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^1H MAS NMR Spectra of Transition Metal Carbonyl Hydrides

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Introduction

The measurement of high-resolution ^1H NMR spectra from powdered or microcrystalline samples typically requires the use of special experimental techniques in order to reduce the adverse effects of $^1H-^1H$ dipole−dipole interactions which are a major cause of broadening of the resonances. Pfeifer and co-workers[2] obtained resolution of ^1H chemical shifts of OH groups in dehydated zeolites using magic angle spinning (MAS) to reduce this broadening. However MAS alone is not usually sufficient to eliminate the broadening, and the best resolved spectra are obtained with the combination of MAS with ^1H multiple pulse methods (CRAMPS[3]) or with MAS combined with isotopic dilution[4] (random substitution of ^1H by ^2H). Both combinations are demanding, CRAMPS requiring instrumentation which as yet is nonroutine, and the isotopic dilution method may require lengthy synthetic procedures. It was recently shown[5] that the narrowest ^1H resonance ($\Delta\nu_{1/2}$ = 0.18 ppm = 72 Hz) was obtained for the residual protons of a deuterated methyl group in solid alanine using MAS. We present here results which show that important structural information on a wide range of molecular organometallic hydrido carbonyl complexes may be obtained by solid state ^1H MAS NMR without recourse either to the multiple pulse method or to isotopic dilution by synthesis. The success in obtaining the high-resolution ^1H spectra reported herein is attributed to the fact that the protons are dilute *intramolecularly* or that certain proton-bearing substituents undergo rapid intramolecular motion in the solid state which significantly reduces dipole−dipole interactions.

Results and Discussion

We have measured the ^1H MAS NMR spectra of the transition metal carbonyl hydride complexes $H_2Os_3(CO)_{10}$ (**I**), $H_2FeRu_3(CO)_{13}$ (**II**), $HRu_3(CO)_9TBA$ (**III**) (the ligand TBA is *tert*-butylethynyl), $H_2Os_3(CO)_{11}$(**IV**), and $H_2Os_3(CO)_{10}NH_3$ (**V**), for $Fe_3(CO)_{12}$ chemisorbed onto γ-alumina, and for $[NHEt_3]^+[HFe_3(CO)_{11}]^-$ (**VI**).

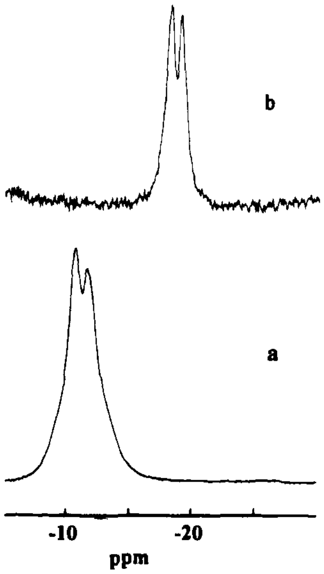

Figure 1. 300 MHz solid state ^1H MAS NMR spectra: (a) $H_2Os_3(CO)_{10}$ (**I**), MAS rate = 8.1 kHz, 48 scans, recycle delay = 20 s; (b) $H_2FeRu_3(CO)_{13}$ (**II**), MAS rate = 9.5 kHz, 914 scans, recycle delay = 60 s.

Complexes **I** and **II** are dihydrides wherein the hydrogen ligands bridge two metal atoms. **I** crystallizes with one molecule as the asymmetric unit, as determined by a neutron diffraction study,[6] and the interproton distance is 2.38 Å. This distance corresponds[7] to an interproton dipolar coupling constant of 8.91 kHz. As expected on the basis of the solid state structure, **I** shows (Figure 1a) two chemical shifts in the ^1H MAS spectrum at δ −10.9 and −12.5, *cf.* one resonance at δ −11.4 in solution.[8] The separation of the two peaks was invariant to changing the MAS rate from 8.1 kHz to the range 3.7−4.7 kHz (there was some loss of resolution at these lower spin rates), and therefore this separation is not due to the homonuclear dipolar coupling phenomenon on a *single* chemical shift recently reported by Wu and Wasylishen.[9] The resolution of the two chemical shifts in spectra where the MAS rate is significantly less than the dipolar coupling is suprising and merits further study. There are suggestions of shoulders on the resonances shown in Figure 1a, and this must be due to the MAS rate (8.1 kHz) being somewhat less than the dipolar coupling and not sigificantly greater than it. Such line shapes have been reprted by Wu and Wasylishen[10,11] and are dependent on the magnitude and orientation of the ^1H chemical shift tensors as well as their orientation with respect to the interproton dipolar vector. The ^1H spin−lattice relaxation time for the two resonances was measured by the inversion−recovery technique to be 11.9 s

