CH_2Cl_2). Anal. Calcd for $C_{18}H_{24}As_2PdS_2$: C, 38.6; H, 4.3. Found: C, 38.5; H, 4.3. ^1H NMR (CD_2Cl_2, -78 °C): δ 1.26 (s, 6 H, AsMe), 1.90-2.88 (m, 8 H, CH_2CH_2), 7.01-7.47 (m, 10 H, aromatics). ^1H NMR (CD_2Cl_2, 25 °C): δ 1.26 (s, 2.3 H, AsMe), 1.80 (s, 3.7 H, AsMe), 1.93-2.91 (m, 8 H, CH_2CH_2), 7.01-7.80 (m, 10 H, aromatics). ^1H NMR ($CDCl_3$): δ 1.27 (s, 1.2 H, AsMe), 1.80 (s, 4.8 H, AsMe), 2.30-2.89 (m, 4 H, CH_2CH_2), 7.37-7.80 (m, 10 H, aromatics). ^1H NMR (benzene-d_6): δ 1.37 (s, 6 H, AsMe), 1.93-2.91 (m, 8 H, CH_2CH_2), 7.01-7.80 (m, 10 H, aromatics). ^1H NMR (toluene-d_8): δ 1.38 (s, 6 H, AsMe), 2.09-2.94 (m, 8 H, CH_2CH_2), 7.04-7.73 (m, 10 H, aromatics). ^1H NMR (nitrobenzene-d_5, 100 °C): δ 1.37 (s, 2.0 H, AsMe), 1.83 (s, 4.0 H, AsMe), 2.40-2.96 (m, 8 H, CH_2CH_2), 7.38-8.17 (m, 10 H, aromatics).

[*SP*-4-1-(*R,*S**)]-Bis[2-(methylphenylarsino)ethanethiolato]palladium(II) (*meso-trans*-[Pd(AsS)$_2$]).** This compound was isolated in 44% yield as orange prisms, mp 171-173 °C, with use of (±)-AsSH as ligand. Anal. Calcd for $C_{18}H_{24}As_2PdS_2$: C, 38.6; H, 4.3. Found: C, 38.7; H, 4.4. ^1H NMR (CD_2Cl_2, -78 °C): δ 1.86 (s, 6 H, AsMe), 2.32-2.87 (m, 8 H, CH_2CH_2), 7.30-7.87 (m, 10 H, aromatics). ^1H NMR (CD_2Cl_2, 25 °C): δ 1.26 (s, 1.71 H, AsMe), 1.73 (s, 0.87 H, AsMe), 1.80 (s, 1.71 H, AsMe), 1.86 (s, 1.71 H, AsMe), 2.32-2.87 (m, 8 H, $AsCH_2CH_2$), 7.30-7.87 (m, 10, aromatics). ^1H NMR (benzene-d_6): δ 1.374 (s, 3 H, AsMe), 1.378 (s, 3 H, AsMe), 1.93-2.91 (m, 8 H, $AsCH_2CH_2$), 7.01-7.80 (m, 10 Hz, aromatics). ^1H NMR ($CDCl_3$): δ 1.27 (s, 0.6 H, AsMe), 1.71 (s, 0.3 H, AsMe), 1.80 (s, 2.55 H, AsMe), 1.82 (s, 2.55 H, AsMe), 2.30-2.94 (m, 4 H, CH_2CH_2), 7.37-7.83 (m, 10 H, aromatics).

[*SP*-4-1-(*R,*R**)]-Bis[2-(methylphenylphosphino)ethanethiolato]palladium(II) (*rac-cis*-[Pt(PS)$_2$]).** A solution of K_2PtCl_4 (1.13 g) in water (15 mL) was slowly added to a solution of (±)-PSH (1.0 g) in ethanol (20 mL) containing 1 M NaOH (5 mL). The reaction mixture was stirred for 30 min, whereupon the pale yellow precipitate was filtered off and recrystallized from hot ethanol. The pure racemic-cis diastereomer was thus isolated as pale yellow needles in 46% yield (0.7 g); mp 248-252 °C. Anal. Calcd for $C_{18}H_{24}P_2PtS_2$: C, 3.5; H, 4.3. Found: C, 38.7; H, 4.4. ^1H NMR ($CDCl_3$): δ 1.30 (s, 6 H, J_{PH} = 9.8 Hz, $^3J_{PtH}$ = 29.4 Hz, PMe), 2.07-2.34 (m, 8 H, CH_2CH_2), 7.35-7.56 (m, 10 H, aromatics).

The following compounds were prepared similarly. **[*SP*-4-2-[*R*-(*R**,*R**)]]-(+)-Bis[2-(methylphenylarsino)ethanethiolato]platinum(II) ((+)-*cis*-[Pt(AsS)$_2$]):** pale yellow needles, mp 267-269 °C, 94% yield, $[\alpha]_D$ +368° (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{18}H_{24}AsPtS_2$: C, 33.3; H, 3.7. Found: C, 33.4; H, 3.9. ^1H NMR ($CDCl_3$): δ 1.35 (s, 6 H, $^3J_{PtH}$ = 17.3 Hz, AsMe), 2.20-2.60 (m, 8 H, CH_2CH_2), 6.73-6.59 (m, 10 H, aromatics). ^1H NMR ($CDCl_3$, after 18 h): δ 1.35 (s, 5 H, $^3J_{PtH}$ = 17.3 Hz, AsMe), 1.87 (s, 1 H, $^3J_{PtH}$ = 20.0 Hz, AsMe), 2.20-2.62 (m, 8 H, CH_2CH_2), 6.73-6.59 (m, 10 H, aromatics). ^1H NMR (nitrobenzene-d_5): δ 1.69 (s, 6 H, $^3J_{PtH}$ = 17.2 Hz, AsMe), 2.54-2.93 (m, 8 H, CH_2CH_2), 7.59-8.30 (7, 10 H, aromatics). ^1H NMR (nitrobenzene-d_5, 100 °C): δ 1.69 (s, 5 H, $^3J_{PtH}$ = 17.2 Hz, AsMe), 2.05 (s, 1 H, $^3J_{PtH}$ = 20.5 Hz, AsMe), 2.53-2.87 (m, 8 H, CH_2CH_2), 7.54-8.30 (m, 10 H, aromatics). **(-)-*cis*-[Pt(AsS)$_2$]:** $[\alpha]_D$ -367° (*c* 1.0, CH_2Cl_2). **[*SP*-4-2-(*R**,*R**)]-(±)-Bis[2-(methylphenylarsino)ethanethiolato]platinum(II) ((±)-*cis*-[Pt(AsS)$_2$]):** pale yellow needles, mp 217-222 °C, 85% yield. Anal. Calcd for $C_{18}H_{24}As_2PtS_2$: C, 33.3; H, 3.7. Found: C, 33.1; H, 3.7. ^1H NMR ($CDCl_3$): δ 1.35 (s, 6 H, $^3J_{PtH}$ = 17.3 Hz, AsMe), 2.20-2.65 (m, 8 H, CH_2CH_2), 6.37-6.59 (m, 10 H, aromatics). ^1H NMR ($CDCl_3$, after 18 h): δ 1.35 (s, 3.6 H, $^3J_{PtH}$ = 17.3 Hz, AsMe), 1.82 (s, 1.4 H, $^3J_{PtH}$ = 18.0 Hz, AsMe), 1.87 (s, 0.5 H, $^3J_{PtH}$ = 20.0 Hz, AsMe), 1.89 (s, 0.5 H, $^3J_{PtH}$ = 20.2 Hz, AsMe), 2.20-2.68 (m, 8 H, CH_2CH_2), 7.10-7.85 (m, 10 H, aromatics).

Note Added in Proof. Ligand (±)-PSH has now been resolved by the method of metal complexation into its optical antipodes: use of the optically pure forms of the tertiary phosphine has validated structural assignments of diastereomers made on the basis of comparisons of chemical shift data between analogous phosphine and arsine complexes.

Registry No. (±)-PSH, 102782-08-1; *rac-trans*-[Ni(PS)$_2$], 102782-02-5; (+)-*trans*-[Ni(AsS)$_2$], 102782-03-6; *meso-trans*-[Ni(AsS)$_2$], 102850-01-1; *rac-trans*-[Pd(PS)$_2$], 102850-02-2; *meso-trans*-[Pd(PS)$_2$], 102782-04-7; *rac-cis*-[Pd(PS)$_2$], 102850-04-4; *meso-trans*-[Ni(PS)$_2$], 102850-05-5; *rac-trans*-[Ni(AsS)$_2$], 102850-06-6; (+)-*trans*-[Pd(AsS)$_2$], 102782-05-8; *meso-trans*-[Pd(AsS)$_2$], 102916-56-3; *rac-cis*-[Pt(PS)$_2$], 102782-06-9; (+)-*cis*-[Pt(AsS)$_2$], 102782-07-0; *rac-cis*-[Pt(AsS)$_2$], 102850-07-7; (-)-*trans*-[Ni(AsS)$_2$], 102850-03-3; *meso-cis*-[Pd(PS)$_2$], 102850-13-5; (-)-*cis*-[Pt(AsS)$_2$], 102850-12-4; *rac-cis*-[Pd(AsS)$_2$], 102850-10-2; *meso-cis*-[Pd(AsS)$_2$], 102850-11-3; *rac-trans*-[Pd(AsS)$_2$], 102916-58-5; (+)-*cis*-[Pd(AsS)$_2$], 102916-57-4; *meso-cis*-[Pt(PS)$_2$], 102850-09-9; *meso-cis*-[Pt(AsS)$_2$], 102850-15-7; *rac-trans*-[Pt(AsS)$_2$], 102916-49-4; *meso-trans*-[Pt(AsS)$_2$], 102850-14-6; (+)-*trans*-[Pt(AsS)$_2$], 102850-08-8; Na[PMePh], 55640-97-6; [$PdCl_2$(MeCN)$_2$], 14592-56-4; $Li_2[PdCl_4]$, 15525-45-8; $K_2[PtCl_4]$, 10025-99-7; ethylene sulfide, 420-12-2.

