Dynamic *Cis*−*Trans* Bridge Isomerism in the Cyclidene Family of Dioxygen Carriers: A Bicyclic Cyclidene with a *Trans* Bridge Orientation

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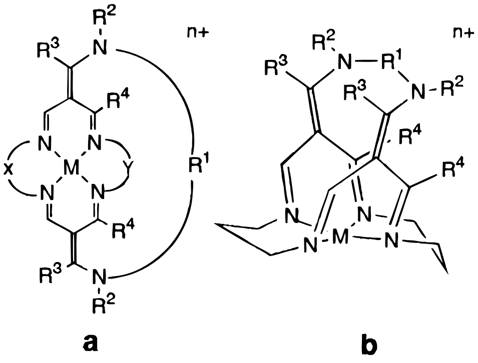
Received October 31, 1996[⊗]

A new type of isomerism has been detected in the cyclidene family of lacunar dioxygen carriers, providing an additional structural variable for the control of their oxygen affinity. In those rare complexes that do not have methyl substituents on the primary macrocycle, NMR and X-ray crystallographic data indicate that, in addition to their usual *cis* orientation, the bridges can also adopt a *trans* orientation. In the crystal structure of [Co(C_8MeHH[16]cyclidene)]$(PF_6)_2$·$3CH_3OH$, the bridge has this *trans* orientation with one end in the "lid-on" configuration while the other end is "lid-off". The *trans* orientation of the bridge is identified as the principal cause of the decreased dioxygen affinity of such unsubstituted cyclidenes.

Introduction

The family of bicyclic [16]cyclidene complexes (Figure 1) forms a class of lacunar complexes with notable ability as dioxygen carriers.[1] Their structures feature a saddle-shaped macrocycle spanned by a bridge (or bridges) stretching between the opposite sides of the macrocycle. These totally synthetic materials provide an almost ideal environment for dioxygen binding to the central atoms, with an additional advantage in the ease with which structural modifications may be carried out on the ligand. This, in turn, allows systematic studies of the effect of structural modifications on dioxygen affinities, rates of binding, dissociation, and autoxidation, and relative efficacies of different conformers.[2−4]

The cyclidenes can be structurally modified by varying the linking chains X, Y, and R^1 and also the substituents R^2−R^4 (Figure 1). Hitherto, attention has focused on R^1, which is usually called the bridging group, with some study of R^2 and R^3, but R^4 has invariably been CH_3. The presence of this methyl group has important consequences on the positioning of R^1 and R^3. In principle, two *cis* geometries are possible (Figure 2), although all previously known cyclidenes have conformation a in which the bridge R^1 is nearest the methyl groups at the R^4 positions. This may be understood by comparison of the molecular structure[4b] of [CoC_6MeMeMe[16]-cyclidene]$^{2+}$ (Figure 2a) with that of the hypothetical molecule (generated by CAChe molecular modeling program) in which the locations of R^1 and R^3 have been interchanged. The closest contact between the methyl groups R^4 and R^3 occurs in structure **2b** (1.806 Å). In contrast, in real structure **2a**, the corresponding distance is 1.904 Å and involves R^4 and the terminal methylene group of the bridge. Furthermore, unlike the contact in **2a**, this steric repulsion can relatively easily be reduced by changing the flexible torsion angle R^3−exocyclic carbon−exocyclic nitrogen−R^2.



Ia R^1 =$(CH_2)_6$, R^2=CH_3 ,R^3= R^4 =H, M=Ni

Ib R^1 =$(CH_2)_6$, R^2=CH_3 ,R^3= R^4 =H, M=Co

IIa R^1 =$(CH_2)_8$, R^2=CH_3 ,R^3= R^4 =H, M=Ni

IIb R^1 =$(CH_2)_8$, R^2=CH_3 ,R^3= R^4 =H, M=Co

Figure 1. Planar (a) and three-dimensional (b) representations of cyclidene complexes. These complexes are denoted below as M($R^1R^2R^3R^4$cyclidene), where M = Ni or Co.

We have recently described[5] the preparation and properties of the unsubstituted cyclidenes with R^3 = R^4 = H. For these materials, both sides of the unsaturated chelate rings are identical and the two bridge orientations described in Figure 2 are identical. However, alternative orientations, with respect to each other, of the *individual* exocyclic vinyl fragments are possible. The first corresponds to the normal *cis* positioning of the bridge, the second, to a *trans*-linked bridge. This *trans* bridge has previously been observed only for the cyclohexyl-fused cyclidene **III** (Figure 3),[6] in which the bridge orientation was dictated by the *trans* conformation of the starting material **IV**.

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[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1997.

