J. Am. Chem. Soc. **1994,** *116,* 7445-7446

Olefin Rotation in the Solid State: A ^{13}C, ^{1}H, and ^{2}H NMR Study of $Rh(acac)(C_2H_4)_2$

Stephanie A. Vierkötter and Craig E. Barnes*

Department of Chemistry, University of Tennessee
Knoxville, Tennessee 37996-1600

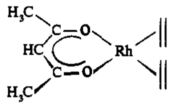
Greta L. Garner and Leslie G. Butler*

Department of Chemistry, Louisiana State University
Baton Rouge, Louisiana 70803-1804

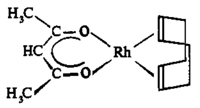
Received March 21, 1994

Motional dynamics in organometallic compounds in solution have been studied intensively for some time.[1] During the last decade, interest has focused on the question of whether analogous molecular motions occur in the solid state and whether such motions are important in initiating solid-state reactions. Solid-state dynamic behavior for organometallic complexes reported thus far has involved primarily motions of carbonyl ligands in metal clusters and rotations of discoidal ("disklike") aromatic ligands such as cyclopentadienyl and arene rings about their binding axes with the metal.[2] Fewer cases involving more asymmetric ligands have been described. While rotation of a coordinated ethylene ligand is frequently observed in solution,[1] we are aware of only one report of this type of motion in the solid state. Gallop et al. studied the molecular dynamics in the triosmium cluster $Os_3(C_2H_4)(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_6H_6)(CO)_8$ in solution and in the solid state.[3] Based on solid-state NMR data, they described evidence for rotation of both the ethylene and benzene ligands in this complex in the solid state.

In this communication we report the results of a detailed study of the solid-state molecular motions of olefin ligands in two monomeric rhodium compounds, $Rh(acac)(C_2H_4)_2$ (**1**) and Rh(acac)(cod) (**2**) (acac = 2,4-pentanedionate; cod = 1,5-cyclooctadiene). Variable-temperature solid-state ^{13}C CP/MAS NMR spectroscopy,[4] ^{2}H NMR powder patterns,[5] and measurements of the ^{1}H relaxation time in the rotating frame, $T_{1\rho}(^{1}H)$,[6,7] all show that the ethylene ligands in **1** rotate in the solid state. Similar measurements on the cod analog **2**, in which olefin rotation is not possible, show that the cod ligand undergoes a small-amplitude motion about its equilibrium binding position.



1



2

Figure 1 shows the solid-state ^{13}C CP/MAS NMR spectra of the ethylene ligands in **1** at temperatures[8] between 235 and 392 K. At 235 K, two distinct resonances are observed for the ethylene carbons (59.4, 60.3 ppm).[9] At 265 K, the signals for the ethylene carbons coalesce, and at room temperature a single signal at $\delta = 59.9$ ppm ($\Delta\nu_{1/2} = 55.6$ Hz[10]) is observed. Line-shape analysis on spectra between 235 and 270 K gives a value for $\Delta G^{\ddagger}$ of 56(6) kJ mol^{-1} (13 kcal mol^{-1}) at 265 K for the process causing coalescence.

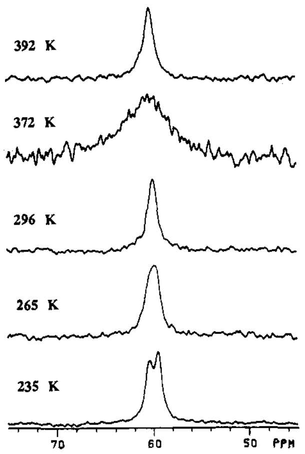


Figure 1. Variable-temperature ^{13}C CP/MAS NMR spectra of the olefin region of **1**. Spinning rate, 4 kHz; contact time, 1 ms; recycle delay, 15 s; proton decoupling field, 50 kHz; spectrometer frequency, ^{13}C 50.31 MHz; line broadening factor, 10 Hz.

The crystal structure of **1** reveals a crystallographically imposed mirror plane which bisects the rhodium-centered square plane and renders the two ethylene *ligands* equivalent in the solid state.[11] However, for the single unique molecule in the unit cell, the two carbon *atoms* of each ethylene ligand are in different environments.[12] Therefore, two ^{13}C resonances can be expected for the ethylene ligands in the solid-state NMR spectrum in the static or slow exchange limit, consistent with the 235 K ^{13}C CP/MAS NMR spectrum.

