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^{13}C CP/MAS NMR Studies of the Stereochemical Nonrigidity of Titanium Tetracyclopentadienyl in the Solid State

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Abstract: Variable-temperature ^{13}C CP/MAS NMR spectroscopy of $Ti(\eta\text{-}C_5H_5)_2(\sigma\text{-}C_5H_5)_2$ has shown that sigmatropic rearrangement of the σ-cyclopentadienyl rings occurs for the molecule in the crystalline state. Magnetization-transfer experiments at 165 K are consistent with [1,2] shifts being the main pathway for the rearrangement, but there is evidence for the possibility of [1,3] shifts as a minor pathway. These measurements, in conjunction with spectral line-shape analysis in the exchange broadening regime, have been used to estimate Arrhenius activation parameters for [1,2] shifts of $E_a = 33.2 \pm 1.0$ kJ mol^{-1} and $A = 2.9 \times 10^{10}$ s^{-1}. The activation barrier is similar to that suggested by solution NMR studies, implying that control of the rearrangement is principally by electronic factors. In contrast to the results of solution NMR studies, only at the highest temperature (369 K) accessible before thermal decomposition of the solid intervenes is there evidence that σ-/η-cyclopentadienyl ligand functionality interchange may be significant on the NMR time scale.

Introduction

Many organometallic compounds have been found to adopt structures that exhibit stereochemical nonrigidity or fluxional behavior. The majority of studies of such processes have been by solution NMR techniques, mainly involving observation of exchange broadening and coalescence, and more recently by magnetization-transfer experiments, using both one- and two-dimensional techniques, in the slow limit of chemical exchange. Many types of fluxional behavior have been implicated, and kinetic and mechanistic information has become available from a wide range of studies.[1-4]

A question of considerable importance is whether such fluxional processes, as identified in solution, persist in the solid state, and if they do, to what extent the activation barriers differ in the two environments. Indeed, it is becoming increasingly apparent from solid-state NMR studies of organometallic and metal cluster compounds that neither molecular reorientation (overall or of a single moeity) nor ligand exchange and rearrangement processes (fluxionality) are necessarily precluded by lattice interactions in the solid state. It has, for example, long been known that reorientation of unsubstituted arene rings π-bonded to a metal atom is often facile ($E_a < 15\text{–}20$ kJ mol^{-1}),[5,6] although substituted rings have much higher activation barriers or tend to be locked into a single orientation in the lattice.[7] Thus, ^1H NMR second-moment studies show an activation barrier to benzene reorientation about its principal axis in solid $Cr(CO)_3(\eta^6\text{-}C_6H_6)$ of ca. 16 kJ mol^{-1},[8] whereas ^{13}C CP/MAS NMR spectra of $M(CO)_3(\eta^6\text{-}C_6H_5Me)$, M = Cr, Mo,[9] are consistent with arene rigidity but rotational motion of the tricarbonyl ligand set at a higher energy ($\Delta G^\ddagger \approx 65\text{–}75$ kJ mol^{-1}). Fyfe and co-workers have detected sigmatropic rearrangements of the (η^1-C_5H_5) rings of $Fe(CO)_2(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)$ and $XHg(\eta^1\text{-}C_5H_5)$ (X = Cl, Br, I, and η^1-C_5H_5) by ^1H wide-line NMR[10,11] and ring reorientations of various types of coordinated cyclooctatetraene in the complexes $Fe(CO)_3(\eta^4\text{-}C_8H_8)$, $Fe_2(CO)_5(\mu\text{:}\eta^8\text{-}C_8H_8)$, and $Ru_3(CO)_4(\mu\text{:}\eta^8\text{-}C_8H_8)_3$ both by ^1H wide-line NMR[12-14] and by ^{13}C CP/MAS NMR.[15,16] Detailed kinetic or mechanistic analyses were not achieved in these studies, but more recently such information has begun to emerge about a variety of problems. Benn et al.[17] have recently detected diene topomerization in $Zr(\eta^5\text{-}C_5H_4Bu^t)_2(\eta^4\text{-}CH_2{=}CH{-}CH{=}CH_2)$ at elevated temperatures by ^{13}C CP/MAS 2D-exchange NMR spectroscopy; from measurement of the cross-peak intensities the activation energy could be estimated. In studies of metal carbonyl cluster compounds, ^{13}C CP/MAS NMR spectra of $Co_2(CO)_8$[18] identified a polytopal reorganization of the ligand polyhedron which effects terminal/bridging carbonyl exchange. Similar studies of fluxionality in $Fe_3(CO)_{12}$[19,20] and $Co_4(CO)_{12}$[21] have been interpreted in terms of metal core reorientation within the CO polytopes causing the effective interchange of terminal and bridging carbonyls. Polytopal rearrangement in the nine-coordinate complex $W(PMe_3)_3H_6$ has been explored by ^{13}C and ^{31}P CP/MAS NMR spectroscopy,[22] and by use of ^{13}C CP/MAS NMR spectroscopy a variety of fluxional processes occurring in the cluster compound $Os_3(CO)_8(\eta^2\text{-}C_2H_4)(\mu_3\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$[23] have been characterized.

Among the best understood of fluxional processes in solution is the rearrangement of σ-polyenyl–metal systems, including the rearrangements of σ-cyclopentadienyl, σ-indenyl, σ-allyl, and σ-cycloheptatrienyl complexes. Most such sigmatropic rearrangements appear to occur by Woodward–Hoffmann allowed *supra*facial [1,5] shifts. In most systems studied to date such shifts are equivalent to [1,2] shifts and are thus indistinguishable from those expected on the principle of least motion. [1,3] shifts are expected to be *antara*facial and therefore highly disfavored. In

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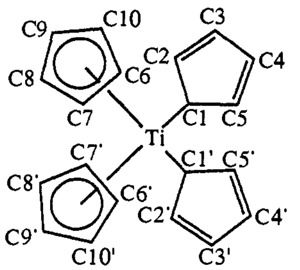

Figure 1. Structure of the titanium cyclopentadienyl molecule, showing the numbering scheme used in the subsequent discussion.

this paper we describe a study by solid-state NMR of the compound $Ti(\eta^5-C_5H_5)_2(\eta^1-C_5H_5)_2$ (**1**). The behavior of **1** in solution is a classic example of stereochemical nonrigidity of an organo-transition-metal compound[24,25] and includes a sigmatropic σ-C_5H_5 ring rearrangement. The comparison of behavior of **1** in the solid and solution states is therefore of particular interest.

