complex a similar absorption band is found at 7200 cm^{-1}.[21]

The other examples of emission from an excited state which is not the lowest are found in the emission spectra of the clusters containing a copper(II) ion. In these clusters the copper(II) center has a broad absorption band with a peak maximum at 11 765 cm^{-1} and a tail which extends well past 13 973 cm^{-1}. This band probably originates from d–d transitions on the copper(II). The emission maximum is at least 1000 cm^{-1} higher in energy than the absorption band maximum.

The emission lifetimes are shortest for those clusters with low-lying M(II)-centered d–d states and longest for those whose Cu(I) excited states lie lower. The Cu_3Co^{II}, Cu_3Cu^{II}, and $Cu_2Cu^{II}Co^{II}$ clusters have lifetimes ranging from 5.4 to 5.9 μs, while those with metals not possessing low-lying d–d states have lifetimes greater than 7.0 μs. The low-lying d–d states provide a deactivation pathway which shortens the lifetime. These low-lying states are obviously not strongly coupled to the states involving the copper, and the magnitude of the effect is small.

Summary

Tetrameric mixed-metal clusters of the type $Cu^I_3M^{II}$ and $Cu^I_2Cu^{II}M^{II}$ are luminescent. The emission from all of the clusters is copper(I) centered and is related to the $3d^94s^1$ excited state strongly modified by copper–copper interactions. In the case of the mixed-metal clusters containing Co(II) or Cu(II) in the core, the emission is not from the lowest excited state of the cluster. In these cases, ligand field states centered on M(II) are lower in energy than the emitting state centered on the Cu(I)'s. Changing of the metal M in the $Cu^I_3M^{II}$ core slightly shifts the emission maximum with respect to the Cu_4 cluster. The emission lifetimes of these clusters are shortest for those clusters containing low-lying d–d states.

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Electronic and Stereochemical Factors Contributing to the Lability of *trans*-Aquomethyl(tetraazamacrocycle)cobalt(III) Complexes. Kinetic and Molecular Mechanics Studies[1]

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Abstract: The origin and variability of the trans-labilizing influence of the Co–alkyl bond have been investigated by using the anation reactions of a series of *trans*-$Co(N_4)(OH_2)CH_3^{2+}$ (N_4 is a tetraazamacrocyclic ligand) complexes as probes. Anation reactions of some related *trans*-$Co(N_4)(OH_2)Cl^{2+}$ complexes have also been examined to provide a basis for comparison with closely related, classical coordination complexes. The coordinated water in the methyl–aquo complexes is 10^4–10^7 times more labile than found in "normal" coordination complexes. Stereochemically uncluttered coordination sites, such as the axial positions when N_4 = 1,4,8,11-tetraazacyclotetradecane, are labilized the most. The labilizing influence of the cobalt–methyl bond is the least at stereochemically conjested coordination sites for which molecular mechanics calculations show that there is considerable relaxation of strain and interligand repulsion in the dissociative transition state; i.e., for those complexes with N_4 = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene ($Me_6[14]dieneN_4$) and in which substitution occurs at a site near equatorial ligand geminal methyl groups. Substitution at the stereochemically uncongested site of an isomer of this complex, obtained by interchanging the axial methyl and water ligands, is at least 10^4 times faster. In such stereochemically complicated ligands, the axial geminal-methyl and other equatorial ligand groups tend to protect the adjacent coordination site from an incoming ligand until the leaving group has moved more than 1 Å away from its coordination site at the metal center. Such an effect could not retard rates in a purely dissociative substitutional mechanism. Rather axial substitution in these complexes is inferred to occur by an interchange mechanism in which the entering and leaving groups become equivalent at a distance (r_{TS}) before the bond to the leaving group is completely broken. A simple electrostatic model for substitution in $Co(N_4)(OH_2)_2^{2+}$, $Co(N_4)(OH_2)CH_3^{2+}$, and $Co(N_4)(OH_2)Cl^{2+}$ complexes suggests that r_{TS} may be only about 0.1 Å longer for substitution at the stereochemically cluttered site of $Co(Me_6[14]dieneN_4)(OH_2)CH_3^{2+}$ than the uncluttered site. The methyl–aquo complexes are in the middle of this correlation, implying that the effective electron density at the cobalt center of these complexes is intermediate between that of the classical Co(III) and Co(II) coordination complexes.

The catalytic roles of the alkylcobalamin compounds have stimulated many studies of the nature and properties of cobalt-alkyl compounds.[3] Much of the recent interest has focused on the properties of the cobalt–alkyl bond and how these properties can be modified through steric and electronic interactions with other coordinated ligands.[3-13] The Co–R bond has been found

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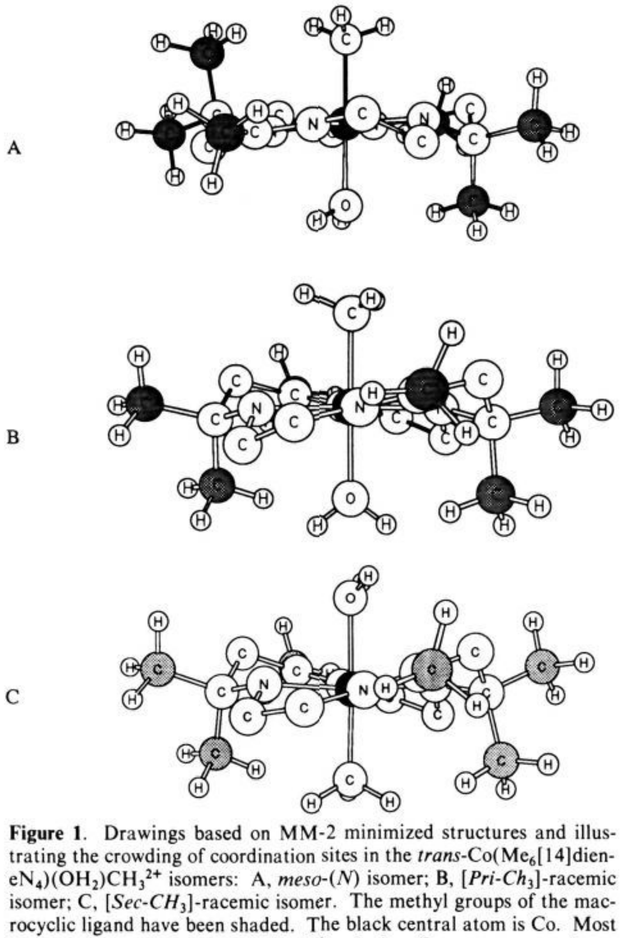

Figure 1. Drawings based on MM-2 minimized structures and illustrating the crowding of coordination sites in the *trans*-$Co(Me_6[14]dieneN_4)(OH_2)CH_3^{2+}$ isomers: A, *meso*-(*N*) isomer; B, [*Pri-Ch*$_3$]-racemic isomer; C, [*Sec-CH*$_3$]-racemic isomer. The methyl groups of the macrocyclic ligand have been shaded. The black central atom is Co. Most hydrogen atoms have been omitted for clarity. Structures were drawn by using the MODEL program at Wayne State University.

to be relatively weak, varying from about 25 kcal mol^{-1} for R = benzyl[9,10,12] to about 45 kcal mol^{-1} for some cobalt–methyl complexes.[14] The biologically important adenosylcobalamin complex has an intermediate bond strength (about 31 kcal mol^{-1}) in the isolated complex, but the rate of Co–C bond cleavage appears to increase enormously, by more than a factor of 10^{10}, in the holoenzyme B_{12}.[10] It has been variously suggested that this apparent weakening of the adenosyl–cobalt bond in the holoenzyme has its origin in some steric factors such as the puckering of the corrin ligand, the "tilt" of the Co–C bond axis with respect to the equatorial ligand N_4 plane, variations of the Co–C–R angles or the N–Co–C–R dihedral angles, etc.[2-11] That steric effects should be important in modulating the chemistry of axial ligands in the cobalamin complexes seems clear. However, their demonstration in simple molecular systems has proved difficult.

It has been observed that even the relatively stable $Co-CH_3$ bond is susceptibile to appreciable variations in its bond dissociation energy depending on the nature of the equatorial ligands.[14,15] The most dramatic effects in a simple system were found for $Co(Me_6[14]dieneN_4)(OH_2)CH_3^{2+}$[16] (ligand structures in Figure 1) complexes in which there may be approximately a 9 kcal mol^{-1} destabilization of the $Co-CH_3$ bond, compared to an analogous tetraimine complex.[14b,d,15] In a purely dissociative process, this would correspond to a factor of 10^6 in homolysis rate. Since two of the geminal methyl groups are in the neighborhood of the axial bonds (see Figure 1) in this complex and since there is some basis for attributing three-center character to the axial CH_3-Co-L bonding interaction,[14a,b] the relative weakness of the $Co-CH_3$ bond in the $Me_6[14]dieneN_4$ complex was attributed to a steric interaction.[14b] However, this steric effect does not manifest itself through any notable increase in the ground-state $Co-CH_3$ or $Co-OH_2$ bond lengths.[17] Rather, the axial bonds are slightly shorter in this than in some related but less congested $Co(N_4)(OH_2)CH_3^{2+}$ complexes.[17]

Stereochemical effects ought to be most readily manifested in their perturbations of substitution reactions of the axial ligands. Thus, steric factors have been postulated to play major roles in the substitution chemistry of coordination complexes in general[18] and, more particularly, in compounds containing macrocyclic ligands.[19-21] Molecular mechanics evaluations of stereochemical interactions in *trans*-$Co(N_4)Cl_2^+$ complexes have resulted in the inference that the complexes with the most strained ground states tend to be the most labile.[20,21] This, and the consideration that the $CH_3-Co-OH_2$ axial bonding interaction was relatively weak in $Co(Me_6[14]dieneN_4)(OH_2)CH_3^{2+}$, led us to expect that this complex should be relatively labile. Simple anation rates revealed a different pattern. To clarify some of the issues involved, we have employed molecular mechanics approaches to evaluate strain energy and other contributions to the reaction coordinate in these systems.

Experimental Section

Reagents. The alkylcobalt compounds were prepared and purified by methods similar to those described previously.[14,22] Trifluoromethanesulfonic acid (3 M) was distilled twice before use. The purified acid was added to Na_2CO_3 to prepare NaO_3SCF_3. In most experiments the ionic strength was adjusted with NaO_3SCF_3 or $NaClO_4$. Deionized, redistilled water was used for making all solutions. Reaction solutions were acidic, at least 10^{-2} M in $HClO_4$ or HO_3SCF_3.

