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Multimethod Investigation of Fluxional Behavior in (Pentachlorocyclopentadienyl)mercurials η^1-C_5Cl_5HgR

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Possible solid-state fluxional behavior in various (pentachlorocyclopentadienyl)mercurials (η^1-C_5Cl_5HgR) has been investigated by using ^{13}C NMR spectroscopy with cross-polarization and magic-angle spinning and by using ^{35}Cl nuclear quadrupole resonance (NQR) spectroscopy. Unusual mercuration reactions are reported which are convenient synthetic methods for these compounds. Fluxional behavior has been established in the solid state for (η^1-pentachlorocyclopentadienyl)(pentamethylphenyl)mercury ($R = C_6(CH_3)_5$) from its variable-temperature magic-angle-spinning ^{13}C NMR spectrum. The expected consequences of fluxional behavior also appear in the ^{13}C NMR spectrum of this compound in CD_2Cl_2 solution and in the ^{35}Cl NQR spectra of this and several other (pentachlorocyclopentadienyl)mercurials. From their NQR fadeout temperatures and NMR spectra the rate of fluxional exchange appears to increase in the order $R = C_5Cl_5 < R = C_6H_5 < R = C_6(CH_3)_5$. Since their time scales are similar, the two solid-state methods serve as complementary methods for studying fluxional behavior: the NMR method is most easily used to obtain fast-exchange data, while NQR is more easily applied at slow-exchange temperatures.

Introduction

Cyclopentadienyl- and (pentamethylcyclopentadienyl)metal compounds include many important catalysts and exhibit a variety of metal–cyclopentadienyl bonding types and properties. Classically the most fascinating property of the (η^1-cyclopentadienyl)metal compounds is fluxional behavior,[2] the relocation of the carbon–metal σ bond among the five cyclopentadienyl ring positions hundreds or thousands of times per second. The rate of this degenerate isomerization is affected by changing the metal bonded to the η^1-cyclopentadienyl ring and by changing the substituents on the metal, in known ways. MO calculations suggest that the influence of pentasubstitution of the C_5 ring may also be substantial,[3] but the experimental evidence is sparse and somewhat surprising: solution fluxional behavior requires only an extra 8 kJ/mol activation energy for $(C_5(CH_3)_5)_nMR_m$ as compared to $(C_5H_5)_nMR_m$ if M = Si, Ge, As, or Sb,[4] but it is reported that pentamethylation completely stops fluxional behavior if M = Hg.[5]

For reasons such as these there is a great interest in the properties of the organometallic derivatives of pentasubstituted cyclopentadienyl groups. An investigation of possible fluxional behavior in the organometallic pentachlorocyclopentadienides is of particular interest since chloro substituents have steric properties similar to but electronic properties quite different from the methyl groups in organometallic pentamethylcyclopentadienides.

Such a study is also of interest as a challenge for spectroscopists, since the most commonly used method of studying fluxional behavior, ^1H NMR spectroscopy, is not applicable. Although solution ^{13}C NMR can be and has been used, it has some severe limitations due to the loss of signal enhancement from neighboring protons (nuclear Overhauser effect), and due to the generally poor solubility of highly chlorinated compounds in most solvents. Hence this study involves additional spectroscopic methods which can respond to fluxional behavior in the *solid state*. Previous ^1H and ^{13}C NMR studies have confirmed that fluxional behavior can also occur in the solid state; in the case of η^1-C_5H_5HgCl the activation energy found in the solid state[6] is only about 8 kJ higher than in solution.[7]

Thus we have studied the (pentachlorocyclopentadienyl)mercurials by use of *solid-state* ^{13}C NMR spectroscopy, employing magic-angle spinning (MAS), sometimes with cross-polarization (CP). This method has been used to investigate fluxional behavior in C_5H_5HgX,[8] metal carbonyls,[9] an organometallic derivative of cyclooctatetraene,[10] and semibullvalene.[11] Since this method also has its limitations (to be discussed later), we have also looked to methods other than NMR. Muetterties pointed out back in 1965 that the time scale of nuclear quadrupole resonance (NQR) spectroscopy was nearly as suitable for the study of fluxional behavior.[12] Hence one purpose of this study is to verify that this technique can also be used to detect fluxional behavior.

Finally, in order to overcome the limitations or take advantage of the opportunities afforded by each of the different spectroscopic methods employed, several new (pentachlorocyclopentadienyl)mercurials, C_5Cl_5HgR, were prepared; these are listed in the Experimental Section. These preparations involved some reactions with unusual characteristics which will be described. Some of our results

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have been presented previously in communication form.[13]

Experimental Section

The solution ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer equipped with a variable temperature controller and an internal ^{2}H lock. Spectra were measured for CD_2Cl_2 solutions in 10 mm o.d. tubes that were degassed on a vacuum line and then sealed under an argon atmosphere. The spectra were collected at 22.5 MHz using a 60° pulse, 5-s repetition rate, and 1256 scans. Chemical shifts were referenced to the CD_2Cl_2 ^{13}C resonance at 53.8 ppm (relative to TMS).

The solid-state ^{13}C NMR spectra were obtained on a Nicolet NT-150 spectrometer at a carbon frequency of 37.735 MHz with a home-built cross-polarization magic-angle spinning (CP-MAS) unit, including the probe. The decoupling field was 55 kHz. The spinner is a modified version of Wind's,[14] with a sample volume of 0.3 cm^3; the samples were spun at 3.8 kHz. Solid samples were loaded into rotors in a glovebox under N_2 and spun with dry N_2 as the drive gas to prevent contamination by water or O_2. The spectra showed no evidence of decomposition over the experiment time. Chemical shifts are relative to external tetramethylsilane, with hexamethylbenzene as a secondary standard (methyl signal at 17.35 ppm). Low-temperature solid-state ^{13}C CP-MAS NMR spectra were obtained on a modified Chemagnetics M-100S′ spectrometer at 2.1 T.

^{35}Cl NQR spectra of the compounds in this study were recorded on a Decca superregenerative NQR spectrometer at a variety of temperatures, which were monitored with a thermocouple inserted into the sample chamber. The temperatures were achieved by use of liquid nitrogen, dry ice/2-propanol, ice water, slush baths of organic solvents, or (between −22 and +100 °C) an Endocal circulating constant-temperature bath connected to a specially designed probe. Temperatures of the baths were also checked by using the known temperature dependence of the NQR frequency of $KClO_3$.[15]

All products were characterized by their infrared spectra, measured between 4000 and 200 cm^{-1} as KBr pellets on a Perkin-Elmer 567 double-beam grating spectrophotometer; these spectra establish unambiguously that all products are η^1 derivatives of the C_5Cl_5 group.[16] Products were also characterized by their ^{1}H NMR spectra, measured in appropriate deuteriated solvents on a Varian EM-390 90-MHz spectrometer. Melting or decomposition points were obtained by using a Mel-Temp melting point apparatus. Approximate solubilities were established by adding increments of solvent to a weighed sample of product and shaking, until the product appeared to be dissolved. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN, the microanalytical lab of the Technische Hochschule Darmstadt, and by Midwest Microlab, Indianapolis, IN. All products were stored in a freezer below 0 °C; samples mailed for ^{13}C NMR spectra were packed in solid CO_2 and mailed by the most rapid method available.

