

Mechanistic Elucidation of the Substitution Behavior of Alkyl Cobaloximes in Water and Methanol as Solvents

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The ligand substitution behavior of *trans*-[Co(Hdmg)₂(R)S] (R = CH₃, PhCH₂; Hdmg = dimethylglyoximate; S = H₂O and/or MeOH) was studied for imidazole, pyrazole, 1,2,4-triazole, *N*-acetylimidazole, 5-chloro-1-methylimidazole, NO₂⁻, Ph₃P, Ph₃As, and Ph₃Sb as entering ligands. In all cases, except for Ph₃As and Ph₃Sb, the observed kinetics shows a linear dependence on the entering nucleophile concentration with no evidence for a back reaction. In the case of Ph₃As and Ph₃Sb as entering nucleophiles, kinetic evidence for a reverse solvolysis reaction is at hand. Activation parameters (ΔH^{\ddagger} , ΔS^{\ddagger} , and ΔV^{\ddagger}) were determined from the temperature and pressure dependence of all studied reactions and support the operation of a dissociatively activated substitution mechanism. The rate and activation parameters show that there is an increase in the dissociative character from a dissociative interchange to a limiting dissociative mechanism that depends on the nature of R and the entering nucleophile. The crystal structure of *trans*-[Co(en)₂(Me)H₂O]²⁺ was determined by X-ray analysis. The Co–O and Co–C bond lengths were found to be 2.153(6) and 1.995(10) Å, respectively. The kinetic and structural data are discussed in reference to a series of earlier studied systems for which data are reported in the literature.

Introduction

Over the past few years, we have developed an active interest in the systematic tuning of the substitution behavior of alkylcobalt(III) complexes for various reasons. First of all, such reactions are relevant to the mechanistic behavior of coenzyme B_{12} , a bio-organometallic cofactor with a cobalt–carbon bond. Second, the introduction of a single cobalt–carbon bond in Co(III) complexes has a profound influence on their substitution lability. Third, such complexes allow a systematic adjustment of their reactivity via steric hindrance and electron donor/acceptor effects of spectator ligands and the coordinated alkyl or aryl group. Such studies are of fundamental interest in the elucidation of inorganic/bioinorganic reaction mechanisms and serve as model systems for tuning the lability of inert metal complexes.

In this respect, it is interesting to note that many investigations in the past have focused on the mechanistic behavior of coenzyme B_{12} itself, or on modified forms of the coenzyme, or on closely related model systems with a quite different chelate arrangement around the Co(III) center. By way of comparison, the substitution behavior of vitamin B_{12}

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derivatives, especially aquacobalamin, was investigated as a reference system in which the cobalt-carbon bond is substituted by a cobalt-water bond that has no labilization effect on the Co(III) center. Work in our laboratories has focused on the substitution behavior of coenzyme B₁₂ and modified alkylcobalamins with R = Et, Pr, Me, CF₃CH₂, NCCH₂, CF₃, and CN,¹ *trans*-[Co(en)₂(Me)H₂O]^{2+,2} *trans*-[Co(en)₂(Me)NH₃]^{2+,2b} *trans*-[Co(BQDI)₂(PPh₃)S]⁺ (BQDI = *o*-benzosemiquinonediimine; S = MeOH, MeCN),³ [Co-(LNHPy)(HLNHPy)(R)]⁺ (HLNHPy = 2-(2-pyridylethyl)amino-3-butanone oxime; R = Et, Me, CF₃CH₂, bridging-CH₂),⁴ and *trans*-[Co(Hdmg)₂(R)S] (Hdmg = dimethylglyoximate; R = *cyclo*-C₅H₉, Et, Me, Ph, PhCH₂, CF₃CH₂; S = H₂O, MeOH).^{5,6} In these studies, detailed kinetic inves-

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tigations enabled the determination of rate and activation parameters, on which basis detailed mechanistic assignments could be made. For instance, for the reaction of cyanide with different alkylcobalamins it was found that the nature of the alkyl group has a marked influence on the thermodynamic stability constants and the kinetics and mechanism of the substitution reactions of the axial ligand *trans* to the alkyl group.^{1,7,8}

The Co–C bond length depends on three contributing factors. First, there are *cis* steric interactions, distortions in the corrin macrocycle or equatorial ligand toward the axial *trans* alkyl ligand resulting in Co–alkyl bond lengthening. Second, a *trans* steric influence occurs when the bulkiness of an axial ligand induces an elongation or weakening of the *trans* metal–ligand bond. Third, the *trans* electronic influence is associated with how the change in basicity of the axial ligand affects the Co–alkyl bond length and/or bond dissociation energy (*trans* effect) and how changes in the σ -donor character of the alkyl group affect the Co–N(ax) bond distance.⁹

It is well-known that high-pressure techniques can assist the elucidation of inorganic and bioinorganic reaction mechanisms through the determination of activation volumes obtained from the pressure dependence of the rate constant and the construction of reaction volume profiles.^{10,11} In the case of Co(III) complexes, activation volume data for complex-formation reactions of trans-[Co(en)₂(Me)H₂O]²⁺ with CN⁻, imidazole,^{2a} and NH₃^{2b} are similar to data for the reactions of aquacobalamin with different ligands such as *N*-acetylimidazole,¹² HN₃, N₃⁻, pyridine and its derivatives, and thiourea and its derivatives.^{13–15} In all these cases, ΔV^{\ddagger} was found to be in the range between +4 and +10 cm³ mol⁻¹, an indication that the reactions follow an I_d mechanism. These values are significantly smaller than those reported for substitution reactions of cobalt(III) porphyrin systems, where it was found that ΔV^{\ddagger} values for ligand substitution on $[Co(TMPP)(H_2O)_2]^{5+}$ and $[Co(TPPS)(H_2O)_2]^{3-}$, TMPP = meso-tetrakis(4-N-methylpyridyl)porphine andTPPS = meso-tetrakis(p-sulfonatophenyl)porphine, are +14.4 and $+15.4 \text{ cm}^3 \text{ mol}^{-1}$, respectively, and these were accordingly assigned to a limiting D mechanism.^{16,17}

