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Observation of Bridging and Terminal Metal Hydrides by Solid-State Deuterium NMR Spectroscopy: Application to Bis(cyclopentadienyl)zirconium Dideuteride

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The solid-state deuterium NMR spectrum of $[(\eta^5\text{-}C_5H_5)_2Zr^2H_2]_x$ has been measured at 46 and 61 MHz. Two deuterium sites were detected: a Zr–^{2}H terminal bond and a Zr–^{2}H–Zr bridging bond. The values found for the deuterium quadrupole coupling constant for the terminal and bridging sites are 46.7 (5) and 32.7 (20) kHz, respectively. A discussion is presented regarding assignment of deuterium quadrupole coupling constants to terminal or bridging metal hydride sites.

Metal–hydrogen bonds are common in organometallic chemistry, contribute to many structurally interesting complexes,[1] and display remarkable variability in bonding modes and bond strengths.[2-4] We propose that solid-state deuterium NMR may be an appropriate technique for the study of M–H bonding. The metal hydride reported here, $[(\eta^5\text{-}C_5H_5)_2Zr^2H_2]_x$, illustrates a useful property of solid-state deuterium NMR: identification of terminal and bridging M–H bonds.

The location of hydrogen atoms in the vicinity of transition-metal atoms can be difficult. The technique of single-crystal neutron diffraction can be frustrated by crystallographic disorder.[2] Vibrational spectroscopy can be rendered ineffective by overlapping carbonyl stretches or weak absorptions.

$[(\eta^5\text{-}C_5H_5)_2Zr^2H_2]_x$ is related to a family of bis(cyclopentadienyl)zirconium(IV) alkyl hydrides used in organic synthesis to activate olefins.[5,6] Structurally, $(\eta^5\text{-}C_5H_5)_2MLL'$ complexes are found as monomeric, bent sandwich structures with a *cis*-L-L′ configuration.[7,8] However, the 16-electron zirconium(IV) hydrides tend to oligomerize; $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ is dimeric in the solid state.[9] The title complex is either dimeric or polymeric in solution; the solid-state structure is also poorly defined.[10,11] The IR spectrum of solid $[(\eta^5\text{-}C_5H_5)_2ZrH_2]_x$ shows two different M–H stretches due to terminal and bridging hydride sites.[11]

In solid-state deuterium NMR, zero-field NMR, or adiabatic demagnetization in the laboratory frame (ADLF) spectroscopy, one obtains the deuterium quadrupole coupling constant, $e^2q_{zz}Q/h$, and the asymmetry parameter, η.[12,13] Here, Q is the deuterium nuclear quadrupole moment.[14] The quantity eq_{zz} is the largest component of the traceless electric field gradient tensor in the principle-axis system. The value of eq_{zz} is a sum of nuclear and electronic contributions, which may be written as an expectation value of the electronic wave function Ψ, shown here in atomic units

$$eq_{zz} = e\sum K_n \frac{3z_n^{\,2} - r_n^{\,2}}{r_n^{\,5}} - e\left\langle \Psi^* \left| \sum \frac{3z_i^{\,2} - r_i^{\,2}}{r_i^{\,5}} \right| \Psi \right\rangle \qquad (1)$$

where e is the absolute value of the electronic charge, the index n is over the other atoms with nuclear charge K_n, and the index i is over the electrons of the molecule. As noted in other NMR studies of charge distribution, additional interest in deuterium electric field gradients accrues from the absence of excited-state effects since only occupied molecular orbitals affect the electric field gradient.[15] We expect that deuterium quadrupole coupling constants and asymmetry parameters will depend on the metal–hydride bond geometry and charge.

Experimental Section

$[(\eta^5\text{-}C_5H_5)_2Zr^2H_2]_x$ was prepared according to a literature procedure.[11] Initially, the product was contaminated with aluminum powder that was traced to the LiAl^{2}H$_4$ reagent (Aldrich). The contamination was prevented by recrystallizing LiAl^{2}H$_4$ from THF prior to use. Preliminary solid-state deuterium NMR spectra taken with a Bruker AM400 spectrometer indicated that aluminum contamination (~2%) had little effect on the NMR spectrum.

Table I. $[(\eta^5\text{-}C_5H_5)_2Zr^2H_2]_x$ Deuterium NMR Spectral Parameters

parameters	Zr–^{2}H	Zr–^{2}H–Zr
$e^2q_{zz}Q/h$, kHz	46.7 (5)	32.7 (20)
η	0.0	<0.1
relative area, %	77	23
Gaussian broadening, kHz	1.5	5
chem shift,[a] ppm	0 (10)	0 (30)

[a] Relative to Me$_4$Si.