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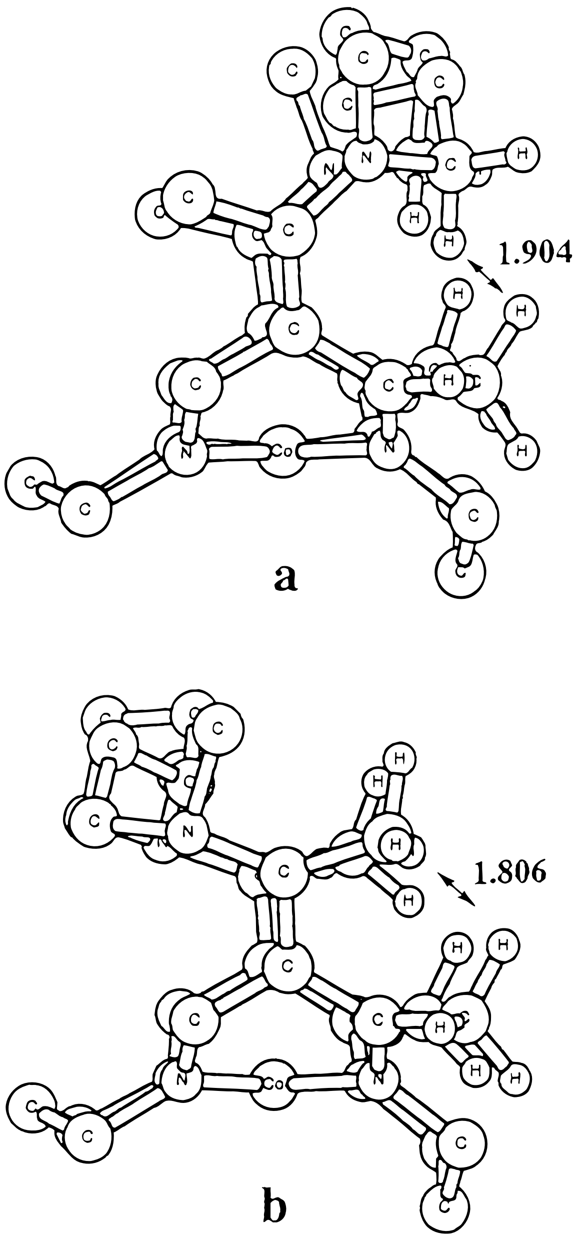

Figure 2. Comparison of the shortest distances between R¹/R³ and R⁴ atoms in (a) X-ray structure of [Co(C$_6$MeMeMe[16]cyclidene)]$^{2+}$ and (b) CAChe-generated hypothetical molecule with inverted orientations for R^1 and R^3.

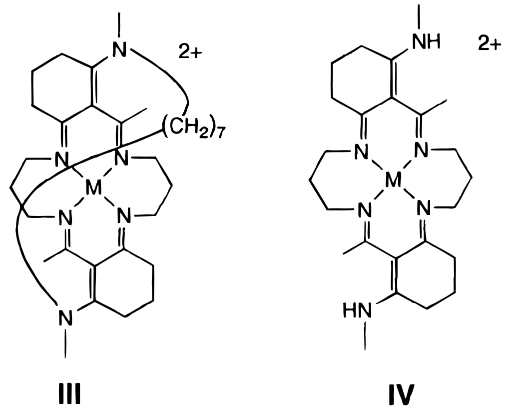

Figure 3. Cyclohexyl-fused cyclidenes and their precursors.

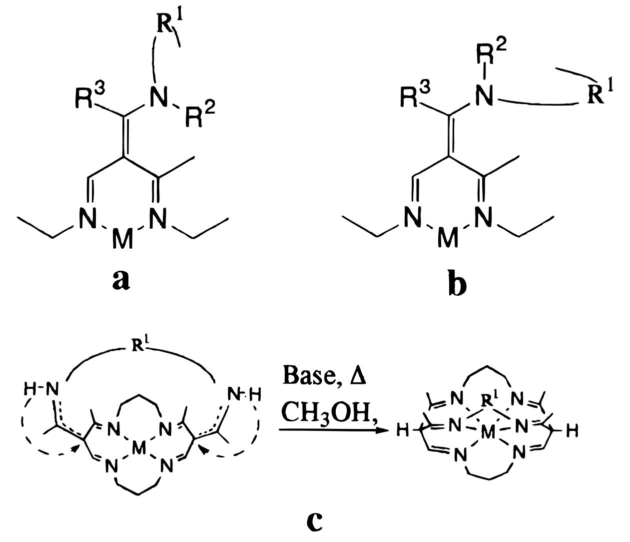

Figure 4. Types of isomerism reported for the cyclidene complexes: (a) lid-on isomer, (b) lid-off isomer, and (c) cyclidene−clathro-chelate isomerization.