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Syntheses and Spectral Properties of Tropocoronands, a New Class of Versatile Metal-Complexing Macrocycles Derived from Aminotropone Imines

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The synthesis and spectral properties of tropocoronands, TC-*n*,*n*′, a new class of metal-complexing macrocycles derived from two aminotropone imine moieties bridged by two polymethylene linker chains (*n*,*n*′ = 2,2; 3,3; 4,4; 5,5; 6,6), two ether linker chains (*n*,*n*′ = 2-O-2,2-O-2), or two thioether linker chains (*n*,*n*′ = 2-S-2,2-S-2) are described. The tropocoronands were prepared by linking two tropone rings (Tp) through the reaction of 2-(tosyloxy)- or 2-chlorotropone with α,ω-diamino alkanes, ethers, or thioethers; the dimeric 2-aminotropone was then converted to dimeric 2-alkoxytropone imine and reacted with a second molecule of the α,ω-diamino linker to yield TC-*n*,*n*′. The condensation of Tp substituted at position 2 by $-NH(CH_2)_4NH_2$ with the aminotropone imine substituted by $=N(CH_2)_4NH_2$ and $-NH(CH_2)_4NH_2$ yielded TC-*n*,*n*′,*n*″ comprised of three aminotropone imine moieties joined by $-(CH_2)_4-$ linker chains. TC-*n*,*n*′ readily forms a complex with first-row transition-metal ions. Spectral data (^1H NMR, ^{13}C NMR, UV-vis) and single-crystal X-ray diffraction studies of the nickel(II) complexes reveal an interesting transition from nearly planar (diamagnetic) to nearly tetrahedral (paramagnetic) coordination geometry as the length of the linker chain is increased. The planar diamagnetic complexes (*n*,*n*′ = 3,3; 4,4) exhibit NMR resonances in the normal range while signals of tetrahedral paramagnetic complexes (*n*,*n*′ = 5,5; 6,6; 2-O-2,2-O-2) are spread out over field widths of 400 and 2000 ppm, respectively, for ^1H and ^{13}C.

Since their appearance more than two decades ago, nitrogen-containing macrocyclic ligands (coronands[1]) have attracted widespread interest.[2] Their metal-complexing abilities have been used extensively in coordination chemistry to convey unusual redox, spectroscopic, or reactivity properties onto transition-metal ions[3]

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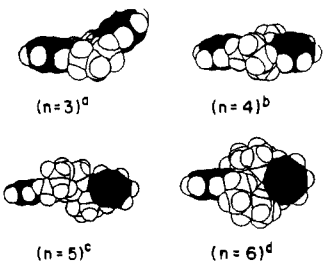
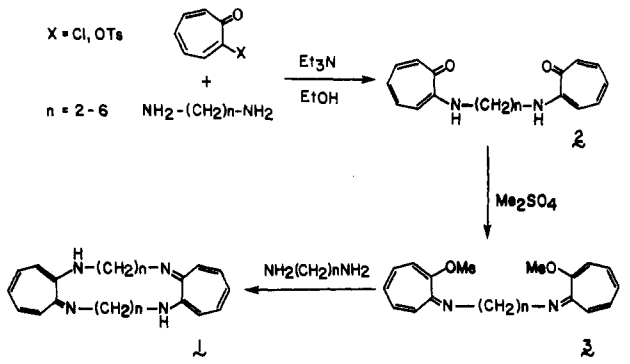


Figure 1. Geometric transition of Nickel(II) tropocoronands:[8] (a) θ = 8.33°; (b) θ = 28.9°; (c) θ = 70.1°; (d) θ = 85.2°. θ = dihedral angle between planes defined by nickel and the nitrogens of each aminotropone imine ring.

Scheme I. Preparation of Tropocoronands **1**



and in numerous model studies of metal centers in bioactive macromolecules.[4] Recently, the binucleating ability of these ligands has been investigated to probe the unique properties of bimetallic centers.[5]

While for the most part entries into coronand systems have been realized by syntheses utilizing C–N bond formation by Schiff base condensation reactions or nucleophilic displacements with sodium sulfonamides,[6] we envisioned a route (Scheme I) that would allow for ready manipulation of the electronic and steric factors of the coronands, a feature often lacking in the above methods. We reasoned that the unique electronic structure and diverse chemical reactivities of the aromatic tropone system[7] would make it amenable to the construction of a class of readily synthesizable ligands (tropocoronands **1**) having a variety of stereochemical and electronic features. X-ray analysis of the nickel(II)–tropocoronand complexes has revealed an intriguing transition from planar to tetrahedral geometry as the number of bridging methylene groups was changed from 3 to 6 (Figure 1).[8] Furthermore, the regioselective γ-substitution reactivity of aminotropone imine moieties allows for the attachment of electron-donating and -withdrawing groups to the ring, thereby altering the electronic properties of the nitrogen donor atoms.[7,9]

The variable coordination geometry and electronic properties obtainable within a single homologous series such as the tropocoronands has potential utility as a means of probing the interrelationship between the physical and spectroscopic properties of a metal and its coordination environment. Such a study would be especially relevant to metal-bearing proteins as their complex structure most often necessitates that information about the metal environment be obtained indirectly via physical and spectroscopic studies. Preliminary results have shown that the tropocoronands form stable copper(II) complexes having a planar to tetrahedral transition similar to that of the nickel(II) series (vide infra) and that the larger tropocoronands **1** (n = 6, 7) are binucleating.[8,10] The properties of these complexes should provide insight into the nature of the binding sites of the numerous mono- and binucleating copper proteins involved in electron transport, oxidation, and oxygen transport processes.[5,11]

Results and Discussion

Synthesis. Our synthesis scheme involves the tethering of two or more troponoid rings with an appropriate organic linker chain followed by addition of a final bridging group under high-dilution conditions to complete and close the macrocycle (Scheme I). Using this approach, one can construct a series of tropocoronands that are comprised of two or more aminotropone imine moieties linked by methylene, ether, or thioether chains with high efficiency and in reasonable yield.

The reactivity of troponoids that allows for the above synthesis route is the facile displacement of an appropriate leaving group from the 2-position of tropones and tropone imines by amines. In this way, two tropone rings can be linked by reaction of an α,ω-diaminoalkane with 2-(tosyloxy)-[12] or 2-chlorotropone to give the dimeric 2-aminotropones **2**.[13,14] Similarly, α,ω-diamino ethers (e.g., 1,5-diamino-3-oxapentane[15]) or thioethers (e.g., 1,5-diamino-3-thiapentane[16]) can be used. Yields for the yellow to orange highly crystalline compounds are ca. 50%.

To complete the ligand, one must allow for addition of another diamine by conversion of the 2-aminotropone moiety to the corresponding 2-alkoxytropone imine by treatment with dimethyl sulfate in refluxing toluene[17] or with triethyloxonium tetrafluoroborate[18] in refluxing chloroform/hexamethylphosphonamide. The resulting alkoxy leaving group then undergoes facile amine

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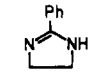
displacement at 25 °C in ethanol. Under high-dilution conditions and with dropwise addition of an ethanolic solution of diamine to a solution of dimeric 2-alkoxytropone imine **3**, tropocoronands **1** were obtained in 20–40% yield.

Although the application of the above scheme generally proceeded smoothly, in two cases complications arose. Conversion of the 2-aminotropone dimer **2** (n = 2) to the corresponding tropocoronand occurred in only 2% yield. The major product, 2-phenyl-2-imidazoline (**4**),[19] presumably formed via an undesired



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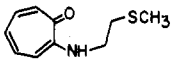

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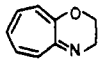

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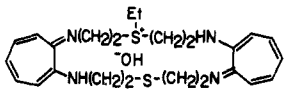

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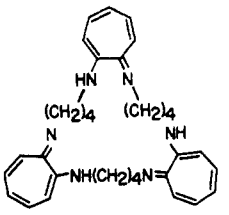
but well-precedented troponoid rearrangement,[7] was obtained in 51% yield. Reaction of thioether-linked 2-aminotropone **2** ((n = 2)–S–(n = 2)) with dimethyl sulfate led to the two products **5** and **6**, formed via S-alkylation. Fortunately, treatment with triethyloxonium tetrafluoroborate[18] led to the desired tropocoronand **1** ((n = 2)–S–(n = 2)) in 25% yield, along with only a minor amount (6%) of the S-ethylated macrocycle **7**.

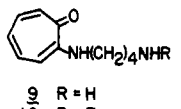
Tropocoronands are yellow to orange crystalline solids and are soluble in moderately polar organic solvents such as chloroform and benzene. Most importantly, addition of ethanolic solutions of first-row divalent transition-metal ions (Fe^{2+}–Zn^{2+}) to tropocoronand solutions result in dark solutions indicative of complex formation. We have succeeded in isolating the nickel(II) n = 3–6 and copper(II) n = 3–5 complexes as black shiny crystals by recrystallization from chloroform/ethanol. The NMR and UV–visible data (vide supra) and the X-ray structures of the nickel(II) complexes reveal a fascinating transition from planar (diamagnetic) to tetrahedral (paramagnetic) coordination geometry as the number of bridging methylene groups increases from three to six (Figure 1).[8] Similarly, recently obtained results for the paramagnetic copper(II) complexes from X-ray analysis show that an analogous planar to tetrahedral transition occurs upon increasing the number of methylene groups from 3 to 5.[10] We had been unable to synthesize the copper(II) n = 6 tropocoronand complex and ascribed this to the reluctance of copper(II) to form tetrahedral coordination complexes. Instead both the n = 6 and n = 7 ligands have been found to be binucleating for Cu(II); that is, rather than yield to the tetrahedral demands of the ligand, two coppers inhabit the binding site.[10] This result is especially significant in light of vigorous research efforts to model the binucleating copper proteins hemocyanin (oxygen transport) and tyrosinase (oxidation).[11]

