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.

Acknowledgment. We are indebted to Dr. Kai C. Su for allowing us to use the FT-Raman facilities at the Advanced Technology Division, CIBA-Vision, Alpharetta, GA. The work was supported in part by National Institutes of Health Grants GM18894 (N.-T.Y.) and GM29225 (L.G.M.).

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

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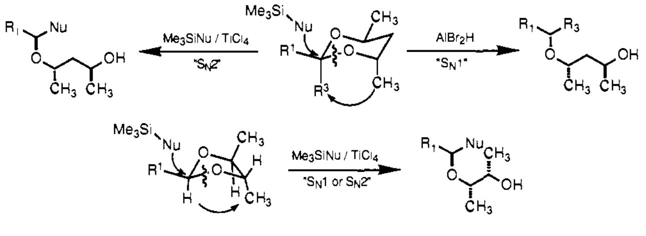
The reaction of acetals with silicon-containing nucleophiles (allylsilanes,[1] enol silanes,[2] TMSCN,[3] silyl acetylenes[4]) has proven to be a powerful method for carbon–carbon bond formation.[5] Based on Johnson's landmark studies of acetal-initiated, cationic polyolefin cyclizations,[6] both Kishi[7] 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]

Scheme I



Scheme II

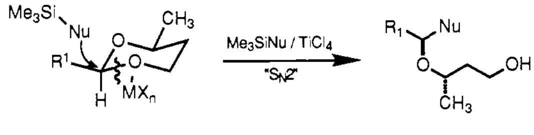


Chart I

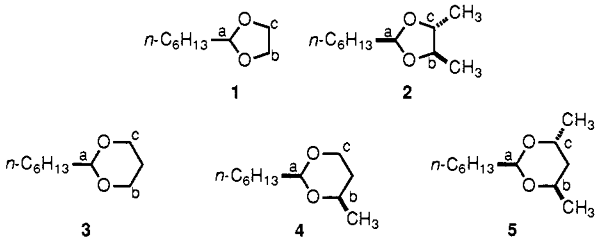
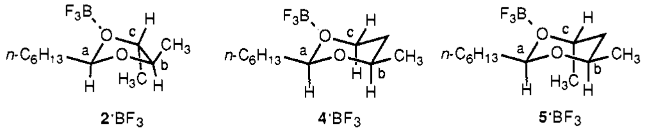


Chart II



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

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

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0002-7863/89/1511-9258$01.50/0

Table I. Summary of Spectroscopic Data for BF_3 Complexes of **1**–**5**

			^{13}C $\Delta\delta$,[c,d] ppm			NOE (saturate/observe), %		
complex	T,[a] °C	solvent[b]	C(a)	C(b)	C(c)	HC(a)/HC(b)	HC(b)/HC(a)	HC(a)/HC(c)
1·BF_3	−80	$CDCl_3/CD_2Cl_2$	8.1	2.1	2.6			
2·BF_3	−80	CD_2Cl_2[e]	7.4	−0.7	5.9			
2·BF_3	−80	toluene-d_8	6.4	−0.4	3.2	0.8[f]		
3·BF_3	−95	$CDCl_3/CD_2Cl_2$	10.1[g]	5.6[g]	5.6[g]			
4·BF_3	−95	$CDCl_3/CD_2Cl_2$	10.9	2.2	6.8			
5·BF_3	−95	CD_2Cl_2	11.0	1.9	11.4	−8.5	−6.8	−2.2[h]
5·BF_3	−95	*F*-toluene/CD_2Cl_2	*i*	2.5	11.4	−13.2	−14.8	−3.0[h]

[a] Calibrated probe temperature for spectra of both ligand and complex. [b] Solvent for both ligand and complex. [c] $\Delta\delta = \delta(\text{complex}) - \delta(\text{neutral})$. [d] For assignments, see Charts I and II. [e] Spectrum of **2** taken in $CDCl_3/CD_2Cl_2$. [f] Enhancement in aromatic acetal, ref 18. [g] Resonances in complex very broad; C(b) and C(c) not resolved. [h] Rough estimates, see ref 22. [i] Obscured by solvent in complex.

