

## SUBSTITUENT EFFECTS ON THE FLUXIONAL BEHAVIOUR OF CYCLOPENTADIENYL DERIVATIVES OF MERCURY

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### SUMMARY

Two new substituted cyclopentadienyl compounds of mercury have been prepared and their fluxional behaviour investigated by variable temperature proton magnetic resonance spectra. The influence of the substituents on the dynamics of cyclopentadienylmercury derivatives is reported.

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### INTRODUCTION

It has been shown recently that the introduction of five methyl substituents into each ring of dicyclopentadienylmercury has a considerable inhibiting effect on the fluxional behaviour of this compound<sup>1</sup>. Since the influence of steric and polar factors as well as of the solvent effects on the dynamic process have been little studied so far, we have started an investigation on the fluxional behaviour of some mono- and poly-substituted cyclopentadienyl derivatives of mercury. In this paper the preparation and the investigation by variable temperature NMR spectroscopy of (tert-butylcyclopentadienyl)mercury chloride and bis(methylcyclopentadienyl)mercury are described.

### EXPERIMENTAL

#### *General data*

Unless otherwise indicated, all manipulations were carried out under dry nitrogen or *in vacuo*. Infrared spectra were recorded on potassium bromide pellets or liquid films or Nujol mulls between NaCl plates, on a Perkin-Elmer 257 or a Beckmann IR 20 spectrometer.

NMR spectra were recorded at 60 MHz on a Varian Associates spectrometer and at 100 MHz on a JEOL spectrometer equipped with variable temperature probes. Temperature calibrations were made with methanol or ethylene glycol. TMS was used as an internal standard. Mass spectra were obtained with an AEI MS 12 spectrometer.

#### *Cyclopentadiene derivatives*

Methylcyclopentadiene was obtained by the distillation of the 70–75° fraction

from the freshly cracked methylcyclopentadiene dimer and used immediately. *tert*-Butylcyclopentadiene was prepared by literature methods<sup>2</sup>. The two compounds were characterized by their infrared and NMR spectra.

The infrared spectrum of the freshly distilled methylcyclopentadiene was recorded on a liquid film between NaCl plates, and was found to be in very good agreement with the data in the literature<sup>3,4</sup>, in which it is described as a mixture of 1- and 2-methylcyclopentadiene. The NMR spectrum of methylcyclopentadiene shows a complex system of multiplets in the olefinic region ( $\tau$  3.95–3.60) and complex signals of the two methylenic protons at  $\tau$  7.8<sup>5</sup>. The methyl group gives a peak at  $\tau$  8.05<sup>6</sup>.

The infrared spectrum of *tert*-butylcyclopentadiene was recorded on a liquid film between NaCl plates, and shows the following bands ( $\text{cm}^{-1}$ ): 625 s, 680 s, 760 s, 810 s, 855 m, 890–900 s, 955 s, 980 s, 1120 m, 1145 m, 1200 s, 1230 s, 1260 s, 1290 m, 1365 s, 1460 s, 1520 m, 1595 s, 2860–2970 s, 3070 s. The NMR spectrum shows a complex system of multiplets between  $\tau$  3.3–4.2, a quartet at  $\tau$  7.2, and a singlet at  $\tau$  8.9; the area ratio is 3/2/9.

#### *Bis(methylcyclopentadienyl)mercury*

A solution of 3 g (0.038 mol) of methylcyclopentadiene monomer in 30 ml of anhydrous THF was added dropwise, with stirring, under nitrogen, to 20 ml of a 20–25% solution of butyllithium in hexane (Fluka). The resulting white suspension was cooled at  $-70^\circ$ , and treated dropwise with a solution of 4.0 g (0.015 mol) of anhydrous mercuric chloride (Erba RP). The gray suspension was kept half an hour at  $-70^\circ$  with stirring, then was rapidly filtered, and the solvent evaporated under reduced pressure at a temperature between 0–10 $^\circ$ . The white solid was dissolved in cold  $\text{CCl}_4$ , and the solution filtered and evaporated to dryness; this operation was repeated to give a pure compound. Pale yellow crystals were obtained; these are stable for several weeks at  $-70^\circ$ , but decompose at room temperature in the solid state or in solution. (Found: C, 40.33; H, 3.51.  $\text{C}_{12}\text{H}_{14}\text{Hg}$  calcd.: C, 40.15; H, 3.65%.)