Other types of isomerism of cylidene complexes have already been investigated in detail. The so-called “lid-on−lid-off” isomerism is very common for long-bridged cyclidenes, involving two different orientations of bridge R^1 and substituent R^2 (Figure 4a,b). It is associated with the planar configuration of the vinyl exocyclic nitrogen atom.[7] The carbon−nitrogen bond to the bridging group R^1 is directed away from the cavity in the lid-off isomer, while that same C−N bond directs the bridge upward in the lid-on isomer, in the latter case positioning the bridge more nearly above the O$_2$ binding site. In the bicyclic lacunar complexes, the lid-on or lid-off structure is locked in by the bicyclic structure. A further type of isomerism in cyclidene chemistry involves hydrogen transfer from the exocyclic nitrogen to the bridgehead carbon, accompanied by formation of a novel clathro-chelate structure; the overall change is essentially a tautomerization reaction (Figure 4c).[8]

In the present work, we describe a new type of dynamic isomerism in cyclidene chemistry arising from the *cis* or *trans* orientation of the two bridge terminals; we also report the X-ray structure of [CoC$_8$MeHH[16]cyclidene]$^{2+}$ in which the *trans* bridge orientation is found.

Experimental Section

The synthesis of unsubstituted nickel(II) and cobalt(II) cyclidene complexes has been previously described.[5]

NMR Measurements. NMR spectra were obtained on a General Electric QE-300 spectrometer and a Bruker AM-500 spectrometer. Signal positions are reported in parts per million (ppm) relative to residual solvent signals. Temperature was controlled with a standard Bruker temperature control unit having an accuracy ±1 °C.

X-Ray Structural Analysis. Crystal Data. C$_{27}$H$_{52}$N$_6$O$_3$CoP$_2$F$_{12}$ (**IIb**), $M = 857.62$, triclinic, $P\bar{1}$, $a = 9.7098(3)$ Å, $b = 11.9499(3)$ Å, $c = 17.3534(5)$ Å, $\alpha = 84.052(2)°$, $\beta = 76.140(2)°$, $\gamma = 79.171(2)°$, $U = 1916.47(9)$ Å^3, $Z = 2$, $D_c = 1.486$ g cm^{-3}, Mo Kα radiation, $\lambda = 0.710\ 73$ Å, μ (Mo Kα radiation) $= 0.63$ mm^{-1}, $T = 230(2)$ K.

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Table 1. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $[CoC_8MeHH[16]cyclidene \cdot MeOH](PF_6)_2 \cdot 2MeOH$ (**IIb**)

	x	y	z	*U*(eq)[a]
Co(1)	7794.8(9)	5803.1(6)	7276.4(5)	39(1)
P(1)	1628(2)	3040.1(17)	8879.9(12)	60(1)
P(2)	13042(2)	7857.0(16)	5191.8(12)	58(1)
F(11)	195(5)	3478(4)	8596(3)	92(1)
F(12)	3096(5)	2584(4)	9162(3)	101(2)
F(13)	825(5)	2345(4)	9599(3)	113(2)
F(14)	1964(6)	2002(5)	8359(4)	138(3)
F(15)	2455(6)	3746(6)	8170(3)	139(2)
F(16)	1285(8)	4061(4)	9433(4)	145(2)
F(21)	14604(5)	7165(4)	4876(3)	103(2)
F(22)	11506(6)	8539(5)	5465(4)	153(3)
F(23)	13401(9)	8110(5)	5958(4)	197(4)
F(24)	12694(5)	7587(4)	4403(3)	119(2)
F(25)	13564(6)	8965(4)	4770(3)	123(2)
F(26)	12592(8)	6710(5)	5582(4)	177(3)
N(1)	7576(5)	6103(4)	8375(3)	42(1)
C(2)	8247(7)	7007(5)	8581(4)	51(2)
C(3)	9865(7)	6761(5)	8291(4)	54(2)
C(4)	10346(7)	6772(5)	7386(4)	54(2)
N(5)	9815(6)	5873(4)	7072(3)	46(1)
C(6)	10771(7)	5057(5)	6758(4)	45(2)
C(7)	10479(6)	4152(5)	6365(4)	40(2)
C(8)	9245(7)	4375(5)	6023(4)	42(2)
N(9)	8139(5)	5147(4)	6258(3)	39(1)
C(10)	7030(7)	5375(5)	5784(4)	47(2)
C(11)	5645(7)	4987(5)	6236(4)	48(2)
C(12)	4967(7)	5610(5)	6982(4)	48(2)
N(13)	5891(5)	5410(4)	7556(3)	40(1)
C(14)	5508(6)	4792(5)	8199(4)	42(2)
C(15)	6200(6)	4598(5)	8851(4)	40(2)
C(16)	7047(6)	5427(5)	8947(4)	42(2)
C(17)	5855(7)	3668(5)	9369(4)	44(2)
N(18)	6346(5)	3190(4)	9999(3)	47(1)
C(19)	7416(7)	3603(6)	10306(4)	61(2)
C(20)	5944(7)	2092(6)	10348(4)	58(2)
C(21)	7155(9)	1102(6)	10113(5)	74(2)
C(22)	7629(9)	1018(7)	9173(5)	83(3)
C(23)	8901(10)	128(6)	8919(5)	84(3)
C(24)	9152(9)	−15(6)	8026(4)	70(2)
C(25)	9610(7)	985(5)	7474(4)	55(2)
C(26)	9922(7)	720(5)	6606(4)	47(2)
C(27)	10248(7)	1721(5)	6026(4)	52(2)
C(28)	12884(7)	1302(6)	5999(5)	66(2)
N(29)	11539(5)	2151(4)	6082(3)	43(1)
C(30)	11538(7)	3195(5)	6278(4)	47(2)
O(31)	7102(5)	7556(3)	6895(3)	58(1)
C(32)	7689(9)	8155(6)	6192(5)	80(2)
O(01A)	4959(10)	925(8)	7976(6)	99(5)
O(01B)	5889(18)	900(16)	7004(11)	93(7)
C(001)	5559(11)	1725(11)	7388(7)	104(3)
O(002)	4783(8)	8841(4)	7700(3)	94(2)
C(002)	3365(13)	8824(8)	7685(6)	111(4)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Selected Bond Lengths and Angles for $[CoC_8MeHH[16]cyclidene \cdot MeOH](PF_6)_2 \cdot 2MeOH$ (**IIb**)[a]

