Zimmerman ascribed the regioselectivity to a greater spin density at the α-position of excited naphthalenes,[10] as has since been made more evident from measured hyperfine interactions in triplet naphthalenes.[12]

If this reaction of triplet naphthalenes involves weak charge-transfer (CT) interaction of the excited aromatic with the double bond followed by radical addition to form a five-membered ring, as appears to be the case for the similar singlet reactions[5] and for analogous triplet benzenes,[1,13] both steps would be affected by the relative unpaired spin density at the carbon bearing the alkenoxy group. As in all such two-step processes,[14] it must be determined which step is rate-determining. We first must deal with any consequences of the slightly lower triplet energy of **2a** relative to **1a**. This difference would not affect the first step, since **2a**'s reduction potential is lower than **1a**'s, but it might affect the second step if bond formation were becoming endothermic. However, the di-π-methane rearrangement has no such energy difference yet shows the same selectivity. We suggest that the low rate constants and the high regioselectivity indicate a low driving force for the first CT step, such that the second step (biradical formation) is facilitated only slightly by charge separation and therefore dominates rate constants. The fact that terminal alkyl substitution on the double bond slightly enhances k_q^{INT} while a 3-methyl depresses it is further evidence for radical cyclization character in the rate-determining step.[12,15] The values of k_q^{INT} deduced for **1a** and **2a**, 8×10^5 and 2×10^5 s^{-1}, are in exactly the same ratio as the spin densities at the 1- and 2-positions in triplet naphthalenes, 0.23 and 0.06,[12] respectively; the **1b**/**2b** rate ratio is twice as large.

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Near-Infrared Fourier Transform Raman Spectroscopy of Photolabile Organocobalt B_{12} and Model Compounds. 1. Detection of the Cobalt-Carbon Stretching Mode in the Solid State and in Solution

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The discovery that coenzyme B_{12} contains a stable Co-C bond[1] and the subsequent recognition of the homolysis of this bond in B_{12}-dependent catalysis[2] have stimulated a considerable amount of work aimed at elucidating factors promoting the enzymatic cleavage of this organometallic bond.[2] Valuable insights have come from structural studies of well-defined organocobalt B_{12} models by X-ray diffraction methods in the solid state and NMR spectroscopy in solution.[3] While vibrational spectroscopic techniques (i.e., IR and Raman) hold the promise of providing molecular information in both the solid state and solution, their utility in directly probing the nature of the Co-C moiety has been rather limited. Early IR studies of organocobalt complexes containing the $(DH)_2$ equatorial ligand system (DH = monoanion of dimethylglyoxime) revealed a Co-C-related absorption band.[4] Its assignment to the Co-C stretching mode remains controversial because the 320-cm^{-1} value is too low compared to those found in other organocobalt complexes and its isotopic shift (6 cm^{-1}, CH_3 vs CD_3) is significantly smaller than that expected for a stretching mode. Resonance Raman investigations of organocorrins with visible laser excitations inevitably ran into the trouble of photoinduced sample decomposition.[5] Even though photolysis could be alleviated by using the rapid-flow technique, the resonance Raman spectra obtained yielded no information about the Co-C bond.[6] A recent report[7] tentatively identified a Raman line at 506 cm^{-1} as the Co-CH_3 stretching mode in solid (4-*tert*-butylpyridine)$Co(DH)_2CH_3$, but the resonance Raman spectrum recorded with 514.5-nm excitation exhibited severe fluorescence interference and was further complicated by photolysis.[8]

We describe here the first application of near-infrared-excited Fourier transform (FT) Raman spectroscopy[9] to study photolabile organocobalt compounds. By using near-IR excitation at 1.064 μm, this new technique precludes electronic transitions and thus completely eliminates fluorescence interference and Co-C bond photolysis, problems encountered with visible laser excitations. As a result, high-quality FT-Raman spectra have been obtained for coenzyme B_{12} itself and for a number of organocobalt B_{12} models[10] of the type $LCo(DH)_2R$ (where L = neutral axial ligand, R = alkyl axial ligand) both in the solid state and in solution. Although interpretation of the B_{12} coenzyme spectrum requires additional studies, the nonresonant FT-Raman spectra of the models provide particularly rich information about the Co-C bond and allow several important issues concerning this organometallic bond to be addressed, such as conclusive identification of the Co-C stretching frequency, the trans ligand influence, and the environmental effect.

