Studies of Fluxionality in Pentachlorocyclopentadienylmercurials $RHgC_5Cl_5$ by Solution and Solid State ^{13}C NMR and by ^{35}Cl NQR Spectroscopy *, **

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Solution and magic-angle-spinning solid-state ^{13}C NMR spectra are reported for η^1-(pentachlorocyclopentadienyl)(pentamethylphenyl)mercury, $C_6Me_5HgC_5Cl_5$ (II). The latter suggests that II is fluxional in the solid state. Some expected consequences of fluxional behavior also appear in the ^{35}Cl NQR spectra of II and several related pentachlorocyclopentadienylmercurials.

*Monohapto*cyclopentadienyl metal compounds, η^1-$C_5X_5MR_n$, show fluxional behavior – rapid relocation of the carbon-metal bond among the five ring positions as in Fig. 1, each relocation generating an equivalent structure [2, 3]. To date fluxional behavior in such compounds has been detected only by NMR spectroscopy, the time scale of which corresponds to the typical jumping rate near ambient temperatures (hundreds or thousands of times per second). But Muetterties [4] pointed out in 1965 that the time scale of nuclear quadrupole resonance (NQR) spectroscopy should also be suitable for studying fluxional behavior. We summarize here results of a study, including the use of NQR spectroscopy, of possible fluxional behavior in organomercury pentachlorocyclopentadienylmercurials C_5Cl_5HgR.

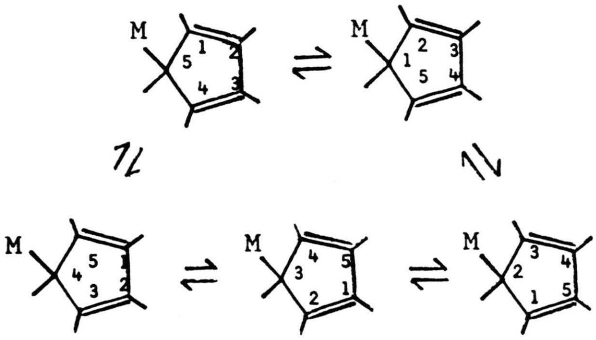

Fig. 1. Fluxional behavior (stereochemical nonrigidity, ring whizzing, pseudorotation, valence isomerism) in a *monohapto*-C_5X_5 compound.

Perchlorination of the cyclopentadienyl ring generates difficulties for the use of NMR spectroscopy: ^1H NMR cannot be used, and ^{13}C NMR signals are weakened, so that the limited solubilities of this type of compound at low temperatures usually preculde the observation of the low-temperature limiting spectra showing three kinds of ring carbon atoms [5]. Such spectra have been obtained for the very soluble phenylmercury derivative $C_5Cl_5HgC_6H_5$ (I) [6]; we have confirmed these spectra. However, partial overlap of one of the three ring carbon signals with phenyl signals prevents determination of whether the two vinylic carbon NMR signals collapse unsymmetrically with increasing temperature. Since ^{13}C-^{199}Hg coupling constants were also not observed either in the fast or slow exchange limiting spectra, the possibility remains that the five C_5Cl_5 carbon atoms are rendered equivalent by *inter*molecular exchange.

To eliminate the ^{13}C NMR interference of the phenyl carbon atoms, we have synthesized the pentamethylphenyl derivative $C_6Me_5HgC_5Cl_5$ (II) [7]. The ^{13}C NMR spectrum of II in CD_2Cl_2 solution in sealed 5 mm tubes at 28 °C was recorded on

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Table 1. ^{13}C NMR frequencies (ppm from TMS) of η^1-cyclopentadienyls.

Compound, Reference	C_5 [a]	$C_{14,23}$	Average	C_{phenyl}	C_{methyl}
C_5H_5HgCl, −122° [b]	60.0	131.3, 128.1	115.8		
+22°		116.3	116.3		
$(C_5Cl_5)_2$ [c]	72.9	131.8, 130.8	119.6		
C_5Cl_6 [c]	82.2	132.0, 131.0	121.6		
$C_5Cl_5Mn(CO)_5$ [d]		118.0	118.0		
$C_5Cl_5HgC_6H_5$, −75° [e]	88.5	124.8, 129?	119?	129.2, 129.7, 136.7, 157.7	
+50°		119.8	119.8		
$C_5Cl_5HgC_6Me_5$, +28°		120.2	120.2	133.9, 136.8, 137.5, 156.1	16.7, 17.3, 26.0
Solid state		118.8	118.8	134.6, 137.2 157.7	18.6, 19.4, 20.5, 25.3, 29.2
$(C_5Cl_5)_2Hg$, +28°	not observed				
Solid state	94.3	131.3	123.3?		