of 1.0 equiv of $BF_3(g)$ to **1** at −80 °C resulted in the near-quantitative formation of a new species characterized by a strong downfield shift of C(a), Table I. Interestingly, the ring methylenes are anisochronous, which together with the presence of a trace of **1**, implies an unsymmetrical structure for this complex, which is static on the NMR time scale. The chiral dioxolane acetal **2** formed a *single*, *static 1:1 complex* at −80 °C with 1.2 equiv of $BF_3(g)$, as evidenced by a single set of diastereotopic methine carbons, one of which is significantly more downfield shifted (spectra A and B, Figure 1; Table I). We assume that this is the methine attached to the complexed oxygen. In toluene-d_8, the same species is formed, and it displayed well-separated resonances for the ring protons, aiding assignment of structure. A HETCOR spectrum of **2**·BF_3 (toluene-d_8) established the connection between the lower field methine C(c) (82.9) and HC(c) (3.92) and between the higher field methine C(b) (80.0) and HC(b) (3.02) (Chart II). Unfortunately, no difference NOE enhancements could be detected for **2**·BF_3 in any solvent.[17] However, a small (0.8%) NOE enhancement could be observed between HC(a) and HC(b) in a related aromatic acetal.[18] Thus, we *tentatively* assign the structure of **2**·BF_3 as shown in Chart II with the BF_3 complexed to OC(c).

The dioxanes were expectedly weaker Lewis bases,[19] and a temperature of −95 °C was required to observe static complexes. For **3**, even this temperature gave broadened resonances due to dynamic exchange. Fortunately, the substituted dioxanes **4** and **5** were well behaved. In the presence of 1.2 equiv of $BF_3(g)$, **4** formed a single complex,[20] characterized by significant downfield shifts of C(a) and C(c) (spectra C and D, Figure 1; Table I). The assignment of structure for this complex (**4**·BF_3) is shown in Chart II. The unique complexation to the OC(c) was easily established by APT spectra, which confirmed that the more downfield shifted ring resonance is a methylene.

The disubstituted dioxane **5** also formed a single complex upon addition of 1.2 equiv of $BF_3(g)$ at −95 °C.[20] The difference in downfield shift of the ring carbons is much larger than in **2**·BF_3, with the methine attached to the complexed oxygen moving 11.4 ppm downfield (spectra E and F, Figure 1; Table I). The assignment of structure for **5**·BF_3 follows similar logic as for **2**·BF_3 but with a higher confidence level. A HETCOR spectrum established the connection between the lower field methine C(c) (79.1) and HC(c) (5.20) and between the higher field methine C(b) (69.0) and HC(b) (4.16), with C(c) obviously bonded to the complexed oxygen. The results of difference NOE spectra taken in two solvents at −95 °C clearly display a much stronger (negative)[21] enhancement from HC(a) to HC(b).[22] Thus HC(b) must be in the axial position, requiring that BF_3 is coordinated to the oxygen bonded to the methine bearing the axial methyl group (OC(c)), Chart II. Finally, it is noteworthy that, at most, only traces of open, oxocarbenium ions were ever detected in any of these spectra.