Bond Lengths (Å)			
Co(1)−N(5)	1.924(5)	Co(1)−N(9)	1.938(5)
Co(1)−N(13)	1.929(5)	Co(1)−O(31)	2.162(4)
Co(1)−N(1)	1.931(5)		
Bond Angles (deg)			
N(5)−Co(1)−N(13)	168.1(2)	N(1)−Co(1)−N(9)	167.0(2)
N(5)−Co(1)−N(1)	90.3(2)	N(5)−Co(1)−O(31)	96.7(2)
N(13)−Co(1)−N(1)	88.5(2)	N(13)−Co(1)−O(31)	95.2(2)
N(5)−Co(1)−N(9)	88.6(2)	N(1)−Co(1)−O(31)	95.2(2)
N(13)−Co(1)−N(9)	89.9(2)	N(9)−Co(1)−O(31)	97.8(2)

[a] Symmetry transformations used to generate equivalent atoms.

Data Collection and Processing. Crystal character red plates; crystal dimensions 0.35 × 0.18 × 0.10 mm, The crystals are unstable on removal from methanol and were mounted in perfluoro ether oil. A Siemens SMART (Siemens, 1994) three-circle system with CCD area detector was used. The crystal was held at 230(2) K with the Oxford Cryosystem Cryostream Cooler.[9] Maximum θ was 28.66°. The *hkl* ranges were −7/13, −15/13, −18/22. A total of 11 394 reflections were measured, 7948 unique [$R(\text{int}) = 0.0551$], no absorption correction, and no crystal decay.

Structure Analysis and Refinement. Space group $P\bar{1}$ was chosen on the basis of intensity statistics and shown to be correct by successful refinement. The structure was solved by direct methods using SHELXS[10] (TREF) with additional light atoms found by Fourier methods. The PF_6 groups were poorly ordered, and their P−F and F···F distances were restrained. As well as the coordinated methanol, two solvent MeOH molecules were found, of which the first has alternative oxygen positions [0.64(2) and 0.36 occupancy]. O002 is hydrogen bonded to O31 (bound) and O001 (lattice). Ready loss of these additional methanol molecules is a probable cause of the instability of **IIb** on removal from mother liquor.

Hydrogen atoms were added at calculated positions (excluding the disordered methanol carbon and the OH groups) and refined using a riding model with freely rotating methyl groups. Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl hydrogen atoms) times the equivalent isotropic displacement parameter of the atom to which the H-atom is attached. The weighting scheme was calculated: $w = 1/[\sigma^2(F_o^2) + (0.1040P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. Goodness of fit on F^2 was 0.996; R1[for 3451 reflections with $I > 2\sigma(I)$] = 0.0826; wR2 (all reflections) = 0.2374; data/restraints/parameters were 7948/18/470; largest difference peak and hole 0.656 and −0.424 e A^{-3}. Refinement used SHELXTL 96.[10] Final atomic coordinates are given in Table 1 and selected bond lengths and angles in Table 2.