[a] C_5 and $C_{14,23}$ refer to the NMR frequencies of the allylic and vinylic carbons, respectively, of the C_5Cl_5 ring; "average" refers to their weighted average. [b] Ref. [8].

[c] G. E. Hawkes, R. A. Smith, and J. D. Roberts, J. Org. Chem. **39**, 1276 (1974). [d] Ref. [5]. [e] Ref. [6].

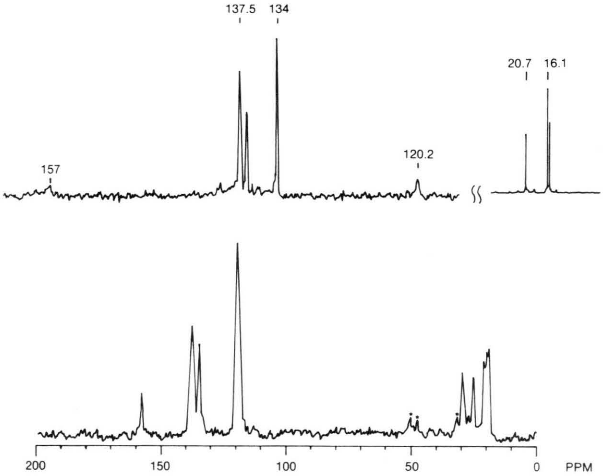

Fig. 2. (a) Above, the ^{13}C NMR spectrum of $C_6Me_5HgC_5Cl_5$ (II) in CD_2Cl_2 solution at 28° (methyl region recorded at reduced signal amplitude); (b) Below, the ^{13}C NMR spectrum of II recorded in the solid state at ambient temperature using cross polarization and magic angle spinning; spinning sidebands are indicated with asterisks (*).

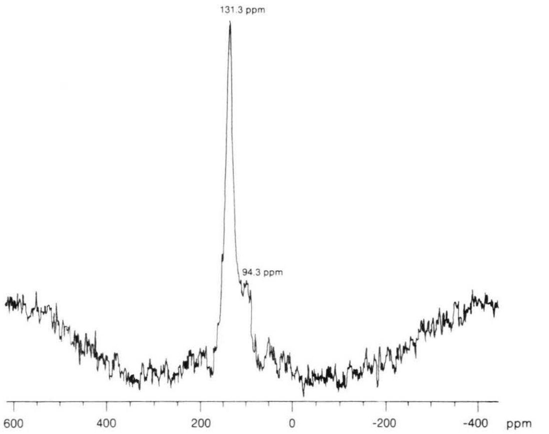

Fig. 3. The solid-state ^{13}C NMR spectrum of $(C_5Cl_5)_2Hg$ (III) at ambient temperature. The spectrum was recorded in a Kel-F spinner and stator, which contributes the broad hump in the center of the spectrum.

a JEOL FX-90Q spectrometer at 22.50 MHz (Fig. 2a and Table 1). A single signal at 120.2 ppm can be assigned to the rapidly equilibrating C_5Cl_5 carbon atoms; this signal disappears on cooling to −30 °C, but the compound also crystallizes out of solution.

To reduce the likelihood of intermolecular exchange of C_5Cl_5 groups and to overcome the solubility problem, we have investigated fluxional behavior of II and a related compound, bis(pentachlorocyclopentadienyl)mercury, $(C_5Cl_5)_2Hg$ (III), in the *solid state*. (The activation energy for fluxional motion in C_5H_5HgCl in the solid state [8] is only about 8 kJ mol^{-1} higher than in solution [9].)

The magic-angle spinning solid-state ^{13}C NMR spectrum of III was obtained at ambient temperature on a modified Nicolet NT-150 spectrometer (Table 1 and Fig. 3); 5600 scans were collected with a 3 ms contact time, a spinning rate of 3800 rps, and 30 sec and 0.5 sec repetition times (the spectrum shown is a difference spectrum of these). The spec-

Table 2. ^{35}Cl NQR data for C_5Cl_5HgR.