Two dynamic processes were considered to explain the observed coalescence behavior observed in **1**: small amplitude libration[13] or libration accompanied by full rotation (180° jumps) of the ethylene ligands about their binding axes with the rhodium atom. The free energy of activation of 56 kJ mol^{-1} for this process is similar to that found for ethylene rotation in **1** in toluene solution (51.7 kJ mol^{-1} at 265 K).[14] Small angle librations are usually low-energy processes which have megahertz or higher frequencies[15] in contrast to the coalescence process, for which the rate

---

[1] Mann, B. E. Non-rigidity in Organometallic Compounds. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York; Vol. 3, Chapter 20, pp 89-168.

[2] Braga, D. *Chem. Rev.* **1992,** *92,* 633-665.

[3] (a) Gallop, M. A.; Johnson, B. F. G.; Keeler, J.; Lewis, J.; Heyes, S. J.; Dobson, C. M. *J. Am. Chem. Soc.* **1992,** *114,* 2510-2520. (b) Heyes, S. J.; Gallop, M. A.; Johnson, B. F. G.; Lewis, J.; Dobson, C. M. *Inorg. Chem.* **1991**, *30*, 3850. (c) Braga, D.; Grepioni, F.; Johnson, B. F. G.; Lewis, J.; Martinelli, M. *J. Chem. Soc., Chem. Commun.* **1990,** 1847.

[4] CP/MAS, cross-polarization/magic angle spinning. For a review of variable-temperature CP/MAS spectroscopy, see: Lyerla, J. R.; Yannoni, C. S. *Acc. Chem. Res.* **1982,** 208-216.

[5] Altbach, M. I.; Hiyama, Y.; Wittebort, R. J.; Butler, L. G. *Inorg. Chem.* **1990,** *29,* 741-747.

[6] Fyfe, C. A. *Solid State NMR For Chemists*; C. F. C. Press: Guelph, Ontario, Canada, 1983.

[7] (a) Slichter, C. P.; Ailion, D. *Phys. Rev. A.* **1964,** *135,* 1099. (b) Ailion, D. In *Advances in Magnetic Resonance*; Waugh, J. S., Ed.; Academic Press: New York, 1971; Vol. 5, pp 177-227.

[8] Temperatures below room temperature were calibrated according to the method reported in the following: Haw, J. F.; Campbell, G. C.; Crosby, R. C. *Anal. Chem.* **1986,** *58,* 3172.

[9] Three singlets are observed for the acac ligand in **1**: 29.4 (CH_3), 101.5 (CH), and 188.1 ppm (C=O). The chemical shifts found in the solid state match approximately those found for $Rh(acac)(C_2H_4)_2$ in solution: δ(^{13}C, ppm; $CDCl_3$, $\delta(CDCl_3) = 77.0$ ppm, 62.90 MHz): 27.21 (CH_3, s), 59.54 (C_2H_4, d, $^{1}J(Rh\text{–}C) = 13.75$ Hz), 99.05 (CH, s), 186.46 (CO, s).

[10] Line broadening factors have been removed from quoted line widths.

[11] Evans, J. A.; Russell, D. R. *J. Chem. Soc., Chem. Commun.* **1971,** 197-198. We have redetermined the structure of **1** at -100 °C and room temperature. The results of these studies, including an analysis of atomic displacement parameters, will be described in a future publication: Vierkötter, S. A.; Barnes, C. E.; Butler, L. G.; Garner, G.; Fronczek, F., manuscript in preparation.

[12] The average $Rh\text{–}C_{(ethylene)}$ bond length in **1** is 2.144 ± 0.005 Å, and the tilt angle of the ethylene ligands off the perpendicular to the rhodium square plane is 0.5°. Furthermore, due to the molecular packing arrangement in the crystal, the ethylene carbon atoms above the plane of the molecule are in a different "intermolecular environment" than those below the plane.

[13] Symmetrical libration of the ethylene ligands about their binding axes with the rhodium atom would produce time-averaged mirror symmetry in the plane of the molecule. Under these conditions, all ethylene carbons become equivalent and, if *inter*molecular differences are small, chemical shift equivalent.

[14] Herberhold, M.; Kreiter, C. G.; Wiedersatz, G. O. *J. Organomet. Chem.* **1976,** *120,* 103-130.