Results and Discussion

Variable-temperature ^{13}C and ^1H spectra of unsubstituted $[NiC_6MeHH[16]cyclidene]^{2+}$ (**1a**) are shown in Figure 5. They are in a good agreement with structure **1a**, apart from the broadening or splitting of three of the most downfield peaks (assigned to unsaturated tertiary carbons and adjacent hydrogens; a−c in Figure 5). At higher temperatures, these doublets collapse to broadened singlets. These splittings indicate the presence of dynamic isomerism influencing the unsaturated chelate rings and adjacent vinyl-like groups. Although isomerism at the bridgehead nitrogens has been previously observed in long-chain cyclidenes (lid-on−lid-off isomers),[7] this does not explain the present observations.

(a) In known examples, lid-on−lid-off isomerism differentiates the NMR signals h for the R^2 methyls that have the "on" and "off" orientations in addition to the signals for the terminal CH_2 groups of the bridge.[11] This differentiation is not observed in the $NiC_6MeHH[16]cyclidene^{2+}$ NMR spectra; i.e., a single $N-CH_3$ resonance is observed.

(b) Based on many known structures, the probability of lid-on−lid-off isomerism for C_6 polymethylene bridges is rather low. In the solid state, many complexes of the general formula $MC_nMeMeMe[16]cyclidenes$ exclusively exist as the lid−off conformers for $n < 9$. For $n = 9$, one side of the bridge is connected in lid-off conformation and the other is disordered, involving both lid-on and lid-off forms; for $n = 10$ the ordered end is lid-on, while longer bridges have lid-on conformations at both ends.

(c) Lid-on−lid-off isomerism should cause larger splittings of the signals attributable to the hydrogen atoms b than for

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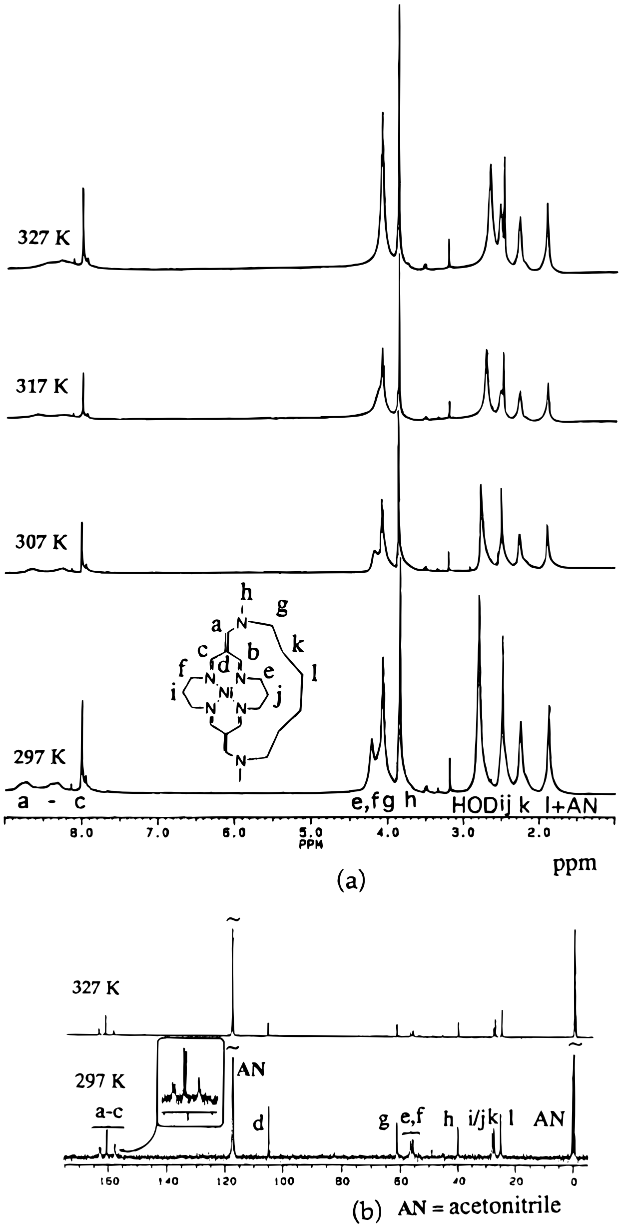

Figure 5. Temperature dependencies of ^{1}H and ^{13}C NMR spectra of $[Ni(C_6MeHH[16]cyclidene)](PF_6)_2{\cdot}CH_3OH$ in acetonitrile. For complete assignment see ref 5.

signals c (for assignments, see Figure 5) because of relative spatial proximities. For unsubstituted cyclidene **1a**, the distance between components in both doublets is approximately equal and comparable with the line width of the third broadened signal.