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(7) The magnitude of the homonuclear dipolar interaction between the two protons is given (for example see: Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*; Longman Scientific & Technical: Harlow, U.K., **1986**; pp 97, 145) by $^3/_2R(3\cos^2\theta - 1)$ where θ is the angle between the internuclear vector and the magnetic field direction. For static powdered samples θ may assume a full range of values determined by the random particle orientation in the magnetic field. R is the dipolar coupling constant given by $(\mu_0/4\pi)(h/4\pi^2)\gamma^2r^{-3}$ Hz, where μ_0 is the permeability constant, γ is the proton magnetogyric ratio, and r is the interproton distance.

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(11) These ^1H line shapes are the subject of continuing investigation. It is relevant that the ^1H chemical shift anisotropy is similar in order of magnitude to the dipolar coupling and to the MAS rate—Nicol and Vaughan (Nicol, A. T.; Vaughan, R. W. *J. Am. Chem. Soc.* **1979**, *101*, 583) determined that the principal values of the ^1H shielding tensor for **I** are 4.4, −9.9, and −21.6 ppm, which at the 300 MHz observation frequency gives the shielding anisotropy as *ca.* 6.0 kHz.

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(±0.5 s), and a good signal/noise ratio was obtained in the spectrum (Figure 1a) using 90° observe pulses separated by 20 s.

An early X-ray structural study on **II** reported[12] that the compound crystallizes as an orange form with two molecules in the asymmetric unit, while a later X-ray study[13] reported just one molecule in the asymmetric unit for a dark-brown form. We crystallized both forms: the orange-red modification could show up to four resolved ^1H chemical shifts but just two are observed at δ −18.1 and −18.9 (presumably due to accidental overlap of resonances); the dark-brown form displays the two expected resonances at the same chemical shifts. These values compare closely with the single resonance at δ −18.4 in solution.[14] The coordinates of the protons reported by Hsu *et al.*[13] give an interproton distance of 2.63 Å, which in turn yields[7] the dipolar coupling constant as 6.60 kHz. There is no evidence of unusual line shape in the spectrum of **II** (Figure 1b), and it is noteworthy that the spin rate for this spectrum is 9.5 kHz and therefore significantly greater than the dipolar coupling. In contrast to the dihydride complexes above, **III** is a monohydride complex which because of the presence of the nine protons of the TBA ligand may not be considered as "proton dilute". An X-ray study has shown[15] that the complex crystallizes with one molecule in the asymmetric unit, and from the published atomic coordinates derived from a neutron diffraction study[16] we estimate[7] dipolar couplings in the range 0.4−1.7 kHz (average 0.7 kHz) between the hydride ligand and the nine protons of the TBA ligand. In spite of the large number of protons in the molecule two sharp resonances are observed (Figure 2a) in the ^1H MAS spectrum at δ 1.4 (*tert*-butyl) and δ −21.2 (hydride), *cf.* δ 1.4 and δ −21.8, respectively, for the solution state.[17] The full widths at half height ($\Delta\nu_{1/2}$) for these two resonances in the solid state are 220 Hz = 0.73 ppm (*tert*-butyl) and 90 Hz = 0.31 ppm (hydride), which for the latter is not much greater than that reported by Zheng *et al.*[5] for a partially deuterated methyl group (*vide supra*). The spin−lattice relaxation times measured for **III** by the inversion−recovery technique are 0.2 s (*tert*-butyl) and 2.9 s (hydride). The latter value is significantly shorter than that anticipated from recording spectra of **I** and indicates that dipolar coupling between the methyl groups and the hydride ligand does provide an efficient spin−lattice relaxation pathway. However the internal mobility of the methyl groups[18] means that the magnitude of the dipolar coupling is such that a high-resolution spectrum can be obtained using MAS alone.