		^{35}Cl NQR frequencies at 77 K, MHz					Taft	Temperature (K) of	
R=	*a*	Allylic	Vinyl 1	Vinyl 2	Vinyl 3	Vinyl 4	σ^* [b]	Fadeout	Decomp.
$C_6H_5CH_2$	2	37.591	36.837	36.233	36.120	35.757	−2.3	244	343
		37.760	36.524	36.437	35.972	35.881	−2.4	293	
C_6Me_4H-o	1	37.030	36.852	36.591	36.398	35.940	−1.3	303	400
C_6Me_5	1	37.412	36.831	36.534	36.444	36.230	−1.0	256	416
C_6H_5	1	37.350	36.865	36.737	36.265	36.212	−1.0	327	393
Cl. diglyme [c]	1	38.364	36.613	36.592	36.570	36.543	−0.7	[d]	342
C_6Me_4Cl-p	1	37.515	37.054	36.579	36.467	36.352	−0.6	243	420
		33.781 [e]						[d]	420
C_6H_4Cl-p	1	37.174	36.897	36.829	36.492	36.270	−0.5	[d]	373
		34.154 [e]						[d]	
C_5Cl_5	2	39.050	37.055	36.900	36.674	36.333 [f]	0.2	[d]	342
		38.850	36.900	36.732	36.674	36.246 [f]		[d]	
[g]	1½	38.600	36.804	36.748	36.539	36.101	−0.9	[d]	
		38.956	37.116	37.019			1.5	268	
Cl	4 [h]	39.564	37.410	37.185	36.954	36.300 [f]	1.6	[d]	402
		39.318	37.265	37.145	36.888	36.267 [f]		[d]	
		39.228	37.223	37.093	36.854	36.233 [f]		[d]	
		39.158	37.185	37.056	36.786	36.161 [f]		[d]	

[a] Number of C_5Cl_5 groups in the asymmetric unit of the unit cell.
[b] Taft polar substituent constant (± 0.4), calculated from average NQR frequency of vinylic chlorines (Ref. [14]).
[c] Diglyme = ligand $MeO(CH_2CH_2O)_2Me$.
[d] No fade-out below the highest temperature studied (333−343 K).
[e] Chlorine in *para* position of phenyl group.
[f] Assigned to coordinating organochlorine atom; deleted from calculation of σ^*.
[g] This compound is $4C_5Cl_5HgOOCMe \cdot (C_5Cl_5)_2Hg$.
[h] Additional weak signals observed in the allylic region at 77 K only may indicate a more complex unit cell, or the additional presence of a second modification.

trum shows quite broad unresolved peaks (131 ppm; an apparent shoulder at 94 ppm), and is subject to different interpretations. A drawback to solid-state ^{13}C NMR of such compounds is that, in the absence of rapid solid-state reorientations, magic-angle spinning does *not* remove the coupling of the carbon to *quadrupolar* nuclei such as ^{35}Cl [10].

The solid-state ^{13}C NMR spectrum (with cross polarization and magic-angle spinning) of II, however, gives much more satisfactory results (Figure 2b). For this spectrum 124 scans were collected with a 10 ms contact time, 60 s repetition time, and spinning rate of 3800 rps. The spectrum of II exhibits five methyl peaks (due to apparent crystallographic and chemical inequivalence), three phenyl peaks (only chemical inequivalence being resolved), and a single *sharp* peak at 119 ppm. This peak position is close to the weighted average of the resolved peaks in the solution spectra of non-fluxional cyclopentadienyls (Table 1) and the observed spectra of possibly-fluxional I and $C_5Cl_5Mn(CO)_5$ [2]; thus all C_5Cl_5 carbons evidently are equivalent on the ^{13}C NMR time scale. The sharpness of the peak suggests that there is rapid motion in the solid, which averages out the coupling of the carbon to the quadrupolar chlorine. It is difficult to imagine any other explanation other than that fluxional motion occurs in II in the solid state.