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In the present study, we have extended the work on *trans*-[Co(Hdmg)₂(R)S] to R = Me and PhCH₂ (S = H₂O and/or MeOH) and to a wide range of different entering nucleophiles (viz. imidazole, pyrazole, 1,2,4-triazole, *N*-acetylimidazole, 5-chloro-1-methylimidazole, NO₂⁻, Ph₃P, Ph₃As, and Ph₃-Sb) in order to determine the role of the nucleophilicity of the entering ligand and the nature of R on the reactivity of the Co(III) center. These data allow us to present an overall comparison of steric and electronic effects that control the reactivity of alkyl and aryl Co(III) complexes, in reference to a series of earlier studied systems for which data are reported in the literature.

Experimental Section

Materials. All chemicals were of p.a. grade and used as received. Imidazole, pyrazole, 1,2,4-triazole, *N*-acetylimidazole, and methylhydrazine were purchased from Fluka, 5-chloro-1-methylimidazole from Acros, TAPS buffer from Sigma, and Ph₃Sb from Strem. Triphenylphosphine, cobalt(II) nitrate hexahydrate, and sodium nitrite were purchased from Merck, and Ph₃As from Aldrich. Ultrapure water was used in the kinetic measurements. *trans*-[Co-(Hdmg)₂(R)H₂O] (R = CH₃, PhCH₂) and *trans*-[Co(en)₂(Me)H₂O]-S₂O₆ were prepared as previously reported and were characterized by elemental analysis and UV-vis and NMR spectroscopy; the results were in agreement with literature data.^{18,19} Preparation of solutions and all measurements were carried out in the dark because the investigated complexes are light sensitive.

All the reactions in aqueous solution were studied at pH 9.0 by using TAPS buffer. The pH of 9.0 was selected to prevent protonation of the nitrogen donor nucleophiles and formation of the corresponding hydroxo complexes.

X-ray Structure Determination. Intensity data were collected on a Nonius CAD4 Mach3 diffractometer with graphite monochromated Mo K α radiation in the $\omega/2\theta$ scan mode at room temperature. The structure of *trans*-[Co(en)₂(Me)H₂O]S₂O₆ was solved by direct methods using SIR-97²⁰ and refined by full-matrix least-squares on F^2 using SHELXL-97.²¹ Complete crystallographic details, bond lengths, bond angles anisotropic temperature factors, and hydrogen atom coordinates are available as a CIF file as Supporting Information. Some crucial bond lengths and bond angles are summarized in Table 1.

Crystal data: CoC₅H₂₁N₄S₂O₇, fw = 372.3 g mol⁻¹, *a* = 19.913-(10) Å, *b* = 12.094(10) Å, *c* = 11.754(10) Å, $\alpha = \beta = \gamma = 90^{\circ}$, V = 2831(4) Å³, orthorhombic, space group = *Iba*2 (No. 45), Z = 8, $D_c = 1.738$ g cm⁻³, μ (Mo K α) = 1.5 mm⁻¹, T = 298 K, R1 = 0.066 for the data $F_o > 2\sigma(F_o)$, ²² ($R_{int} = 0.050$ for 2335 unique reflections). The minimum and maximum electron densities on the final difference Fourier map were -0.51 and 0.89 e Å⁻³, respectively.

Instrumentation. The pH of the solution was measured using a Mettler Delta 350 pH meter. The pH meter was calibrated with

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Table 1. Bond Lengths (Å) and Bond Angles (deg) with Standard Deviations for the Complex *trans*-[Co(en)₂(Me)H₂O]S₂O₆

bond distance (Å)		bond angle (deg)	
bond di Co-O1 Co-N1 Co-N2 Co-N3 Co-N4 Co-C5 N1-C1	2.153(6) 1.999(7) 1.995(8) 1.931(7) 1.927(7) 1.995(10) 1.453(12)	01-Co-N1 01-Co-N2 01-Co-N3 01-Co-N4 01-Co-C5 N1-Co-N2 N1-Co-N3 N1-Co-N3	8 (deg) 88.2(3) 89.5(3) 90.2(3) 87.8(3) 177.6(3) 84.2(3) 176.3(3)
N2-C2 N3-C3 N4-C4 C1-C2	1.437(12) 1.553(11) 1.480(12) 1.512(14)	N1-Co-N4 N1-Co-C5 N2-Co-N3 N2-Co-N4 N2-Co-C5 N3-Co-N4 N3-Co-C5 N4-Co-C5 Co-N1-C1 Co-N2-C2	$\begin{array}{c} 96.0(3)\\ 89.4(3)\\ 92.5(3)\\ 177.2(3)\\ 90.6(4)\\ 87.3(3)\\ 92.2(3)\\ 92.1(3)\\ 108.4(5)\\ 109.1(6) \end{array}$

standard buffer solutions at pH 4.0, 7.0 and 10.0. UV-vis spectra were recorded on Shimadzu UV-2101 and Hewlett-Packard 8452A spectrophotometers.

