

The Co–CH₃ Bond in Imine/Oxime B₁₂ Models. Influence of the Orientation and Donor Properties of the *trans* Ligand As Assessed by FT-Raman Spectroscopy

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Near-IR FT-Raman spectroscopy was used to probe the properties of three types of methyl imine/oxime B₁₂ model compounds in CHCl₃ solution. These types differ in the nature of the 1,3-propanediyl chain and were selected to test the influence of electronic and steric effects on the Co–CH₃ stretching ($\nu_{\text{Co-CH}_3}$) frequency, a parameter related to Co–C bond strength. For the first type studied, [LCo((DO)(DOH)pn)CH₃]^{0/+} ((DO)(DOH)pn = *N*²,*N*²-propane-1,3-diylbis(2,3-butanedione 2-imine 3-oxime)), $\nu_{\text{Co-CH}_3}$ decreased from 505 to 455 cm⁻¹ with stronger electron-donating character of the *trans* axial ligand, L, in the order Cl⁻, MeImd, Me₃Bzm, 4-Me₂-Npy, py, 3,5-Me₂PhS⁻, PMe₃, and CD₃⁻. This series thus allows the first assessment of the effect of negative axial ligands on $\nu_{\text{Co-CH}_3}$; these ligands (L = Cl⁻, 3,5-Me₂PhS⁻, CD₃⁻) span the range of *trans* influence. The CH₃ bending (δ_{CH_3}) bands were observed at 1171, 1159, and 1150/1105 cm⁻¹, respectively. The decrease in C–H stretching frequencies (ν_{CH}) of the axial methyl suggests that the C–H bond strength decreases in the order Cl⁻ > 3,5-Me₂PhS⁻ > CD₃⁻. This result is consistent with the order of decreasing ¹³C–¹H NMR coupling constants obtained for the axial methyl group. The trend of lower $\nu_{\text{Co-CH}_3}$ and ν_{CH} frequencies and lower axial methyl C–H coupling constant for stronger electron-donating *trans* axial ligands can be explained by changes in the electronic character of the Co–C bond. The symmetric CH₃–Co–CH₃ mode ($\nu_{\text{CH}_3\text{-Co-CH}_3}$) for (CH₃)₂Co((DO)(DOH)pn) was determined to be 456 cm⁻¹ (421 cm⁻¹ for (CD₃)₂Co((DO)(DOH)pn)). The L–Co–CH₃ bending mode ($\delta_{\text{L-Co-CH}_3}$) was detected for the first time for organocobalt B₁₂ models; this mode, which is important for force field calculations, occurs at 194 cm⁻¹ for ClCo((DO)(DOH)pn)CH₃ and at 186 cm⁻¹ for (CH₃)₂Co((DO)(DOH)pn). The $\nu_{\text{Co-CH}_3}$ frequencies were all lower than those reported for the corresponding cobaloxime type LCo(DH)₂CH₃ (DH = monoanion of dimethylglyoxime) models for planar N-donor L. This relationship is attributed to a steric effect of L in [LCo((DO)(DOH)pn)CH₃]⁺. The puckered 1,3-propanediyl chain in [LCo((DO)(DOH)pn)CH₃]⁺ forces the planar L ligands to adopt a different orientation compared to that in the cobaloxime models. The consequent steric interaction bends the equatorial ligand toward the methyl group (butterfly bending); this distortion leads to a longer Co–C bond. In a second imine/oxime type, a pyridyl ligand is connected to the 1,3-propanediyl chain and oriented so as to minimize butterfly bending. The $\nu_{\text{Co-CH}_3}$ frequency for this new lariat model was close to that of pyCo(DH)₂CH₃. In a third type, a bulkier 2,2-dimethyl-1,3-propanediyl group replaces the 1,3-propanediyl chain. The $\nu_{\text{Co-CH}_3}$ bands for two complexes with L = Me₃Bzm and py were 2–5 cm⁻¹ lower in frequency than those of the corresponding [LCo((DO)(DOH)pn)CH₃]⁺ complexes. The decrease in the axial $\nu_{\text{Co-CH}_3}$ frequencies is probably due to the steric effect of the equatorial ligand. Thus, the $\nu_{\text{Co-CH}_3}$ frequency can be useful for investigating both steric and electronic influences on the Co–C bond.

Introduction

The two types of cobalamin (B₁₂) coenzymes, methylcobalamin (MeCbl) and deoxyadenosylcobalamin (AdoCbl), transfer a methyl group and promote skeletal rearrangements, respectively.¹ During the mechanism of action, the Co–C bond is broken for both types.^{1–4} For both types, the *trans* ligand has been hypothesized to modulate coenzyme function.^{1,5,6} A recent

X-ray structural determination of the cobalamin-binding domain of *Escherichia coli* methionine synthase has revealed that the “nucleotide loop” of bound MeCbl was in the base-off conformation and was involved primarily in the binding of the cobalamin to the protein.⁶ The axial site was coordinated by an imidazole from a histidine residue instead of the 5,6-dimethylbenzimidazole (DMBz) of the isolated base-on cofactor. The imidazole differs from DMBz in both electronic and steric properties. Thus it is of some interest to probe how the *trans* ligand influences the Co–C bond since this bond must be broken during turnover.

Since near-infrared (near-IR) Fourier transform (FT) Raman spectroscopy is a good method for assessing the bonding, we are exploring the use of this method both with models, in studies presented here, and in corrinoid derivatives.⁷ Using a near-IR beam for the excitation eliminates electronic transitions and thus fluorescence and photolysis of the axial methyl group. Raman and IR frequencies give information about bond strength, and

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employing these spectroscopic methods in solution removes the uncertainty of solid-state lattice effects.

Imine/oxime B₁₂ model compounds seemed to hold promise for assessing the electronic influence of the *trans* ligands, since very diverse types of axial ligands can be incorporated.⁸⁻¹⁰ Furthermore, unlike other model systems, the steric influence of planar N-donor ligands has been clearly established with these types of complexes.⁸⁻¹⁰