$Ti(C_5H_5)_4$ has been shown by a single-crystal X-ray diffraction study[25] to contain two *pentahapto*cyclopentadienyl rings that show an essentially symmetrical M–(C_5H_5) interaction and two genuine, well-defined *monohapto*cyclopentadienyl rings[26] (see Figure 1). The dynamic behavior of **1** has been extensively studied by ^1H NMR in solution at 100 MHz.[24] At temperatures below ambient, spectral changes indicative of sigmatropic ring rearrangement were observed, though at the lowest temperature studied, 134 K, the slow limit of the rearrangement has not been attained. Although kinetic parameters for this process were not determined, comparison of the spectra with those of $(\eta^1-C_5H_5)M(CO)_2((\eta-C_5H_5)$ (M = Fe, Ru) suggests an activation energy of $E_a < \approx 40$ kJ mol^{-1}. At temperatures above ambient, spectral changes due to interchange of *monohapto*- and *pentahapto*cyclopentadienyl rings were observed, and line-shape analysis yielded activation parameters of $E_a = 67.6 \pm 1.3$ kJ mol^{-1} and $A = 3.2 \times 10^{13}$ s^{-1}. That ring interchange may occur in **1** is attributed to the 16 valence electron configuration of the Ti atom. The low-lying empty valence shell orbital characteristic of this configuration may be used to stabilize the transition state for exchange in which one ring is intermediate in character between η^1 and η^5 (as is found for $(C_5H_5)_3MoNO$ in the ground state[27]).

Experimental Section

Preparation of $Ti(C_5H_5)_4$. All compounds were handled on a dual vacuum/nitrogen line using standard Schlenk techniques[28] and in a drybox containing an inert nitrogen atmosphere. Toluene and tetrahydrofuran were predried over molecular sieves and then distilled from potassium; 40–60 petroleum ether was predried over molecular sieves and then distilled from a sodium/potassium alloy. Solution-state ^1H NMR spectra were recorded at 300 MHz on Bruker WH300 or AM300 spectrometers. Air-sensitive samples were made up under an inert dry nitrogen atmosphere and sealed under vacuum. All spectra were referenced internally to TMS ($\delta = 0$) by using the solvent resonance. Microanalyses were performed by the analytical service of this laboratory.

Sodium cyclopentadienide was prepared by reaction of cyclopentadiene monomer with sodium sand in tetrahydrofuran.[29] **1** was prepared from the reaction of $Ti(\eta-C_5H_5)_2Cl_2$ (Aldrich) and $Na(C_5H_5)$ by the method of Calderon et al.[24] The resultant crystals were green-black, with a hint of violet when viewed in transmitted light. Purity was checked by ^1H NMR at 300 MHz in toluene-d_8 solution; broad resonances of equal intensity were observed at 5.895 (σ-C_5H_5) and 5.270 ppm (η-C_5H_5). In addition, a sharp resonance at 5.705 ppm, accounting for <0.5% of proton intensity, was observed; this may be attributed to the presence of trace amounts of $Ti(\eta-C_5H_5)_3Cl$. **1** is extremely oxygen and moisture sensitive and was handled under dry nitrogen.

Solid-State NMR Spectroscopy. All solid-state NMR spectra were recorded on a Bruker CXP200 pulse NMR spectrometer with an Oxford Instruments 4.7-T wide-bore (98 mm) superconducting solenoid magnet (200.13 MHz for ^1H NMR) and equipped with an Aspect 2000 data system. ^{13}C CP/MAS NMR spectra were recorded at 50.32 MHz by using a multinuclear, proton-enhanced, double-bearing magic angle sample spinning probe (Bruker Z32-DR-MAS-7DB) and a high-power proton decoupler. A single-contact spin-lock CP sequence[30] with alternate cycle spin–temperature inversion and flip-back of ^1H magnetization[31] and a proton radio frequency field of 1.7 mT ($\omega_1 = 72$ kHz), resulting in a 90° pulse length of 3.5 μs, was used. Temperature regulation, utilizing a Bruker B-VT1000 unit equipped with a copper–constantan thermocouple and digital reference, was of the bearing gas, and temperature measurement was of the bearing exhaust close to the sample. Temperature calibration below room temperature was achieved with the samarium ethanoate tetrahydrate Curie law chemical shift thermometer[32] previously calibrated against the phase transition of camphor-d^{32} and above room temperature with the phase transitions of cobaltocenium hexafluorophosphate[33] and 1,4-diazabicyclo[2.2.2]octane.[32] The system was allowed to equilibrate at each new temperature for 1 h before spectral accumulation was commenced. The setting of the spinner angle was checked at each temperature by using the ^{79}Br resonance of a small amount of KBr,[34] separated from the sample by a plastic disk. Approximately 200 mg of **1** was packed into a 7-mm zirconia rotor with a Kel-F top, under an inert atmosphere of dry nitrogen. ^{13}C CP/MAS NMR spectra were recorded at a range of temperatures from 165 to 369 K at a typical MAS rotation rate of $\approx$2.8 kHz. Typically up to 1500 transients with a contact time of 2.5 ms and a relaxation delay of 5 s were accumulated for each spectrum. Chemical shifts are reported on the δ scale with respect to δ(TMS) = 0 and were referenced to the secondary standard adamantane. The principal components of chemical shift tensors, defined by using the standard convention,[35] were recovered from the spinning side-band manifold, measured in at least two slow spinning speed MAS NMR spectra, using both the Maricq and Waugh moment analysis[36] and the Herzfeld and Berger graphical analysis.[37] Iterative comparison of the experimental and simulated MAS NMR spectra was then used for refinement of the tensor components,[38] and such refined values are quoted with error limits derived from the fitting process. Magnetization-transfer experiments used the rotationally synchronized, selective magnetization-transfer experiment of Conner et al.,[39,40] which monitors longitudinal polarization transfer between two selected resonances. In each experiment the MAS rotation rate was adjusted such that the evolution time of the experiment was an integral number of spinner rotation periods.[41] Kinetic data were obtained from the magnetization data following the analysis of Jeener et al.[42] for spin exchange between two sites of equal population, in which the ratio of intensities of the resonances after a mixing time, τ, is given by $M_B/M_A = r = [1 - \exp(-k\tau)]/[1 + \exp(-k\tau)]$ such that a plot of $\ln[(1 + r)/(1 - r)]$ versus τ yields k, the rate of magnetization transfer, as the slope. For the ^{13}C NMR experiments performed here magnetization transfer due to spin diffusion could be neglected,[43] and the rate of chemical exchange is obtained directly from the rate of magnetization transfer. The program DNMR4 (QCPE No. 466)[44] was used to calculate the exchange-broadened line shapes for coupled spin systems from the static (chemical shifts, coupling constants, and equilibrium populations of each of the accessible configurations of