Kinetic measurements were carried out on an Applied Photophysics SX 18MV stopped-flow instrument coupled to an online data acquisition system. At least eight kinetic runs were recorded under all conditions, and the reported rate constants represent the mean values. All kinetic measurements were carried out under pseudo-first-order conditions; i.e., the ligand concentration was in at least a 10-fold excess. Measurements at high pressure were carried out using a homemade high-pressure stopped-flow unit.²³ Kinetic data were analyzed with the OLIS KINFIT program. All instruments used were thermostated to the desired temperature (± 0.1 °C).

Results and Discussion

The kinetics of the ligand substitution reactions (eq 1) of *trans*-[Co(Hdmg)₂(R)S] (R = CH₃, CH₂Ph; S = H₂O, MeOH) were studied for different nucleophiles L to form *trans*-[Co(Hdmg)₂(R)L]. The UV-vis absorption spectra of *trans*-[Co(Hdmg)₂(R)S] and *trans*-[Co(Hdmg)₂(R)L] complexes, where L = imidazole, pyrazole, 1,2,4-triazole, *N*-acetylimidazole, 5-chloro-1-methylimidazole, NO₂⁻, Ph₃P, Ph₃As, and Ph₃Sb, are summarized in Table 2.

trans-[Co(Hdmg)₂(R)S] + L
$$\frac{k_a}{k_b}$$

trans-[Co(Hdmg)₂(R)L]^{0/-} + S (1)

Figures 1–3 and S1 (Supporting Information) report plots of the pseudo-first-order rate constant k_{obs} versus [L] for the reactions with imidazole, pyrazole, 1,2,4-triazole, *N*-acetylimidazole, 5-chloro-1-methylimidazole, NO₂⁻, and Ph₃P at 25 °C. The linear plots have negligible intercepts, indicating that a reverse or parallel reaction does not contribute significantly under the selected experimental conditions. This behavior can be expressed by the rate law given in (eq 2) with a negligible contribution from k_b . The second-order rate constants for substitution of the solvent (k_a) were found to be 70.3, 90.7, 70.6, 48.2, 105.1, and 113.9 M⁻¹ s⁻¹ for L =

Table 2. UV–Vis Spectral Data for trans-[Co(Hdmg)₂(R)(L)] in H₂O and MeOH at Room Temperature

L	λ , nm (10 ⁻³ ϵ , M ⁻¹ cm ⁻¹)	$\lambda^f(\mathrm{nm})$
H_2O^b	278 ^{sh a} (4.94), 384 (1.43),	
	and 440 (1.22)	
imidazole ^b	282 (5.48), 372 (2.14),	450
	and $416^{\text{sh}}(0.85)$	
pyrazole ^b	280 (5.84), 374 (1.91),	450
	and 420 ^{sh} (0.87)	
1,2,4-triazole ^b	282 (5.74), 372 (2.11),	450
	and 416 ^{sh} (0.78)	
N-acetylimidazole ^b	372 (2.19) and 420 ^{sh} (0.82)	450
5-chloro-1-methylimidazole ^b	358 (3.37) and 414 ^{sh} (1.06)	450
NO ₂ ^{-b}	$422^{\text{sh}}(1.04)$ and $464^{\text{sh}}(0.25)$	445
MeOH ^c	284 ^{sh} (6.45), 384 (1.70),	
	and 444 (1.64)	
Ph ₃ P ^c	370 ^{sh} (4.15) and 420 ^{sh} (1.23)	445
imidazole ^c	288 (7.08), 372 (2.68),	445
	and 420 ^{sh} (0.93)	
Ph ₃ As ^{c,d}	308 ^{sh} , 378 ^{sh} , and 444	332
Ph ₃ Sb ^{c,d}	316 ^{sh} , 372 ^{sh} , and 448	335
MeOH ^e	274 ^{sh} (12.95), 358 (6.64),	
	and 470 (1.06)	
Ph ₃ P ^e	360 ^{sh} (14.43)	410

^{*a*} sh = shoulder. ^{*b*} trans-[Co(Hdmg)₂(Me)(L)] in H₂O (pH 9.0, I = 0.1 M NaClO₄ and 0.5 M for NO₂⁻ as nucleophile). ^{*c*} trans-[Co(Hdmg)₂(Me)(L)] in MeOH. ^{*d*} No extinction coefficients are specified since only partial formation of the corresponding complex could be reached due to the unfavorable equilibrium position (see ratio of rate constants for the forward and reverse reactions given in Table 3). ^{*e*} trans-[Co(Hdmg)₂(PhCH₂)(L)] in MeOH. ^{*f*} Wavelength at which kinetic data were recorded.



