Deuterium NMR Studies of (μ_3-C^{2}H)[Co(CO)$_3$]$_3$

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Abstract: Deuterium quadrupole coupling constant ($e^2q_{zz}Q/h$) of (μ_3-C^{2}H)[Co(CO)$_3$]$_3$ was determined by using solid-state deuterium MAS NMR spectroscopy. The small quadrupole coupling constant of bridging methyne unit relative to sp-acethylene in propyne is discussed in terms of the C-H bond length and the negative charge on the carbon.

INTRODUCTION

Many experimental techniques have been used to study surface chemistry,[1] including solid-state NMR spectroscopy. Triply bridging methylenes and bridging methynes occur in surface chemistry, although the methylene units are particularly difficult to observe.[2] Solid-state ^{13}C NMR study has provided remarkable details of the surface chemistry of absorbed ethylene and acethylene on Pt/Al$_2$O$_3$.[3] The NMR observables for ^{13}C NMR are mainly chemical shielding and dipolar coupling; these are not sensitive in a useful sense to obtain the information on the electronic structure at carbon. For that reason, we are exploring the potential of solid-state ^{2}H NMR where the quadrupole coupling constant is a known measure of electronic structure. Herein, the objective is acquisition of the solid-state ^{2}H NMR spectrum of (μ_3-C^{2}H)[Co(CO)$_3$]$_3$ and investigation of the interpretative model for the analysis of ^{2}H quadrupole coupling constant. Assigned orbital model[4,5] will be explored.

EXPERIMENTAL

Sample Preparation.

(μ_3-C^{2}H)[Co(CO)$_3$]$_3$ was prepared according to literature procedures.[6] The solution ^{2}H NMR spectrum in CCl$_4$/C^{2}HCl$_3$ shows the characteristic peak at 12.15 ppm (referenced to the C^{2}HCl$_3$ peak at 7.26 ppm) for the deuterium at the methyne site. The solution ^{13}C NMR spectrum in CCl$_4$ shows a broad peak at 199.2 ppm for the terminal carbonyls; no peak was detected for the methyne carbon, a fact that is not unusual for triply bridging carbons bound to cobalt. The IR spectrum (KBr pellet) shows peaks at 2050, 2030, 2020, and 2010 cm^{-1} for the carbonyls; no peaks for bridging carbonyls were observed, consistent with the desired product. The mass spectrum shows the molecular ion peak at 442.8 m/e and nine peaks separated by 28 m/e corresponding to the loss of each of the nine carbonyls.

Solid-State Deuterium NMR Spectroscopy.

Solid-state ^{2}H wideline spectrum was acquired at 61.4 MHz on a modified Bruker WH-400 NMR spectrometer at about 300K. The quadecho pulse sequence ($90_{x,-x}$-t$_1$-90_y-t$_2$-acq$_{x,-x}$) was used. The 90° ^{2}H pulse length was 2.2 μs. The first delay between 90° pulses, t$_1$, was 50 μs and the second delay before echo acquisition, t$_2$, was 35 μs. A relaxation delays of 60s was used.

Solid-state ^{2}H MAS spectrum was acquired at 30.709 MHz on a Bruker MSL 200 solid-state NMR spectrometer using a 7 mm CP/MAS probe at about 300K. Simple Bloch decay was used. A spin rate of 8 kHz was used; the spin rate was stable to within 10 Hz during the acquisition. The angle of the spinning axis with respect to the magnetic field was set using the method of Frye and Maciel with KBr.[7] The 90° ^{2}H pulse length of 2 μs was used with a delay (inverse of the spinning rate) of 125 μs. A relaxation delays of 60s was used.

RESULTS AND DISCUSSION

Solid-state ^{2}H wideline NMR spectrum is composed of two contributions from the triply bridging methyne site in (μ_3-C^{2}H)[Co(CO)$_3$]$_3$ and the impurity shown in Fig. 1a. A rough estimate of the spin lattice relaxation times (T$_1$) shows that the innermost peak has a short T$_1$ (ca. 0.15s) while the outermost peak has a long T$_1$ (ca. 30 s). The outermost peak was assigned to the deuterium in the methyne unit based on the splitting expected for a static C-^{2}H bond and on the characteristic long T$_1$ value as found in bridging methylene metal dimers. The innermost peak is tentatively assigned to a deuterated impurity in the sample which could not be identified. Even small amounts of impurity can yield very intense signals in the solid-state spectrum with respect to the

