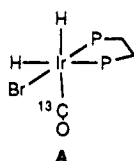


produced by coherent transfer of the reactant parahydrogen spin state, $\alpha\beta$ - $\beta\alpha$.¹⁸ A striking feature of the present study is the observation that larger enhancements result from less sample. Thus, a 4.6-mg sample of IrBr(CO)(dppe) in C₆D₆ under 3 atm of p-H₂ at a probe temperature of 342 K gives hydride resonances that are 40-fold greater in relative total signal area than unpolarized IrH₂Br(CO)(dppe), but 95-fold enhancements are produced with 0.3 mg of complex.^{2,19} With IrCl(CO)(PPh₃)₂ (Vaska's complex), the oxidative addition process is less facile than for the dppe analog; nevertheless, 40-fold enhancements were observed with 1 mg under the same conditions.

The non-Boltzmann spin populations of the hydride resonances were transferred to ¹³C and ³¹P nuclei in the product complexes via polarization-transfer pulse sequences with striking results. When a 3-mg sample of labeled IrBr(¹³CO)(dppe) in C₆D₆ under p-H₂ was examined at 342 K using the INEPT+²⁰ sequence, the spectrum shown in Figure 1a was obtained after 32 scans. The ¹³C carbonyl resonance of IrH₂Br(¹³CO)(dppe), A, exhibits a large

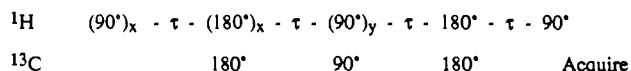


trans proton coupling (47.8 Hz), normal cis couplings to the nearly equivalent phosphine donors (4.3 and 3.3 Hz), and an extraordinary antiphase coupling to the cis hydride nucleus of 5 Hz. For comparison, Figure 1b shows a 256-transient ¹³C{INEPT+} NMR spectrum of the same sample with n-H₂. On the basis of the observed 158-fold enhancement in signal strength, a single scan collected in the presence of p-H₂ is equivalent to 25 000 scans acquired under normal hydrogen (n-H₂).^{21,22} In a different experiment, using the same INEPT+ pulse sequence, IrCl(¹³CO)(PPh₃)₂ (6 mg) and p-H₂ produced a ¹³C carbonyl resonance that was 25-fold stronger in S/N than that produced with n-H₂.

The observation that smaller amounts of sample yielded larger ¹H resonance amplification suggested the possibility of observing the ¹³C carbonyl resonance using unlabeled complex under p-H₂. This was indeed the case. Specifically, the spectrum in Figure 1c corresponds to that of a 0.3-mg sample of IrH₂Br(CO)(dppe) under p-H₂ after only 32 transients at 342 K. Thus, less than 1 mg or 1.5 μmol of complex with naturally abundant ¹³C in the carbonyl ligand yields a spectrum in less than 2 min of spectrometer time, a truly amazing degree of signal amplification. The magnitude of ¹³C enhancement in these two experiments (Figure 1b,d) can be compared through their S/N ratios after normalization for ¹³C label content. Calculation thus shows that the ¹³C resonance amplification observed with the unlabeled sample was really 18 times larger than that produced with the more concentrated labeled counterpart.

From a vector analysis, we can follow the effect of the INEPT+ pulse sequence on the non-Boltzmann spin population of the hydride ligands formed using p-H₂.²³ For the purposes of this analysis, we can ignore coupling to ³¹P, thereby simplifying the nuclear spins of IrH₂Br(¹³CO)(dppe) to an AMX system. Without

³¹P coupling, the spectrum in Figure 1a would consist of a doublet of antiphase doublets with the larger splitting due to $J_{\text{CH}(\text{trans})}$ (47.8 Hz) and the smaller to $J_{\text{CH}(\text{cis})}$ (5 Hz). Figure 2a shows the spin function energy levels for the AMX system of A with spin labels corresponding, respectively, to H_{trans}, H_{cis}, and ¹³C. The overpopulation of $\alpha\beta$ and $\beta\alpha$ ¹H spin states arises from the oxidative addition of p-H₂; at this point, there is no enhancement of ¹³C resonances, as the inverted populations are between levels relating to ¹H transitions. Application of the pulse sequence



where τ is $(4J_{\text{CH}(\text{trans})})^{-1}$ leads to the relative spin populations shown in Figure 2b when acquisition commences. Inverted populations now exist between levels corresponding to ¹³C transitions, thus explaining why the ¹³C carbonyl resonance is enhanced.