Figure 1 shows the solid-state deuterium NMR spectrum for $[(\eta^5\text{-}C_5H_5)_2Zr^2H_2]_x$ taken at 300 K. The spectrum was obtained at 46.1 MHz on a Bruker CXP300 spectrometer. With use of a solenoidal coil, a simple quadrupolar echo pulse sequence (90° pulse (^{2}H) = 3.6 μs) gave good results. However, significant increase in the intensity of the wings of the powder pattern occurred with a composite pulse sequence,[16] which was used for the reported spectrum. The deuterium spin–lattice relaxation time was on the order of 10 s; presumably rapid cyclopentadienyl ring rotation contributed to a dipolar relaxation mechanism.[17] Also shown in Figure 1 are simulations derived by assuming two separate deuterium quadrupole coupling constants. Table I lists the final values of the powder pattern spectral simulation.

In a solid-state deuterium NMR experiment, values for the quadrupole coupling constant and the relative areas of multiple components are influenced by motional averaging and differential deuterium spin–lattice relaxation times.[12] In this work, a solid-state deuterium NMR spectrum taken at 185 K was similar to the room-temperature spectra, thus showing that the quadrupole coupling constants listed in Table I are static values and are not reduced by motional averaging. At room temperature, solid-state deuterium NMR spectra taken with different relaxation delays gave similar powder patterns, indicating that the relative areas reported

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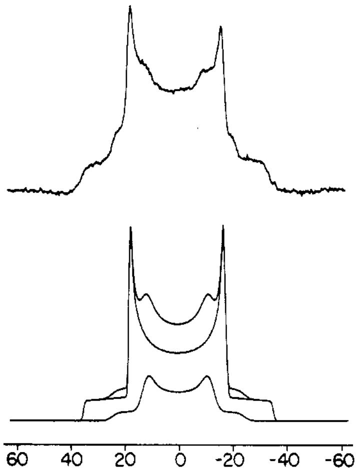

Figure 1. Solid-state deuterium NMR spectrum of $[(\eta^5\text{-}C_5H_5)_2Zr^2H_2]_x$ at room temperature. Top trace is experimental spectrum taken at 46 MHz by using the composite pulse sequence given in ref 16 (sequence I; 90° pulse length = 3.7 μs; delay between composite 90° pulses 25 μs; delay after second composite 90° pulse 23.2 μs before quadrature detection with 1-MHz spectral width; relaxation delay 20 s; 3286 scans). Bottom trace is best fit of two deuterium powder patterns to the observed spectrum.

in Table I are not dominated by differential deuterium spin-lattice relaxation times but rather represent the relative abundance of the two deuterium sites. Finally, deuterium exchange into positions on the cyclopentadienyl ring can occur with early-transition-metal complexes. This would yield a powder pattern with an apparent deuterium quadrupole coupling constant of about 95 kHz.[18] However, no ring deuteriation was found in $[(\eta\text{-}C_5H_5)_2Zr^2H_2]_x$.

Nevertheless, the areas of the two powder patterns do vary in a nonpredictable manner with sample preparation. We attribute this latter feature to a variability in the extent of polymer formation of $[(\eta^5\text{-}C_5H_5)_2Zr^2H_2]_x$ due to a weak bridging hydride bond. A solution NMR study of $[(\eta^5\text{-}C_5H_5)_2ZrH_2]_2$ shows that at 60 °C, rapid exchange occurs between terminal and the weakly bound bridging hydrides.[10]

Results and Discussion

Assignment of the observed deuterium powder patterns to terminal and bridging hydride sites is accomplished by first estimating the value of the deuterium quadrupole coupling constant for a terminal Zr–^{2}H site and then noting that the value of the quadrupole coupling constant will be less for a Zr–^{2}H–Zr bond. For a terminal X–^{2}H bond, the value of the deuterium quadrupole coupling constant can be predicted from the vibrational stretching force constant,[19–21] a correlation first noted by Salem. An updated correlation is shown in Figure 2.[19] Using the Zr–H stretching frequency of 1520 cm^{-1},[11] we expect a deuterium quadrupole coupling constant of about 40 kHz. Having established an estimate of the deuterium quadrupole coupling constant for a terminal Zr–^{2}H bond, we now turn to the bridging Zr–^{2}H–Zr bond. A bridging metal hydride will have a smaller quadrupole coupling constant than a deuterium atom in a simple terminal bond with the same metal. The reduction in the value of the deuterium quadrupole coupling constant is a result of three factors: (1) The formation of a bridging metal hydride bond is accompanied by an increased internuclear distance between the metal and deuterium atoms; for example, *d*(Mn–H) = 1.601 Å for $HMn(CO)_5$[22] and *d*(Cr–H) = 1.675–1.750 Å for $[HCr_2(CO)_{10}]^-$.[23] (2) The positive, nuclear contribution to the electric field gradient (eq 1) is larger in magnitude that the negative, electronic term. Li^{2}H has a positive quadrupole coupling constant,[24] as does ^2H_2O.[25] Since there are no large deviations from the line drawn in Figure 2, we can assume that all terminal X–^{2}H bonds will have a positive deuterium quadrupole coupling constant. In fact, the only report of a negative deuterium quadrupole coupling constant comes from a calculation of the bridging hydride site in diborane.[26] (3) The nuclear term of the electric field gradient is a stronger function of the X–^{2}H distance than the electronic term.