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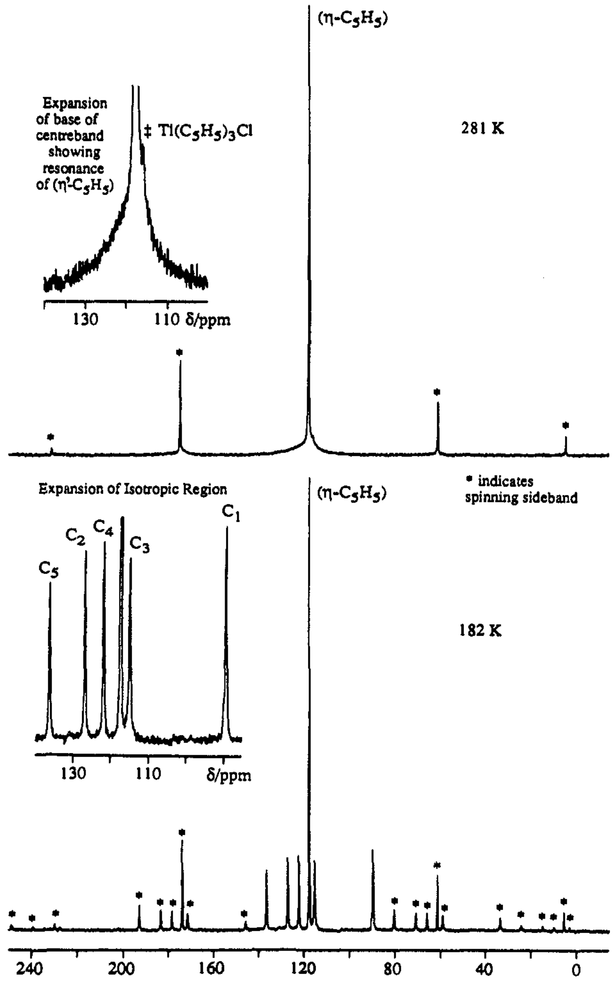

Figure 2. ^{13}C CP/MAS NMR spectra of $Ti(C_5H_5)_4$ at 281 and 182 K.

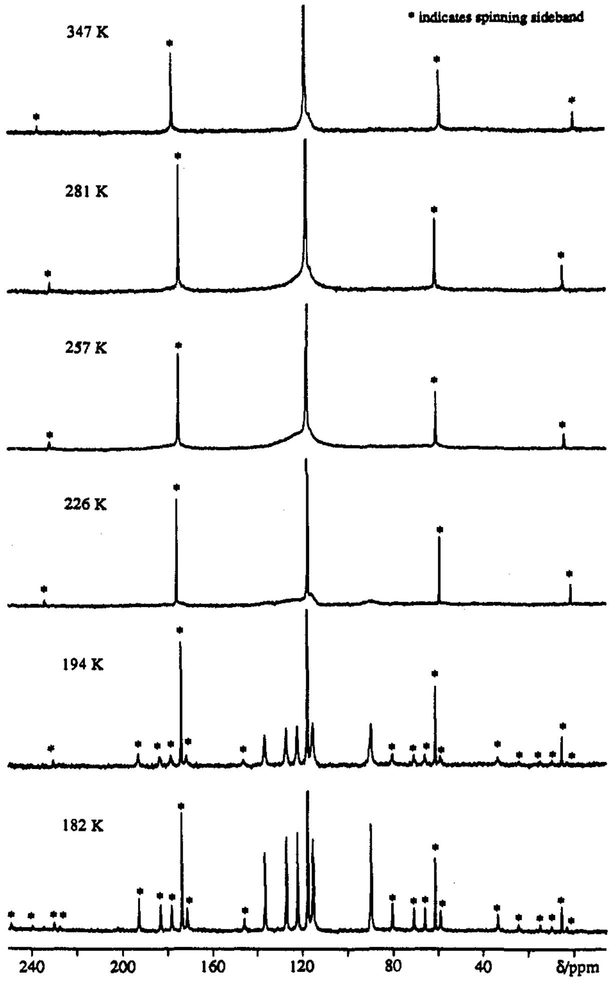

Figure 3. ^{13}C CP/MAS NMR spectra of $Ti(C_5H_5)_4$ showing full anisotropic information. The isotropic peak for the η-C_5H_5 functionality is plotted to the same height in each spectrum but is truncated in these plots.

the system) and dynamic (relaxation and exchange matrices) input parameters in a full density matrix treatment.