#### *(tert-Butylcyclopentadienyl)mercury chloride*

A 20–25% solution of butyllithium (10 ml) in hexane was added slowly to a cooled solution of 3.8 g (0.031 mol) of *tert*-butylcyclopentadiene in 50 ml of anhydrous THF. The temperature was raised to room temperature, and after half an hour a solution of 7.5 g (0.03 mol) of  $\text{HgCl}_2$  in anhydrous THF was added. The gray suspension was stirred at room temperature for one hour and the solvent was then evaporated off and the residue extracted with petroleum ether 50–60 $^\circ$ .

Evaporation gave a pale yellow solid. Elemental analysis indicated this was a mixture of (*tert*-butylcyclopentadienyl)mercury chloride and bis(*tert*-butylcyclopentadienyl)mercury. The solid was recrystallized several times from acetone. Pale yellow crystals, m.p. 88–89 $^\circ$ , were obtained, which do not decompose at room temperature in the solid state. (Found: C, 30.63; H, 3.73; Hg, 56.6.  $\text{C}_9\text{H}_{13}\text{HgCl}$  calcd.: C, 30.25; H, 3.67; Hg, 56.2%.)

The infrared spectrum shows the following bands ( $\text{cm}^{-1}$ ): 645 s, 730 s, 800 s, 900 m, 980 s, 1000 m, 1125 m, 1200 w, 1250 w, 1285 w, 1365 s, 1455–1470 s, 1575 m, 2850–2950 s.

The mass spectrum of the compound shows the most prominent peaks in the range 362–355 *m/e*. The observation that the mass spectrum of the compound shows

clearly defined parent ions suggests that there are no dimeric or more highly aggregated species, and that the mercury is  $\sigma$ -bonded to the cyclopentadienyl ring<sup>7</sup>.  $\pi$ -Cyclopentadienyl metal compounds usually show prominent peaks corresponding to  $C_5H_5M^+$  cation<sup>8</sup>.

## RESULTS AND DISCUSSION

The fluxional behaviour of (tert-butylcyclopentadienyl)mercury chloride was investigated by variable temperature NMR spectroscopy in deuterated acetone in the range  $+30$  to  $-100^\circ$ . The complete NMR spectrum is shown in Fig. 1. At room temperature the spectrum shows the characteristic singlet of the tert-butyl group at  $\tau$  8.84, and two bands in the olefinic region in the range  $\tau$  4.55–5.00 and 4.10–3.90, respectively. The area ratios are 9/2/2, respectively.