An attractive feature of the tropocoronands is that methodology exists for regiospecific γ-substitution of their aminotropone imine moieties.[7,9] For example, treatment of aminotropone imines with bromine gives in excellent yield only 4-bromoaminotropone imines.[9a] Bromine, in turn, can be replaced by direct nucleophilic displacement or via metalation followed by reaction with electrophiles to give a range of γ-substituted aminotropone imines.[9b] Since the metal-coordinating nitrogens are directly attached to the rings, variations in the electronic properties of the nitrogens can be effected by placement of electron-donating/electron-withdrawing substituents on the ring. This option should prove useful in studies of the effects of nitrogen basicity on the properties of metal–tropocoronand complexes. This will be particularly interesting for the copper(II) complexes as the effects can be related to the structures of the metal-bearing sites of biologically active copper proteins found in nature.[11]

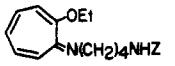
Extension of the above synthesis scheme to the preparation of hexaazatropocoronands **8** was accomplished by simply using a diamine containing an aminotropone imine moiety to complete and close the macrocycle. These ligands contain three amino-



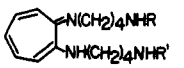
8



9 R = H
10 R = Z



11



12 R = H R' = Z
13 R = R' = Z
14 R = R' = H

tropone imine moieties linked by methylene bridges and are potential octahedral metal chelators.[20] Preparation of the diamine involved the following transformations. Reaction of 2-chlorotropone with excess 1,4-diaminobutane under high-dilution conditions gave the 2-aminotropone **9**, the free amino group of which was protected by a carbobenzoxy group.[21] The resulting yellow crystalline material **10** was treated with triethyloxonium tetrafluoroborate[18] in refluxing chloroform/hexamethylphosphoramide to give the crude ethoxytropone imine **11** as a brown oil. High-dilution reaction with 1,4-diaminobutane gave the aminotropone imine **12**, whose free amino group was protected as above to facilitate purification and characterization. Treatment of **13** with 25% hydrogen bromide in acetic acid gave the desired diamine **14**. Reaction of this material with bis(2-ethoxytropone imine) **3** under high-dilution conditions as described previously gave orange cubes of the aminotropone imine trimer **8** (n = 4).

Nuclear Magnetic Resonance Spectra. NMR studies of the series of nickel(II) tropocoronand complexes revealed an abrupt and striking change in chemical shift frequencies upon transition from planar to tetrahedral coordination geometry. While the diamagnetic, planar complexes n = 3, 4 exhibited resonances in the normal ranges, the paramagnetic, tetrahedral complexes n = 5, 6 and (n = 2)–O–(n = 2) required field widths of up to 400 ppm in the proton region and 2000 ppm in the carbon region. These results are reminiscent of previous studies on transition-metal complexes of (dialkylamino)tropone imines and salicylaldimines.[22] However, in the present series, the bridging alkyl groups give rise to a number of unique properties previously unobserved (vide supra). In addition, we have identified two previously unobserved carbon signals for the aminotropone imine moiety, completing, for the first time, the assignment of the carbon resonances of this ring system in a paramagnetic environment.

The shift from diamagnetism to paramagnetism upon transition from planar to tetrahedral geometry stems from a reordering of nickel(II) d-orbital energy levels with concomitant unpairing of two electrons. Interaction of paramagnetic nickel(II) with an appropriate ligand delocalizes the unpaired spin density of the metal through the ligand σ and π framework, giving rise to isotropic shifts (contact shifts) in the ligand ^1H and ^{13}C NMR spectra.[23] Despite the paramagnetic environment of the tetrahedral nickel complexes these resonances are relatively sharp and are readily interpreted due to the short electronic relaxation time of nickel(II).[24]

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Table I. ^{1}H NMR Data for Ligands **1** and Their Ni(II) Complexes

1	α	β	γ	1-CH_2	2-CH_2	3-CH_2
$n = 3$						
ligand	6.24	6.78	6.12	3.48	2.27	
complex	6.31	6.83	6.16	2.93	2.02	
$n = 4$						
ligand	6.20	6.79	6.14	3.28	1.98	
complex	6.26	6.76	6.12	3.35	1.91	
$n = 5$						
ligand	6.27	6.73	6.13	3.38	1.79	1.79
complex	−99.7	+60.7	−134.7	16.05	16.05	12.9
$(n = 2)_2$–O						
ligand	6.22	6.74	6.12	3.48	3.89	
complex	−101.3	+62.3	−136	16.6	unobsd	
$n = 6$						
ligand	7.76	6.25	6.13	3.25	1.67	1.67
complex	−97.9	+61.9	−136.2	244.4	0	17.2
				262.9	18.9	26.4

Contact shifts for the nickel(II) tropocoronand complexes are observed toward both higher and lower field. As in previous NMR observations of nickel(II) aminotropone iminates[22a] the α- and γ-protons of the aminotropone imine ring experience upfield shifts due to a localization of positive unpaired spin density. This situation is reversed for the β position; namely, a downfield proton shift resulting from a concentration of negative unpaired spin density occurs.

In general, the unpaired spin density has the opposite effect on the shifts of ^{13}C NMR signals.[24] We have identified, for the first time, ^{13}C NMR signals corresponding to the C-1 and γ positions and have found that they are consistent with spin density arguments. Thus, a complete set of ^{13}C NMR peak assignments consisting of downfield α- and γ-carbon resonances and upfield β and C-1 resonances have now been obtained.

Complete chemical shift values for the tropocoronands and their nickel(II) complexes are tabulated in Tables I (^{1}H) and II (^{13}C). Ring assignments were made largely on the basis of the spin density arguments discussed above. Similarly, the known decrease of unpaired spin density through a σ system led to the assignments for the methylene chains.[24,25] Integral intensities and selective proton–proton and proton–carbon decoupling were used to corroborate the assignments.

Studies on unbridged nickel(II) complexes of aminotropone imines and salicylaldimines have shown that there exists an equilibrium between the planar and tetrahedral forms.[22] We have found that this equilibrium is radically altered by the addition of bridging linker chains. The equilibrium position of the unbridged complexes is dependent on temperature and the steric bulk of the nitrogen substituents. The tetrahedral form is favored by bulky substituents while increases in temperature favor the higher energy conformations. Equilibrium positions were determined by observations of changes in the magnitude of the NMR contact shifts. In contrast, a 110 °C temperature rise (295–405 K) caused no significant chemical shift changes in the nickel(II) $n = 4$ tropocoronand complex. In this case the short methylene chain's inability to stretch further toward the tetrahedral structure kept the complex locked in a planar/diamagnetic configuration. However, the increased flexibility of the linker chain for the nickel(II) $n = 6$ complex allowed access to both the planar and tetrahedral array. A rise in temperature caused substantial decrease in the magnitudes of the ^{1}H NMR contact shifts, indicating a shift in equilibrium toward the higher energy planar conformation.

The deviation of the tropocoronand complexes from purely planar or tetrahedral geometry imparts a helical twist to the molecule. This twist results in a chirality that is manifested in several properties of the paramagnetic members of the series. The most straightforward evidence of chirality was the enantiomerically pure crystals grown from the nickel(II) $n = 5$ and $(n = 2)$–O–$(n = 2)$ complexes. X-ray structural studies grouped these crystals in chiral space groups.[8] Dissolution of an enantiomerically pure crystal ($n = 5$) gave no discernible CD spectra. Presumably, racemization occurs in solution through the planar conformation, from which both enantiomers are accessible. The existence of a planar intermediate is substantiated by studies carried out on complexes of monomeric nickel(II) aminotropone iminates[22] and by the variable-temperature ^{1}H NMR studies carried out on the nickel(II) $n = 6$ complex (vide infra).

Chirality was expressed in the nickel(II) $n = 6$ complex in solution through the methylene group attached to nitrogen. In only this complex do the diastereotopic methylene protons appear as separate signals in the ^{1}H NMR spectra. Two peaks were observed at δ 244.4 and 262.9 for the methylene group adjacent to nitrogen. This assignment was confirmed by preparing the octadeuterio ligand and observing the disappearance of these signals in the ^{1}H NMR spectra of the nickel(II) complex. Attempts to separate the enantiomers of the nickel(II) $n = 6$ complex by HPLC on chiral supports failed. Both Chiralpak-(+)[26] and Pirkle[27] columns yielded traces showing a single peak. Material collected corresponding to these peaks showed no discernible CD spectrum.

The NMR-nonequivalent diastereotopic protons of the nickel(II) $n = 6$ complex afforded an opportunity to study the rate of racemization using the techniques of spin magnetization transfer and signal coalescence.[28] Both of these methods rely on the interchange of the protons on any one methylene group upon conversion of one complex into its enantiomer. Spin magnetization transfer showed no crossover (i.e., no decrease in intensity of the signal at δ 262.9 upon irradiation of the signal at 244.4 ppm), indicating a slow rate of racemization. However, T_1 values for these signals were on the order of milliseconds (δ 243, 0.498 ms; δ 262, 2.34 ms).[29] Therefore, the data from this experiment can set only an upper limit on the rate of racemization since the protons are able to relax prior to interconversion at a racemization rate slower than the T_1 values. Attempts to obtain accurate racemization rate values by coalescence of the resolved signals were hindered by shifts toward the diamagnetic peak positions (i.e., upfield shifts). Interestingly, the two peaks shifted independently of each other. An increase in temperature to 100 °C caused the peaks to overlap upfield at δ 212, an apparent coalescence. However, a further rise of 29 °C again resolved the signals at 200 and 195 ppm.

