78 *Inorg. Chem.* **1987**, *26*, 78–83

Contribution from the Chemistry Department,
The Ohio State University, Columbus, Ohio 43210

Cobalt(II) Complex of a Novel Pentadentate Half-Clathro Half-Cyclidene Ligand Produced by a Base-Catalyzed Ligand Rearrangement

Maureen L. Caste, Colin J. Cairns, Jeffrey Church, Wang-Kan Lin, Judith C. Gallucci, and Daryle H. Busch*

Received December 26, 1985

A low-spin cobalt(II) complex of an unsaturated, 16-membered tetradentate macrocycle containing four imine donors has been synthesized by reaction of the protonated ligand with cobalt(II) under basic conditions. The tetradentate ligand rapidly rearranges in the presence of cobalt(II) to give a product in which one of the secondary amines, which are usually peripheral substituents, becomes coordinated as an appended axial imine group. An X-ray crystal structure determination has confirmed the nature of this rearrangement. [3-(1-(Methylamino)ethylidene)-11-(1-(methylimino)ethyl)-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-κ^4N]cobalt(II) hexafluorophosphate–acetonitrile crystallizes in the monoclinic space group $P2_1/n$ with $a = 18.186$ (2) Å, $b = 7.296$ (1) Å, $c = 25.279$ (3) Å, and $\beta = 110.66$ (1)°. The structure was solved by the heavy-atom method and refined to final agreement indices of $R = 6.0\%$ and $R_w = 11.6\%$ for 2922 reflections. The macrocyclic ligand occupies five vertices of a slightly distorted square pyramid, with an acetonitrile of solvation weakly interacting at the sixth coordination site. Spectroscopic and electrochemical studies on the cobalt(II) complex, and on the chemically oxidized cobalt(III) product, confirm that the cyclidene ligand retains its structure in solution.

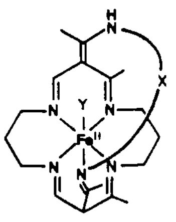
Introduction

Encapsulation reactions, in which a metal ion is completely entrapped by a polycyclic ligand, have been known and studied for several years and were first predicted over 20 years ago.[1] The systems that have undergone the most detailed study range from the cryptates and cryptands of Lehn et al.,[2] in which the donor atoms are mostly ether oxygens, through the sepulchrates of Sargeson and his co-workers,[3] containing saturated nitrogen donors, to the tris(α-diimine) clathrochelate complexes synthesized by Boston and Rose[4] and by Goedken and Peng.[5] Transition-metal complexes of the latter two categories are synthesized by way of the coordination template effect and are relatively inert toward substitution reactions. This stability has made them useful in studies of the thermodynamics and kinetics of electron-transfer processes.[3] A disadvantage of these complexes lies in this same inertness, since once made they are not often amenable to the metal-exchange reactions that would produce entrapped complexes of other metal ions.

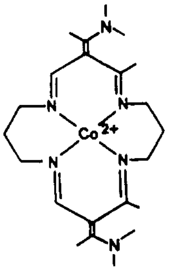
In previous studies we have described the synthesis and properties of some iron(II) clathrochelate complexes of macrocyclic cyclidene ligands in which the enclosed six-coordinate complex is formed by the rearrangement of the superstructure of a precursor complex.[6] This process, which has been proven to occur via a base-induced tautomerism, is represented in Scheme I.

In this process, proton transfers occur from the uncoordinated secondary amine groups to the nearby γ-carbons, followed by coordination of the two new imine groups. This rearrangement has been observed in both bridged (X = $-(CH_2)_5$ or $-(CH_2)_6$) and unbridged (X = $-(CH_3)_2$) complexes. A variation of the rearrangement has been observed that is particularly pertinent to the work reported here. It appears that a monodentate axial ligand that binds strongly enough can prevent rearrangement. In the presence of carbon monoxide, that strongly bound axial ligand remains coordinated and the rearrangement is limited to just one side of the macrocycle, producing a pentadentate, rather than a hexadentate ligand (structure I).

This report represents an extension of the earlier studies to complexes of cobalt(II) and cobalt(III). In the presence of excess base (acetate) we have found that an internal rearrangement of one peripheral secondary amine moiety occurs, and this allows an additional nitrogen to coordinate to the metal center, forming a five-coordinate cobalt(II) complex (Scheme II).[7]



I, X = $-(CH_2)_5$ Y = CO



II

In fact, this rearrangement occurs sufficiently rapidly that the intermediate, unrearranged complex is observed only by a fleeting orange color that appears immediately upon mixing the ligand (as the tetraprotonated chloride tris(hexafluorophosphate) salt) with cobalt(II) acetate in a methanol solution containing excess sodium acetate. This behavior appears to be unique to the unbridged complex, since the corresponding reaction has not been observed for the lacunar cobalt(II) complexes or in unbridged cobalt(II) cyclidene complexes where the amine does not possess acidic hydrogens (structure II).[8] Oxidation of this pentadentate complex to the cobalt(III) derivative does not reverse the rearrangement process, as confirmed by ^1H NMR and ^{13}C NMR spectroscopy.

The reaction of the pentadentate complex with dioxygen to give a 1:1 adduct can also be followed spectrophotometrically. Again there is no evidence for a reversal of the ligand rearrangement. The extra electron density supplied to the metal center by the hybrid ligand makes this complex extremely susceptible to oxidation, as reflected in the facile electrochemical oxidation of the metal to the +3 state and in the rapid decomposition of the initially formed superoxo adduct at temperatures much above 233 K. This behavior is in marked contrast to that observed for the hexaene–iron(II) complexes (product in Scheme III). The latter compounds are remarkably stable toward electrochemical and air oxidation, presumably due to the back-bonding associated with the six isolated imine donors, which results in a thermodynamically and kinetically inert low-spin iron(II) system.

Experimental Section

Materials. All metal salts, organic reagents, and solvents were reagent grade. Solvents were dried by following recommended procedures,[9] distilled under dry nitrogen, and thoroughly degassed before use. The synthesis of the cobalt(II) complex was carried out in a Vacuum Atmospheres glovebox under an atmosphere of dry nitrogen.

---

(1) Busch, D. H. *Rec. Chem. Prog.* **1964**, *25*, (2), 107.