The three isomers of $Co(Me_6[14]dieneN_4)(OH_2)CH_3^{2+}$ were prepared by approaches capitalizing on the kinetic and thermodynamic properties

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(16) Ligand abbreviations: $[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane; $Me_4[14]tetraeneN_4$ = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; *ms*-(*N*)-$Me_6[14]dieneN_4$ = *meso*-(1,8)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; *rac*-(*N*)-$Me_6[14]dieneN_4$ = *rac*-(1,8)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; $dmgH^-$ = 3,4-dimethylglyoximate. We have used [*Pri-X*] and [*Sec-X*] to specify the axial binding site of the least labile axial ligand in the *trans*-Co(*rac*-(*N*)-$Me_6[14]dieneN_4)(OH_2)X^{2+}$ complexes. The *Pri* site is relatively uncongested, Figure 1b, and the *Sec* site is stereochemically congested, Figure 1c.

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Table I. Methyl ^{1}H NMR Peaks Observed for *trans*-Co(Me$_6$[14]aneN$_4$)(OH$_2$)CH$_3^{2+}$ Isomers[a]

isomer	Co–CH$_3$	imine	geminal equatorial	geminal axial
meso-(*N*)	1.765	2.32, 2.30	1.358	1.222, 1.092
[*Pri-CH*$_3$]-rac-(*N*)	1.481	2.289	1.372	1.166
[*Sec-CH*$_3$]-*rac*-(*N*)	1.737	2.318	1.359	1.121

[a] Resonances relative to sodium 3-(trimethylsilyl)propionate-*2,2,3,3-d*$_4$ (TSP). All spectra recorded in 0.01 M DSO$_3$CF$_3$/D$_2$O; HDO (4.80 ppm) presaturation. All spectra were determined with a QE300 spectrometer.

of the several Co(II) and Co(III) species. The two least stable methyl–aquo isomers were prepared from the isomerically pure (*meso-* or *rac*-Me$_6$[14]diene)cobalt(II) complexes.

[*trans*-Co(*ms*-(*N*)-Me$_6$[14]dieneN$_4$)(OH$_2$)$_2$](ClO$_4$)$_2$. The Rillema synthesis reported previously[23] produces this isomer in reasonably pure form.[24-27] The most definitive, routine determination of isomeric composition is based on oxidation to Co(III) in acidic solution followed by NMR or other product characterization. The *ms* ⇌ *rac* isomerizations involve NH inversion and are base catalyzed; these isomerization rates are relatively slow in acidic solutions.

Warning: The perchlorate salts described here are potentially explosive and should be handled with care.

[*trans*-Co(*rac*-(*N*)-Me$_6$[14]dieneN$_4$)OH$_2$](ClO$_4$)$_2$. Our initial syntheses of this complex used Cr^{2+} to reduce [*Pri-Cl*]-*trans*-Co(*rac*-(*N*)-Me$_6$[14]dieneN$_4$)(OH$_2$)Cl^{2+} in acidic aqueous solution.[26] We have found that the synthesis of (Me$_6$[14]dieneN$_4$)cobalt(II) reported by Goedken et al.[28] produces almost exclusively the racemic isomer, and this is a much more convenient route. We modified the published[28] procedure slightly: (a) about 25 mL of 2-propanol was added to the preparative mixture in methanol to precipitate the product; (b) the resulting solid was recrystallized from aqueous 0.1 M HClO$_4$ containing a very small amount of NH$_4$ClO$_4$.

[*trans*-Co(*ms*-(*N*)-Me$_6$[14]dieneN$_4$)(OH$_2$)CH$_3$](ClO$_4$)$_2$. We have found that a slight modification of the procedure of Bakac and Espenson[29] afforded the most reproducible preparative method. Equal mass amounts (typically 0.5 g) of [Co(*ms*-(*N*)-Me$_6$[14]dieneN$_4$)(OH$_2$)$_2$](ClO$_4$)$_2$ and *trans*-Co(dimethylglyoximate)$_2$(OH$_2$)CH$_3$ were dissolved into 20 mL of 0.1 M HClO$_4$ in a stoppered Pyrex flask through which a steam of N$_2$ was passed. The solution in this flask was irradiated for 4 h with an iLC Technology LX1500 V 150-W Xe arc lamp. The radiation was filtered by a Pyrex glass optic and 5 cm of water. The reddish-tan precipitate was filtered, washed with cold water, and air dried. The complex was recrystallized from 0.1 M HClO$_4$/NH$_4$ClO$_4$. The overall yield was about 47%, but we did not attempt to recover all the solid formed at each stage owing to the explosion hazard of the prechlorate salt.

[[*Sec-CH*$_3$]-*trans*-Co(*rac*-(*N*)-Me$_6$[14]dieneN$_4$)(OH$_2$)CH$_3$](ClO$_4$)$_2$.[30] The above procedure was repeated substituting [Co(*rac*-(*N*)-Me$_6$[14]dieneN$_4$)(OH$_2$)$_2$](ClO$_4$)$_2$ for the meso isomer. The overall yield of the isomerically pure product after recrystallization was about 50%. The X-ray crystal structure of this complex was determined at Brookhaven National Laboratory and is being reported elsewhere.[30b] Absorption spectra: λ_{max} (ϵ) [nm (M^{-1} cm^{-1})] 462 (192), 272 (399), 290 (2700).

[[*Pri-CH*$_3$]-*trans*-Co(*rac*-(*N*)-Me$_6$[14]dieneN$_4$)(OH$_2$)CH$_3$](ClO$_4$)$_2$. Of our several synthetic approaches to this complex, the equilibration of either of the other isomers in NaCN, as described by Roche,[22] has been found to be the cleanest route. The [[*Pri-CH*$_3$]-*trans*-Co(*rac*-(*N*)-Me$_6$[14]dieneN$_4$)(CN)CH$_3$]ClO$_4$ precipitate was dissolved in water, and the aquo complex was precipitated by the addition of HClO$_4$.

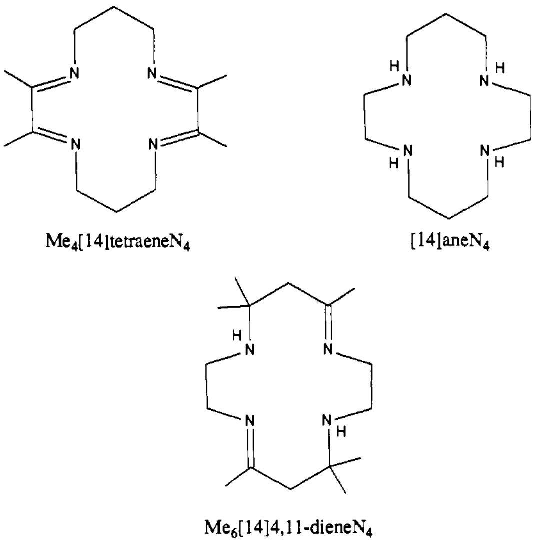

Figure 2. Skeletal structures of macrocyclic ligands. Abbreviations are explained in ref 16.

The methyl–aquo complexes were characterized on the basis of their ^{1}H NMR spectra. The important spectral features are summarized in Table I.

Kinetic Methods. Reaction rates have been monitored by using variations on standard spectrophotometric and NMR techniques.

The spectrophotometric determinations employed an Aminco stopped flow apparatus for reactions with half-lives of less than 30 s and a Guilford 250 spectrophotometer for the slower reactions. All these reactions were run using an excess of NCS$^-$ and thermostated at 25 °C. Complex concentrations were generally about 10^{-3} M, and [NCS$^-$] was varied as necessary to obtain [NCS$^-$]-dependent, pseudo-first-order rate constants. Second-order rate constants for the anations were obtained from linear correlations of the pseudo-first-order rate constants with [NCS$^-$]. Intercepts of these correlations were taken as measures of the back (or hydrolysis) reactions. The anation reactions were observed for the substrates (wavelengths, in nanometers):[13] Co([14]aneN$_4$)(OH$_2$)CH$_3^{2+}$ (360); [*Pri-CH*$_3$]-Co(*rac*-(*N*)-Me$_6$[14]dieneN$_4$)(OH$_2$)CH$_3^{2+}$ (365); [*Pri-Cl*]-Co(*rac*-(*N*)-Me$_6$[14]dieneN$_4$)(OH$_2$)Cl^{2+} (550); Co(Me$_4$[14]tetraeneN$_4$)(OH$_2$)CH$_3^{2+}$ (490). Reaction products were identified by their electronic or NMR spectra. The anation reactions were found to be first order in Co(III) complex and NCS$^-$.

Anations of [*Sec-CH*$_3$]-Co(*rac*-(*N*)-Me$_6$[14]dieneN$_4$)CH$_3^{2+}$ were initially examined at Wayne State and more thoroughly examined at Brookhaven National Laboratory by using Hi-Tech Scientific stopped flow equipment. The BNL system was comprised of a SF-40 Canterbury stopped flow, SU-40 spectrophotometer unit, and OPL-10 optical platform.

^{1}H NMR spectra were determined by using a Nicolet QE-300 and a NT-300 MHz instrument equipped with a variable-temperature unit. A curve analysis program (CAP) was used to determine peak areas. The equilibrium constant for the meso ⇌ racemic isomerization of Co(Me$_6$[14]dieneN$_4$)(OH$_2$)CH$_3^{2+}$ was determined by equilibrating the complex at pD ≃ 10 in D$_2$O for 5 min in the dark, adjusting the pD to about 1 with HO$_3$SCF$_3$, and comparing the peak areas of the Co–CH$_3$ resonances from each isomer in solution.

