

# Molecular Dynamics of Fluxional Molecules in the Solid State. Organometallic Complexes Containing Monohapto ( $\sigma$ -Bonded) Cyclopentadienyl Rings

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**Abstract:** The monohapto cyclopentadienyl rings in the fluxional molecules  $(h^1-C_5H_5)(h^5-C_5H_5)Fe(CO)_2$  and  $(h^1-C_5H_5)HgX$  ( $X = Cl, Br, I, (h^1-C_5H_5)$ ) have been shown by "wide line" nuclear magnetic resonance spectroscopy to reorient in the solid state. The nature of the motion has been deduced and estimates have been made of the activation energies involved.

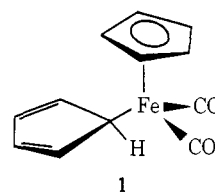
In recent years there has been considerable interest in the structure and bonding of fluxional organometallic molecules.<sup>2</sup> In these compounds, the bonding between the metal atom and the organic ligand is localized at some point in the latter, as evidenced by X-ray diffraction studies in the solid state, but the bonding in these molecules in solution is of a dynamic nature, the point of attachment continually changing and the static structure being observed only at low temperatures.

Certain fluxional molecules containing one or more cyclooctatetraene rings bonded to the metal atom have recently been investigated by solid state (wide line) nmr.<sup>3,4</sup> It was shown by these studies that the cyclooctatetraene rings reorient by a 1,2 shift mechanism at room temperature in the solid state as well as in solution.<sup>3,4</sup> The bonding in these compounds between the metal atoms and the cyclooctatetraene rings is similar to that observed in metal-butadiene complexes, *i.e.*, delocalized over several carbon atoms.

Another important class of fluxional molecules is that where the localization of the bonding is extreme, *i.e.*, where the static structure contains a metal-to-carbon  $\sigma$  bond. We have carried out a solid state (wide line) nmr study of a number of organometallic molecules containing monohapto cyclopentadienyl rings which are known to show "fluxional" behavior in solution in order to observe whether or not they would show reorientation of the organic moieties in the solid state, which here would involve the breaking of a  $\sigma$  bond with a simultaneous reorientation of the cyclopentadienyl ring. The compounds chosen for study were  $(h^1-C_5H_5)(h^5-C_5H_5)Fe(CO)_2$  and the series of compounds  $(h^1-C_5H_5)HgX$  where  $X = Cl, Br, I,$  and  $(h^1-C_5H_5)$ .

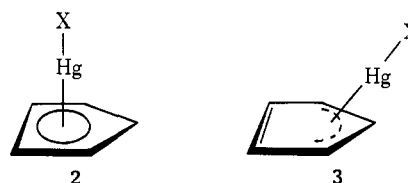
The first of these compounds,  $(h^5-C_5H_5)(h^1-C_5H_5)Fe(CO)_2$ , has been shown by X-ray diffraction studies to have structure **1** in the solid state.<sup>5</sup>

The room-temperature proton nmr spectrum<sup>6</sup> of **1** showed only *two* proton resonances, indicating that the monohapto ring was in a dynamic equilibrium, with the  $\sigma$  bond from the metal being continually formed and broken. The complete temperature dependence



of the spectrum<sup>6</sup> showed that the static structure for the monohapto ring was attained at approximately  $-75^\circ$  (on the nmr time scale).

Cyclopentadienylmercury compounds exhibit similar behavior and have been extensively investigated.<sup>7-16</sup> Preliminary work on  $(C_5H_5)_2Hg$ , although generally favoring a monohapto structure **4**, was not completely unambiguous, and several groups of workers have proposed a pentahapto structure **2**,<sup>8,12,13</sup> while another proposed di(trihapto) (di( $\pi$  allyl)) bonding to mercury (structure **3**,  $X = C_5H_5$ ).<sup>9</sup>