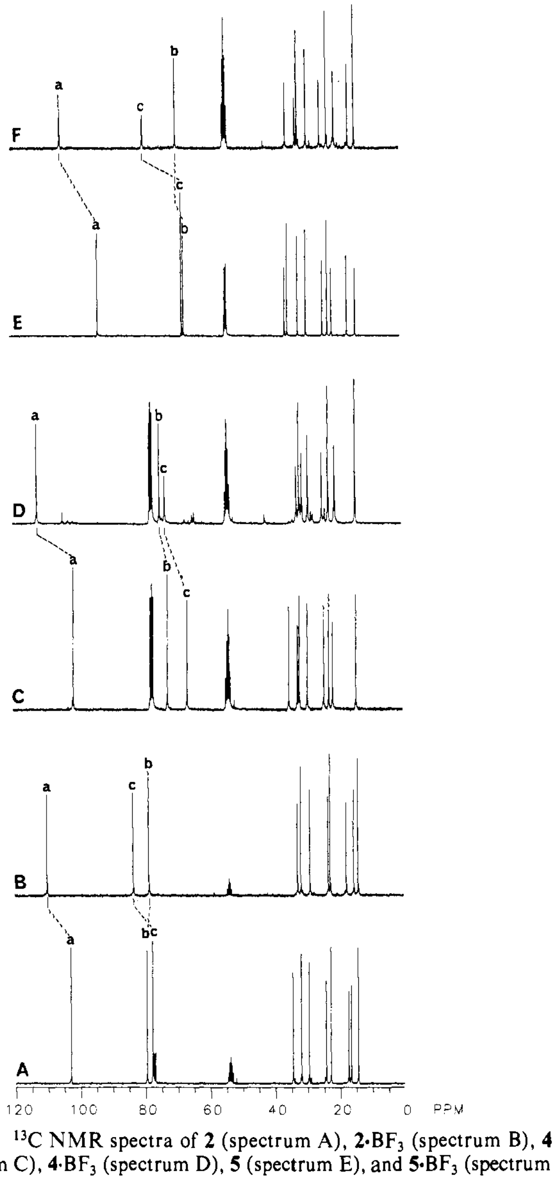

Figure 1. ^{13}C NMR spectra of **2** (spectrum A), **2**·BF_3 (spectrum B), **4** (spectrum C), **4**·BF_3 (spectrum D), **5** (spectrum E), and **5**·BF_3 (spectrum F).

The unidirectional complexation of **2**, **4**, and **5** is striking in magnitude and structural similarity. Further, it is in agreement with the observed stereochemical course of opening. While easily explained on steric grounds for **4**, the strong biases in **2** and **5** merit more careful analysis. We assume that upon coordination the oxygen atom rehybridizes toward sp^2, giving a planar or weakly pyramidal complex, by analogy to the structure of Lewis acid–ether complexes.[23] In this trigonal-like configuration, the BF_3

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(17) Uncomplexed **2** showed only a 1% NOE at −80 °C.

(18) *d,l*-1-(3,5-Dimethylphenyl)-3,4-dimethyldioxolane.

(19) $\Delta H^\circ_{BF_3}$ (298 K): THF = 21.6 kcal/mol, THP = 20.4. Anomeric effects are also expected to reduce the basicity of dioxanes more. Maria, P.-C.; Gal, J.-F. *J. Phys. Chem.* **1985**, *89*, 1296.

(20) Equilibration of this complex required 6–8 h at −80 °C.

(21) A negative NOE is expected at low temperatures in high-viscosity media. Neuhaus, D.; Williamson, M. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*; VCH: Weinheim, 1989; Chapter 2.

(22) The NOE for HC(a)/HC(c) could not be accurately determined due to the proximity of the resonances.

experiences stronger eclipsing interactions with the equatorial group and thus prefers to coordinate next to an axial substituent (Chart II).[24]

In summary, we have demonstrated a strong preference for complexation of unsymmetrical cyclic acetals and have provided an experimentally based explanation for the unidirectional ring opening of these species.

Acknowledgment. We gratefully acknowledge financial support by grants from the National Science Foundation (NSF CHE 8818147, CHE 8515371, and Presidential Young Investigator Award (1985–1990)) and A. P. Sloan Foundation (1985–1989). We thank Professor Eric N. Jacobsen for his technical advice on handling BF$_3$ and Dr. Benjamin Shoulders (Texas–Austin) for advice on low-temperature, difference NOE experiments.

Supplementary Material Available: Full characterization of **1–5** along with COSY and HETCOR spectra for **2**, **2**·BF$_3$, **5**, and **5**·BF$_3$ and APT spectra for **4**·BF$_3$ (12 pages). Ordering information is given on any current masthead page.

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Crystal Structure of the Expanded-Metal Compound ^{7}Li(ND$_3$)$_4$