Other previously established conformational peculiarities of the cyclidene family such as chair−boat "isomerism" for the saturated six-membered rings cannot explain the changes in the low-field region of the NMR spectra. The chair−boat conformational changes have never been found to cause a splitting of the azomethine signals, and it would be difficult to explain why the elimination of methyl substituents (making the molecule more symmetrical) would cause such a splitting. Even though, when the temperature is increased, changes are observed in the vicinity of resonances associated with the saturated six-membered chelate rings, these changes are not simultaneous with the changes in the spectral behaviour of signals a and b. At the temperature where i/j signals became unequivalent (due to possible coexistence of chair and boat forms) any signs of splitting within the a and b signals disappear. Under the chair-boat model, at lower temperature the i and j protons are equivalent, and no splitting should be observed for the a and b signals, which is not the case.

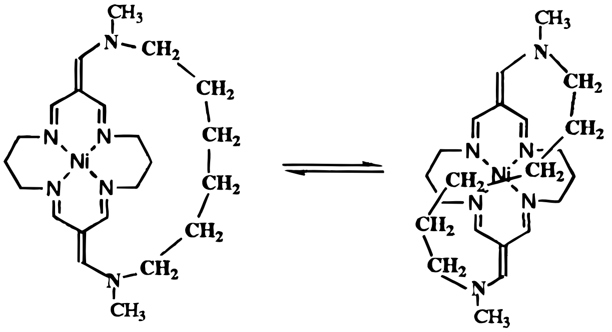

Figure 6. *Cis−trans* bridge isomerism in $[Ni(C_6MeHHcyclidene)]^{2+}$.

A rational explanation of the NMR spectra is based on *cis* and *trans* isomerization of the bridge and the conformation at the exocyclic carbon a. Although the two sides of the unsaturated chelate rings are equivalent in unsubstituted cyclidenes (R^4 = H), once the orientation at one end of the bridge has been established two orientations are then possible for the other end; this leads to *cis* or *trans* orientation of the bridge (Figure 6, the *cis* or *trans* orientation is most easily recognized in the corresponding N-methyl groups). The close proximity in energy of the *trans* isomer is apparent in this as in the structure of the C_8 bridged complex (see below). The presence of the two isomers then gives two different azomethine signals for resonances a, b, and, probably, c in the ^{13}C and ^{1}H spectra of **Ia**. The similar intensities of the doublet components indicate comparable concentrations of the isomers in solution. In the solid state, however, the bridge takes up the *cis* conformation exclusively for C_6 bridged complex[5] (and the *trans* conformation exclusively for C_8 bridged complex). The transformation barrier between the two isomers must depend, in part, on the bond order of the exocyclic carbon−carbon bond, which approximates 1.5, on the basis of the average C−C distance (1.383 Å, compared to a typical aromatic bond of 1.395 Å). While the reason for the ease of rotation about this partial double bond may not be clear, it is well demonstrated in the behavior of the N,N-dimethyl, unbridged cyclidene complexes. Their NMR spectra at room temperature give only a single resonance for the two methyl groups.[12]

For the complex having the longer C_8 bridge, the room-temperature ^{13}C and ^{1}H spectra are substantially more complicated $[[NiC_8MeHH[16]cyclidene]^{2+}$ (Figure 7)], though the mean chemical shifts are typical of cyclidene complexes. Most of the individual signals are broadened and the number of signals is substantially larger than expected for either lid-on−lid-off isomerism or *cis−trans* bridge isomerism alone.

The regions around 40 ppm in the carbon spectrum and 3.2 ppm for the proton spectrum (NCH_3 area) are especially informative (Figure 7). Multiple signals were detected for both spectra in these areas, strongly suggesting the simultaneous existence of both lid-on−lid-off and *cis−trans* bridge isomerism. Each NCH_3 group may have either the lid-on or lid-off configuration, which in combination with either *cis* or *trans* bridge orientation gives six different types of NCH_3 groups in (**IIa**). Similarly, several closely located signals were detected in the ^{13}C spectrum for the bridgehead carbons d. This model suggests 24 individual peaks for the region farthest downfield, in which the signals for the two azomethyne groups and the "vinyl" hydrogens are located. This complicated pattern is given in the inset for Figure 7.

