D. MacNual, Eds.; Oxford Univ. Press: Oxford, U.K., in press.

Scheme I



on those with a 16-membered ring ($\text{Y} = (\text{CH}_2)_3$ in Figure 1B) with some investigation of the 15-membered ($\text{Y} = (\text{CH}_2)_2$ in Figure 1B) macrocycles.^{14,15} In both cases, the shape of the deep saddle conformation of the parent cyclidene ring facilitates the formation of the bridged derivatives (Figure 1C). In contrast, the cyclidene precursor with a 14-membered ring is virtually planar.¹⁶ The bridging reaction in these complexes is likely to be less favorable, and the cavities in the resulting lacunar complexes can be expected to be very different in shape from those of the [15]- and [16]cyclidenes, leading to distinctive and perhaps valuable properties.

This study has therefore examined the synthesis of the nickel(II) and cobalt(II) complexes of [14]cyclidene, with a polymethylene bridging group at the R^1 position, the structure of the nickel complex, and the dioxygen binding ability, autoxidation and other properties of the cobalt(II) complex.

Results and Discussion

Synthesis. The reaction sequence leading to the 14-membered bridged cyclidene complexes is shown in Scheme I. The neutral square planar nickel(II) complex that serves as starting material 1 was first synthesized by Jaeger.¹⁷⁻¹⁹ Methylation proceeded as in other cyclidenes,²⁰ but the bridging reaction proved difficult. Route A²⁰ failed (with $\text{X} = \text{OTs}$, Br or Cl), but route B, using a secondary amine to attach R^1 and R^2 simultaneously, was

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

(15) Thomas, R.; Fendrick, C. M.; Lin, W. K.; Glogowski, M. W.; Chavan, M. Y.; Alcock, N. W.; Busch, D. H. *Inorg. Chem.*, **1988**, *27*, 2534.

(16) Alcock, N. W.; Lin, W.-K.; Jircitano, A.; Mokren, J. D.; Corfield, P. W. R.; Johnson, G.; Novotnak, G.; Cairns, C.; Busch, D. H. *Inorg. Chem.* **1987**, *26*, 440.

(17) Jaeger, E. *Z. Anorg. Allg. Chem.* **1966**, *346*, 76.

(18) Jaeger, E. *Z. Chem.* **1968**, *8*, 30.

(19) Jaeger, E. *Z. Chem.* **1968**, *8*, 392.

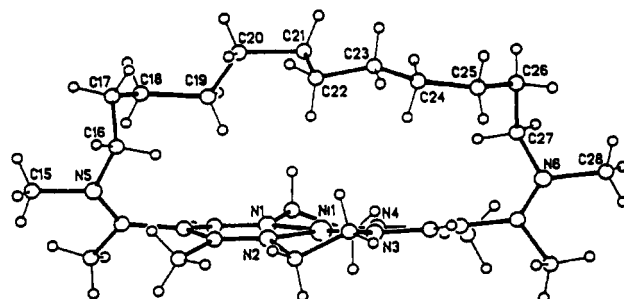


Figure 2. Front view of $[\text{Ni}(\text{MeNMeC}_{12}[\text{14}]\text{cyclidene})](\text{PF}_6)_2$ structure from X-ray determination.

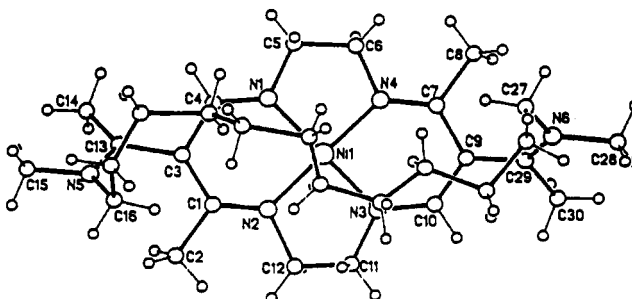


Figure 3. Top view of $[\text{Ni}(\text{MeNMeC}_{12}[\text{14}]\text{cyclidene})](\text{PF}_6)_2$ structure from X-ray determination.

Table I. Selected Dimensions (Å) for $[\text{Ni}(\text{MeNMeC}_{12}[\text{14}]\text{cyclidene})](\text{PF}_6)_2$ (3)

Ni1-N1	1.83(3)	Ni1-N2	1.86(2)
Ni1-N3	1.86(3)	Ni1-N4	1.87(2)
N1-C4	1.27(3)	N1-C5	1.48(4)
N2-C1	1.28(3)	N2-C12	1.55(3)
N3-C10	1.32(4)	N3-C11	1.45(4)
N4-C7	1.29(3)	N4-C6	1.43(3)
C1-C3	1.42(4)	C3-C4	1.44(4)
C7-C9	1.44(4)	C9-C10	1.36(4)
C3-C13	1.48(4)	C9-C29	1.37(4)
C13-N5	1.31(3)	C29-N6	1.30(4)
N5-C16	1.44(4)	N6-C27	1.45(4)

successful though only with the longest chain ($(\text{CH}_2)_n$, $n = 12$) and not with $n = 8$ or 10. The preparation of the free ligand salt 4 from the nickel(II) complex 3 followed the procedure used for the [16]cyclidenes,²⁰ and $[\text{Co}(\text{MeNMeC}_{12}[\text{14}]\text{cyclidene})]^{2+}$ 5 was prepared by mixing solutions of cobalt(II) acetate and the ligand salt in an inert atmosphere box as described earlier for other cyclidenes.²² Elemental analysis suggested that its crystals include lattice methanol and water.

X-ray Structural Analysis of $[\text{Ni}(\text{MeNMeC}_{12}[\text{14}]\text{cyclidene})](\text{PF}_6)_2$. Although crystal quality was poor, with considerable disorder in both the anions and the $(\text{CH}_2)_{12}$ bridge, the overall structure is clearly defined. Figures 2 and 3 show the front and top views of the cation, and Table I gives selected dimensions. As already noted, in contrast to the 15- and 16-membered homologs, the ring methyl groups occupy *trans* positions in this [14]cyclidene derivative. The 14-membered macrocycle ring in $[\text{Ni}(\text{MeNMeC}_{12}[\text{14}]\text{cyclidene})](\text{PF}_6)_2$ (complex 3 in Scheme I) is almost perfectly flat; the only apparent deviations from planarity are in the saturated chelate rings where the $(\text{CH}_2)_2$ groups are twisted to relieve the eclipsing of the C-C bonds (torsional angles C5-C6 and C11-C12, 36.0° and 42.3° , respectively). The bridgehead vinyl groups are forced far from

(20) Korybut-Daszkiwicz, B.; Kojima, M.; Cameron, J. H.; Herron, N.; Chavan, M. Y.; Jircitano, A. J.; Coltrain, B. K.; Neer, G. L.; Alcock, N. W.; Busch, D. H. *Inorg. Chem.* **1984**, *23*, 903.