The Co-CH₃ stretching ($\nu_{\text{Co-CH}_3}$) mode for a B₁₂ model compound was first assigned by IR spectroscopy to a band at 320 cm⁻¹ for a methylcobaloxime, LCo(DH)₂CH₃ (DH = monoanion of dimethylglyoxime).¹¹ However, the reported 6 cm⁻¹ frequency shift for the methyl-*d*₃ derivative¹¹ was unreasonably small. Later, the $\nu_{\text{Co-CH}_3}$ band was found by near-IR FT-Raman spectroscopic studies of LCo(DH)₂CH₃ compounds; e.g., the Co-C band at 504 cm⁻¹ for pyCo(DH)₂CH₃ in CHCl₃ shifted 27 cm⁻¹ for pyCo(DH)₂CD₃.¹² Frequency differences between solution and solid-state spectra of the models were observed in $\nu_{\text{Co-CH}_3}$, *trans* axial ligand, and equatorial ligand modes, indicating a conformational change upon solvation of the solids.¹⁴ The $\nu_{\text{Co-CH}_3}$ frequency for MeCbl was later determined by FT-Raman spectroscopy to be 500 cm⁻¹, a value very close to those of the models.¹³ Recently, the $\nu_{\text{Co-CH}_3}$ frequency of [H₂OC_o(1,2-bis(2-pyridinecarboxamido)benzene)CH₃] in the solid state was also found to have a similar value.¹⁴ The $\nu_{\text{Co-CH}_3}$ frequency for [Co(*meso*-tetraphenylporphyrin)CH₃] was found to have a normal value of 504 cm⁻¹, but the value of 459 cm⁻¹ for [Co(*meso*-tetramesitylporphyrin)CH₃] was taken to indicate that the steric bulk of this porphyrin macrocycle exerts a profound influence on the axial Co-C bond.¹⁴

Recently, resonance Raman spectroscopy was used for the first time to assign a band of a protein to the $\nu_{\text{Co-CH}_3}$ mode.¹⁵ The band at 429 cm⁻¹ was detected for a methylated corrinoid/iron sulfur protein. This significantly lower $\nu_{\text{Co-CH}_3}$ frequency than those for free methylcobalamin and other hexacoordinated organocobalt B₁₂ model compounds was attributed to a weaker Co-C bond in the protein.¹⁵

Here we investigate several types of methyl derivatives of imine/oxime type B₁₂ model compounds (Figure 1) in CHCl₃ solution. We compare the effect of L on vibrations involving the Co-CH₃ bonds with those of the analogous LCo(DH)₂CH₃ organocobalt models.

Experimental Section

Materials. All previously described methyl complexes, [LCo((DO)(DOH)pn)CH₃]⁺ ((DO)(DOH)pn = *N*²,*N*²-propane-1,3-diylbis(2,3-butanedione 2-imine 3-oxime)), [LCo((DO)(DOH)Me₂pn)CH₃]⁺ ((DO)(DOH)Me₂pn = *N*²,*N*²-2,2-dimethylpropane-1,3-diylbis(2,3-butanedione 2-imine 3-oxime)), and [CH₃Co(C₁py)]⁺ (C₁py = 2,3,9,10-tetramethyl-6-(2-pyridylmethyl)-1,4,8,11-tetrazaundeca-1,3,8,10-tetraene-

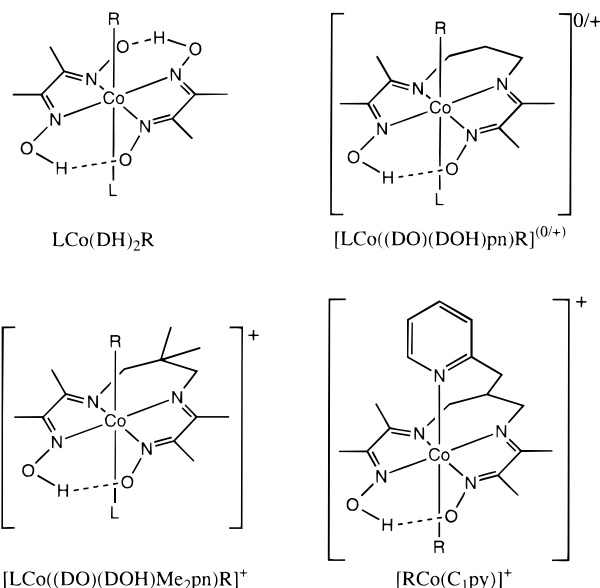


Figure 1. Schematic representation of B₁₂ model compounds.

1,11-diolo), were prepared and reported from this laboratory.^{8-10,16-18} The CD₃ complexes were synthesized by the same method but using methyl-*d*₃ iodide. (CH₃(CD₃)Co((DO)(DOH)pn) was prepared by a modification of a reported method.¹⁹ The purity of all samples was confirmed by ¹H NMR spectra in CDCl₃. PMe₃ (1.0 M solution in toluene) was purchased from Aldrich. Methyl-*d*₃ iodide (99.5 atom % for D) was purchased from Cambridge Isotope Labs. Analytical results listed in the Supporting Information were obtained through Atlantic Microlabs.

[Me₃PCo((DO)(DOH)pn)CH₃]PF₆. In an inert atmosphere, 1.0 M PMe₃ in toluene (0.37 mL, 0.37 mmol) was added to a suspension of [H₂OC_o((DO)(DOH)pn)CH₃]PF₆¹⁷ (0.16 g, 0.33 mmol) in CH₂Cl₂ (20 mL). The bright orange solution was stirred overnight, and the CH₂-Cl₂ was then removed to give a yellow solid. The air-stable product was washed with diethyl ether and vacuum-dried. Yield: 79%.

(3,5-Me₂PhS)Co((DO)(DOH)pn)CH₃. The synthesis of this compound, which gave satisfactory elemental analysis and NMR spectra, will be reported later.²⁰

ClCo((DO)(DOH)pn)CH₃. This orange compound was prepared in 81% yield using a procedure analogous to that reported for IC_o((DO)(DOH)pn)(*neo*-C₃H₁₁),²¹ but with an excess of NaCl.

[Me₃BzmCo((DO)(DOH)Me₂pn)CH₃]ClO₄. This compound was prepared in 95% yield as an orange powder in the same manner as the corresponding PF₆⁻ salt,¹⁰ using NaClO₄ (5-fold excess) in place of KPF₆.

(CH₃(CD₃)Co((DO)(DOH)pn). This compound was prepared by modifications of reported methods.^{22,23} An orange mixture of ClCo((DO)(DOH)pn)CH₃ (0.080 g, 0.18 mmol) with THF (25 mL), H₂O (17 mL), ether (17 mL), and NaOH (0.15 g, 3.75 mmol) was degassed with N₂ (15 min) and then CO (30 min) at 0 °C. Methyl-*d*₃ iodide (0.065 mL, 1.04 mmol) was introduced. After 2 h of stirring, much of the product had dissolved into the ether layer. The aqueous phase was extracted with additional diethyl ether, and the combined ether layer was concentrated under reduced pressure. The solid was collected by

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filtration, washed with H₂O, and vacuum-dried. Deuterated samples were prepared from [H₂OCo((DO)(DOH)pn)CH₃]ClO₄, and their purity was confirmed by comparison of their ¹H NMR spectra with those of nondeuterated samples in CDCl₃. Yield: 43%.