The recent solution nmr results of Rausch, *et al.*,<sup>15</sup> have conclusively shown that the cyclopentadienylmercury halides  $C_5H_5HgX$  ( $X = Cl, Br, I$ ) have monohapto  $C_5H_5$  rings, the chloride yielding a completely resolved limiting spectrum at low temperature. These workers also observed some broadening in the single resonance of  $(C_5H_5)_2Hg$  below  $-100^\circ$  and concluded

- (1) Author to whom correspondence should be addressed.
- (2) F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).
- (3) A. J. Campbell, C. A. Fyfe, and E. Maslowsky, Jr., *Chem. Commun.*, 1032 (1971); *J. Amer. Chem. Soc.*, **94**, 2690 (1972).
- (4) C. E. Cottrell, C. A. Fyfe, and C. V. Senoff, *J. Organometal. Chem.*, **43**, 203 (1972).
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- (9) F. A. Cotton, *Proc. Robert A. Welch Found. Conf. Chem. Res.*, **9**, 213 (1966).
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- (11) E. Maslowsky, Jr., and K. Nakamoto, *Inorg. Chem.*, **8**, 1108 (1969).
- (12) G. G. Dvoryantseva, K. F. Turchin, R. B. Materikova, Yu. N. Sheinker, and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, **166**, 868 (1966).
- (13) A. N. Nesmeyanov, L. A. Fedorov, R. B. Materikova, E. I. Fedin, and N. A. Kochetkova, *Chem. Commun.*, 105 (1969).
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- (15) P. West, M. C. Woodville, and M. D. Rausch, *J. Amer. Chem. Soc.*, **91**, 5649 (1969).
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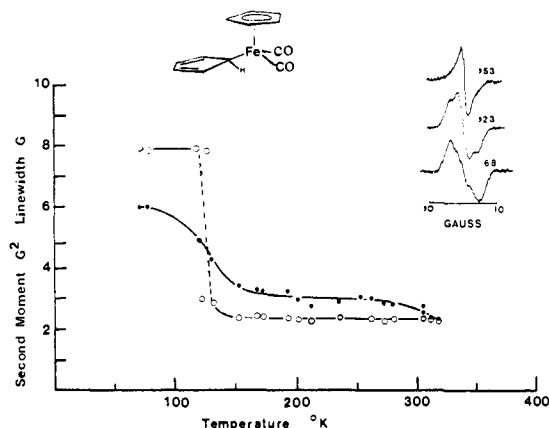


Figure 1. The temperature dependence of the line width (open circles) and second moment (filled circles) parameters of the proton resonance of  $(h^1-C_5H_5)(h^3-C_5H_5)Fe(CO)_2$  in the solid state with (inset) representative spectra recorded at the temperatures indicated.

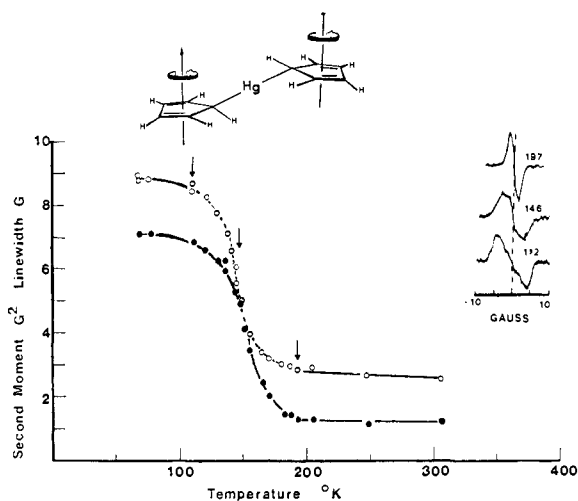
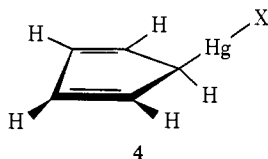


Figure 2. The temperature dependence of the line width (open circles) and second moment (filled circles) parameters of the proton resonance of  $(h^1-C_5H_5)_2Hg$  in the solid state with (inset) representative spectra recorded at the temperatures indicated by the vertical arrows.

that it too had monohapto  $C_5H_5$  rings bonded to Hg. More recently, Campbell and Green<sup>16</sup> have studied the spectrum of bis(methylcyclopentadienyl)mercury and have shown unambiguously that the rings in this compound are indeed monohapto. Hence one can conclude that the series of compounds have the common structure 4. Both 1,2 and 1,3 shifts have been



proposed as possible rearrangement pathways.<sup>2,5,14</sup> Recent calculations by Su<sup>17</sup> employing the Woodward-Hoffmann rules predict a 1,2 shift mechanism for the rearrangement pathway.