(2) Lehn, J.-M. *Acc. Chem. Res.* **1978**, *11*, 49.

(3) Sargeson, A. M. *Pure Appl. Chem.* **1984**, *56*, 1603 and references therein.

(4) Boston, D. R.; Rose, N. J. *J. Am. Chem. Soc.* **1968**, *90*, 6859.

(5) Goedken, V. L.; Peng, S. M. *J. Chem. Soc., Chem. Commun.* **1973**, 62.

(6) Herron, N.; Grzybowski, J. J.; Matsumoto, N.; Zimmer, L. L.; Christoph, G. G.; Busch, D. H. *J. Am. Chem. Soc.* **1982**, *104*, 1999.

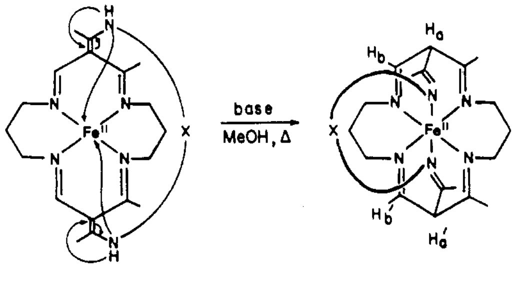
(7) Caste, M. L. Ph.D. Thesis, The Ohio State University, 1982.

(8) Jackson, P. J. Ph.D. Thesis, The Ohio State University, 1981.

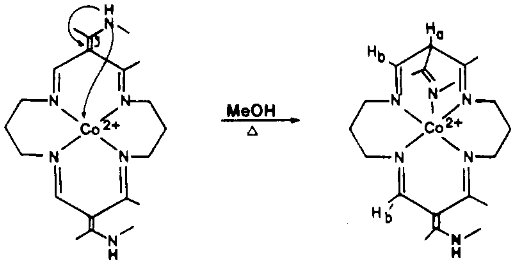
(9) Vogel, A. I. *A Textbook of Practical Organic Chemistry*, 3rd ed.; Wiley: New York, 1966; pp 163–179.

0020-1669/87/1326-0078$01.50/0

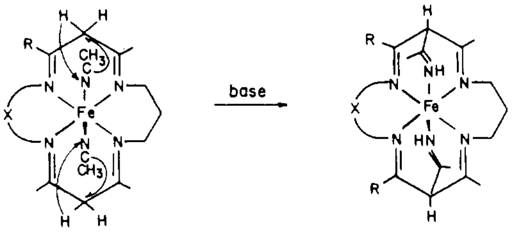
Scheme I



Scheme II



Scheme III



Physical Measurements. ^{1}H NMR spectra were recorded on a Varian 390L continuous wave spectrometer operating at 90 MHz. ^{13}C NMR spectra were obtained by using a Bruker WP80 Fourier transform spectrometer operating at 20.115 MHz. All spectra were run at room temperature (ca. 300 K) with dried, degassed acetonitrile-d_3 used as solvent. Chemical shifts are quoted relative to internal tetramethylsilane at 0.0 ppm.

Electrochemical measurements were performed with a Princeton Applied Research Corp. Model 173 potentiostat/galvanostat and a Model 179 digital coulometer. Current vs. potential curves were measured on a Houston Instruments Model 2000 XY recorder. All measurements were carried out in a Vacuum Atmospheres glovebox under an atmosphere of dry nitrogen. The working electrode for the voltammetric curves was a platinum disk, with potentials measured vs. an $Ag^0/AgNO_3$ (0.1 M in CH_3CN) reference. The working electrode was spun at 600 rpm by a synchronous motor for the rotating platinum electrode (RPE) voltammograms at a 50 mV/s scan rate. These measurements were made in CH_3CN containing tetra-*n*-butylammonium tetrafluoroborate (0.1 M) as supporting electrolyte. Half-wave potentials ($E_{1/2}$) were taken as the potential at one-half the height of the RPE voltammogram. The value $E_{3/4-1/4}$, also obtained from the RPE voltammogram, was used as a measure of the reversibility of the redox couple (for a reversible one-electron couple $E_{3/4-1/4}$ = 60 mV).

Infrared spectra were obtained with a Perkin-Elmer Model 283B recording spectrophotometer operating in the range 4000–200 cm^{-1}. Solid-state spectra were recorded on samples as Nujol mulls or potassium bromide pellets. Visible and ultraviolet spectra were measured on a Cary Model 17D recording spectrophotometer equipped with a variable-temperature cell holder for 10-mm quartz cells. Air-sensitive samples were prepared in an inert atmosphere and run immediately upon removal from the glovebox. Exposure of acetone solutions of the cobalt(II) complex to various partial pressures of dioxygen was achieved by using a series of rotameters (Matheson, East Rutherford, NJ) to accurately mix dioxygen and nitrogen standards. The appropriate gas mixture was first saturated with solvent vapor in a bubbling cell held at the sample temperature, followed by passage of the gas mixture through the sample solution in 10-mm quartz optical bubbling cells (Precision Cells, Inc., Hicksville, NY) equipped with a gas inlet and bubbling tube. The cell was thermostated (±0.3 °C) through the use of a Neslab or FTS constant-temperature circulation system. Methanol was used as coolant and was pumped through a Varian variable-temperature double-jacketed cell holder within the nitrogen-flushed cell compartment of the spectrophotometer. The cell temperature was monitored by a calibrated copper–constantan thermocouple attached to the cell holder.

EPR spectra were recorded with a Varian Model E-112 spectrophotometer in the X-band region at 9.3 GHz on samples prepared as frozen acetone glasses at 77 K in a round quartz sample cell. Values of *A* and *g* were determined relative to a sample of strontium(II) oxide containing manganese(II) impurity.[10]

Elemental analyses were performed by Galbraith, Inc., Knoxville, TN.