X-ray Structure of $[Co(C_8MeHH[16]cyclidene)](PF_6)_2{\cdot}3CH_3OH$ (IIb). The solid-state structures of both the Ni and

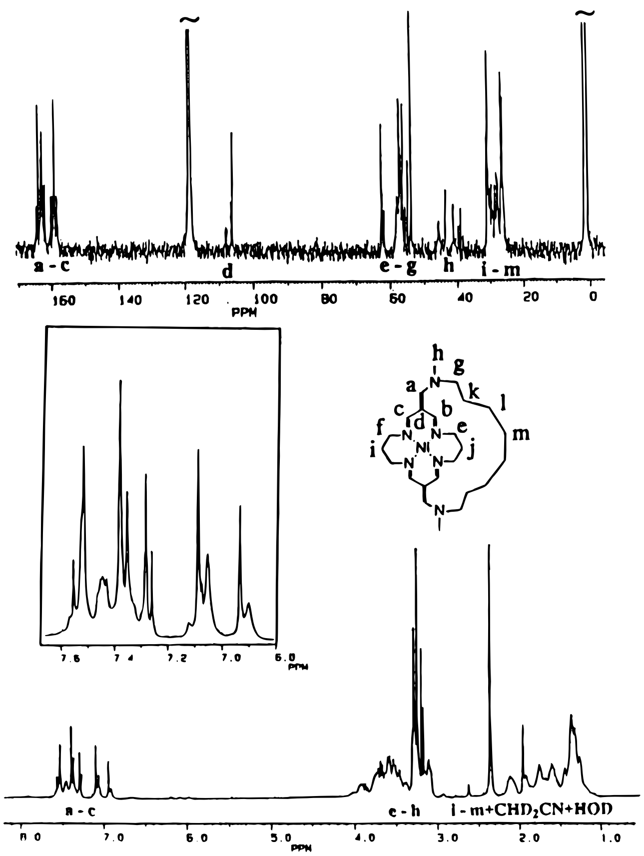

Figure 7. ^{13}C and ^{1}H NMR spectra of $[Ni(C_8MeHH[16]cyclidene)CH_3OH](PF_6)_2{\cdot}2CH_3OH$ in acetonitrile. Inset: magnified portion of ^{1}H NMR spectra.

Co complexes (**IIa/IIb**) with C_8 bridges have been examined, but the Ni complex proved to be highly disordered and the bridge conformation could not be determined. The Co complex is more informative, and a structural representation and atom numbering are shown in Figure 8. The unusual *trans* bridge positioning can clearly be seen in the side view (Figure 8b). The cobalt atom is 0.21 Å out-of-plane away from the bridge. The figure also shows that one of the bridge termini has the lid-on and the other the lid-off conformation. Thus, this structure strongly supports our conclusions on bridge isomerism in unsubstituted cyclidenes, with the likely coexistence in solution of all the possible combinations of lid-on−lid-off and *cis*−*trans* bridge isomers, in agreement with the NMR data.

It is also relevant to consider the effect of a *trans* bridge orientation on the overall structure. It has previously been found that, despite their intrinsic flexibility, the medium-length polymethylene bridges (C_7−C_9) stretch the cyclidene cavity beyond its ideal width.[1,2a,4c] The distance between the two exocyclic nitrogens increases from 6.74 Å for $[CoC_6MeMeMe[16]\text{-}cyclidene]^{2+}$ to 7.81 Å for $[CuC_8MeMeMe[16]cyclidene]^{2+}$; simultaneously, the bridge conformation changes from folded U-shaped to coiled.[4c] The idealized conformation of the bridge in $[CuC_8MeMeMe[16]cyclidene]^{2+}$ is gauche(+)−gauche(+)−gauche(+)−gauche(+)−anti−gauche(−)−gauche(−), which can be described as two fragments of right and left coils connnected in the center. The actual $[CuC_8MeMeMe[16]\text{-}cyclidene]^{2+}$ structure is therefore a compromise between the conformations of the bridge and the macrocyclic backbone. The saddle-shaped macrocycle widens to accommodate the long C_8 bridge, which in turn is coiled, substantially deviating from the most favorable all-*anti* conformation. In contrast, the distance between the exocyclic nitrogens in $[CoC_8MeHH[16]cyclidene]^{2+}$ is 7.49 Å, indicating relatively little stretching of the cavity.

