

A Carbon-13 Nmr Study of the Rearrangement Pathway of the Fluxional Molecule Cyclopentadienylmercury Chloride and Some Related Compounds

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The carbon-13 nmr spectra of $(\eta^1\text{-C}_5\text{H}_5)\text{HgCl}$ and $(\eta^1\text{-C}_9\text{H}_7)_2\text{Hg}$ have been recorded over a temperature range extending from -122°C to 22°C . A comparison of the two low temperature limiting spectra indicates that $(\eta^1\text{-C}_5\text{H}_5)\text{HgCl}$ rearranges via 1,2-shifts. The activation energy for this rearrangement was found to be 7.7 ± 0.7 kcal/mol. Carbon-13 nmr spectra of $(\eta^1\text{-C}_5\text{H}_5)_2\text{Hg}$ have also been recorded from 22°C to -120°C . The line width of the 22°C signal is 10 Hz while at -120°C it is 17 Hz.

Introduction

It was reported in 1956 by Piper and Wilkinson¹ that biscyclopentadienylmercury has a single sharp ^1H nmr signal at room temperature. The same observation has since been made for each of the three compounds $(\text{C}_5\text{H}_5)\text{HgX}$, X = Cl, Br, I. A number of studies aimed at establishing the structural and dynamic characteristics of these molecules are summarized in detail elsewhere.² Suffice it here to say that all four of the molecules mentioned above appear to contain $\eta^1\text{-C}_5\text{H}_5$ rings and the appearance of a single proton resonance at room temperature is a result of fluxional character.

The slow exchange limiting ^1H nmr spectrum of $(\eta^1\text{-C}_5\text{H}_5)\text{HgCl}$ has been reported.³ However due to the very small chemical shift difference between signals in the olefinic portion of the AA'BB'X pattern, no inferences could be drawn about the rearrangement pathway. For the other three compounds the coalescence temperatures are lower and the low temperature limiting spectra have not been observed. The room temperature ^1H nmr spectrum of $(\eta^1\text{-C}_5\text{Me}_5)_2\text{Hg}$ was reported to be consistent with a static monohapto structure.⁴ Apparently no effort was made to see if the fully methylated derivative would undergo "ring whizzing" at higher temperatures.

In all cases so far reported in which a mechanism has been established for the "ring whizzing" of a $(\eta^1\text{-C}_5\text{H}_5)\text{M}$ moiety, that mechanism appears to be a series of 1,2 shifts. In all of these cases, however,

M is either a transition metal which has only one valence shell orbital with which to bind the $\eta^1\text{-C}_5\text{H}_5$ ring and cannot, therefore, readily accommodate multicenter bonding in a transition state, or M is a group IV metal which is already using three of its four valence shell orbitals to bind other groups, as in $(\text{CH}_3)_3\text{Sn}(\eta^1\text{-C}_5\text{H}_5)$. In the case of mercury, the possibility of a transition state in which the ring might be bound through three or five π electrons, because of the potential availability of two more valence shell orbitals beyond those used in the linear ground state of a $(\eta^1\text{-C}_5\text{H}_5)\text{HgCl}$ molecule, must be considered. Thus it could not, by any means, have been considered certain in advance, that the 1,2-shift pathway would prevail for the $(\eta^1\text{-C}_5\text{H}_5)\text{HgX}$ compounds. The other evident possibilities are 1,3 shifts via a quasi-trihapto activated complex, or random shifts via a pentahapto activated complex.

A carbon-13 nmr study of $(\eta^1\text{-C}_5\text{H}_5)\text{HgCl}$, and some related molecules has been conducted with the object of determining the rearrangement pathway.

Experimental

All operations, unless otherwise stated, were carried out under an atmosphere of dry nitrogen. Solvents were appropriately dried and distilled under nitrogen. Literature procedures were used to prepare $(\eta^1\text{-C}_5\text{H}_5)_2\text{Hg}$,⁵ $(\eta^1\text{-C}_5\text{H}_5)\text{HgCl}$,⁶ and $(\eta^1\text{-C}_9\text{H}_7)_2\text{Hg}$.⁷

Carbon-13 nmr spectra were recorded on a Jeol PFT-100/Nicolet 1080 Fourier transform spectrometer at 25.034 MHz. Temperatures are accurate to $\pm 2^\circ\text{C}$.⁸ Spectra of $(\eta^1\text{-C}_5\text{H}_5)_2\text{Hg}$ and $(\eta^1\text{-C}_5\text{H}_5)\text{HgCl}$ were recorded in 2-methyl-tetrahydrofuran with 20% CDCl_3 as an internal lock and 10% TMS as a reference. Spectra of $(\eta^1\text{-C}_9\text{H}_7)_2\text{Hg}$ were recorded in CDCl_3 with 10% TMS as a reference. While samples of $(\eta^1\text{-C}_5\text{H}_5)_2\text{Hg}$ and $(\eta^1\text{-C}_5\text{H}_5)\text{HgCl}$ were kept under an atmosphere of nitrogen, the $(\eta^1\text{-C}_9\text{H}_7)_2\text{Hg}$ sample was not.⁷