The purpose of the present work was to employ "wide line" nmr to investigate possible molecular mo-

(17) C.-C. Su, *J. Amer. Chem. Soc.*, **93**, 5653 (1971).

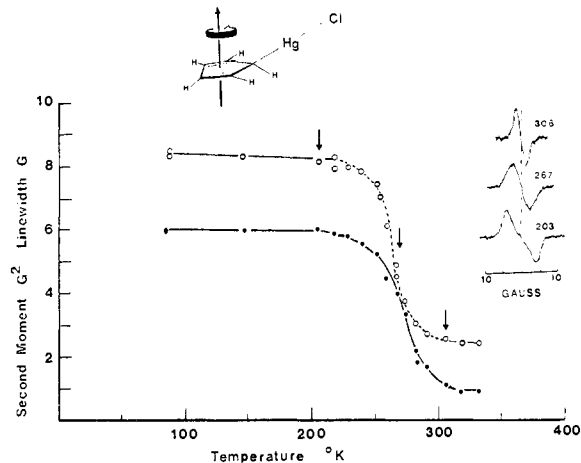


Figure 3. The temperature dependence of the line width (open circles) and second moment (filled circles) parameters of the proton resonance of  $(h^1-C_5H_5)HgCl$  in the solid state with (inset) representative spectra recorded at the temperatures indicated by the vertical arrows.

tion in these complexes in the solid state. If motion of the rings did occur, this would be a situation not previously observed, where a single bond would have to be broken as part of the reorientation process. It was anticipated that the nmr data might also distinguish between the motions of monohapto and pentahapto cyclopentadienyl moieties in these molecules.

### Experimental Section

"Wide line" proton nmr spectra were obtained at 100 MHz using a modified Varian HA-100 spectrometer.<sup>3</sup> Temperature variation was achieved using a standard temperature controlling unit, and temperatures were measured directly using a copper-constantan thermocouple inserted into the bulk of the sample. The samples were sealed in thin-walled 12-mm o.d. glass tubes and kept at low temperatures when not in use. Several samples of each compound were used to obtain the final results. Second moment parameters were obtained from the spectra by a numerical procedure and corrected for modulation broadening. All calculations were performed on an IBM 360-50 computer using Fortran IV programs.

**Preparation of Samples.**  $(h^1-C_5H_5)_2Hg$  was prepared using the method of Nesmeyanov, *et al.*<sup>13</sup> The product was dried under vacuum, in the absence of light, for 1 hr.

$(h^1-C_5H_5)HgCl$  was prepared by a modification of the method suggested by Kitching and Hagarty.<sup>14</sup> A suspension of 10 g of  $(C_5H_5)Tl$  in 100 ml of tetrahydrofuran was cooled in an acetone-Dry Ice bath under a nitrogen atmosphere. A solution of 10.3 g of  $HgCl_2$  in 50 ml of tetrahydrofuran was added with constant stirring over a period of 2 hr; the mixture was then stirred for a further 2 hr in the acetone-Dry Ice bath and for a further 2 hr at room temperature. The solution was filtered to remove  $TlCl$  and unreacted  $(C_5H_5)Tl$ , the solvent removed, and the product recrystallized twice from ethanol and once from  $CCl_4$ . The product was then dried under vacuum, over  $P_2O_5$ , in the absence of light for ca. 12 hr.

$(h^1-C_5H_5)HgBr$  was prepared by a procedure identical with that used for  $(h^1-C_5H_5)HgCl$ .