Results and Discussion

(a) Temperature Dependence of the Spectra. The ^{13}C CP/MAS NMR spectra of **1** at temperatures of 182 and 281 K are shown in Figure 2, and full comparisons of various aspects of the spectra in the temperature range between 182 and 369 K are shown in Figures 3 and 4. The spectrum at ambient temperature consists of a sharp peak at 117.8 ppm, which shows an axially symmetric CSA tensor, consistent with those known for typical $M(\eta$-$C_5H_5)$ moieties,[45] due to averaging by the ring reorientation process. The line width and anisotropy of this resonance remain constant throughout the studied temperature range, and its chemical shift shows only a slight temperature dependence, the value decreasing from 117.8 ppm at 297 K to 117.3 ppm at 182 K. On the basis of the peak intensities the sharp peak may be assigned to the 10 carbon atoms of the two η-C_5H_5 rings, for which rapid reorientation about the fivefold ring axis is expected to average the carbon resonances of each individual ring, and additionally the molecular symmetry found in the diffraction study[25] ensures equivalence of the two rings. Upfield of the sharp resonance there is a weak shoulder at 116 ppm, which is likely to arise from the small amount (<0.5%) of $Ti(C_5H_5)_3Cl$ apparent in the solution ^1H NMR spectrum of the material used here. This impurity peak slightly overlies the downfield portion of the resonance assigned to the η-C_5H_5 carbon atoms in **1**, and this must be borne in mind in the subsequent inspection and analysis of the spectra (vide infra). These resonances are superimposed on a very broad resonance, which is barely distinguishable above the level of the noise. When the material is cooled below room temperature, the broad resonance sharpens somewhat and becomes more distinct; it then broadens again at temperatures below 280 K, reaching maximum line width at about 233 K. At temperatures lower than 233 K the broadened resonance breaks up into five separate resonances, which gradually sharpen with decreasing temperature. At 183 K these five resonances are of equal intensity and as narrow as the resonance of the η-C_5H_5 carbons. Integration of isotropic and side-band resonances shows that each of these five resonances accounts for one-fifth of the intensity of the η-C_5H_5 resonance. These resonances are assigned to the two σ-C_5H_5 functionalities. Evidently the σ-C_5H_5 moiety is fluxional, and this fluxionality is almost frozen out into the slow limit on the exchange broadening time scale at 183 K. Thus, unlike the case for the ^1H NMR studies in solution,[24] the slow exchange limit for σ-C_5H_5 rearrangement has been reached in the present ^{13}C CP/MAS study; this is an important requirement in attempts to obtain kinetic and mechanistic information from the NMR data.

On the basis of the expected symmetry in the bonding of the *monohapto*cyclopentadienyl ligand, and presupposing that the two σ-C_5H_5 rings in each molecule are identical, it might have been expected that three resonances in the ratio 1:2:2, corresponding to C_1, $C_{3,4}$, and $C_{2,5}$, would be observed in the ^{13}C NMR spectrum. Clearly the degeneracy observed in solution NMR studies of such systems has been lifted in the solid state. Recourse to the single-crystal X-ray structure of **1**[25] shows that all the molecules in the structure lie on twofold crystallographic axes, such that the two σ-C_5H_5 rings in each molecule are symmetry related. The different shifts are not, therefore, due to any difference between two such rings with an accidental degeneracy in the case of the C_1 resonance but must reflect the different environments for each

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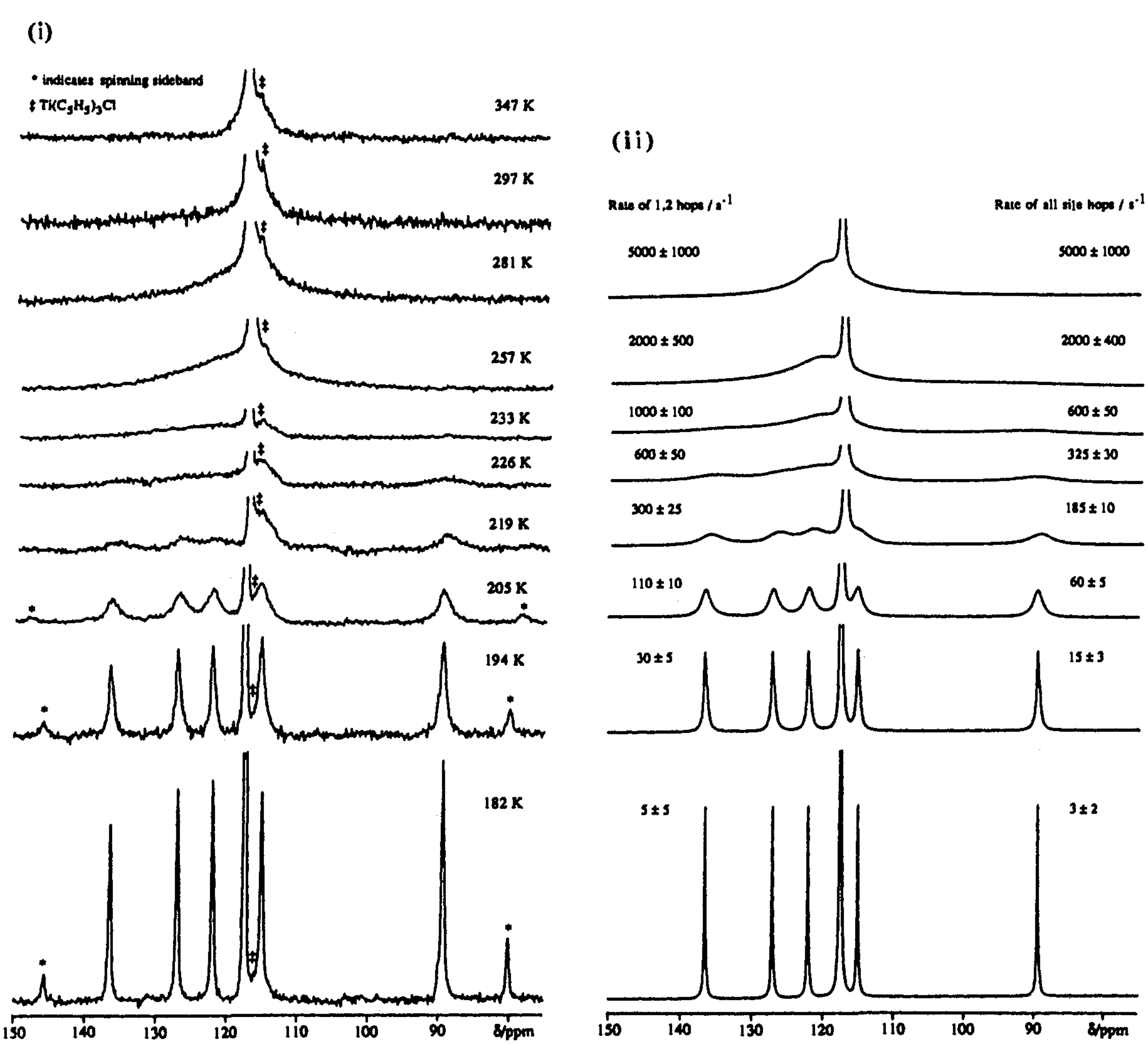

Figure 4. (i) ^{13}C CP/MAS NMR spectra of $Ti(C_5H_5)_4$ at various temperatures showing the isotropic resonances. The spectra are normalized with the intensity of the isotropic resonance of the η-C_5H_5 functionality being constant. This latter resonance is truncated in these plots. (ii) Simulation of the center band of the ^{13}C CP/MAS NMR spectra of $Ti(C_5H_5)_4$ using the program DNMR4.[44] A simple 5-site exchange model was used with the low temperature limiting σ-cyclopentadienyl carbon-13 chemical shifts as the static parameters, and exchange was modeled with [1,2] or with random shifts. This spectrum was added to that simulated for the η-cyclopentadienyl functionality in the specified ratios to take into account the overall proportion of each resonance actually in the center band at that temperature for which the spectrum is to be simulated. The simulations are plotted with the η-C_5H_5 resonance at constant height and truncated.