Solvents were reagent-grade and were generally used as obtained from standard commercial suppliers such as Fisher Scientific Co. and Aldrich. Most of the starting materials were also used as obtained from Aldrich: diphenylmercury, phenylmercury hydroxide, pentamethylbenzene, 1,2,3,4-tetramethylbenzene, 1,2,4,5-tetramethylbenzene, mercuric oxide, mercuric acetate, mercuric chloride, trifluoroacetic acid, trifluoroacetic anhydride, diglyme, and dibenzylmercury (Orgmet, Inc.). Pentachlorocyclopentadiene was prepared by the literature method.[17] **CAUTION**: It has been reported that pentachlorocyclopentadiene undergoes microsomal metabolism to possibly mutagenic tetrachlorocyclopentadienone.[18] Caution should be exercised in handling this liquid.

$C_6H_5HgC_5Cl_5$ (1). 1 was prepared by the reaction of C_6H_5HgOH with HC_5Cl_5 as before[16] (route B) and also by grinding together $(C_6H_5)_2Hg$ (1.06 g, 3 mmol), $Hg(C_5Cl_5)_2$ (2.03 g, 3 mmol), and CCl_4 (5 mL) for 3 min in a glovebag under N_2 (route C). After evaporation, the yield was 2.70 g (84%). Its solubility is approximately 1.1 M in CH_2Cl_2, 0.5 M in $CHCl_3$, and 0.2 M in CCl_4 at room temperature.

$C_6(CH_3)_5HgC_5Cl_5$ (2). $C_6(CH_3)_5HgOOCCF_3$ was prepared according to the literature method.[19] In synthetic route D, this trifluoroacetate (3.5 g, 7.5 mmol) was dissolved in 25 mL of methanol and stirred with HC_5Cl_5 (2.0 g, 8.1 mmol). Fifty milliliters of water was added, and the oily mixture was stirred with a high-torque mechanical stirrer for 1 h. The water layer was discarded, and the IR spectrum of the oil was examined for the strong characteristic bands of the trifluoroacetate group. Twice more 40-mL portions of distilled water were added, the mixtures were stirred for 1 h, the water layers were discarded, and the oil (which gradually became solid) examined by IR until the spectrum showed no trace of trifluoroacetate. The solid product was dried and recrystallized from chloroform/heptane. The yield of 2 was 1.0 g (23% yield). The solubility is approximately 0.4 M in CH_2Cl_2 and $CHCl_3$ and 0.2 M in CCl_4 at room temperature. The ^{1}H NMR spectrum ($CDCl_3$) showed three methyl-proton peaks at 2.19, 2.25, and 2.43 ppm from TMS. Anal. Calcd for $C_{16}H_{15}Cl_5Hg$: C, 32.84; H, 2.58; Cl, 30.29; Hg, 34.28. Found: C, 32.98; H, 2.77; Cl, 30.09; Hg, 34.11.

To prepare 2 by route C, the (pentamethylphenyl)mercury trifluoroacetate was stirred with 5 mol of NaI in ethanol for 2.5 days to give an 85% yield of precipitated bis(pentamethylphenyl)mercury.[20] This product (1.48 g, 3.0 mmol) and $Hg(C_5Cl_5)_2$ (2.02 g, 3.0 mmol) were dissolved in 50 mL of CH_2Cl_2, which was stirred for 20 min under N_2 and evaporated to give 2 (1.52 g, 43% yield).

2,3,4,5-$(CH_3)_4C_6H(HgC_5Cl_5)$ (3). 1,2,3,4-Tetramethylbenzene (20.86 mL, 140 mmol) was mercurated with a deficiency of mercuric trifluoroacetate (100 mmol, from HgO and CF_3COOH). The product was fractionally recrystallized from methanol to exclude the (presumably less soluble) dimercurated product. A 17.6-g (41% yield) portion of 2,3,4,5-$(CH_3)_4C_6H(HgOOCCF_3)$ was obtained and found to be adequately pure by IR and NMR. This product was then stirred mechanically with HC_5Cl_5, water, and methanol as in route D above to give a 50% yield of 3 after recrystallization from $CHCl_3$. The solubility was approximately 0.3 M in $CHCl_3$. The ^{1}H NMR spectrum ($CDCl_3$) showed methyl-proton peaks at 2.24, 2.27, and 2.40 ppm from TMS and a phenyl-proton peak at 6.72 ppm from TMS. Anal. Calcd for $C_{15}H_{13}Cl_5Hg$: C, 31.55; H, 2.29; Cl, 31.04. Found: C, 31.62; H, 2.34; Cl, 30.74.

$(C_5Cl_5)_2Hg$ (4). To a solution of mercuric trifluoroacetate (from 40 mmol of HgO, 40 mmol of trifluoroacetic anhydride, and excess trifluoroacetic acid as solvent, later removed) in 80 mL of methanol, HC_5Cl_5 (20.97 g, 88 mmol) was added. Eighty milliliters of water was added, and the heterogeneous mixture was stirred under Ar with a high-torque mechanical stirrer. The oily layer containing HC_5Cl_5 gradually turned pasty and then solid. The water layer was replaced every hour until reaction was complete (no trifluoroacetate bands in the IR spectrum of the solid product after ca. 3 h). The product was dissolved in ether, filtered through $MgSO_4$, heptane was added, and ether was removed by rotary evaporation until crystallization began. Cooling gave 11.1 g of the yellow form of 4 (41.0% yield), identified from its known IR and NQR spectra.[16] Its solubility is approximately 0.08 M in CCl_4, 0.2 M in $CHCl_3$, and 0.4 M in CH_2Cl_2.

$C_6H_5CH_2HgC_5Cl_5$ (6). Dibenzylmercury and $HgCl_2$ were stirred together in ether/acetone under N_2 for 2 h and then cooled to give crystalline $C_6H_5CH_2HgCl$. This was reacted with NaOH to give $C_6H_5CH_2HgOH$.[21] A 3.09-g (10 mmole) sample of this

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product, 2 mL of triethyl orthoformate, and 20 mL of petroleum ether were stirred together and then cooled to −78 °C. HC_5Cl_5 (2.38 g, 10 mmol) was added and stirred, but no apparent reaction occurred within 1 h, so the solution was warmed to 0 °C. An orange solution quickly resulted. After being stirred for 2 h, the solution was filtered at 0 °C under N_2. The precipitate was redissolved in 40 mL of petroleum ether + 40 mL of ether. When the solution was cooled to −78 °C, some grayish precipitate (Hg^0?) formed which was filtered off. The solvent was distilled off in vacuo until white needles formed. After the solution was cooled at −78 °C overnight, the crystals of 6 (1.32 g, 25% yield) were filtered off. Anal. Calcd for $C_{12}H_7Cl_5Hg$: C, 27.24; H, 1.33. Found: C, 27.07; H, 1.39.