FT-Raman Measurements. FT-Raman spectra were acquired on a Nicolet Raman 950 spectrometer, equipped with a 1.064 μm Nd:YVO₄ laser head, a liquid-nitrogen-cooled germanium detector, and a CaF₂ beamsplitter. The mirror velocity and the laser power were 0.4747 cm/s and 1 W (at the sample point), respectively, for all measurements. Samples were saturated in ~0.2–0.3 mL of CHCl₃ and were placed in an NMR tube. The CHCl₃ solvent spectrum was subtracted from the complex solution spectra to cancel the intensities of the solvent bands as much as possible. Accumulation time was 26–261 min according to the solubility of the complex in CHCl₃. The resolution of all spectra was ±1 cm⁻¹.

¹³C–¹H Coupling Constant Measurements. The ¹³C–¹H coupling constants were obtained by the new *J*-coupled heteronuclear multiple quantum coherence (JHMQC) NMR method to be described in a later publication.

Results

As mentioned above, the imine/oxime complexes afford the opportunity to vary greatly the nature of the *trans* ligand. In the past, relatively little dependence of the ν_{Co–CH₃} frequency on the nature of various neutral *trans* ligands was found, although the complexes examined spanned a broad range of equatorial groups.^{12,14,24} Because of the broader range of spectral effects found for these neutral complexes, we carried out a number of isotopic substitution studies to facilitate the assignments.

FT-Raman spectra in the 1200–150 cm⁻¹ region for neutral LCo((DO)(DOH)pn)CH₃ and the methyl-*d*₃ analogs were compared (Figure 2). For ClCo((DO)(DOH)pn)CH₃ only three bands (194, 505, and 1171 cm⁻¹, Figure 2Aa) shifted in the CD₃ analog (to 185, 478, and 890 cm⁻¹, respectively, Figure 2Ab). Frequencies and the frequency shifts for the 505 and 1171 cm⁻¹ bands were very close to those reported for the Co–CH₃ stretching (ν_{Co–CH₃}) and CH₃ bending (δ_{CH₃}) bands of LCo(DH)₂CH₃ compounds and methylcobalamin.^{12–14,25}

The spectrum of (3,5-Me₂PhS)Co((DO)(DOH)pn)CH₃ has several bands in the 600–400 cm⁻¹ region (Supporting Information, Figure S-1). However, since only the 496 cm⁻¹ band shifted in the CD₃ analog, this band is assigned to ν_{Co–CH₃}. Another intense band at 424 cm⁻¹, not seen for the L = Cl⁻ complex (Figure 2A), is probably a 3,5-Me₂PhS⁻ ligand vibration. At higher frequencies, the 1135 cm⁻¹ band changed intensity in the CD₃ analog spectrum but did not shift. The band at 1159 cm⁻¹ shifted to 879 cm⁻¹ in the CD₃ analog; we assign it to the δ_{CH₃} mode. These frequencies were 11–12 cm⁻¹ lower than those of the corresponding bands for chloro complexes.

Bands at 186, 456, and 1151/1103 cm⁻¹ in the spectrum of (CH₃)₂Co((DO)(DOH)pn) shifted to 177, 421, and 853 cm⁻¹, respectively (Figure 2B), for (CD₃)₂Co((DO)(DOH)pn). The bands at 456 and 421 cm⁻¹ are assigned to the CH₃–Co–CH₃ symmetric stretching mode (ν_{CH₃–Co–CH₃}). Spectral bands of (CH₃)(CD₃)Co((DO)(DOH)pn) at 455 and 435 cm⁻¹ are assigned to ν_{Co–CH₃} for Co–CH₃ and Co–CD₃, respectively. The 186 cm⁻¹ band for (CH₃)₂Co((DO)(DOH)pn) shifted to 181 cm⁻¹ for (CH₃)(CD₃)Co((DO)(DOH)pn). The spectra of (CH₃)₂Co((DO)(DOH)pn) and (CH₃)(CD₃)Co((DO)(DOH)pn) showed two bands for δ_{CH₃}, at 1151/1103 and 1150/1105 cm⁻¹, respectively. The frequencies and methyl-*d*₃ frequency shifts

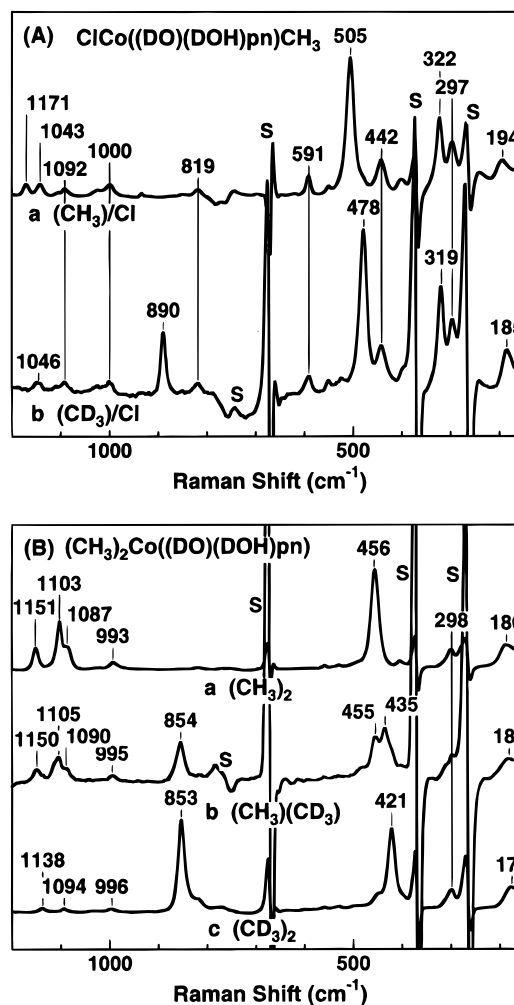


Figure 2. FT-Raman spectra in the 1200–150 cm⁻¹ region for LCo((DO)(DOH)pn)R for R = CH₃ and CD₃. L: Cl⁻ (A) and CD₃⁻ or CH₃⁻ (B). The ordinate scales are normalized by the intensity of the equatorial ligand modes in each spectrum. Peaks marked S denote the residual solvent bands. Experimental conditions for all figures: excitation, 1.064 μm, 1 W at the sample point; saturated CHCl₃ solution.

were close to those of the δ_{CH₃} mode of ClCo((DO)(DOH)pn)CH₃. Only one δ_{CH₃} band was seen for (CD₃)₂Co((DO)(DOH)pn) (Figure 2Bc). Two δ_{CH₃} bands for (CH₃)₂Co((DO)(DOH)pn) and for (CH₃)(CD₃)Co((DO)(DOH)pn) could be caused by a vibrational coupling of the δ_{CH₃} band with another band. Since a band at 1138 cm⁻¹ for (CD₃)₂Co((DO)(DOH)pn) is close to the δ_{CH₃} band for (CH₃)₂Co((DO)(DOH)pn) and (CH₃)(CD₃)Co((DO)(DOH)pn), the 1138 cm⁻¹ band is probably the band involved in the coupling.