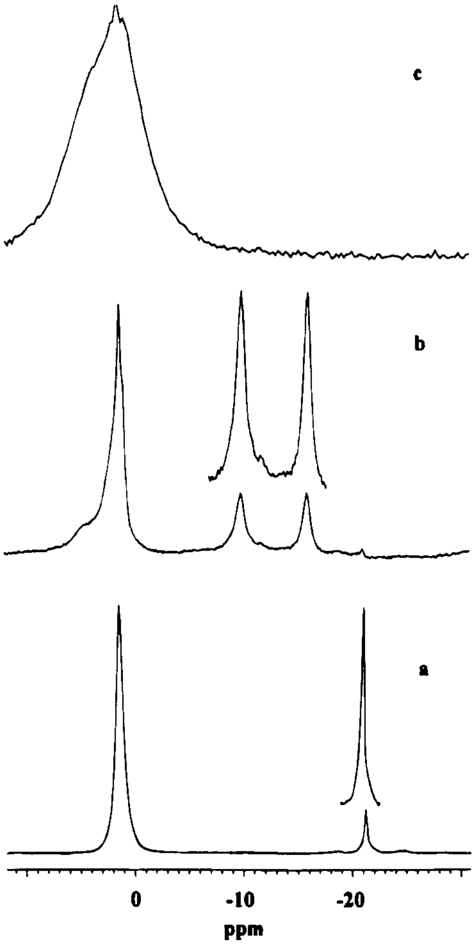

Figure 2. 300 MHz solid state ^1H MAS NMR spectra: (a) $HRu_3(CO)_9$-TBA (**III**), MAS rate = 11.0 kHz, 72 scans, recycle delay = 2 s; (b) $H_2Os_3(CO)_{10}NH_3$ (**V**), MAS rate = 10.8 kHz, 112 scans, recycle delay = 30 s; (c) **V**, static spectrum, 118 scans, recycle delay = 10 s.

For a third type of hydride complex we measured the ^1H MAS spectra of **IV** and **V**, which are obtained by adding CO and NH_3, respectively, to the coordinatively unsaturated $H_2Os_3(CO)_{10}$ (**I**). The electron-precise species so formed contain one terminal and one bridging hydride ligand, which in the case of **IV** in solution are involved in a mutual exchange process that can be "frozen out" at low temperature.[19] The X-ray structure of **IV** has been studied,[20] and while the hydrides were not directly located, their positions were inferred by comparison with the isostructural $Os_3(CO)_{12}$ and the results of an X-ray study[21] of the related $H_2Os_3(CO)_{10}PPh_3$, which gave the interproton distance to be 2.36 Å. From this we calculate[7] a value of 9.1 kHz for the dipolar coupling constant. The ^1H MAS spectrum of **IV** shows well-resolved resonances at δ −10.5 and δ −20.5 ($\Delta\nu_{1/2}$ *ca.* 300 Hz) due to the terminal and bridging hydrides, respectively. The assignments were made by comparison with the solution state assignments, and the chemical shifts are close to those found[17] (−10.3 and −20.0 δ) in the low-temperature solution spectrum. The introduction of the NH_3 ligand to form complex **V** increases the degree of intramolecular dipolar coupling; however the ^1H MAS spectrum shows (Figure 2b) three well-resolved resonances at δ 1.2, −10.1 and −16.2, which compare with δ 0.19, −10.5 and −16.4 in solution.[22] The solid state structure of **V** has not been determined, but it is reasonable to expect the dipolar coupling between the hydride ligands to be similar to that estimated for **IV** and therefore MAS alone could lead to the relatively narrow resonances observed. The observation of a narrow resonance for the NH_3 protons must be due to rapid internal rotation of this group about the metal-nitrogen bond which reduces the interproton dipolar interaction (*cf.* the situation for the *tert*-butyl

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group in **III**). To test this idea, the static solid state ^1H spectrum of **V** was recorded which shows (Figure 2c) just one broad line ($\Delta\nu_{1/2}$ *ca.* 2.1 kHz), centered at the chemical shift found for the NH_3 ligand in the MAS spectrum, which is compatible only with rapid rotation of the NH_3 group. There is no evidence of either hydride ligand resonance in the static spectrum because their mutual dipolar interaction, not moderated by any intramolecular motion, results in much broader lines than that for NH_3.