Line-shape analyses to estimate activation parameters were carried out using the program, EXCHSYS, written by Krieger and Whitesides.⁹

Results and Discussion

$(\eta^1\text{-C}_5\text{H}_5)\text{HgCl}$

Carbon-13 nmr spectra of $(\eta^1\text{-C}_5\text{H}_5)\text{HgCl}$ have been recorded at several temperatures and representative examples are shown in Figure 1. The quality of the spectra are not as good as one would like, but they are the best that could be obtained using ^{13}C at the natural abundance level without collecting a very large number of transients. The two factors principally responsible for poor quality of the spectra are the low solubility of $(\eta^1\text{-C}_5\text{H}_5)\text{HgCl}$, even in polar solvents such as THF, and the small number of each type of carbon atom per molecule.

The low temperature limiting spectrum was obtained at -122°C , and consists of three signals, at 131.3, 128.1, and 60.0 ppm downfield from TMS. The amplitudes of the three singlets are in an approximate 2:2:1 ratio. This pattern is consistent with the $\text{A}_2\text{B}_2\text{X}$ system of a $\eta^1\text{-C}_5\text{H}_5$ ring. As the temperature is raised the lowest field singlet and the highest field singlet begin to broaden. In fact the signal due to the unique aliphatic carbon, X, was observed only at temperatures below -114°C . At -99°C both of the olefinic signals have broadened with the lower field signal appearing almost as a shoulder on the side of the higher field

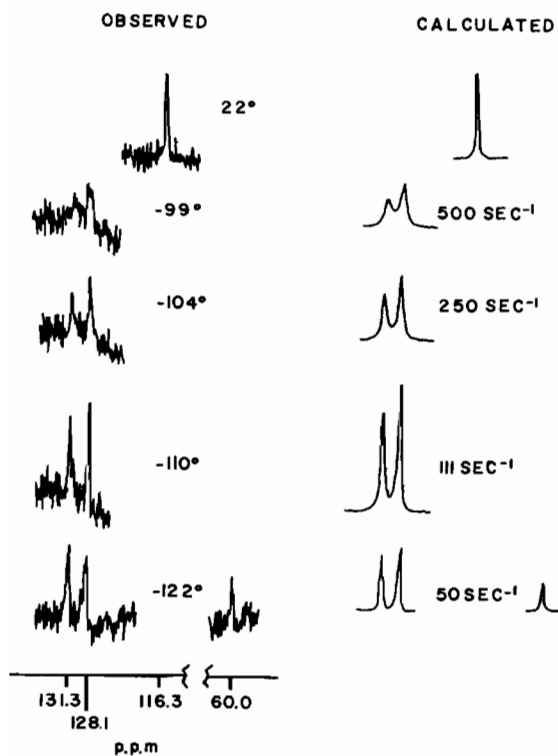


Figure 1. Observed carbon-13 nmr spectra of $(\eta^1\text{-C}_5\text{H}_5)\text{HgCl}$ are on the left. Calculated spectra are on the right.

signal. Line-broadening at -90°C is sufficient to have caused the two signals to disappear into the baseline. The spectrum at 22°C shows the expected sharp singlet at 116.3 ppm. This position compares quite favorably with that expected from a weighted average of the peaks of the -122°C spectrum, namely 115.8 ppm.

With the above observations the possibility of "ring whizzing" by any process, or processes, which cause random scrambling can be eliminated from consideration. It is quite clear that the two downfield signals undergo initial broadening at quite different rates, and from this it follows^{2,11} that one of the two selective processes, that is, 1,2 shifts or 1,3 shifts, is responsible for the signal averaging. The problem of distinguishing between these is the now classic one² for such systems, namely, determining how to assign the two downfield signals to the A and B type carbon atoms of the $\eta^1\text{-C}_5\text{H}_5$ ring. If the peak at 131.3 ppm is assigned to carbons at position A (Figure 2a) and the 128.1 ppm peak is assigned to carbons at position B, then rearrangement proceeds *via* 1,2-shifts. A reversal of this assignment of the olefinic carbon resonances would indicate rearrangement *via* 1,3-shifts.