Electronic Spectra. The effects of the bridging methylene groups on the geometric and electronic properties of the nickel(II) tropocoronand complexes are again revealed in their electronic spectra (Table III). The spectra of the tetragonal complexes $n = 3, 4$ contain a single observable d–d transition at 610 and 751 nm, respectively. The lower wavelength transition for the complex $n = 3$ is reflective of its shorter nickel–nitrogen bond length.[30] The pseudotetrahedral complexes $n = 5, 6$ and $(n = 2)$–O–$(n = 2)$ give rise to several d–d bands between 580 and 700 nm plus a longer wavelength transition (1000–1250 nm) diagnostic of pseudotetrahedral structures.[30,31] All of the complexes exhibit intense brown colors, which are the result of highly probable ($\epsilon = 10^4$ M^{-1} cm^{-1}) transitions in the 400–520-nm region. These are tentatively assigned as charge-transfer bands as they are absent in the spectra of the free ligands. The electronic spectra of the tropocoronands and their nickel(II) complexes are reminiscent

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(31) Parks, J. E.; Holm, R. H. *Inorg. Chem.* **1968**, *7*, 1408.

Table II. ^{13}C NMR Data for Ligands **1** and Their Ni(II) Complexes

1	α	β	γ	1-C	1-CH_2	2-CH_2	3-CH_2
$n = 3$							
ligand	110.3	133.5	117.4	153.6	48.5	28.9	
complex	111.9	132.7	116.6	165.2	45.5	31.4	
$n = 4$							
ligand	109.9	132.9	117.0	152.8	45.2	28.0	
complex	112.5	132	115.5	164	48.3	26.6	
$n = 5$							
ligand	110.0	132.9	117.4	153.0	46.1	30.2	26.4
complex	+940	−411	+1091	−814	460	316	29.0
$(n = 2)_2$–O							
ligand	110.1	133.0	117.8	153.6	46.6	70.6	
complex	+942	−418	+1102	−833	+397	+297	
$n = 6$							
ligand	109.9	132.9	117.2	152.6	45.6	30.6	28.4
complex	+955	−412	+1132	−843	+326	+136	−20.7

Table III. Electronic Spectra of the Nickel(II) Tropocoronands[a]

$n = 3$	$n = 4$	$n = 5$	$(n = 2)_2$–O	$n = 6$	assign[b]
281 (33 200)	280 (28 100)	281 (43 900)	280 (41 500)	279 (45 200)	L
318 (16 400)	321 (17 800)	378 (27 100)	374 (26 300)	375 (28 100)	L
367 (19 100)	380 (18 500)				
476 (20 300)	480 (11 200)	430 (29 500)	429 (28 800)	439 (36 500)	CT
504 (22 600)	510 (10 700)				CT
610 (1550)	751 (1550)	588 (1710)	582 (1520)	585 (1530)	d–d
		643 (1890)	642 (1580)	611 (1260)	d–d
		701 (1470)	690 (870)	697 (450)	d–d
		1125 (130)	1110 (110)	1210 (75)	d–d

[a] Absorption maxima are given in nm with molar extinction coefficients (M^{-1} cm^{-1}) in parentheses. [b] Legend: L, ligand; CT, charge transfer; d–d, metal d-orbital internal transitions.

of those observed for the monomeric aminotropone imines and their nickel(II) complexes.[22a]

Experimental Section

Instrumentation. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL 100, Bruker WM 250, or Bruker WM 300 spectrometer operating at 100, 250, or 300 MHz, respectively. Deuteriochloroform was used as a solvent with residual chloroform serving as the internal standard. Pulse widths of 2.5 μs (45°) and 7 μs (60°) were used for ^1H NMR and ^{13}C NMR spectra, respectively. For ^{13}C NMR spectra a delay of 80 μs was allowed between the pulse and acquisition to avoid pulse breakthrough. UV–visible spectra were recorded on a Perkin-Elmer TE-320 spectrophotometer using chloroform as solvent. Mass spectra were recorded on a Hitachi M-80 or a JEOL JMS-01SG-2 mass spectrometer. Infrared spectra were recorded on an IBM IR/85 spectrometer using chloroform as solvent.

General Procedure: 2,2′-(Ethylenediamino)di-2,4,6-cycloheptatrien-1-one (2 (n = 2)). 2-Chlorotropone[13,14] (7.31 mmol, 1.03 g), triethylamine (7.37 mmol, 746 mg), and 1,2-diaminoethane (3.91 mmol, 235 mg) in absolute ethanol (15 mL) were heated at reflux for 6 h. Concentration in vacuo gave a syrup, which was dissolved in chloroform, washed with saturated aqueous sodium bicarbonate, dried over magnesium sulfate, and concentrated to give an oil. This material was chromatographed (silica gel, chloroform:ether 5:1) and recrystallized to give **2** (n = 2) as yellow leaflets (yield 409 mg, 42%; mp 229–230 °C). ^1H NMR: δ 3.69 (m, 4 H), 6.53 (d, 2 H, J = 6 Hz), 6.69 (dd, 2 H, J = 5 Hz), 7.18–7.30 (m, 6 H), 7.33 (bd s, 2 H). ^{13}C NMR: δ 41.4, 108.5, 123.0, 129.5, 136.0, 137.4, 155.2, 176.9. IR: 3280 (s), 1605 (m), 1590 (m), 1542 (s), 1445 (s), 1259 (m), 1247 (m) cm^{-1}. Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.88; H, 6.01; N, 10.52.

2,2′-(Trimethylenediamino)di-2,4,6-cycloheptatrien-1-one (2 (n = 3)). 2-(Tosyloxy)tropone[12,14] (0.109 mol, 30 g), triethylamine (0.125 mol, 12.7 g), and 1,3-diaminopropane (61.5 mmol, 4.56 g) in absolute ethanol (300 mL) was treated as above to give **2** (n = 3) as yellow crystals (yield 7.1 g, 46%; mp 125–126 °C). ^1H NMR: δ 2.19 (d, 2 H, J = 7 Hz), 3.49 (q, 4 H, J = 7 Hz), 6.49–6.80 (m, 4 H), 7.09–7.43 (m, 8 H). ^{13}C NMR: δ 27.3, 40.1, 108.7, 122.5, 128.8, 136.2, 137.3, 155.3, 176.6. IR: 3290 (w), 1632 (s), 1605 (s), 1593 (s), 1509 (s), 1451 (s), 1280 (s), 714 (m) cm^{-1}. Mass spectrum: m/e 282 (34%, M^+), 161 (100), 148 (65), 135 (39), 106 (36), 77 (52). Anal. Calcd for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N, 9.92. Found: C, 72.30; H, 6.43; N, 9.79.

2,2′-(Tetramethylenediamino)di-2,4,6-cycloheptatrien-1-one (2 (n = 4)). 2-(Tosyloxy)tropone[12,14] (0.109 mol, 30 g), triethylamine (0.125 mol, 12.7 g), and 1,4-diaminobutane (61.5 mmol, 7.24 g) in absolute ethanol (300 mL) was treated as above to give **2** (n = 4) as yellow leaflets (yield 10.2 g, 63%; mp 130–132 °C). ^1H NMR: δ 1.72–2.01 (m, 4 H), 3.38 (bq, 4 H, J = 6 Hz), 6.47–6.79 (m, 4 H), 7.07–7.41 (m, 8 H). ^{13}C NMR: δ 25.9, 42.2, 108.4, 122.1, 128.5, 136.1, 137.1, 155.3, 176.3. IR (CHC^{13}): 3300 (m), 1590 (s), 1444 (s), 1385 (m), 891 (w), 874 (w) cm^{-1}. Mass spectrum: m/e 296 (18, M^+), 175 (100), 174 (78), 147 (12), 146 (13), 132 (20), 122 (17), 106 (18), 77 (23). Anal. Calcd for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45. Found: C, 73.12; H, 6.81; N, 9.43.

2,2′-(Pentamethylenediamino)di-2,4,6-cycloheptatrien-1-one (2 (n = 5)). 2-Chlorotropone[13,14] (7.16 mmol, 1.00 g), triethylamine (7.57 mmol, 766 mg), and 1,5-diaminopentane (4.10 mmol, 419 mg) in absolute ethanol (20 mL) was treated as above to give **2** (n = 5) as orange rods (yield 551 mg, 50%; mp 159–161 °C). ^1H NMR: δ 1.49–1.97 (m, 6 H), 3.25 (q, 4 H, J = 6 Hz), 6.41–7.79 (m, 4 H), 7.11–7.41 (m, 8 H). ^{13}C NMR: δ 24.7, 28.2, 42.6, 108.5, 122.2, 128.5, 136.2, 137.3, 155.5, 176.6. IR: 3300 (m), 1595 (s), 1590 (s), 1496 (m), 1445 (s), 1386 (m), 872 (m) cm^{-1}. Mass spectrum: m/e 310 (18, M^+), 189 (68), 188 (100), 148 (31), 134 (47), 122 (37), 106 (53), 77 (75). Anal. Calcd for $C_{19}H_{22}N_2O_2$: C, 73.52; H, 7.14; N, 9.03. Found: C, 73.51; H, 7.15; N, 8.90.

2,2′-(Hexamethylenediamino)di-2,4,6-cycloheptatrien-1-one (2 (n = 6)). 2-(Tosyloxy)tropone[12,14] (50 mmol, 13.8 g), triethylamine (57.4 mmol, 5.81 g), and 1,6-diaminohexane (28.2 mmol, 3.28 g) in absolute ethanol (140 mL) was treated as above to give yellow leaflets of **2** (n = 6) (yield 5.36 g, 66%; mp 161–164 °C). ^1H NMR: δ 1.40–1.90 (m, 8 H), 3.31 (q, 4 H, J = 6.5 Hz), 6.48–6.78 (m, 4 H), 7.09–7.40 (m, 8 H). ^{13}C NMR: δ 26.8, 28.3, 42.7, 108.5, 122.0, 128.4, 136.2, 137.2, 155.6, 176.6. IR: 3300 (m), 1590 (s), 1495 (m), 1440 (s), 1385 (m), 1085 (w), 890 (w). Mass spectrum: m/e 324 (48, M^+), 202 (69), 148 (64), 134 (100), 122 (72), 106 (98), 77 (100). Anal. Calcd for $C_{20}H_{24}N_2O_2$: C, 74.04; H, 7.46; N, 8.64. Found: C, 73.80; H, 7.50; N, 8.70.