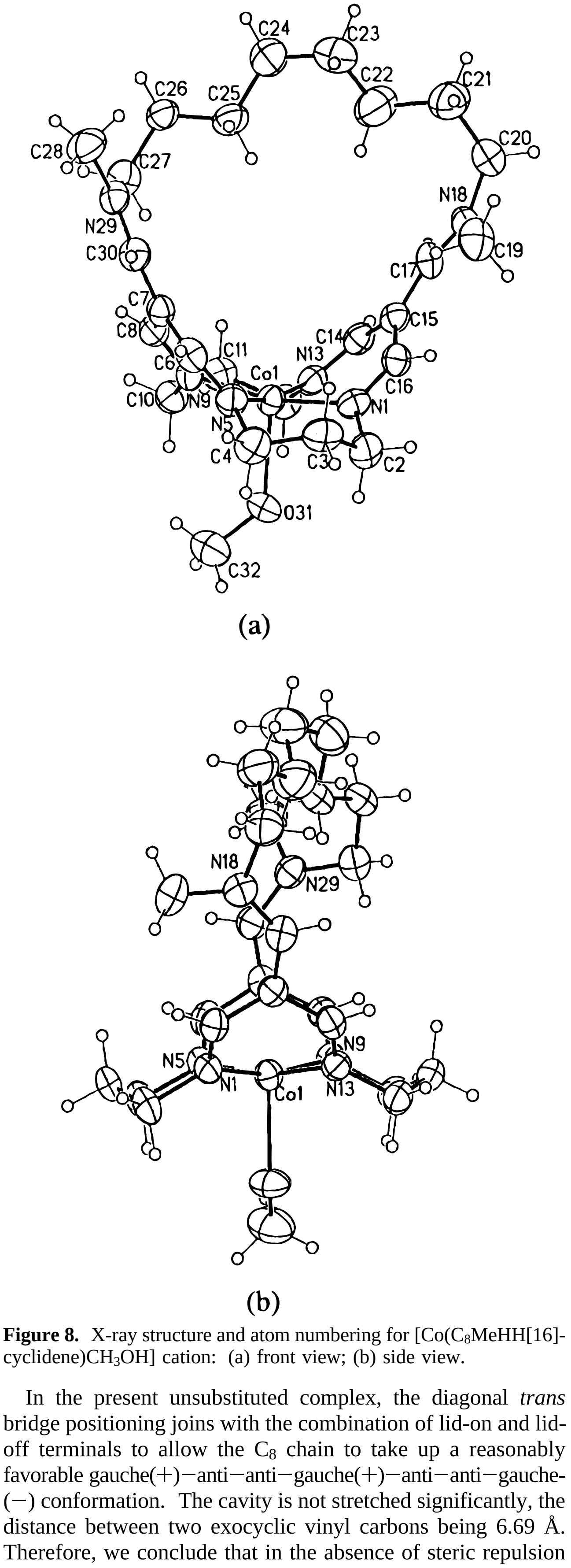

Figure 8. X-ray structure and atom numbering for $[Co(C_8MeHH[16]\text{-}cyclidene)CH_3OH]$ cation: (a) front view; (b) side view.

In the present unsubstituted complex, the diagonal *trans* bridge positioning joins with the combination of lid-on and lid-off terminals to allow the C_8 chain to take up a reasonably favorable gauche(+)−anti−anti−gauche(+)−anti−anti−gauche-(−) conformation. The cavity is not stretched significantly, the distance between two exocyclic vinyl carbons being 6.69 Å. Therefore, we conclude that in the absence of steric repulsion caused by the methyl group at R^4 positions, both these parameters (bridge conformation and cavity width) can be quite close to the ideal.

The bridge in $[Co(C_8MeHH[16]cyclidene)]^{2+}$ passes directly over the top of the cavity, and the distance from the cobalt to

Table 3. Selected Dioxygen Affinities for the Cobalt Cyclidenes[a]

$R^1R^2R^3R^4$	K_{O_2} (Torr^{-1})	ref
C_6MeMeMe	1.3	12
C_6MeHH **(Ib)**	0.0032	5
III	0.0024 (−16.5 °C)	6
C_8MeMeMe	5.92	12
C_8MeHH **(IIb)**	0.092	5

[a] In acetonitrile/1.5 M methylimidazole, 0 °C.

the midpoint C23/C24 is 6.93 Å. The effect of this moderately close bridge is enhanced by its direct overhead location. Consequently, in order for a dioxygen molecule to be bound, a substantial rearrangement must take place; this is almost certainly the main reason for the relatively low dioxygen affinity of the complex (Table 3).[5] Interestingly, the cyclohexyl-fused cyclidene (**III**, M = Co)[6], which also has a *trans* bridge, has very low dioxygen affinity as well.

In both of the structurally characterized unsubstituted cyclidenes, **Ib** and **IIb**, the bridge conformations are straighter than those in the corresponding R^4 methyl substituted analogs. Thus, the R^1-R^4 repulsion plays a key role in producing folded bridge conformations, which, in turn, is highly favorable for dioxygen binding, because those conformations favor the lid-off, *cis*-oriented bridge structure.

Acknowledgment. This material is based upon work supported by the NSF under Grant OSR-9255223 and matching support from the state of Kansas. The collaboration between The University of Kansas and The University of Warwick has been supported by a NATO travel grant. We thank EPSRC and Siemens Analytical Instruments for grants in support of the diffractometer. The authors also greatly appreciate the contributions of Dr. Martha Morton to the NMR studies.

Supporting Information Available: Tables of bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacement factors for **1** (4 pages). Ordering information is given on any current masthead page. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and the remaining bond lengths and angles.

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