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^{13}C Chemical Shift Anisotropy, Proton Spin–Lattice Relaxation Time Measurements, and the Barriers to Rotation in Crystalline Pentacarbonyl(methyl)manganese(I) and Pentacarbonyl(methyl)rhenium(I) Complexes

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Proton spin–lattice relaxation times and ^{13}C chemical shift anisotropy measurements have been made on the complexes pentacarbonyl(methyl)manganese(I) and -rhenium(I), $CH_3M(CO)_5$, (M = Mn, Re). The barrier to rotation of the methyl group in the manganese complex is 21.7 kJ mole^{-1}, and the chemical shift anisotropies are not averaged in either complex. The disorder that exists in these complexes is, therefore, probably a static disorder without overall molecular rotation.

INTRODUCTION

The pentacarbonylmethyl complexes of manganese(I) and rhenium(I) [$CH_3M(CO)_5$, M = Mn, Re] are the simplest organometallic systems containing a metal–carbon σ bond and serve as prototypes for organometallic catalyzed reactions. However, structural studies and the solid state behavior have proven to be quite complex. An X-ray diffraction study of the crystal structure of the manganese compound (1) showed the presence of statistical disorder with each octahedral coordination site occupied by one-sixth of a methyl carbon and five-sixths of a carbonyl group. The disorder could be either static, with random occupancy of each lattice site, or dynamic, with an averaging over all sites due to molecular rotation. In the latter case, a phase transition to an ordered structure is possible, but no transition was observed with temperature down to 10 K, although a variable-pressure study (2) showed second-order phase transitions at 9 and 22 kbar in the manganese and rhenium complexes, respectively.

A second point of interest lies in determining the barrier to rotation of the methyl group, both in the gas phase and in the solid. This has been extensively discussed (1, 3–5), but no direct measurement has been reported. Vibrational spectroscopic studies of both complexes in the vapor phase showed that the barrier to internal rotation of the methyl group is extremely low and results from the out-of-plane motions of the carbonyl groups (3, 4), The CH_3 rocking mode is very sensitive to the change of phase from the gas to the solid, which shows that a change in barrier must occur. An early estimate (5) of the barrier in the solid, 11 ± 2 kJ mole^{-1}, based upon the temperature broadening of the asymmetric C–H stretch, was criticized (1) as being too high, since the derivation of the nonrotationally broadened bandwidth was taken as the value observed in solid $CH_3Mn(CO)_5$ at -140°C, which could be broadened by the disorder in the solid. Estimates based upon the torsional modes (1) observed in the Raman spectrum and by neutron scattering measurements, were also challenged (3) on the grounds that a low V_{12} barrier cannot be reconciled with the low torsional frequencies in the crystal, since a very large barrier would be needed in order for well-defined torsional levels to occur, and torsional–rotational transitions, therefore, must be spread over a wide region of the spectrum.

To address these long-standing questions regarding the disorder and the barrier to rotation, we have undertaken proton spin–lattice relaxation time and ^{13}C chemical shift anisotropy measurements on the solid pentacarbonylmethyl complexes of manganese and rhenium.

EXPERIMENTAL SECTION

The compounds were prepared by literature methods (6, 7), as described previously (2). Solution ^{13}C NMR spectra were measured using a Varian XL-300 spectrometer, and solid state CP-MAS spectra were obtained on a Chemagnetics CMX-300 spectrometer, both at 75.43 MHz. Proton spin–lattice relaxation time measurements were performed at 33 MHz, using a Spin-Lock CPS-2 spectrometer, by the inversion–recovery method. The temperature was controlled using a flow of cooled nitrogen gas and measured with a digital thermocouple.

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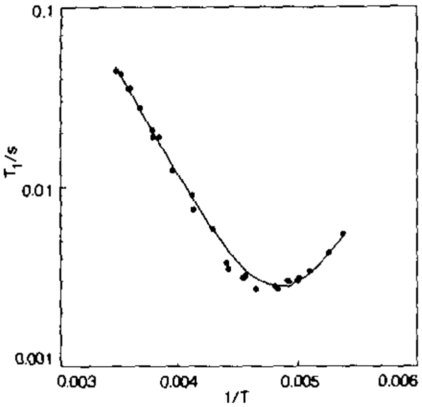

FIG. 1. Pentacarbonyl(methyl)manganese(I): Proton spin–lattice relaxation time (sec) versus reciprocal temperature (K^{-1}). The solid line is the fit to the BPP equation.

RESULTS AND DISCUSSION

Solution ^{13}C NMR chemical shifts for both compounds have been reported previously and the present results are in excellent agreement in the case of $CH_3Re(CO)_5$ (8): *trans*-CO 181.2 ppm, *cis*-CO 185 ppm, methyl −38.1 ppm from TMS, in deuteriochloroform. The earlier results for the manganese derivative reported (9) identical chemical shifts for the *cis*- and *trans*-carbonyl groups at 213.4 ppm, but these resonances were clearly separated in the present study: *trans*-CO 206.9 ppm, *cis*-CO 210.1 ppm, methyl −23.4 ppm, in deuterated methylene chloride. In the solution spectra, no couplings were observed between the carbonyl groups and the metal nuclear spins (^{55}Mn, ^{185}Re, and ^{187}Re), presumably as a result of rapid quadrupole relaxation (10).