Syntheses. The synthesis of the unbridged nickel(II) complex and the demetalation procedure used to make the ligand salt have been described in previous reports.[11-13]

[3-(1-(Methylamino)ethylidene)-11-(1-(methylimino)ethyl)-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-κ^4N]cobalt(II) Hexafluorophosphate, [Co((MeNIminoethyl)(HMeNEthi)Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$. In a typical reaction 2.0 g (0.0024 mol) of the ligand salt $H_4[(HMeNEthi)_2[16]tetraeneN_4](PF_6)_3Cl$ was slurried in 20 mL of refluxing methanol. Cobalt(II) acetate tetrahydrate (0.60 g, 0.0024 mol) and sodium acetate trihydrate (0.98 g, 0.0072 mol) were dissolved in 20 mL of refluxing methanol and added dropwise to the ligand slurry. The color of the reaction mixture changed quickly through an initial orange to a dark green; during this change all of the ligand salt dissolved. The reaction mixture was refluxed with constant stirring for 30 min and filtered hot. Upon cooling, dark green crystals of the product were obtained. This product was filtered and recrystallized from acetonitrile/ethanol to yield 1.60 g (76%). Anal. Calcd for $CoC_{20}H_{34}N_6P_2F_{12}$: C, 33.96; H, 4.84; N, 11.88; Co, 8.33. Found: C, 33.94; H, 4.83: N, 12.00; Co, 8.19.

[3-(1-(Methylamino)ethylidene)-11-(1-(methylimino)ethyl)-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-κ^4N]cobalt(III) Hexafluorophosphate–Acetonitrile, [Co((MeNIminoethyl)(HMeNEthi)-Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_3$·CH$_3$CN. A 0.2-g (0.00028-mol) sample of the cobalt(II) complex was dissolved in 5 mL of dry acetonitrile and 20 mL of dry methanol in an inert-atmosphere box. Ammonium hexakis(nitrato)cerate(IV) (0.163 g, 0.00028 mol), dissolved in 10 mL of methanol, was added dropwise to this solution over ca. 2 h. During this time the color of the reaction mixture changed from dark green to a deep purple. The reaction mixture was filtered and then removed to the open atmosphere. Ammonium hexafluorophosphate (0.09 g, 0.00056 mol) in 10 mL of methanol was added dropwise to give a purple crystalline product when the mixture was allowed to stand overnight; yield, 0.20 g (83%). Anal. Calcd for $CoC_{22}H_{37}N_7P_3F_{18}$: C, 29.50; H, 4.18; N, 10.97; Co, 6.59. Found: C, 29.74; H, 4.14; N, 11.29; Co 6.24. $^{13}C\{^1H\}$ NMR data (δ) in CD_3CN, Me_4Si reference: 183.1, 178.3, 177.5, 171.7, 171.0, 162.9, 109.5, 68.0, 55.2, 52.9, 49.5, 47.6, 32.5, 26.7, 25.4, 25.2, 24.2, 21.1, 17.8.

Crystal Data and Structure Refinement. Dark red-brown crystals of the cobalt(II) complex [Co((MeNIminoethyl)(HMeNEthi)Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$·CH$_3$CN suitable for X-ray diffraction were prepared by slow crystallization from an acetonitrile/methanol solution. A long rectangular tabular crystal of dimensions 0.15 × 0.60 × 0.90 mm was mounted in a glovebox on a quartz fiber with its *b* axis approximately along the spindle direction. The crystal was coated with several thin layers of epoxy cement. Intensity data were collected at room temperature on a Syntex P$\bar{1}$ diffractometer, equipped with a molybdenum target X-ray tube (Mo K$\bar{\alpha}$ = 0.71069 Å) and a graphite-crystal monochromator. The lattice constants were determined from a least squares refinement of the setting angles for 41 high-angle reflections with $17 < 2\theta < 30°$. Intensity data were collected by the ω–2θ scan technique with a variable scan rate between 4 and 24°/min in 2θ, depending on the intensity of the reflection. The stability of the crystal was monitored by measuring six check reflections after every 100 reflections during the course of data collection. No significant changes were observed over this period.

A total of 5560 unique reflections was collected, of which 2922 ($I/\sigma(I) > 3.0$) were used in the refinement. The data were corrected for Lorentz and polarization effects; no corrections were made for absorption effects. The molecule crystallizes in the monoclinic system. Systematic absences $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, uniquely determined the space group as $P2_1/n$. The position of the cobalt atom was obtained from a

---

(10) Rosenthal, J.; Yarmus, L. *Rev. Sci. Instrum.* **1966**, *37*, 381.

(11) Busch, D. H.; Olszanski, D. J.; Stevens, J. C.; Schammel, W. P.; Kojima, M.; Herron, N.; Zimmer, L. L.; Holter, K. A.; Mocak, J. *J. Am. Chem. Soc.* **1981**, *103*, 1472.

(12) Korybut-Daszkiewicz, 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.

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

Table I. Summary of Crystallographic Data for $[Co((MeNIminoethyl)(HMeNEthi)Me_2[16]tetraeneN_4)](PF_6)_2 \cdot CH_3CN$

M_r	748.45
a, Å	18.186 (2)
b, Å	7.296 (1)
c, Å	25.279 (3)
β, deg	110.66 (1)
V, Å^3	3138
T, K	295
Z	4
space group	$P2_1/n$ ($\equiv C_{2h}^5$)
d_{calcd}, g cm^{-3}	1.58
d_{obsd},[a] g cm^{-3}	1.51
cryst dimens, mm	0.15 × 0.60 × 0.90
abs coeff (μ), cm^{-1}	7.4
radiation, Å	Mo K$\bar{\alpha}$ = 0.71069
$2\theta_{max}$, deg	50
no. of unique data	5560
no. of data used in refinement [$I/\sigma(I) > 3$]	2922
no. of variables	397
R	0.060
R_w[b]	0.116
GOF	2.2
data collcd	$+h,+k,\pm l$

[a] By flotation in benzene/chloroform. [b] $R_w = [\sum w^2(|KF_o|^2 - |F_c|^2)^2/\sum w^2|KF_o|^4]^{1/2}$ with $w = 1/\sigma(F_o^2)$.