2,2′-(3-Oxapentamethylenediamino)di-2,4,6-cycloheptatrien-1-one (2 ((n = 2)–O–(n = 2))). 2-Chlorotropone[13,14] (20.1 mmol, 2.91 g), triethylamine (25.6 mmol, 2.59 g), and 1,5-diamino-3-oxapentane[15] (13.6 mmol, 1.41 g) in absolute ethanol (50 mL) was treated as above to give **2** ((n = 2)–O–(n = 2)) as yellow needles (yield 1.70 g, 53%; mp 96–97 °C). ^1H NMR: δ 3.80 (t, 4 H, J = 6 Hz), 3.57 (q, 4 H, J = 6 Hz), 6.53–6.78 (m, 4 H), 7.08–7.53 (m, –NH–, 8 H). ^{13}C NMR: δ 42.4, 68.8, 108.5, 122.3, 128.7, 136.1, 137.1, 155.4, 176.5. IR: 3325 (w), 1611 (s), 1599 (s), 1548 (m), 1516 (s), 1458 (s), 1263 (w), 1133 (m) cm^{-1}. Anal. Calcd for $C_{18}H_{20}N_2O_3$: C, 69.21; H, 6.45; N, 8.97. Found: C, 69.42; H, 6.54; N, 9.09.

2,2′-(3-Thiapentamethylenediamino)di-2,4,6-cycloheptatrien-1-one (2 ((n = 2)–S–(n = 2))). 2-Chlorotropone[13,14] (7.25 mmol, 1.02 g), triethylamine (7.45 mmol, 754 mg), and 1,5-diamino-3-thiapentane[16] (4.04

mmol, 486 mg) in absolute ethanol (15 mL) was treated as above to give **2** ((*n* = 2)–S–(*n* = 2)) as yellow crystals (yield 616 mg, 52%; mp 128–129 °C). ^{1}H NMR: δ 2.91 (t, 4 H, *J* = 7 Hz), 3.57 (q, 4 H, *J* = 7 Hz), 6.48–6.79 (m, 4 H), 7.06–7.41 (m, 6 H), 7.49 (bs, 2 H). ^{13}C NMR: δ 30.6, 42.3, 108.5, 122.5, 128.9, 135.0, 137.2, 154.9, 176.6. IR: 3300 (m), 1604 (s), 1593 (s), 1540 (s), 1501 (s), 1450 (s), 1410 (m), 1392 (m), 1263 (m). Mass spectrum: *m/e* 328 (100%, M^+), 164 (34), 134 (15), 97 (12), 67 (9). Anal. Calcd for $C_{18}H_{20}N_2O_2S$: C, 65.83; H, 6.13; N, 8.51. Found: C, 65.56; H, 6.01; N, 8.33.

General Procedure: 6,7,8,9,16,17,18,19-Octahydrodicyclohepta[*b*,*i*][1,4,8,11]tetraazacyclotetradecene (1 (*n* = 3)). To a mixture of **2** (*n* = 3) (2.03 mmol, 573 mg) and toluene (10 mL) at reflux was added dimethyl sulfate (4.37 mmol, 551 mg) dropwise over 1 min. The reaction mixture was heated at reflux for 45 min. A dark water-miscible oil was deposited during the reaction. When it was cooled to 25 °C the reaction mixture was extracted with water and the aqueous phase was washed with chloroform and then made alkaline with 5% aqueous sodium carbonate. The aqueous phase was extracted with chloroform and the chloroform layer dried over anhydrous potassium carbonate. Concentration gave crude **3** (*n* = 3) as a green oil. ^{1}H NMR: δ 2.16 (d, 2 H, *J* = 7 Hz), 3.57 (t, 4 H, *J* = 7 Hz), 3.84 (s, 6 H), 6.1–6.6 (m, 10 H). This material was dissolved in ethanol (75 mL), and a solution of 1,3-diaminopropane (2.22 mmol, 165 mg) in ethanol (50 mL) was added dropwise over 3 h. After 12 h the reaction mixture was concentrated and then passed through a column of neutral alumina (chloroform:ether 5:1). A dark orange solid (yield 282 mg, 44%) was obtained, which was dissolved in hot toluene. Norit was added and the hot mixture filtered through Celite. Recrystallization (toluene/ethanol) gave **1** (*n* = 3) as fine yellow orange needles (yield 157 mg, 25%; mp 214–229 °C dec). ^{1}H NMR and ^{13}C NMR spectral data are tabulated in Tables I and II, respectively. IR: 3270 (s), 1590 (s), 1499 (m), 1465 (s), 1395 (m), 1131 (w) cm^{-1}. Mass spectrum: *m/e* 320 (93), 173 (28), 159 (28), 145 (60), 131 (100), 118 (23), 104 (42), 91 (30), 77 (29). UV (λ (ε)): 267.5 (34 500), 272 (s, 34 200), 360 (s, 25 900), 366.5 (31 500), 403 (s, 13 900), 413 (s, 14 600), 432 (s, 9400), 462 nm (s, 3300). Anal. Calcd for $C_{20}H_{24}N_4$: C, 74.96; H, 7.55; N, 17.49. Found: C, 75.07; H, 7.56; N, 17.41.

6,7,8,9,10,17,18,19,20,21-Decahydrodicyclohepta[*b*,*j*][1,4,9,12]tetraazacyclohexadecene (1 (*n* = 4)). Dimethyl sulfate (4.37 mmol, 551 mg), **2** (*n* = 4) (2.03 mmol, 600 mg), and toluene (10 mL) were reacted as above to give **3** (*n* = 4) as a green oil. ^{1}H NMR: δ 1.74–1.92 (m, 4 H), 3.47 (bd t, 4 H), 3.84 (s, 6 H), 6.0–6.8 (m, 10 H). This material in ethanol (75 mL) was treated with 1,4-diaminobutane (2.22 mmol, 196 mg) in ethanol (50 mL) as described above to give after chromatography and recrystallization **1** (*n* = 4) as orange prisms (yield 212 mg, 30%; mp 197–202 °C dec). ^{1}H NMR and ^{13}C NMR spectral data are tabulated in Tables I and II, respectively. IR: 3210 (w), 1590 (s), 1502 (m), 1460 (s), 1391 (s), 1274 (m), 1121 (m), 975 (m) cm^{-1}. Mass spectrum: *m/e* 348 (73), 228 (100), 200 (28), 171 (52), 131 (58), 104 (28), 78 (38), 77 (24). UV (λ (ε)): 268.5 (30 300), 335 (s, 11 000), 348.5 (17 100), 361.5 (22 300), 404 (s, 10 800), 416 (11 700), 432 (s, 9100), 462 nm (s, 3200). Anal. Calcd for $C_{22}H_{28}N_4$: C, 75.82; H, 8.10; N, 16.08. Found: C, 75.82; H, 8.10; N, 15.92.

6,7,8,9,10,11,18,19,20,21,22,23-Dodecahydrodicyclohepta[*b*,*k*][1,4,10,13]tetraazacyclooctadecene (1 (*n* = 5)). Dimethyl sulfate (4.31 mmol, 543 mg), **2** (*n* = 5) (2.0 mmol, 620 mg), and toluene were reacted as above to give **3** (*n* = 5) as a green oil. ^{1}H NMR: δ 1.48 (p, 2 H, *J* = 7 Hz), 1.80 (p, 4 H, *J* = 7 Hz), 3.41 (t, 4 H, *J* = 7 Hz), 3.84 (s, 6 H), 7.0–7.7 (m, 10 H). This material in ethanol (75 mL) was treated with 1,5-diaminopentane (2.22 mmol, 227 mg) in ethanol (75 mL) as described above to give after chromatography and recrystallization **1** (*n* = 5) as yellow needles (yield 248 mg, 33%; mp 199–207 °C dec). ^{1}H NMR and ^{13}C NMR spectral data are tabulated in Tables I and II, respectively. IR: 3225 (w), 1594 (s), 1502 (m), 1463 (s), 1391 (m), 1277 (m). Mass spectrum: *m/e* 376 (100), 256 (71), 213 (34), 185 (50), 145 (38), 131 (89), 104 (42), 77 (28). UV (λ (ε)): 263 (31 500), 268 (s, 30 900), 332 (10 500), 348 (17 000), 360 (20 200), 403 (s, 11 200), 426 (12 000), 434 (s, 9000), 462 nm (s, 3200). Anal. Calcd for $C_{24}H_{32}N_4$: C, 76.55; H, 8.57; N, 14.88. Found: C, 76.48; H, 8.54; N, 14.88.

6,7,8,9,10,11,12,19,20,21,22,23,24,25-Tetradecahydrodicyclohepta-[*b*,*l*][1,4,11,14]tetraazacycloeicosene (1 (*n* = 6)). Dimethyl sulfate (4.37 mmol, 551 mg), **2** (*n* = 6) (6.63 mmol, 2.15 g), and toluene (20 mL) were reacted as above to give **3** as a green oil. ^{1}H NMR: δ 1.32 (m, 4 H), 1.73 (m, 4 H), 3.39 (t, 4 H, *J* = 7 Hz), 3.81 (s, 6 H), 5.9 (d, 2 H, *J* = 9 Hz), 6.22–6.62 (m, 8 H). This material in ethanol (250 mL) was treated with 1,6-diaminohexane (7.36 mL, 855 mg) in ethanol (175 mL) as described above to give after chromatography and recrystallization **1** (*n* = 6) as yellow needles (yield 926 mg, 35%; mp 197–200 °C dec). ^{1}H NMR and ^{13}C NMR spectral data are tabulated in Tables I and II, respectively. IR: 3190 (w, N–H), 1585 (s), 1499 (m), 1455 (s), 1267 (m) cm^{-1}. Mass spectrum: *m/e* 404 (23, M^+), 159 (23), 145 (31), 131 (100), 104 (24), 77 (11). UV (λ (ε)): 264 (34 400), 269 (s, 33 700), 332 (s, 11 300), 348 (18 100), 361 (22 000), 404 (s, 12 000), 418 (13 300), 434 (s, 10 700), 462 nm (s, 3900). Anal. Calcd for $C_{26}H_{36}N_4$: C, 77.18; H, 8.97; N, 13.85. Found: C, 77.35; H, 8.97; N, 13.78.