[15] Dunitz, J. D.; Maverick, E. F.; Trueblood, K. N. *Angew. Chem., Int. Ed. Engl.* **1988,** *27,* 880-895. Braga, D.; Anson, C. E.; Bott, A.; Johnson, B. F. G.; Marseglia, E. *J. Chem. Soc., Dalton Trans* **1990,** 3517-3524.

0002-7863/94/1516-7445$04.50/0

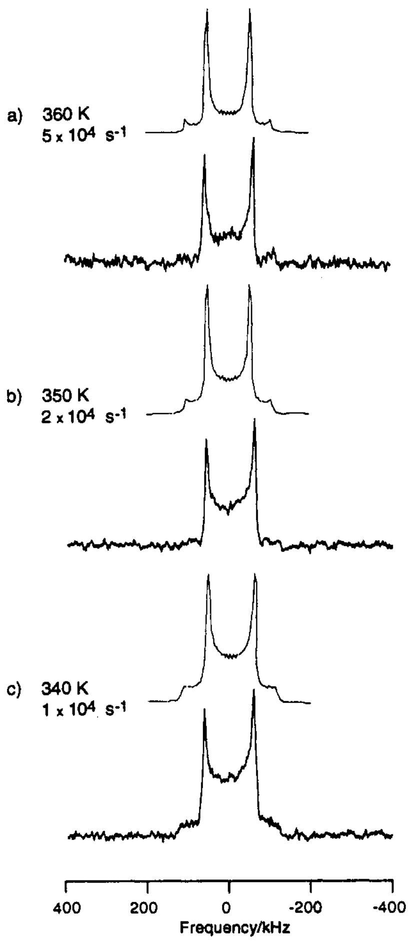


Figure 2. Solid-state ^2H NMR spectra of $Rh(acac)(C_2D_4)_2$ and simulations. The spectra were acquired with a quad echo pulse sequence (recycle delay, 60 s; 2.5-μs 90° rf pulses; interpulse spacing, 30 μs; average of 500–2000 transients). Simulations were done with TURBOPOWDER[21] based on a deuterium quadrupole coupling constant of 160 kHz, asymmetry parameter of zero, EFG aligned with C–D bond, and bendback angle of 12°.

constant is approximately 100 Hz at 265 K. Thus, the observed coalescence of the ethylene carbon resonances is most consistent with ethylene rotation.

When **1** is heated to temperatures above room temperature, the ethylene resonance first broadens significantly (Figure 1, T = 372 K) and then resharpens again at higher temperatures, while the signals associated with the acac ligand are not affected. The observed line broadening is consistent with motional modulation of the CH dipolar decoupling of the ethylene resonances[16] and is further indication for a type of dynamic behavior in $Rh(acac)(C_2H_4)_2$ which involves only the ethylene ligands.

Further evidence for the rotation of the ethylene ligands in **1** was obtained from solid-state ^2H NMR. Deuterium NMR accesses a different range of exchange rates than the ^{13}C CP/MAS experiment, and the line shape of the ^2H powder pattern can be analyzed to determine the type of molecular motion, i.e., small angle libration or 180° jumps. Powder patterns for $Rh(acac)(C_2D_4)_2$[17] were recorded at several temperatures in the range of 300–370 K (Figure 2). As the temperature is increased, the characteristic ^2H powder pattern for the low-temperature limit (static or slow motion) evolves with loss of intensity in the central portion of the line shape. Also shown in Figure 2 are simulated ^2H line shapes based on a model with 180° rotational motion for the olefin bound to rhodium at the rates indicated in the figure.[18] At 350 K, the rate constant is estimated to be 2×10^4 s^{-1}. Simulations were also done with the assumption that the olefin ligands execute small angle librational motion on the order of ±5° to ±15°; however, rate constants obtained from this model were inconsistent with the ^{13}C CP/MAS results, and this model was not accepted.