Figure 1. Plots of k_{obs} versus [5-chloro-methylimidazole] (A), [pyrazole] (B), and [*N*-acetylimidazole] (C) for the reaction with 1×10^{-4} M *trans*-[Co(Hdmg)₂(Me)H₂O] at 25.0 °C, pH 9.0, and I = 0.1 M NaClO₄.

imidazole, pyrazole, 1,2,4-triazole, *N*-acetylimidazole, 5-chloro-1-methylimidazole, and NO₂⁻, respectively ($R = CH_3$, $S = H_2O$); 23.6 and 19.6 M⁻¹ s⁻¹ for L = imidazole and Ph₃P, respectively ($R = CH_3$, S = MeOH); and 252 M⁻¹ s⁻¹ for L = Ph₃P ($R = PhCH_2$ and S = MeOH) at 25 °C.

$$k_{\rm obs} = k_{\rm a}[\rm L] + k_{\rm b} \tag{2}$$

Kinetic data for the reaction of *trans*-[Co(Hdmg)₂(R)-MeOH] with Ph₃As and Ph₃Sb are reported in Figures 4 and 5, from which it follows that good linear plots with significant intercepts are obtained within the experimental error limits. This behavior can also be expressed by the rate law given in eq 2, where k_a and k_b represent the rate constants

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Figure 2. Plots of k_{obs} versus [imidazole] for the reaction with 1×10^{-4} M *trans*-[Co(Hdmg)₂(Me)S] where S = H₂O (A) and MeOH (B) at 25.0 °C, pH 9.0, and I = 0.1 M NaClO₄ for aqueous solution.



Figure 3. Plots of k_{obs} versus [Ph₃P] for the reaction with $(0.5-1) \times 10^{-4}$ M *trans*-[Co(Hdmg)₂(R)MeOH] where R = PhCH₂ (A) and CH₃ (B) at 25.0 °C.

for the forward and reverse reactions in eq 1, respectively. Direct evidence for a reversible complex-formation reaction was obtained from the overall spectral changes observed during the reaction, which increased significantly with increasing entering nucleophile concentration. Unfortunately, the solubility of both Ph₃As and Ph₃Sb in methanol is too low to enable a direct spectrophotometric determination of the overall equilibrium constant. In the most favorable case, the ratio of k_a/k_b (=12 M⁻¹ at 25 °C, see Table 3) in the case of Ph₃As as entering ligand is such that a 1 M solution of the ligand will be required to shift the equilibrium over to the product side, whereas the solubility is limited to only 0.08 M at 25 °C.

Tables 3 and S1–S3 (Supporting Information) summarize the kinetic data obtained as a function of temperature and pressure for the series of reactions investigated. In the case of Ph₃As and Ph₃Sb as entering nucleophiles, the temperature and pressure dependence was studied at low and high nucleophile concentrations in order to determine the effect on k_a and k_b , respectively. The values of k_a and k_b as a



Figure 4. Plots of k_{obs} versus [Ph₃As] for the reaction with *trans*-[Co-(Hdmg)₂(Me)MeOH] as function of temperature. Experimental conditions: $[Co^{III}] = 1 \times 10^{-4}$ M and T = 5.0 (A), 10.0 (B), 15.0 (C), 20.0 (D), and 25.0 (E) °C.



Figure 5. Plots of k_{obs} versus [Ph₃Sb] for the reaction with *trans*-[Co-(Hdmg)₂(Me)MeOH] as function of temperature. Experimental conditions: [Co^{III}] = 1 × 10⁻⁴ M and *T* = 5.0 (A), 10.0 (B), 15.0 (C), 20.0 (D), and 25.0 (E) °C.

function of temperature and pressure, along with the corresponding activation parameters, are summarized in Table S3 (Supporting Information). Plots of ln k_a and ln k_b versus pressure gave good linear relationships as shown in Figure S2 (Supporting Information) for the reaction of *trans*-[Co-(Hdmg)₂(R)MeOH] with Ph₃As, and the constructed volume profile is shown in Figure 6. Plots of ln k_a versus pressure gave good linear relationships as shown in Figure S3 for the reaction of *trans*-[Co(Hdmg)₂(R)H₂O] with imidazole, pyrazole, 1,2,4-triazole, *N*-acetylimidazole, 5-chloro-1-methylimidazole, and NO₂⁻. Similar plots are presented in Figure S4 (Supporting Information) for the reactions between *trans*-[Co(Hdmg)₂(R)MeOH] and Ph₃P where (R = CH₃ and PhCH₂).

Second-order rate constants (k_a) for substitution of *trans*-[Co(Hdmg)₂(R)S] by the series of entering ligands in Table 3 at 25 °C do not depend strongly on the nature of the entering ligand either in aqueous or in methanol solution. The data in Table 4 show a similar trend except for

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Table 3. Kinetic Data for the Reaction of *trans*-[Co(Hdmg)₂(R)S], for $R = CH_3$ and PhCH₂, and $S = H_2O$ and MeOH, with Different Nucleophiles (L)

