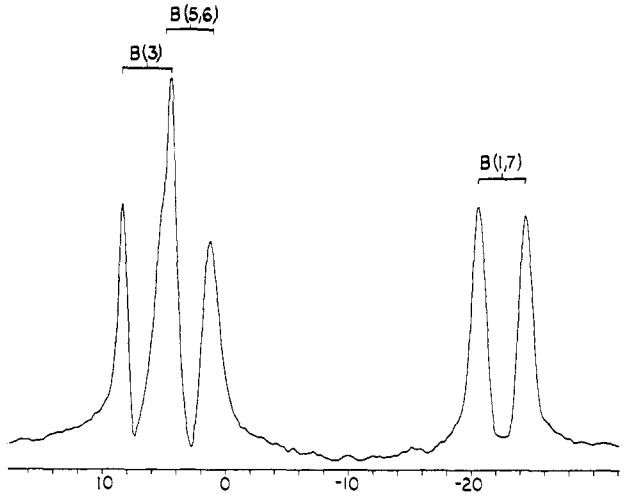

Figure 3. Projection on the y axis of Figure 2 showing the ^{11}B doublets due to ^{11}B–^{1}H coupling.

is performed on this matrix to give a 2D NMR spectrum having orthogonal frequency axes (^{11}B and ^{1}H), simultaneously displaying the chemical-shift spectra of both ^{11}B and ^{1}H. A peak in the "map" will correspond to a BH pair (or part of a BH pair if no decoupling is employed) with chemical shifts indicated on the appropriate axes.

In Figure 2 the spectrum of the *closo*-carborane 2,4-$C_2B_5H_7$ is shown, which to our knowledge represents the first reported ^{11}B–^{1}H 2D NMR experiment. The compound selected is typical of boron cage systems in that it exhibits large terminal B–H scalar coupling and minor long range (>1 bond) coupling. The resolution of ^{11}B signals over two distinct axes is clearly visible; since no decoupling is employed, the BH pairs appear as three doublets of quartets having relative areas of 2:2:1 corresponding to the three distinct boron environments in the molecule.

The two components of each of the doublets appearing in the boron dimension are 180° out of phase, although this is masked in the absolute value spectrum. This effect arises owing to the progressive and regressive nature of the modulation by the protons which allows no net transfer of magnetization between the spin systems. The 1:−1 intensity pattern can be explained by classical spin pumping arguments used previously to account for the ^{13}C multiplets of methyl and methylene groups.[5,11]

One striking feature of the spectrum is the approximate 3:1:1:3 intensity pattern for the ^{11}B-coupled ^{1}H quartets, which differs from the familiar 1:1:1:1 pattern ordinarily seen for a nucleus coupled to a single spin $I = 3/2$ nucleus. Density matrix analysis[12] predicts a 3:1:−1:−3 pattern for a coupled ^{11}B–^{1}H pair of spins if 90° pulses are applied to both ^{11}B and ^{1}H nuclei.

Projection of the 2D spectra on the ^{11}B axis (Figure 3) and the ^{1}H axis (Figure 4b) produce 1D spectra which resemble the normal NMR spectra. However, an important difference exists between the proton projection and the normal 1D NMR of the same sample (Figure 4a): the 2D projection has eliminated the C–H protons (δ 5.5), organic impurities in the sample (1.5–3.0), and multiplets due to ^{10}B–^{1}H decoupling; the reason, of course, is that only ^{11}B–^{1}H pairs are observed in this type of experiment.

It is evident that 2D NMR spectroscopy is capable of resolving heavily overlapped ^{11}B signals and of correlating the resonances of individual ^{11}B and ^{1}H nuclei which are scalar-coupled to each other. A further advantage is that ^{1}H spectra are simplified by elimination of resonances of protons (e.g., in organic substituents and in solvents) that are not coupled to boron. Modifications of this procedure, such as decoupling