(21) Alcock, N. W.; Padolik, P. A.; Pike, G. A.; Kojima, M.; Cairns, C. J.; Busch, D. H. *Inorg. Chem.* **1990**, *29*, 2600.

(22) Cameron, J. H.; Kojima, M.; Korybut-Daszkiwicz, B.; Coltrain, B. K.; Meade, T. J.; Alcock, N. W.; Busch, D. H. *Inorg. Chem.* **1987**, *26*, 427.

Table II. Calculated Steric Energies for [14], [15], and [16] Jaeger and Unbridged Cyclidene Complexes of Nickel(II)^a

ring size	Z-shape			U-shape			$E_Z - E_U$
	E_{Steric}	$d_{\text{CA}-\text{CA}'}$	δ	E_{Steric}	$d_{\text{CA}-\text{CA}'}$	δ	
[Ni{Ac ₂ Me ₂ tetraenatoN ₄ }]							
[14]	36.9	9.35	19.2	41.0	8.59	15.8	-4.1
[15]	44.9	9.06	17.2	48.9	7.31	15.1	-4.0
[16]	46.6	8.81	14.0	46.2	6.46	15.5	+0.4
[Ni(MeNMeHcyclidene)] ²⁺							
[14]	48.0	9.33	38.2	51.9	8.88	38.9	-3.9
[15]	55.2	9.04	33.7	59.0	7.15	26.8	-3.8
[16]	56.5	8.73	18.8	55.2	6.23	20.5	+1.3
[Ni(MeNMeMecyclidene)] ²⁺							
[14]	59.7	9.35	61.7	62.6	8.80	61.6	-2.9
[15]	65.9	9.13	60.5	70.0	7.53	61.0	-4.0
[16]	67.8	8.96	58.7	66.8	6.79	61.2	+1.0

^a E_{Steric} is the minimized steric energy, in kcal/mol; $d_{\text{CA}-\text{CA}'}$ is the distance between the acyl or vinyl carbon atoms, in Å; the torsion angle δ is the average of two values, in deg. For the meanings of $d_{\text{CA}-\text{CA}'}$ and δ , see Figure 5.

coplanarity with the unsaturated chelate rings to which they are attached, and the C3–C13 and C9–C29 bond distances, 1.42 and 1.48 Å respectively, approach single bond dimensions. The dodecamethylene group traverses directly across the macrocycle, striking a jagged line that very nearly bisects the planar macrocyclic nickel complex.

It is important to contrast the 3-dimensional structure of the [14]cyclidene with those of the [15]- and [16]cyclidenes, especially the latter. As Figure 1C shows, the unsaturated chelate rings of the [16]cyclidene combine with the bridging group to form a protected cavity within which an O₂ molecule is confined when it binds to the metal ion. In contrast, the entire parent macrocycle of [14]cyclidene is essentially flat and the O₂ bound to its metal ion will project up from that plane, finding only limited protection, and that from the bridging group alone.

The *trans* ring methyl configuration of the [14]cyclidene is probably established at the ring closure step, which leads to complex 1 (Scheme I), as shown by X-ray structure determination.¹⁶ In contrast, the ring methyl configuration of the acyclic precursor to 1, Ni{N₂O₂}, is almost certainly *cis* since it can be closed by H₂N(CH₂)₃NH₂ to give a 15-membered ring with *cis* methyl groups.¹⁶ Therefore, the closure reaction must be associated with a number of competing reactions. Molecular mechanics calculations indicate that the minimized total steric energies of the *trans* and *cis* isomers of the 14-membered complex 1 in Scheme I are about the same ($E_{\text{cis}} - E_{\text{trans}} = 0.1$ kcal/mol).

In earlier X-ray and molecular mechanics studies,^{15,16,23–26} we have shown that the 16-membered ring cyclidenes, Jaegers and related macrocycles, favor the deep saddle, or U-shape over the relatively flat Z-shape, while for the 15-membered cyclidenes, either structure may be more stable. Similar calculations for the 14-membered ring derivatives have now been performed on the Jaeger complexes ([Ni{Ac₂Me₂tetraenatoN₄}] and the unbridged cyclidene complexes (both [Ni(MeNMeH[14]cyclidene)]²⁺ and [Ni(MeNMeMecyclidene)]²⁺) (Table II). Results are compared with those for the corresponding 15- and 16-membered ring derivatives. The steric energies of the 14-membered Z-shape, or planar structures, are always the lowest in any series. Further the energy differences, $E_Z - E_U$, support the expected preference for planarity over the saddle shape for the 14-membered macrocyclic complexes. Comparing results for the ligands

(23) Alcock, N. W.; Lin, W.-K.; Cairns, C.; Pike, G. A.; Busch, D. H. *J. Am. Chem. Soc.* **1989**, *111*, 6630.

(24) Jackson, P. J.; Cairns, C.; Lin, W. K.; Alcock, N. W.; Busch, D. H. *Inorg. Chem.* **1986**, *25*, 4015.

(25) Chia, P. S. K.; Alcock, N. W.; Nosco, D.; Masarwa, M.; Warburton, P. R.; Wu, W.; Busch, D. H. Paper in preparation.

(26) Lin, W.-K.; Alcock, N. W.; Busch, D. H. *J. Am. Chem. Soc.* **1991**, *113*, 7603.

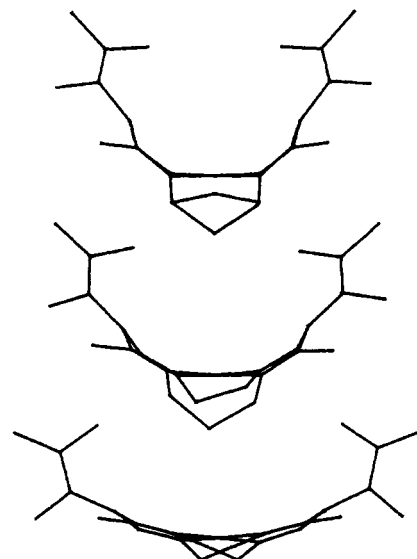


Figure 4. Profile of the cleft in cyclidene complexes based on molecular mechanics energy minimized structures. The cleft widths increase from [16]- (top) to [15]- (middle) to [14]-membered derivatives (bottom). This pattern occurs for all three families of compounds listed in Table II. Hydrogens were omitted for clarity.