L^a	$k_{\rm a}$ at 25 °C, M ⁻¹ s ⁻¹	$\Delta H^{\ddagger},$ kJ mol ⁻¹	ΔS^{\ddagger} , J mol ⁻¹ K ⁻¹	$\Delta V^{\ddagger},$ cm ³ mol ⁻¹
imidazole ^{b,c}	70.3 ± 0.5	74 ± 2	$+40 \pm 8$	$+3.7 \pm 0.2$
pyrazole ^{b,c}	91 ± 2	79 ± 2	$+56 \pm 7$	$+4.5 \pm 0.4$
1,2,4-triazole ^{b,c}	70.6 ± 0.7	72 ± 3	$+31 \pm 9$	$+4.0 \pm 0.1$
N-acetylimidazole ^{b,c}	48 ± 1	70 ± 1	$+22 \pm 3$	$+3.1 \pm 0.2$
5-chloro-1-methylimidazole ^{b,c}	105.1 ± 0.5	89 ± 2	$+92 \pm 6$	$+2.5 \pm 0.1$
$NO_2^{-b,c}$	113.9 ± 0.8	84 ± 3	$+78 \pm 10$	$+2.3 \pm 0.1$
$Ph_3P^{d,e}$	19.6 ± 0.1	94 ± 2	$+97 \pm 8$	$+12.3 \pm 0.4$
imidazole ^{d,e}	23.6 ± 0.2	74 ± 2	$+29 \pm 5$	$+7.3 \pm 0.1$
$Ph_3As_{(forward reaction)}^{d,e}$	20.1 ± 1.1	103 ± 4	$+126 \pm 14$	$+10.6 \pm 0.5$
$Ph_3As_{(reverse reaction)}^{d,e}$	$1.66 \pm 0.03 \ \mathrm{s^{-1}}$	114 ± 5	$+143 \pm 18$	$+15.9 \pm 0.2$
Ph ₃ Sb _(forward reaction) ^{d,e}	20.3 ± 1.7	89 ± 3	$+77 \pm 10$	
$Ph_3Sb_{(reverse reaction)}^{d,e}$	$10.24 \pm 0.04 \ \mathrm{s^{-1}}$	95 ± 3	$+95 \pm 9$	$+11.3 \pm 0.4$
$Ph_3P^{f,g}$	252.0 ± 0.8	92 ± 1	$+109 \pm 3$	$+15.2 \pm 0.3$

^a The two superscripts (b-e) given in the first column of the table refer to the experimental conditions selected for the temperature and pressure dependence studies, respectively (see Supporting Information). ^b trans-[Co(Hdmg)₂(Me)H₂O] = 1×10^{-4} M, imidazole, pyrazole, 1,2,4-triazole, and N-acetylimidazole = 0.01-0.5 M, 5-chloro-1-methylimidazole = 1.88×10^{-2} to 0.3 M, and NO₂⁻ = 6.25×10^{-2} to 0.5 M, pH 9.0, and I = 0.1 M NaClO₄ and 0.5 M for NO_2^- as ligand. ^c trans-[Co(Hdmg)₂(Me)H₂O] = 2 × 10⁻⁴ M, imidazole, pyrazole, 1,2,4-triazole, and N-acetylimidazole = 0.01 M, 5-chloro-1-methylimidazole $= 3.75 \times 10^{-2}$ M, and NO₂⁻ = 6.25 $\times 10^{-2}$ M, T = 25.0 °C, pH 9.0, and I = 0.1 M NaClO₄ and 0.5 M for NO₂⁻ as ligand. ^d trans-[Co(Hdmg)₂(Me)MeOH] = 1 × 10⁻⁴ M, [imidazole] = 0.05-0.5 M, [Ph₃P] = (0.5-2.5) × 10⁻² M, [Ph₃As] and [Ph₃Sb] = (0.5-4.0) × 10⁻² M. ^e trans-[Co(Hdmg)₂(Me)MeOH] $= 2 \times 10^{-4}$ M, [imidazole] = 0.05 M, [Ph₃P] = 0.01 M, [Ph₃As] $= (0.5-4.0) \times 10^{-2}$ M, T = 25.0 °C, and [Ph₃Sb] = 0.02 M at 15.0 °C. ^f trans- $[Co(Hdmg)_2(PhCH_2)MeOH] = 5 \times 10^{-5} \text{ M} \text{ and } [Ph_3P] = (0.5-2.5) \times 10^{-2} \text{ M}.$ *g trans*- $[Co(Hdmg)_2(PhCH_2)MeOH] = 5 \times 10^{-5} \text{ M} \text{ and } [Ph_3P] = 0.01 \text{ M}.$ at 25.0 °C.



N-acetylimidazole as entering ligand (see further in Discussion). This is typical for a process that is dissociatively activated, either via a dissociative interchange (Id) or limiting dissociative (D) mechanism, in which bond breakage with the leaving group largely controls the rate and nature of the substitution mechanism. Similarly, the rate constants for the backward reaction were found to be 1.7 and 10.2 s^{-1} at 25 °C for the displacement of Ph₃As and Ph₃Sb, respectively, indicating that the release of the nucleophile does depend on its nucleophilicity, again in line with a dissociatively activated mechanism controlled by bond cleavage with the leaving group. The most important factors that account for the increase in k_b from Ph₃P to Ph₃As and Ph₃Sb are the basicity and π -acceptor ability of these nucleophiles that decrease in this order. A more detailed discussion of the activation parameters given below reveals that a dissociative interchange mechanism (I_d) is favored, in terms of which the overall second-order rate constant k_a is a composite of a

precursor formation constant (K) and an interchange rate constant (k). This will further account for some of the differences in the values of k_a especially in cases where precursor formation is favored by the nature of the entering nucleophile and so affects the value of k_a .

Substitution reactions of trans-[Co(Hdmg)₂(R)S] show a strong dependence on the nature of the alkyl group. The second-order rate constant for substitution of S = methanol by Ph₃P was found to be 19.6 and 252 M⁻¹ s⁻¹ at 25 °C for $R = CH_3$ and PhCH₂, respectively, and that for substitution of water by imidazole was found to be 70.3 and 20.9 M^{-1} s^{-1} at 25 °C for R = CH₃ and CH₂Cl,²⁴ respectively. The lability of these complexes is affected by the size and electronic structure of the alkyl group. The second-order rate constant for substitution of trans-[Co(Hdmg)₂(R)H₂O] by pyrazole, 1,2,4-triazole, and N-acetylimidazole was found to be 1309, 1200, and 135 $M^{-1} s^{-1}$ for R = Et, 755, 691, and 119 M^{-1} s⁻¹ for R = PhCH₂, and 0.36, 0.35, and 0.07 M^{-1} s⁻¹ for R = CF₃CH₂ at 25 °C, respectively, as summarized in Table 4.25 The second-order rate constants show that the kinetic trans effect decreases in the order Et > PhCH₂ > CH₃ > CH₂Cl > CF₃CH₂ according to the donor properties of the alkyl group.