General Procedure: 6,7,8,15,16,17-Hexahydrodicyclohepta[*b*,*h*][1,4,7,10]tetraazacyclododecene (1 (*n* = 2)). Hexamethylphosphoramide (1.2 g, HMPA, toxic and cancer suspect), triethyloxonium tetrafluoroborate[18] (5.80 mmol, 1.05 g), and **2** (*n* = 2) (1.47 mmol, 395 mg) in dry chloroform (60 mL) were heated at reflux under nitrogen for 22 h, and the reaction mixture was allowed to cool to 25 °C and then extracted with water. The aqueous extract was washed with chloroform and then made alkaline with 5% aqueous sodium carbonate and extracted with chloroform. The second chloroform extract was dried over anhydrous potassium carbonate and concentrated to give a yellow solid (530 mg). This material was dissolved in absolute ethanol (80 mL) and treated with a solution of 1,2-diaminoethane (1.93 mmol, 116 mg) in absolute ethanol (50 mL) dropwise over 1.5 h. After 12 h at 25 °C a yellow precipitate (136 mg) was collected. Recrystallization (benzene/ethanol) gave **1** (*n* = 2) as yellow needles (yield 9 mg, 2%; mp 243–245 °C dec). ^{1}H NMR: δ 3.63 (s, 8 H), 6.15 (t, 2 H, *J* = 9.0 Hz), 6.35 (d, 4 H, *J* = 11.2 Hz), 6.79 (dd, 4 H, *J* = 9.0 Hz). ^{13}C NMR: δ 46.2, 110.4, 117.7, 133.3, 153.7. IR: 3260 (m), 1593 (s), 1458 (s), 1392 (m), 1361 (m), 1045 (m) cm^{-1}. UV (λ (ε)): 263.5 (31 000), 270 (s, 30 000), 353 (s, 18 600), 361.5 (21 900), 403 (s, 14 300), 413 (15 500), 429 (s, 11 500), 459 nm (s, 4200). The filtrate was concentrated in vacuo and chromatographed (7 g silica gel deactivated with triethylamine, chloroform (100–90%)/triethylamine (0–10%)). The chloroform eluant gave **3** (*n* = 2) as an orange oil (86 mg) contaminated with HMPA.

The chloroform (90%)/triethylamine (10%) eluant gave an orange oil (221 mg), which was sublimed in vacuo to give pale yellow crystals (yield 109 mg, 51%; mp 98.6–101.2 °C) of 2-phenyl-2-imidazoline.[19] ^{1}H NMR: δ 3.79 (s, 4 H), 4.57 (bd s, 1 H), 7.30–7.53 (m, 3 H), 7.70–7.89 (m, 2 H). ^{13}C NMR: δ 50.3, 126.9, 128.3, 130.5, 164.7. IR: 3410 (m), 1617 (s), 1572 (m), 1443 (s), 1412 (m), 1285 (s), 980 (m) cm^{-1}. Mass spectrum (field desorption): *m/e* 146 (100).

7,8,11,18,19,20,22,23-Octahydro-6*H*,10*H*-dicyclohepta[*e*,*n*][1,10,4,7,13,16]dioxatetraazacyclooctadecene (1 ((*n* = 2)–O–(*n* = 2))). **2** ((*n* = 2)–O–(*n* = 2)) (3.32 mmol, 1.04 mg), HMPA (1.5 g), and triethyloxonium tetrafluoroborate[18] (8.40 mmol, 1.53 g) in dry chloroform (40 mL) were reacted as above to give **3** (*n* = 2)–O–(*n* = 2) contaminated with HMPA (1.5 g). This material was treated with 1,5-diamino-3-oxapentane[15] (5.76 mmol, 600 mg) as described above. A yellow precipitate (463 mg) was collected, eluted through a column of neutral alumina with chloroform, and then recrystallized (chloroform/ethanol) to give **1** (*n* = 2)–O–(*n* = 2) as yellow needles (yield 406 mg, 32%; mp 223–230 °C dec). ^{1}H NMR and ^{13}C NMR spectral data are tabulated in Tables I and II, respectively. IR: 2250 (w), 1618 (w), 1598 (s), 1515 (s), 1473 (s), 1279 (m), 1129 (s) cm^{-1}. UV (λ (ε)): 263 (28 500), 268 (s, 28 000), 334 (s, 10 200), 348 (15 600), 260.5 (18 300), 406 (s, 10 400), 414.5 (10 800), 430 (s, 8700), 458 nm (s, 3300). Anal. Calcd for $C_{22}H_{28}N_4O_2$: C, 69.44; H, 7.42; N, 14.73. Found: C, 69.40; H, 7.41; N, 14.60.

7,8,11,18,19,20,22,23-Octahydro-6*H*,10*H*-dicyclohepta[*e*,*n*][1,10,4,7,13,16]dithiatetraazacyclooctadecene (1 ((*n* = 2)–S–(*n* = 2))). HMPA (1.4 g), **2** ((*n* = 2)–S–(*n* = 2)) (3.13 mmol, 1.03), and triethyloxonium tetrafluoroborate[18] (8.05 mmol, 1.46 g) in dry chloroform (50 mL) were reacted as above to give **3** ((*n* = 2)–S–(*n* = 2)) contaminated with HMPA (1.36 g). This material was reacted with 1,5-diamino-3-thiapentane[16] (3.70 mmol, 445 mg) as described above. An orange precipitate (427 mg) was collected and chromatographed (7 g of neutral alumina, chloroform) to give, upon recrystallization (chloroform/ethanol), **1** ((*n* = 2)–S–(*n* = 2)) as yellow needles (yield 320 mg, 25%; mp 210 °C dec). ^{1}H NMR: δ 3.12 (t, 8 H, *J* = 6 Hz), 3.60 (t, 8 H, *J* = 6 Hz), 6.19 (t, 2 H, *J* = 9 Hz), 6.30 (d, 4 H, *J* = 10 Hz), 6.60 (dd, 4 H, *J* = 9, 10 Hz). ^{13}C NMR: δ 33.4, 47.9, 110.8, 118.5, 133.3, 153.0. IR: 3225 (w), 1595 (s), 1534 (m), 1509 (s), 1482 (s), 1278 (m), 1141 (m) cm^{-1}. Mass spectrum: *m/e* 412 (100), 206 (63), 73 (17). UV (λ (ε)): 262 (34 300), 269 (s, 33 500), 334 (s, 12 900), 348 (19 300), 361 (22 300), 401 (s, 12 200), 413 (13 100), 429 (s, 10 400), 460 nm (s, 3600). Anal. Calcd for $C_{22}H_{28}N_4S_2$: C, 64.04; H, 6.84; N, 13.58. Found: C, 63.94; H, 6.83; N, 13.45.

Concentration of the above filtrate gave a yellow syrup, which was chromatographed (10 g of neutral alumina, benzene/chloroform) to give an orange oil (412 mg), which was crystallized (chloroform/benzene/ethanol) to give 9-ethyl-7,8,11,18,19,20,22,23-octahydro-6*H*,10*H*-dicyclohepta[*e*,*n*][1,10,4,7,13,16]dithiatetraazacyclooctadecenium hydroxide (**7**) as yellow crystals (yield 85 mg, 6%; mp 142–143 °C dec). ^{1}H NMR: δ 1.43 (t, $-CH_3$, 3 H, *J* = 7 Hz), 2.95–3.05 (m, –SCH–, 2 H), 3.39 (q, $-CH_2CH_3$, 2 H, *J* = 7), 3.49–3.64 (m, $-SCH_2-$, 4 H), 3.73–3.89 (m, 8

H), 6.14 (d, 2 H, J = 11 Hz), 6.33 (t, 2 H, J = 11 Hz), 6.55 (d, 2 H, J = 12 Hz), 6.87–6.96 (m, 4 H). ^{13}C NMR: δ 9.63, 31.16, 31.43, 41.26, 42.57, 42.69, 105.34, 118.16, 119.59, 134.16, 134.89, 150.98, 155.89. IR: 3240 (m), 1592 (s), 1505 (s), 1429 (s), 1392 (m), 1278 (m), 1058 (bd s) cm^{-1}. Mass spectrum (field desorption): m/e 441 (M^+ – OH, 100). Anal. Calcd for $C_{24}H_{34}N_4S_{20}\cdot 4H_2O$: C, 54.31; H, 7.98; N, 10.56. Found: C, 54.63; H, 6.23; N, 10.53.

Treatment of 2 ((*n* = 2)–S–(*n* = 2)) with Dimethyl Sulfate. Dimethyl sulfate (1.82 mmol, 230 mg) and **2** ((*n* = 2)–S–(*n* = 2) (0.79 mmol, 258 mg) in toluene (30 mL) were heated at reflux for 17.5 h. The reaction mixture was then washed with water. The organic layer was concentrated to give an orange oil (80 mg), which was chromatographed on silica gel (4 g). Elution with chloroform gave 2-[[2-(methylthio)-ethyl]amino]-2,4,6-cycloheptatrien-1-one (**5**) as a yellow oil (22 mg). ^{1}H NMR: δ 2.18 (s, 3 H), 2.84 (t, 2 H), 3.56 (q, 2 H), 6.51–6.80 (m, 2 H), 7.07–7.42 (m, 3 H), 7.42 (bs, 1 H). ^{13}C NMR: δ 15.4, 32.3, 41.7, 108.4, 122.3, 128.8, 137.3, 136.0, 155.0, 176.6. IR: 3310 (w), 1608 (s), 1598 (s), 1545 (s), 1504 (s), 1455 (s) cm^{-1}. Mass spectrum: m/e 195 (M^+). Elution with ethyl acetate gave **2** ((*n* = 2)–S–(*n* = 2)) (30 mg) as yellow needles.