Table I. Isotropic and Anisotropic Chemical Shift Data for Titanium Tetracyclopentadienyl

	δ_i/ppm	δ_{11}/ppm	δ_{22}/ppm	δ_{33}/ppm	$\Delta = \delta_{11}-\delta_{33}$/ppm	η
η^5-C_5H_5	117.3	158 ± 1	158 ± 2	36 ± 2	122	0
C_1	89.3	164 ± 2	72 ± 5	32 ± 3	132	0.54
C_3	114.9	195.5 ± 2	122 ± 4	27 ± 3	168.5	0.83
C_4	121.8[5]	206 ± 1	127.5 ± 5	32 ± 2	174	0.87
C_2	126.8[5]	208 ± 1	140 ± 5	32.5 ± 3	175.5	0.72
C_5	136.3	235.5 ± 1	151 ± 7	22.5 ± 5	213	0.74

of the carbon atoms in an individual ring. Assignment of the individual resonances is not, however, straightforward. Comparison with previous ^{13}C solution NMR studies of $Fe(CO)_2(\eta$-$C_5H_5)(\sigma$-$C_5H_5)$[46] and $Mo(\sigma$-$C_5H_5)(\eta$-$C_5H_5)(NO)(S_2CNBu^n{}_2)$[47] suggests that the saturated carbon C_1 is likely to be the most upfield resonance and that C_2 and C_5 will resonate downfield of C_3 and C_4. Further evidence that we can make this distinction is provided by the measured ^{13}C NMR CSA tensors for each of the resonances (Table I) which indicate more similar asymmetry parameters within each pair of resonances 114.9/121.8[5] ppm and 126.8[5]/136.3 ppm than between pairs. Individual assignment of each resonance within a pair to a particular carbon atom can only be tentative, but the C_2 and to a lesser extent C_3 carbons lie above the plane of an adjacent η-C_5H_5 ring of the same molecule and therefore might be expected to undergo upfield ring current shifts in contrast to the C_5 and C_4 atoms. Futhermore, study of the intermolecular packing shows that C_5 and C_4 lie in the vicinity

Table II. Magnetization-Transfer Rates between ^{13}C NMR Resonances of the σ-Cyclopentadienyl Carbons of Titanium Tetracyclopentadienyl at 165 K

	rate/s^{-1}
$C_1 \leftrightarrow C_3$	0.3 ± 0.05
$C_1 \leftrightarrow C_4$	0.3 ± 0.05
$C_1 \leftrightarrow C_2$	0.55 ± 0.1
$C_1 \leftrightarrow C_5$	0.7 ± 0.05

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Table III. σ-Cyclopentadienyl Ring Rearrangement Data for Titanium Tetracyclopentadienyl

temp/K	rate of 1,2 hops/s^{-1}	rate of all-site hops/s^{-1}
182	5 ± 5	3 ± 2
194	30 ± 5	15 ± 3
205	110 ± 10	60 ± 5
219	300 ± 25	185 ± 10
226	600 ± 50	325 ± 30
233	1000 ± 100	600 ± 50
257	2000 ± 500	2000 ± 400
281	5000 ± 1000	5000 ± 1000

of the C=C bond joining C_5 and C_4 atoms of an adjacent molecule and would therefore be expected to be shifted downfield by the magnetic anisotropy of the double bond.[48] The assignments are detailed in Table I.

(b) Kinetic Analysis of the σ-C_5H_5 Rearrangement. That the C_2 and C_5 and the C_3 and C_4 resonances are not degenerate within each pair, in contrast to the general case for solution NMR studies, means that there are no differential broadening effects to enable discrimination of the [1,2] and [1,3] shift mechanisms by line-shape analysis in the intermediate time scale of the exchange broadening regime.[2,4] As the σ-C_5H_5 ring rearrangement is clearly in the low-temperature limit of the exchange broadening regime at temperatures below 180 K, magnetization-transfer experiments provide a means to probe possible chemical exchange effects between specific resonances. Experiments were performed at 165 K, in order that the exchange should be slow enough to allow distinction between the postulated rearrangement mechanisms. The rates of magnetization transfer from the C_1 resonance at 89.3 ppm to all the other σ-C_5H_5 carbon resonances were measured, as were the rates of transfer from each of these resonances to the C_1 resonance.