One approach to the verification of assignments in a $(\eta^1\text{-C}_5\text{H}_5)\text{M}$ system is to investigate also the corresponding 1-indenyl system, $(\eta^1\text{-C}_9\text{H}_7)\text{M}$, as first suggested¹⁰ for the iron system and subsequently used in other cases^{2,12} (Figure 2). Cotton and Marks have reported the ^1H nmr spectra of $(\eta^1\text{-C}_9\text{H}_7)_2\text{Hg}$ ⁷ at various temperatures. The low temperature spectrum is consistent with the monohapto formulation. The spectra change with increasing temperature in a manner indicative of an overall 1,3-shift (*i.e.* positions X and B, a and a', b and b', and c and c' (Figure 2b) approach equivalency).

Carbon-13 nmr spectra were recorded from -41°C to $+58^\circ\text{C}$. The low temperature limiting spectrum (Table I) is consistent with the $(\eta^1\text{-C}_9\text{H}_7)_2\text{Hg}$ formulation. A complete assignment of the peaks could not be made for two reasons. First, the sample decomposed above 50°C during the time necessary to collect data. Second, even at 50°C the peaks seen in the -41°C spectrum (except the one at 133.8 ppm) are still in the process of broadening, and it was not possible to find out which pairs coalesce. However, as can be seen from the data in Table I the positions observed agree quite well with those of $\text{Me}_3\text{Sn}(\eta^1\text{-C}_9\text{H}_7)$,¹⁴ the only other $(\eta^1\text{-C}_9\text{H}_7)\text{M}$

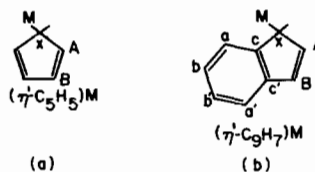


Figure 2. The $(\eta^1\text{-C}_5\text{H}_5)_2\text{M}$ and $(\eta^1\text{-C}_9\text{H}_7)\text{M}$ systems.

TABLE I. Peak Assignments (relative to Figure 2b) of the Low Temperature Limiting Carbon-13 Nmr Spectra of ($\eta^1\text{-C}_9\text{H}_7$)₂Hg and Me₃Sn($\eta^1\text{-C}_9\text{H}_7$)^a.

Position	Hg	Sn
X	66.2 ^b	44.9 ^c
A	133.8	134.4
B	125.8(?)	125.8
a	120.9(?)	124.3
a'	124.1(?)	124.8
b	122.8(?)	122.1
b'	122.8(?)	122.1
c	142.9	142.9
c'	144.9	146.6

^a Taken from reference 13. ^b ppm downfield from internal TMS.

^c Shifts in reference 13 were reported relative to external CS₂. These shifts have been re-referenced here to TMS assuming that CS₂ is 192.8 ppm downfield from TMS.¹⁴

system for which a ¹³C-nmr spectrum has been reported. Although a complete assignment of the -41°C spectrum of ($\eta^1\text{-C}_9\text{H}_7$)₂Hg cannot be made at this time, the peak at 133.8 ppm can unequivocally be assigned to the A position carbon since that peak remains sharp above -41°C.

Therefore if the assumption that a $\eta^1\text{-C}_5\text{H}_5$ ring is similar enough to the five-membered ring of a $\eta^1\text{-C}_9\text{H}_7$ that their chemical shifts will be similar can be made,^{2,10,12} then the 131.3 ppm signal in the low temperature spectra of ($\eta^1\text{-C}_5\text{H}_5$)HgCl (Figure 1) can be assigned to carbon atoms of type A. As mentioned earlier, this assignment indicates that the "ring whizzing" of ($\eta^1\text{-C}_5\text{H}_5$)HgCl proceeds *via* 1,2-shifts.

Carbon-13 nmr spectra of ($\eta^1\text{-C}_5\text{H}_5$)₂Hg were recorded from 22°C to -120°C. The only difference between the spectra was that the line width of the singlet at 116.0 ppm downfield from TMS changed: at 22°C the line width was 10 Hz while at -120°C it was 17 Hz.

Calculated spectra for an uncoupled A₂B₂X system were matched with the observed spectra of ($\eta^1\text{-C}_5\text{H}_5$)HgCl (Figure 1). The calculated rates and observed temperatures were then least-squares fitted to an Arrhenius plot to give an activation energy of 7.7 ± 0.7 kcal/mol and a frequency factor, LogA = 11.37 ± 0.70. The activation energy is comparable to that determined for ($\eta^1\text{-C}_5\text{H}_5$)SiMe₃ (6.4 ± 1.0 kcal/

mol),¹⁵ but is lower than that of ($\eta^1\text{-C}_5\text{H}_5$)GeMe₃ (10.7 ± 0.9 kcal/mol)¹⁵ and ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)₂($\eta^1\text{-C}_5\text{H}_5$) (10.7 ± 0.5,¹⁶ 9.8 ± 0.1,¹⁷ or 8.5 ± 0.8¹⁸ kcal/mol).

Acknowledgement

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