$(C_5Cl_5)_2Hg$-$n$$C_5Cl_5HgOOCCH_3$ (7). HC_5Cl_5 was prepared from 0.25 mol of C_5Cl_6 and extracted into 50 mL of CCl_4 according to the literature method.[17] Methanol (100 mL) was added to the CCl_4 solution under N_2, then mercuric acetate (31.9 g, 0.10 mmol) was added in four portions, allowing each to dissolve completely. The solution was tested for the presence of free Hg^{2+} (with NaOH to give yellow HgO) until the test was negative. Water was added to the solution; the CCl_4 layer was separated, dried, combined with double its volume of petroleum ether, and then cooled to give 51.85 g of 6. The NMR and IR spectra showed the presence of acetate groups in addition to the C_5Cl_5 groups.

Microscopic examination of the product showed the main body of larger crystals to be contaminated with a much smaller volume of needlelike crystals; the two could not be separated by fractional recrystallization or washing. Hence the analytical results varied with the sample but suggested an overall composition of the mixture corresponding approximately to $n = 4$ in the above formula for 7: Calcd for $C_{38}H_{12}Cl_{30}O_8Hg_5$: C, 17.14; H, 0.45; Cl, 39.94. Found: C, 17.23 and 16.61; H, 0.43 and <0.30; Cl, 41.04, 39.03, 39.40, and 38.33. Hence the mercuric acetate did not completely react with the excess of HC_5Cl_5.

When the preparation of 7 was repeated in the presence of water (conditions as for the synthesis of 4 but using mercury(II) acetate instead of mercury(II) trifluoroacetate) much smaller crystals were obtained which showed acetate IR bands and (weakly) the NQR spectrum of 7. The elemental analysis was reasonably consistent for $n = 0.5$. Calcd for $C_{27}H_3Cl_{25}O_2Hg_3$: C, 17.55; H, 0.16; Cl, 47.98; Hg, 32.57. Found: C, 17.49; H, 0.26; Cl, 48.05; Hg, 31.50. Although microscopic examination showed no sign of the needlelike crystals, we cannot be sure that this product is a single compound either. Evidently the mercuration was facilitated by the presence of water but was still incomplete.

$(C_5Cl_5)_2$ (5), C_5Cl_5HgCl (8), $C_5Cl_5HgCl\cdot$diglyme (9), and C_5Cl_5R (R = CMe_3, $CHMe_2$, CH_2Me). These compounds were prepared according to literature methods.[16,22]

4-$ClC_6H_4HgC_5Cl_5$ (10). Bis(4-chlorophenyl)mercury was prepared by the method of Nesmeyanov;[23] it was identified by its infrared spectrum and its ^{35}Cl NQR spectrum (34.100 MHz at 77 K, in agreement with the literature.[24]) Bis(4-chlorophenyl)mercury (0.635 g, 1.50 mmol) and 4 (1.00 g, 1.50 mmol) were dissolved in 5 mL of CH_2Cl_2 in a Schlenk tube under argon and were stirred for 30 min; crystals formed. Five milliliters of heptane was added and the volume of the solution was reduced. Cooling produced 1.3 g of 10 (80% yield). Anal. Calcd for $C_{11}H_4Cl_6Hg$: C, 24.05; H, 0.73; Cl, 38.71. Found: C, 24.06; H, 0.84; Cl, 38.52. Its solubility was too low to attempt low-temperature solution ^{13}C NMR: 0.06 M in $CHCl_3$ and 0.2 M in CH_2Cl_2.

4-Cl-2,3,5,6-$(CH_3)_4C_6HgC_5Cl_5$ (11). Chlorodurene was prepared and purified by the literature method.[25] Twelve grams (70 mmol) of chlorodurene was added to a solution of HgO (24.5 g, 110 mmol) in 50 mL of trifluoroacetic acid. This reaction mixture was stirred for 1 h, then 20 mL of water was added. The brown precipitate which formed was filtered and washed with a small quantity of ethanol. The residue was dissolved in 250 mL of methanol containing 1 mL of trifluoroacetic acid, NaI (18.6 g, 124 mmol) was added, and the solution was stirred overnight. The resulting precipitate was washed twice with 20-mL portions of methanol and recrystallized from chloroform. The yield of moderately pure bis(chloroduryl)mercury was 7.5 g (40%). Anal. Calcd for $C_{20}H_{24}Cl_2Hg$: C, 44.83; H, 4.51; Cl, 13.23. Found: C, 43.97; H, 4.24; Cl, 13.17. ^1H NMR: 2.39 and 2.58 ppm from TMS. ^{35}Cl NQR frequencies at 77 K (and signal-to-noise ratios in parentheses): 33.873 MHz (5) and 33.397 MHz (6).

Inside a N_2-filled glovebag, bis(chloroduryl)mercury (1.00 g, 1.86 mmol) and 4 (1.26 g, 1.86 mmol) were ground together with 5 mL of CCl_4 in a mortar and pestle for 10 min. After evaporation of the solvent, 1.95 g of 11 was obtained (86% yield). This was recrystallized from chloroform, in which its solubility is 0.1 M. Anal. Calcd for $C_{15}H_{12}Cl_6Hg$: C, 29.75; H, 2.00; Cl, 35.13. Found: C, 29.40; H, 2.01; Cl, 35.01. ^1H NMR: 2.35 and 2.51 ppm from TMS.

Discussion of Syntheses

The original synthetic route ("A") for $RHgC_5Cl_5$ (R = organic group) required difficult manipulations at very low temperatures and gave very low yields;[16] hence we have been concerned with improving the syntheses of these compounds

route A:

$$RHgCl + Tl^+C_5Cl_5^- \rightarrow RHgC_5Cl_5 + TlCl$$

The second route ("B") mentioned in our earlier work[16]

route B:

$$RHgOH + HC_5Cl_5 \rightarrow RHgC_5Cl_5 + H_2O \text{ (pentane solution, 0 °C)}$$

is much more satisfactory, but still has some deficiencies in that (1) yields still do not exceed 40% and substantial amounts of metallic mercury are usually also produced and (2) the RHgOH products sometimes cannot be produced due to the nature of other functional groups. Even when they can be produced, their solubility or insolubility in the reaction mixture is difficult to predict, since some apparently dehydrate to oxides $(RHg)_2O$, or even to oxonium salts $(RHg)_3O^+$. Hence isolation and purification of these intermediates are not routine. Use of organomercury methoxide intermediates did not give the hoped-for improvement; hence completely new syntheses were investigated.