These results, given in Table II, indicate that the magnetization transfer from C_1 to the resonances tentatively assigned to C_2 and C_5 is significantly faster than that to the resonances assigned to C_3 and C_4. This illustrates that a random shift mechanism does not operate, since this would result in identical transfer rates between the different resonances. Instead, the data are consistent, on the basis of the assignments described above, with the dominant mechanism of rearrangement occurring via [1,2] shifts.[51] The data indicate a rate for these at 165 K of ca. 0.6 ± 0.1 s^{-1}. The measured rate of magnetization transfer from C_1 to C_3 or C_4 (ca. 0.3 ± 0.05 s^{-1}) is, however, significantly higher than that anticipated to arise merely from successive [1,2] shifts (ca. 0.1^5 s^{-1}) and therefore implicates the presence of an additional concurrent mechanism involving [1,3] shifts. The proportion of [1,2] to [1,3] shifts is estimated from the magnetization-transfer rates to be approximately 3:1, which is rather lower than expected. [1,2] shifts are implicated as the exclusive mechanism for most such rearrangements that have been studied in solution,[4,47] and Wemmer et al.[52] have calculated from a CSA line-shape analysis study a ratio of [1,2] to [1,3] jumps for the reorientation of the η-cyclopentadienyl aromatic rings in decamethylferrocene as ca. 10:1. The [1,2] sigmatropic shifts favored by the principle of least motion, which is likely to be at its most relevant in the solid state, are indistinguishable in their effect from the [1,5] *supra*facial shifts favored by the Woodward–Hoffmann rules.[4] [1,3] shifts are only Woodward–Hoffmann allowed when the shift is *antara*facial, such a possibility may be reasonably dismissed for a densely packed crystalline solid, and in addition are not favored on "distance of travel" grounds either. It is thus surprising that the magnetization experiments apparently implicate such a high proportion of [1,3] shifts in the rearrangement mechanism. One possible reason for this could be that spin diffusion makes a significant contribution to the magnetization-transfer results. In this case, subtraction of the rate due to spin diffusion would reduce the measured chemical exchange rates and might well reduce the rate of [1,3] shifts proportionately more than the rate of [1,2] shifts. To determine if spin diffusion were to be significant in this system would require magnetization-transfer experiments to be carried out at a temperature low enough that chemical exchange rates are insignificant. Such measurements were not possible with our apparatus, and it is therefore necessary to consider the ratio of 3:1 for the proportion of [1,2] to [1.3] shifts a minimum value. An alternative, and particularly interesting, possibility is, however, that the 16 electron nature of the compound studied here allows the accessibility of an η^3-C_5H_5 bonded transition state. Such a transition state has been postulated in the mechanism of η^1/η^5 ring interchange[24,53] but could also facilitate [1,3] shifts about the σ-cyclopentadienyl ring. A mechanism of this type would not be significant for the 18 electron compounds for which sigmatropic rearrangements have so far been studied in detail.[54]

The simulated exchange-broadened NMR spectra for [1,2] shifts and for random shifts of the σ-C_5H_5 rings (the two extremes of the spectrum of likely rearrangement mechanisms) at various rates were calculated by using the program DNMR4.[44] The simulations were generated on the assumption that the static site frequencies remain the same as those measured from the low-temperature limiting spectrum at 183 K throughout the whole temperature range. Though the shifts are experimentally certain to be somewhat temperature dependent, the simulations apparently fit well with the form of the experimental spectra. The fact that the η-C_5H_5 resonance is unchanged by temperature is of considerable use for the accurate fitting of the experimental and simulated spectra since it acts as an intensity standard; the spectra recorded at different temperatures are plotted with the η-C_5H_5 resonance at equal intensity in Figure 4. The simulations for rearrangement of the σ-C_5H_5 carbons at each rate on a particular mechanistic assumption were added to a simulated η-C_5H_5 resonance in the 0.9:1 proportion suggested by integration of the isotropic region of the low-temperature limiting spectrum, except in the case of the simulation of the spectra at 257 and 281 K, where side-band analysis indicates an increased proportion of the intensity in the center band for the averaged σ-C_5H_5 resonance and a ratio of 1.3:1 was used.

The line-shape changes in the simulations are similar for both [1,2] and random shifts of the σ-C_5H_5 rings, but the equivalent exchange-averaged line shapes are attained at slightly lower individual jump rates for the random exchange case. The sets of simulations were fitted to the experimental spectra and the derived rates at each temperature are reproduced for each mechanism on an Arrhenius diagram in Figure 5. Over the temperature range 165–233 K excellent linear plots are obtained. The analysis for a [1,2] shift mechanism gives E_a = 33.2 ± 1.0 kJ mol^{-1} with A = 2.9 × 10^{10} s^{-1} and for a random shift mechanism gives E_a = 34.1 ± 0.9 kJ mol^{-1} with A = 2.5 × 10^{10} s^{-1}. The extrapolation

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(48) In fact, the differences in the chemical shifts for these apparently electronically identical carbon atoms (δ_5-δ_2 ≈ 10 ppm and δ_4-δ_3 ≈ 7 ppm) are remarkably large, and the *intra*- and *inter*molecular distances involved are too great to allow expectation of such marked shifts from ring current[49] or other magnetic anisotropy effects. Although differences in ^{13}C NMR shifts of up to ca. 12 ppm could be expected from general positional influences on the diamagnetic shift term,[50] it is still appropriate to suggest that other factors must influence the observed chemical shift differences δ_2/δ_5 and δ_3/δ_4. Due to the symmetry of the bonding in **1**, of the mechanisms that might be considered, the most reasonable suggestions in this situation still involve through-space rather than through-bond interactions. We might therefore suggest that the near presence of an aromatic η^5-C_5H_5 ring perturbs the electron density about the most proximate carbons of the σ-C_5H_5 ring, namely C_2 and C_3. The larger difference between the shifts δ_2 and δ_5 than between δ_3 and δ_4 may readily be explained on any through-space effect model because the differential difference involved for the C_2 and C_5 carbons is larger than the equivalent distance for the C_3 and C_4 carbon atoms. Clearly, free or restricted rotation about the M-σ-C_5H_5 bond is not of sufficient rate to be of any consequence at this temperature.

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(50) Ditchfield, R.; Ellis, P. D. In *Topics in Carbon-13 NMR Spectroscopy*; Levy, G. C., Ed.; Wiley: New York, 1974; Vol. 1, pp 1–47.

(51) That [1,2] shifts are the dominant rearrangement mechanism is to be expected given the results of solution NMR studies on such systems. This observation may also be used in reverse to suggest that the carbon resonaces of the σ-C_5H_5 group have been correctly assigned.

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(54) We are grateful to a referee for this suggestion.