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Received June 16, 1989

The structure of the expanded-metal compound Li(ND$_3$)$_4$ has been one of the most important and elusive unsolved problems in metal–ammonia chemistry.[1,2] This unique compound has the lowest melting point of any known metal (89 K), possesses unusual electrical[3] and magnetic[4] properties, and is just on the metallic side of the metal–nonmetal transition.[5] Mammano and Sienko were the first to recognize that 20 mol% metal solutions of lithium in ammonia formed a stable crystalline solid below 90 K.[6] They concluded that there were two crystalline phases: a cubic phase with $a = 9.55$ Å, stable between 82 and 89 K, and a hexagonal phase with $a = 7.0$ Å and $c = 11.1$ Å existing below 82 K. These distinct phases will be referred to as phase I and phase II, respectively. Chieux et al.[7] performed several low-temperature neutron powder diffraction (NPD) data collections on both ^{7}Li(NH$_3$)$_4$ and ^{7}Li(ND$_3$)$_4$ over the range 3–85 K using the D1B spectrometer at the Institut Laue-Langevin. They found that the protonated compound changed from phase I to phase II upon cooling from 85 to 60 K, which corroborates the previous X-ray studies, although the assignment of the lattice for phase II was different. However, no phase change was observed in the range 60–85 K for the deuterated compound. The diffraction patterns indicated that both phases were body-centered cubic (bcc), with $a = 15.03$ Å at 85 K and $a = 14.93$ Å at 60 K. This isotope effect has been verified by careful thermodynamic measurements.[8] Below 25 K, additional reflections appear in the diffraction patterns of ^{7}Li(ND$_3$)$_4$ corresponding to the formation of a superstructure having a period $2a$ (phase III), which coincides with the onset of antiferromagnetic behavior below about 25 K.[5,9] Although the study of Chieux et al.[7] has been the most informative structural investigation of this intriguing compound to date, no detailed structural analysis could be performed on the data due to overwhelming preferred orientation, as evidenced by the poor reproducibility of peak intensities (>30%). Recently, Stacy and Sienko[9] reevaluated all previous structural data. They found that the X-ray data for both phases I and II are better indexed as a single bcc phase and suggested the probable space group, $I\bar{4}3d$, as well as a hypothetical structure. The elucidation of the structure of ^{7}Li(ND$_3$)$_4$ above the antiferromagnetic transition temperature is the subject of this investigation. These results confirm the idealized model proposed by Stacey and Sienko.[9]

Table I. Fractional Coordinates and Isotropic Thermal Parameters for Li(ND$_3$)$_4$[a]

atom	x	y	z	U_{iso}
Li	1094 (6)	1094	1094	1.4 (4)
N(1)	2064 (2)	2064	2064	1.8 (1)
D(1)	2614 (4)	1749 (3)	2229 (3)	5.8 (2)
N(2)	1697 (2)	−79 (2)	1328 (2)	2.8 (1)
D(11)	2324 (4)	−119 (4)	1545 (3)	5.2 (2)
D(12)	1311 (3)	−472 (3)	1689 (3)	3.5 (1)
D(13)	1794 (3)	−379 (4)	718 (4)	5.8 (2)

[a] Fractional coordinates are listed in 10^4 Å. Isotropic thermal parameters are given in 10^2 Å^2.

The sample was prepared by condensing sodium-dried ND$_3$ (Cambridge Isotope Laboratories, 99.5%) into 7.5 cm × 1.2 cm i.d. quartz sample cells containing ^{7}Li (Oak Ridge, 99.94%), to yield 3.84 g of ^{7}Li(ND$_3$)$_{4.0}$. In addition, an ample amount of quartz wool was included in the sample cell to inhibit large crystal growth. Time-of-flight (TOF) NPD data were collected on the general purpose powder diffractometer[10] at IPNS. Initial data collections showed a high degree of preferred orientation, i.e., some reflections were present in some detectors and not in others. Most of this effect was eliminated by rotating the sample in 5° intervals (360° total coverage) while data were collected for 5 min/interval.

The structure was refined by using the generalized structure analysis system (GSAS).[11] The space group was uniquely determined to be $I\bar{4}3d$, with $a = 14.8131$ (28) Å. However, the coincidence of reflections caused by the bcc lattice hampered Patterson and direct-methods solution attempts. After considering how this tetrahedrally shaped molecule would have to fit into the asymmetric unit according to the constraints imposed by space-group requirements, we decided to begin refinement by using rigid bodies. An idealized Li(ND$_3$)$_4$ unit was assembled while the Li atom and one N atom of an ND$_3$ group were kept on the body-diagonal axis, as required by space-group symmetry. Fractional coordinates were refined, while isotropic temperature factors were held constant at 0.06 Å^2. After this refinement converged, the reflections for interplanar spacings >1.4 Å fit well, but those <1.4

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