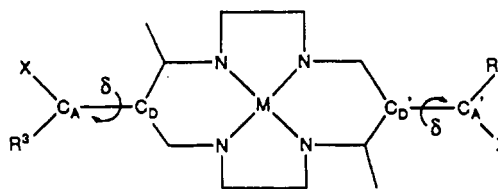


Figure 5. Torsional angle δ for the C3–C13 and C9–C29 Bonds.

(MeNMeHcyclidene) and (MeNMeMecyclidene), it seems that the bulkiness of the substituents has little effect on the steric energy pattern (in all cases, $E_Z - E_U$ is negative for [14] and [15], positive for [16]).

The distance between the pair of acyl or vinyl carbon atoms, in any given structure, is a fair measure of the width of the cleft for these structures (U-shape only) and these values are also reported in Table II. The width of the cleft among the three U-shaped complexes decreases from [14] to [16] (Figure 4). Since the dioxygen affinities of the cobalt(II) and iron(II) [16]cyclidene complexes depend strongly on the cavity widths,^{6,11} one might expect that the dioxygen affinities of the [16], [15], and [14] cyclidene complexes at the same polymethylene bridge length would follow the same trend as the cleft width. This is true for corresponding pairs of [15]- and [16]cyclidene complexes, both of which have the U-shape,²⁷ but the relative dioxygen affinity of the [14] complexes is complicated by existence of that species in the Z-shape, which produces a different set of strong interactions between the bridge and the bound dioxygen (vide infra).

From the crystal structure of [Ni(MeNMeC₁₂[14]cyclidene)](PF₆)₂ the C3–C13/C9–C29 torsional angles (δ in Figure 5 and Table II) are 51° and 58°, respectively; these values are substantially larger than those in [16]cyclidenes (24–42° in the absence of cavity-bound ligands).²³ It is reasonable to assume that the δ value results from compromise between good overlap in the conjugated π system and steric interactions between substituents, as modified by packing forces in the crystalline compound. Analysis of the δ values in Table II suggests that the most important factor in determining these torsional angles is the steric hinderance between the attached acyl or vinyl groups and the ring methyl groups. In the cases of [Ni(MeNMeMecyclidene)]²⁺, the number of methylene groups in the saturated chelate

(27) Warburton, P. R.; Busch, D. H. Unpublished results.

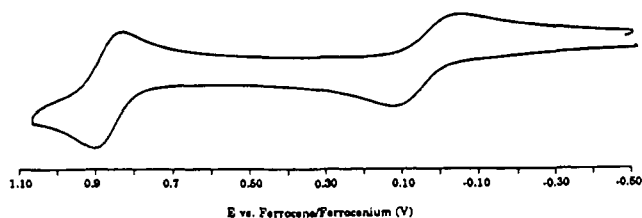


Figure 6. Cyclic voltammogram of $[\text{Co}(\text{MeNMeC}_{12}[14]\text{cyclidene})](\text{PF}_6)_2$ in CH_3CN with 0.5 M tetrabutylammonium tetrafluoroborate.

rings, the parent macrocycle conformations, and the orientations of bridge-head nitrogens are all unimportant; i.e., the torsion angle is the same for all 6 structures Z/U [14]/[15]/[16]. Molecular mechanics calculation on complex 3 ($[\text{Ni}(\text{MeNMeC}_{12}[14]\text{cyclidene})]^{2+}$) also gave a very similar averaged δ value of 61.2° . The fact that many [16]cyclidene complexes with very different bridge lengths give similar δ values²³ indicates that the effects of bridges on δ are also minimal. The large δ values in complex 3 will hinder π overlap in the C3–C13 and C9–C29 bonds, and lead to a charge separation in the macrocycle, placing charge density on the nitrogen atoms that bind the metal ion.²⁸ This should enhance the dioxygen affinities of the cobalt complexes.

Because of the flat shape of the parent macrocycle, the $(\text{CH}_2)_{12}$ chain in Figure 3 is almost completely extended, that extension being moderated mainly by the lower energies of gauche, compared to eclipsed C–C conformations. The twisting of N5 and N6 toward *trans* orientations makes the required minimum bridge length (R , Figure 1A) even longer by demanding that the bridge be somewhat S-shaped. The difficulty of bridging the 14-membered macrocyclic complex with shorter chains is clear; they are either too short for closure to occur, or they force the parent macrocycle to deviate from its favored flat conformation. The resulting cavity of complex 3 is wide but very shallow (Ni to C22, 3.971 Å; C16 to C27, 9.739 Å; N5 to N6, 10.671 Å, as contrasted to a minimum observed height of about 4.5 Å and maximum width of about 7.8 Å for a [16]cyclidene complex). From the low cavity it is anticipated that dioxygen binding of the cobalt complex will be subject to significant steric hinderance (reversing the predictions based on electronic considerations).

Electrochemistry. Cyclic voltammograms of $[\text{Co}(\text{MeNMeC}_{12}[14]\text{cyclidene})](\text{PF}_6)_2$ were obtained in acetonitrile in an inert atmosphere box (Figure 6). On scanning anodically, two oxidative processes were observed, the first of which was identified as a metal-centered reaction and the second as a ligand centered oxidation, by analogy with the [16]cyclidene complexes.²⁹ The cobalt(III)/(II) couple is quasi-reversible, ($E_{1/2} = 0.095$ V vs Fc/Fc⁺, $\Delta E_p = 230$ mV); the large peak separation probably arises from the well-known coordination number change (from five to six) by cobalt complexes upon oxidation. Analogous behavior has been observed for the [16]cyclidene complexes of cobalt in acetonitrile.²⁹ The more drawn-out shape of the Co(III)/II cathodic peak is also consistent with a so-called CE process,³⁰ involving association of the sixth ligand (probably CH_3CN) with the cobalt(II) prior to oxidation to cobalt(III). In contrast to the metal centered oxidation, the voltammogram of the ligand oxidation process is notably more reversible ($E_{1/2} = 0.865$ V, $\Delta E_p = 90$ mV). The excess in ΔE_p over 60 mV may arise from ohmic drop, as is frequently found when using resistive non-aqueous solvents. The much smaller peak separation of the ligand centered redox couple compared to the metal centered process is consistent with the lesser geometrical rearrangement associated