Molecular Mechanics Calculations. The Allinger-Yuh MM2 program (No. 395; updated Jan 1980) from the Quantum Chemistry Program Exchange (University of Indiana, Bloomington, IN)[31] was modified at Ohio State University to accommodate six-coordinate transition-metal ions. Further modifications were made by the authors to accommodate metal coordination numbers greater than six and to allow for multiple metal–ligand parametrization. The calculations reported here assumed that the π-systems were not significantly delocalized. The initial atomic coordinates were based on X-ray crystal structures of [*Pri-CH*$_3$]-Co(*rac*-(*N*)-Me$_6$[14]dieneN$_4$)(OH$_2$)CH$_3^{2+}$,[17] Co(*meso*-(*N*)-Me$_6$[14]dien-

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$eN_4(OH_2)_2^{2+}$,[23] Co(Me_4[14]tetraeneN_4)$(OH_2)_2^{2+}$,[23] and Co([14]aneN_4)$(ClO_4)_2$[23] (skeletal structures of the ligands are shown in Figure 2). The last three of these were converted to the corresponding methyl–aquo complexes by using the Evans-Sutherland PS-300 graphics system and other facilities of the Ohio State University Chemistry Department's Image Center. Coordinates for the additional water molecules needed for the seven-coordinate model were calculated manually and then refined by the program. The [*Pri-CH*$_3$]-Co(*rac*-(*N*)-Me_6[14]dieneN_4)$(OH_2)CH_3^{2+}$ complex was converted to the [*Sec-CH*$_3$] isomer on the WSU system by interchanging the CH_3 and H_2O coordinates.

The MM2 program parameters[31] were employed for all interactions not involving the central metal. Interaction parameters involving the metal were based on values published by Brubaker and Johnson.[32] Small variations ($\approx$30%) in metal–ligand bending constants did not significantly affect the ground state–intermediate state energy difference. No charge was assigned to the Co atom, but all calculations were performed including dipole interactions but excluding the interaction of dipoles with an atom in common. Metal–Ligand dipoles were varied over a range of 0 to 1.5 D, and these variations did slightly alter some of the results. As is customary,[32] torsional constants were set equal to zero for deformations around the metal.[33]

The calculational strategy was designed to assess the labilizing effects due to the relaxation of strain in the *coordinated macrocycle*. "Disconnecting" the H_2O ligand resulted in the aesthetically unappealing rotation of the water molecule (apparently to maximize van der Waals attractions) so that a proton was between, and approximately collinear with Co and O. This orientation has a small effect on atomic positions within the macrocycle. Partly to avoid this rotation and to better elucidate the Co–OH_2 separations over which macrocyclic ligand relaxation and ligand substitution occurred, we "moved" the water molecule away from the complex in a systematic manner by redefining the unstrained-equilibrium Co–OH_2 bond length, r_0, in 10–15-pm increments. The total structure was minimized for each incremental change in Co–OH_2 bond length. All interaction energies with the water molecule were subtracted from the calculated results to determine the energy changes within the R–Co(macrocycle) fragment. These energy changes were evaluated with and without the Co–O and O–H dipoles included in the minimization procedure.[33] The O–Co–N and H–O–Co bending force constants were set equal to zero for the Me_6[14]dieneN_4 complexes, to allow the departing water molecule to find the pathway with the smallest nonbonded repulsions. Some small H–O–Co angle constraints ($\approx$0.05 mdyn Å/rad^2) were required to maintain a sensible Co–OH_2 orientation for the [14]aneN_4 and Me_4[14]tetraeneN_4 complexes. The contribution to the total energy from this constraint was very small (ca. 0.01 kcal mol^{-1}) and was subsequently removed in evaluating E(Co(N_4)X).[33]

To model the point at which the axial and bulk water become indistinguishable, the axial water was placed 5 Å from the metal and another water was coordinated at this same distance. The entire seven-coordinate molecule was then minimized. No torsional or bending constraints were used for the Co–O moieties except for the previously mentioned H–O–Co bending constant. The unstrained Co–OH_2 bond length, r_0, was then shortened by 0.5-Å increments to determine the point at which equatorial ligand reorganization, as judged by the total steric energy, became necessary to accommodate the additional water molecule. Interwater repulsions were consistently about 1 kcal mol^{-1} for each series of calculations. Consequently these contributions had no effect on the comparison.

Results

A. Kinetic Studies. 1. General Features. The pseudo-first-order absorbance increases were well behaved for most of the reactions. However, the anation of [*Pri-CH*$_3$]-Co(*rac*-(*N*)-Me_6[14]dieneN_4)$(OH_2)CH_3^{2+}$ was biphasic, with only the rapid initial phase exhibiting the expected first-order dependence on [NCS^-]; the slower second phase ($k \approx 0.06$ s^{-1}) was nearly independent of [NCS^-].[34] The anation rates found for this compound and its chloro–aquo analogue were slower than expected based on either qualitative stereochemical arguments or on water exchange rates inferred from the previously reported aquation rates and equilibrium constants.[19b] The possibilities that these reactions could be complicated by substitution in the different axial sites of the Co(*rac*-(*N*)-Me_6[14]dieneN_4)$(OH_2)Cl^{2+}$ complex, or by *rac–meso* isomerization of the macrocyclic ligand, led us to follow the reactions using ^1H NMR techniques and to examine the anation of [*Sec-CH*$_3$]-Co(*rac*-(*N*)-Me_6[14]dieneN_4)$(OH_2)CH_3^{2+}$.

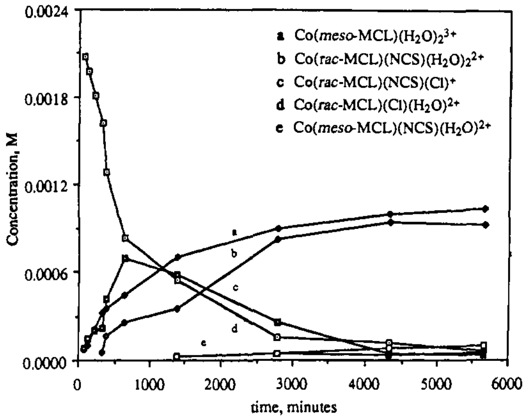

Figure 3. Plot of concentration vs time for species observed in the reaction of [*Pri-Cl*]-Co(*rac*-Me_6[14]4,11-dieneN_4)(Cl)$(H_2O)^{2+}$ with NaSCN. Data determined by NMR at 25 °C; [Co^{3+}] = 2.2 × 10^{-3} M, [NCS^-] = 1.0 × 10^{-3} M, and [H^+] = 0.5 M.

We were unable to determine rates of anation for [*Sec-CH*$_3$]-Co(*rac*-(*N*)-Me_6[14]dieneN_4)$(OH_2)CH_3^{2+}$. After several attempts using different stopped flow systems and after careful consideration of reactant and product absorption spectra, we have concluded that the anation reactions were complete on mixing ($\leq 5 \times 10^{-3}$ s) in solutions with [NCS^-] = 0.05 M. These final determinations were made with the Hi-Tech stopped flow spectrophotometer at Brookhaven National Laboratory. From the absorbance changes at 270 nm at several [NCS^-] $\leq$ 0.5 M (variable ionic strength) we infer that the formation constant of [*Sec-CH*$_3$]-Co(*rac*-(*N*)-Me_6[14]dieneN_4)(NCS)CH_3^+ is approximately 10^2 M^{-1} at 25 °C.

The rates of hydrolysis of the Co(Me_6[14]dieneN_4)$(OH_2)Cl^{2+}$ complexes were slow enough that they could be followed by using the NMR technique. However, these reactions were found to be very complex, with the *rac* $\rightleftharpoons$ *meso* isomerizations competing with or following the aquation and/or anation steps. Fortunately, it was possible to identify all the species involved by using different conditions of medium or different starting materials,[26] and each species was found to have a unique NMR spectrum. The reaction products were identified by observation of reactions of [*Pri-Cl*]Co(*rac*-(*N*)-Me_6[14]dieneN_4)$(OH_2)Cl^{2+}$ with thiocyanate for different concentrations of NaCl and HO_3SCF_3. An example of the time dependence of the concentrations of the various species is shown in Figure 3. The concentration of the NaSCN was kept low (approximately half the [Co^{3+}]) so the reactions would progress at slow rates and allow the accumulation of accurate NMR data. Figure 3 demonstrates that the decay of [*Pri-Cl*]-Co(*rac*-(*N*)-Me_6[14]dieneN_4)$(OH_2)Cl^{2+}$ results from competitive aquation and anation reactions. The anation was slightly faster than the aquation (for the conditions noted in Figure 3), and the metastable chloro–thiocyanato product typically rose to a maximum concentration, then decayed into an aquo–thiocyanato species. Pseudo-first-order rate constants, based on starting material decay, were [NCS^-] dependent, but plots of [NCS^-] vs the pseudo-first-order rate constants had small intercepts. From

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[32] Brubaker, G. R.; Johnson, D. W. *Coord. Chem. Rev.* **1984**, *53*, 1.

[33] (a) A typical MM2 parameter set is included in the supplementary material (see paragraph at the end of this paper). While the total steric energy was strongly dependent on the choice of metal–ligand interaction parameters, the energy differences between six-coordinate and five-coordinate species, $\Delta E = E(M(N_4)XY - E(M(N_4)X)$, and between different complexes, $\Delta E' = E(M(N_4)XY) - E(M(N'_4)XY)$, were quite insensitive ($\pm$0.3 kcal mol^{-1}) to these choices provided the paramatrization was consistent among systems compared. For example, inclusion of X–C–N–Co torsional parameters resulted in total steric energies of about 40 kcal mol^{-1} (supplementary material and Table III). While their omission resulted in steric energies of about 20 kcal mol^{-1} for the Co(Me_6[14]dieneN_4)$(OH_2)CH_3^{2+}$ complexes (Table III); however, $\Delta E'$ was 1.6 and 2.0 kcal mol^{-1}, respectively, for the steric energy difference between the meso and [*Pri-CH*$_3$]-racemic isomers, and the ΔE values agreed to about 0.1 kcal mol^{-1}. (b) We have represented the total steric energy of the complex by E(M(N_4)XY and steric energy of the M(N_4)X fragment (after subtracting all interactions of Y) by E(M(N_4)X).

[34] Such "slow" first-order processes were usually found to vary with the instrument used for measurement and are probably photochemical decompositions.