deuterium in $(\mu_3\text{-}C^2H)[Co(CO)_3]_3$ when the difference in T_1 is large. Solid-state ^2H MAS NMR spectrum taken at a spin rate of 8 kHz shown in Fig. 1b offers some unique advantage relative to the wideline spectrum for obtaining the better signal-to-noise ratio and acquisition of ^2H electric field gradient (EFG) parameters; thus we used ^2H MAS spectrum to extract the quadrupole coupling constant.
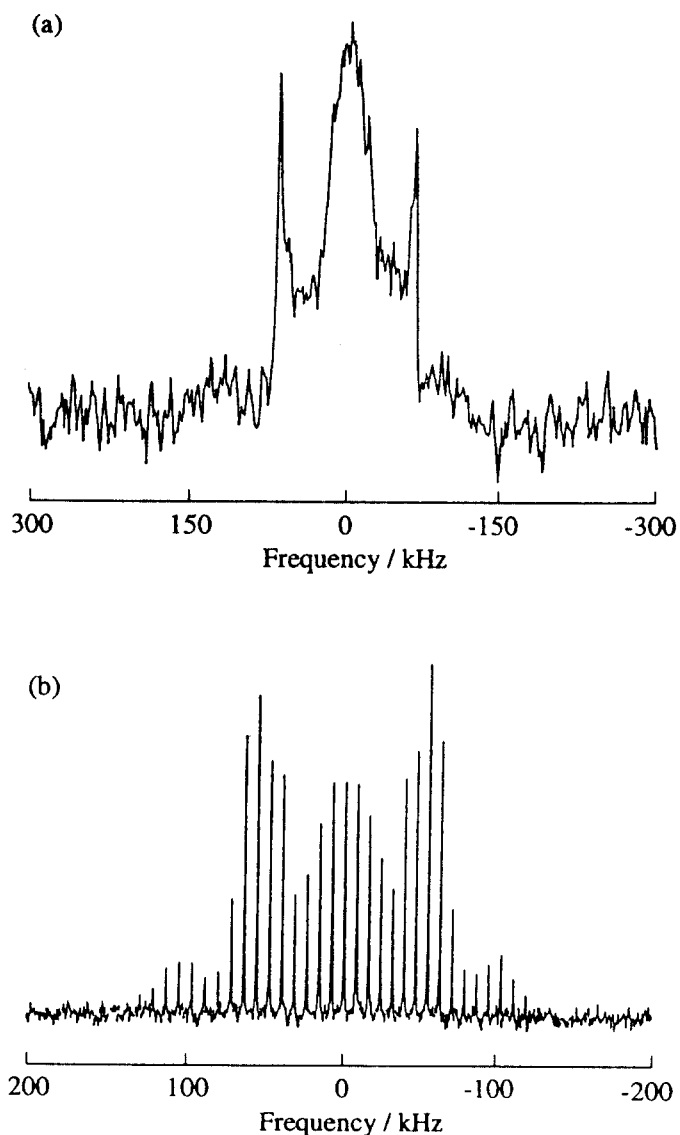

Fig. 1. Solid-state ^2H NMR spectra of $(\mu_3\text{-}C^2H)[Co(CO)_3]_3$. (a) wideline spectrum and (b) MAS spectrum taken at a spin rate of 8 kHz.

The experimental symmetrized stick spectrum in Fig. 2a was obtained by averaging each pair of spinning sidebands of the MAS NMR spectrum that are related to each other about the isotropic chemical shift.   Shown in Fig. 2b is the simulated stick spectrum using quadrupole coupling constant of 178 kHz and asymmetry parameters of 0. Simulated MAS centerband and spinning sidebands intensities were calculated using a Herzfeld-Berger method with minor modifications[8] for the quadrupolar interaction.   The residuals between the experimental and calculated stick spectra is shown in Fig. 2c. The large deviations in centerband and four spinning sidebands is due to the impurity in sample.