Figure 1 depicts FT-Raman spectra of $pyCo(DH)_2CH_3$ (py = pyridine) and its deuterated derivative, $pyCo(DH)_2CD_3$, obtained in the solid state. Three isotopically sensitive lines are detected. The symmetric stretching and deformation modes of the axial

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(10) Organocobalt complexes, $LCo(DH)_2CH_3$ (L = pyridine, H_2O, triphenylphosphine, trimethylphosphine, and tricyclohexylphosphine), were reported previously; see ref 3a.

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Table I. Co–C Stretching Frequencies in Some Organocobalt B_{12} Complexes of the Type $LCo(DH)_2R$ in the Solid State and in Chloroform

	L/R					
	py/CH_3	py/CD_3	H_2O/CH_3	PPh_3/CH_3	PMe_3/CH_3	$P(C_6H_{11})_3$/CH_3[a]
solid	522	492	512	491	498	505
solution	504	477	*b*	487	495	481
difference	18	15		4	3	24

[a] $P(C_6H_{11})_3$ = tricyclohexylphosphine. [b] Not determined due to its low solubility in chloroform.

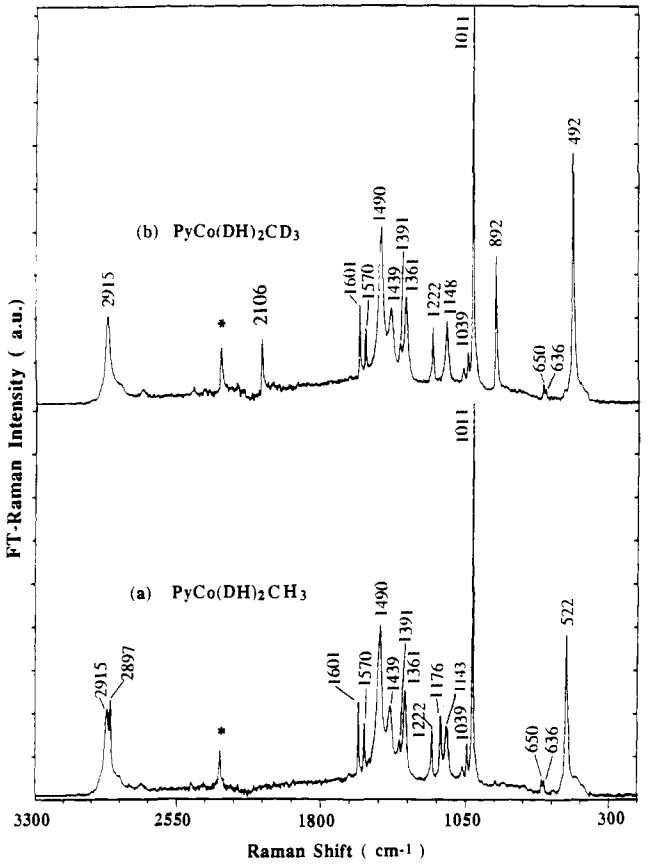

Figure 1. FT-Raman spectra of $pyCo(DH)_2CH_3$ and $pyCo(DH)_2CD_3$ obtained in the solid state. Conditions: laser power = 1.0 W; data acquisition time = 3.5 min; spectral resolution = 4.0 cm^{-1}. FT-Raman spectra were recorded by using a Bomem DA3.02 spectrophotometer equipped with a liquid nitrogen cooled InGaAs detector. Near-infrared excitation at 1.064 μm was provided by a Quantronix CW Nd:YAG laser. Scattered Raman photons were collected at 180° by using an ellipsoidal mirror. Solid polycrystalline samples were placed between two sapphire plates, while solution samples were put in a glass tube. (*): spurious lines.