Transfer of polarization from ¹H to ³¹P using p-H₂ and INEPT+ has also been accomplished with IrH₂Br(CO)(dppe). The ortho phenyl and methylene bridge protons were decoupled during data acquisition. For a system composed of 1 mg of IrBr(CO)(dppe) under 3 atm of p-H₂ at 342 K, the ³¹P resonance, corresponding to the position trans to hydride, is 61 times more intense than that produced under n-H₂.²⁴

The amazing parahydrogen-aided resonance transfer (PART)²⁵ reported here opens the possibility of detecting species never seen before in catalytic hydrogenation and H₂ oxidative addition reactions. Our efforts are now progressing in that vein.

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(24) The 61-fold enhancement in S/N was obtained by comparison with a partially decoupled spectrum. If a fully decoupled ³¹P{¹H} spectrum is used in the comparison, the enhancement drops by a factor of 4 because the signal intensity of the ³¹P resonance increases 4-fold on removal of the hydride couplings.

(25) Chemical Abstracts Service advises us that parahydrogen is one word, any acronymic difficulties thus being avoided.

Determination of the Equilibrium Constant for Coordination of an Amide Carbonyl to a Metal Complex in Water

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Over the years, there has been considerable interest in developing artificial metalloproteases that hydrolyze unactivated amides under mild conditions.¹ Sequence specific hydrolytic cleavage of protein molecules has recently been achieved under oxidative conditions.² The mechanism of this remarkable hy-

(18) Parahydrogen with its nondegenerate spin state has no magnetic moment and is NMR silent.

(19) The 95-fold signal enhancement is lower than the theoretical maximum value.

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(21) The degree of signal enhancement was calculated using the signal-to-noise ratios obtained from the spectra with and without p-H₂ according to the equation $[(S/N_1)/(S/N_2)]^2 = N_1/N_2$ where N_1 and N_2 are the respective numbers of scans.

(22) The ratios of S/N values obtained after 4, 16, and 32 scans, respectively, were 1:1.7:1.7 rather than the 1:2:2.8 ratio theory predicts because during the period of observation there is relaxation of the spin distribution of p-H₂. These enhancements correspond to single scan equivalents of 25 000, 21 000, and 10 000, respectively.

(23) A more rigorous analysis of the spin physics associated with p-H₂ during polarization transfer is beyond the scope of this communication.

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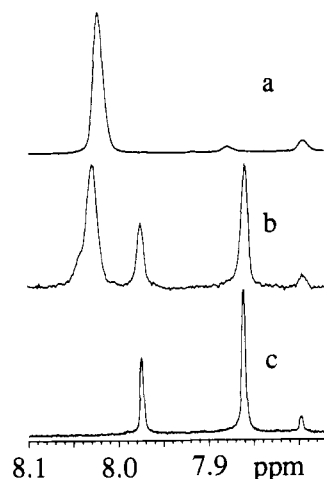
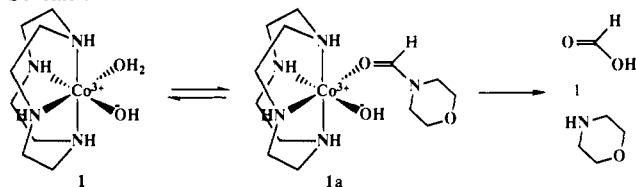


Figure 1. ^1H NMR of formylmorpholine or sodium formate in a 0.1 M solution of **1** in D_2O : (a) formylmorpholine (0.1 M) at pD 2, 25 °C; (b) formylmorpholine (0.05 M) at pD 5.9, 60 °C, 72-h reaction time; (c) sodium formate (0.05 M) at pD 5.9.