The proton spin–lattice relaxation time dependence on reciprocal temperature is shown in Fig. 1 for the manganese complex. The low signal-to-noise ratio for the rhenium complex precluded accurate measurement of T_1 in this case. A fit of the observed T_1 behavior to the BPP equation gave a barrier of 21.7 kJ mole^{-1} and a preexponential term of 8.7×10^{-15} sec. The value of the T_1 minimum (2.7 msec) was in poor agreement with that expected from the calculated changes in second moment for an isolated methyl group undergoing either rotation about the C_3 axis or isotropic rotation (about 19 and 14 msec, respectively, for a resonance frequency of 33 MHz). However, due to the disorder, it is possible that a distribution of correlation times exists. A barrier as high as 20 kJ mole^{-1} might favor rotation of the whole molecule and dynamic disorder, since the barrier to internal rotation of the methyl group is small. This possibility can be examined by testing whether the chemical shift anisotropy is averaged.

Initially, we were unable to obtain resolved spinning side-bands in the solid state spectra at 4.7 T (50.3 MHz) but spectra were obtained at higher field, 7.05 T (75.5 MHz). Since the ^{13}C isotropic chemical shifts of the *cis*- and *trans*-carbonyl nuclei differed by only a few ppm, they could not be separated in the solid state spectra. Thus the sidebands due to the *cis*-carbonyls, which should

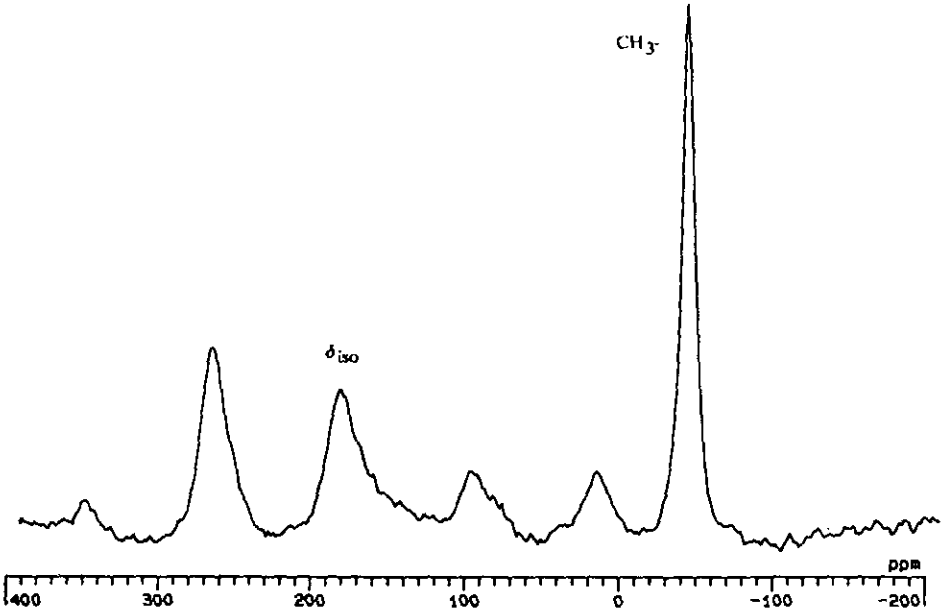

FIG. 2. ^{13}C CP-MAS spectrum of pentacarbonyl(methyl)rhenium(I) at room temperature. Contact time 5 msec, spinning speed 6.3 kHz, 11,000 scans accumulated with recycle delay of 5 sec.

have a noncylindrically symmetric shift tensor, overlap those of the *trans*-carbonyl, which would have a cylindrically symmetric tensor. The spectra are complicated by a combination of additional factors since ^{55}Mn and the two isotopes of rhenium all have spin $\frac{5}{2}$ and high nuclear quadrupole moments. Residual dipolar coupling to the metal nuclear spins and quadrupolar interactions could add additional broadening. The indirect coupling is not averaged by magic-angle spinning, and the spectrum of the carbonyl groups in the rhenium complex should contain overlapping sextets arising from coupling to the two isotopes, but such splittings were not observed, either because the sidebands were too broad, or rapid quadrupolar relaxation still occurred in the solid. The analysis of the spinning side-band pattern for spin $\frac{1}{2}$ nuclei coupled to quadrupolar nuclei has been recently discussed (11, 12).

Unfortunately, although sideband patterns were observed in the spectra of the manganese complex, no satisfactory solutions to the Herzfeld–Berger method could be obtained. However, the overall width of the spectra exceeded 20 kHz and, therefore, the chemical shift anisotropy is not averaged by molecular motions. For the rhenium complex, spectra obtained at different spinning rates between 4 and 6 kHz were analyzed satisfactorily using the Herzfeld and Berger graphical method (13) and gave consistent results: $\delta_{11} = 335 \pm 5$, $\delta_{22} = 285 \pm 5$, and $\delta_{33} = 65 \pm 5$ ppm, from TMS. These values are in the range found for other metal carbonyl complexes (14–17), where the shift tensors for nonbridging carbonyl groups vary only slightly with the transition metal. For example, the average values cited by Duncan (14) are: $\delta_{11} = 327 \pm 22$, $\delta_{22} = 320 \pm 21$, and $\delta_{33} = -64 \pm 28$ ppm for a wide variety of compounds, including metal hexacarbonyl complexes, metal cluster carbonyls, and surface-bound complexes.

Since the full chemical shift anisotropic spectrum was observed, the rate of any motional averaging of the carbonyl resonance must be limited to the width of the shift anisotropy, 400 ppm at 75 MHz, which places an upper limit of about 30 kHz on the frequency of whole molecule motion.

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