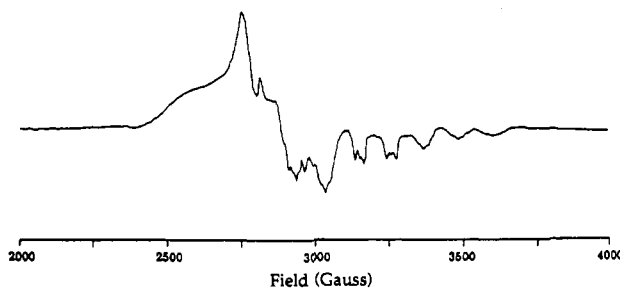


Figure 7. ESR spectrum of $[\text{Co}(\text{MeNMeC}_{12}[14]\text{cyclidene})](\text{PF}_6)_2$ in CH_3CN with 1.5 M *N*-methylimidazole at 77 K.

with electron transfer. Similar behavior has been discussed by Mu and Schultz with reference to porphyrin complexes.³¹

The redox potentials for the [16]cyclidene complexes of cobalt(II) span the range from 0.21 to 0.50 V (vs Fc/Fc⁺), depending on bridge length.²⁹ Comparison of the redox potential of $[\text{Co}(\text{MeNMeC}_{12}[14]\text{cyclidene})]^{2+}$ ($E_{1/2} = 0.095$ V) with that of the 16-membered analogues places the value for the [14]cyclidene at the cathodic extremity of the group of [16]cyclidenes. The variations in the potentials for the complexes of the [16]cyclidenes have been ascribed to accessibility of the lacunae to solvent and other small ligands.²⁹ The open structure of the [14]cyclidene complex suggests that the metal atom in [14]cyclidenes is easily approached by such ligands. However, the relatively cathodic potential of the [14]cyclidene complex also supports the hypothesis that the twisting of the so-called vinyl groups leads to an increase in electron density at the metal ion.

ESR Spectra. The ESR spectrum (Figure 7) for $[\text{Co}(\text{MeNMeC}_{12}[14]\text{cyclidene})]^{2+}$ in acetonitrile with 1.5 M *N*-methylimidazole at 77 K is qualitatively very similar to those of the cobalt(II) [16]cyclidenes.¹ The tensor g_{\parallel} is split into an eight line pattern by interaction of the unpaired electron spin with the ⁵⁹Co nucleus ($I = 7/2$), with a hyperfine coupling constant (A_{\parallel}) of about 110 Gauss. Several of these hyperfine lines are themselves split into triplets by superhyperfine coupling of the electron spin with the nitrogen atom (¹⁴N $I = 1$) of a single axial *N*-methylimidazole with a coupling constant (A_N) of about 16 Gauss. These spectral parameters are consistent with a low spin, five-coordinate cobalt(II) d^7 configuration, with the unpaired electron in the d_{z^2} orbital. The spectrum closely approximates axial symmetry and has values for g_{\parallel} of about 2.064 and g_{\perp} of about 2.272, again similar to those for the [16]cyclidenes.⁶ Thus the ring size of the parent macrocycle has little effect on the ESR spectral parameters.

The ESR spectrum for the dioxygen adduct of $[\text{Co}(\text{MeNMeC}_{12}[14]\text{cyclidene})]^{2+}$ in acetonitrile with 1.5 M *N*-methylimidazole was obtained after bubbling dioxygen gas through a solution of the respective cobalt(II) cyclidene complex, followed by freezing in liquid nitrogen. The spectrum (Figure 8, $g_{\parallel} = 2.119$, $g_{\perp} = 2.022$, $A_{\parallel} = 19$ Gauss, $A_{\perp} = 14$ Gauss) is similar to those of the dioxygen adducts of the cobalt(II) [16]cyclidenes⁶ and highly characteristic of 1:1 mononuclear cobalt(II) dioxygen adducts,^{1,32–34} but notably different from that of the initial five-coordinate cobalt(II) complex.

Reversible Dioxygen Binding by $[\text{Co}(\text{MeNMeC}_{12}[14]\text{cyclidene})(N\text{-ethylimidazole})]^{2+}$. At temperatures below -10°C , the autoxidation rate for $[\text{Co}(\text{MeNMeC}_{12}[14]\text{cyclidene})]^{2+}$ is sufficiently slow to allow accurate measurements of the dioxygen binding equilibrium constant, K_{O_2} . For this complex, K_{O_2} values have been measured at 240.6, 250.1, and 255.4 K in CH_3CN with 1.5 M *N*-methylimidazole (*N*-MIm) as the axial base, giving

(28) Masarwa, M.; Sauer-Masarwa, A.; Ye, N.; Busch, D. H. Paper submitted to *J. Coord. Chem.*, in review.

(29) Chavan, M. Y.; Meade, T. J.; Busch, D. H.; Kuwana, T. *Inorg. Chem.* **1986**, *25*, 314.

(30) Saveant, J. M.; Vianello, E. *Electrochim. Acta* **1963**, *8*, 905.

(31) Mu, X. H.; Schultz, F. A. *Inorg. Chem.* **1990**, *29*, 2877.

(32) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139.

(33) Smith, T. D.; Pilbrow, J. R. *Coord. Chem. Rev.* **1981**, *39*, 295.

(34) Torrog, B. S.; Kitko, D. J.; Drago, R. S. *J. Am. Chem. Soc.* **1976**, *98*, 5144.

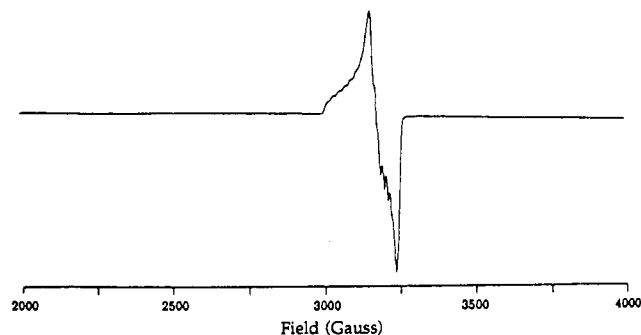


Figure 8. ESR spectrum of the dioxygen adduct of $[\text{Co}(\text{MeNMeC}_{12}[14]\text{cyclidene})](\text{PF}_6)_2$ in CH_3CN with 1.5 M *N*-methylimidazole at 77 K.