The solvent has a significant effect on the rate constant of the ligand substitution reaction. The second-order rate constant for substitution of the solvent in trans-[Co(Hdmg)₂(R)S] by imidazole was found be 70.3 and 23.6 M^{-1} s⁻¹ at 25 °C for S = H₂O and MeOH, respectively. The slower reaction in methanol is ascribed to solvent effects and the fact that we are dealing with a totally different leaving group. The values of the second rate constant k_a in MeOH are again independent of the nature of the entering nucleophile.

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Table 4. Comparison of Rate and Activation Parameters for the Reaction of trans-[Co(chel)₂(R)H₂O] and Aquacobalamin with Imidazole, Pyrazole,1,2,4-Triazole, and N-Acetylimidazole as Entering Nucleophiles

ligand	ΔH^{\ddagger} , kJ mol ⁻¹	ΔS^{\ddagger} , J K ⁻¹ mol ⁻¹	$\Delta V^{\ddagger}, \mathrm{cm}^3 \mathrm{mol}^{-1}$	$k_{\rm a},{ m M}^{-1}{ m s}^{-1}$	
		trans-[Co(Hdmg) ₂ (Me)H ₂ O] ^a			
imidazole	74 ± 2	$+40 \pm 8$	$+3.7 \pm 0.2$	70.3 ± 0.5	
pyrazole	79 ± 2	$+56 \pm 7$	$+4.5 \pm 0.4$	90.7 ± 2.0	
1,2,4-triazole	72 ± 3	$+31 \pm 9$	$+4.0 \pm 0.1$	70.6 ± 0.7	
N-acetylimidazole	70 ± 1	$+22 \pm 3$	$+3.1 \pm 0.2$	48.2 ± 1.0	
	tran	s-[Co(Hdmg) ₂ (CH ₃ CH ₂)H ₂ O] ^{25,}	1		
pyrazole	69 ± 0.6	$+46 \pm 2$	$+4.6 \pm 0.3$	1309 ± 14	
1,2,4-triazole	65 ± 1	$+31 \pm 3$	$+4.9 \pm 0.3$	1200 ± 7	
N-acetylimidazole	72 ± 0.6	$+36 \pm 2$	$+4.1 \pm 0.3$	135 ± 2	
	tra	$ns-[Co(Hdmg)_2(PhCH_2)H_2O]^{25,a}$			
pyrazole	70 ± 2	$+46 \pm 8$	$+6.2 \pm 0.5$	755 ± 16	
1,2,4-triazole	66 ± 1	$+31 \pm 3$	$+7.5 \pm 0.4$	691 ± 13	
N-acetylimidazole	72 ± 1	$+38 \pm 5$	$+4.3 \pm 0.3$	119 ± 4	
	trar	as-[Co(Hdmg) ₂ (CF ₃ CH ₂)H ₂ O] ^{25,c}	ı		
pyrazole	83 ± 1	$+23 \pm 3$	$+4.4 \pm 0.3$	0.358 ± 0.006	
1,2,4-triazole	86 ± 2	$+37 \pm 6$	$+2.3 \pm 0.3$	0.348 ± 0.002	
N-acetylimidazole	87 ± 2	$+26\pm5$	$+3.4 \pm 0.3$	0.069 ± 0.001	
<i>trans</i> -[Co(en) ₂ (Me)H ₂ O] ^{2+1,29}					
imidazole ^a	53 ± 2	-22 ± 7	$+4.7 \pm 0.1$	198 ± 13	
$pyrazole^b$	67 ± 6	$+27 \pm 19$		284 ± 10	
1,2,4-triazole ^b	59 ± 2	$+1 \pm 6$		318 ± 5	
N-acetylimidazole ^b	72 ± 4	$+23 \pm 14$		24 ± 3	
		aquacobalamin ^{12,30a}			
imidazole		1		21.2 ± 0.7	
pyrazole	85 ± 4	$+69 \pm 13$		35.0 ± 0.8	
1,2,4-triazole	90 ± 2	$+83 \pm 6$		24.0 ± 0.4	
N-acetylimidazole	108 ± 12	$+135 \pm 40$	$+7.2 \pm 0.3$	6.6 ± 1.6	

^a The second rate constants were determined at 25.0 °C. ^b The second-order rate constants were calculated from the activation parameters for 25.0 °C.