Table II. Kinetic and Equilibrium Parameters for Anation Reactions: $Co(N_4)(OH_2)X^{2+} + NCS^-$

N_4	X	k_f, $M^{-1}\ s^{-1}$ (T, °C)	k_r, s^{-1}	K_f, M^{-1}
[14]aneN_4	CH_3	386 ± 30 (5)[a]	≈0	
		966 ± 32 (15)[a]	≈0	
		2330 ± 160 (25)[a,b]	≈0	
Me_4[14]tetraeneN_4	CH_3	414 ± 8 (15)[c]	2.6 ± 0.4 (15)	160 ± 3
		762 ± 12 (25)[c]	4.2 ± 0.6 (25)	180 ± 3
		1642 ± 40 (35)[c,d]	10.6 ± 0.8 (35)	150 ± 1
	Cl	$\leq 1 \times 10^{-3}$ (25)[e]		
ms-(*N*)-Me_6[14]dieneN_4	CH_3	11 ± 3 (25)[a]	0.10	1×10^2
[*Pri-X*]-*rac*-(*N*)-Me_6[14]dieneN_4	CH_3	4.6 ± 0.2 (25)	≈0	
	Cl	3.4×10^{-3} (25)		
[*Sec-X*]-*rac*-(*N*)-Me_6[14]dieneN_4	CH_3	$\geq 10^4$ (25)		
$(dmgH)_2^{2-}$	CH_3	50 (10)[f]		

[a] k_f obtained from the slope of the average of three or more determinations of the anation rate for each of three or more [NCS^-]; in 1 M $NaCF_3SO_3$, 10^{-2} M H^+. [b] $\Delta H^\ddagger = 15 \pm 1$ kcal mol^{-1} and $\Delta S^\ddagger = 5.6 \pm 3.0$ eu for k_f. [c] 0.5 M $NaCF_3SO_3$; otherwise as in note *a*. [d] $\Delta H^\ddagger = 12 \pm 2$ kcal mol^{-1} and $\Delta S^\ddagger = 8.0 \pm 0.3$ eu for k_f. [e] Upper limit based on NMR studies in 1 M HCl. [f] Crumbliss, A. L.; Wilmarth, W. K. *J. Am. Chem. Soc.* **1970**, *92*, 2593.

these observations $k_{an} = 3.4 \times 10^{-3}\ M^{-1}\ s^{-1}$, and from the intercept, $k_b = 1.2 \times 10^{-5}\ s^{-1}$, at 25 °C in 0.01 M HCF_3SO_3/0.5 M $NaCF_3SO_3$. This value of k_b is in the range of values estimated for hydrolysis of Co(*rac*-(*N*)-Me_6[14]dieneN_4)$(OH_2)Cl^{2+}$ under similar conditions.

Extrapolation to [NCS^-] = 0 of the plots of pseudo-first-order anion rate constants vs [NCS^-] for Co(Me_4[14]tetraeneN_4)-$(OH_2)CH_3^{2+}$ resulted in a nonzero intercept, $k_{obsd} = k_f[NCS^-] + k_r$, where we have interpreted k_r as the reverse or hydrolysis reaction rate constant. The rate and equilibrium constant data are summarized in Table II.

2. ^1H NMR Studies of the Chloro Complexes. Our NMR studies have indicated that all reactions of $Co(N_4)(OH_2)Cl^{2+}$ complexes, where N_4 = Me_6[14]dieneN_4 or Me_4[14]tetraeneN_4, are complicated by hydrolytic equilibria and isomerizations. These reactions are especially complicated when N_4 = Me_6[14]dieneN_4, and the detailed studies of the anation and aquation reactions of those complexes will be reported elsewhere.[26] Very briefly, whether the racemic or meso isomer is the most stable species depends strongly on the symmetry of the axial coordination. For axially symmetric Co(III) complexes, the meso isomer is favored, while the racemic isomer is usually the most stable for the axially asymmetric complexes. Thus the meso isomers are most stable for Co(Me_6[14]dieneN_4)$(OH_2)_2^{3+}$ and Co(Me_6[14]dieneN_4)Cl_2^+, while the [*Pri-X*]-racemic isomers are most stable for Co(Me_6[14]dieneN_4)$(OH_2)X^{2+}$. Fortunately, we were able to observe the buildup and decay of Co(*ms*-(*N*)-Me_6[14]dieneN_4)(NCS)Cl^+, thereby establishing the direct anation of Co(*ms*-(*N*)-Me_6[14]dieneN_4)$(OH_2)Cl^+$ as one of the faster reactions in this system. The rate of formation of Co(*ms*-(*N*)-Me_6[14]dieneN_4)(NCS)Cl^+ was indistinguishable from the initial rate of decay of Co(*ms*-(*N*)-Me_6[14]dieneN_4)$(OH_2)Cl^{2+}$. We have based the anation rate in Table II on the rate of disappearance of this chloro–aquo starting material (Figure 3). The NMR spectra of solutions of Co(Me_4[14]tetraeneN_4)Cl_2^+ demonstrated the dichloro– and aquo–chloro complexes to be much less stable than expected stepwise formation constants, K_f = 0.19 and 34 M^{-1}, respectively, in 1 M NaCl at 25 °C).

Our NMR studies of base-equilibrated Co(Me_6[14]dieneN_4)$(OH_2)CH_3^{2+}$ solutions have indicated that the [*Pri-CH*$_3$]-racemic isomer is favored by a factor of 5 ± 1 over the meso isomer. This may be compared to a calculated equilibrium constant of 14 for [*Pri-CH*$_3$]-racemic:meso and 16 for meso:[*Sec-CH*$_3$]-racemic (energies calculated are summarized in the supplementary material (see paragraph at end of paper) and Table III).

Our spectrophotometric studies of the NCS^- anation of Co-(Me_4[14]tetraeneN_4)$(OH_2)Cl^{2+}$ seemed to indicate a straightforward process. However, the NMR studies demonstrated that this chloro–aquo complex was in relatively labile equilibrium with Cl^- in solution and that anation of Co(Me_4[14]tetraeneN_4)-$(OH_2)_2^{3+}$ was the dominant process. Consequently, we were able to obtain only an uppler limit for anation of the chloro–aquo complex.[27]

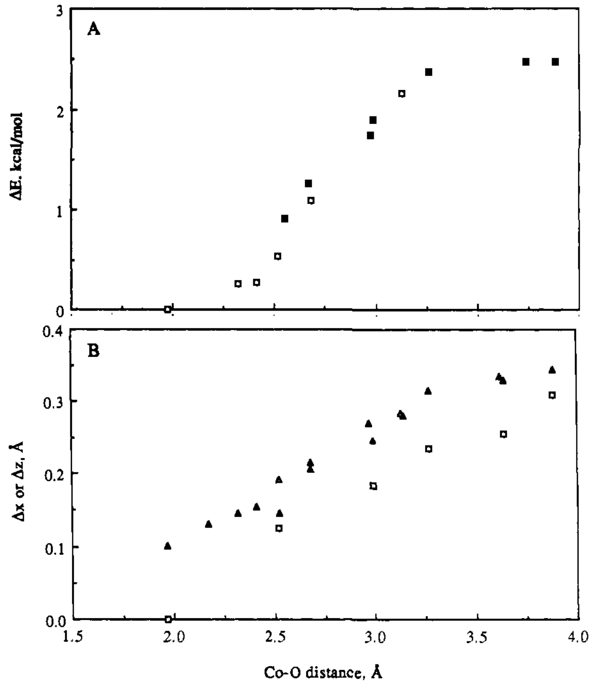


Figure 4. Variations in strain energy with Co–O distance in the Co(*rac*-(*N*)-Me_6[14]dieneN_4)CH_3^{2+} fragment (upper plot), and correlated changes in the X- or Z-coordinated, respectively, of the axial–geminal methyl (■ or □) or methylene (▲ or △) hydrogens nearest to the Co–OH_2 coordination site (plot B). Closed points (■ or ▲) are used for calculations that employed finite values of the Co–O and O–H dipoles; open points are for calculations that set these dipoles equal to zero.

B. MM-2 Calculations. We have examined the energy and conformational changes in the coordinated macrocycle that accompany Co–OH_2 bond breaking in $Co(N_4)(OH_2)CH_3^{2+}$ complexes. Six complexes have been examined, and these complexes exhibit a considerable range of behavior. The contributions of the macrocyclic ligand are largest for the [*Pri*]-Co(*rac*-(*N*)-Me_6[14]dieneN_4)$(OH_2)CH_3^{2+}$, smallest for Co(Me_4[14]tetraeneN_4)$(OH_2)CH_3^{2+}$ and Co([14]aneN_4)$(OH_2)CH_3^{2+}$ complexes. Table III surveys and summarizes the results of the calculations. Some features of the individual calculations warrant detailed comment.

1. [*Pri-CH*$_3$]-Co(*rac*-(*N*)-Me_6[14]dieneN_4)$(OH_2)CH_3^{2+}$. Some important features of this system are illustrated in Figure 4. There is an appreciable relaxation of $Co(N_4)CH_3^{2+}$ strain energy when H_2O is removed from the coordination sphere ($\Delta E = 2.6 \pm 0.1$ kcal mol^{-1}). These energy changes are accompanied by an appreciable decrease in the volume of the coordination site as the neighboring axial geminal methyl groups and some of the methylene groups (from the five-membered chelate rings) fold into the space vacated by water. Four hydrogen atoms close to the coordination site move 0.3–0.5 Å each, and these motions

Table III. Survey of Characteristic MM2 Calculations for Water Dissociation from *trans*-$Co(N_4)(OH_2)CH_3^{2+}$

equatorial ligand	$Co-OH_2$ parameters varied[a]	d(Co–O),[b] Å	$E(Co(N_4)OH_2CH_3)$,[c] kcal mol^{-1}	$E(Co(N_4)CH_3)$,[d] kcal mol^{-1}
[*Pri-CH*$_3$]-*rac*-(*N*)-Me_6[14]dieneN_4	in	1.97	18.0	22.6
	out	1.97	22.1	22.1
	out	2.68	20.4	21.2
	in	2.98	17.1	20.4
	out	3.13	19.1	20.2
	in	>3.25	16.3[e]	19.9[e]
	(in	1.96	7.6	12.4)[f]
	(in	2.45	8.2	11.5)[f]
	(in	2.86	7.2	10.6)[f]
	(in	3.22	7.9	10.8)[f]
	in[g]	1.97	38.9	
[*Sec-CH*$_3$]-*rac*-(*N*)-Me_6[14]dieneN_4	in[g]	1.97	40.6	37.3
		4.02		35.0
ms-(*N*)-Me_6[14]dieneN_4	in	1.99	20.0	26.3
	in	3.98	19.9	24.4
	in[g]	1.97	37.4	
Me_4[14]tetraeneN_4	out	2.00	26.8	28.9
	out	3.90	28.2	28.8
[14]aneN_4	out	1.99	15.2	13.3
	out	3.5	13.8	12.6

[a] Co–O and O–H dipoles; N–Co–O, C–Co–O, and Co–O–H angle constraints: "in" indicates that these parameters were used in the minimization; "out" that they were not. All torsions involving Co set to zero except as noted. [b] Distance after minimization. [c] Minimized energy of the Co-$(N_4)(OH_2)CH_3^{2+}$ complex. [d] Minimized energy with all H_2O interactions removed. [e] Averaged values for calculations with *d*(Co–O) between 3.25 and 4.0 Å. [f] Calculations for *trans*-Co(*rac*-(*N*)-Me_6[14]dieneN_4)$(OH_2)Cl^{2+}$. Co–Cl dipole moment set equal to −1.5 D. Other parameters as described in supplementary material. [g] Values of C–C–N–Co, H–C–N–Co torsions included in calculation; see supplementary material.

continue until the $Co-OH_2$ bond length has increased by at least 1.25 Å (see Figure 4). The departing water molecule moves nearly along the Co–C axis.