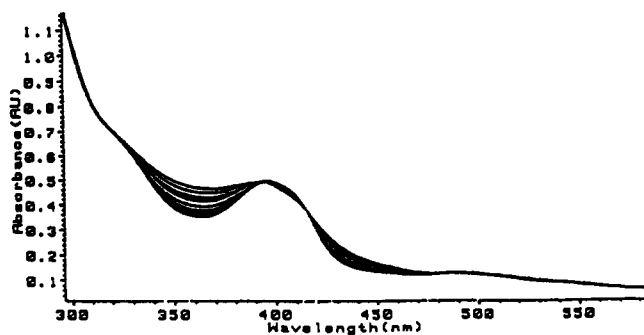


Figure 9. UV-visible spectral change for $[\text{Co}(\text{MeNMeC}_{12}[14]\text{cyclidene})](\text{PF}_6)_2$ upon oxygenation in CH_3CN with 1.5 M *N*-methylimidazole at -17.6°C .

values of 0.62, 0.11, and 0.050 Torr⁻¹, respectively. The estimated errors in K_{O_2} values are about 10%. The spectroscopic changes accompanying dioxygen titration (Figure 9) are similar over the temperature range; increases in absorbance occur around 362 nm and 440 nm, a decrease around 410 nm, and isobestic points at 500 nm, 415 nm, 390 nm and 310 nm. The K_{O_2} values were obtained by the method of Stevens^{2,35} from a double reciprocal plot of the absorbance change versus dioxygen concentration at 362 nm; excellent straight-line plots were obtained in all cases.

The values of K_{O_2} for $[\text{Co}(\text{MeNMeC}_{12}[14]\text{cyclidene})]^{2+}$ are much greater than those of $[\text{Co}(\text{MeNMeC}_4[16]\text{cyclidene})]^{2+}$, but a factor of about 10 smaller than those of $[\text{Co}(\text{MeNMeC}_5[16]\text{cyclidene})]^{2+}$.³⁶ It is likely that the affinity reflects substantial, but not extreme steric interactions between the bound dioxygen and the bridge, since electronic considerations suggest that dioxygen affinities of $[\text{Co}(\text{MeNMeC}_{12}[14]\text{cyclidene})]^{2+}$ should be at the high end of those of cobalt(II) [16]cyclidene complexes. This postulate is supported by molecular mechanics calculations. Dioxygen affinities of the cobalt(II) [16]cyclidene complexes have been successfully correlated to the steric energy differences ($E_6 - E_5$) between a 6-coordinated dioxygen adduct and its 5-coordinated deoxy form.²⁶ In order to study how its bridge affects the dioxygen affinity of $[\text{Co}(\text{MeNMeC}_{12}[14]\text{cyclidene})]^{2+}$, we compared its ($E_6 - E_5$) with that of $[\text{Co}(\text{MeNMeC}_4[16]\text{cyclidene})]^{2+}$. The value of ($E_6 - E_5$) for the bridged complex was calculated to be 5.5 kcal/mol higher. This difference should certainly be ascribed to the repulsive interactions between the bridge and the dioxygen ligand. Our modeling studies also show that the bridge-dioxygen interactions produce significant distortions of the whole molecule (Figure 10). In order to accommodate the dioxygen moiety, the C_{12} bridge of $[\text{Co}(\text{MeNMeC}_{12}[14]\text{cyclidene})]^{2+}$ is displaced upward (away from the CoN_4 coordination plane, Figure 10A) and toward one side of the structure (Figure 10B), and its parent macrocycle is forced to bend into a shallow U-shape (Figure

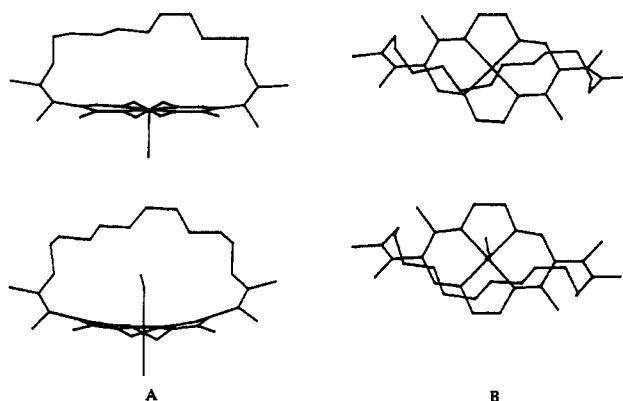


Figure 10. Comparison of the dioxygen adduct of $[\text{Co}(\text{MeNMeC}_{12}[14]\text{cyclidene})]^{2+}$ and its deoxy form: (A) view into cavity looking edgewise at the coordination plane; (B) view looking down onto coordination plane. Hydrogens are omitted for clarity, and, for modeling purposes, the axial base is a chloride ion. Drawings are based on results of molecular mechanics calculations.

Table III. Dependence of Autoxidation Rates on Temperature and Dioxygen Concentration^a

P , Torr	T , K	k , s ⁻¹	P , Torr	T , K	k , s ⁻¹
152	255.0	9.3×10^{-5}	1.9	298.1	1.8×10^{-4}
152	266.9	3.1×10^{-4}	7.6	298.1	3.5×10^{-4}
152	277.3	6.4×10^{-4}	38	298.1	1.2×10^{-3}
152	283.2	8.0×10^{-4}	152	298.1	1.2×10^{-3}

^a P : pressure of dioxygen used to saturate the solution of cobalt(II) cyclidene complex. k : observed autoxidation rate; estimated uncertainty <10%.

10A). The distances from cobalt to the two middle carbon atoms are 5.5 and 6.1 Å in the dioxygen adduct but only 4.0 and 4.9 Å in the deoxy species. Further, the $\angle\text{C}_A\text{-Co-C}_{A'}$ for the dioxygen adduct is 161.3° ; that for its deoxy form, 174.2° , where C_A and $\text{C}_{A'}$ are the vinyl carbon atoms, see Figure 5. For the unbridged counterpart, such distortion is minimal ($\angle\text{C}_A\text{-Co-C}_{A'}$ for the dioxygen adduct, 171.4° ; for its deoxy form, 176.5°). It should be recalled that for the [16]cyclidenes, steric control of dioxygen affinity is exerted by changes in the width of the cavity within which the dioxygen is bound. In contrast for the [14]cyclidene case, the bridge itself directly repels the O_2 molecule.

Autoxidation. The autoxidation of dioxygen carriers involves net oxidation of the metal and/or ligand. Consequently, the more cathodic $\text{Co}(\text{III}/\text{II})$ redox potential of $[\text{Co}(\text{MeNMeC}_{12}[14]\text{cyclidene})]^{2+}$, when compared to its 15- and 16-membered ring homologs, might be expected to result in more rapid autoxidation; that expectation is fulfilled. At temperatures above -10°C , in the presence of *N*-methylimidazole, and at fixed O_2 partial pressure, $[\text{Co}(\text{MeNMeC}_{12}[14]\text{cyclidene})]^{2+}$ was observed to undergo rapid autoxidation, and the rate data accord with the simple first order rate law. In agreement with the larger ring cyclidene derivatives, the O_2 dependence showed a saturation behavior.³⁷ Compared with the corresponding pentamethylene bridged [16]cyclidene complex ($[\text{Co}(\text{MeNMeC}_5[16]\text{cyclidene})]^{2+}$),³⁷ the autoxidation of the 14-membered cyclidene complex is much faster ([14]: $k = 1.2 \times 10^{-3} \text{ s}^{-1}$ at 25°C , 20% dioxygen concentration; [16]: $k = 2.0 \times 10^{-4} \text{ s}^{-1}$ at 30°C). The observed autoxidation rate constants for different temperatures and dioxygen concentrations are listed in Table III.