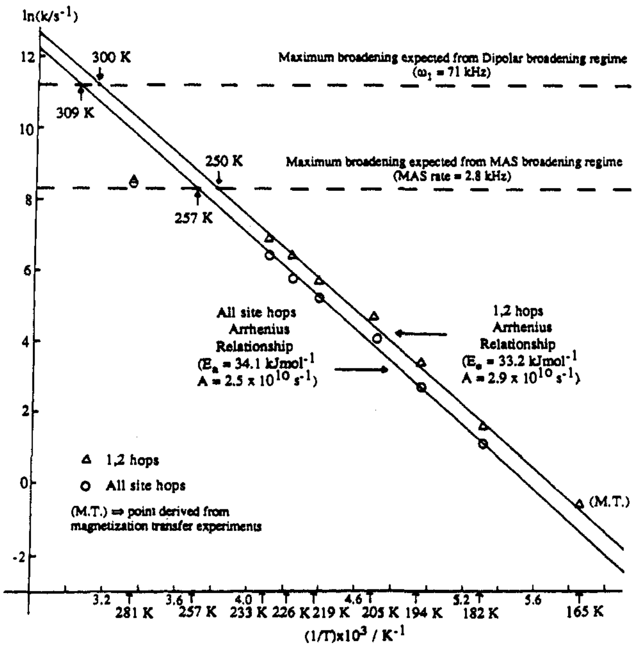

Figure 5. Arrhenius plot for σ-cyclopentadienyl ring reorientation data from fitting of exchange-broadened simulations to the experimental spectra and showing the predicted temperatures of maximum broadening in the MAS and dipolar broadening regimes, as determined by extrapolation of the Arrhenius law behavior observed at lower temperatures in the exchange broadening regime.

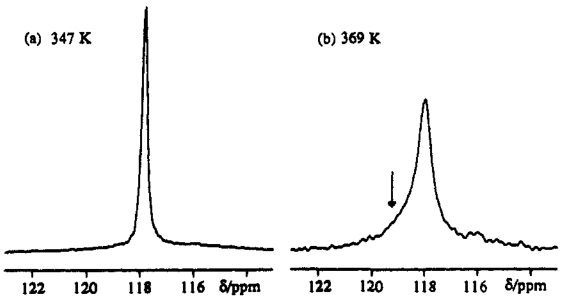

Figure 6. Comparison of the center-band region of the ^{13}C CP/MAS NMR spectrum of **1** at 347 and 369 K, showing the broadening of the η-C_5H_5 resonance at higher temperatures and the appearance of the shoulder to lower field, where the averaged resonance for the σ-cyclopentadienyl carbons would be expected from the weighted average of the low-temperature shifts.

of the Arrhenius relation derived for [1,2] shifts to low temperature is, however, more closely consistent with the rate of rearrangement measured by magnetization transfer at 165 K than is that for the random shift mechanism. The C_2/C_5 and C_3/C_4 resonances show no sign of pairwise coalescence in addition to the line-shape changes resulting from the general σ-C_5H_5 rearrangement, thus indicating that reorientation, restricted or otherwise, of the cyclopentadienyl ring about its twofold axis is not of significance in the averaging process.

The form of the experimental spectra shows that the averaged σ-C_5H_5 resonance does not sharpen above the coalescence point, approximately 233 K, as rapidly as would be expected for a system passing into the fast limit on the exchange broadening time scale. In addition, above 281 K it actually starts to broaden again until it is essentially indistinct from the baseline. The Arrhenius plots (Figure 5) confirm that the rates indicated purely on the basis of exchange broadening become progressively too low to conform to an Arrhenius rate law expression as the temperature increases above ca. 230 K. Extrapolation of the low-temperature Arrhenius rate law expressions (see Figure 5) to the higher temperatures at which this broadening is apparent shows the projected rates of exchange to be of the order of the MAS rotation rate (2.8 kHz) in the CP/MAS NMR experiment. This suggests that the motion of sigmatropic rearrangement of the σ-C_5H_5 ring is destructively interfering with the MAS averaging of the CSA.[55] Such broadening is expected to be at a maximum when $\sqrt{2}\omega_r\tau_c \approx 1$, where ω_r is the MAS rotation rate and τ_c is the motional correlation time. This mechanism for the broadening was confirmed by accumulation of the spectrum at 257 K with different MAS rotation rates, while keeping all other parameters identical, and noting the expected changes in the line width of the averaged σ-cyclopentadienyl resonance. Experimentally, a maximum in the linewidth is not observed in the expected temperature region (250 K), which may be attributed to the fact that the experimental spectra reflect the combined effects of the broadening resulting from the rearrangement rate reaching the MAS regime and the sharpening of the resonance as the rearrangement approaches the fast limit on the exchange broadening time scale. Also of note is that the broad resonance in the spectrum at 257 K now accounts for rather more intensity than the isotropic resonance of the η-C_5H_5 carbon atoms. This may be rationalized by considering that the CSA of the σ-C_5H_5 carbon resonance is averaged by the motion of the rearrangement, such that a greater proportion of the intensity of the σ-C_5H_5 carbon atoms is reflected in the isotropic resonance of the MAS NMR spectrum.[56]

Above 285 K the σ-C_5H_5 resonance broadens substantially again, and in the spectra at 325 and 347 K it is essentially broadened into the baseline. The rates of motion expected at these temperatures, as obtained by extrapolation of the low-temperature Arrhenius behavior, are well above those expected to interfere with the CSA averaging by MAS. They are, however, of the order of the frequency of the high-power proton-decoupling radio frequency field applied during acquisition of the CP NMR spectrum, and motion at such frequencies is expected to interfere with the averaging of the dipolar coupling to the protons by high-power radio frequency irradiation;[58] this broadening is expected to be substantial. In addition, in the region of maximum broadening, $T_{1\rho}(^1H)$ is decreased to such an extent that cross-polarization becomes ineffective and affected resonances may not necessarily be observed in the CP NMR spectrum at all, particularly in the presence of carbon atoms that are unaffected by the motion and so still cross-polarizing efficiently. The maximum broadening in the dipolar regime is expected when $\omega_1\tau_c \approx 1$; and for the decoupling field of $\omega_1 \approx 71$ kHz used in these experiments may be predicted by extrapolation to be at ≈300–309 K. In fact, since both [1,2] and [1,3] shifts occur, and have different rates at any given temperature, they would be expected to lead to broadening in both the MAS and dipolar decoupling regimes in an independent manner. The σ-C_5H_5 ^{13}C NMR resonance is therefore expected, as observed experimentally, to be severely broadened over an extended temperature range by the different mechanisms. The extreme broadeness and asymmetry of the resonance in this temperature region precludes, however, line-width deconvolution of sufficient accuracy to provide additional information about the sigmatropic rearrangement mechanisms.