2. [*Sec-CH*$_3$]-Co(*rac*-(*N*)-Me_6[14]dieneN_4)$(OH_2)CH_3^{2+}$. Dissociation of H_2O resulted in a decrease of strain energy of ΔE = 2.3 kcal mol^{-1}. Most of this was the result of decreased geminal methyl–axial methyl (Co) van der Waals interactions. Intermediate energies were not calculated.

3. Co(*ms*-(*N*)-Me_6[14]dieneN_4)$(OH_2)CH_3^{2+}$. Substantial but smaller strain relaxation energies were found for this molecule. Strain relaxation energy in the metallo fragment amounted to 1.6 ± 0.1 kcal mol^{-1} at the dissociation limit. As the water molecule departed, there was an appreciable contraction on one side of the coordination site. Substantial changes in strain energy and atomic positions within the macrocyclic ligand continued until the departing water molecule had moved 1.0 ± 0.1 Å. The departing water molecule moved in an arc away from the proximate axial geminal methyl group that closed in on the coordination site.

4. Co([14]aneN_4)$(OH_2)CH_3^{2+}$. Both strain relaxation and macrocyclic ligand atomic motions were small when water was removed from the coordination site: 0.6 ± 0.1 kcal mol^{-1} and ≤ 0.1 Å, respectively. Some very small changes in strain energy and atomic position continued until the water molecule had moved 0.7 Å.

5. Co(Me_4[14]tetraeneN_4)$(OH_2)CH_3^{2+}$. Changes in the steric energy or atomic positions within the macrocyclic ligand as the $Co-OH_2$ bond length was increased were smallest for this complex: $\Delta E \leq 0.17 \pm 0.1$ kcal mol^{-1}; the maximum amplitude of any atomic motion was less than 0.1 Å. There was no change in atomic positions within the ligand after the $Co-OH_2$ bond had been lengthened by 0.3 Å.

6. [*Pri-Cl*]-Co(*rac*-(*N*)-Me_6[14]dieneN_4)$(OH_2)Cl^{2+}$. When a Co–Cl dipole moment of −1.5 D was used, ΔE = 1.6 ± 0.2 kcal mol^{-1} (for μ(Co–Cl) = 0.0, ΔE = 1.9 kcal mol^{-1}). The behavior found for this complex as the water was removed further differed from that found for [*Pri-CH*$_3$]-Co(*rac*-(*N*)-Me_6[14]dieneN_4)-$(OH_2)CH_3^{2+}$ in that the changes in energy were largely complete for a 0.9-Å increase in $Co-OH_2$ bond length. It appears that the large Co–Cl and N–H dipole–dipole coupling and the smaller van der Waals repulsions make the chloro–aquo more rigid than the methyl–aquo complex.

7. Evaluation of Stereochemical Interactions for an Interchange Pathway. To evaluate possible contrasts in stereochemical interactions for interchange pathways (see Scheme I and Discussion), we have examined the effects of adding a second water molecule to the coordination spheres of [*Pri-CH*$_3$]Co(*rac*-(*N*)-Me_6[14]-dieneN_4)$(OH_2)CH_3^{2+}$, [*Pri-Cl*]Co(*rac*-(*N*)-Me_6[14]dieneN_4)-$(OH_2)Cl^{2+}$, and Co(Me_4[14]tetraeneN_4)$(OH_2)CH_3^{2+}$. The stereochemical repulsions become small for $Co-OH_2$ distances of 2.5 Å for the Co(Me_4[14]tetraeneN_4)$(OH_2)CH_3^{2+}$ system and of about 4 Å for the Co(*rac*-(*N*)-Me_6[14]dieneN_4)$(OH_2)X^{2+}$ complexes (Figure 5). Clearly, ligand stereochemistry is a severe impediment to an interchange pathway in these Me_6[14]dieneN_4 complexes but not in the Me_4[14]tetraeneN_4 complex.

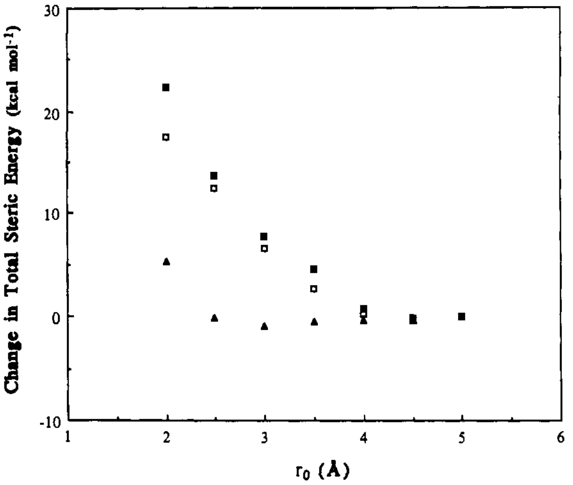
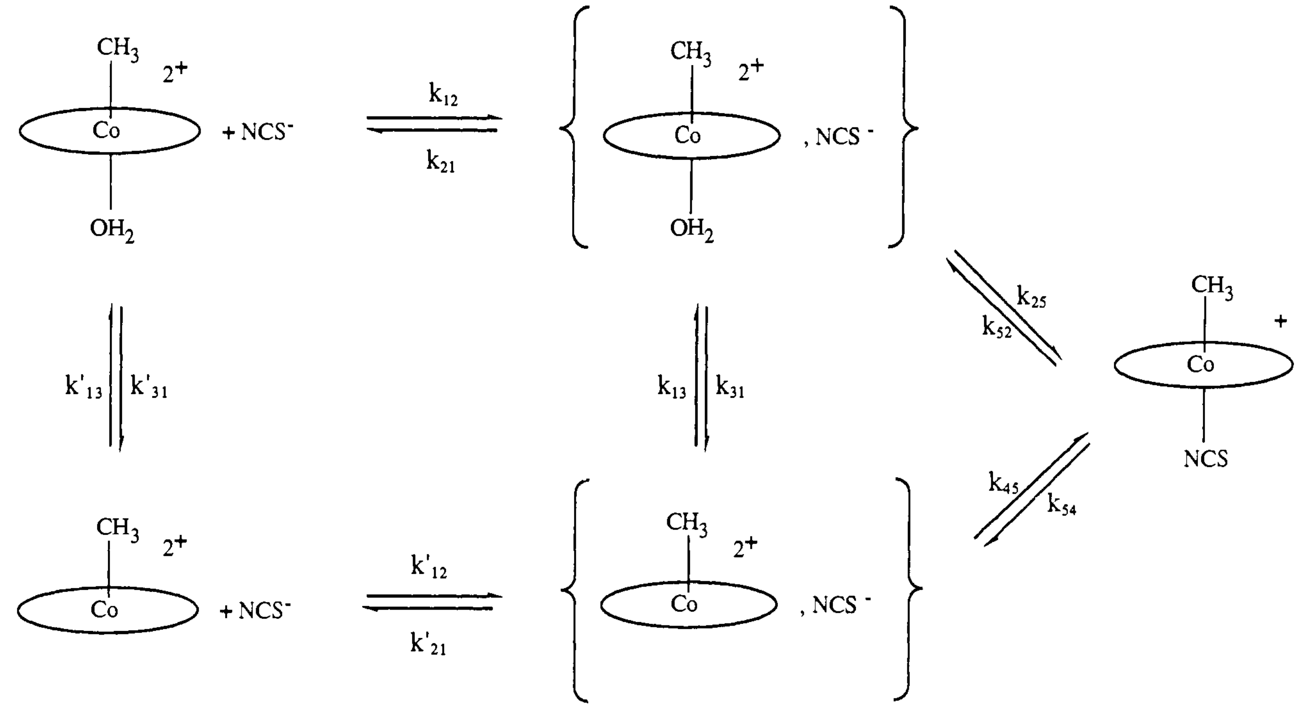


Figure 5. Variations in stereochemical repulsions for two equivalent water molecules near the coordination site of $Co(N_4)X^{2+}$ (a model for dissociative interchange): [*Pri-CH*$_3$]Co(*rac*-(*N*)-Me_6[14]dieneN_4)CH_3^{2+}, ■; [*Pri-Cl*]Co(*rac*-(*N*)-Me_6[14]dieneN_4)Cl^{2+}, □; Co(Me_4[14]tetraeneN_4)Cl^{2+}, △.

In addition to the strain relaxation energies within the $Co(N_4)X$ fragment that are described above, we found the macrocyclic ligand–coordinated water interactions to be small, largely attractive, and increasingly negative as the Co–O distance increased. These effects varied from ΔE_{vdW} = 0.2 kcal mol^{-1} for the [14]-aneN_4 complex to approximately 1.6 kcal mol^{-1} for the *rac*-(*N*)-Me_6[14]dieneN_4 complex. (Note that our sign convention is based on $\Delta E = E(Co(N_4)XY) - E(Co(N_4)X)$.[33] This component of ΔE_{vdW} does not always approach a well-defined limit in these calculations when the atomic motions within the ligand do. We have not used these variations of ΔE_{vdW} in our analysis of strain relaxation. Their incorporation does not change the

Scheme I



nature of our argument. Since some contribution of ΔE_{vdW} must enter into the dissociation pathway, the relaxation energies employed in the Discussion should be regarded as underestimates by 0–2 kcal mol^{-1}, with the smaller values found for the Me$_4$-[14]tetraeneN$_4$ and [14]aneN$_4$ complexes and the larger ones for the Me$_6$[14]dieneN$_4$ complexes.

There was some tendency for these complexes to fold slightly in the direction of departing water molecule. However, the dipole–dipole interaction forces tended to keep the distance small between the Co atom and the mean N$_4$ plane so that most of the atomic motion was confined to the paraffinic backbone of the ring. The actual value selected for the Co–N dipole moment (2 D $\geq \mu \leq$ 0.2 D) was not a major factor in this behavior.