Temperature variation is less routine in magic-angle-spinning NMR than in NQR spectroscopy, which also takes advantage of the quadrupolar chlorine nuclei rather than being hindered by them. ^{35}Cl NQR spectra of many compounds of the general type C_5Cl_5HgR have been recorded on a Decca superregenerative spectrometer at temperatures ranging from 77 K to 343 K [11]. The temperature dependence of the NQR frequencies of these compounds is normal except for the fact that the signals broaden and lose intensity (fade out) over a relatively short temperature range, disappearing well below the melting or decomposition points of the compounds. (The temperatures at which the signals disappear, and at which the compounds decompose, are summarized in Table 2.) This behavior is characteristic of hindered solid-state reorientations of functional groups about their symmetry axes [12]; fluxional motion can be regarded as a five-fold reorientation of the η^1-C_5Cl_5 ring hindered by the Hg-C covalent bond.

Although not by themselves conclusive evidence of fluxional behavior, the fade-out phenomena summarized in Table 2 exhibit several characteristics expected with fluxional behavior, but which are not likely with alternate causes of fade-out. Firstly, it has been noted that fluxional behavior is accelerated by the presence of electron-donating R groups in $C_5H_5MR_n$ [13]. The electron-donating tendencies of the R groups studied (as Taft σ^* parameters) have been calculated from the 77 K spectra of these compounds [14], and are shown in Table 2. Although solid-state packing effects must also have an influence, with but one exception we have observed fade-out if and only if electron-donating R groups ($\sigma^* < -0.5$) are present in C_5Cl_5HgR.

Secondly, fluxional behavior would not be expected if mercury has an equatorial ligand which sterically interferes with the C_5Cl_5 group. Molecular models indicate that the compound $C_5Cl_5HgCl:CH_3O(CH_2CH_2O)_2CH_3$ should have such interference and, even though the ligand is electron-donating, the compound shows no fluxional behavior below its decomposition point.

Thirdly, fluxional motion should not involve the HgR group, which is much too bulky to be likely to move in the solid state; instead it should involve reorientations of the pseudo-symmetric C_5Cl_5 group. This is supported by the solid-state NMR spectrum of II. Also, in the NQR spectrum of $C_5Cl_5HgC_6(CH_3)_4Cl$-p, the weaker (at 77 K) signal of the *para*-chlorine persists in intensity to much higher temperatures than the signals of the C_5Cl_5 chlorines (Table 2). This suggests that the fade-out is not due to approach to a phase transition, and is not due to a reorientation of the whole molecule.

We conclude that fluxional behavior can be studied by methods other than NMR spectroscopy, and that the use of NQR spectroscopy may be advantageous in certain kinds of systems, such as organometallic derivatives of chlorocarbons, or perhaps transition-metal carbonyls, since many transition-metal nuclei and ^{17}O also have quadrupolar nuclei.

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[1] (a) MTSU, (b) Chemistry Division, ORNL, (c) Analytical Chemistry Division, ORNL, (d) THD.
[2] F. A. Cotton, Acc. Chem. Res. **1,** 257 (1968).
[3] J. W. Faller, Adv. Organometal. Chem. **16,** 211 (1977).
[4] E. L. Muetterties, Inorg. Chem. **4,** 769 (1965).
[5] K. J. Reimer and A. Shaver, Inorg. Chem. **14,** 2707 (1975).
[6] A. G. Davies, J. P. Goddard, M. B. Hursthouse, and N. P. C. Walker, J. Chem. Soc., Dalton Trans., **1985,** 471.
[7] Syntheses and characterization of this and other new compounds will be reported elsewhere.
[8] F. A. Cotton, D. L. Hunter, and J. D. Jamerson, Inorg. Chim. Acta **15,** 245 (1975).
[9] A. J. Campbell, C. E. Cottrell, C. A. Fyfe, and K. R. Jeffrey, Inorg. Chem. **15,** 1326 (1976).
[10] W. W. Fleming, C. A. Fyfe, J. R. Lyerla, H. Vanni, and C. S. Yannoni, Macromolecules **13,** 460 (1980).
[11] Further details will be reported elsewhere.
[12] R. Sh. Lotfullin and G. K. Semin, Adv. Nuclear Quadrupole Resonance **2,** 1 (1975).
[13] P. West, M. C. Woodville, and M. D. Rausch, J. Amer. Chem. Soc. **91,** 563 (1969).
[14] G. Wulfsberg, J. Organometallic Chem. **86,** 321 (1975).