Patterson synthesis. Subsequent cycles of structure factor and Fourier syntheses revealed all non–hydrogen atoms. In the least-squares refinement the function minimized was $\sum w^2(K^2|F_o|^2 - |F_c|^2)^2$, where $w = 1/\sigma(F_o^2)$. Refinement with isotropic thermal parameters was carried out, and the discrepancy index

$$R = \sum||KF_o| - |F_c||/\sum|KF_o|$$

was calculated to be 12.4%. Most of the methyl hydrogen atoms were located on a difference electron density map, and the positions of the remaining methyl hydrogen atoms were calculated by using a least-squares fit of the positions of the observed atoms. Coordinates for all non-methyl hydrogen atoms were calculated by using the structural parameters of the connecting atoms with the restriction C–H and N–H = 0.95 Å. The positions and isotropic thermal parameters of all hydrogen atoms were held constant during the refinement. The final refinement cycle with anisotropic thermal parameters for all non-hydrogen atoms yielded values of 6.0% and 11.6% for R and R_w, respectively. A final difference electron density map showed no significant features, with a maximum peak of 0.43 e Å^{-3}.

All computations used in the above structure determination were carried out on an Amdahl 470 computer at the Instruction and Research Computer Center of The Ohio State University with the CRYM crystallographic package.[14] Neutral-atom scattering factors and anomalous dispersion factors were taken from ref 15 for C, H, N, P, F, and Co. Table I summarizes the crystal characteristics and X-ray diffraction methodology used in the determination. Final positional and anisotropic thermal parameters are given in Table II, and bond lengths and bond angles of the macrocyclic cation in Table III. Listings of calculated and observed structure factors and metrical parameters for the PF_6^- counterions are available as supplementary material.

Discussion

The remarkable rearrangement[6] of the long-known cyclidene ligand into the unusual clathrochelate and half-clathro structures is remarkably metal ion specific. It is clearly a case of the ligand structure being determined by the stereochemical preferences associated with a given metal ion electronic structure. The d^8 nickel(II) ion forms an extremely stable, low-spin, 4-coordinate, square-planar complex with the cyclidene ligand, and that complex shows no tendency to rearrange. The d^6 iron(II) ion promotes rearrangement of the ligand in order to form an equally stable, low-spin, 6-coordinate complex within which the rearranged ligand is a hexadentate clathrochelating species. We now report the clear link between the nickel(II) and iron(II) structures. Cobalt(II) tends to combine with unsaturated nitrogen donors to form low-spin, 5-coordinate complexes, and this tendency produces an intermediate degree of rearrangement of an unbridged cyclidene ligand. The product is a pentadentate ligand, half of whose structure corresponds to that of the *clathrochelate* while the other half retains the characteristic structural features of the *cyclidene*. This is shown in Scheme II.

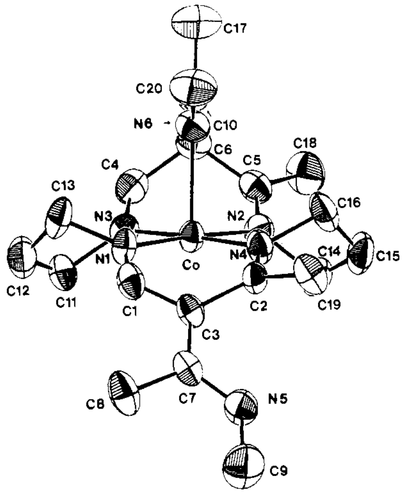


Figure 1. Atom-labeling scheme and ORTEP plot of the cobalt(II) complex, emphasizing the conformation of the saturated portion of the macrocycle.

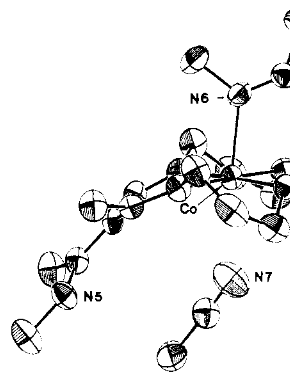


Figure 2. ORTEP plot of the cobalt(II) complex, emphasizing the axial coordination of the rearranged imine nitrogen.

Structure of $[Co((MeNIminoethyl)(HMeNEthi)Me_2[16]tetraeneN_4)](PF_6)_2 \cdot CH_3CN$. Two different ORTEP representations of the structure of the new cobalt(II) complex are shown in Figures 1 and 2. The latter view shows the axial coordination provided by the rearranged peripheral group (N(6)) particularly clearly. The angles involving the axial imine nitrogen, the metal, and the four equatorial nitrogens range from 86.7 to 96.1°. This relatively narrow range indicates that the structure is a fair approximation to a tetragonal pyramid with the imine nitrogen in a true axial site, as further suggested by the ORTEP drawing. The four equatorial nitrogens share an average bond length of 1.93 Å, appreciably less than the axial bond distance of 2.15 Å; however, this latter distance is still well within the limits known for a Co–N bond. These four nitrogens form a rather well-defined plane with the cobalt atom displaced only 0.05 Å toward the apical coordination site. A molecule of acetonitrile (from solvent) is situated near the unrearranged peripheral substituent. The nitrogen atom of the acetonitrile is no closer than 2.645 Å from the metal atom, and the solvent molecule is so oriented that the nitrogen is closest to the cobalt atom. Strictly speaking, the complex may be described as having a distorted-octahedral geometry. It is interesting to find the distortion accumulated in a single metal ligand bond rather than along both axial bonds.

Other bond lengths and bond angles (Table III) lie within expected ranges, although the imine C=N bond lengths merit

---

(14) Modified by G. G. Christoph at The Ohio State University, from: DuChamp, D. J. "Program and Abstracts"; American Crystallographic Association Meeting, Bozeman, MT, 1964; Paper B14.