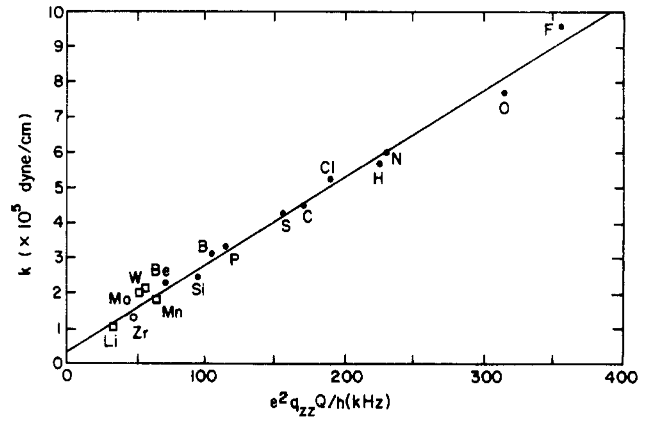

Figure 2. X–H stretching force constants and deuterium quadrupole coupling constants (adapted from Wei and Fung[34]). Symbols: ●, diatomic and small molecules; □, metal hydrides [Li^{2}H, $(\eta^5\text{-}C_5H_5)_2Mo^2H_2$, $(\eta^5\text{-}C_5H_5)_2W^2H_2$, $^2HMn(CO)_5$]; ○, this work.

The relationship between geometry and the deuterium quadrupole coupling constant has been well studied in 3-centered, 4-electron O–^{2}H···O bonds.[15c,27–30] Here, gas-phase microwave spectroscopy of water provides a reference value of 313.2 kHz.[31] The weakest hydrogen bond yet studied has a quadrupole coupling constant of 245.2 (1) kHz;[32] the very strong hydrogen bond in rubidium oxodiacetate has a quadrupole coupling constant of 41 (1) kHz.[33] In summary, the formation of a hydrogen bond causes a large reduction in the value of the deuterium quadrupole coupling constant for deuterium bound to oxygen. And in metal–hydride bonds, going from a terminal M–^{2}H bond to a M–^{2}H–M bond should also result in a reduction in the deuterium quadrupole coupling constant.

$[(\eta^5\text{-}C_5H_5)_2Zr^2H_2]_x$ shows two different powder patterns. We assign the powder pattern with the larger value of the deuterium quadrupole coupling constant, 46.7 (5) kHz, to a terminal Zr–^{2}H site. This value is close to that reported for $(\eta^5\text{-}C_5H_5)_2Mo^2H_2$, 39 (2) kHz.[20c] The powder pattern with the smaller value of the quadrupole coupling constant, 32.7 (20) kHz, is assigned to a bridging Zr–^{2}H–Zr site. This work represents the first report of solid-state deuterium NMR for a bridging metal hydride site.

Conclusion

Solid-state deuterium NMR spectroscopy can be used to dif-

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(18) The motionally averaged value of $e^2q_{zz}Q/h$ observed for $(\mu\text{-CO})_2[FeCp^d(CO)]_2$ (Cp^d = deuteriated cyclopentadienyl): Altbach, M. I.; Hiyama, Y.; Gerson, D. J.; Butler, L. G., unpublished results.

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ferentiate between terminal and bridging metal hydride sites and quantify the relative populations of M–^{2}H and M–^{2}H–M sites. Before assignment of bridging metal hydride resonances involving a transition metal can be attempted, an approximate value of the deuterium quadrupole coupling constant for a simple, terminal metal hydride of that metal is required. In the absence of the deuterium NMR spectrum for a terminal metal hydride site, an estimate of the deuterium quadrupole coupling constant can be made from the vibrational M–H stretching force constant.