The frequencies of the bands that showed frequency shifts upon deuterium substitution into the axial methyl group of LCo((DO)(DOH)pn)R with L = Cl⁻, 3,5-Me₂PhS⁻, or CH₃⁻ (or CD₃⁻) and R = CH₃ or CD₃ are summarized in Table 1, together with the ¹³C–¹H coupling constants. Figure 3 shows the FT-Raman spectra in the 600–400 cm⁻¹ region for various [LCo((DO)(DOH)pn)CH₃]^{0/+} complexes. The band for the ν_{Co–CH₃} mode has usually been found at ~500 cm⁻¹ (Table 2).^{12–14,25} Since the isotopic shift of 27 cm⁻¹ for the band around 500 cm⁻¹ for LCo((DO)(DOH)pn)CH₃ (L = Cl⁻, 3,5-Me₂PhS⁻) was close to the calculated value (35 cm⁻¹) for the Co–CH₃ diatomic model, this band is assigned to ν_{Co–CH₃}. The smaller than expected frequency shift indicates that the band is not from a pure ν_{Co–CH₃} mode. Furthermore, an even smaller frequency shift (20 cm⁻¹) was observed for (CH₃)(CD₃)Co((DO)(DOH)pn) (ν_{Co–CH₃} at 455 and ν_{Co–CD₃} at 435 cm⁻¹,

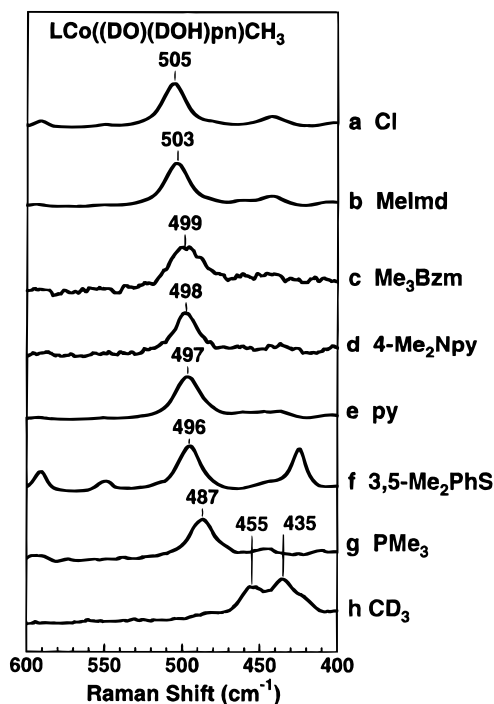
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Table 1. Observed Axial CH₃ Related Frequencies and ¹³C-¹H Coupling Constants of the Axial Methyl Group in CHCl₃ for LCo((DO)(DOH)pn)R

L	$\delta_{L-Co-CH_3}, \text{cm}^{-1}$			$\nu_{Co-CH_3}, \text{cm}^{-1}$			$\delta_{CH_3}, \text{cm}^{-1}$			ν_{CH}, cm^{-1}		$^1J_{C-H}, \text{Hz}$ R = CH ₃
	R = CH ₃	R = CD ₃	diff	R = CH ₃	R = CD ₃	diff	R = CH ₃	R = CD ₃	diff	R = CH ₃	R = CD ₃	
Cl ⁻	194	185	9	505	478	27	1171	890	281	2902	2246	138.0
3,5-Me ₂ PhS ⁻	<i>a</i>	<i>a</i>		496	469	27	1159	879	280	2896	2240	136.1
CH ₃ ⁻ /CD ₃ ⁻		181		455	435	20	1150	854		<i>b</i>	2108	
R	186	177	9	456	421	35	1151	853		<i>b</i>	2216	131.0
							1103				2093	

^a Overlapped with ligand-related modes. ^b Overlapped with equatorial CH₃ symmetric stretching bands.

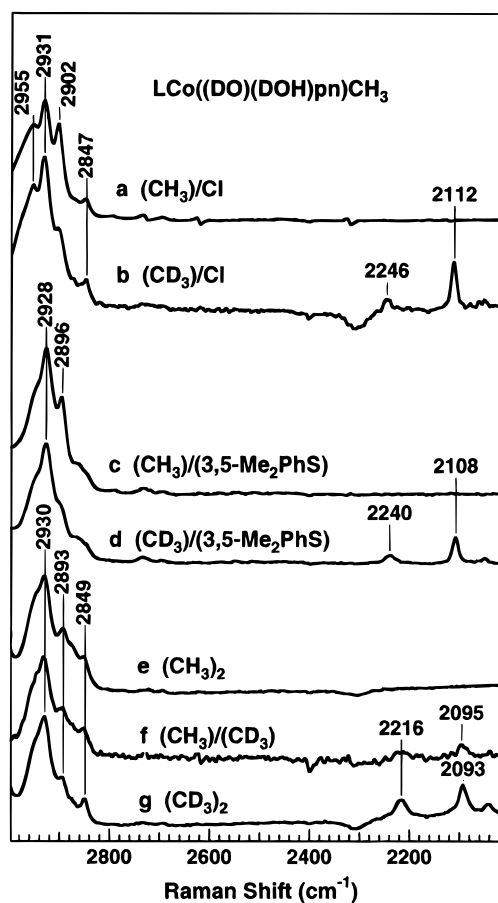
**Figure 3.** FT-Raman spectra in the 600–400 cm⁻¹ region for [LCo((DO)(DOH)pn)CH₃]^{0/+} compounds. The ordinate scales are normalized by the intensity of the ν_{Co-CH_3} bands.**Table 2.** Co-CH₃ Stretching Frequencies in CHCl₃ of [LCo((DO)(DOH)pn)CH₃]^{0/+} and LCo(DH)₂CH₃

L	$\nu_{Co-CH_3}, \text{cm}^{-1}$	
	(DO)(DOH)pn	(DH) ₂ ^a
Cl ⁻	505	
1-MeImd	503 ^b	508
Me ₃ Bzm	499 ^b	506
4-Me ₂ Npy	498 ^b	504
py	497 ^b	504
3,5-Me ₂ PhS ⁻	496	
PMe ₃	487 ^c	
CD ₃ ⁻	455	

^a Reference 25. ^b ClO₄⁻ salt. ^c PF₆⁻ salt.