The lability of organo cobaloximes is much higher than that of inorganic cobaloximes due to the alkyl group in the axial position that significantly increases the length of the Co-OH₂ bond in the ground state and increases its pK_a value. pK_a values were found to be 10.96²⁶ and 12.68²⁷ for trans-[Co(Hdmg)₂(CF₃CH₂)H₂O] and trans-[Co(Hdmg)₂(Me)H₂O], respectively. The activation enthalpy values for substitution of trans-[Co(Hdmg)₂(R)H₂O] by pyrazole, 1,2,4-triazole, and *N*-acetylimidazole for $R = PhCH_2$, CH_3 , and CF_3CH_2 were found to be in the ranges 66-72,²⁵ 72-79, and 83-86 kJ mol⁻¹,²⁵ respectively, as summarized in Table 4. The activation entropies in Table 3 are in general significantly positive and in line with a dissociatively activated reaction mechanism. A plot of ΔH^{\ddagger} versus ΔS^{\ddagger} gives a good linear relationship for the reaction of *trans*-[Co(Hdmg)₂(Me)S] with imidazole, pyrazole, 1,2,4-triazole, N-acetylimidazole, 5-chloro-1-methylimidazole, and NO₂⁻ in water as shown in Figure 7, and for the reaction with imidazole, Ph₃P, Ph₃As, and Ph₃-Sb in MeOH as shown in Figure S5 (Supporting Information). The good compensation correlation between ΔH^{\dagger} and ΔS^{\ddagger} suggests that an isokinetic relationship exists, which supports the claim that a single mechanism operates for the series of nucleophiles.²⁸

The activation volumes for substitution of coordinated water in *trans*-[Co(Hdmg)₂(Me)H₂O] by imidazole, pyrazole, 1,2,4-triazole, *N*-acetylimidazole, 5-chloro-1-methylimida-



Figure 7. Correlation between ΔH^{\ddagger} and ΔS^{\ddagger} for the second-order rate constant for substitution of H₂O in *trans*-[Co(Hdmg)₂(Me)H₂O] by *N*-acetylimidazole (1), 1,2,4-triazole (2), imidazole (3), pyrazole (4), NO₂⁻ (5), and 5-chloro-1-methylimidaziole (6).

zole, and NO₂⁻ were found to be between +2.3 and +4.5 cm³ mol⁻¹. The relatively small positive values suggest that the reaction follows an I_d mechanism in which the entering nucleophile is weakly bound in the transition state. The substitution of coordinated water by py and 4-CNpy in *trans*-[Co(Hdmg)₂(CF₃CH₂)H₂O] proceeds according to the same mechanism since ΔV^{\ddagger} was found to be +5.7 and +7.4 cm³ mol⁻¹, respectively.⁶ Similarly, ΔV^{\ddagger} values between +3.6 and +9.7 cm³ mol⁻¹ were reported for displacement of water in *trans*-[Co(en)₂(Me)H₂O]^{2+ 2,29} and in aquacobalamin^{14,30}

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by different nucleophiles. ΔV^{\ddagger} values for the substitution of water by N-acetylimidazole in trans-[Co(Hdmg)₂(Me)H₂O] and aquacobalamin¹² were found to be +3.1 and +7.2 cm³ mol⁻¹, respectively. Similar data for ligand substitution reactions of trans-[Co(Hdmg)₂(R)H₂O] by 1,2,4-triazole for $R = CF_3CH_2$ ²⁵ CH₃, and PhCH₂²⁵ were found to be +2.3, +3.2, and +7.5 cm³ mol⁻¹, respectively, as summarized in Table 4. These values all favor a dissociative interchange mechanism that consists of rapid precursor formation and a rate-determining interchange reaction. The consequence is that the overall second-order rate constant k_a is a composite value of the precursor formation constant (K) and the interchange rate constant (k), such that $k_a = kK$ as mentioned above. This naturally complicates the interpretation of k_a and its activation parameters since it was not possible to separate k and K (and their thermodynamic parameters) kinetically in the studied reactions, as could be done in other cases.^{6,13}

As mentioned before, activation volumes for ligand substitution reactions on [Co(TMPP)(H₂O)₂]⁵⁺ and [Co(TPPS)- $(H_2O)_2$ ³⁻ (TMPP = meso-tetrakis(4-N-methylpyridyl)porphine and TPPS = *meso*-tetrakis(*p*-sulfonatophenyl)porphine) are +14.4 and +15.4 cm³ mol⁻¹, respectively,^{16,17} and were assigned to a limiting D mechanism. The activation volumes for the substitution of methanol in *trans*-[Co(Hdmg)₂(R)-MeOH] by Ph₃P for $R = CH_3$ and PhCH₂ were also found to be more positive, viz. +12.3 and +15.2 cm³ mol⁻¹, respectively, which could suggest the operation of a limiting dissociative mechanism. However, this trend could also be due to the larger partial molar volume of methanol as compared to water, since this will affect the magnitude of ΔV^{\ddagger} for a dissociatively activated process. By way of comparison, it is interesting to note that the reaction of trans-[Co(Hdmg)₂(CH₃)MeOH] with imidazole is characterized by a significantly smaller activation volume than that found for Ph₃P, which suggests the operation of a dissociative interchange mechanism. The reason for this apparent difference in mechanism may be related to the formation of a precursor complex with imidazole, which would then favor a dissociative interchange mechanism in which precursor formation will contribute to the overall activation parameters found for $k_{\rm a}$ since $k_{\rm a} = kK$.

In one system, it was possible to construct a volume profile for the reaction between *trans*-[Co(Hdmg)₂(Me)MeOH] and Ph₃As (Figure 6), from which the dissociative character of the substitution process is clearly seen. The larger ΔV^{\ddagger} for the back reaction is related to the larger partial molar volume of the leaving ligand Ph₃As, which also accounts for the overall negative reaction volume. Although these larger activation volumes tend to suggest the operation of a limiting D mechanism, this suggestion is speculative due to the uncertain contribution of the larger partial molar volumes of the leaving groups for both the forward and back reactions as outlined above. In the case of a dissociative interchange I_d mechanism, the volume of activation for the forward reaction will include contributions arising from precursor formation and the interchange reaction step since $k_a = kK$



Figure 8. Crystal structure of the cation trans-[Co(en)₂(Me)H₂O]²⁺.