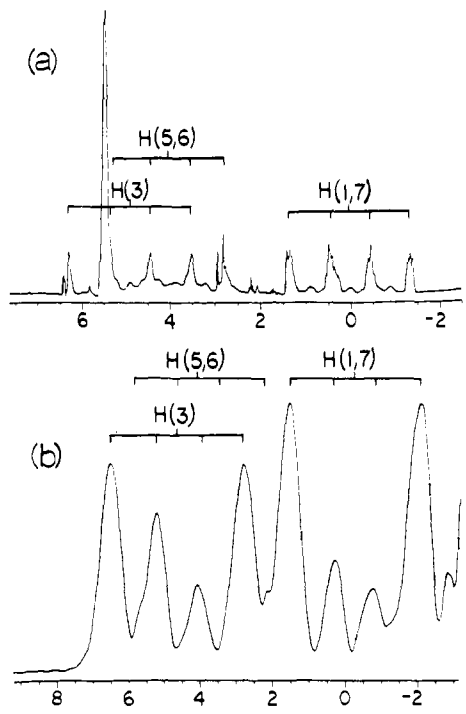

Figure 4. ^{1}H NMR spectra of 2,4-$C_2B_5H_7$: (a) 1D spectrum at 200 MHz; (b) projection on the x axis of Figure 2. For assignments see ref 13.

experiments, are expected to increase still further the information that can be extracted by this technique.

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Preferential Anion Binding to the Lactim Tautomers of 2-Hydroxypyridines

Sir:

Considerable attention has been devoted to the lactim-lactam tautomeric equilibria;[1-3] in part this is because the Watson-Crick model for nucleic acid structure and function involves specific base pairing of the *lactam* forms of the hydroxypyrimidines and hydroxypurines. Indeed, these are

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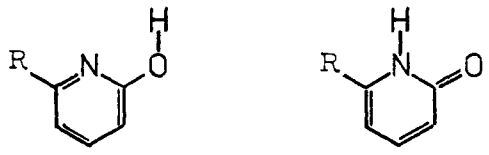

lactim lactam

R = -Cl, -OMe

commonly by far the most abundant species in solution. However, it is now well known that the position of the equilibrium is highly sensitive to solvent.[1-3] The 2-hydroxypyridines[4,5] and some hydroxypyrimidines[5] predominate in the vapor phase. It seems that preferential solute-solvent interactions with the lactam are responsible for such behavior. Indeed, self-association[6] or stoichiometric associations with water,[7] alcohols,[8] carboxylic acids,[9] and cations[10] have been shown to favor the lactam tautomers. In this paper we report the effect of halide ion binding which shifts the tautomeric equilibrium in favor of the *lactim* form, at least for 2-hydroxypyridines possessing an electroattractive substituent at carbon 6.

The UV spectra of 2-hydroxypyridines usually display two absorption bands characteristic of the lactam tautomer ($\lambda \sim 310$ nm) and the lactim tautomer ($\lambda \sim 280$ nm). Therefore, the marked spectral changes observed when tetraalkylammonium halides are added to solutions of tautomerizable 2-hydroxypyridines in polar aprotic solvent (Figure 1) can reasonably be attributed to a shift of the tautomeric equilibrium toward the lactim form. It is unlikely that a modification of the dielectric properties due to salt addition influences the lactim-lactam equilibria since equilibrium constants remain in the same range in aprotic solvents of different polarities.[7]

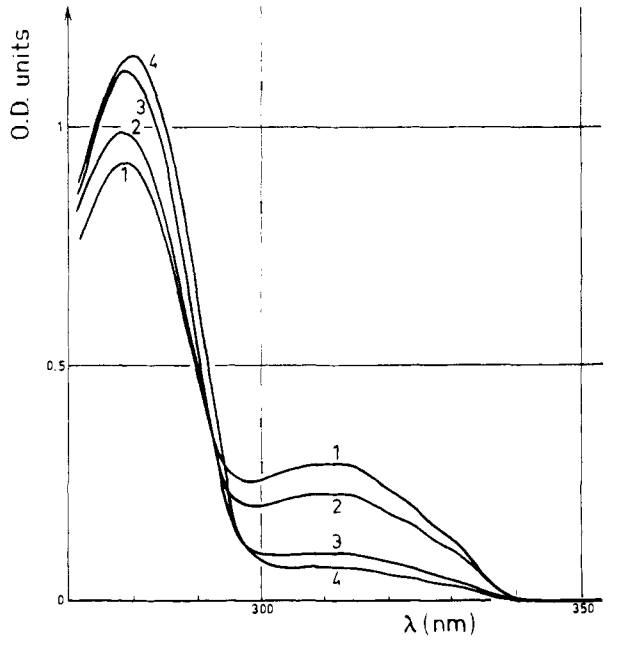

Figure 1. Influence of tetrabutylammonium halides on the UV spectrum of 6-methoxy-2-pyridone (1.7×10^{-4} M) in acetonitrile. Absorption in the 300-350-nm range is attributed to the lactam tautomer, whereas the lactim tautomer displays an absorption maximum near 280 nm. The lactim is favored in the presence of the salts: $N(Bu)_4^+I^-$ (0.25 M) (curve 2), $N(Bu)_4^+Br^-$ (0.23 M) (curve 3), and $N(Bu)_4^+Cl^-$ (0.06 M) (curve 4). In the presence of $N(Bu)_4^+ClO_4^-$, the spectrum is the same as in the pure solvent (curve 1). Spectra are recorded at room temperature in 1-cm path-length cells.