It is known that mercury compounds (especially arylmercury compounds) often undergo rapid intermolecular exchange reactions.[26] Hence we speculated that exchange reactions between alkyl- or arylmercury compounds and $(C_5Cl_5)_2Hg$ (4) might also be rapid. The exchange reaction of 4 and diphenylmercury is very rapid, going nearly to completion in 3 min simply upon grinding the two reactants together with a little CCl_4 under N_2 or on stirring solutions of the two reactants for 15 min

route C:

$$(C_5Cl_5)_2Hg + Ar_2Hg \rightarrow 2ArHgC_5Cl_5$$

The corresponding reaction between 4 and dibenzylmercury was too slow to be of value; although there was evidence that 6 was being formed, it is not a very stable product at room temperature and decomposed as it was being formed.

Route C requires the presynthesis of 4 and of the diarymercury compound; although the latter gives little

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Table I. ^{13}C NMR Frequencies (ppm from TMS) of η^1-Cyclopentadienyls

			cyclopentadienyl carbons[b]			
compound	state or temp[a]	ref	C_5	$C_{14,23}$	av	other carbons (Me = methyl, Ph = phenyl)
C_5H_5HgCl	−122 °C	*c*	60.0	131.3, 128.1	115.8	
	+22 °C	*c*		116.3	116.3	
$(C_5Cl_5)_2$	RT	*d, e*	72.9	131.8, 130.8	119.6	
	solid		73[f]	131[f]		
C_5Cl_6	RT	*d, e*	82.2	132.0, 131.0	121.6	
$C_5Cl_5CCl_3$	RT	*d, e*	78.2	131.1, 133.5	121.5	97.4
$C_5Cl_5CMe_3$	RT	*d*	79.4	129.4, 134.2	121.3	40.1; 26.2 (Me)
$C_5Cl_5CHMe_2$	RT	*d*	76.2	128.4, 133.2	119.9	35.7; 16.6 (Me)
$C_5Cl_5CH_2Me$	RT	*d*	73.2	128.3, 132.7	119.0	30.6; 7.8 (Me)
$C_5Cl_5Mn(CO)_5$	RT	*g*		118.0	118.0	
$C_5Cl_5HgC_6H_5$	−75 °C	*h*	88.5	124.8, 129?	119?	129.2, 129.7, 136.7, 157.7 (Ph)
	+50 °C	*h*		119.8	119.8	unchanged
	solid	*d*		*i*		129.5, 131.0, 138.4, 157.1 (Ph)
$C_5Cl_5HgC_6Me_5$	+28 °C	*d*		120.2	120.2	134.0, 136.8, 137.5, 157 (Ph); 16.7, 17.3, 26.0 (Me)
	solid	*d*		118.8	118.8	134.6, 137.2, 157.7 (Ph); 18.6, 19.4, 20.5, 25.3, 29.2 (Me)
$(C_5Cl_5)_2Hg$	+28 °C	*d*		*i*		
	solid	*d*	*i*	131[f]		

[a] Solid-state data are for ambient temperature; if temperatures are given the data are for the compound in solution. RT = solution data at ambient temperature. [b] C_5 and $C_{14,23}$ refer to the NMR frequencies of the allylic and vinylic carbons, respectively, of the C_5Cl_5 ring; "av" refers to their weighted average. [c] Reference 6. [d] This work. [e] Similar data reported first in ref 31. [f] Chemical shifts of peaks broadened (and split) by coupling to quadrupolar chlorine nuclei. [g] Reference 32. [h] Reference 33. [i] Not observed.

difficulty, our previous synthesis of 4[16] uses an intermediate, $Hg(OCH_3)_2$, which is unstable, being prone to decomposition to mercury metal and radicals.[27] Although we had previously made 4 without difficulty from mercury(II) acetate and lithium methoxide,[16] we were unable to carry out the reaction by using the more readily available sodium methoxide. Hence a new synthesis of 4 seemed worth investigating.

Since cyclopentadiene itself is readily mercurated by mercury(II) acetate, even giving rise to a hexamercurated product,[28] we investigated the direct reaction of HC_5Cl_5 with $Hg(OOCCH_3)_2$. The reaction proceeded readily in methanolic solution, without producing mercury metal as a byproduct, to give an impure crystalline product 7, the elemental analyses of which suggested about 60% replacement of acetate groups on mercury by C_5Cl_5 groups. When the mercuration was conducted in a heterogeneous methanol–water suspension, replacement of acetate with C_5Cl_5 groups went further (about 83%) but was still incomplete.

Since mercury(II) trifluoroacetate is known to be a more powerful mercurating agent than the acetate, the mercuration was attempted using the trifluoroacetate. The reaction in this case proceeds to completion, but only in the presence of water, which results in a heterogeneous suspension

$$2HC_5Cl_5(l) + Hg(OOCCF_3)_2(aq) \rightarrow Hg(C_5Cl_5)_2(s) + 2CF_3COOH(aq)$$

Interestingly, it proved possible to generalize this reaction as a new synthetic route D:

route D:

$$RHgOOCCF_3 + HC_5Cl_5 \rightarrow RHgC_5Cl_5 + CF_3COOH$$

Again the presence of water was necessary for this reaction. For arylmercury derivatives this is a convenient synthesis, since the $RHgOOCCF_3$ can be rapidly obtained in good yield by the reaction of mercury(II) trifluoroacetate with the appropriate arene.

We are not aware of any previous case in the literature in which an arylmercury species (e.g. trifluoroacetate) has been usable as a mercurating agent to give a diorganomercurial RR′Hg. Indeed, in one study in which a second substitution on mercury should have been favored (using excess arene, reaction times of 40–2000 h, and temperatures of 110–160 °C) there was exchange of the first aryl group rather than replacement of the acetate group with a second aryl group.[29] Of course diarylation may not be the true mechanism (perhaps $RHgOOCCF_3$ desymmetrizes in the heterogeneous medium to R_2Hg and $Hg(OOCCF_3)_2$, which undergoes further reaction), but the result is still novel. Possibly the high acidity of HC_5Cl_5[30] gives it an unusual ease of mercuration.

Solution ^{13}C NMR Spectra

The solution ^{13}C NMR spectra of some simple C_5Cl_5R compounds (R = nonmetallic group) have been reported;[31] we measured the spectra of these and some additional compounds of this type for reference purposes (Table I). But for reasons cited in the Introduction, the measurement of the spectra of fluxional organometallic derivatives of the C_5Cl_5 group is not so simple. Thus the room-temperature ^{13}C NMR spectrum reported for $C_5Cl_5Mn(CO)_5$ shows only one peak besides those assignable to the carbonyl carbons, which suggests but does not prove fluxional behavior; poor solubility (and the absence of protons) prevented the recording of low-temperature spectra.[32] The compound $C_5Cl_5HgC_6H_5$ (1) has exceptionally high solubility in CD_2Cl_2, so that ^{13}C NMR spectra were obtained down to −75 °C.[33] These spectra (which we have also confirmed) show the pattern expected for fluxional behavior: besides phenyl carbon signals, there is only one C_5Cl_5 ring signal at room temperature, which fades out at lower temperatures and then reappears as (in theory) three signals at the lowest temperatures. Unfortunately one of these low-temperature peaks virtually coincides with a phenyl-carbon peak. Hence it could not be ascertained whether the two vinylic carbon NMR signals collapse unsymmetrically with increasing temperature, which is one of the criteria commonly used to exclude the possibility that the five C_5Cl_5

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carbon atoms are rendered equivalent by *inter*molecular exchange (neither could ^{13}C–^{199}Hg coupling constants be observed either in the fast or slow exchange limiting spectra).