From the first four data points one can estimate that the enthalpy of activation for autoxidation ΔH^\ddagger is about $47 \text{ kJ}\cdot\text{mol}^{-1}$, and the apparent entropy of activation is about $25 \text{ eu}\cdot\text{mol}^{-1}$. However, R^2 is only 0.985 for this linear fit of the temperature data.

(35) Stevens, J. C., Thesis, The Ohio State University, 1979.

(36) Jackson, P. J., Thesis, The Ohio State University, 1981.

(37) Mararwa, M.; Evans, W. E.; Busch, E. H. Unpublished results.

Experimental Section

Materials. Solvents used in the synthesis of nickel(II) complexes were of reagent grade and used without further purification unless otherwise noted. Solvents used in the synthesis of cobalt(II) complexes were dried using standard techniques,³⁸ and distilled under nitrogen and degassed under vacuum prior to use. Benzene and *N*-methylimidazole (Aldrich) were dried over CaH₂. All other reagents were used without further purification.

Physical Measurements. Manipulations of air-sensitive compounds were performed in a Vacuum Atmospheres Corporation inert atmosphere box equipped with a nitrogen recirculating and dioxygen removal system. Dioxygen concentrations were maintained below 1 ppm. Elemental analyses were performed at The University of Kansas or Galbraith Laboratories, Inc., Knoxville, TN. ¹H NMR and ¹³C NMR spectra were obtained on either a Varian XL-300 or a General Electric QE-300 spectrometer. Infrared spectra were obtained using a Perkin-Elmer Model 1610 Fourier transform spectrophotometer with range of 4000 – 400 cm⁻¹. Samples were examined as potassium bromide disks. Fast atom bombardment (FAB) mass spectra were obtained on a VG ZAB HS mass spectrometer equipped with a Xenon gun. Several matrices were used, including NBA (nitrobenzyl alcohol) and TG/G (thioglycerol/glycerol). UV-visible spectrophotometric studies were conducted using a 1 cm gastight quartz cell, fitted with a gas inlet and a bubbling tube. Spectra were recorded on a Hewlett Packard Model 8452A diode array spectrophotometer with a 9000 (300) Hewlett Packard Chem. Station. Installed in the spectrophotometer is a flow-through, temperature-regulated cell holder connected to a Neslab constant temperature circulation system, giving a temperature precision of ±0.3 °C. Oxygen/nitrogen gas mixtures were mixed using Tylan FC-260 mass flow controllers. ESR spectra were obtained using a Model E-112 spectrometer operating in the X band at a frequency of approximately 9.132 GHz. Samples were prepared in an inert atmosphere box and sealed in quartz tubes equipped with greased, ground-glass joints. For low temperature spectra, the solutions were frozen in quartz tubes submerged in liquid nitrogen at -196 °C and then transferred to a liquid nitrogen dewar which was placed in the sample cavity of the spectrometer. Electrochemical experiments were performed inside a glove box, using a single compartment cell. The working electrode was a 3 mm diameter glassy carbon electrode in Kel-F (Bioanalytical systems), the secondary electrode was a platinum wire and a silver wire was used as the reference electrode. Potentials were measured versus ferrocene, which was used as an internal standard. The experiments were undertaken using a Princeton Applied Research (PAR) programmer Model 175, PAR potentiostat Model 173. The redox couple for [Co(MeNMeC₆[16]cyclidene)]²⁺/²⁺ has been related to ferrocene, assuming Fc/Fc⁺ = -0.16 V vs Ag/Ag⁺.

Autoxidation Experiments. The kinetic experiments on the autoxidation of the cobalt(II) [14]cyclidene complex were performed by bubbling 20% dioxygen through a solution of the cobalt(II) cyclidene complex in acetonitrile containing 1.5 M *N*-methylimidazole over a range of temperatures or by bubbling various concentrations of dioxygen through the solution at room temperature, 25.1 °C. The decay curves may be closely approximated by first order kinetics, and observed rate constants *k* were obtained using a first-order fit.

Molecular Mechanics. Molecular mechanics calculations were performed with Lin's modification of the MM2/MMP2 program of Allinger,^{26,39-41} running on a VAX 9000-210VP computer. Lindoy's⁴² nickel(II) parameters were adopted. The calculated results were visualized in the SYBYL program of TRIPOS Associates, Inc. of St. Louis, Missouri.

X-ray Structure Determination of Complex 3. The crystals were grown by the slow diffusion of ethanol into an acetonitrile solution of the complex at room temperature. On standing for about a week, red needle-like crystals formed, which were washed with a small amount of ethanol.

Crystal data are listed in Table IV. Crystal character: weakly diffracting laths. Data were collected with a Siemens R3M four circle diffractometer in ω-2θ mode. Maximum 2θ was 50° (reduced during collection to 42°) with scan range +0.7°(ω) around the K_{α1}-K_{α2} angles, scan speed 2.4-15°(ω) min⁻¹, depending on the intensity of a 2s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan

Table IV. Brief X-ray Details for Complex 3

empirical formula	NiC ₃₀ H ₅₂ N ₆ P ₂ F ₁₂	<i>V</i> , Å ³	3682
fw	845.1	<i>Z</i>	4
cryst system	orthorhombic	<i>D</i> (calc), g/cm ³	1.52
space group	<i>Pna</i> 2 ₁	λ, Å	0.710 69
<i>a</i> , Å	24.543(11)	Mo K _α , mm ⁻¹	6.7
<i>b</i> , Å	8.077(4)	<i>R</i> , ^a <i>R</i> _w	0.086, 0.112
<i>c</i> , Å	18.576(8)	<i>T</i> , K	290

$$^a R = (\sum ||F_o| - |F_c||) / (\sum |F_o|)$$

time. *hkl* ranges were: 0/29; 0/8; 0/22. Three standard reflections were monitored every 200 reflections, and showed no significant decrease during data collection. Unit cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections (16 < 2θ < 20°). Reflections were processed using profile analysis to give 2144 unique reflections, of which 1192 were considered observed (1/σ(*I*) ≥ 2.0). These were corrected for Lorentz, polarization and absorption effects (by the Gaussian method); minimum and maximum transmission factors were 0.89 and 0.97.