Table 1 shows the C-H bond lengths and the corresponding ^{2}H quadrupole coupling constants for $(\mu_3\text{-}C^2H)[Co(CO)_3]_3$, (1-^2H) propyne, and $cis\text{-}(\mu\text{-}C^2H_2)(\mu\text{-}CO)[FeCp(CO)]_2$. In this table, the C-H bond length in $cis\text{-}(\mu\text{-}C^2H_2)(\mu\text{-}CO)[FeCp(CO)]_2$ was obtained from a linear correlation between the C-H bond lengths and the C-H
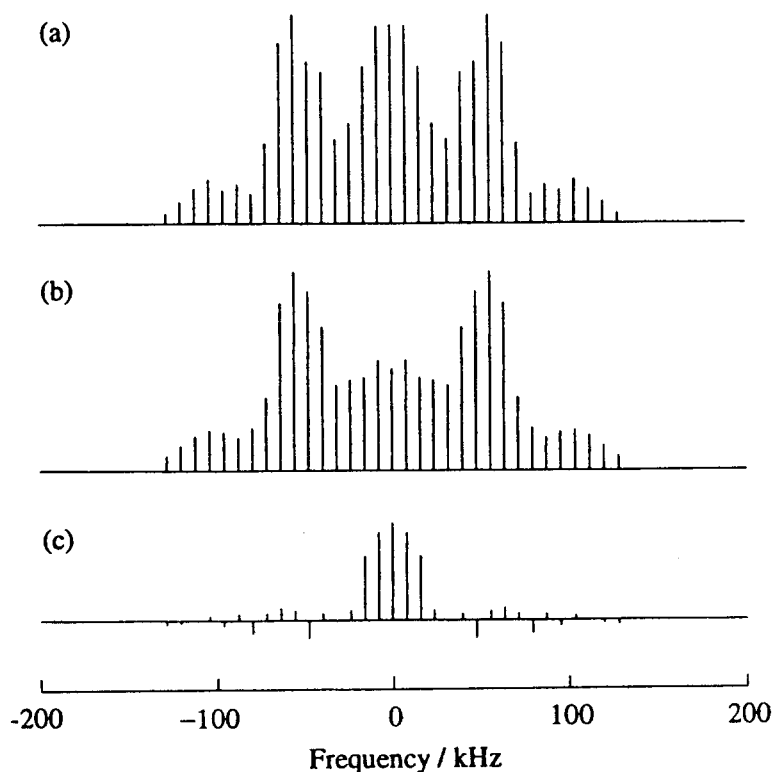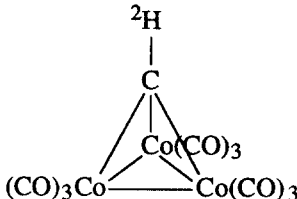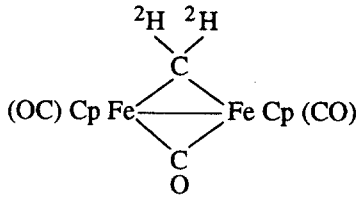

Fig. 2.   Solid-state ^{2}H MAS stick spectra of $(\mu_3\text{-}C^2H)[Co(CO)_3]_3$.   (a) Experimental symmetrized stick spectrum recreated from spinning sideband integrals of the MAS spectrum.   (b) Calculated stick spectrum using $e^2q_{zz}Q/h$ = 178 kHz and η = 0.   (c) The residuals between the experimental and calculated stick spectra.

streching frequency for a kinetically "isolated" C-H bond.   This correlation method was developed by McKean[9,10] and applied to other metal alkyls such as $CH_3Mn(CO)_5$ and $CH_3Re(CO)_5$.   The slope of the correlation is -0.0001 Åcm^{-1}, making precise, relative assessments of C-H bond lengths possible.   The ^2H quadrupole coupling constant of (1-^2H) propyne was measured in the gas phase from microwave spectroscopy.[11]   Care must be taken in extrapolating the values of the quadrupole coupling constant obtained in the gas phase to the solid state since vibrational effects slightly modulate the value of the quadrupole coupling constant.[12]   As shown in the table, the ^2H quadrupole coupling constants for bridging methylene (M-C^2H_2) and methyne (M-C^2H) units are so similar that they can not be distinguished.

Fig. 3 shows a plot of ^2H quadrupole coupling constants vs. C-H bond lengths.   In this figure, the trace represents the empirical fit to the experimental and calculated quadrupole coupling constants for 37 X-^2H sites based on the Huber's work.[13]   Small deviations in ^2H quadrupole coupling constants between the trace and three compounds may be due to negative charge on carbon. The charge on carbon can be determined by

Table 1.   The ^2H quadrupole coupling constants for C-^2H sites.