Temperature studies of $T_{1\rho}(^1H)$ are highly useful as a survey for the presence or absence of solid-state motions in the vicinity of 5×10^4 s^{-1}, the Larmor frequency of the rotating frame in the spin–lock experiment.[6,7] Measurements of $T_{1\rho}(^1H)$ for **1** and **2** reveal that their temperature dependencies are markedly different. At 253 K, both **1** and **2** have long $T_{1\rho}(^1H)$ values of about 1 s. At 353 K, however, $T_{1\rho}(^1H)$ remains long for **2** but is 200-fold shorter for **1**; this can be taken as evidence for a motional process in **1** with a rate of the order of 5×10^4 s^{-1}. Based on the ^{13}C and ^2H NMR work, the motional process is that of olefin rotation. The constant value of $T_{1\rho}(^1H)$ for the cod complex **2** is also consistent with the absence of a motional process like olefin rotation in this complex.[19]

In summary, variable-temperature ^{13}C and ^2H solid-state NMR data and $T_{1\rho}(^1H)$ relaxation time measurements for **1** and **2** show that the ethylene ligands in $Rh(acac)(C_2H_4)_2$ (**1**) undergo not only librational motion but also 180° flips (rotation), while the cod in Rh(acac)(cod) undergoes only librational motion.[19] At 265 K, the olefin rotation rate in **1** is such that coalescence occurs for the two ^{13}C resonances; at 350 K, the ^2H NMR spectrum shows evidence of 180° olefin rotations at a rate of 2×10^4 s^{-1}. An Eyring plot using both the ^{13}C and the ^2H data gives a $\Delta G^{\ddagger}$ value of 56.5(3) kJ mol^{-1} at 298 K.[20] Thus, ethylene rotation in the mononuclear rhodium bisethylene complex **1** is a type of molecular motion which can occur not only in solution but also in the solid state. Furthermore, lattice interactions in solid **1** neither prevent ethylene rotation nor increase the barrier to rotation significantly above that observed in solution. From our studies, it is apparent that reorientational motion in the solid state is not limited to ligands of discoidal shape but is also accessible to more asymmetric ligands such as ethylene. Molecular motion studies involving $Rh(acac)(C_2H_4)(CO)$ and analogous iridium complexes are in progress to evaluate in more detail the roles of intra- and intermolecular forces in the solid state.

Acknowledgment. S.A.V. and C.E.B. gratefully acknowledge the generous loan of rhodium salts from Johnson Matthey Aesar Alfa. G.L.G. and L.G.B. gratefully acknowledge support from the National Science Foundation (CHE-9119871). S.A.V. and C.E.B. would also like to acknowledge helpful discussions with Dr. Edward Hagaman (Oak Ridge National Laboratories, Oak Ridge, TN).

---

(16) Voelkel, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1468–1483 and ref 13, 14 and 20 therein. Maximum motional broadening is observed when the frequency of the motion matches the strength of the proton field $B_1(^1H)$ (50 kHz).

(17) $Rh(acac)(C_2D_4)_2$ was prepared from the dimeric complex $[RhCl(C_2D_4)_2]_2$ (Haddleton, D. M.; McCamley, A.; Perutz, R. N. *J. Am. Chem. Soc.* **1988**, *110*, 1810–1817) according to the procedure reported in the following: Cramer, R. *Inorg. Synth.* **1974**, *15*, 14.

(18) A 12° bend-back angle was assumed for the ethylene deuteriums in the ^2H NMR simulations for **1**-d_8. This value was obtained from a low-temperature structure determination of **1** (ref 11).

(19) ^{13}C CP/MAS spectra of **2** acquired at temperatures ranging from 299 to 372 K show that the cod ligand undergoes librational motion about its equilibrium binding position: at room temperature, the spectrum of **2** shows four resonances for the olefinic carbons (75.7, 76.7, 77.4, 78.4 ppm) and three for the aliphatic carbons of the cod ligand (30.5, 31.5, 32.7 ppm). At higher temperatures, the peak envelopes of both the olefinic and the aliphatic cod carbons become narrower, and only three olefinic resonances are resolved at 372 K. In contrast to the ethylene complex **1**, no motional broadening of the resonances for the olefinic carbons in **2** is observed in these spectra.

(20) The enthalpy and entropy of activation from this analysis are $\Delta H^{\ddagger}$ = 51.5(2) kJ mol^{-1}; $\Delta S^{\ddagger}$ = −16.7(5) J mol^{-1} K^{-1}.

(21) The ^2H NMR line-shape simulation program TURBOPOWDER was generously provided by Prof. R. G. Griffin (Wittebort, R. J.; Olejniczak, E. T.; Griffin, R. G.; *J. Chem. Phys.* **1987**, *86*, 5411).