$(h^1-C_5H_5)HgI$ . When using the method used for  $(h^1-C_5H_5)HgCl$  and  $(h^1-C_5H_5)HgBr$ , a mixture of  $(h^1-C_5H_5)_2Hg$  and  $(h^1-C_5H_5)HgI$  was always obtained. Therefore  $(h^1-C_5H_5)HgI$  was prepared from  $(h^1-C_5H_5)_2Hg$  using the method of Nesmeyanov, *et al.*<sup>13</sup> The product was recrystallized and dried using the same method employed in the recrystallization and drying of  $(h^1-C_5H_5)HgCl$ .

$(h^1-C_5H_5)(h^3-C_5H_5)Fe(CO)_2$  was prepared as described by Piper and Wilkinson.<sup>7</sup> It was purified by recrystallizing from low-boiling petroleum ether and dried under vacuum before use.

The purity of all the samples was checked by comparison of their ir and nmr spectra with known data, and by chemical analysis where the compounds were sufficiently stable.

**Table I.** Limiting Values of Line Width (G) and Second Moment Parameters ( $G^2$ ) at the Temperatures Indicated for the Transitions in the Proton Resonances of Solid Monohapto Cyclopentadienylorganometallics Together with Estimates of the Associated Activation Energies

Compound	Line width (temp, °K)	Second moment (temp, °K)	Activation energy, kcal/mol BPP <sup>a</sup>	Waugh <sup>b</sup>
$(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$	2.2 (306)	2.7 (306)		4.6 <sup>c</sup>
	8.0 (77)	5.9 (77)		
$(\eta^1\text{-C}_5\text{H}_5)\text{HgCl}$	2.5 (306)	1.3 (306)	14.0	9.8
	8.2 (200)	6.3 (200)		
$(\eta^1\text{-C}_5\text{H}_5)\text{HgBr}$	2.6 (306)	1.3 (306)	8.5	8.9
	8.5 (160)	7.6 (160)		
$(\eta^1\text{-C}_5\text{H}_5)\text{HgI}$	2.8 (306)	1.3 (306)	11.4	8.6
	8.5 (160)	7.6 (160)		
$(\eta^1\text{-C}_5\text{H}_5)_2\text{Hg}$	2.6 (306)	1.3 (306)	2.7	5.7
	8.8 (77)	7.1 (77)		

<sup>a</sup> By the procedure of ref 19 and 20. <sup>b</sup> By the procedure of ref 21. <sup>c</sup> Activation energy for the pentahapto ring.

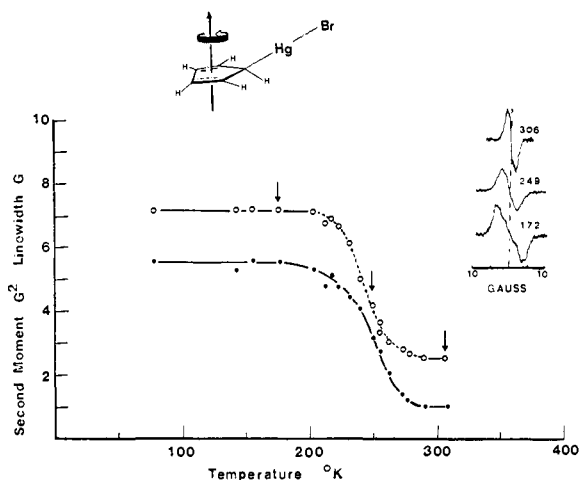


Figure 4. The temperature dependence of the line width (open circles) and second moment (filled circles) parameters of the proton resonance of  $(\eta^1\text{-C}_5\text{H}_5)\text{HgBr}$  in the solid state with (inset) representative spectra recorded at the temperatures indicated by the vertical arrows.