Scheme I



drolysis reaction is not yet understood. The half-life of a typical amide bond in protein molecules at neutral pH and 25 °C is about 7 years.³ Because of the stability of amides, most studies on amide hydrolysis have been focused on model systems involving activated amides or intramolecular catalysis.⁴ It has been recognized for over 40 years that Lewis acid activation likely plays an important role in many of the simple metal complex and metalloenzyme catalyzed hydrolyses of esters and amides.⁵ Therefore it is of fundamental importance to determine the equilibrium constant for coordination of the amide carbonyl group to metal complexes. In this communication, we report on the first direct measurement of the equilibrium constant for coordination of an amide carbonyl group to a metal complex (**1**) and the rate constant for the metal complex promoted hydrolysis of the amide under mild conditions (Scheme I). The determination of the equilibrium constant for coordination of formylmorpholine to **1** and the measurement of the rate of cleavage of the amide bond allow for a detailed dissection of the factors responsible for the significant rate enhancement observed for the hydrolysis of formylmorpholine in the presence of **1**.

The perchlorate salt of **1** was synthesized by acidification of the corresponding carbonato complex.⁶ The equilibrium constant for coordination of formylmorpholine to the diaqua form of **1** was measured by ^1H NMR (Figure 1a). In a typical experiment, formylmorpholine (0.1 M) was added to a solution of $[(\text{cyclen})\text{Co}(\text{OH}_2)_2](\text{ClO}_4)_3$ (0.1 M) in D_2O (DSS) at pD 2 and 25 °C (cyclen-: 1,4,7,11-tetraazacyclododecane). The formyl proton signal for the free amide appears at δ 8.02 ppm while those due to coordinated formylmorpholine (**1a**) appear at δ 7.79 ppm and δ 7.87 ppm. Two isomers of the coordinated complex are formed

because the cyclen tetraamine ligand coordinates to Co(III) in an asymmetric fashion.⁶ The upfield shift of the formyl proton signal in **1a** is in agreement with the previous observation that coordination of dimethyl formamide to Co(III) results in an upfield shift of the ^1H NMR signal for the formyl proton.⁷ From the relative areas of the ^1H NMR signals of the free and bound forms of formylmorpholine the equilibrium constant for complexation of formylmorpholine to the diaqua form of **1** was estimated to be $0.4 \pm 0.1 \text{ M}^{-1}$.

At low pD, coordination of formylmorpholine to **1** is not accompanied by any hydrolysis of the amide bond. However, at pD values close to the $\text{p}K_a$ of the cobalt-bound water molecule ($\text{p}K_a$ for $[(\text{cyclen})\text{Co}(\text{OH}_2)_2]^{3+}$ is 5.9 in D_2O), hydrolysis of the amide bond can be easily detected, indicating that the active form of the cobalt complex is the aqua-hydroxy form. The rate of **1**-promoted hydrolysis of formylmorpholine was monitored by ^1H NMR. When formylmorpholine (0.05 M) is added to a solution of $[(\text{cyclen})\text{Co}(\text{OH}_2)_2](\text{ClO}_4)_3$ (0.1 M) in D_2O (DSS) at pD 5.9 and 60 °C, the intensities of the signals due to formylmorpholine decrease with concomitant increases in the signals due to coordinated formates. The formyl region of the ^1H NMR after 3 days of reaction shows (Figure 1b) signals due to formylmorpholine (δ 8.02 ppm) and cobalt-bound formates (δ 7.79 ppm, δ 7.86 ppm, and δ 7.98 ppm). Under the above conditions, the initial rate of product formation as measured by ^1H NMR is $(1.8 \pm 0.1) \times 10^{-7} \text{ M s}^{-1}$ (disappearance of formylmorpholine as well as appearance of formate was monitored for the first 10% of the reaction). Therefore the second-order rate constant for hydrolysis of formylmorpholine promoted by the aqua-hydroxy form of **1** is $(7.2 \pm 0.4) \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$.