The aqueous layer was washed with chloroform, made alkaline with 5% aqueous sodium carbonate, and extracted with chloroform. The second chloroform extract was dried over potassium carbonate and concentrated to give an orange oil (95 mg), which was dissolved in ethanol (30 mL) and treated dropwise with a solution of 1,5-diamino-3-thiapentane (0.46 mmol, 55 mg) in ethanol (20 mL) over 4 h at 25 °C. After 12 h the reaction mixture was concentrated to a syrup and then passed through a column of alumina (5 g, $CHCl_3$) to give an orange oil, which was chromatographed on alumina (2 g). Elution with benzene gave an orange oil (56 mg), which contained mostly 2,3-dihydrocyclohepta[*b*]-1,4-oxazine (**6**). This material crystallized (benzene/methanol) to give **1** ((*n* = 2)–S–(*n* = 2)) (7 mg, 2%). Elution with chloroform gave pure **6** as an orange oil (44 mg). ^{1}H NMR: δ 3.71–3.84 (m, 2 H), 3.93–4.04 (m, 2 H), 6.14–6.53 (m, 3 H), 6.61–6.85 (m, 2 H). ^{13}C NMR: δ 48.5, 62.1, 112.9, 126.7, 129.1, 131.3, 135.6, 154.5, 159.0. IR: 1595 (m), 1543 (s), 1333 (m), 1273 (s), 1170 (s) cm^{-1}. Mass spectrum: m/e 147 (M^+).

General Procedure: [6,7,8,9,16,17,18,19-Octahydrodicyclohepta[*b*,*i*][1,4,8,11]tetraazacyclotetradecenato(2–)-N^6,N^{10},N^{20}]nickel. To **1** (n = 3) (0.059 mmol, 19 mg) in dichloromethane (10 mL) was added nickelous acetate tetrahydrate (0.080 mmol, 20 mg) in ethanol (5 mL). After 5 min most of the methylene chloride was removed on a water bath, resulting in the formation of black needles. These were collected, dissolved in methylene chloride, and passed through a column of silica gel to give black crystals (24 mg). Recrystallization from methylene chloride/ethanol gave black needles of the nickel(II) complex (23 mg, quantitative). ^{1}H NMR, ^{13}C NMR, and UV spectral data are tabulated in Tables I, II, and III, respectively. IR: 1587 (s), 1512 (m), 1506 (s), 1413 (s), 1402 (s), 1286 (m), 1231 (s), 1141 (w), 1075 (w), 1038 (w) cm^{-1}.

[6,7,8,9,10,17,18,19,20,21-Decahydrodicyclohepta[*b*,*j*][1,4,9,12]tetraazacyclohexadecenato(2–)-N^6,N^{11},N^{17},N^{22}]nickel. Nickelous acetate tetrahydrate (0.069 mmol, 17 mg) and **1** (n = 4) (0.069 mmol, 24 mg) were treated as above to give black needles of the nickel(II) complex (yield 22 mg, 79%). ^{1}H NMR, ^{13}C NMR, and UV spectral data are tabulated in Tables I, II, and III, respectively. IR: 1584 (s), 1512 (s), 1501 (s), 1431 (s), 1411 (s), 1395 (s), 1288 (m), 1276 (m), 1261 (m), 1226 (m), 1089 (w), 993 (w), 972 (w), 720 (m) cm^{-1}.

[6,7,8,9,10,11,18,19,20,21,22,23-Dodecahydrodicyclohepta[*b*,*k*]-[1,4,10,13]tetraazacyclooctadecenato(2–)-N^6,N^{12},N^{18},N^{24}]nickel. Nickelous acetate tetrahydrate (0.133 mmol, 33 mg) and **1** (n = 5) (0.090 mmol, 34 mg) were reacted as above. Purification as above gave black rods of the nickel(II) complex (yield 37 mg, 95%). ^{1}H NMR, ^{13}C NMR, and UV spectral data are tabulated in Tables I, II, and III, respectively. IR: 1584 (m), 1502 (s), 1427 (s), 1405 (m), 1263 (m), 1226 (m), 1201 (w), 1051 (w), 717 (m) cm^{-1}.

[6,7,8,9,10,11,12,19,20,21,22,23,24,25-Tetradecahydrodicyclohepta-[*b*,*l*][1,4,11,14]tetraazacycloeicosenato(2–)-N^6,N^{13},N^{19},N^{26}]nickel. Nickelous acetate tetrahydrate (0.100 mmol, 25 mg) and **1** (n = 6) (0.069 mmol, 28 mg) were treated as above to give black needles of the nickel(II) complex (yield 27 mg, 85%). ^{1}H NMR, ^{13}C NMR, and UV spectral data are tabulated in Tables I, II, and III, respectively. IR: 1584 (m), 1506 (s), 1428 (s), 1418 (s), 1390 (m), 1346 (w), 1337 (w), 1277 (w), 1264 (s), 1233 (m), 1209 (m), 989 (w), 884 (w), 722 (m) cm^{-1}.

2-[(4-Aminobutyl)amino]-2,4,6-cycloheptatrien-1-one (9). A solution of 1,4-diaminobutane (116 mmol, 10.2 g) in methanol (250 mL) was heated at reflux while a solution of 2-chlorotropone[13,14] (28 mmol, 4.0 g) in methanol (200 mL) was added dropwise over 3.5 h. The reaction mixture was cooled and then concentrated in vacuo. The resulting brown residue was dissolved in chloroform, washed with saturated aqueous sodium bicarbonate and water, and then dried over potassium carbonate. Concentration in vacuo gave a brown oil (8.51 g), which was chromatographed (50 g of silica gel, chloroform/methanol 1/1) to give **9** as a yellow oil (yield 3.68 g, 66%). ^{1}H NMR: δ 1.39–1.93 (m, 4 H), 2.75 (t, 2 H), 3.30 (bq, 2 H), 6.47–6.75 (m, 2 H), 7.05–7.38 (m, 4 H). ^{13}C NMR: δ 25.4, 30.5, 41.2, 42.2, 108.1, 121.5, 127.8, 135.8, 136.7, 155.1, 176.0. IR: 3300 (m, N–H), 1595 (s), 1541 (s), 1506 (s), 1446 (s), 1257 (m), 875 (m) cm^{-1}. Mass spectrum: m/e 192 (100), 175 (83), 162 (22), 148 (71), 134 (97), 123 (100), 122 (100), 106 (40).

Benzyl [4-[(7-Oxo-1,3,5-cycloheptatrien-1-yl)amino]butyl]carbamate (10). To **9** (19.1 mmol, 3.68 g) and pyridine (25 mmol, 2.0 g) in chloroform (100 mL) at 0 °C was added benzyl chloroformate (25 mmol, 4.2 g) in chloroform (100 mL) dropwise. The reaction mixture was then allowed to warm to 25 °C. After 7 h the reaction mixture was passed through a column of alumina (3 g). Concentration gave an orange oil (7.27 g), which was chromatographed (70 g of silica gel, chloroform/ethyl acetate 1/1) to give a yellow solid (5.29 g). Recrystallization (benzene/hexane) gave **10** as yellow needles (yield 4.83 g, 52%; mp 91.2–92.3 °C). ^{1}H NMR: δ 1.45–1.87 (m, 4 H), 3.13–3.39 (m, 4 H), 5.11 (s, 2 H), 5.18 (bs, 1 H), 6.46–6.77 (m, 2 H), 7.08–7.35 (m, 8 H), 7.35 (s, 1 H). ^{13}C NMR: δ 25.5, 27.5, 40.4, 42.2, 66.5, 108.5, 122.0, 127.9, 128.3, 136.1, 136.5, 137.1, 155.4, 156.4, 176.4. IR: 3450, 3320 (w, N–H), 1710 (s), 165 (s), 1593 (s), 1510 (s), 1450 (s), 1160 (m). Anal. Calcd for $C_{19}H_{22}O_3N_2$: C, 69.92; H, 6.79; N, 8.58. Found: C, 70.07; H, 6.70; N, 8.44.

[4-[[2-[[4-(Carboxyamino)butyl]amino]-2,4,6-cycloheptatrien-1-ylidene]amino]butyl]carbamic Acid, Dibenzyl Ester (13). HMPA (2.13 g), **10** (5.95 mmol, 1.94 g), and triethyloxonium tetrafluoroborate[18] (11.0 mmol, 1.98 g) in chloroform (100 mL) were heated at reflux for 19.5 h. The reaction mixture was then washed with water and 5% aqueous sodium carbonate, dried over anhydrous potassium carbonate, and concentrated to give benzyl [4-[(2-ethoxy-2,4,6-cycloheptatrien-1-ylidene)-amino]butyl]carbamate (**11**) contaminated with HMPA.

This material was dissolved in ethanol and added to a solution of 1,4-diaminobutane (73 mmol, 6.0 g) in ethanol (300 mL) dropwise over 3 h. After 12 h, concentration gave a syrup, which was dissolved in chloroform, washed with water, dried over anhydrous potassium carbonate, and concentrated to give benzyl [4-[[7-[(4-aminobutyl)imino]-1,3,5-cycloheptatrien-1-yl]amino]butyl]carbamate (**12**, 4.36 g).

Pyridine (7 mL) and **12** were dissolved in chloroform, cooled to 0 °C, and treated with a solution of benzyl chloroformate (13.5 mmol, 2.3 g) in chloroform (30 mL) dropwise over 30 min. The reaction mixture ws then allowed to warm to 25 °C. After 1.5 h it was passed through a column of alumina (30 g) and concentrated to give a brown oil (7.12 g). This material was chromatographed (silica gel, chloroform/methanol 1/1) and recrystallized (ethanol) to give **13** as yellow needles (yield 950 mg, 32%; mp 80.0–80.5 °C). ^{1}H NMR: δ 1.39–1.93 (m, 8 H), 3.01–3.14 (m, 8 H), 5.09 (s, 2 H), 5.12 (bs), 6.22 (t, 2 H, J = 9.3 Hz), 6.31 (d, 4 H, J = 11.0 Hz), 6.83 (dd, 4 H, J = 9.3, 11.0 Hz), 7.33 (s, 10 H). ^{13}C NMR: δ 26.8, 27.9, 40.8, 45.5, 66.4, 110.7, 118.4, 127.8, 128.3, 133.5, 136.6, 152.7, 156.4. Anal. Calcd for $C_{31}H_{38}N_4O_4$: C, 70.16; H, 7.22; N, 10.56. Found: C, 70.21; H, 7.19; N, 10.26.