Figure 3). In (CH₃)(CD₃)Co((DO)(DOH)pn), the CH₃ has CD₃ as a *trans* ligand while CD₃ has CH₃ as a *trans* ligand. Therefore, the smaller frequency difference between ν_{Co-CH_3} and ν_{Co-CD_3} indicates that ν_{Co-CH_3} is influenced by the mass of the *trans* axial ligand and that this mode is probably vibrationally coupled with the Co-L (L = *trans* axial ligand) stretching mode.

In the high-frequency region (3000–2000 cm⁻¹) in the FT-Raman spectra for LCo((DO)(DOH)pn)CH₃ and LCo((DO)(DOH)pn)CD₃ for L = Cl⁻, 3,5-Me₂PhS⁻, and CH₃⁻ or CD₃⁻ (Figure 4), the small peaks and troughs around 2320, 2620, and

**Figure 4.** FT-Raman spectra in the high-frequency region, 3000–2000 cm⁻¹, for [LCo((DO)(DOH)pn)R] compounds. The ordinate scales are normalized by the intensity of the equatorial ν_{CH_3} bands.

2720 cm⁻¹ are instrumental artifacts. Although other bands around 3000 cm⁻¹ did not shift between [LCo((DO)(DOH)pn)CH₃] (L = Cl⁻, 3,5-Me₂PhS⁻) and the methyl-*d*₃ analog, the 2902 and 2896 cm⁻¹ bands were shifted and appeared as two new bands at 2246/2112 and 2240/2108 cm⁻¹, respectively (Figure 4). The frequencies and methyl-*d*₃ frequency shifts for these 2902 and 2896 cm⁻¹ bands were close to those observed for the axial ν_{CH} band of methylcobaloximes¹² and thus are assigned to the axial ν_{CH} mode. The axial ν_{CH} band was overlapped with the equatorial ν_{CH} band for (CH₃)₂Co((DO)(DOH)pn) but was seen at ~2216/2095 and 2216/2093 cm⁻¹ for (CH₃)(CD₃)Co((DO)(DOH)pn) and (CD₃)₂Co((DO)(DOH)pn), respectively. This band was definitely lower in frequency than those of the L = Cl⁻ and 3,5-Me₂PhS⁻ derivatives. The intensity of the ~2216/2095 cm⁻¹ bands for (CH₃)(CD₃)Co((DO)(DOH)pn) is lower than that of the 2216/2093 cm⁻¹ bands in (CD₃)₂Co((DO)(DOH)pn), since only one methyl group is

Table 3. Comparison of Co–CH₃ Stretching Frequencies in CHCl₃ and Co–C Bond Lengths of [CH₃Co(C₁py)]⁺ and [LCo(CHEL)CH₃]^{0/+} with CHEL = (DO)(DOH)pn, (DO)(DOH)Me₂pn, and (DH)₂ and L = py and Me₃Bzm

	C ₁ py		(DO)(DOH)Me ₂ pn		(DO)(DOH)pn		(DH) ₂	
	py	Me ₃ Bzm	py	Me ₃ Bzm	py	Me ₃ Bzm	py	Me ₃ Bzm
$\nu_{\text{Co-CH}_3}$, cm ⁻¹	506 ^a	493 ^a	495 ^b	499 ^a	497 ^a	506 ^c	504 ^c	
Co–C, Å	1.99, 2.05 ^d	2.014 ^e	2.017 ^e	2.011 ^f	2.003 ^g	1.989 ^h	1.998 ⁱ	

^a ClO₄⁻ salt. ^b PF₆⁻ salt. ^c Reference 25. ^d Reference 8. ^e Reference 10. ^f Reference 9. ^g Reference 16. ^h Reference 27. ⁱ Reference 28.

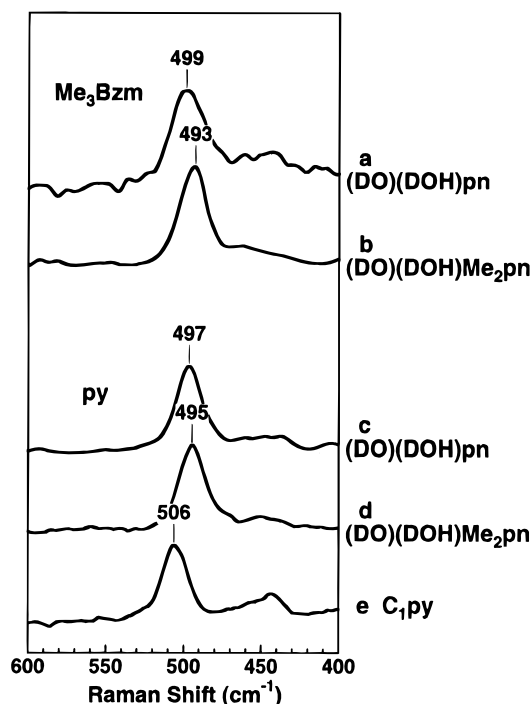


Figure 5. FT-Raman spectra in the 600–400 cm⁻¹ region for [LCo(CHEL)CH₃]⁺ and [CH₃Co(C₁py)]⁺ complexes. The ordinate scales are normalized by the intensity of the $\nu_{\text{Co-CH}_3}$ bands.

labeled in the former compound; the position of the weak ~2216 cm⁻¹ band was difficult to define precisely.

In Figure 5, we compare the $\nu_{\text{Co-CH}_3}$ bands for the three types of imine/oxime complexes studied here. The $\nu_{\text{Co-CH}_3}$ band for [CH₃Co(C₁py)]⁺ was detected at 506 cm⁻¹, a frequency close to that for pyCo(DH)₂CH₃ (504 cm⁻¹).¹²

Discussion

Influence on Co–CH₃ Bond Strength by the Electronic Properties of the *trans* Axial Ligand. For a diatomic model, the frequency ($\bar{\nu}$) of the bond follows the relationship

$$\bar{\nu} \propto (k/m)^{1/2} \quad (1)$$

where k and m are the force constant of the bond and the reduced mass, respectively. Since the force constant is related to the bond strength, the frequency reflects bond strength. There are also good correlations between bond strength and bond length. Thus, the stretching frequency is a very useful probe into the nature of a bond.

The $\nu_{\text{Co-CH}_3}$ frequencies for [LCo((DO)(DOH)pn)CH₃]⁺ were all lower than those of the corresponding LCo(DH)₂CH₃²⁵ model compounds for planar L ligands (Table 2). In general, the Co–C bond lengths for imine/oxime compounds are longer than those for the analogous cobaloximes (Table 3).