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Delocalization As Evidenced by Absorption, Luminescence, and Excitation Spectra of $Ru(bpy)_3^{2+}$ in $Zn(bpy)_3(PF_6)_2$ and Ethanol/Methanol Glasses

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The metal–ligand excited states of the $Ru(bpy)_3^{2+}$ chromophore in $Zn(bpy)_3(PF_6)_2$ can only be effectively described by a delocalized D_3 model. This is in spite of the fact that the chromophore is at a low-symmetry site with only approximate C_2 symmetry. Polarized spectra are completely inconsistent with a localized C_2 model. Luminescence excitation polarization spectra detected at different energies within the emission profile are presented for 4:1 ethanol/methanol glasses at 110 K, and a resolution of the conflict among interpretations of luminescence polarization ratios, excited-state Raman spectra, and a larger body of spectroscopic evidence is given.

Introduction

A large number of spectral techniques have been brought to bear on the $Ru(bpy)_3^{2+}$ chromophore, but there appears to be a continued controversy about the nature of the excited states of this complex ion.[1-3] Although it is uniformly agreed that the visible absorption bands involve transfer of an electron from the metal ion to the ligands, two types of spectral evidence have been used to support arguments for the inequivalent involvement of the ligands in both absorption and emission processes, i.e., a localized rather than a delocalized description. The purpose of this paper is to report new data, which establish beyond reasonable doubt that localization arguments are flawed and all of the charge-transfer states are intrinsically delocalized, even in crystals where strict D_3 symmetry is not maintained between the ligands.

The strongest argument for localization comes from excited-state resonance Raman (ERR) spectra observed in fluid solutions.[4,5] The evidence seems unequivocal in its support of localization of charge in the luminescent states. ERR spectra resemble free-radical bpy$^-$ Raman spectra and are *not* dependent on substitution of one or two bpys with completely different electrophobic ligands. However, this localization process has been shown[6] to be the result of a fast environmental relaxation that traps the electron on a single ligand which is inhibited in solid phases. Time-resolved luminescence (TRL) spectra can be observed and change markedly upon formation of a glass.[6] ERR spectra taken of $Ru(bpy)_3^{2+}$ in solid phases are completely different from those observed in solution[7] and in fact show a quasi-continuum scattering.

The second argument is older and stems from a number of observations of the luminescence polarization ratio in glycol/water and other glass-forming mixtures. They were originally reported by Fujita and Kobayashi,[8] confirmed by Felix et al.,[9] and further extensively investigated by DeArmond et al.[1,2] These results consistently show a region of anomalously high polarization ratio at about 21 000 cm^{-1}, too high for a planar oscillator in both absorption and emission $(>{}^1/_7)$. The fact that the polarization is greater than $^1/_7$ suggests that the symmetry of the chromophore is not D_3 but lower, so as to involve linear rather than planar oscillators.

Most recently, Braterman et al.[3] have used the observations of solution ERR, anomalous polarization ratios, and evidence from excited-state absorption spectra in fluid solutions[10] to propose a localized description for the triplet states and "part" of the singlet states. In their view the spin-allowed transitions are considered to be either "trapped" at lower energies or "untrapped" at higher energies, thus explaining the anomalously high polarization ratio observed around 21 000 cm^{-1} where a changeover from "trapped" to "untrapped" absorption is considered to occur. The bulk of the spin-allowed band is considered "untrapped". It was further speculated[3,10] that transitions in the "trapped" region are followed by radiationless decay to a luminescent state in which the electron resides on the same ligand; i.e., the complex retains a memory of the initial absorption process. On the other hand, absorption to higher energies leads to a loss of memory by the excited ion and there is a random selection of the luminescent states.

This proposal by Braterman et al.[3] attempts to interpret the polarization result in glassy media without giving sufficient consideration to a larger body of spectroscopic data. In particular, the measurement of CD in the same spectral region in single crystals[11] of $Zn(bpy)_3(BF_4)_2$:Ru is quite inconsistent with their proposal. The absence of detailed structural information for the $Zn(bpy)_3(BF_4)_2$ host crystal tends to weaken the case, and a similar lack of crystal structure information for the host $Zn(bpy)_3(PF_6)_2$ could perhaps be used to dismiss some of the conclusions reached from a study of the spectroscopy in this host as well.[12,13] Fortunately, the crystal structure of $Zn(bpy)_3(PF_6)_2$ has now been solved,[14] and the basic structural features predicted from the previous spectroscopic analysis have in fact been confirmed. We are therefore in a strong position to use the crystallographically

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