Intermolecular exchange reactions of arylmercury compounds are known to be relatively fast[26] and have been observed in cyclopentadienyltin compounds in the presence of Lewis bases[34] and in C_5H_5HgX solutions.[35] This possibility concerned us when we discovered how facile synthetic route C is.

In order to eliminate the ^{13}C NMR interference of the meta and para phenyl carbon atoms, we synthesized the pentamethylphenyl derivative $C_6Me_5HgC_5Cl_5$ (**2**). The ^{13}C NMR spectrum of **2** in CD_2Cl_2 solution in sealed 5-mm tubes at 28 °C was recorded on a JEOL FX-90Q spectrometer at 22.50 MHz (Table I; see also Figure 2a in ref 13). 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 unfortunately the compound crystallizes out of solution, so that conclusive slow-exchange solution spectra could not be obtained. Hence we also prepared the less fully methylated (pentachlorocyclopentadienyl)(2,3,4,5-tetramethylphenyl)mercury (**3**). Unfortunately its solubility was more like that of **2** than **1**; hence solution ^{13}C NMR spectroscopy was not attempted on it. Several attempts to obtain room-temperature solution ^{13}C NMR spectra in $CDCl_3$ or CD_2Cl_2 on the slightly soluble **4** and **8** failed. (It should be noted that, although C_5Cl_5 mercurials such as these are generally considerably more soluble in polar donor solvents than in $CDCl_3$ or $CDCl_2$, they also decompose readily in those solvents.)

Solid-State ^{13}C NMR Spectra

To overcome the solubility problem and to reduce the likelihood of intermolecular exchange of C_5Cl_5 groups, we obtained ^{13}C NMR spectra of solid samples of **1**, **2**, bis(pentachlorocyclopentadienyl)mercury (**4**), and (1,2,3,4,5-pentachlorocyclopentadienyl) (**5**). The last serves as a model compound for a nonfluxional C_5Cl_5 group.

Magic-angle spinning (MAS) effectively averages chemical shift anisotropy and long-range dipolar coupling between spin-$^1/_2$ nuclei, but dipolar coupling between spin-$^1/_2$ and quadrupolar nuclei is not in general averaged to zero. This effect has been thoroughly examined for ^{14}N–^{13}C couplings,[36] for which splitting and broadening of the ^{13}C peak are common. Chlorine atoms in organic compounds are expected to cause more severe perturbations, since the quadrupole coupling constants are generally more than an order of magnitude larger than those typically observed for ^{14}N in organic amines.[37] At higher magnetic field strength the quadrupole splitting is a smaller perturbation of the Zeeman energy, and the effect is diminished. In C_5Cl_5 groups the quadrupole splitting is greater than or comparable to the Zeeman splitting at any accessible magnetic field strength.

Figure 1 shows the ^{13}C MAS NMR spectrum of **5** at 3.5 and 8.45 T, taken on modified NT-150 and NT-360 spectrometers, respectively. The rotor material, poly(chlorotrifluoroethylene), contributes a broad signal centered at 113 ppm in the single-pulse mode; this signal is suppressed in the cross-polarization mode. Even at the highr magnetic field strength the ^{13}C peaks are split by about 250 Hz (7 ppm). The splitting and residual broadening obscure the anticipated chemical shift difference of 1 ppm for the two types of vinylic carbon. The averaged shifts for the two doublets, 131 and 73 ppm, agree well with solution ^{13}C shifts for **5** (Table I). At the lower magnetic field strength the isotropic chemical shifts are quite obscured by the quadrupole effect. This suggests that a stationary C_5Cl_5 ring may not yield an observable signal at magnetic field strengths less than 3.5 T. The ^{13}C longitudinal relaxation time, T_1, is on the order of 1 min, which is consistent with the absence of large-amplitude rapid motion in **5**.

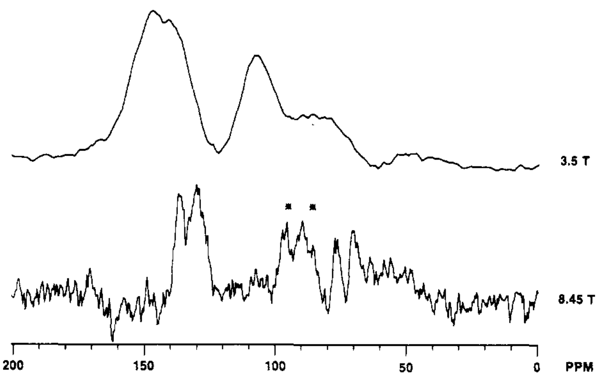

Figure 1. ^{13}C MAS NMR spectra of $(C_5Cl_5)_2$ (**5**) at 3.5 T (top) and 8.45 T (bottom). A total of 1600 scans were obtained with 5-μs pulses with a repetition time of 60 s. A broad background signal, arising from the poly(chlorotrifluoroethylene) in the rotor and stator, has been subtracted. The spinning speed was 3.6–4.0 kHz, and spinning sidebands (*) were identified by varying the spinning rate.

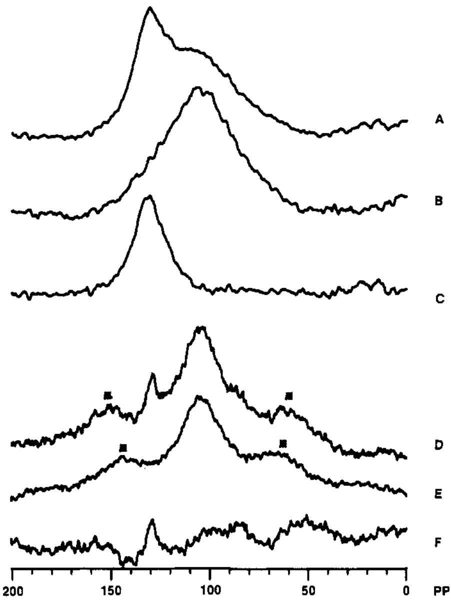

Figure 2. ^{13}C MAS NMR spectra of $Hg(C_5Cl_5)_2$ (**4**) at B_0 = 3.5 T (A–C) and 8.45 T (D–F). A and D are the raw spectra; B and E are blanks without sample; C and F are difference spectra to cancel the background peak. A total of 900 scans were taken with 60-s repetition time.