Coordination of PMe₃ decreased the $\nu_{\text{Co-CH}_3}$ frequency significantly compared to that of other *trans* ligand derivatives except the CD₃ derivative of [LCo((DO)(DOH)pn)CH₃]^{0/+} (Table 2). A decrease in the $\nu_{\text{Co-CH}_3}$ frequency upon PMe₃

coordination was found in studies of other models;^{14,25} thus, the decrease seems to be characteristic of organocobalt model compounds. The low $\nu_{\text{Co-CH}_3}$ frequency for the PMe₃ derivative could be due to the strong electron-donating effect of the PMe₃ ligand. Coordination of CD₃⁻ decreased the $\nu_{\text{Co-CH}_3}$ frequency more than coordination of PMe₃, since CD₃⁻ has a stronger electron-donating character. Coordination of Cl⁻, which has only very weak electron-donating character, exhibited the highest $\nu_{\text{Co-CH}_3}$ frequency among the derivatives studied. The stronger electron-donating *trans* axial ligand seems to cause a decrease in the $\nu_{\text{Co-CH}_3}$ frequency, i.e., a weakening of the Co–C bond.

The low $\nu_{\text{Co-CH}_3}$ frequency observed for (CH₃)(CD₃)Co((DO)(DOH)pn) is consistent with results obtained from crystal structures. The Co–C bond was significantly longer for (CH₃)₂Co((DO)(DOH)pn) (2.045 and 2.049 Å) than those for [(Me₃Bzm)Co((DO)(DOH)pn)CH₃]⁺ (2.011 Å) and [pyCo((DO)(DOH)pn)CH₃]⁺ (2.003 Å).^{9,16,26} The lower $\nu_{\text{Co-CH}_3}$ frequency for (CH₃)₂Co((DO)(DOH)pn) in CHCl₃ solution indicates that in solution this compound must have a Co–C bond longer than those of the other derivatives studied.

These changes involve relatively large changes in the nature of the *trans* ligand, including even the identity of the ligating atom. In B₁₂ coenzymes, the *trans* ligand is a heterocyclic N-donor. Since 4-Me₂Npy is a better electron donor than py and since 4-Me₂Npy and py have about the same steric effect, one would expect that the $\nu_{\text{Co-CH}_3}$ frequencies would be significantly different for 4-Me₂Npy and py complexes. The close $\nu_{\text{Co-CH}_3}$ frequencies for analogous complexes with the two ligands (Table 2) indicate that the difference in the electronic effect of the *trans* axial ligand between 4-Me₂Npy and py is too small to cause a change in the Co–C bond strength. Other evidence suggests that the electronic difference between these N-donors is small. For example, the first-order rate constant for the dissociation of L from LCo(DH)₂CH₃ (in CH₂Cl₂) is only ~18 times greater for py than for 4-Me₂Npy.²⁷ Indeed, formation constants in DMSO for LCo(DH)₂CH₃ differ by only an order of magnitude.²⁷

Influence on Co–CH₃ Bond Strength by the Steric Properties of the *trans* Axial Ligand. The steric influence of one ligand on the bonding between the Co and the *trans* axial ligand is called the steric *trans* influence. This influence is transmitted through interactions between the bulkier ligand and the equatorial ligand. Since large, bulky ligands such as tripodal P-donors can distort the equatorial ligand, these L have readily detectable primary steric *trans* influences. The planar N-donor ligands normally do not exhibit this primary influence. However, in some cases, the equatorial ligand can control the orientation of the N-donor ligand such that its positioning creates steric repulsions. In these cases of a secondary steric *trans* influence, the bonding of the other axial ligand can be affected.

To assess whether the secondary steric *trans* influence could affect the $\nu_{\text{Co-CH}_3}$ frequencies, several model systems were compared. The $\nu_{\text{Co-CH}_3}$ frequencies and Co–C bond lengths of [CH₃Co(C₁py)]⁺ and [LCo(CHEL)CH₃]^{0/+}, with CHEL =

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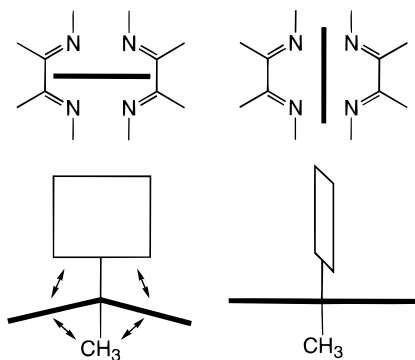


Figure 6. Schematic representation of the relationship of planar N-ligand orientation to butterfly bending.

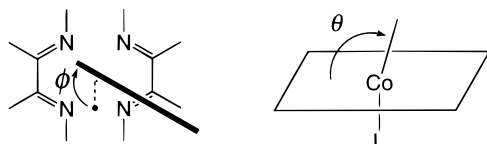


Figure 7. Orientation of the planar L ligand defined by the ϕ angle (left) and schematic drawing of the Co-C bending parameter, θ (right).

(DO)(DOH)pn, (DO)(DOH)Me₂pn, and (DH)₂ and L = Me₃Bzm and py, are listed in Table 3. The increase in the $\nu_{\text{Co-CH}_3}$ frequencies corresponds very well with the decrease in the Co-CH₃ bond lengths, even though these are affected by the crystal lattice. Since the $\nu_{\text{Co-CH}_3}$ frequencies increased in the order (DO)(DOH)Me₂pn < (DO)(DOH)pn < (DH)₂ \approx C₁py, the Co-C bond length in CHCl₃ solution must decrease in this order also.

The dependence of Co-C bond length on the nature of these equatorial ligands can be attributed to the different orientation of the planar L ligand (Figure 6). The orientation of L is specified with the improper torsion angle ϕ (Figure 7), C(axial ligand)-N(axial ligand)-Co-Z (Z is a dummy atom at the midposition of the equatorial oxime N-donors). In cobaloximes, ϕ is close to 0°, while it varies from 76 to 115° in traditional imine/oxime compounds.⁹ When ϕ is close to 0°, the *trans* ligand is not in an orientation that allows L to affect the planarity of the equatorial ligand, but when ϕ is near 90°, the *trans* ligand is positioned such that it can cause the equatorial ligand to bend toward the axial methyl group (Figure 6). In turn, the steric clashes created by this bending can cause the methyl group to move away from the Co atom. Because of the consequent weakening of the Co-C bond, the $\nu_{\text{Co-CH}_3}$ frequency would decrease. For [CH₃Co(C₁py)]⁺, the $\nu_{\text{Co-CH}_3}$ frequency was close to that of pyCo(DH)₂CH₃. This is because the ϕ angle is close to 0° for both [CH₃Co(C₁py)]⁺ and pyCo(DH)₂CH₃, and both complexes have less butterfly bending for the equatorial ligand.^{8,28}

These solution FT Raman results suggest that the conformational differences found in the solid between these types of complexes also exist in solution. Indeed, analysis of the anisotropic shift effects of the equatorial ligands on the NMR signals of the L protons also suggests that the solid and solution orientations of the L ligand are the same or nearly so.^{9,10,16}

The $\nu_{\text{Co-CH}_3}$ frequencies for the L = Me₃Bzm and py complexes having a (DO)(DOH)Me₂pn equatorial ligand are lower by 2–6 cm⁻¹ than those of the corresponding complexes having a (DO)(DOH)pn ligand (Figure 5, Table 3), although the Co-N bond length does not differ much between the two

series.^{10,16,17} The lower $\nu_{\text{Co-CH}_3}$ frequencies for the complexes with a (DO)(DOH)Me₂pn equatorial ligand could be explained by the steric effect of the *syn* Me₂pn methyl group pushing the axial CH₃ group away from the Co atom.