Compounds	QCC / kHz	d(C–H) / Å
^2H │ C △ Co(CO)$_3$ (CO)$_3$Co————Co(CO)$_3$	178 (2) [a]	1.084 [b]
H_3C—C≡C—^2H	208 (10) [c]	1.056 [c]
^2H ^2H \ / C (OC) Cp Fe————Fe Cp (CO) C O	174 (2) [d]	1.1 [e]

[a] from this work.   [b] from neutron diffraction method.[15]   [c] from microwave spectroscopy.[11,17]   [d] from solid-state ^2H NMR spectroscopy.[5]   [e] from IR method.[5,9,10,16]
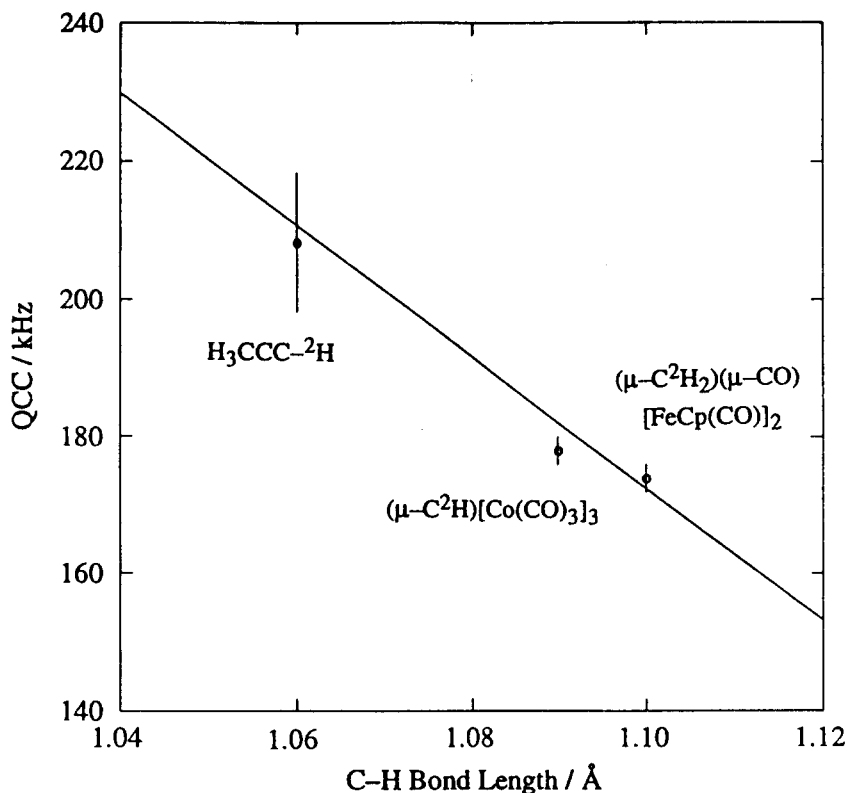
Fig. 3.   Plot of ^{2}H quadrupole coupling constants versus C-H bond lengths.   The trace represents empirical fit to experimental and calculated ^{2}H quadrupole coupling constants for 37 X-^{2}H sites.   The C-H bond lengths for three compounds are obtained from the IR methods.

using the assigned orbital model,[4,5] in which the equation modified for the calculation of the quadrupole coupling constant is as follows;

$$e^2q_{zz}Q/h \text{ (sample)} = e^2q_{zz}Q/h \text{ (ref)} + \frac{2 e^2 Q \Delta q}{a_0^3 h} \left\langle \psi_p^* \left| \sum_i \frac{3z_i^2 - r_i^2}{r_i^5} \right| \psi_p \right\rangle$$

where $e^2q_{zz}Q/h$ (ref) is the scaled ^{2}H quadrupole coupling constant for the reference, the factor of two in the second term of the equation accounts for the distribution of charge over the two carbon p orbitals of the apical carbon in $(\mu_3\text{-C}^2\text{H})[Co(CO)_3]_3$, and Δq

is the change in the occupancy in the carbon p orbitals relative to the reference molecule. An increase in occupancy of the carbon 2p orbital reduces $\Delta(e^2q_{zz}Q/h)/\Delta q$ to -61.2 kHz. The sp-acetylenic carbon in propyne was chosen as reference. The rate of increase of ^2H quadrupole coupling constant with the C-H bond distance is 1 kHz per 0.001 Å;[12,15] thus the scaled quadrupole coupling constants in (1-^2H)propyne are 180 kHz. Thus, the charge on the methyne carbon is -0.03 e with respect to the acetylenic carbon in (1-^2H)propyne. This observation supports the idea that the bonding in methyne unit is described as an sp hybrid and its charge is close to that of an acetylenic carbon but slightly more negative.

CONCLUSIONS

Triply bridging methyne in $(\mu_3\text{-}C^2H)[Co(CO)_3]_3$ has small deuterium quadrupole coupling constant of 178 (2) kHz which depends on C-H bond length and slightly negative charge on carbon relative to acetylenic carbon in (1-^2H)propyne. It would be difficult to distinguish between bridging methylene and methyne units, since both have similar values for deuterium quadrupole coupling constant.

Acknowledgments

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