

Bis(pentamethylcyclopentadienyl)mercury

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CYCLOPENTADIENYL derivatives involving ring-carbon-metal σ -bonds may undergo rapid metal 1,2-shifts around the ring,¹ which are responsible for the n.m.r. equivalence of the cyclopentadienyl protons.^{2,3}

Characteristic n.m.r. patterns for nonequivalent protons can only be observed when the lifetime of the molecule is long as compared with the time scale of the measurement.⁴ Thus, whereas dicyclopentadienylmercury displays a simple pattern consisting of a single peak at room temperature,^{2,5} slowing down of the metal shifts at lower temperature is expected to give rise to three peaks whose areas should be in the ratio 2:2:1. Results in this direction were indeed reported by Maslowsky and Nakamoto⁶ although they have recently been questioned by Nesmeyanov *et al.*⁶

Davison and Rakita⁴ found that replacement of all ring hydrogens with methyl groups in $\text{Me}_5\text{SnC}_5\text{H}_5$ produces a single peak for the methyl protons of the ring. This result clearly indicates that the bond-rearrangement process does not require the ring hydrogens and can still be quite fast even in overcrowded structures. We now report on the different behaviour of a similar structure in the Hg series.

We have synthesised bis(pentamethylcyclopentadienyl)mercury by the reaction of lithium pentamethylcyclopentadienide with HgCl_2 in tetrahydrofuran solution. The product was recrystallised from petroleum as colourless crystals, m.p. 125–126°. The u.v. spectrum displays a band at 270 nm. ($\log \epsilon$ 3.91) and a shoulder at 248 nm. The main i.r. bands (cm^{-1}) attributable to the diene system are as follows: 1655 (m), 997–1122 (including a strong peak at 1066) and 695–841 (w). From a comparison of these spectral data with those of pentamethylcyclopentadiene⁷

and from the analogous behaviour of related cyclopentadienyl derivatives,^{2,8} a σ -bonded structure is indicated.

Furthermore, at variance with what is observed for the unsubstituted parent compound, the room-temperature

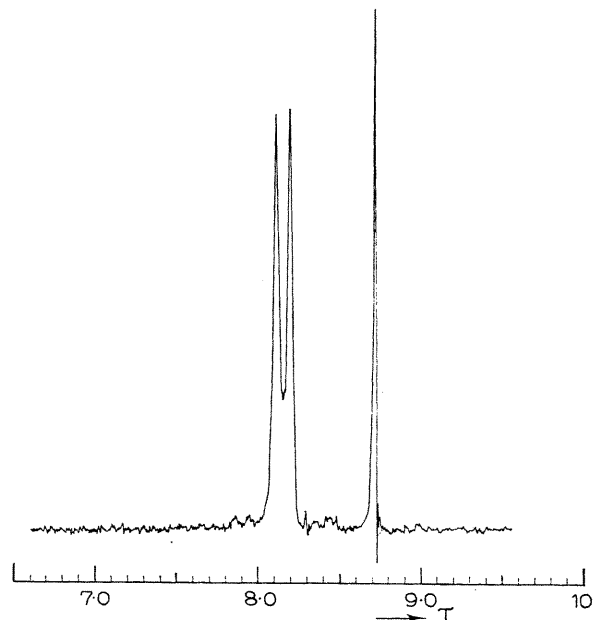


FIGURE. The ^1H n.m.r. spectrum of bis(pentamethylcyclopentadienyl)mercury in benzene at room temperature.

n.m.r. spectrum of $\text{Hg}(\text{C}_5\text{Me}_5)_2$ is that expected for a "static" σ -bonded structure since it displays the nonequivalence of the methyl protons. It is in fact the simplest spectrum recorded so far for this kind of structure, since complexities resulting from ring proton *versus* methyl proton coupling interactions are absent. In CDCl_3 solution only two peaks with a 4:1 pattern are observed; the spectrum is better resolved in benzene solution showing three singlets (τ 8.10, 8.18, 8.70; Me_4Si internal standard), whose areas are in the ratio of 2:2:1 (Figure).

Obviously, the compound need not consist of a truly static structure. The n.m.r. spectrum simply shows that here the lifetime of the molecule is long as compared with the time scale of the measurement. We also have unequivocal proof that the five methyl substituents at each ring have a considerable retarding effect on the molecular dynamics of dicyclopentadienylmercury.

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¹ These shifts are alternatively classified as [1,5]-sigmatropic rearrangements (ref. 3b; see also R. B. Woodward and R. Hoffman, *J. Amer. Chem. Soc.*, 1965, **87**, 2511).

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

³ (a) H. P. Fritz and C. G. Kreiter, *J. Organometallic Chem.*, 1965, **4**, 313; (b) R. Hüttel, V. Raffay, and H. Reinheimer, *Angew. Chem. Internat. Edn.*, 1967, **6**, 862; (c) B. Fusch, M. Ishaq, and M. Rosenblum, *J. Amer. Chem. Soc.*, 1968, **90**, 5293.

⁴ A. Davison and P. E. Rakita, *J. Amer. Chem. Soc.*, 1968, **90**, 4479.

⁵ M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Adv. Organometallic Chem.*, 1965, **3**, 114.

⁶ E. Maslowsky and K. Nakamoto, *Chem. Comm.*, 1968, 257; A. N. Nesmeyanov, L. A. Fedorov, R. B. Materikova, E. I. Fedin, and N. S. Kochetkova, *ibid.*, 1969, 105.

⁷ L. de Vries, *J. Org. Chem.*, 1960, **25**, 1838.

⁸ H. P. Fritz, *Adv. Organometallic Chem.*, 1964, **1**, 239.