Valence Tautomerism in Dicyclopentadienylmercury

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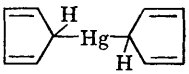
DICYCLOPENTADIENYLMERCURY has been formulated as containing the mercury atom bonded to the carbon atoms of the cyclopentadienyl rings by



means of σ-bonds. This structure was suggested on the basis of both spectral and chemical evidence.[1,2] Some experimental results, namely the ^{1}H n.m.r. spectrum, at first seem to be at variance with this structure. The n.m.r. spectrum at room temperature consists of a single sharp peak ($\tau \sim 4{\cdot}2$), which is indicative of π-bonded rather than σ-bonded cyclopentadienyl compounds.[3] Similar results have been obtained for other cyclopentadienyl compounds, where the metal is bonded to the ring carbon through σ-bonds, namely, $(C_5H_5)CuPEt_3$[2], $(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C_5H_5)$,[4] and $(\pi\text{-}C_5H_5)Cr(NO)_2(\sigma\text{-}C_5H_5)$.[5]

When, however, the n.m.r. spectra of these compounds were obtained at lower temperatures, the single peak assigned to the cyclopentadienyl protons became resolved into three peaks whose areas were in the expected ratio of 2 : 2 : 1. The explanation for this phenomenon is that originally advanced by Piper and Wilkinson,[2] namely that while the metal atom is indeed σ-bonded to the ring, the point of attachment changes at such a rate that the protons on the rings appear equivalent in the n.m.r. spectrum. This rate of exchange, however, can be slowed down sufficiently at low enough temperatures so that the protons no longer appear equivalent. On the basis of the pattern of the resolved spectrum as a function of temperature it is also possible to suggest the mechanism by which the metal atom exchanges,[6] the possibilities being a series of 1,2-shifts, 1,3-shifts, or a combination of both types of shifts of the metal atom about the ring.

The low-temperature n.m.r. spectrum of dicyclopentadienylmercury had previously been measured in a tetrahydrofuran solution at $-70°$. However, no splitting was observed in the signal of the cyclopentadienyl protons.[7] Since the splitting has been shown to be a function of the solvent used,[6] we have measured the n.m.r. spectrum of dicyclopentadienylmercury in various solvents down to $-70°$. In triethylamine, no splitting was observed; the peak remaining as a sharp singlet. In CS_2, the peak was noticeably broadened as the temperature reached $-70°$. However, no splitting was observed. In SO_2 solution, splitting does occur producing three peaks as is shown in the Figure.

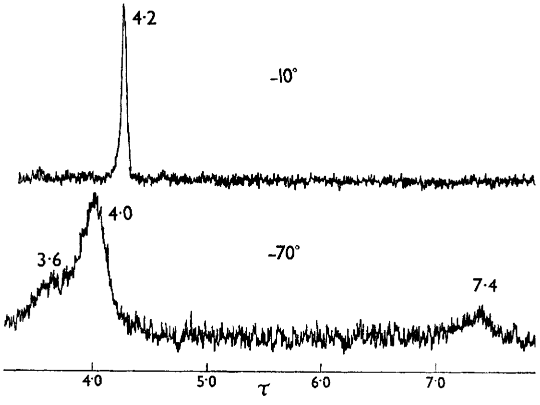


FIGURE. *The* ^{1}H *n.m.r. spectrum of* $(C_5H_5)_2Hg$ *in solution as a function of temperature.*

Evidence is thus presented that dicyclopentadienylmercury belongs to that group of compounds where the metal atom migrates around the cyclopentadienyl ring, as originally predicted by Piper and Wilkinson.[2] The pattern of the spectrum is seen to be the opposite of that observed for $(C_5H_5)CuPEt_3$;[6] namely, in the unsymmetrical collapse of the vinyl proton peak into two peaks, the one at lower field is less intense when the splitting begins to occur. Assuming that the assignments of the peaks by Whitesides and Fleming[6] are correct, our spectrum can be interpreted as indicating that the mercury atom rotates around the rings by a series of 1,2-shifts.

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[1] G. Wilkinson and T. S. Piper, *J. Inorg. Nuclear Chem.*, 1956, **2**, 32.

[2] T. S. Piper and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.

[3] M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Adv. Organometallic Chem.*, 1965, **3**, 114.

[4] M. J. Bennett, jun., F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Amer. Chem. Soc.*, 1966, **88**, 4371.

[5] F. A. Cotton, A. Musco, and G. Yagupsky, *J. Amer. Chem. Soc.*, 1967, **89**, 6136.

[6] G. M. Whitesides and J. S. Fleming, *J. Amer. Chem. Soc.*, 1967, **89**, 2855.

[7] G. G. Dvoryantseva, K. F. Turchin, R. B. Materikova, Yu. N. Sheinker, and A. N. Nesmeyanov, *Doklady Akad. Nauk S.S.S.R.*, 1966, **166**, 868.