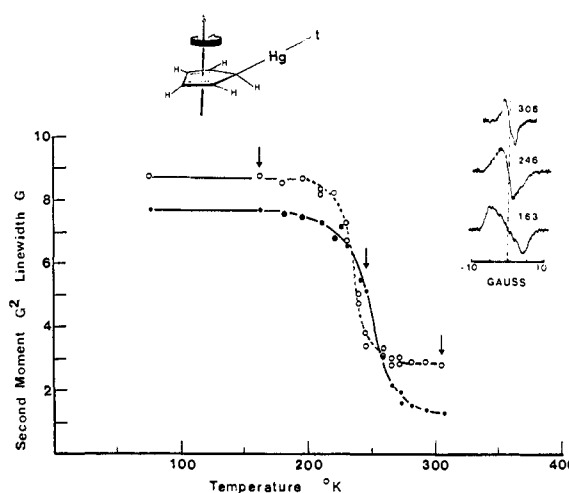


Figure 5. The temperature dependence of the line width (open circles) and second moment (filled circles) parameters of the proton resonance of  $(\eta^1\text{-C}_5\text{H}_5)\text{HgI}$  in the solid state with (inset) representative spectra recorded at the temperatures indicated by the vertical arrows.

## Results

$(\eta^1\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ . The proton resonance of  $(\eta^1\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$  in the solid state is found to be temperature dependent (Figure 1 inset), indicating the presence of some motional process. The complete temperature dependences of the line width and second moment<sup>18</sup> parameters over the temperature range 68–320°K are shown in Figure 1.

$(\eta^1\text{-C}_5\text{H}_5)\text{HgX}$ . The proton resonances of each of the compounds in the series  $(\eta^1\text{-C}_5\text{H}_5)\text{HgX}$  were also found to be significantly temperature dependent. The line width and second moment parameters as functions of temperature for this series of compounds are shown in Figures 2–5. In all cases, the spectrum is quite narrow at room temperature, indicating that appreciable molecular motion exists at this temperature.

The dotted lines shown in the line-width curves in the region of the transitions represent least-squares fits to the experimental data using the BPP equation<sup>19</sup> as modified by Smith.<sup>20</sup> The activation energies thus

(18) The second moment  $(\Delta H)^2$  of a curve is defined as  $(\Delta H)^2 = \int_0^\infty (H - H_{av})^2 f(H) dH$ , where  $(H - H_{av})$  is the distance from the center of the curve and  $f(H)$  the height of the curve at this point. The usefulness of this particular parameter lies in the fact that it can be calculated theoretically and compared with experimental values.

(19) N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, **73**, 679 (1948).

(20) G. W. Smith, *J. Chem. Phys.*, **50**, 3595 (1969).

obtained are given in Table I together with those obtained from the Waugh estimate.<sup>21</sup>

## Discussion

$(\eta^1\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ . The room-temperature solid state proton nmr spectrum of  $(\eta^1\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$  is a fairly narrow curve tailing off gently to the base line (see insert Figure 1). The values of the line width and second moment are 2.2 G and 2.7  $G^2$ , respectively. At temperatures below 80°K, the limiting values of the line width and the second moment were found to be 7.6 G and 5.9  $G^2$ , respectively.

A theoretical value of the second moment for a completely rigid structure can be calculated by the procedure of Van Vleck.<sup>22</sup> Such a calculation utilizing the crystal structure data<sup>5</sup> and assuming a C–H bond length of 1.08 Å yielded a value of 5.1  $G^2$  for the second moment, assuming that the lattice is rigid. The difference between this value and the observed experimental value of 5.9  $G^2$  can be attributed, in part at least, to an uncertainty in the positioning of the hydrogen atom attached to the  $sp^3$  carbon atom of the mono-

(21) J. S. Waugh and E. I. Fedin, *Sov. Phys. Solid State*, **4**, 1633 (1963).

(22) J. H. Van Vleck, *Phys. Rev.*, **74**, 1168 (1948).

hapto ( $C_5H_5$ ) ring (no hydrogen coordinates were available from the X-ray analysis).