Finally, the MM2 calculations indicate that [*Pri-CH*$_3$]-Co-(*rac*-(*N*)-Me$_6$[14]dieneN$_4$)(OH$_2$)CH$_3$$^{2+}$ should be about 1.6 kcal mol^{-1} more stable than Co(*ms*-(*N*)-Me$_6$[14]dieneN$_4$)(OH$_2$)CH$_3$$^{2+}$, while the meso isomer should be about 1.6 kcal mol^{-1} more stable than the [*Sec-CH*$_3$]-racemic isomer (see also the comparison of equilibrium constants, above).

Discussion

The labilizing influence of the trans-methyl group is clearly manifested in these Co(N$_4$)(OH$_2$)CH$_3$$^{2+}$ complexes. However, the effects of any variations in electron density near the metal are complicated by the manner in which stereochemical interactions between the atoms on the macrocyclic ligand and the departing water molecules modify the reaction rate. These rate modifications are reversed from expectation based on the energetic effects of the decrease in repulsive energies when the metal complex becomes five-coordinate; the system in which the loss of H$_2$O results in the largest decrease in nonbonded repulsions and intraligand strain, [*Pri-CH*$_3$]-Co(*rac*-(*N*)-Me$_6$([14]dieneN$_4$)(OH$_2$)CH$_3$$^{2+}$, actually is the least labile of the complexes studied. This observation seems at least superficially different from the conclusions of earlier studies of the hydrolysis of Co-(N$_4$)Cl$_2$$^+$ complexes,[20,21] and we have been led to a more critical evaluation of the substitutional behavior of these systems.

Scheme I is a very general description of possible substitutional pathways in the methyl–aquo complexes. The pathway with the primed rate constants is usually described as the limiting dissociative ("D" or SN$_1$) pathway. Depending on which step dominates the relaxation time, substitution along the pathways with unprimed rate constants can be described as D, limiting associative ("A") or interchange ("I$_A$" or "I$_D$" if the dominating characteristics are associative or dissociative, respectively).[18,35-37] General solutions of the rate equations for Scheme I can be obtained in the pseudo-first-order limit (great excess of [NCS$^-$]), but simple limiting solutions are adequate for our purposes. It is very reasonable to assume that the primed and corresponding unprimed rate constants are approximately equal (i.e., $k_w' \cong k_w$, $k_{12}' \cong k_{12}$, etc.). It is then convenient to classify limiting cases in terms of the mean lifetimes of key intermediate species: τ_{1P} for the ion pairs (i.e., the entities in curly brackets); τ_d for the five-coordinate Co(N$_4$)CH$_3$$^{2+}$ complex. Then the limiting dissociative pathway dominates when $\tau_d > \tau_{1P}$,[38] while all other limits require $\tau_{1P} > \tau_d$. There are two limiting possibilities for the D pathway: (a) $k_{45} > k_{21}$ so that k_{D1}(obsd) $\cong K_w k_{12}$ ($K_w = k_{13}/k_{31}$); (b) Co-(N$_4$)CH$_3$$^{2+}$ relatively stable (k_{12}, k_{21}, $> k_{45}$) so that k_{D2}(obsd) $\cong K_w K_{12} k_{45}$. Similarly, there are three simple limiting situations along the unprimed pathway: (a) an associative limit in which $k_{25} > k_{k13}$ and k_A(obsd) $\cong K_{12} k_{25}$; (b) a dissociative limit ($k_{45} > k_{31}$), k_{D2}(obsd) $\cong K_w K_{12} k_{45}$; (c) an I$_D$ pathway in which $k_{45} >$ (k_{31}, k_{21}), so that k_{1D}(obsd) $\cong K_{12} k_{13}$. From a qualitative point of view, the D pathway will be favored for relatively stable Co-(N$_4$)CH$_3$$^{2+}$ moieties, and many discussions about the influence of stereochemical strain energies on substitution rates can be interpreted as arguments that the D pathway dominates and that strain relaxation on forming the five-coordinate intermediate is a major factor in the stabilization of this species. This view has some support, among the systems considered here, in the observations that the aquo complex of (*rac*-(*N*)-Me$_6$[14]dieneN$_4$)cobalt(II) is five-coordinate with the conjested, [*Sec*], site unoccupied.[27] However, it contrasts to the prevailing view that most substitution is Co(III) complexes proceeds by means of an interchange mechanism.[35-37]

A. Contrast in Labilities of Alkyl–Aquo and Chloro–Aquo Complexes. We have examined the anations of several *trans*-Co(N$_4$)(OH$_2$)Cl^{2+} complexes to be able to contrast the behavior of "normal" Co(III) complexes to that of the alkyls. While the

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(37) Swaddle, T. W. *Adv. Inorg. Bioinorg. Mech.* **1983**, *2*, 95.

(38) For our systems this condition would require Co(N$_4$)X intermediate lifetimes of less than about 10 ns.

spectroscopic studies of these complexes did not reveal much that was out of the oridinary, our NMR studies have shown that each of the reactions investigated was actually very complex. The principal difficulty was the relatively facile aquation of the chloro–aquo complexes and the rapid anation of the resulting diaquo species. However, this is only a complication of detail, since all of these reactions were much slower than anations of the methyl–aquo complexes. We have been able to obtain a reasonable estimate $k_f/K_0 = 1.0 \times 10^{-3}$ s^{-1}, where K_0 is the estimated value of K_{12}) for the water lability of [*Pri-Cl*]-Co(*rac*-(*N*)-Me$_6$[14]dieneN$_4$)(OH$_2$)Cl^{2+} and an upper limit ($k_f/K_0 \leq 3 \times 10^{-4}$ s^{-1}) for the Co(Me$_4$[14]tetraeneN$_4$)(OH$_2$)Cl^{2+} complex. The trans-labilizing effect of CH$_3$ can then be inferred to contribute a factor of 10^3–10^7 to the rates of substitution in the corresponding methyl–aquo complexes.

There is a striking inversion in the ratio of labilities of the Co(*rac*-(*N*)-Me$_6$[14]dieneN$_4$)(OH$_2$)X^{2+} and Co(Me$_4$[14]tetraeneN$_4$)(OH$_2$)X^{2+} complexes when X is changed from CH$_3$ to Cl: the rate ratio k_f(N$_4$):k_f(N$_4'$) changes from 6×10^{-3} to ≥ 3. This inversion can be partly attributed to the smaller differences in the relaxation of equatorial ligand strain (ΔE) for the chloro–aquo complexes. However, our calculated energy differences would account for no more than 5% of the change in rate ratio. There are two simple ways in which such a marked change in rate ratios might come about: (a) the substitutional pathway is different for [*Pri-CH$_3$*]-Co(*rac*-(*N*)-Me$_6$[14]dieneN$_4$)(OH$_2$)CH$_3$$^{2+}$ (and for the meso analogue) than for any of the other Co(N$_4$)(OH$_2$)CH$_3$$^{2+}$ complexes (e.g., D rather than I$_D$); or (b) the major fraction (on the order of 90%) of these differences in water lability should be attributed to variations in the H$_2$O–Co–X bond dissociation energies (ΔU; see below), and the H$_2$O–Co–CH$_3$ and H$_2$O–Co–Cl bond dissociation energies respond differently to changes of the equatorial ligand.

B. Influences of the Equatorial Ligands on the Substitutional Behavior: Electronic vs Steric Effects. It is useful to employ the k_f/K_0 ratios in our discussion. In the limiting D or I$_D$ pathways, $k_f/K_0 \cong k_w$ (the water-exchange rate constant) and would be free of any contributions from the equilibrium constants of the substitution reactions. The k_f/K_0 ratio is also a natural parameter in other limiting substitutional pathways. The lability of Cl$^-$ in several of the *trans*-Co(N$_4$)(OH$_2$)Cl^{2+} complexes has complicated some of the attempted comparisons. Nevertheless, it is clear that k_f/K_0 is small for these complexes. It is not clear that there is much variation in k_f/K_0 for the different Co(N$_4$)(OH$_2$)Cl^{2+} complexes.

A much larger range of substitution rates, about 10^4-fold, has been reported for aquation of the corresponding dichloro complexes. In these reactions, the Me$_6$[14]dieneN$_4$ and the Me$_4$[14]tetraeneN$_4$ complexes are of comparable lability and much more labile than the [14]aneN$_4$ complex. However, this observation turns out to be of little use since there are large differences in the equilibrium constants for these reactions and the reaction rates are expected to vary with the equilibrium constants.[35,37] In fact the least stable complexes are the most labile, as expected. The magnitudes of the differences in stability constants or the significance of the isomer problems was not clear until we began our NMR studies.

The pattern of rates in the anations of the Co(N$_4$)(OH$_2$)CH$_3$$^{2+}$ complexes was surprising to us. Since the complexes all have the same charge and since they are comparable in size, values of the outer-sphere association constants (K_0) should be very nearly identical, and the observed rates should be directly proportional to the water exchange rates in the I$_D$ limit, as defined above. Values inferred for k_f/K_0 are presented in Table III.

That the Co([14]aneN$_4$)(OH$_2$)CH$_3$$^{2+}$ and Co([14]tetraeneN$_4$)(OH$_2$)CH$_3$$^{2+}$ complexes have somewhat comparable values of k_f/K_0 indicates that equatorial ligand unsaturation does not play a major role in labilizing the CH$_3$–Co–OH$_2$ axis. The slightly smaller value of k_f/K_0 found for the Me$_4$[14]tetraeneN$_4$ complex is consistent with the smaller strain relaxation calculated for the Co(Me$_4$[14]tetraeneN$_4$)CH$_3$$^{2+}$ than the Co([14]aneN$_4$)CH$_3$$^{2+}$ fragment. However, this consistency is deceptive since even in the dissociative limit other factors must be considered. The contributions to the energy required to form the dissociative transition state (SDE) can be approximately represented as the sum of the appropriate energy contributions:[39]

$$\mathrm{SDE} \cong \Delta U - \Delta E_{\mathrm{st}} - \Delta E_{\mathrm{vdW}} - E_{\mathrm{solv}} \qquad (1)$$

where ΔU is the "intrinsic" Co–OH$_2$ heterolytic bond dissociation energy (i.e., the value of SDE in the absence of any stereochemical interactions), ΔE_{st} and ΔE_{vdW} are the energies of relaxation of strain within the CH$_3$–Co(MCL)$^{2+}$ fragment and interligand van der Waals repulsions, respectively, as H$_2$O leaves the coordination sphere and ΔE_{solv} is the difference in solvation energies of the ground state and the dissociated fragments. An expression similar to eq 1 should apply to the homolytic dissociation of CH$_3$. Since the photochemically determined bond dissociation energy is about 5 kcal mol^{-1} smaller for homolysis of Co([14]aneN$_4$)(OH$_2$)CH$_3$$^{2+}$ than for Co(Me$_4$[14]tetraeneN$_4$)(OH$_2$)CH$_3$$^{2+}$,[14] the axial bond is probably 2–4 kcal/mol^{-1} weaker in the former than in the latter. The weaker bond also appears to be slightly longer and more labile (Table III). These complexes behave very much in accord with reasonable expectation for the D and probably for the I$_D$ limits.