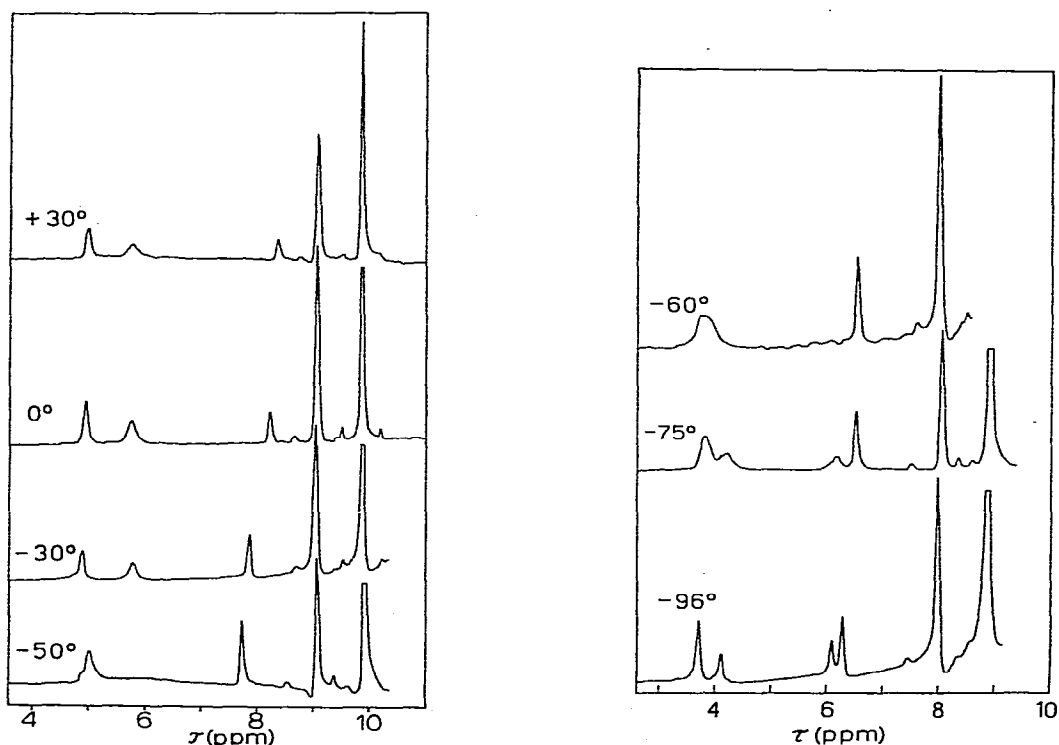


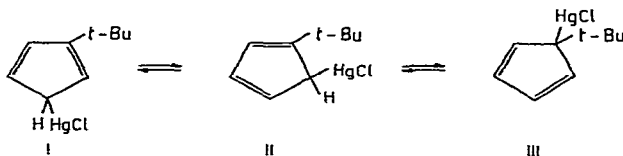
Fig. 1. The proton magnetic resonance spectra of (tert-butylcyclopentadienyl)mercury chloride at several temperatures. The peak at  $\tau$  8.02 is the solvent signal.

There is no evidence of signals due to methylenic hydrogens in the region  $\tau$  7, while the spectrum shows a singlet at  $\tau$  7.35. This peak is due to the HOD present in the solvent, as it was confirmed by the spectrum of the solvent, and the shifts to lower fields with the decrease of temperature confirm the nature of this signal. The decrease in temperature from  $+30$  to  $-96^\circ$  gives rise to some changes in the spectra, which indicate that some rearrangement process is taking place. Notably, the sharpest changes are observed from  $-60$  to  $-96^\circ$ : the two bands of the olefinic hydrogens,

which broaden continuously from  $+30$  to  $-60^\circ$  collapse in a large band at  $-65^\circ$ , which at  $-96^\circ$  splits into two signals centered at  $\tau$  3.7 and 4.1, respectively. At the same time, at  $-75^\circ$  a peak in the region  $\tau$  5.80 begins to appear near the HOD peak, which is due to a methylenic hydrogen. At  $-96^\circ$  this signal becomes sharp; at this temperature the NMR spectrum shows four peaks, at  $\tau$  8.86 (tert-butyl group), 6.08 (methylenic hydrogen), 4.1 and 3.7 (olefinic hydrogens); the area ratios are 9/1/1/2, respectively. [It is noteworthy that these changes in the NMR spectra are nearly the same as those reported for (methylcyclopentadienyl)trimethylgermane in the temperature range from  $-40^\circ$  to  $+130^\circ$ ]<sup>9</sup>. The reversibility of the process was established by the observation that when the solution at  $-96^\circ$  is allowed to warm to room temperature, the NMR spectrum is identical to that of the original solution.

No evidence is available from the spectra for t-BuCp<sup>199</sup>HgCl proton resonances, although they were carefully looked for. A reasonable explanation is that they are covered by the two broad vinylic bands (the quadrupole moment of the mercury gives also some contribution to this broadening), since these satellite peaks are reported to lie between 6.1 and 7.0 ppm<sup>10</sup>; the upfield satellites of the methylenic proton can be found only with difficulty, since they are extremely low and broad.

The interpretation of the NMR spectrum is consistent with the view that (tert-butylcyclopentadienyl)mercury chloride is a fluxional molecule, with the cyclopentadienyl moiety  $\sigma$ -bonded to the mercury atom, and with the following configurations rapidly interconverting among themselves. At  $-96^\circ$  the molecule is frozen in one of



its lowest free energy configurations, which is revealed by the NMR spectra to be either (I) or (II), since these are the only ones possessing a methylenic hydrogen; configuration (III) must be destabilized by the steric repulsion between tert-butyl and HgCl groups.