Methyl-B₁₂ has a very long axial Co-N bond (~2.19 Å),²⁹ considerably longer (by 0.1–0.2 Å) than in typical models.²⁹ This lengthening is very likely solely a *cis* electronic influence. The orientation of the DMBz ligand is fixed by its attachment to the corrin. The $\nu_{\text{Co-CH}_3}$ frequency for methyl-B₁₂ has been found at 500 cm⁻¹ for the solid¹³ and at 504 cm⁻¹ for the solution.⁷ These values are similar to those for models with *trans* N-donor ligands. Thus, although the large *cis* electronic influence of the corrin ring lengthens the Co-N bond, it has little effect on the $\nu_{\text{Co-CH}_3}$ band frequency. The major N-donor equatorial ligand influence appears to be the secondary *cis* steric influence; this steric trend is most clearly identified in models.

Axial δ_{CH_3} and ν_{CH} Modes and C-H Bond Strength of Axial CH₃. The axial δ_{CH_3} mode was more intense for the methyl-*d*₃ complexes than for the protio methyl complexes (Figure 2). This characteristic, also apparent in the reported spectra of pyCo(DH)₂CH₃,¹² appears to be a common feature for methyl-B₁₂ model compounds.

It is well established that, in general, the C-H stretching (ν_{CH}) frequency becomes higher as the C-H bond strength increases and bond length decreases. The axial ν_{CH} frequency is thus a very good probe for properties of the C-H bond of the axial methyl group. For the B₁₂ model compounds studied here, the axial ν_{CH} mode was difficult to detect for some nondeuterated samples, since the bands of the axial and the equatorial ν_{CH} modes overlap. On the other hand, for all of the methyl-*d*₃ complexes studied, the ν_{CH} bands had two different frequencies (Figure 4): 2246 and 2112 cm⁻¹ for ClCo((DO)(DOH)pn)CD₃; 2240 and 2108 cm⁻¹ for (3,5-Me₂PhS)Co((DO)(DOH)pn)CD₃; and 2216 and 2093 cm⁻¹ for (CD₃)₂Co((DO)(DOH)pn). These frequencies suggest that the order of the C-H bond strength for the axial methyl group of LCo((DO)(DOH)pn)CH₃ is L = Cl⁻ > 3,5-Me₂PhS⁻ > CH₃⁻; the C-H bond length follows the opposite trend.

Assignments of Symmetric $\nu_{\text{CH}_3-\text{Co}-\text{CH}_3}$ and $\delta_{\text{L}-\text{Co}-\text{CH}_3}$ Modes. From IR spectroscopy, the $\nu_{\text{CH}_3-\text{Co}-\text{CH}_3}$ stretching band of (CH₃)₂Co((DO)(DOH)pn) has been assigned to a broad band at 488 cm⁻¹.¹⁹ Upon bis(methyl-*d*₃) substitution, the band shifted only to 467 cm⁻¹,¹⁹ a significantly larger shift is expected. This disparity was attributed to a coupling of the $\nu_{\text{CH}_3-\text{Co}-\text{CH}_3}$ mode with another mode.¹⁹ In the Raman spectra of (CH₃)₂Co((DO)(DOH)pn) and (CD₃)₂Co((DO)(DOH)pn), the isotopic frequency shift of the 456 cm⁻¹ band to 421 cm⁻¹ is clear (Figure 2B). This 35 cm⁻¹ shift is very close to the calculated value of 40 cm⁻¹ for the pure $\nu_{\text{CH}_3-\text{Co}-\text{CH}_3}$ symmetric stretch; we thus assign this 456 cm⁻¹ band to the $\nu_{\text{CH}_3-\text{Co}-\text{CH}_3}$ symmetric stretching mode. We could not detect bands for any other axial CH₃ mode, including the antisymmetric CH₃-Co-CH₃ stretching mode.

For ClCo((DO)(DOH)pn)CH₃, the band at 194 cm⁻¹ exhibits an isotopic shift, the low frequency suggesting that it may be due to the L-Co-CH₃ (L = Cl⁻) bending mode ($\delta_{\text{L}-\text{Co}-\text{CH}_3}$) (Figure 2A). This frequency is close to the reported CH₃-M-CH₃ (M = Hg, Zn) bending frequencies.³⁰ Since the bending mode is not Raman active in a linear A-B-A type molecule, the intensity of the bending band in Raman scattering tends to

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be low.³¹ The lower intensity of this 194 cm⁻¹ band compared to that of the $\nu_{\text{Co}-\text{CH}_3}$ band in the same spectrum also supports the $\delta_{\text{L}-\text{Co}-\text{CH}_3}$ assignment. A similar (CH₃)₂Co(DO)(DOH)pn band detected at 186 cm⁻¹ (181 and 177 cm⁻¹ for (CH₃)(CD₃)Co(DO)(DOH)pn and (CD₃)₂Co(DO)(DOH)pn), respectively) is likewise assigned to the CH₃-Co-CH₃ bending mode ($\delta_{\text{CH}_3-\text{Co}-\text{CH}_3}$) (Figure 2B). However, this $\delta_{\text{L}-\text{Co}-\text{CH}_3}$ band was not detectable for (3,5-Me₂PhS)Co(DO)(DOH)pnCH₃, since it overlapped with another band, possibly at 183 cm⁻¹ (not seen in other compounds) from a -Me₂PhS⁻ ligand-related mode.