In contrast, the MM2 calculations indicate that stereochemical effects should be much more important for the Co(Me$_6$[14]dieneN$_4$)(OH$_2$)CH$_3$$^{2+}$ complexes, but the values of k_f/K_0 are relatively small. Reasoning as above, ΔU is probably as much as 4 kcal mol^{-1} smaller in the Me$_6$[14]dieneN$_4$ complexes than in Co(Me$_4$[14]tetraeneN$_4$)(OH$_2$)CH$_3$$^{2+}$ (i.e., simple stereochemical factors may account for half or more of the difference reported for Co–CH$_3$ in homolytic bond dissociation energies). This, coupled with the relatively large strain relaxation energies when water dissociates, should result in extremely rapid anation reactions. This reasoning is clearly consistent with the observed facile substitution at the stereochemically uncongested site of [*Sec-CH$_3$*]-Co(*rac*-(*N*)-Me$_6$[14]dieneN$_4$)(OH$_2$)CH$_3$$^{2+}$ ($k_f \geq 10^4$ M^{-1} s^{-1}) but not with the very slow substitution at the congested site of the [*Pri-CH$_3$*]-racemic isomer ($k_f = 4.6$ M^{-1} s^{-1}). These stereoisomers are respectively the most labile and the least labile methyl aquo complexes that we have examined. This contrast in reactivities is not readily attributed to variations in any components of eq 1. Rather, the simplest way to account for this retarding effect of the Me$_6$[14]dieneN$_4$ ligand in the [*Pri-CH$_3$*]-racemic (and in the meso) isomer is to postulate that the stereochemical clutter of the equatorial ligand interferes with approach of the entering group so that the departing water molecule must move a relatively great distance from the metal center before the departing, and entering water molecules become equivalent in the exchange of coordinated and bulk water (e.g., see Figure 5). This requires that substitution at stereochemically less cluttered sites in the macrocyclic ligand complexes occur by an interchange pathway in which the entering ligand approaches the coordination site before the bond to the departing ligand is completely broken, while substitution at the stereochemically conjested sites of Me$_6$[14]dieneN$_4$ complexes requires more complete bond breaking to the leaving group. For example, substitution at the "open" sites could be I$_D$ in character, while conjested site substitution may be more nearly D. The I$_D$ mechanism is usually postulated for substitution in Co(III) complexes,[18,35-37] but much of the discussion of substitution in macrocyclic ligand complexes has assumed five-coordinate transition state.[20,21,40] It is likely that some of this confusion has come from

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(39) Equation 1 addresses only variations in energy contributions. Entropic contributions are also expected (see eq 2 and Discussion), however, these are expected to be relatively small, and they are more difficult to systematically estimate. The *signs* of entropy changes for the D pathway are reasonably predictable: (a) $\Delta S_{\mathrm{B}} > 0$ for Co–OH$_2$ dissociation; (b) $\Delta S_{\mathrm{Str}} < 0$ for relaxation of sterecochemical strain; (c) ΔS_{solv} is probably less than zero for the difference in solvation of Co(N$_4$)(OH$_2$)CH$_3$^{2} and (Co(N$_4$)CH$_3$$^{2+}$ + H$_2$O). Clearly there will be some cancellation of terms. Only ΔS_{str} is expected to show large percentage changes from one complex to another, but this contribution is expected to be proportional to ΔE_{str} and will have the effect of increasing the stereochemical influence on the reaction rate. The energy to enthalpy correction is simply a constant and will not affect the relative rate considerations.

(40) (a) Poon, C. K.; Tobe, M. L. *Inorg. Chem.* **1968**, *7*, 2398; (b) *J. Chem. Soc. A* **1968**, 1549.

Table IV. Comparison of Water Exchange Rates (k_w) and Co–O Ground-State Bond Lengths of $Co^{III}(N_4)(OH_2)X$ Complexes

equatorial ligand	X	k_f/K_0,[a] s^{-1}	Co–O bond length r_0,[b] Å	Co–C bond length r_0,[b] Å
[14]aneN_4	CH_3	6.6×10^2	2.16[c]	1.99[c]
Me_4[14]tetraeneN_4	CH_3	2.2×10^2	2.11[c]	2.01[c]
	Cl	$\leq 3 \times 10^{-4}$	(1.91)[d]	
$(dmgH)_2^{2-}$	CH_3	1.2×10^2[e]	2.06[f]	1.99[f]
ms-(*N*)-Me_6[14]dieneN_4	CH_3	3.1		
[*Pri-CH*$_3$]-*rac*-(*N*)-Me_6[14]dieneN_4	CH_3	1.3	2.12[c]	1.97[c]
	Cl	1.0×10^{-3}	(1.91)[d]	
[*Sec-CH*$_3$]-*rac*-(*N*)-Me_6[14]dieneN_4	CH_3	$>3 \times 10^3$	2.09[g]	
Me_4[14]tetraeneN_4(Co^{II})[h]	H_2O	$\approx 3.5 \times 10^8$[i]	2.29[j]	
ms-(*N*)-Me_6[14]dieneN_4(Co^{II})[h]	H_2O	$\approx 10^9$[k]	2.48[j]	

[a] Calculated values of K_0 are 3.5 and 0.4 M^{-1}, respectively, for the neutral and $(dmgH)_2^{2-}$ ligand complexes in 1 M ionic strength, 25 °C. [b] Based on X-ray crystal structure determination in the references cited. [c] Reference 17. [d] Co–O bond lengths in several $Co(N_4)(OH_2)_2^{3+}$ complexes have been found to be about 1.91 Å. See ref 24b. [e] Crumbliss, A. L.; Wilmarth, W. K. *J. Am. Chem. Soc.* **1970**, *92*, 2593. [f] McFadden, D. L.; McPhail, A. T. *J. Chem. Soc., Dalton Trans.* **1974**, 363. [g] Reference 30b. [h] For *trans*-$Co(N_4)(OH_2)_2^{2+}$. [i] Based on the rate of reaction with $\cdot CH_3$ radicals.[14c] [j] Reference 24a. [k] Representative values on the rates reported for the reaction with CH_3 radicals; see ref 14c, 24a, and 44.

considering aquation reactions in which the net free energy changes make differing contributions.

A point to emphasize is that the nearly dissociative substitution behavior inferred for the *meso-* and [*Pri-CH*$_3$]-racemic-Me_6-[14]dieneN_4 complexes is most likely a function only of the manner in which the equatorial ligand shelters the coordination site and not a property of the cobalt-alkyl bond. Similarly, the variations observed in substitutional reactivity among the methyl–aquo complexes are dominated by variations of the detailed mechanism (i.e., kinetic effects) rather than by variations of bond energy (i.e., thermodynamic effects). Further to this point, there is very little change in Co–OH_2 bond lengths through this series of compounds, and what change there is does not correlate with the anation rates (or k_f/K_0). Analogous effects have been found in the aquation reactions of the Co(*rac*-, and *ms*-(*N*)Me_6[14]dieneN_4)Cl_2^+ complexes.[26]

C. Electronic Effects Attributable to the Co–CH_3 Bond. That there is more electron density at the cobalt center in the methyl-aquo complexes than is common in Co(III) complexes is demonstrated by the 0.15–0.25 Å longer bond distances in the methyl–aquo than in the diaquo complexes[17,23,39–41] (see Table IV) and by the 10^5–10^7-fold greater values of k_f/K_0 in the methyl–aquo than in the chloro–aquo complexes. In fact the methyl–aquo complexes are intermediate between Co(II) and Co(III) behavior in both regards (see Table IV). This is a somewhat unique, but relatively sensitive series of compounds since the equatorial Co–N bond lengths remain the same (±0.02 Å), for a given macrocyclic ligand, through this sequence, while any added electron density is manifested by an increase of axial bond lengths.[17,24,27]

Inspection of Table IV indicates that k_f/K_0 increases as the ground-state bond lengths increase. This is expected for either a limiting D or an I_D mechanism since much of the work required to dissociate H_2O is electrostatic. Thus, eq 1 may be modified[18]

$$\Delta G^{\ddagger} = \Delta U - T\Delta S^{\ddagger} + \Delta G^{\ddagger}_{str} + \Delta G^{\ddagger}_{vdW} + \Delta(\Delta G_{solv}) \quad (2)$$

where $\Delta U = \Delta U_{LF} + \Delta U_{el}$, $\Delta U_{el} = -Ze\mu/r^2 + \Delta U'$, ΔU_{LF} and ΔU_{el} are the ligand field and electrostatic contributions to the Co–OH_2 heterolytic bond dissociation energy, respectively, Ze is the charge on the metal complex fragment ($Co(N_4)CH_3^{2+}$), μ is the effective dipole moment of H_2O, r is the center-to-center distance between Co and OH_2, $\Delta U'$ contains dipole–dipole and other higher order terms, $\Delta(\Delta G_{solv})$ is the difference in solvation free energy of the transition and ground states (including the entering and leaving groups), ΔU is the difference between the Co–OH_2 bond energies of the substitutional transition state and the ground state, and $\Delta G^{\ddagger}_{str}$ and $\Delta G^{\ddagger}_{vdW}$ are stereochemical free energy changes. If the electrostatic terms make relatively large contributions to $\Delta G^{\ddagger}$ and if the Co–OH_2 distance at which "solvent" and "bound" water are indistinguishable (r_{TS}) is comparable in all the complexes considered, then eq 2 can be put into the simpler form

$$\Delta G^{\ddagger} \cong \alpha(r_0^{-2} - r_{TS}^{-2}) + \beta + \Delta E_{str} + \Delta E_{vdW} \quad (3)$$

where α and β are approximately constant, and r_0 is the ground-state bond length.