It is important to determine the equilibrium constant for coordination of amides to metal complexes since this is thought to be a key step for many simple metal complex and metalloenzyme catalyzed hydrolyses of amides.⁵ Although amides coordinated to Co(III) complexes have been synthesized,⁷ the equilibrium constants for their formation have not been measured. The basicities of a water molecule and the amide carbonyl oxygen in formylmorpholine are comparable. It is interesting that the equilibrium constant for coordination of formylmorpholine to **1** in competing solvent water molecules is large enough to be easily detected.

The active form of the cobalt complex for hydrolyzing esters, nitriles, phosphate diesters, and amides is the aqua-hydroxy form (**1**).⁸ The pseudo-first-order rate constant for hydrolysis of formylmorpholine in **1a** ($3.6 \times 10^{-4} \text{ s}^{-1}$ at 60 °C) can be estimated from the equilibrium constant for coordination of formylmorpholine to **1** (0.2 M^{-1})⁹ and the second-order rate constant for **1**-promoted hydrolysis of formylmorpholine ($7.2 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$). By comparison, the pseudo-first-order rate constant for deuteroxide-catalyzed hydrolysis of free formylmorpholine is $9 \times 10^{-12} \text{ s}^{-1}$ (at pD 5.9 and 60 °C). Formylmorpholine in **1a** is hydrolyzed almost 10^8 times more rapidly than free formylmorpholine under the above conditions. In order to determine whether this rate acceleration is due to Lewis acid activation or metal-hydroxide activation, we also measured the rate of hydrolysis of formylmorpholine in the substitutionally inert cobalt complex (**2**).⁷ The pseudo-first-order rate constant for deuteroxide-catalyzed hydrolysis of the formylmorpholine in **2** is $2 \times 10^{-6} \text{ s}^{-1}$ (at pD 5.9 and 60 °C).¹⁰ The formylmorpholine in **1a** hydrolyzes more rapidly than that in **2** despite the fact that the cobalt center in **2** is slightly more Lewis acidic than that in **1a** ($\text{p}K_a$ values of the cobalt-bound water in $[(\text{NH}_3)_5\text{Co}(\text{OH}_2)]^{3+}$ and

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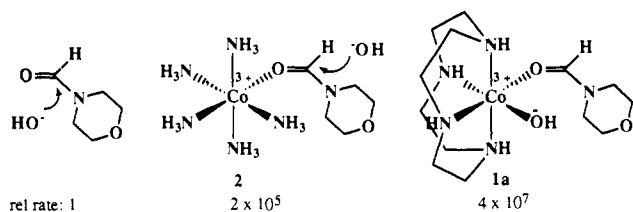
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(10) Synthesis and hydrolysis of **2** was accomplished by following the procedures in ref 7.

[(cyclen)Co(OH)(OH)]²⁺ are 6 and 8, respectively).⁸ Therefore, the metal-hydroxide in **1a** provides significant rate acceleration for the amide hydrolysis reaction.



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Rigid Bowlic Liquid Crystals Based on Tungsten-Oxo Calix[4]arenes: Host-Guest Effects and Head-to-Tail Organization

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New methodologies for the creation of noncentrosymmetric structures in molecular solids and liquids are critical to the development of new materials with ferroelectric and second order nonlinear optical (NLO) properties.^{1,2} Liquid crystalline methods are particularly attractive since liquid crystalline materials are easily deposited for device construction and are readily aligned.² Bowl-shaped (bowlic) liquid crystals³ are natural noncentrosymmetric building blocks since a head-to-tail organization maximizes the interactions between bowlic cores. Columnar phases are also conducive to polar order since their symmetry does not readily accommodate antiferroelectric arrangements.^{3c} We present herein a new type of columnar liquid crystal with a rigid bowlic core based on tungsten-oxo calix[4]arene complexes. These complexes display mesophases of unusually high stability and novel host-guest effects, which suggests that head-to-tail organization occurs in the mesomorphic state.