Systematic reflection conditions *Ok*l, *k* + *l* = 2*n*; *h*0*l*, *h* = 2*n* indicate either space group *Pnam* (non-standard setting of *Pnma*) or *Pna*2₁. The likely value of *Z* (4) and the probable absence of mirror symmetry in the molecule suggested the latter, which was initially examined and proved correct from successful refinement.

The Ni and two P atoms were located by the Patterson interpretation section of SHELXTL and the light atoms then found successive Fourier syntheses. The [PF₆]⁻ groups had high thermal parameters; one was modelled with anisotropic thermal parameters for F, the other with two anisotropic trans F atoms with occupancy 1.0, combined with two sets of four isotropic atoms with occupancy 0.5. All P-F distances were constrained to 1.55(3) Å by using DFIX constraints.

Because of the small number of reflections, anisotropic thermal parameters were used only for P, Ni and F (as noted above). Hydrogen atoms were given fixed isotropic temperature factors, *U* = 0.08 Å², and not refined. Those defined by the molecular geometry were inserted at calculated positions; methyl groups were generated as rigid CH₃ units, with their orientation based on a staggered configuration. No attempt was made to assign the absolute structure of the individual crystal chosen. The *z* coordinate of the Ni atom was fixed to define the origin. Final refinement was on *F* by least squares methods refining 275 parameters (effectively reduced by the DFIX constraints). Largest positive and negative peaks on a final difference Fourier synthesis were of height +1.0 and -0.5 e. Å⁻³.

A weighting scheme of the form *W* = 1/(σ²(*F*) + *gF*²) with *g* = 0.011 was used and shown to be satisfactory by a weight analysis. Final *R* = 0.086, *R*_w = 0.112, *S* = 0.94. Maximum shift/error in final cycle 0.6. Such relatively high final *R*-values are frequently found in similar compounds which often suffer, as here, from weak diffraction and disorder. Computing with SHELXTL PLUS⁴³ on a DEC Microvax-II. Scattering factors in the analytical form and anomalous dispersion factors used as stored in the program. Final atomic co-ordinates are given in supplementary Table 5.

Syntheses. [6,13-Diacetyl-5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraeno(2-)-κ⁴N]nickel(II), [Ni(Ac₂Me₂[14]-tetraenatoN₄)] (1). This 14-membered macrocyclic nickel(II) complex was synthesized using a previously published procedure.⁴⁴ The complex was isolated as very stable orange needles, insoluble in water, ethanol, and methanol, but soluble in chloroform and dichloromethane. The complex shows two very broad and intense bands in its infrared spectrum, centered at 1623.8 cm⁻¹ and 1576.4 cm⁻¹, assigned respectively as the C=O stretching mode and C=C and C=N stretching vibrations. The ¹H NMR in CDCl₃ shows resonances in four regions: 7.70 ppm (vinyl), 3.34 ppm (methylene), 2.40 ppm (methyl) and 2.28 ppm (methyl).

[(5,12-Dimethyl-6,13-bis(1-(methyloxy)ethylidene)-1,4,8,11-tetraazacyclotetradeca-4,7,11,14-tetraene-κ⁴N)nickel(II)]hexafluorophosphate, [Ni(MeOEt₂Me₂[14]tetraeneN₄)](PF₆)₂ (2). To 7.3 g of the nickel(II) Jaeger complex 1, previously dried in a vacuum oven overnight in a 1-liter round-bottomed flask with a calcium chloride drying tube, was added dichloromethane (250 mL, dried over calcium hydride). To this red solution was added 10 g methyl trifluoromethane sulfonate. *Caution: this powerful methylating agent may be very dangerous. It replaces a notorious reagent, methyl fluorosulfonate.* The reaction was stirred for

(38) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: New York, 1980.

(39) Allinger, N.; Yuh, Y. *QCPE* 1980, No. 423.

(40) Allinger, N.; Sprague, J. *J. Am. Chem. Soc.* 1973, 95, 3893.

(41) Allinger, N. *J. Am. Chem. Soc.* 1977, 99, 8129.

(42) Adam, K. R.; Antolovich, M.; Brigden, L. G.; Lindoy, L. F. *J. Am. Chem. Soc.* 1991, 113, 3346.

(43) Sheldrick, G. M., SHELXTL PLUS user's manual. Nicolet Instr. Co.: Madison, WI, 1986.

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

18 h, and 50 mL of methanol was added to the brown mixture which was stirred for another 10 min. The mixture was concentrated to about 50 mL by rotary evaporation. (25 mL of methanolic KOH was placed in the receiving flask to destroy any residual methyl trifluoromethane sulfonate.) The thick green oil was redissolved in a minimum amount of methanol. Ammonium hexafluorophosphate (8.2 g) dissolved in 40 mL of methanol was slowly added to this mixture with vigorous stirring. A light green crystalline product formed after refrigeration for 6 h, and the product was collected by suction filtration. Recrystallization of the methylated Jaeger product from 1:2 CH₃CN–MeOH, to remove the small amount of deacetylated material still present, produced bright green needles of the purified product. Yield 5.8 g, 42%. The yellow-green crystals are soluble in acetonitrile, less soluble in methanol or ethanol, and insoluble in less polar solvents. Elemental analysis. Calcd for C₁₈H₂₈N₄NiO₂P₂F₁₂: C, 31.74; H, 4.14; N, 8.23. Found: C, 32.04; H, 4.15; N, 7.99. The IR spectrum shows two characteristic bands of almost equal intensity at 1637.6 cm⁻¹ and 1545.0 cm⁻¹, due to C=C and C=N stretching vibrations. This pattern is useful in estimating the purity of the product and the absence of the deacetylated nickel(II) complex of 1, which has a strong band at 1675 cm⁻¹ and a much weaker one at 1640 cm⁻¹. ¹³C NMR spectrum in CD₃CN: 188.1, 172.6, 162.7, 115.1, 61.0, 59.5, 56.7, 24.1, 17.2 ppm.