The room temperature NMR spectrum (Fig. 2) of bis(methylcyclopentadienyl)mercury in  $\text{CCl}_4$  shows three signals at  $\tau$  4.15, 4.75, and 8.10, with area ratios 2/2/3, and is completely different from that of pure methylcyclopentadiene. The two peaks at low fields, which are due to olefinic hydrogens, are symmetrical and do not show any fine structure; no resonance in the region at  $\tau$  7 due to a methylenic hydrogen is observed. The same pattern is also observed in the NMR spectrum of (methylcyclo-

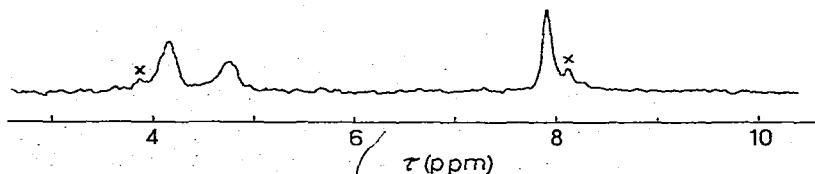
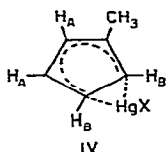


Fig. 2. The room temperature proton magnetic resonance spectrum of bis(methylcyclopentadienyl)mercury. The small peaks marked X may be due to impurities produced by a little thermal decomposition.

pentadienyl)trimethylsilane<sup>9</sup> and -germane<sup>9</sup> at temperatures high enough to reveal the fluxional behaviour of these molecules, and it, together with the easy decomposition of the product at room temperature<sup>11</sup>, indicates the presence of a dynamic  $\sigma$ -cyclopentadienyl group.

As expected from the above behaviour of (tert-butylcyclopentadienyl)mercury chloride, the introduction of a methyl group does not affect the fluxional character of dicyclopentadienylmercury and so further NMR analysis of this compound at low temperatures was neglected. The presence of the two symmetrical signals in the olefinic region may be explained by structure (IV), for which only the signals of the two types of hydrogen, H<sub>A</sub> and H<sub>B</sub>, would be detected when the rotation is sufficiently fast compared with the NMR time-scale.

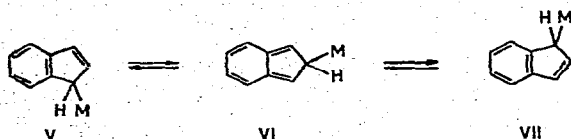


It was recently reported<sup>10</sup> that the fluxional behaviour of some molecules of the type CpHgX is influenced by the nature of the X group because it was found that the less electronegative is substituent X, the more facile is the intramolecular ring-whizzing of the mercury atom about the Cp ring, *i.e.*, Cp<sub>2</sub>Hg > CpHgI > CpHgBr > CpHgCl.

The comparison of the fluxional character of some derivatives such as dicyclopentadienylmercury, bis(methylcyclopentadienyl)mercury, bis(pentamethylcyclopentadienyl)mercury, cyclopentadienylmercury chloride, and (tert-butylcyclopentadienyl)mercury chloride suggests that the dynamic process is affected also by steric factors. The Cp<sub>2</sub>Hg compound shows a decrease in its fluxional character at temperatures below  $-100^{\circ}$ , but its static structure could not be observed<sup>10</sup>. The introduction of a methyl group in each ring does not greatly affect this character, while the introduction of ten methyl substituents has a considerable retarding effect. Cyclopentadienylmercury chloride<sup>10</sup> and (tert-butylcyclopentadienyl)mercury chloride show their static structures at  $-113^{\circ}$  and  $-96^{\circ}$ , respectively. The comparison reveals that the tert-butyl group may exert a very slight steric retardation on the metal migration, since its polar influence would have an accelerating effect because of the better interaction of the  $5p$  or  $6d$  unfilled metal orbitals with the diene system<sup>12</sup>. However, this comparison does not take into account that different solvents were used (tetrahydrofuran and acetone, respectively), and that their basicities may also play some role in the fluxional behaviour.

In their study of the non-fluxional molecule  $(\sigma\text{-C}_9\text{H}_7)(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ , Cotton and coworkers<sup>13</sup> calculated that a 1,2 shift for a  $\sigma$ -bonded indenyl group would give rise to an isoindenyl structure (VI) which is 9 kcal/mol less stable than either (V) or (VII). In contrast, a 1,2 shift in the corresponding unsubstituted cyclopentadienyl compound occurs between equivalent, low-energy structures. Since the activation energy for the fluxional indenylmercury is 12.9 kcal/mol<sup>12</sup>, assuming that 9 kcal/mol is required for the formation of the less stable isoindenyl structure, the fluxional process requires 4 kcal/mol; for the cyclopentadienylmercury compounds an activa-

tion energy of 4 kcal/mol is consistent with the observation of dynamic spectra at temperatures as low as ca.  $-100^{\circ}$ .



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