Compound **4** also exhibits a field-dependent line width (Figure 2). The background peak also clearly narrows at the higher magnetic field strength. The vinylic carbon signal is not split and broadened as much as in the spectrum of **5**. Dipolar coupling of carbon to chlorine can be averaged if there is sufficiently rapid solid-state motion; this has been observed in the case of poly(chlorotrifluoroethylene).[38] Hence there may be more local motion

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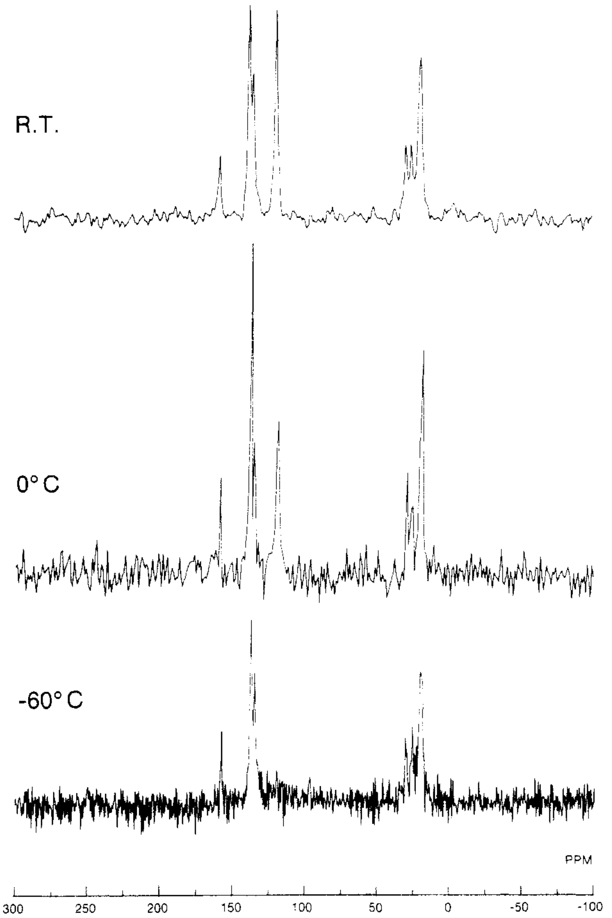

Figure 3. ^{13}C NMR CP-MAS spectra of $C_6Me_5HgC_5Cl_5$ (**2**) at (a) room temperature, (b) 0 °C, and (c) −60 °C. Spectra recorded below −60 °C were substantially unchanged from spectrum c. A total of 124 scans were obtained with a repetition time of 60 s, a 10-ms CP contact time, and a spinning speed of 3.8 kHz.

in **4** than in **5**. The observed chemical shift of 131 ppm indicates that the vinylic and allylic carbons are not exchange-averaged. The absence of the allylic carbon signal could arise from an extremely long ^{13}C T_1, extreme broadening by the attached Cl atom, or perhaps extreme broadening by the attached Hg atom by an interaction other than Hg–C J or dipolar coupling.

The ^{13}C spectrum of **2** (Figure 3) exhibits a single relatively sharp weighted-average peak at 118.8 ppm for the C_5Cl_5 group, consistent with rapid fluxional motion at room temperature in the solid state. This motion does not average the five distinct methyl signals (see Figure 2b in ref 13). Low-temperature MAS spectra were then obtained for **2**; on cooling, the 118.8 ppm peak broadens and finally disappears at −60 °C. But the resolved slow-exchange limit spectrum does not appear even at −185 °C. Since the fluxional motion surely must be very slow at this temperature, we conclude that the splitting and broadening effect of the chlorine nuclei have broadened the ^{13}C signal into the base line for the static case. (Variable-temperature capability was not available for the higher-field spectrometers.)

Compound **1** (Figure 4) shows no signal clearly attributable to the coordinated C_5Cl_5 group. Since it is unlikely that the quadrupole effect or relaxation time is a more severe problem for **1** than for **5**, we suggest that **1** is undergoing fluxional averaging more slowly than is **2**, and the C_5Cl_5 signals are exchange-broadened into the base line at room temperature. Superambient temperature MAS is not currently available to us, and subambient MAS would be subject to the same problem as for **2**.

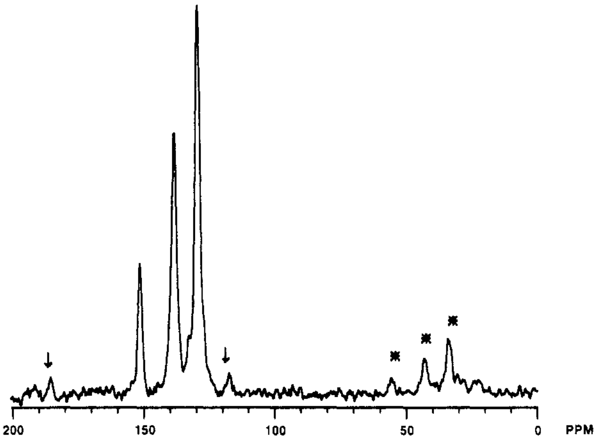

Figure 4. ^{13}C NMR CP-MAS spectrum of $C_6H_5HgC_5Cl_5$ (**1**) at 3.5 T. A total of 3600 scans were taken with a 5-ms contact time and a 20-s repetition time. Spinning sidebands and impurity peaks are labeled with asterisks and arrows, respectively.

Although the spectrum of **2** is aesthetically satisfying and seems very consistent with the presence of rapid fluxional motion, the spectra of the other compounds (in which slower or no fluxional motion is apparently involved) are much more difficult to interpret due to the broadening effects of coupling of the ^{13}C nucleus to the quadrupolar chlorine nuclei. Thus it seemed useful to supplement the NMR measurements with a method which takes advantage of the quadrupolar nuclei, ^{35}Cl NQR spectroscopy.

^{35}Cl NQR Spectra

Although NQR has not yet been used to detect fluxional behavior in organometallic compounds, it has long been used as a method for studying solid-state molecular reorientations;[39,40] fluxional motion can be regarded as a 5-fold reorientation of the η^1-C_5Cl_5 ring hindered by the Hg–C chemical bond. Such reorientations first manifest themselves in the NQR spectra when the reorientation rates become comparable to the line widths of the NQR signals (typically a few kilohertz for ^{35}Cl NQR spectra); the signals then are broadened and lose intensity ("fade out") within a moderate temperature range. In contrast, the NQR signals of compounds with reasonably intense spectra at low temperatures normally persist (although gradually lose intensity) to near their melting, decomposition, or phase-transition temperatures.