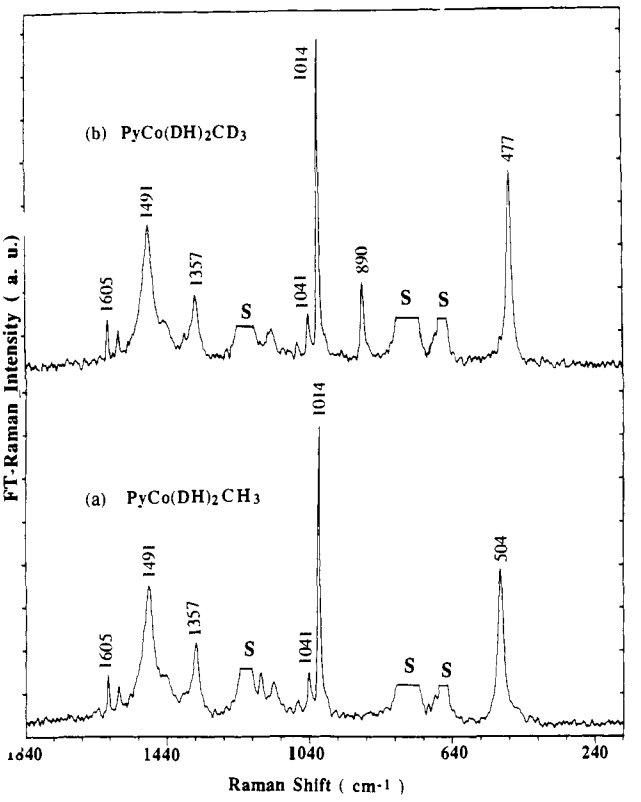

Figure 2. FT-Raman spectra of $pyCo(DH)_2CH_3$ and $pyCo(DH)_2CD_3$ obtained in chloroform solution. Data acquisition conditions were the same as in Figure 1. S: solvent Raman lines.

methyl group appear at 2897 and 1176 cm^{-1}, respectively, and their deuterium isotopic shifts to 2106 and 892 cm^{-1} are in agreement with theoretical calculations.[11] Attention now is focused on the third isotopically sensitive line at 522 cm^{-1}, since vibrational analysis indicates the absence of internal methyl vibrational modes in this region.[11] This prominent Raman line is conclusively assigned to the vibrational normal mode that consists predominantly of the Co–C stretching motion, on the basis of the following theoretical and experimental evidence: (1) the observed isotopic shift (30 cm^{-1}) is in close agreement with the theoretical value of 36 cm^{-1} calculated by approximating the methyl group as a point mass;[12] (2) this line completely disappears if the axial methyl group is absent, as in $pyCo(DH)_2Cl$; (3) a survey of B_{12} model complexes with N-, O-, and P-donor ligands reveals the correlation of such a Raman line with the presence of Co–CH_3 (see Table I). The FT-Raman results (Table I) also clearly show that the nature of the trans ligand profoundly influences the Co–C stretching frequency. For example, replacement of axial pyridine by triphenylphosphine (PPh_3) leads to a decrease of ca. 31 cm^{-1} in ν(Co–C). Furthermore, the trans ligand exerts a significant effect on the Raman scattering intensity of the Co–C stretching mode (a factor of ~6 from $H_2OCo(DH)_2CH_3$ to $P(Ph_3)Co(DH)_2CH_3$), as will be presented in detail in a forthcoming publication.

The ability to acquire highly resolved and accurate vibrational spectra for various B_{12} compounds also permits unambiguous assignments of axial pyridine and equatorial DH vibrational modes. Briefly, replacement of the axial H_2O ligand in $H_2OCo(DH)_2CH_3$ with pyridine results in the appearance of pyridine Raman lines at 1601, 1570, 1222, 1039, 1011, 650, and 636 cm^{-1}, while DH vibrational modes are located at 1490, 1439, 1361, and 1143 cm^{-1} (Figure 1a).

The sampling flexibility of Raman spectroscopy affords the possibility of obtaining structural information both in the solid state and in solution. In Figure 2 are shown FT-Raman spectra of saturated $pyCo(DH)_2CH_3$ and $pyCo(DH)_2CD_3$ solutions in chloroform. Interestingly, the Co–C stretching mode exhibits a large frequency difference (18 cm^{-1}) between solid and solution. In contrast, Kerr[13] found no difference in the stretching frequency of the Fe–C bond between solid and solution in pyFe(TPP)CO (TPP = tetraphenylporphyrin). Results shown in Table I establish that such a frequency downshift is a general phenomenon for B_{12}

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(12) The isotopic shift was calculated by using the conventional formula

$$\Delta\tilde{\nu} = \tilde{\nu}_{(Co-CH_3)}[1 - (\mu_{Co-CD_3}/\mu_{Co-CH_3})^{1/2}] = 36\ cm^{-1}$$

(13) Kerr, E. A. Ph.D. Thesis, Georgia Institute of Technology, 1984, p 187–188.

complexes of the type $LCo(DH)_2CH_3$. The effect of solvation on pyridine and DH vibrational modes, albeit considerably smaller, is also noticeable. This finding is highly significant in that it provides a vibrational spectroscopic probe for the effects of the environment on the Co–C bond. The determination of force constants useful in the derivation of a force field for molecular mechanics calculations on organocobalamins is now also feasible.