(c) η-C_5H_5/σ-C_5H_5 Ring interchange. In the 100-MHz ^1H NMR spectrum in solution[24] σ-C_5H_5/η-C_5H_5 ring interchange is observed to be fast on the exchange broadening time scale at temperatures above 335 K. Observation of the η-C_5H_5 resonance in the ^{13}C CP/MAS NMR spectra from 182 to 347 K reveals little measurable change in line width. However, by 369 K the η-C_5H_5 resonance has clearly broadened and the σ-C_5H_5 resonance has not sharpened at a temperature where the sigmatropic rearrangement process might be expected to be sufficiently fast for the broadening mechanisms operative at lower temperatures to be ineffective. This could be a consequence of ring interchange

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(56) Calculations taking account of simple exchange broadening and of side-band averaging of the CSA are complicated, but have been successfully performed for some two-site exchange problems.[57] The data here are not suitable for such an analysis, due to the complications of deconvoluting the spectral effects of various interactions.

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starting to become significant on the exchange broadening time scale at 369 K, although the experimental data are insufficient to demonstrate this conclusively. The separation between the resonance of the η-C_5H_5 carbon atoms and the shoulder to low field, which could perhaps be the averaged resonance for the σ-C_5H_5 carbon atoms, is approximately 70 Hz. This compares to a 75-Hz separation between the resonances of the σ- and η-cyclopentadienyl protons in the 100-MHz NMR spectrum in toluene at 240 K.[24] Since in solution the ligand functionality interchange reaches the fast limit on the exchange broadening time scale above about 330 K, this implies that the ring-interchange process is significantly slowed in the crystalline state in comparison to in solution.

Conclusions

The ^{13}C CP/MAS NMR spectrum of **1** indicates that the rate of sigmatropic rearrangement of the σ-C_5H_5 ring is significant on the NMR time scale at temperatures above 180 K. This rearrangement could be followed through the exchange broadening, MAS broadening, and dipolar broadening regimes. Magnetization-transfer experiments in the slow exchange limit are consistent with [1,2] sigmatropic shifts being the dominant rearrangement mechanism, although interestingly some contribution from [1,3] shifts is indicated by the data. Exchange rates for this rearrangement process, calculated from fitting of the exchange-broadened line shapes to those expected for a [1,2] shift process, follow an Arrhenius relation with activation energy $E_a = 33.2 \pm 1.0$ kJ mol^{-1} and frequency factor $A = 2.9 \times 10^{10}$ s^{-1}. This rearrangement, therefore, appears to occur with similar facility in the solid state and in solution, suggesting that the activation energy for this process is determined principally by electronic factors, which are expected to be similar in the two states. By contrast, the ring-interchange process appears substantially retarded in the crystalline state as compared with that in the solution state. This indicates that the activation energy for this motion, which involves substantial rearrangement of atoms and disruption to the molecular packing, is significantly increased by the intermolecular interactions present in the crystalline state.

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Solid-State ^{199}Hg and ^{113}Cd NMR Studies of Mercury- and Cadmium–Thiolate Complexes. Spectroscopic Models for $[Hg(SCys)_n]$ Centers in the Bacterial Mercury Resistance Proteins

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Abstract: ^{199}Hg CP/MAS-NMR spectra have been measured for representative examples of the major coordination geometries available to monomeric mercury thiolate complexes: $[Hg(SR)_2]$, $[Hg(SR)_3]^{1-}$, and $[Hg(SR)_4]^{2-}$. Solid-state ^{113}Cd NMR spectra have been measured for related $[Cd(SR)_3]^{1-}$ compounds. $[(n\text{-}Bu)_4N][Cd(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3]$ and $[Ph_4P][Hg(S\text{-}2,3,5,6\text{-}Me_4C_6H)_3]$ were structurally characterized by X-ray crystallography. The metal ions in both compounds are three-coordinate with distorted Y-shaped, planar $[MS_3]$ units. These structures are discussed in relationship to a second conformational isomer, the symmetric C_{3h} $[M(SR)_3]^{1-}$ anion. The shielding tensor, isotropic chemical shift (σ_{iso}), the chemical shielding anistropy ($\Delta\sigma$), and the asymmetry parameter (η) vary in a systematic manner as a function of coordination number and coordination geometry. ^{199}Hg and ^{113}Cd CP/MAS-NMR data for selected compounds (σ_{iso}, $\Delta\sigma$, η) are as follows: $[Hg(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2]$ (−1015, 4256, 0.16); $[Ph_4P][Hg(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3]$ (−267, 1408, 0.30), $[(n\text{-}Bu)_4N][Hg(SPh)_3]$ (−341, 1273, 0.97), $[Et_4N]_2[Hg(S\text{-}2\text{-}PhC_6H_4)_4]$ (−433, 86.5, 0.86), and $[Ph_4P][Cd(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3]$ (668, 483, 0.24). The implications of this study to solution and solid-state ^{199}Hg and ^{113}Cd NMR studies of Hg– and Cd–cysteine proteins are discussed.

The proteins which are involved in bacterial mercury resistance are encoded in a single operon which is regulated under the control of a mercury-sensing DNA-binding protein (MerR).[1] The mer gene encodes a series of proteins which detoxify organomercurials (organomercury lyase) and inorganic mercuric salts (mercuric reductase) by enzymatic conversion to Hg metal. The study of these proteins has stimulated interest in structural and spectroscopic probes which might be used to determine the nature of the coordination of the Hg^{2+} ion to the proteins. Among such probes is ^{199}Hg NMR. As has been shown in numerous studies, NMR is uniquely sensitive to the coordination and environment of metal ions bound to proteins. Thus ^{113}Cd has been used to probe the nature of metal binding in metallothionein, liver alcohol dehydrogenase, and most recently in the DNA-binding proteins gene 32 and GAL4.[2-7] Given the success of such studies, it is reasonable to consider whether ^{199}Hg, an isotope with a somewhat lower gyromagnetic ratio and natural abundance, but nonetheless favorable compared with, say ^{13}C, might similarly be used to probe mercury binding proteins. The feasibility of such studies hinges critically on the size of the chemical shielding tensor of mercury in typical protein coordination sites. In solution NMR of heavy metals, the chemical shielding tensor is usually the dominant mode

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