The ^1H MAS (12.0 kHz) spectrum of $Fe_3(CO)_{12}$ chemisorbed onto hydroxylated γ-alumina displayed a single hydridic signal at δ −17.5 ($\Delta\nu_{1/2}$ *ca.* 600 Hz). The chemisorbed species is believed (for a recent discussion see Reven and Oldfield[23]) to have a structure similar to that of the anion $[HFe_3(CO)_{11}]^-$, wherein the hydride ligand bridges two iron atoms. We have measured the ^1H solid state spectrum of $[NHEt_3]^+[HFe_3(CO)_{11}]^-$ (**VI**), which showed the hydride resonance at δ −15.3 ($\Delta\nu_{1/2} \approx$ 250 Hz) and a broad resonance ($\Delta\nu_{1/2} \approx$ 1100 Hz) centered at δ 1.2 for the cation. A previous report[24] of the solid state ^1H spectrum of $Fe_3(CO)_{12}$ on γ-Al_2O_3 gave a signal at δ −13.6 but did not include any other detail (e.g. line width, MAS or not). Solution state ^1H shifts for $[HFe_3(CO)_{11}]^-$ are in the same region as the above values but are dependent upon the cation, e.g. at δ −14.5 when the cation is[25] $[(Ph_3P)_2N]^+$ and δ −18.4 when it is[26] $[H_3O^+ \cdot nH_2O]$.

Experimental Section

NMR Spectra. The 300 MHz ^1H MAS NMR spectra were recorded with a Bruker MSL-300 spectrometer using the single-pulse acquisition method or the 90°−τ −180°−τ−acquire spin echo sequence. The 90° pulse width was 4.0 μs, τ values were adjusted to the rotor period (e.g. 103.5 μs for MAS rate of 9.5 kHz or 93.5 μs for 10.8 kHz), and relaxation delays in the range 20−60 s were used to optimize signal/noise. The ^1H chemical shifts were referenced to (external) liquid tetramethylsilane (TMS) by measurement of the liquid in the MAS rotor immediately prior to the measurement of the solid state sample. No correction has been applied to the measured chemical shifts to account for differences in bulk susceptibility between samples; this provides a potential source of error in the chemical shifts quoted, but this error is expected to be less than 0.5 ppm. For the molecular structures **I**−**VI**, we estimate the error on the reported hydride ligand shifts to be *ca.* ± 0.3 ppm (about half the $\Delta\nu_{1/2}$ values), while for the broader resonance of the hydrated $Al_2O_3/Fe_3(CO)_{12}$ sample, the error is estimated to be *ca.* ± 1.0 ppm. The digital resolution in all spectra was 0.15 ppm or better.

Compounds. Complexes **I**−**V** were synthesized according to published procedures: Johnson *et al.*[27] for **I**; Yawney and Stone[28] for **II**; Sappa *et al.*[27] for **III**; Deeming and Hasso[8] for **IV**; Aime *et al.*[22] for **V**; Case and Whiting[29] for **VI**. $Fe_3(CO)_{12}$ chemisorbed onto γ-Al_2O_3 was prepared according to Reven and Oldfield.[23]

Conclusion

In summary, these observations demonstrate that ^1H MAS NMR spectra of a range of organometallic hydride complexes are sufficiently resolved to yield structural information without recourse either to multiple-pulse methods or to isotopic (^2H) dilution. The criteria for resolution in the spectra are that the hydride ligands constitute a "dilute spin" situation, i.e. no other proximal proton-containing ligands, or that if such ligands are present, they have sufficient internal motion in the solid state to significantly reduce their dipolar effect to the point where MAS is effective. It is not necessary that the MAS rate is much greater than the dipole coupling constant; rather, the MAS rate must be at least comparable in magnitude to it. Therefore ^1H MAS NMR may prove a valuable complement to the well-established applications of solid state ^{13}C and ^{31}P NMR in organometallic chemistry.

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