N,N'-Dimethyl-1,12-diaminododecane, [CH₃NH(CH₂)₁₂NHCH₃]. This compound was synthesized according to a previously published procedure.¹⁵

[(2,3,16,17,19,25-Hexamethyl-3,16,20,23,26,29-hexaazabicyclo-[16.6.6]triaconta-1,17,19,23,25,29-hexaene-κ⁴(N^{20,23,26,29}))nickel(II)] Hexafluorophosphate, [Ni(MeNMeC₁₂[14]cyclidene)](PF₆)₂ (3). This complex was synthesized in a manner similar to that reported for the 15-membered complexes.¹⁵ Acetonitrile (500 mL, dried over CaH₂) was placed in a dry three-necked, 2-liter, round-bottomed flask fitted with a reflux condenser connected to N₂ gas, and the solvent was heated to reflux. Solutions of methylated 14-membered Jaeger nickel(II) complex 2 (2.87 g) in 250 mL CH₃CN and the stoichiometric amount of *N,N'*-dimethyldiaminododecane (0.96 g) in 250 mL CH₃CN were dripped into the stirred, refluxing CH₃CN over a period of 24 h by using a peristaltic pump in order to maintain high dilution reaction conditions. The reaction produced a very dark solution. The volume of the solution was reduced to about 20 mL with a rotary evaporator and chromatographed on neutral alumina, eluting with CH₃CN. This produced a yellow or red fast-moving band followed by, but not separated from, a darker material. The fast yellow band was collected. After reduction in volume to less than 15 mL, CH₃OH was added to induce crystallization of the PF₆⁻ salt. Yield 1.35 g, 38%. Elemental analysis. Calcd for C₃₀H₅₂N₆NiP₂F₁₂: N, 9.95; C, 42.64; H, 6.21. Found: N, 9.83; C, 42.80; H, 6.49. The complex is insoluble in CH₃OH and water, but soluble in acetonitrile. ¹³C NMR spectrum in CD₃CN: 182.5, 163.8, 156.5, 107.9, 59.9, 57.7, 55.9, 41.8, 31.8, 30.7, 28.3, 26.7, 26.6, 26.3, 25.4, 21.5 ppm. (For ¹³C NMR assignments for the nickel cyclidene complexes, see refs 45 and 46.) The FAB mass spectrum in NBA for this complex shows no dimer or polymer. A peak at 699 corresponds to the molecular ion minus one PF₆⁻, and at 553, to the molecular ion minus (PF₆⁻ + HPF₆).

[(2,3,16,17,19,25-Hexamethyl-3,16,20,23,26,29-hexaazabicyclo-

[16.6.6]triaconta-1,17,19,23,25,29-hexaene)] Tris(hydrogen hexafluorophosphate), [H₃(MeNMeC₁₂[14]cyclidene)](PF₆)₃ (4). This ligand salt was synthesized according to a previously published procedure.²⁰ The bridged nickel(II) complex (0.63 g) (3) was dissolved in 120 mL of CH₃CN, and HBr gas was bubbled through the solution for about 2 min, during which time the color of the solution changed from red to green, indicating the presence of NiBr₄²⁻. Some white-yellow solid was formed but redissolved into the solution after standing for two hours and removal of the excess HBr gas. Removal of the solvent on a rotary evaporator yielded a white-yellow sticky solid. This product was dissolved with stirring in a mixture of 50 mL of water and 5 mL of ethanol. It was cooled to -5 °C and a solution containing 2 g of NH₄PF₆ in 20 mL of water was added in small portions over 1 h, during which time a white-yellow solid precipitated out. The white-yellow solid was collected by suction filtration and washed with a small amount of cold water, followed by diethyl ether to remove any residual HBr. Drying in vacuo (60 °C) gave 0.45 g of a white-yellow ligand salt which, although not analytically pure, is suitable for preparation of the cobalt(II) complex. Yield: 0.45 g, 65%. N–H stretching vibrations at 3626.7 cm⁻¹ and 3451.1 cm⁻¹, C=C and C=N stretching vibrations at 1639.9 cm⁻¹ and 1591.0 cm⁻¹; peaks at 830.8 cm⁻¹ and 558.4 cm⁻¹ due to PF₆⁻. FAB mass spectroscopy in NBA shows peaks at 789, 643, and 497, due to the molecular ion losing one PF₆⁻, PF₆⁻ + HPF₆, and PF₆⁻ + 2HPF₆, respectively.

[(2,3,16,17,19,25-Hexamethyl-3,16,20,23,26,29-hexaazabicyclo-[16.6.6]triaconta-1,17,19,23,25,29-hexaene-κ⁴(N^{20,23,26,29}))cobalt(II)]hexafluorophosphate, [Co(MeNMeC₁₂[14]cyclidene)](PF₆)₂ (5). This reaction was carried out under nitrogen in an oxygen-free inert atmosphere glove box using predried and degassed solvents, as described in an earlier report.²² Ligand salt (0.45 g) 4 was slurried in 15 mL of methanol in a 50 mL flask, and the suspension was heated to boiling. A solution containing 0.119 g of cobalt(II) acetate tetrahydrate and 0.119 g of sodium acetate trihydrate in 10 mL of hot methanol was added to the suspension. As the ligand salt dissolved, the color of the mixture changed quickly to deep orange and the product began to crystallize within a few minutes. The reaction mixture was boiled gently for 10 min, cooled to room temperature and stirred overnight. Suction filtration of the mixture gave a red microcrystalline solid and this product was recrystallized from CH₃CN/CH₃OH to remove excess Co(OAc)₂ and NaOAc. The product was washed with a little methanol and dried. Yield was greater than 90%. The cobalt(II) cyclidene product is sufficiently stable toward oxidation in the solid state that a solid state IR spectrum could be obtained by rapid manipulation in the atmosphere. The spectrum is almost identical to that of the corresponding nickel(II) cyclidene complex. Peaks at 1622.9 cm⁻¹ and 1575.9 cm⁻¹ (C=C and C=N stretch); 838.9 cm⁻¹ and 558.0 cm⁻¹ (PF₆⁻). FAB mass spectrum in TG/G shows peak at 700, due to the molecular ion minus one PF₆⁻, and at 554, due to molecular ion minus one PF₆⁻ and one HPF₆. Elemental analysis. Calcd for C₃₀H₅₂N₆CoP₂F₁₂: N, 9.94; C, 42.61; H, 6.20; Co, 6.97. Calcd for C₃₀H₅₂N₆CoP₂F₁₂·CH₃OH·H₂O: N, 9.38; C, 41.57; H, 6.53; Co, 6.58. Found: N, 9.45; C, 41.65; H, 6.98; Co, 6.23.

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Supplementary Material Available: Lists of data collection details, atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters, H-atom coordinates, and full bond lengths and angles (6 pages). Ordering information is given on any current masthead page.

(45) Meade, T. J.; Fendrick, C. M.; Padolik, P. A.; Cottrell, C. E.; Busch, D. H. *Inorg. Chem.* **1987**, *26*, 4252.

(46) Alcock, N. W.; Padolik, P. A.; Pike, G. A.; Kojima, M.; Cairns, C. J.; Busch, D. H. *Inorg. Chem.* **1990**, *29*, 2599.