Calculation of the intramolecular second moment for cyclopentadiene itself, where the hydrogen coordinates are known from an X-ray study,<sup>23a</sup> and including only one of the hydrogen atoms bonded to the  $sp^3$  carbon atom, yielded a value of 3.3  $G^2$ , which is substantially larger than that calculated for the "intra" value for the monohapto ( $C_5H_5$ ) ring in the iron complex.<sup>23b</sup> If one were to substitute this value for that of the monohapto ring, it would raise the theoretical value to  $\sim 5.5 G^2$ . Because of the large size of the iron atom in  $(h^1-C_5H_5)(h^5-C_5H_5)Fe(CO)_2$  compared to that of the other atoms in the system, it might be expected that the hydrogen atom attached to the  $sp^3$  carbon would be "pushed" even further toward the center of the ring, which would further increase the contribution of this hydrogen atom to the second moment. The difference between the observed and experimental second moments is thought to be within the uncertainties in the calculation and, at these low temperatures, the whole system appears to be quite rigid in the lattice.

At higher temperatures, a transition is observed at about 120°K where the second moment drops to a constant value of about 3.2  $G^2$ . Motion of only one  $C_5H_5$  ring is thought to be involved in the change in the spectra (since motion of both rings would be expected to yield a much narrower spectrum with a second moment of about 1–1.5  $G^2$  as is observed for ferrocene.)<sup>24</sup> Since the crystal structure shows no disorder, the only allowed motions must be "jumping" of the carbon atoms between equivalent sites. The pentahapto ( $C_5H_5$ ) ring is believed to be moving rather than the monohapto ring, because motions of  $\pi$ -bonded ring systems occur at comparable temperatures. A theoretical value for the second moment for the case of pentahapto ring rotating and the monohapto ring being rigid was calculated after the formulation of Michel, *et al.*<sup>25</sup> A value of 3.4  $G^2$  was obtained (Table I), in reasonable agreement with the experimental value, taking into account the uncertainties involved in the calculations.

Between room temperature and the melting point of the compound, the second moment decreases further to a value of about 2.6  $G^2$  at 50°, suggesting that the monohapto ring is also undergoing motion. Calculation of a theoretical value for the second moment for both rings moving yields a value of 1.2  $G^2$ , and it is thought that the transition is not complete before melting. However, since the nmr measurements are "kinetic" measurements, the transitions thus detected must occur at temperatures at, or above, the temperature where the molecules *begin* to reorient. The limiting lower line width will thus only be observed when *all* the molecules have reoriented on the nmr time scale, and it is thought from the drop in second moment observed before the melting point, that the monohapto ring is also able to reorient at ambient temperatures.

(23) (a) G. Liebling and R. E. Marsh, *Acta Crystallogr.*, **19**, 202 (1965). (b) A similar calculation for the monohapto ring in  $(C_5H_5)_2MoNO(h^1-C_5H_5)_2^{20c}$  yields a value of 2.8  $G^2$ , but the uncertainties in the positions of the hydrogen atoms as indicated by the large differences in the C–H bond lengths found suggest there may be a substantial error in this value. (c) J. L. Calderon, F. A. Cotton, and P. Legzdins, *J. Amer. Chem. Soc.*, **91**, 2528 (1969).

(24) L. N. Mulay and A. Attalla, *J. Amer. Chem. Soc.*, **85**, 702 (1963).

(25) J. Michel, M. Drifford, and P. Rigny, *J. Chim. Phys. Physicochim. Biol.*, **67**, 31 (1970).