(15) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

Table II. Final Positional and Anisotropic Thermal Parameters for the Non-Hydrogen Atoms of the Half-Clathro Half-Cyclidene Cobalt(II) Complex[a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	49557(5)	92012(13)	73948(4)	318(5)	398(5)	369(5)	24(6)	174(4)	-26(5)
N1	44946(28)	103054(72)	78917(21)	303(32)	466(40)	451(34)	5(28)	184(28)	-68(9)
N2	54233(29)	79399(73)	69120(21)	422(35)	451(38)	385(34)	66(31)	201(28)	-34(30)
N3	39969(29)	78983(71)	70136(22)	392(35)	390(37)	493(37)	60(30)	189(30)	52(31)
N4	59359(28)	104170(72)	77991(20)	380(33)	515(41)	380(32)	-16(30)	221(28)	-9(29)
N5	67788(32)	101135(80)	95178(21)	498(38)	669(43)	355(34)	25(35)	176(30)	-4(32)
N6	45423(31)	112158(70)	67362(22)	570(39)	336(39)	481(36)	49(31)	259(31)	4(29)
N7	96045(37)	114413(104)	68834(27)	689(48)	1200(68)	612(45)	52(47)	286(41)	-114(47)
C1	48736(37)	107428(94)	83969(26)	459(42)	450(45)	461(41)	-4(43)	282(35)	-65(42)
C2	61895(33)	109862(90)	83123(25)	276(35)	391(42)	446(40)	-35(36)	152(31)	15(38)
C3	57041(35)	107604(93)	86701(24)	388(39)	360(41)	366(37)	-109(40)	181(31)	-64(37)
C4	37604(38)	77397(93)	64808(29)	415(45)	435(48)	574(49)	18(39)	119(39)	-2(41)
C5	50698(39)	78062(92)	63867(27)	526(48)	419(46)	402(42)	-24(40)	229(38)	-13(38)
C6	42429(40)	85491(93)	61618(26)	498(47)	463(49)	376(43)	-29(85)	116(36)	-14(35)
C7	60265(38)	105382(91)	92507(26)	462(42)	431(47)	419(41)	-85(40)	238(34)	-33(37)
C8	55417(41)	106508(111)	96246(28)	624(50)	779(59)	551(46)	-126(50)	381(40)	-101(47)
C9	71823(45)	99243(130)	101200(30)	633(55)	1119(73)	454(48)	13(55)	97(43)	-39(49)
C10	42619(38)	106622(103)	62356(27)	467(45)	506(51)	449(44)	76(43)	168(36)	44(43)
C11	35269(38)	71477(103)	73378(29)	381(44)	614(55)	649(51)	-103(42)	207(39)	124(44)
C12	32273(40)	86435(115)	76301(29)	420(47)	891(69)	569(49)	-28(47)	238(39)	15(46)
C13	36312(36)	104603(104)	76733(28)	313(41)	686(60)	563(46)	108(41)	179(35)	-96(42)
C14	62457(41)	73282(110)	71968(29)	450(48)	767(61)	578(50)	228(46)	256(40)	46(46)
C15	67967(39)	89598(128)	73555(28)	404(46)	1140(76)	499(46)	173(53)	271(38)	64(52)
C16	64136(39)	107322(111)	74352(26)	503(46)	729(55)	458(43)	-122(48)	298(36)	4(46)
C17	39435(51)	117314(117)	57032(33)	960(69)	686(61)	627(56)	71(57)	154(50)	183(49)
C18	53717(45)	70124(111)	59623(30)	770(59)	674(58)	581(51)	66(50)	371(45)	-106(45)
C19	69217(42)	121079(103)	85413(28)	602(52)	627(54)	547(48)	-151(45)	309(41)	-26(43)
C20	46006(49)	131806(99)	68635(32)	966(67)	356(48)	716(56)	58(49)	304(51)	0(42)
C21	91451(49)	107064(112)	58343(31)	1000(67)	545(53)	642(54)	133(55)	271(50)	-43(49)
C22	94063(41)	110989(106)	64275(31)	582(50)	594(57)	532(48)	64(45)	272(43)	33(46)
P1	15338(13)	99527(36)	59511(9)	579(15)	883(19)	533(14)	49(14)	179(12)	-3(13)
P2	33965(13)	78398(33)	42020(9)	641(17)	668(17)	618(15)	-39(14)	246(13)	51(13)
F11	18922(41)	100933(117)	54834(31)	2028(71)	2834(97)	1217(50)	-1217(70)	1211(53)	-810(57)
F12	8031(34)	90721(108)	55182(25)	945(43)	2276(81)	1271(49)	-602(53)	90(38)	-481(54)
F13	11769(40)	97790(85)	64222(24)	2082(66)	1316(54)	1253(47)	142(50)	1208(49)	49(41)
F14	18718(39)	79494(93)	61026(30)	1568(62)	1315(56)	1865(65)	550(51)	727(53)	-52(51)
F15	11848(43)	118675(87)	58375(28)	2010(73)	1008(49)	1744(65)	520(52)	590(56)	671(47)
F16	23002(32)	107658(103)	63751(24)	842(40)	2125(76)	1252(48)	-122(50)	-103(37)	-576(53)
F21	30566(40)	84863(91)	46580(24)	2051(71)	1471(61)	1270(50)	1(53)	1022(51)	-361(44)
F22	42064(36)	82668(133)	46008(29)	868(46)	3107(111)	1643(66)	-471(63)	-227(44)	497(71)
F23	25385(36)	74056(107)	38281(27)	1136(51)	2074(80)	1384(55)	-395(54)	61(43)	-295(54)
F24	36978(44)	71181(95)	37423(26)	2384(78)	1641(64)	1452(56)	769(61)	1463(58)	433(49)
F25	32961(39)	97456(82)	39402(29)	1723(63)	1001(48)	1987(66)	208(46)	903(56)	688(47)
F26	34357(43)	58669(82)	44479(30)	2152(74)	995(48)	2327(74)	494(53)	1627(65)	638(52)

[a] Atomic coordinates and thermal parameters have been multiplied by 10^5 and 10^4, respectively. The anisotropic thermal parameters are expressed in the form $\exp[-2\pi^2(h^2U_{11}a^{*2} + k^2U_{22}b^{*2} + l^2U_{33}c^{*2} + 2hkU_{12}a^*b^* + 2hlU_{13}a^*c^* + 2klU_{23}b^*c^*)]$.

mention. One would expect the three localized C═N bonds to be somewhat shorter than the other two bonds (C(2)–N(4) and C(1)–N(1)), which are in conjugation with the carbon–carbon double bond (C(3)–C(7)). The results do not bear out this expectation, and suggest that steric as well as electronic factors may affect the observed lengths of these bonds.

The two hexafluorophosphate counterions exhibit some disorder, as is evident from the large and very anisotropic thermal parameters for the fluorine atoms listed in Table II. The equivalent B values for the fluorine atoms vary from 10.9 to 16.2 Å^2, as compared to the values of 5.0 and 5.3 Å^2 for B_{eq} for the phosphorus centers. The P–F bond lengths range from 1.495 to 1.580 Å. The final large R and R_w values obtained for this structure are most likely a consequence of the disordered PF_6^- groups.