Work is in progress to assess systematically the importance of various factors affecting the Co–C vibration and to delineate interactions among axial and equatorial ligands.

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The Origin of Stereoselective Opening of Chiral Dioxane and Dioxolane Acetals: Solution Structure of Their Lewis Acid Complexes†

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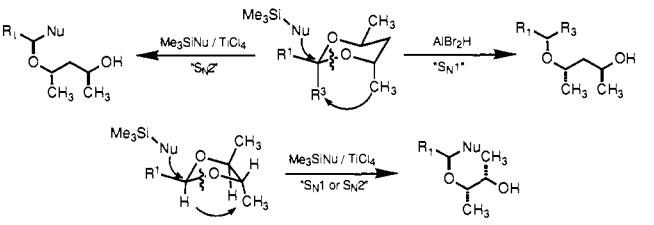
The reaction of acetals with silicon-containing nucleophiles (allylsilanes,[1] enol silanes,[2] TMSCN,[3] silyl acetylenes[4]) has proven to be a powerful method for carbon–carbon bond formation.[5] Based on Johnson's landmark studies of acetal-initiated, cationic polyolefin cyclizations,[6] both Kishi[7] and Johnson and Bartlett[8] reported remarkable levels of stereoselection in the Lewis acid promoted, nucleophilic opening of chiral dioxolane and dioxane acetals derived from optically active 2,3-butanediol and 2,4-pentanediol. In recent years, the reaction has been intensively studied and optimized.[9]

Early rationalization of the unidirectional opening of the chiral dioxane acetals focused on relief of strain due to the axial standing methyl group[10] or related van der Waals interactions in the dioxolane,[8] Scheme I. While this explanation was supported by the selective reduction of ketone acetals by Richter[11] and Yamamoto,[9c,12] it failed to explain the selective opening of monosubstituted dioxanes in the same sense,[9a,10,13] Scheme II. The current rationale proposes that the reaction occurs through an invertive S_N2-type substitution on an intermediate Lewis acid complex or ion pair in which the breaking bond is attached to the sterically most accessible oxygen.[10,9c] Because of our interest in the mechanism of this reaction[14,15a] and in the stereochemical significance of Lewis acid–base complexes,[15b,c] we undertook an extensive study of the solution structure of Lewis acid acetal complexes of this type.

Our study involved both aliphatic and aromatic aldehyde acetals of acyclic (Me) and cyclic (five and six membered) structure with and without ring substituents. Five different Lewis acids were examined, but only the results with BF_3(g) and the cyclic acetals **1–5** (Chart I) will be discussed here. Variable-temperature ^{13}C NMR analysis of the complexes was most informative.[16] Addition

Scheme I



Scheme II

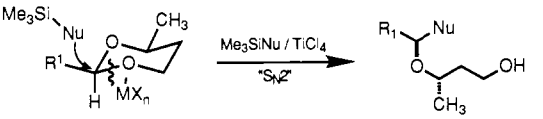


Chart I

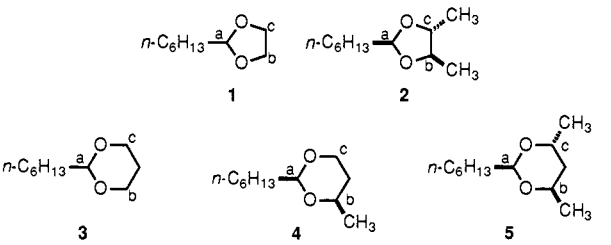
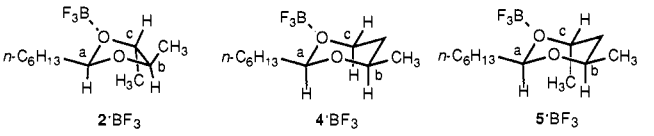


Chart II



† Dedicated to the memory of Roger Adams in the centennial year of his birth, 1989.

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(16) All ^{13}C spectra were recorded at either 75.5 or 125.0 MHz, using temperature-calibrated probes. All resonances were assigned by 2D NMR methods. See Supplementary Material.

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