There are a number of known causes of fade-out of NQR signals. In general terms, NQR signals will fade out when the relaxation times of the nuclei involved become too short (or too long) as a function of temperature. (This can be important, for example, in paramagnetic transition-metal compounds.) Some of the causes of fade-out can be classified as order-to-disorder phase transitions. Most of the types listed by Chihara and Nakamura[40] (displacive ferroelectric transitions due to ion displacement, cell-doubling transitions due to ion rotation, hydrogen-bonded ferroelectric transitions) are not relevant to this study; the last category (orientational order–disorder transition) could include the specific cases of hindered reorientation and fluxional behavior.

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Among the types of molecular motion which can produce fade-out[40] are (1) the self-diffusion of molecular species, (2) the reorientation of molecules or ions as a whole, and (3) the reorientation of functional groups within a molecule, including fluxional behavior. The authors are not aware of cases corresponding to type 1. Type 2 is found in, for example, *trans*-1,2-dichloroethane, the NQR spectrum of which fades out above about 140 K due to the tumbling of the molecule about its Cl–Cl molecular axis,[41] and in penta- or hexasubstituted benzenes, which can undergo 6-fold rotation. Type 3 occurs commonly when $—CCl_3$ or $=PCl_3$ groups undergo hindered rotations about their 3-fold axes. Type 3 differs from types 1 and 2 and an order–disorder phase transition in that only NQR signals in the functional group itself fade-out; those from quadrupolar nuclei in other parts of the molecule, or in like functional groups which are crystallographically inequivalent, will not fade out at the temperature in question.

Compounds **1**, **2**, and **4** have no chlorines outside of the C_5Cl_5 group, and have no crystallographically inequivalent molecules, so it was useful to synthesize compounds with chlorines substituted in the phenyl group, **10** and **11**. No fade-out occurred in **10** below the temperature at which the sample began to decompose, but the results with **11** were more useful. Figure 5 shows the temperature variation of the NQR frequencies of **11**. As is normal, the frequencies decrease with increasing temperature. By comparison with the 33.873- and 33.397-MHz frequencies of bis(chloroduryl)mercury, the low frequency of **11** can be assigned to the para chlorine in the phenyl group. This NQR signal persists up to the highest temperature measured, 324 K, while the NQR signals of the C_5Cl_5 group fade-out between 243 and 254 K. Hence the motion or disorder responsible for fade-out in **11** is confined to the C_5Cl_5 group; the group attached to the mercury (and by implication the mercury itself) is not in motion.

Our communication of this work[13] gives the 77 K ^{35}Cl NQR spectra of the mercurials included in this study. Most of the compounds have five ^{35}Cl NQR signals and hence only one crystallographically inequivalent molecule per unit cell. Compounds **4**, **6**, **8**, and maybe **7**[42] show more than five ^{35}Cl NQR signals and hence have crystallographically distinct C_5Cl_5 groups in the asymmetric units of their unit cells. **4** and **8** show no fade-out below their decomposition points or the highest temperature studied. In **6** the NQR signals found at 77 K at 37.591, 36.837, 36.233, 36.120, and 35.757 MHz fade out by 244 K while the other five signals retain their intensity; these then fade out by 293 K. This behavior seems unlikely for an order–disorder phase transition but is consistent with functional-group or molecular reorientation which has different intermolecular hindrance at the crystallographically different sites.

The NQR fade-out behavior of compounds **1**, **2**, and **4** is consistent with reasonable interpretations of their solid-state ^{13}C NMR spectra. Thus **4**, which showed only a quadrupole-split and broadened vinylic ^{13}C NMR peak at room temperature, shows no sign of fade-out up to its temperature of decomposition, 342 K. **1**, which showed no NMR peak for the C_5Cl_5 group at room temperature, does show fade-out above room temperature in its NQR spectrum; this is complete at about 327 K. And **2**, which shows a single sharp solid-state NMR peak for a fluxional C_5Cl_5 group at room temperature and at 273 K but not at 213 K, shows fade-out of its NQR spectrum by 256 K. The similarity in the temperatures involved in the NMR and NQR changes suggests that, at least in this system, the time scales for detecting fluxional behavior of chlorine NQR and of carbon NMR are similar (on the order of a few kilohertz).

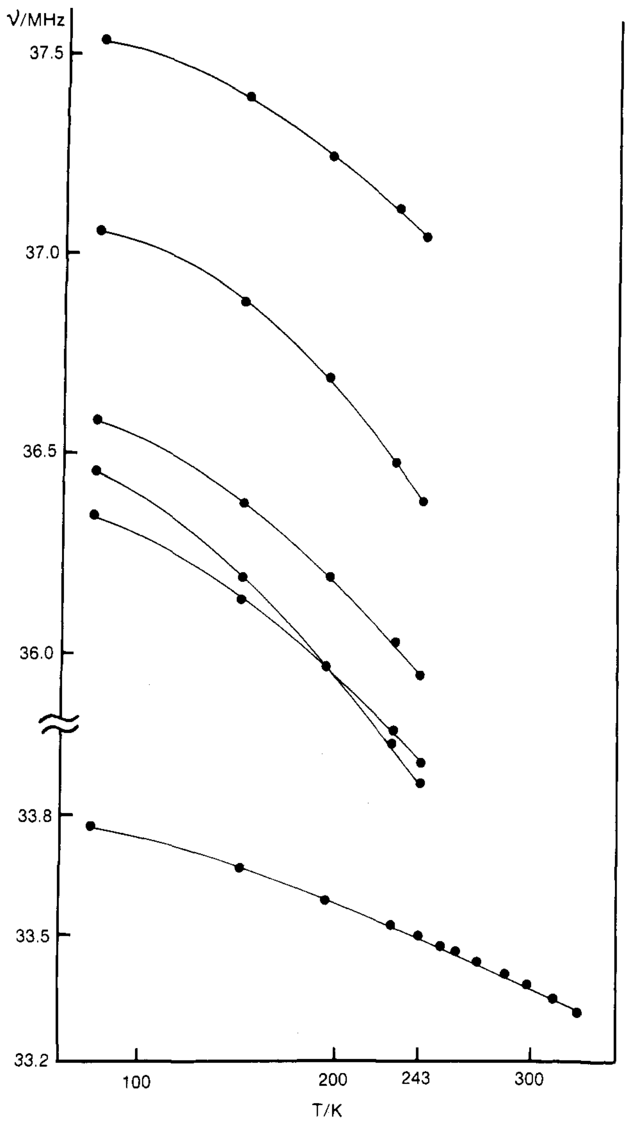

Figure 5. Temperature dependence of the ^{35}Cl NQR spectrum of $4\text{-}ClC_6(CH_3)_4HgC_5Cl_5$ (**11**). Frequencies are in megahertz. Spectra were measured up to 324 K.

Since NQR fade-out can be due to causes other than molecular reorientation or fluxional behavior, the observation of fade-out by itself is not conclusive evidence for fluxional behavior. The NMR and NQR evidence taken together, however, would be very difficult to explain in any other manner. Thus ^{35}Cl NQR should be a nicely complementary technique to solid-state ^{13}C NMR for compounds in which quadrupolar nuclei similar to chlorine are bonded to the NMR nucleus. Both techniques should involve similar time scales of a few kilohertz, but the NMR will be best used in the rapid-exchange limit, while NQR will be most useful in the slow-exchange limit.[43] It appears that the time scales of the two spectroscopic methods are close enough to each other in this type of compound that, between them, characteristics of the fluxional motion (i.e.