Figure 3 (supplementary material) presents a stereo packing diagram of the complex, showing all non-hydrogen atoms. No hydrogen bond interactions involving the hexafluorophosphate counterions are observed. The diagram, like Figure 1, shows that the saturated carbon atoms in the trimethylene chains have assumed a skew conformation rather than the chair and boat conformations commonly found among the lacunar cyclidene complexes. Similar skew conformations have been observed in the X-ray crystal structure of a closely related low-spin iron(II) complex,[16] formed by the base-promoted, electrophilic attack of two coordinated acetonitrile molecules at the apical carbons of the parent macrocyclic ligand in the presence of an iron(II) salt (Scheme III).[17] The same kinds of skew conformations have also

---

(16) Mertes, K. B.; Corfield, P. W. R.; Busch, D. H. *Inorg. Chem.* **1977**, *16*, 3226.

(17) Bowman, K.; Riley, D. P.; Busch, D. H.; Corfield, P. W. R. *J. Am. Chem. Soc.* **1975**, *97*, 5036.

Table III. Bond Distances (Å) and Angles (deg) with Their Estimated Standard Deviations for the Title Complex

A. Bond Distances			
(a) Coordination Sphere			
Co–N(1)	1.917 (4)	Co–N(4)	1.930 (4)
Co–N(2)	1.947 (4)	Co–N(6)	2.148 (5)
Co–N(3)	1.921 (4)		
(b) Imine N=C Double Bonds			
N(1)–C(1)	1.260 (8)	N(4)–C(2)	1.283 (8)
N(2)–C(5)	1.258 (8)	N(6)–C(10)	1.253 (8)
N(3)–C(4)	1.266 (9)		
(c) Ligand			
C(1)–C(3)	1.422 (7)	C(5)–C(6)	1.508 (7)
C(3)–C(7)	1.385 (8)	C(6)–C(10)	1.552 (10)
C(7)–C(8)	1.505 (8)	C(10)–C(17)	1.485 (10)
C(7)–N(5)	1.331 (7)	C(6)–C(4)	1.506 (8)
N(5)–C(9)	1.444 (9)	C(11)–C(12)	1.522 (10)
C(3)–C(2)	1.479 (7)	N(6)–C(20)	1.465 (9)
C(2)–C(19)	1.495 (8)	C(12)–C(13)	1.501 (10)
C(16)–C(15)	1.516 (11)	C(15)–C(14)	1.516 (11)
C(5)–C(18)	1.484 (9)		
N(1)–C(13)	1.474 (6)	N(3)–C(11)	1.481 (7)
N(2)–C(14)	1.482 (7)	N(4)–C(16)	1.489 (7)
(d) Acetonitrile of Crystallization			
N(7)–Co	2.645 (8)	C(21)–C(22)	1.433 (10)
N(7)–C(22)	1.108 (10)		
B. Bond Angles			
(a) Coordination Sphere			
N(1)–Co–N(2)	176.6 (2)	N(2)–Co–N(6)	87.0 (2)
N(1)–Co–N(3)	90.4 (2)	N(2)–Co–N(4)	91.3 (2)
N(1)–Co–N(4)	89.8 (2)	N(3)–Co–N(4)	177.4 (2)
N(1)–Co–N(6)	96.1 (2)	N(3)–Co–N(6)	86.7 (2)
N(2)–Co–N(3)	88.4 (2)	N(4)–Co–N(6)	95.8 (2)
(b) Ligand			
C(1)–N(1)–Co	124.2 (3)	C(3)–C(1)–N(1)	127.0 (5)
C(13)–N(1)–Co	116.2 (4)	C(19)–C(2)–N(4)	121.5 (5)
C(13)–N(1)–C(1)	119.3 (4)	C(19)–C(2)–C(3)	117.8 (5)
C(5)–N(2)–Co	121.6 (4)	C(3)–C(2)–N(4)	120.2 (4)
C(14)–N(2)–Co	115.3 (4)	C(2)–C(3)–C(1)	117.7 (5)
C(14)–N(2)–C(5)	122.8 (5)	C(2)–C(3)–C(7)	122.7 (4)
C(4)–N(3)–Co	119.1 (4)	C(1)–C(3)–C(7)	119.6 (5)
C(4)–N(3)–C(11)	120.6 (5)	C(6)–C(4)–N(3)	119.4 (5)
C(11)–N(3)–Co	120.3 (4)		
C(2)–N(4)–Co	128.3 (3)	C(18)–C(5)–N(2)	127.7 (5)
C(2)–N(4)–C(16)	119.6 (4)	C(6)–C(5)–C(18)	116.2 (5)
C(16)–N(4)–Co	112.0 (4)		
C(9)–N(5)–C(7)	127.3 (5)	N(2)–C(5)–C(6)	116.1 (5)
C(10)–N(6)–Co	118.0 (5)	C(5)–C(6)–C(4)	110.4 (5)
C(20)–N(6)–Co	121.4 (4)	C(10)–C(6)–C(4)	108.5 (5)
C(10)–N(6)–C(20)	120.6 (6)	C(5)–C(6)–C(10)	109.6 (5)
N(5)–C(7)–C(8)	114.8 (5)	C(8)–C(7)–C(3)	122.4 (5)
N(5)–C(7)–C(3)	122.7 (5)		
C(6)–C(10)–C(17)	115.3 (6)	N(6)–C(10)–C(17)	129.5 (7)
N(6)–C(10)–C(6)	115.2 (6)	N(3)–C(11)–C(12)	112.3 (6)
C(11)–C(12)–C(13)	114.8 (4)	N(1)–C(13)–C(12)	112.9 (5)
N(2)–C(14)–C(15)	110.6 (6)	C(14)–C(15)–C(16)	114.4 (4)
N(4)–C(16)–C(15)	110.2 (6)		
(c) Acetonitrile			
C(21)–C(22)–N(7)	178.5 (9)		

been observed in a 15-membered unbridged macrocycle.[18] That case is interesting as the conformational restraints at the saturated 5- and 6-membered chelate rings results in the adoption of an overall Z-shaped conformation for the macrocycle. In the present case the reverse is true; the internal rearrangement of one end of the ligand produces a Z-shape for the two unsaturated portions of the macrocycle, and this forces the two 6-membered saturated chelate rings to adopt a skewed arrangement.