Calix[4]arenes are a well-known class of bowlic compounds which have been of interest due to their ease of preparation and propensity to exhibit host-guest complexes.⁵ We have synthesized

azo-substituted calix[4]arene derivatives **2a** and **2b** as shown in Scheme I which have 8 and 12 side chains, respectively.⁶ **2a** and **2b** are flexible macrocycles which, after recrystallization from solution, melt to give a transient mesophase which is only observed on first heating. Once heated into the isotropic phase, these compounds lose their mesomorphism and cooling produces only nonbirefringent glasses. Apparently, the crystal phase exhibits conformations compatible with a liquid crystal phase which are lost in the isotropic phase.⁷

Capping **2a** and **2b** with a tungsten-oxo group⁴ to form **1a** and **1b** produces a mesogen with a rigid bowl conformation which promotes liquid crystallinity. Both **1a** and **1b** display columnar mesophases (M , M_1 , and M_2) which are stable over a very wide temperature range as shown in Scheme II. The nature of the mesophases has been investigated by DSC, and optical textures were viewed with a polarizing microscope. The M to isotropic transition enthalpy for **1a** is fairly small (1.5 kcal/mol), indicating that this mesophase is likely a disordered phase with liquid-like correlation between mesogens. Cooling **1a**'s isotropic phase produces a texture for M characteristic of a columnar phase.⁸ However, due to partial decomposition in the isotropic phase, we have not been able to generate textures by this method suitable for further analysis. **1b** displays two columnar phases M_1 and M_2 , and the additional four side chains lower the clearing point to give a stable isotropic phase. The M_2 -I transition enthalpy for **1b** is 5.1 kcal/mol, a value considerably greater than the isotropic transition enthalpy observed for **1a**. Miscibility studies determined that M and M_2 have different structures. By slow cooling of **1b**'s M_2 phase, a texture is produced with digitized contours, leaf patterns, and large regions of uniform extinction. The large areas of extinction are suggestive of a uniaxial structure, and the observation of digitized stars with 6-fold symmetry and 120° facets confirms a hexagonal arrangement of the columns in M_2 .⁹ The birefringence decreases with increasing temperature for both **1a** and **1b**, and there is a particularly large change between the mesophase and the crystal phase. This effect is likely the result of twisting motions of the azophenyls, which is also consistent with the observation that the mesophases of both complexes are yellow whereas the crystal phases are red. The large M_2 -I transition enthalpy for **1b** and the spherulitic growth of the phase suggest that the mesogens are ordered in the columns, and therefore we characterize M_2 as a bowlic D_{ho} (these types of phases have also been termed $P_A^{3c,f}$ and B_{ho}^{3g}). The small enthalpy of the M_1 - M_2 phase transition and the absence of textural changes suggest that the structures of M_1 and M_2 are closely related.

The combination of the rigid cavity and the Lewis acidic nature of the square pyramidal tungsten produces a pronounced tendency for **1a** and **1b** to display host-guest interactions with Lewis bases.⁴ Although a number of compounds may serve as guests, we have focused on DMF complexes due to their strong association, and 1:1 complexes are obtained by recrystallization from anhydrous DMF. Infrared spectroscopy confirms that DMF forms a Lewis base complex. The W=O band undergoes a characteristic shift from 1074 cm⁻¹ (¹⁸O 1019 cm⁻¹) to 990 cm⁻¹ (¹⁸O 938 cm⁻¹) with DMF complexation.¹⁰ Likewise, the C=O band of the DMF

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