7,8,9,10,17,18,19,20,21,28,29,30,31,32-Tetradecahydro-6*H*-tricyclohepta[*b*,*j*,*r*][1,4,9,12,17,20]hexaazacyclotetracosene (15). At 0 °C, **13** (1.47 mmol, 745 mg) was dissolved in 40 mL of 25% hydrobromic acid/75% acetic acid. After 7 h at 25 °C diethyl ether was added. A yellow precipitate formed, which was collected, washed with diethyl ether, and dissolved in water. The aqueous solution was washed with chloroform and then made alkaline with 5% aqueous sodium carbonate and extracted into chloroform. The second chloroform extract was dried over potassium carbonate and concentrated to give *N*-[2-[(4-aminobutyl)-amino]-2,4,6-cycloheptatrien-1-ylidene]-1,4-butanediamine (**14**) as a yellow oil (404 mg, quantitative).

To **3** (n = 4) (541 mg, prepared from 1.68 mmol, 498 mg, of **2** (n = 4)) in ethanol (250 mL) was added **14** (1.54 mmol, 404 mg) in ethanol (100 mL) dropwise over 3 h. After 12 h a yellow precipitate (439 mg) was collected and passed through a column of alumina with benzene to give a yellow solid (330 mg). Recrystallization (benzene/ethanol) gave **15** as orange cubes (yield 311 mg, 39%; mp 187.5–189.4 °C). ^{1}H NMR: δ 2.69–3.05 (m, 12 H), 3.09–3.29 (m, 12 H), 6.02–6.39 (m, 9 H), 6.63–6.91 (m, 6 H). ^{13}C NMR: δ 28.0, 46.0, 110.2, 117.6, 133.0, 152.9. Mass spectrum: m/e 523 (55), 522 (100), 256 (14), 164 (4). UV (λ(ε)): 262 (49 900), 268 (s, 48 400), 334 (s, 17 200), 349 (26 600), 361 (37 000), 405 (s, 19 300), 416 (20 400), 431 (s, 16 600), 460 (s, 6100). Anal. Calcd for $C_{33}H_{42}N_6$: C, 75.82; H, 8.10; N, 16.08. Found: C, 75.75; H, 8.04; N, 15.90.

Registry No. **1** (n = 2), 103590-84-7; **1** (n = 3), 84927-34-4; **1** (n = 4), 84927-35-5; **1** (n = 5), 84927-36-6; **1** (n = 6), 84927-37-7; **1** ((*n* = 2)–O–(*n* = 2)), 84927-38-8; **1** ((*n* = 2)–S–(*n* = 2)), 84927-39-9; **2** (n = 2), 103590-85-8; **2** (n = 3), 103590-86-9; **2** (n = 4), 86007-90-1; **2** (n = 5), 86007-91-2; **2** (n = 6), 86017-13-2; **2** ((*n* = 2)–O–(*n* = 2)), 87345-

76-4; **2** ((*n* = 2)–S–(*n* = 2)), 87345-77-5; **3** (*n* = 3), 103590-87-0; **3** (*n* = 4), 103590-88-1; **3** (*n* = 5), 103590-89-2; **3** (*n* = 6), 103590-90-5; **3** ((*n* = 2)–O–(*n* = 2)), 103590-91-6; **3** ((*n* = 2)–S–(*n* = 2)), 103590-92-7; **4**, 936-49-2; **5**, 103590-93-8; **6**, 103590-94-9; **7**, 84927-40-2; **9**, 103590-95-0; **10**, 103590-96-1; **11**, 103590-97-2; **12**, 103590-98-3; **13**, 103590-99-4; **14**, 103591-00-0; **15**, 103591-01-1; Ni[**1** (*n* = 3)]$^{2+}$, 103591-02-2; Ni[**1** (*n* = 4)]$^{2+}$, 103591-03-3; Ni[**1** (*n* = 5)]$^{2+}$, 103591-04-4; Ni[**1** (*n* = 6)]$^{2+}$, 103591-05-5; Ni[**1** (*n* = 2)$_2$–O]$^{2+}$, 103591-06-6; 2-chlorotropone, 3839-48-3; 1,2-diaminoethane, 107-15-3; 2-(tosyloxy)tropone, 38768-08-0; 1,3-diaminopropane, 109-76-2; 1,4-diaminobutane, 110-60-1; 1,5-diaminopentane, 462-94-2; 1,6-diaminohexane, 124-09-4; 1,5-diamino-3-oxapentane, 2752-17-2; 1,5-diamino-3-thiapentane, 871-76-1.

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Coordinatively Saturated Cationic Ruthenium(II) Complexes. Preparation, Characterization, and Reaction with Potassium Superoxide

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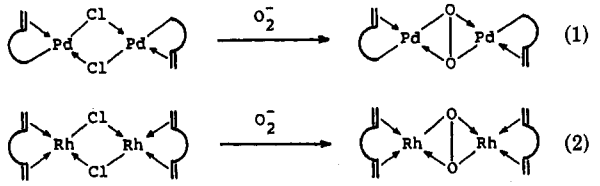
Coordinatively saturated cationic ruthenium(II) complexes, [(η^5-C_5H_5)(η^6-C_6H_6)Ru^{II}][BF_4] (**1**), [(η^5-C_5Me_5)(η^6-C_6H_6)Ru^{II}][BF_4] (**2**), [(1–5-η^5-C_6H_7)(η^6-C_6H_6)Ru^{II}][BF_4] (**3**), [(1–5-η^5-C_7H_9)(η^6-C_6H_6)Ru^{II}][BF_4] (**4**), [(1–3:5,6-η^5-C_8H_{11})(η^6-C_6H_6)Ru^{II}][BF_4] (**5**), and [(6-EtO–1–5-η^5-C_7H_8)(η^6-C_6H_6)Ru^{II}][BF_4] (**7**), are prepared by the reaction of [(η^6-C_6H_6)$RuCl_2$]$_2$ with cyclopentadiene, pentamethylcyclopentadiene, 1,3-cyclohexadiene, 1,3-cycloheptadiene, 1,5-cyclooctadiene, and 1,3,5-cycloheptatriene, respectively, in ethanol in the presence of $AgBF_4$. Superoxide anion attacks at the terminal position of the dienyl moiety of **3**–**5** to yield ruthenium(0) complexes **8**–**10**, containing cyclic dienone ligand.

Introduction

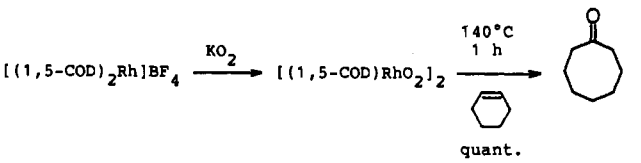
Interaction between dioxygen and transition-metal complexes has become an important area of investigation over the last two decades primarily since this may be a key step for catalytic oxygenation reactions.[1] Numbers of peroxo complexes can be obtained by the reaction of molecular oxygen with low-valent transition-metal complexes containing tertiary phosphines or isonitriles as auxiliary ligands. Transfer of coordinated dioxygen to olefins giving epoxides or ketones was examied by interaction of the peroxo complexes with cyanoolefins, and several intermediary peroxometallacyclic adducts were isolated.[2] Not only dioxygen but superoxide (O_2^-) and peroxide (O_2^{2-}), resulting from electron transfer from the metal species to dioxygen, deeply participate in the metal-catalyzed oxidation. In previous papers, we reported that the reaction of coordinatively unsaturated (16 e) palladium(II) and rhodium(I) olefin complexes with superoxide ion (O_2^-) afforded the corresponding μ-peroxo complexes via a nucleophilic attack of superoxide ion on the metal center (eq 1 and 2).[3] Superoxide ion may also attack the metal center of the



(1)

(2)

coordinatively unsaturated (16 e) cationic rhodium(I) complex to yield dimeric peroxo complexes, e.g. [(1,5-COD)RhO_2]$_2$, which liberates cyclooctanone on pyrolysis in benzene solution in the presence of cyclohexene (eq 3).[4] We have also reported the



(3)

reaction of *tert*-butylperoxide anion (*t*-BuOO$^-$) with cationic rhodium(I) and palladium(II) complexes.[5] In the reaction with electronically saturated cationic complexes, *t*-BuOO$^-$ attacks the coordinated olefinic ligand, whereas it attacks the cationic metal center directly in the reaction with the complexes with 16e configurations. Thus, the number of electrons around the metal center, 16 or 18, may determine the reaction site of superoxide ion toward the metal–olefin complex, i.e. at the metal center as opposed to the coordinated olefin. We have expanded our studies to clarify the reaction of superoxide ion with coordinatively saturated metal–olefin complexes. In this paper we describe the preparation and characterization of novel cationic ruthenium complexes of 18-electron configuration and their reactions with superoxide ion.

Experimental Section

All manipulations were carried out under an atmosphere of dry argon, using either standard Schlenk or vacuum techniques. All solvents used were dried by conventional techniques[6] and were distilled under an atmosphere of dry argon prior to use. Unless otherwise noted, all reagents were obtained from commercial suppliers. Potassium superoxide[7] and potassium 1,2,3,4,5-pentakis(methoxycarbonyl)cyclopentadienide[8] were freshly prepared prior to use by the literature procedures. The ruthenium complexes [(η^6-C_6H_6)$RuCl_2$]$_2$[9] and [(η^5-C_5Me_5)$RuCl_2$]$_n$[10] were prepared

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