**( $h^1-C_5H_5$ )HgX Series of Compounds.** The nature of the changes in line width and second moment parameters with temperature (shown in Figures 2–5) for the compounds in this series can be understood by comparison with the corresponding data for  $(h^1-C_5H_5)(h^5-C_5H_5)Fe(CO)_2$  above, and by considering the limiting second moment values above and below the transitions. Although the crystal structures of these compounds have not, as yet, been determined by X-ray diffraction, values for the rigid lattice second moments can be estimated with a reasonable degree of accuracy, since the contribution to the second moment from within a given molecule depends only on the molecular structure and is independent of the actual disposition of the molecules in the lattice, and the contribution from the other molecules is very much a function of the density of protons and can be estimated from those of related compounds. Thus for  $(h^1-C_5H_5)_2Hg$  one would expect an "intra" contribution to the second moment from within the molecule of  $\sim 3 \pm 1 G^2$  and an intermolecular value due to the effect of the other molecules of  $\sim 4 \pm 1 G^2$  by comparison with ferrocene<sup>22</sup> which has similar numbers of protons. There will also be a small contribution to the second moment from  $^{199}Hg$  of spin  $1/2$  (16.8%) and  $^{201}Hg$  (13.2%) of spin  $3/2$  yielding an overall value of about  $7 \pm 2 G^2$  which compares favorably with the experimentally determined values (see Table I), and at temperatures below 80°K the whole molecule is thought to be rigid in the lattice (on nmr time scale). Movement of the  $C_5H_5$  rings in their approximate planes must be invoked to explain the extreme narrowing of the spectrum at higher temperatures, and this movement must involve a simultaneous rotation and distortion of the ring together with breaking and forming of the  $\sigma$  bond. Values for the second moments associated with this type of motion, estimated by comparison with ferrocene and  $(h^1-C_5H_5)(h^5-C_5H_5)Fe(CO)_2$ , would be of the order of  $1 \pm 0.5 G^2$  in agreement with that determined experimentally (Table I). It is very unlikely that motion of the whole molecule would occur as it is so unsymmetrical, and from the results it is predicted that when a crystal structure is determined it will show discrete positions for all the atoms with relatively large thermal factors for the carbon atoms in the  $C_5H_5$  rings.

In the case of  $(h^1-C_5H_5)HgCl$ , an estimated value for the "rigid lattice" second moment is  $6 \pm 2 G^2$  based on an intramolecular contribution of  $2.7 \pm 0.8 G^2$ , an intermolecular of  $2.5 \pm 1 G^2$  plus a small contribution from the mercury atom as before and a contribution from  $^{37}Cl$  (24.4%) of spin  $3/2$ . (Since the spin of each of the Cl is  $3/2$ , then a small amount of broadening will result from quadrupolar interaction also estimated as  $0.2 \pm 0.1 G^2$ .) Hence the total value will be of the order  $6.7 \pm 2 G^2$  in agreement with the observed value of 6.3  $G^2$ . As with  $(h^1-C_5H_5)_2Hg$ , movement of the  $C_5H_5$  ring is thought to be involved in the extreme narrowing of the spectrum, and the most probable type of motion is considered to be rotation in the plane of the ring with the ring undergoing simultaneous rotation and distortion. An estimated value of the second moment for this type of motion would again be of the order of  $1 \pm 0.5 G^2$  in agreement with the observed value of 1.3  $G^2$ . Again it is considered unlikely that the whole molecule would move.

( $h^1\text{-C}_5\text{H}_5$ )HgBr and ( $h^1\text{-C}_5\text{H}_5$ )HgI may be treated similarly, for the same estimates can be made taking into account the larger size of the Br atoms hindering the packing, giving a slightly smaller intermolecular contribution and the contribution of  $^{79}\text{Br}$  (50.5%) spin  $3/2$  and  $^{81}\text{Br}$  (49.5%) spin  $3/2$  being slightly different from that of Cl (see Table I). The large size of the iodine atom in ( $h^1\text{-C}_5\text{H}_5$ )HgI is slightly offset by the fact that  $^{127}\text{I}$  has a spin of  $5/2$  which tends to increase its contribution to the second moment. In both cases the low value of the high-temperature second moment is thought due to the motion of the  $\text{C}_5\text{H}_5$  rings in their approximate molecular planes.

