Absence of Valence Tautomerism in Dicyclopentadienylmercury

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THE discussion on the nature of the C_5H_5–M bond in dicyclopentadienylmercury has continued for 12 years. A whole range of spectroscopic evidence[1] is in disagreement with the original suggestion of a localised σ-bond between the cyclopentadienyl ring and Hg.[2] Recently we have suggested the existence of a "π-complex" bond of a "sandwich" type on the basis of n.m.r. studies.[3]

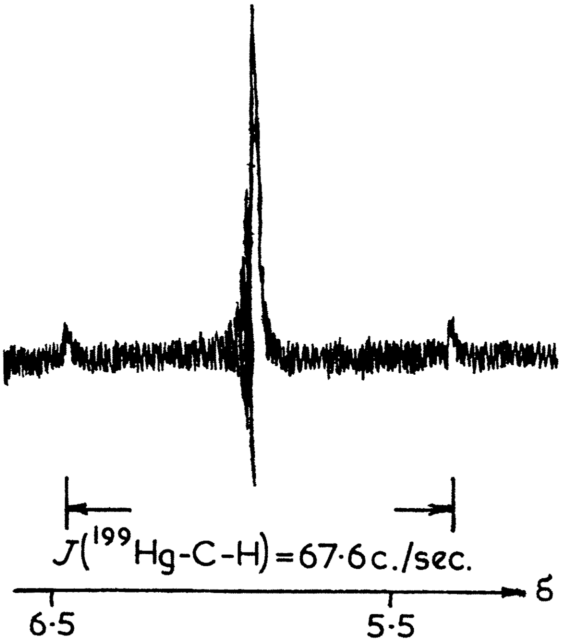

FIGURE 1. *The ^1H n.m.r. spectrum of dicyclopentadienylmercury in C_6D_6 after 20 days at room temperature.*

We report the study of the ^1H n.m.r. spectra of $(C_5H_5)_2Hg$ in weak and strong solvating media, in protic and aprotic solvents, in aromatic hydrocarbons and in solvents with lone electron pairs of different activities. In addition, the effect of temperature on the spectra was studied; the details will be published elsewhere.

In none of the solvents, at none of the temperatures studied (+35— −100°), was the splitting of the cyclopentadienyl proton singlet (δ 5·85—6·15 depending on the solvent) observed, which would be attributed to a σ-structure or to a 1,2-Hg rearrangement.[2] In particular, at −100° the C_5H_5 singlet was the same width as at −30° (in tetrahydrofuran).

The solvents may be classified into two groups depending on their effect on $(C_5H_5)_2Hg$. Nonsolvating and weak solvating media stabilise this compound. Thus dicyclopentadienylmercury dissolved in C_6D_6, $CDCl_3$, or CCl_4 may be stored without decomposition much longer than the solid compound at the same temperature (see Figure 1, the ^1H n.m.r. spectrum of $(C_5H_5)_2Hg$ in C_6D_6 after 20 days at room temperature). On the other hand, strong solvating media accelerate the irreversible process of decomposition, shown by the appearance of metallic mercury (sometimes a hard resin can also be formed) and the appearance of impurity signals in the spectrum (in the vinyl and allyl proton regions). The impurity signals strengthen progressively with time and have no reversible temperature dependence. The easier it is to remove a proton from the solvent molecule, the closer the chemical shifts of these signals agree with the free cyclopentadiene signals.[4] Thus, the impurity signals (δ 6·44 and 2·93) in the spectrum of dicyclopentadienylmercury in $CDCl_3$ arise after storage for many days at room temperature. In contrast, even at −70° a solution of $(C_5H_5)_2Hg$ in liquid SO_2, freed from H_2O and O_2, exhibits a symmetrical singlet 10 min. after being prepared (Figure 2a), but shows a noticeable quantity of

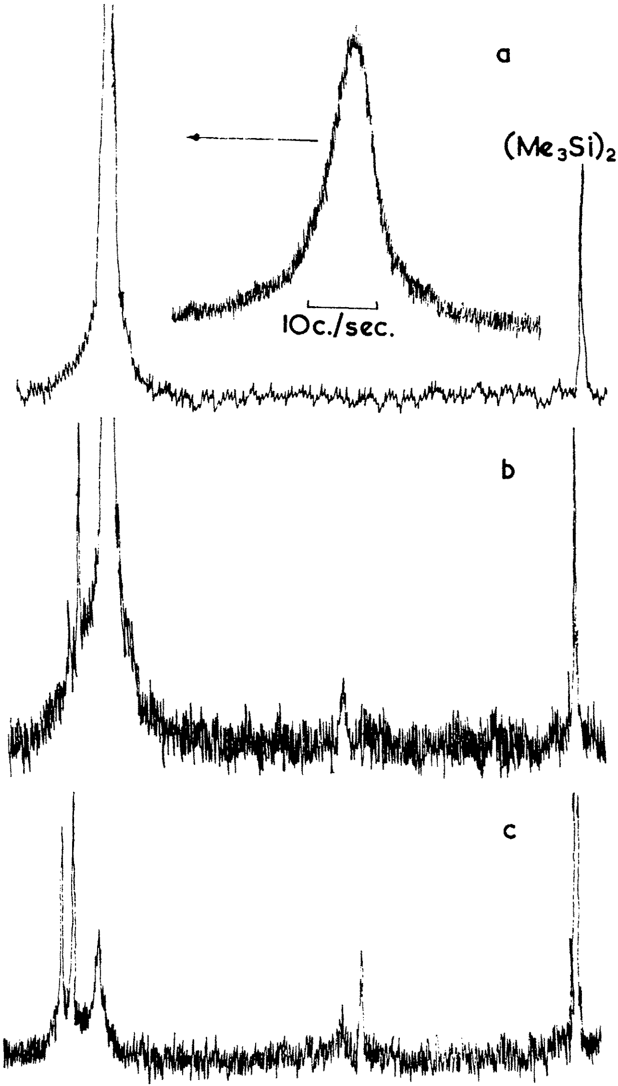

FIGURE 2, a—c. *The ^1H n.m.r. spectra of dicyclopentadienylmercury in SO_2 at −70° after storage of the sample for* 10 *min.* (a), 3 *hr.* (b), *and* 7—8 *hr.* (c).

impurities after 3 hr. (Figure 2b), and the impurities (δ 6·75; 6·60; 3·11 and 2·89) predominate several hours later (Figure 2c). If the temperature of the sample (*vide* Figure 2a) is gradually increased to −10°, after 40 minutes impurity signals similar to the preceding ones could be observed. If subsequently one decreases the temperature these signals do not disappear, but strengthen gradually with time, which demonstrates the irreversible character of the decomposition. These were probably the signals observed by Maslowsky and Nakamoto.[5]

The n.m.r. spectra were taken with the NMR-2305 spectrometer (SKB, Leningrad).

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[1] A. N. Nesmeyanov, G. G. Dvoryantseva, N. S. Kochetkova, R. B. Materikova, and Yu. N. Sheinker, *Doklady Akad. Nauk S.S.S.R.*, 9164, **159**, 847; 1966, **166**, 868.

[2] G. Wilkinson and T. S. Piper, *J. Inorg. Nuclear Chem.*, 1956, **2**, 32; 1956, **3**, 104.

[3] A. N. Nesmeyanov, L. A. Fedorov R. B. Materikova, E. I. Fedin, and N. S. Kochetkova, *Tetrahedron Letters*, 1968, 3753.

[4] M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1959, 3759.

[5] E. Maslowsky and K. Nakamoto, *Chem. Comm.*, 1968, 257.