Table 5. Structural Parameters for Complexes of the Type *trans*- $[Co(chel)_2(X)H_2O]$, Where chel Represents the Equatorial Chelate Ligand

Х	Co-O (Å)	Co-X(Å)	O-Co-X (deg)	
trans- $[Co(en)_2(X)H_2O]^{2+}$				
CH ₃	2.153(6)	1.995(10)	177.6(3)	
trans-[Co((DO)(DOH)pn)(X)H ₂ O] ⁺				
CH334	2.14(2)	1.99(4)		
trans-[Co((EMO)(EMOH)pn)(X)H ₂ O] ⁺				
CH331	2.102(3)	1.997(4)		
trans-[Co(Hdmg) ₂ (X)H ₂ O]				
CH333	2.058(3)	1.990(5)	178.0(2)	
CH ₂ CMe ₃ ³²	2.056(5)	2.044(7)	172.4(3)	
CN ³²	1.992(4)	1.906(5)		
NO_{2}^{32}	1.980(5)	1.881(9)		
Br ³²	1.955(11)	2.364(2)	180.0	

and $\Delta V^{\ddagger}(k_{a}) = \Delta V^{\ddagger}(k) + \Delta V(K)$. Due to our inability to separate *k* and *K* kinetically in the present case, no further details can be included in the volume profile.

The labilization of the ligand in the position trans to the cobalt-carbon bond can in many cases be observed in the ground state as a result of the trans influence. In the present study, it was possible to crystallize *trans*-[Co(en)₂(Me)H₂O]-S₂O₆ of which the structure, determined by X-ray analysis, is shown in Figure 8. The crystal consists of organometallic cations and dithionate anions. The structure of the complex is a distorted octahedron, the cobalt atom and the four nitrogen atoms are located in the equatorial plane, and the water molecule and methyl group occupy the axial positions as shown in Figure 8. The Co-O and Co-C bond lengths in trans-[Co(en)₂(Me)H₂O]²⁺ were found to be 2.153(6) and 1.995(10) Å, respectively, and the Co-N bond lengths for N(1), N(2), N(3), and N(4) were found to be 1.999(7), 1.995-(8), 1.931(7), and 1.927(7) Å, respectively. The significantly larger Co-N(1) and Co-N(2) distances can be ascribed to the influence of hydrogen bonding to the oxygen atoms of the $S_2O_6^{2-}$ anion, which is located close to these amines in the crystal structure.

A comparison of the crystal structure data with closely related complexes is given in Table 5. The bond lengths depend on the nature of alkyl group and the equatorial ligands, the hybridization state of the carbon bond attached to the cobalt center, and steric interactions between the axial alkyl and the equatorial ligands (steric *cis* influence).^{31,32} In addition, the overall charge on the complexes changes from

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2+ to zero, which will also affect the metal-ligand bond lengths and complicate the following comparison. The X-ray structure data show that the bond lengths of Co-O are 2.058-(3),³³ 2.102(3),³¹ 2.14(2),³⁴ and 2.153(6) Å for *trans*-[Co-(Hdmg)₂(Me)H₂O], trans-[Co((EMO)(EMOH)pn)(Me)H₂O]⁺, trans-[Co((DO)(DOH)pn)(Me)H₂O]⁺, and trans-[Co(en)₂- $(Me)H_2O]^{2+}$, respectively, where (DO)(DOH)pn = diacetylmonoxime-diacetyl monoximato-propane-1,3-diyldiimino and (EMO)(EMOH)pn = 3,9-dimethyl-2,10-diethyl-1,4,8,11tetraazaundeca-1,3,8,10-tetraen-11-ol-1-olato. These data show that the $Co-OH_2$ bond is stronger in the ground state in the case of *trans*-[Co(Hdmg)₂(Me)H₂O]. The Co-O bond length increases from 1.955(4) Å for X = Br to 2.058(3) Å for X = CH_3 in the complex *trans*-[Co(Hdmg)₂(X)H₂O] as shown in the Table 5.³² A comparison of the data in Table 5 indicates that several kinds of structural changes arise from changes in the electron-donating ability of R and from the interactions between the alkyl group and the equatorial moiety, and the nature of the equatorial ligand. The Co-C bond lengthens from 1.990 to 2.044 Å as the bulk of the alkyl group increases from CH₃ to CH₂CMe₃ in the case of the dimethylglyoximate complex, and clearly depends on the steric interaction between the axial alkyl and the equatorial

ligands.³¹ In addition, the hybridization of the carbon atom affects the Co–C bond length, which was found to be 2.00, 1.96, and 1.90 Å for sp³, sp², and sp hybridization, respectively.³² Distortion arising from the interaction of the axial alkyl group with the equatorial ligand can be ascribed to (a) changes in the C–Co–N(eq) bond angles; (b) widening of the Co–CH₂–R' angles and shortening of the Co–R bond lengths; (c) lengthening of the Co–C bond; (d) deformation of the equatorial ligand unit.³²

It can be concluded that the variety of chelates, R groups, entering ligands, and solvents selected in this and our earlier studies¹⁻⁶ enables a systematic tuning of the lability of alkyl cobalt(III) complexes, which results in a systematic tuning of the ligand displacement process in terms of a dissociative interchange (I_d) and a limiting dissociative (D) mechanism.

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Supporting Information Available: Crystallographic data in CIF format. Additional tables and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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