Table I. Anion Binding Constants Determined from Eq 2[a]

compd		Cl^-	Br^-	I^-
6-methoxy-2-pyridone	K_C	1 ± 0.5	0.3 ± 0.15	≤ 0.05
	K_E	50 ± 2	11 ± 1	2 ± 0.2
6-chloro-2-pyridone	K_C	5 ± 1	3 ± 0.5	
	K_E	65 ± 3	18 ± 1	

[a] Data given in M^{-1} for acetonitrile solutions at room temperature.

Consequently, the observed effects should result from specific salt interactions with the lactim or the lactam tautomers. In the polar media used, salts are dissociated. Therefore, since the bulky tetraalkylammonium (methyl and *n*-butyl) cations have no influence on the UV spectra,[10] our results are interpreted in terms of specific anion binding and analyzed quantitatively by assuming that this interaction modifies little or not at all the extinction coefficients. An apparent tautomeric equilibrium constant, K_{ap}, is determined from the UV spectra:

$$K_{ap} = \frac{(\text{lactam}) + (\text{lactam}, \alpha\ \text{anion})}{(\text{lactim}) + (\text{lactim}, \beta\ \text{anion})} = K_T \left[\frac{1 + K_C(\text{anion})^\alpha}{1 + K_E(\text{anion})^\beta}\right] \quad (1)$$

K_T = (lactam)/(lactim) is equal to the tautomeric equilibrium constant measured in the absence of salt (the pure solvent), α and β are the stoichiometric numbers, and K_C and K_E are association constants[11] of the anion with the lactam and the lactim tautomer, respectively. If $\alpha = \beta = 1$, eq 1 becomes

$$\frac{K_{ap} - K_T}{(\text{anion})} + K_E \cdot K_{ap} = K_T \cdot K_C \quad (2)$$

which is verified experimentally and from which K_C and K_E may be determined. Thus, 1:1 stoichiometric ion-molecule associations of the halide anions with *both* the lactim and the lactam tautomers are held responsible for the observed phenomena. Results for two 2-hydroxypyridines which display easily observable lactim-lactam equilibria are given in Table I. As interactions appear stronger with chloride and in the order $Cl^- > Br^- > I^-$, we suggest that this is associated with the decreasing H-bond acceptor character of the anions in this group.[12]

High salt concentrations are known to have dramatic influence on DNA physicochemical properties in aqueous solutions, and it has been suggested[13] that this is due to the formation of specific complexes between the anions and the nucleotide bases.[14] The order of the anion-binding strength is the reverse of that observed here, but solvation by water is well known to invert the reactivity of anions, whereas under our present conditions these are "naked". One cannot tell whether this anion binding will increase the lactim proportions or not, since the solvent influences upon nucleic acid-base tautomeric equilibria seem somewhat different[15] from those on 6-substituted 2-hydroxypyridines. We believe that more detailed studies in this area would help to increase our knowledge of ion-molecule interactions and consequences on the chemical reactivity of tautomers.[16]

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(11) Defined as
$$K_C = \frac{(\text{lactam, } \alpha \text{ anion})}{(\text{lactam}) \cdot (\text{anion})^{\alpha}} \text{ and } K_E = \frac{(\text{lactim, } \beta \text{ anion})}{(\text{lactim}) \cdot (\text{anion})^{\beta}}$$
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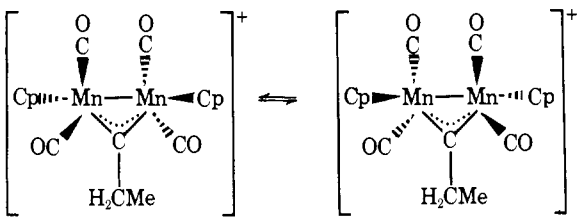
Nucleo- and Electrophilicity of $(C_5H_5)_2Mn_2(CO)_4(\mu\text{-}\eta^1\text{-}CCH_2)$. New Paths to Carbyne and Allene Ligands

Sir:

We have recently reported[1] the synthesis and structure of $Cp_2Mn_2(CO)_4(\mu\text{-}\eta^1\text{-}CCH_2)$, Ia, a rare example of a complex of the unsubstituted vinylidene ligand. This complex is unusual in that the carbon–carbon double bond of the vinylidene ligand does not donate directly to either metal atom. We report here the results of a study of the nucleophilic and electrophilic reactivity of this bond.[2]

Compound Ia offers a variety of sites for addition of H^+: the Mn—Mn bond, the carbonyl oxygen, the vinylidene C=C bond, and the magnanese-vinylidene σ bond. Addition of 4 equiv of CF_3CO_2H to compound Ia in CD_3CN results in complete conversion into violet $[HCp_2Mn_2(CO)_4CCH_2]$-O_2CCF_3, IIa, characterized by sharp ^1H NMR singlets at δ 5.27 (Cp, 10 H) and 4.45 (3 H); no hydride resonance is evident.[3] The ^1H NMR of a CD_3CN solution formed by addition of 1 equiv of CF_3CO_2H to Ia exhibits four broad resonances due to proton exchange of IIa with Ia.[4] To further confirm that the protonation site is the β carbon of the vinylidene bridge, we have examined an alternative substrate. The dimer $Cp_2Mn_2(CO)_4(\mu\text{-}CCHMe)$,[5] Ib, exhibits inequivalent cyclopentadienyl rings up to 100 °C since the asymmetrically substituted vinylidene bridge does not participate in any facile dynamic process. Addition of 4 equiv of CF_3CO_2H to this dimer in CD_3CN forms IIb, characterized by a cyclopentadienyl *singlet* (δ 5.28) and an ABX_3 ethyl pattern (CHH′ at 4.84 and 4.36, with CH_3 at 1.61). The same behavior is observable in CD_2Cl_2 or CD_3NO_2. The diastereotopic character of the methylene protons in IIb indicates that the enantiomerization process shown in Scheme I is slow. Taken together, these results demonstrate a new synthesis of the μ-carbyne unit by β addition to a vinylidene bridge

Scheme I



$$[CpMn(CO)_2]_2(\mu\text{-}CCHR) + H^+ \rightarrow [CpMn(CO)_2]_2(\mu\text{-}CCH_2R)^+ \quad (1)$$

This method contrasts with all previous carbyne syntheses, which involve *removal* of one or more groups from the α carbon.[6] The extension of this new procedure to the terminal vinylidene–terminal carbyne transformation (IV → V) merits further study as a step in the sequential conversion[2] of coordinated acetylide into carbyne (III → V), using electrophiles E^+.

$$[M\text{—}C\equiv CR]^{n+} \xrightarrow{E^+} [M{=}C{=}C(E)R]^{n+1} \xrightarrow{E^+} [M\equiv C\text{—}CE_2R]^{n+2} \quad (2)$$
III IV V

The acidity of the β hydrogens in the cationic carbyne complexes IIa and IIIb, shown by their exchange with $CF_3CO_2^-$ and with I, allows a direct competition experiment (eq 3). Surprisingly, combination of equimolar Ia and IIb in

$$[mn\text{—}mn(\mu\text{-}CCH_2CH_3)]^+ SO_3CF_3^- + mn_2CCH_2 \rightleftharpoons mn_2CC(H)CH_3 + [mn\text{—}mn(\mu\text{-}CCH_3)]^+ SO_3CF_3^- \quad (3)$$
IIb Ia Ib IIa

mn = $CpMn(CO)_2$

CD_3NO_2 results in complete conversion into Ib and IIa; steric factors appear to control this equilibrium.

Complex Ia also reacts with strong nucleophiles. Treatment of Ia with $LiEt_3BH$ in THF,[7] followed by reaction with methyl iodide, yields two carbonyl compounds. Chromatography on Florisil (toluene eluant) brings down a green and then a maroon band (VI). The ^1H NMR spectrum of compound VI, $Cp_2Mn_2(CO)_3C_3H_4$,[8] establishes equivalent cyclopentadienyl rings, but two types of C_3H_4 protons in equal numbers. Remarkably, the IR spectrum of VI suggests the presence of a bridging carbonyl. The exact nature of compound VI, established by X-ray crystallography,[9] is evident in Figure 1. The molecule has approximate twofold rotational symmetry, being comprised of *trans*-CpMnCO groups bridged by both CO and allene. The allene fragment in VI is bent at an angle of 146.5°. This work is the first accurate structural definition of a sym-

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