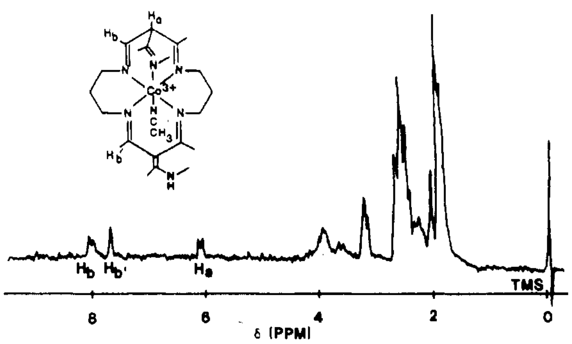


Figure 4. ^1H NMR spectrum of the rearranged cobalt(III) complex in acetonitrile-d_3, referenced to internal Me_4Si.

Characterization of the Pentadentate Cobalt(II) Complex. While the X-ray crystallographic study described above establishes the novel ligand geometry for the cobalt(II) complex in the solid state, it is also necessary to demonstrate that this novel rearranged structure exists in solution. A combination of spectroscopic methods has been used to show that this is, in fact, the case.

The cobalt cyclidene complexes are readily oxidized by cerium(IV) in the presence of suitable monodentate ligands, such as thiocyanate, to give the corresponding 6-coordinate, diamagnetic cobalt(III) compounds.[7] As in the present case, a solvent molecule can occupy the sixth coordination site. Figure 4 presents the ^1H NMR spectrum of the cobalt(III) derivative formed by chemical oxidation of the cobalt(II) complex of the pentadentate clathrochelate ligand. The two doublets centered at 6.15 and 8.15 ppm are due to protons H_a and H_b, respectively. The coupling between these protons gives $^3J_{H-H} \simeq 5.0$ Hz. The singlet at 7.7 ppm, due to $H_{b'}$, indicates that complete rearrangement to a 6-coordinate clathrochelate species has not occurred.

The infrared spectrum of the solid cobalt(III) product confirms the half-clathro structure; a strong band at 3395 cm^{-1} can be assigned to the NH stretching mode of the secondary amine associated with the half-cyclidene part of the ligand, while a band at 2230 cm^{-1} is due to coordinated acetonitrile, the sixth ligand. Bands at 1680 and 1660 cm^{-1}, not present in the spectrum of the analogous (unrearranged) cyclidene nickel(II) complex, are presumably due to the altered unsaturation, including the C=N stretching vibration for the coordinated imine group. The complexity of the ^1H NMR spectrum in the 1.5–4.0 ppm region supports the absence of symmetry elements in this half-clathro complex. All of these spectral features, which are not typical of the cyclidene complexes, are, in fact, reminiscent of those observed in the iron(II) clathrochelate species.[6]

The ^{13}C NMR spectrum of the half-clathro cobalt(III) complex (Experimental Section) supports the preceding arguments. The absence of any symmetry elements results in 20 unique carbon resonances, all of which can be resolved. These resonances have been assigned by using off-resonance decoupling techniques and by comparison with ^{13}C NMR spectra of known unbridged nickel(II) cyclidene complexes. The six methyl groups give rise to resonances between 17.8 and 26.7 ppm. The next six resonances, occurring between 32.5 and 55.2 ppm, are assigned to the six unique methylene carbons. The peak at 68.0 ppm, which splits into a doublet in the off-resonance spectrum, is due to carbon C(6) (Figure 1) and is dramatically shifted from the resonance at 109.5 ppm due to C(3). This shift of over 40 ppm in going from a quaternary to tertiary carbon atom provides a convenient marker for the detection of the base-induced rearrangement process in this and related cyclidene coordination complexes.

The electrochemical behavior of the 5-coordinate cobalt(II) complex is quite simple. Two redox processes are observed. A reversible wave at +1.16 V is associated with the ligand-centered process while a reversible wave at −0.465 V is due to the cobalt(II)/(III) redox couple. This latter potential is the most negative yet observed for a cobalt(II) derivative of a cyclidene ligand. For comparison, $E_{1/2} = -0.145$ V for $[Co\{Me_2NEthi)_2Me_2[16]tetraeneN_4\}](PF_6)_2$ under the same experi-

---

[18] Alcock, N. W.; Lin, W.-K.; Jircitano, A.; Mokren, J. D.; Corfield, P. W. R.; Johnson, G.; Novotnak, G.; Cairns, C.; Busch, D. H., submitted for publication in *Inorg. Chem.*

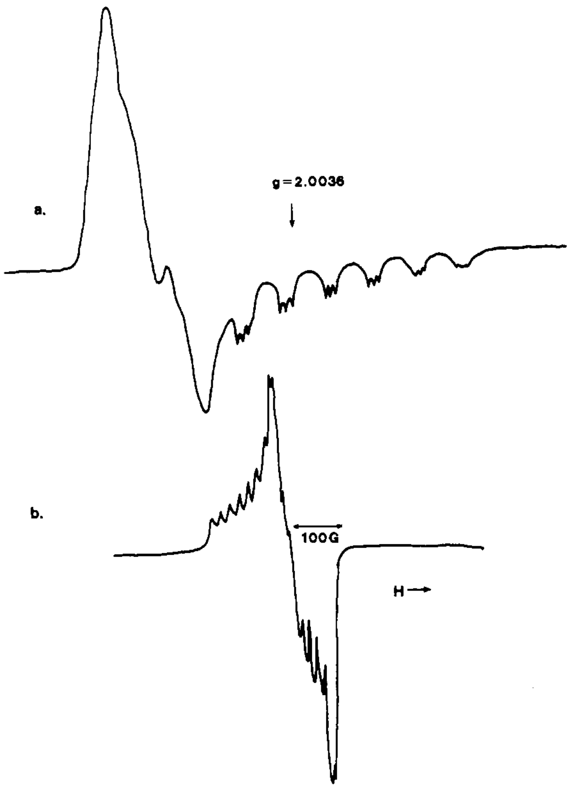


Figure 5. EPR spectra of (a) the half-clathro half-cyclidene cobalt(II) complex and (b) the O_2 adduct of the same complex, in frozen acetone. Both spectra were obtained at 77 K; exposure of the complex to dioxygen was performed at 233 K.