The isotopic frequency shifts of the $\delta_{\text{CH}_3-\text{Co}-\text{CH}_3}$ bands of LCo(DO)(DOH)pnCH₃ (L = Cl⁻, CH₃⁻) were the same (9 cm⁻¹, Table 1). This finding suggests that this mode involves almost exclusively the movement of the axial methyl group, since the mass of the *trans* ligand is not changed in the CD₃ analog for the chloro compound, whereas it becomes heavier in the CD₃ analog for the dimethyl compound. This conclusion is consistent with the assignment of the 194 cm⁻¹ band to the L-Co-CH₃ bending mode, since lateral movement of the Co atom within the equatorial plane is restricted by the equatorial nitrogens. This is the first assignment of $\delta_{\text{L}-\text{Co}-\text{CH}_3}$ for this general class of organocobalt compounds.

The frequency of the $\delta_{\text{L}-\text{Co}-\text{CH}_3}$ bending mode reflects how readily the bands are perturbed from the equilibrium position. The mode should be very important for developing the force field needed for molecular mechanics studies. Since the band gives information on the flexibility of the molecule in the L-Co-CH₃ direction, it could be useful as a probe for environmental effects on the Co-CH₃ bond. From our analysis, this mode reflects primarily the movement of the methyl group with respect to the rest of the molecule. This bending of the Co-C bond from the perpendicular direction is called θ -bending (θ is the angle between the equatorial plane and the Co-C bond, Figure 7). θ -Bending has been the subject of theoretical studies directed in part toward evaluating the hypothesis that θ -bending is an avenue through which coenzyme-enzyme binding energy could weaken the Co-C bond and thereby facilitate B₁₂-dependent reactions.^{32,33} It was concluded that the bending of θ from 90° does not greatly weaken the bond.³² We recently found that θ -bending was a facile process during the formation of a Co-C-N three-membered ring for the imine/oxime type models.²¹ The resulting new organocobalt compounds provided the first opportunity for gaining experimental insight into the likely effects of θ -bending on the Co-C bond strength. Qualitative observations on the highly distorted (θ -bending = 116°) new compounds indicated that they are relatively inert under conditions for which Co-C bond cleavage normally is observed.²¹

Relationship between $\nu_{\text{Co}-\text{CH}_3}$, ν_{CH} and δ_{CH_3} Frequencies and the ¹³C-¹H Coupling Constant of the Axial Methyl Group. The ν_{CH} frequency results were consistent with the ¹³C-¹H coupling constant data for the axial methyl group in LCo(DO)(DOH)pnCH₃ (L = Cl⁻, 3,5-Me₂PhS⁻, CH₃⁻) complexes. The ¹³C-¹H coupling constant decreased in the order L = Cl⁻ > 3,5-Me₂PhS⁻ > CH₃⁻ derivatives; therefore, the C-H bond length is suggested to increase in the order L = Cl⁻ < 3,5-Me₂PhS⁻ < CH₃⁻ derivatives. The $\nu_{\text{Co}-\text{CH}_3}$ and ν_{CH} (ν_{CD}) frequencies and ¹³C-¹H coupling constant of the axial methyl group all decreased for stronger electron-donating *trans* axial ligands in the order Cl⁻ > 3,5-Me₂PhS⁻ > CH₃⁻ (Table 1).

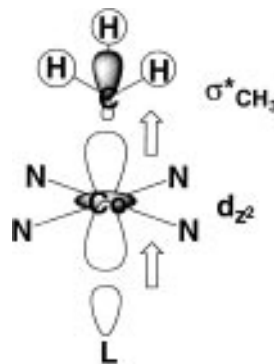


Figure 8. Schematic view of interacting orbitals.

To explain these trends, it is useful to consider a qualitative interpretation of the binding. In this qualitative approach, we view the methyl derivative as a combination of a methyl anion and a Co complex. The methyl anion would have a pyramidal structure with its antibonding $\sigma_{\text{CH}_3}^*$ orbital being the lowest unoccupied molecular orbital (LUMO) (Figure 8).^{34,35} Electron donation from the *trans* L ligand to the Co atom could cause electron donation to the methyl $\sigma_{\text{CH}_3}^*$ orbital through the Co d_{z^2} orbital (Figure 8). This d_{z^2} orbital is an antibonding orbital in octahedral Co complexes.³⁶ As the *trans* ligand becomes a stronger electron donor, there is greater electron occupation in the antibonding Co d_{z^2} orbital. As a result, the Co-C bond strength decreases, explaining the observed $\nu_{\text{Co}-\text{CH}_3}$ frequency decrease. Also since the $\sigma_{\text{CH}_3}^*$ orbital is antibonding for the C-H bond, one would expect that the C-H bond strength decreases and the C-H bond length increases for compounds having stronger electron-donating *trans* axial ligands. These changes would lead to the observed decrease in ν_{CH} frequencies and ¹³C-¹H coupling constants as L becomes a better donor.

Conclusions

Good correlations exist between the X-ray structural data for Co-C bond length and the $\nu_{\text{Co}-\text{CH}_3}$ frequency. Thus, the $\nu_{\text{Co}-\text{CH}_3}$ frequency appears to be a very good means for assessing trends in Co-C bond strength and bond length in solution.

Variations in the N-donor ligand strength have relatively little influence on the $\nu_{\text{Co}-\text{CH}_3}$ frequency and hence Co-C bond strength in the ground state. However, the secondary steric *trans* influence does lead to significant, if small, variations in $\nu_{\text{Co}-\text{CH}_3}$ frequency. The secondary steric *trans* influence appears to be transmitted through butterfly bending of the equatorial ligand. The bending causes a steric clash between the equatorial ligand and the axial methyl group, which weakens the Co-C bond.

Larger variations in the *trans* ligands, including changes in the nature of the ligating atoms, lead to appreciable changes in $\nu_{\text{Co}-\text{CH}_3}$ frequency, indicating that the Co-C bond becomes weaker as the *trans* ligand becomes a stronger electron donor. These changes are also reflected in other bands, particularly ν_{CH} . Furthermore, there appears to be a relationship between these Raman frequencies and the ¹³C-¹H coupling constants for the axial methyl group. These relationships can be understood from a qualitative binding scheme.

The L-Co-CH₃ bending mode ($\delta_{\text{L}-\text{Co}-\text{CH}_3}$), the first assignment of $\delta_{\text{L}-\text{Co}-\text{CH}_3}$ for this general class of organocobalt compounds, involves almost exclusively the movement of the

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axial methyl group. The band could be useful as a probe for environmental effects on the Co-CH₃ bond and of the bending of the Co-C bond from the perpendicular direction (θ -bending).

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Supporting Information Available: Tables giving ¹H NMR data for newly reported compounds and elemental analyses and a figure showing FT-Raman spectra in the 1200–150 cm⁻¹ region for (3,5-Me₂PhS)Co((DO)(DOH)pn)R for R = CH₃ and CD₃ (3 pages). Ordering information is given on any current masthead page.

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