Observations on most of the divalent ions in Table IV are roughly correlated by eq 3 with $\alpha \cong -230$ kJ mol^{-1} $Å^2$ and $\beta - \alpha/r_{TS}^2 \cong -24$ kJ mol^{-1} (substitution of atomic parameters into the expression for ΔU_{el} predicts $\alpha \cong -256$ kJ mol^{-1} $Å^2$).[41–43] The notable exceptions are [*Pri-CH*$_3$]-Co(*rac*-(*N*)-Me_6[14]dieneN_4)(OH_2)CH_3^{2+} and *trans*-Co(*ms*-(*N*)-Me_6[14]dieneN_4)-$(OH_2)_2^{2+}$, both of which have smaller than "expected" values of k_f/K_0. The available data on the Co(II) complexes span a considerable range[22,24,44] and are close to the physical limit for water exchange (ca. 10^{11} s^{-1}, based on the relaxation time of H_2O). If anation of the [*Pri-CH*$_3$]-racemic isomer does require a more nearly dissociative pathway than that found for most of the other complexes (i.e., a larger value of r_{TS}), then this correlation suggests that the retardation of substitution could be accounted for by a 0.1 Å greater than "normal" Co–OH_2 separation required in the transition state for substitution in [*Pri-CH*$_3$]Co(*rac*-(*N*)-Me_6-[14]dieneN_4)(OH_2)CH_3^{3+}.

Conclusions

The importance of access to the coordination site for substitution in coordination complexes with macrocyclic ligands has been most dramatically demonstrated in the greater than 10^3-fold variations of anation rates for the three stereochemical isomers of *trans*-Co(Me_6[14]dieneN_4)(OH_2)CH_3^{2+}. When the leaving group (H_2O) is in the stereochemically conjested coordination site, "protected" by neighboring geminal methyl groups in the [*Pri-CH*$_3$]-racemic isomer, the anation rate is slow ($k_f/K_0 = 1.3$ s^{-1}); when the leaving group is in the opposite, more accessible site, in the [*Sec-CH*$_3$]-racemic isomer, the rate is fast ($k_f/K_0 \geq 3 \times 10^3$ s^{-1}). The effects of relaxation of stereochemical strain or variations in axial ligand bond strength, as might be postulated to "stabilize" the transition state in such systems, are only manifested if the substitution sites compared have nearly identical restrictions on motion of the entering group.

On a much broader scale of comparison, the patterns of anation rates do follow the order of axial bond energies, the weakest bond being longest and most labile, as modified by inter- and intraligand

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(41) For this correlation we assumed that the Co–OH_2 bond length in the *trans*-chloro–aquo complexes is 1.91 Å as found in *trans*-diaquo complexes. Recent X-ray crystallographic studies of *trans*-Cr^{III}(MCL)XY complexes (with MCL = *meso*-(7,14)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) have demonstrated a 0.1 Å longer Cr–O bond length in the chloro–aquo[42] than in the diaquo[43] complex. Thus the 1.91-Å bond length is a lower limit, and 2.01 Å would be an upper limit for the Co–OH_2 bond length in the Co(III)–chloro–aquo complexes. Related correlations, very similar to the one we have used, have been proposed previously: (a) ref 18; (b) ref 36, pp 20–24; (c) Neely, J. W. Ph.D. Thesis, University of California, Berkeley, 1971 (quoted in ref 36). For an alternative approach to eq 1–3 for parameterizing the bond-length dependence of the potential energy function see: Burgi, N.-B.; Dunitz, J. D. *J. Am. Chem. Soc.* **1987**, *109*, 2924.

(42) Temple, R.; House, D. A.; Robinson, W. T. *Acta Crystallogr.* **1984**, *40*, 1789.

(43) Heeg, M. J.; Schwarz, C. L; Endicott, J. F., work in progress.

(44) Bakac, A.; Espenson, J. H., submitted for publication.

repulsions and provided the substitution site is not obstructed by the macrocyclic ligand. An interchange mechanism, with appreciable but not dominant bond making to the entering group is inferred for the transition state for substitution at stereochemically unconjested sites in closely related Co(II) and Co(III) complexes with macrocyclic ligands. The aquo–methyl complexes are intermediate in this series, consistent with relatively incomplete transfer of electron density from Co(II) to the alkyl ligand.

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Registry No. [*trans*-Co([14]aneN_4)(OH_2)CH_3](ClO_4)$_2$, 51240-13-2; [*trans*-Co(Me_4[14]tetraeneN_4)(OH_2)CH_3](ClO_4)$_2$, 64942-11-6; [*trans*-Co(Me_4[14]tetraeneN_4)(OH_2)Cl](ClO_4)$_2$, 121675-81-8; [*trans*-Co(*ms*-(*H*)-Me_6[14]dieneN_4)(OH_2)CH_3](ClO_4)$_2$, 39611-20-6; [[*Pri*-CH_3]-*trans*-Co(*rac*-(*N*)-Me_6[14]dieneN_4)(OH_2)CH_3](ClO_4)$_2$, 39756-78-0; [[*Pri*-Cl]-*trans*-Co(*rac*-(*N*)-Me_6[14]dieneN_4)(OH_2)Cl](ClO_4)$_2$, 121701-58-4; [[*Sec*-CH_3]-*trans*-Co(*rac*-(*N*)-Me_6[14]-dieneN_4)(OH_2)-CH_3](ClO_4)$_2$, 121784-60-9; *trans*-Co(dimethylglyoximate)$_2$(OH_2)CH_3), 25360-55-8; [Co(*ms*-(*N*)-Me_6[14]dieneN_4)(OH_2)$_2$](ClO_4)$_2$, 121675-82-9; [Co(*rac*-(*N*)-Me_6[14]dieneN_4)(OH_2)$_2$](ClO_4)$_2$, 121784-62-1.

Supplementary Material Available: Summaries of MM2 input parameters and minimized energies (2 pages). Ordering information is given on any current masthead page.

Magnesium Dihalide Promoted Addition of Grignard Reagents to the Cyclopentadienyl Rings of Tungstenocene Dichloride

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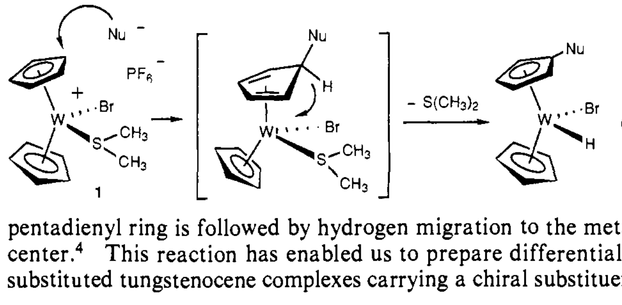
Abstract: Some Grignard reagents, including $CH_2{=}CHCH_2MgCl$, $CH_2{=}C(CH_3)CH_2MgCl$, and $PhCH_2MgCl$, add to a cyclopentadienyl ring of $[W(\eta\text{-}C_5H_5)_2Cl_2]$ (**2**) to give the ring-substituted hydrochlorides $[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)HCl]$ (**3**), $[W\{\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}(\eta\text{-}C_5H_5)HCl]$ (**4**), and $[W(\eta\text{-}C_5H_4CH_2Ph)(\eta\text{-}C_5H_5)HCl]$ (**5**). These reactions are promoted by the addition of $MgCl_2$, which is essential for the reproducible synthesis of **3**, **4**, or **5** in good yield. Grignards which react at the metal to give bis-alkyls $[W(\eta\text{-}C_5H_5)_2R_2]$, including CH_3MgCl and $(CH_3)_3SiCH_2MgCl$, were unaffected by added $MgCl_2$. The hydrochlorides **3**, **4**, and **5** can be converted to the corresponding dichlorides $[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)Cl_2]$ (**6**), $[W\{\eta\text{-}C_5H_4CH_2C(CH_3){=}CH_2\}(\eta\text{-}C_5H_5)Cl_2]$ (**7**), and $[W(\eta\text{-}C_5H_4CH_2Ph)(\eta\text{-}C_5H_5)Cl_2]$ (**8**) by reaction with CCl_4. Further reaction of **6** with $CH_2{=}CHCH_2MgCl$ in the presence of added $MgCl_2$ leads to substitution of the second cyclopentadienyl ligand and formation of $[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)_2HCl]$ (**10**). It is proposed that added magnesium dihalides promote Grignard addition to cyclopentadienyl rings of **2** by complexation of an intermediate cyclopentadiene complex. The presence of a double halide bridge in an adduct such as "$[W(\eta^4\text{-}C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)Cl(\mu\text{-}Cl)(\mu\text{-}Br)MgBr]$" would account for the otherwise surprising observation that reaction of **2** with $CH_2{=}CHCH_2MgBr$ leads to predominant (64%) formation of the hydrobromide $[W(\eta\text{-}C_5H_4CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)HBr]$ (**11**), with the hydrochloride **3** as a minor (7%) product.

Since the first report of electrophilic substitution of a cyclopentadienyl ligand of ferrocene under Friedel–Crafts conditions,[1] there has been continuing interest in the preparation of systems in which the cyclopentadienyl ligand carries additional functional groups, and this area is of particular current interest because additional functional groups can be used to incorporate cyclopentadienyl complexes into organometallic materials.[2] As pointed out in a recent review,[3] however, the extension of electrophilic substitution to the preparation of functionalized cyclopentadienyl complexes of other transition metals has been "severely limited in scope" by the relatively narrow range of complexes which are reactive under Freidel-Crafts conditions. Alternative approaches most typically involve functionalization of the cyclopentadienyl ligand prior to its introduction to the metal center,[3] but this has a number of intrinsic limitations, including the inevitable modification of the reactivity of the intermediate cyclopentadienides and the requirement that the new functional group be inert under the conditions required to produce these cyclopentadienides.

We have recently observed that the cyclopentadienyl ring in the tungstenocene complex $[W(\eta\text{-}C_5H_5)_2(SEt_2)Br]^+$ ($\mathbf{1}^+$) is sufficiently electrophilic to undergo substitution reactions of the type shown in eq 1, in which addition of a heteroanion to the cyclopentadienyl ring is followed by hydrogen migration to the metal center.[4] This reaction has enabled us to prepare differentially substituted tungstenocene complexes carrying a chiral substituent



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