mental conditions (structure II).[7,17,19,20] This extremely negative potential reflects the presence of the fifth coordinated nitrogen atom, which places extra electron density on the metal atom, thereby driving the potential more cathodic. This interpretation is supported by the qualitative observation that a green solution of this complex rapidly turns red when exposed to the atmosphere, suggesting the facile autoxidation to the cobalt(III) state. Basolo et al. have proposed a correlation between the redox potential of the $\mathrm{Co^{II}/Co^{III}}$ couple of certain Schiff base complexes and their dioxygen affinities, such that lower $E_{1/2}$ values give rise to higher K_{O_2} values.[21] The greater the electron density at the metal center the stronger will be the back-bonding and concomitant electron donation to coordinated dioxygen. This provides a rationalization for the ready autoxidation of the half-clathro cobalt(II) complex as compared to unbridged cobalt(II) cyclidene complexes. By way of contrast, the $\mathrm{Fe^{II}/Fe^{III}}$ potential shifts by ca. 90 mV in the anodic direction for the 6-coordinate clathrochelate–iron(II) complexes as compared with the parent cyclidene complexes. This shift reflects the thermodynamic stability of the low-spin, 6-coordinate complex of iron(II). These iron(II) clathrochelates are, as expected, completely unreactive toward dioxygen.

Perhaps the clearest indication of the coordination environment of the cobalt(II) atom in the half-clathro complex is from EPR spectroscopy. The EPR spectrum of the pentadentate cobalt(II) compound in acetone, a noncoordinating solvent for these complexes, measured at 77 K, is similar to those of square-pyramidal low-spin cobalt(II) Schiff base complexes.[21,22] The spectrum (Figure 5) has near-axial symmetry with $g_\perp = 2.22$ and $g_\parallel = 2.01$. These values should be compared to those measured for lacunar cyclidene cobalt(II) complexes, in which $g_\perp$ varies between 2.28 and 2.32 and $g_\parallel$ is 2.00–2.02 when *N*-methylimidazole is the axial base. The $g_\parallel$ component exhibits an eight-line hyperfine coupling, $A = 1.0 \times 10^{-2}$ cm^{-1}, again within the range expected for this type of complex. Most importantly for diagnostic purposes, each of these eight bands is split into an equal-intensity triplet as a result of the interaction with one axial nitrogen donor ($I = 1$). The measured super hyperfine coupling constant, $A_\parallel^{N} = 1.13 \times 10^{-3}$ cm^{-1}, is in accord with other measurements made with *N*-methylimidazole as axial base. Exposure of this green solution to 1 atm of dioxygen at 233 K for 200 s gives the spectrum of Figure 5. This spectrum, in which $g_\parallel = 2.09$ ($A_\parallel = 1.55 \times 10^{-3}$ cm^{-1}) and $g_\perp = 2.02$ ($A_\perp = 1.14 \times 10^{-3}$ cm^{-1}), is typical of a mononuclear dioxygen adduct, where the spin-density distribution leads to a cobalt(III)–superoxo formulation.[8,21] At temperatures much above 233 K, this 1:1 adduct begins to decompose, although it can still be detected in solutions that have been warmed to room temperature for as long as 14 h.

Conclusions

A combination of structural and spectroscopic characterization techniques has been used to identify the first example of a pentadentate *half-clathro* cobalt(II) complex derived from the cyclidene family of macrocyclic ligands. The complex is formed by the same type of base-catalyzed ligand rearrangement that has already been noted for a series of low-spin iron(II) encapsulation complexes. In contrast to the iron(II) clathrochelate complexes, the cobalt(II) half-clathro complex exhibits a marked chemical reactivity toward dioxygen, proceeding through dioxygen adduct formation to autoxidation. This ligand rearrangement process produces a ligand well suited to the demands of the metal ion in question. Nickel(II) favors a square-planar 4-coordinate structure, so the cyclidene binds without rearrangement in its normal tetradentate form. Iron(II) favors an octahedral 6-coordinate structure with the result that the cyclidene ligand rearranges to the hexadentate clathrochelate form. Finally, cobalt(II) favors tetragonal-pyramidal 5-coordination, and it promotes the partial rearrangement of the cyclidene ligand into the pentadentate half-clathro form. It is probable that additional examples of these structures could be produced by variations in the substituents at the R^2 and R^3 positions. Suitable choice of substituents, including both favorable steric and electronic factors, may yield derivatives that are less susceptible to irreversible autoxidation. This goal has been largely achieved in our studies on the family of lacunar iron(II) complexes.[23] In addition, the possibility that other metals, such as manganese(II) and chromium(III), may promote similar ligand rearrangements deserves to be investigated now that these metals have been successfully incorporated in complexes of the lacunar macrobicyclic cyclidene ligands.

Acknowledgment. The support of the National Science Foundation and the National Institutes of Health is gratefully acknowledged. Thanks are also due to Drs. Bill Davis and Madhav Chavan for assistance during the course of this work.

Registry No. [Co((MeNIminoethyl)(HMeNEthi)Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$·CH$_3$CN, 105638-60-6; [Co((MeNIminoethyl)(HMeNEthi)Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_3$·CH$_3$CN, 105638-62-8; H$_4$[(HMeNEthi)$_2$[16]tetraeneN$_4$](PF$_6$)$_3$Cl, 105638-64-0.

Supplementary Material Available: A table of bond distances and angles and a stereodrawing of the unit cell (Figure 3) (2 pages); a table of calculated and observed structure factors (8 pages). Ordering information is given on any current masthead page.

---

(19) Stevens, J. C. Ph.D. Thesis, The Ohio State University, 1979.

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

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

(22) Hoffman, B. M.; Diemente, D. L.; Basolo, F. *J. Am. Chem. Soc.* **1970**, *92*, 61.

(23) Herron, N.; Zimmer, L. L.; Gryzbowski, J. J.; 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.