### Conclusions

The molecular motions detected in the present work are thought to be similar to those found in the case of the cyclooctatetraeneiron tricarbonyls,<sup>3</sup> where the  $\text{C}_8\text{H}_8$  rings reorient in the solid state with simultaneous distortion and breaking of the metal-cyclooctatetraene bond. There may well be some bonding between the metal and the ligand during the motion, but it cannot be that observed in the static structure which is presumably the optimum bonding. The occurrence of bond breaking with reorientation in these compounds was unusual, being the only reported instance to date, and contrary to what one might intuitively expect in the solid at the relatively low temperatures at which it occurred. The cyclopentadienyl compounds investigated here represent an even more extreme example. In these compounds, not only must there be distortion of the rings as they "jump" between potential wells, but there must be a simultaneous change in the localized metal-carbon  $\sigma$  bond. As such, the result is of considerable interest and would seem to warrant further work on these sys-

tems as well as investigation of other potential examples.

For the series of compounds ( $h^1\text{-C}_5\text{H}_5$ )HgX (X =  $\text{C}_5\text{H}_5$ , Cl, Br, I), there is a general correspondence between the solid state results and those from high resolution nmr studies in solution. As the electronegativity of X is increased, the temperature of the transition increases. This implies that the activation energy for the process is increasing. It also implies that in the solid state, intramolecular forces contribute significantly to the barrier to reorientation. Two values for the activation energy in the solid state were obtained; one was obtained by least-squares fit of the experimental data using the BPP equation,<sup>19</sup> as modified by Smith.<sup>20</sup> This is an empirical relationship based on the change in the line width with temperature and usually yields values within 15% of those obtained by other methods. The second value for the activation energy was obtained by use of the Waugh estimate,<sup>21</sup> another empirical relationship, where  $E = 37T$ , where  $T$  is the temperature at the midpoint of the line-width transition. This very empirical formula usually yields values within 20% of those obtained from other methods. The  $E_a$  values for each compound are given in Table I. Although good fits were obtained using the BPP equation, the values from the Waugh estimate appear more "sensible." Measurement of the temperature dependence of  $T_1$ , the spin-lattice relaxation time, for these compounds will provide a much more direct method of obtaining values for the activation energy.

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## New 10- and 11-Atom Polyhedral Metallocarboranes Prepared by Polyhedral Contraction

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**Abstract:** The base degradation of  $[\text{LCo}(\pi\text{-}(3)\text{-}1,2\text{-B}_9\text{C}_2\text{H}_{11})]^+$  followed by oxidation has been found to effect a polyhedral contraction to give  $[\text{LCo}(\pi\text{-}(1)\text{-}2,4\text{-B}_8\text{C}_2\text{H}_{10})]^+$ , where  $\text{L} = \text{C}_5\text{H}_5^-$  and  $z = 0$  or  $\text{L} = (3)\text{-}1,2\text{-B}_9\text{C}_2\text{H}_{11}^{2-}$  and  $z = -1$ . Further degradation of these complexes using  $\text{FeCl}_3$  in ethanol gave  $[(\pi\text{-C}_5\text{H}_5)\text{Co}(\pi\text{-B}_7\text{C}_2\text{H}_9)]$  and  $[(\pi\text{-}(3)\text{-}1,2\text{-B}_9\text{C}_2\text{H}_{11})\text{Co}(\pi\text{-B}_7\text{C}_2\text{H}_9)]^-$ . The former complex eliminates hydrogen at  $150^\circ$  to give  $[(\pi\text{-C}_5\text{H}_5)\text{Co}(\pi\text{-}(2)\text{-}1,10\text{-B}_7\text{C}_2\text{H}_9)]$ .

Previously, metallocarborane complexes have been prepared by two general methods. The first involves deprotonation of a nido carborane which contains acidic hydrogen atoms followed by reaction of the resulting anion with a transition metal ion to give a metallocarborane.<sup>1,2</sup> The second, more general approach

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(2) T. A. George and M. F. Hawthorne, *ibid.*, **91**, 5475 (1969).

involves the direct reduction of a closo carborane to an anionic species using an alkali metal. Reaction of this anion with transition metal ions then gives the desired metallocarborane.<sup>3-5</sup> This second method has been

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