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(42) Due to the uncertainties in the composition and homogeneity of **7**, its spectrum cannot be reliably interpreted.

(43) Although the NQR spectrum of a rapidly rotating group should, in theory, be detectable and quite distinctive,[39] nearly all attempts to detect such spectra have failed.

Table II. Conclusions Based on ^{35}Cl NQR Data for C_5Cl_5HgR

				temp (K) of	
compd	R=	*a*	Taft σ*[b]	fade-out	dec[c]
6	$C_6H_5CH_2$	2	−2.3	244	343
			−2.4	293	343
3	C_6Me_4H-*o*	1	−1.3	303	400
2	C_6Me_5	1	−1.0	256	416
1	C_6H_5	1	−1.0	327	393
9	Cl·diglyme	1	−0.7	*d*	342
11	C_6Me_4Cl-*p*	1	−0.6	243	420
11	C_6H_4Cl-*p*	1	−0.5	*d*	373
4	C_5Cl_5	2	+0.2	*d*	342
8	Cl	4	+1.7	*d*	402

[a] Number of C_5Cl_5 groups in the asymmetric unit of the unit cell, as deduced from the total number of C_5Cl_5 NQR signals. [b] Taft polar substituent constant of HgR (±0.4), calculated from the average NQR frequency of the vinylic chlorines.[44] [c] The temperature of decomposition appear to depend markedly on the rate and duration of heating. [d] No fade-out below the highest temperature studied (333–343 K).

exchange rates and activation energies) can be studied over nearly the complete temperature range of interest in the solid state. This appears to be impractical in this type of compound using either method by itself.

Trends in Fade-Out Temperatures. If NQR signal fade-out is indeed related to fluxional behavior, certain trends ought to be observed in the fade-out temperatures of these compounds, which are listed in Table II. Firstly, it has been noted that the rate of fluxional motion of a η^1-C_5R_5 tends to be accelerated when electron-donating groups are present on the mercury atom.[35] Although solid-state packing effects will certainly interfere, we might expect to see a tendency for lower fade-out temperatures in such compounds.

The electron-donating characteristics of the R groups in $RHgC_5Cl_5$ can be assessed as Taft inductive constants σ* from the NQR frequencies of the vinylic C_5Cl_5 chlorines at 77 K;[44] these are summarized in Table II. Except in the cases of **9**, fade-out occurs in all compounds and only in compounds having electron-donating substituents ($\sigma^* < -0.5$).[45] Molecular models indicate that severe steric hindrance should occur between C_5Cl_5 chlorines and diglyme hydrogens in **9**; this would be expected to hinder fluxional motion.[4]

Conclusions

The room-temperature solid-state CP-MAS ^{13}C NMR spectrum of **2** contains only one line for the chemically inequivalent carbons of the η^1-C_5Cl_5 group. This one line is sharp despite the presence of quadrupolar chlorine atoms, which broaden such lines unless rapid solid-state motion is present. This line loses intensity and then disappears at subambient temperatures. It is difficult to think of explanations of this spectrum other than the presence of fluxional behavior of the C_5Cl_5 group in the solid state. The ^{35}Cl NQR spectra of this and many of the other compounds in this study also include the expected manifestations of fluxional behavior: (1) the spectra fade out over a moderate temperature range well below the melting or decomposition temperature; (2) in substances with more than one crystallographically distinct molecule in the asymmetric unit of the unit cell, the signals of different C_5Cl_5 groups fade out at different temperatures; (3) the signals of chlorine nuclei in the phenyl substituent do not fade out; (4) the fade-out temperature depends on the inductive effect of the R group in $RHgC_5Cl_5$, (5) fade-out is absent when steric hindrance is likely to be present. The NQR data suggest that fluxional motion becomes more rapid in the order $R = C_5Cl_5 < R = C_6H_5 < R = C_6(CH_3)_5$; this order seems consistent with reasonable interpretations of the corresponding solid-state ^{13}C NMR spectra, insofar as these can be deciphered in the presence of quadrupolar broadening.

We conclude that, under certain circumstances, it may be profitable to use other methods in addition to NMR spectroscopy to study fluxional behavior. The circumstances that made this advantageous in this study (poor solubility, broad solid-state ^{13}C NMR signals due to the presence of quadrupolar nuclei) do not just occur in metal derivatives of the C_5Cl_5 group, but also may be found, for example, in many transition-metal carbonyls, for which transition-metal and/or ^{17}O NQR spectra might also prove valuable. As an example of this, $Co_2(CO)_8$, which has been shown to be fluxional in the solid state by solid-state ^{13}C NMR spectroscopy,[9] also shows fade-out of its ^{59}Co NQR signals at 233 K.[46]

Acknowledgment. We thank the Research Corporation, the Alexander von Humboldt Foundation, the North Atlantic Treaty Organization (RG 496/84), and the Deutsche Forschungsgemeinschaft for financial support of this work. We also acknowledge the assistance of the Colorado State University Regional NMR Center, funded by National Science Foundation Grant No. CHE-8208821, in obtaining the CP-MAS NMR spectrum, of A. Schluter and D. Hillenbrand in obtaining the solution ^{13}C NMR spectrum of 1 and the model compounds, and of N. Weiden for helpful discussions.

Registry No. **1**, 33997-14-7; **2**, 102140-86-3; **3**, 102140-87-4; **4**, 33997-11-4; **5**, 2227-17-0; **6**, 67951-83-1; **8**, 33997-12-5; **9**, 56104-46-2; **10**, 102140-89-6; **11**, 102140-88-5; $C_5Cl_5H_9OOCCH_3$, 110614-65-8; $C_5Cl_5CMe_3$, 56118-23-1; $C_5Cl_5CHMe_2$, 16177-50-7; $C_5Cl_5CH_2Me$, 16177-48-3; $(C_6H_5)_2H_9$, 587-85-9; $C_6(CH_3)_5H_9OOCCF_3$, 33814-59-4; HC_5Cl_5, 25329-35-5; 2,3,4,5-$(CH_3)_4C_6H(H_9OOCCF_3)$, 110614-66-9; $C_6H_5CH_2HgOH$, 29239-28-9; HgO, 21908-53-2; bis(pentamethylphenyl)mercury, 56457-48-8; 1,2,3,4-tetramethylbenzene, 488-23-3; mercuric trifluoroacetate, 13257-51-7; mercuric acetate, 1600-27-7; bis(4-chlorophenyl)mercury, 2146-79-4; chlorodurene, 2762-20-1; bis(chlorodiuryl)mercury, 110614-67-0.

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(45) 7 may also be an exception.

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