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ON THE STRUCTURE OF CYCLOPENTADIENYL DERIVATIVES OF NONTRANSITION METALS OF PERIODS V AND VI

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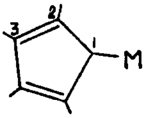
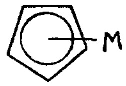
Chemists are not agreed on the nature of the cyclopentadienyl - metal (Cp-M) bond in nontransition metal compounds of periods V and VI. Some chemists believe them to be σ-bonded (structure I, refs 1,2), others consider some of them as ion derivatives (structure II, refs 3,4), still others suggest the existence of " π -coordination" (sandwich structure III, refs 5,6,7).



I

II



III

The third alternative was first proposed by E.Fischer (5,9). We have substantiated it for Cp-Tl (8) and Cp-Hg - compounds (10,11).

The sharp singlet for Cp-protons in the proton magnetic resonance (PMR) spectrum of Cp_2Hg is usually explained by a fast migration of the C-M bond, although even at -70°C no splitting of the proton signal (in THF) is observed (11) *. If the rate of this migration is so high, then the life period of the C-Hg bond is so short ($\tau \leqslant 0.01$ sec) that no spin-spin coupling of $J_{Hg^{199}-C-H}$ can be observed in the PMR spectrum

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* The splitting of this signal at -70°C in liquid SO_2 (12) deserves special consideration.

We did however find one pair of singlet satellites (Table I and Fig.Ib) whose sharpness even increased with decreasing temperature. For structure I one would expect an opposite temperature effect with in the limit three pairs of multiplet satellites arising from the $Hg^{199}-C_1-H$, $Hg^{199}-C_1-C_2-H$, $Hg^{199}-C_1-C_2-C_3-H$ coupling. Using a spectrum accumulator developed by B.A.Kvassov (13) we succeeded in observing satellites from the $C^{13}-H^1$ coupling in the form of one pair of signals similar in shape and splitting to those in benzene (Table I and Fig.1 a), whereas for I one would again expect multiplet satellites or, for very fast migration, one pair of signals but with $J \sim 150$ c/s taking into account the statistical weight of C atoms in sp^2 and sp^3 hybridisation states (14,15).

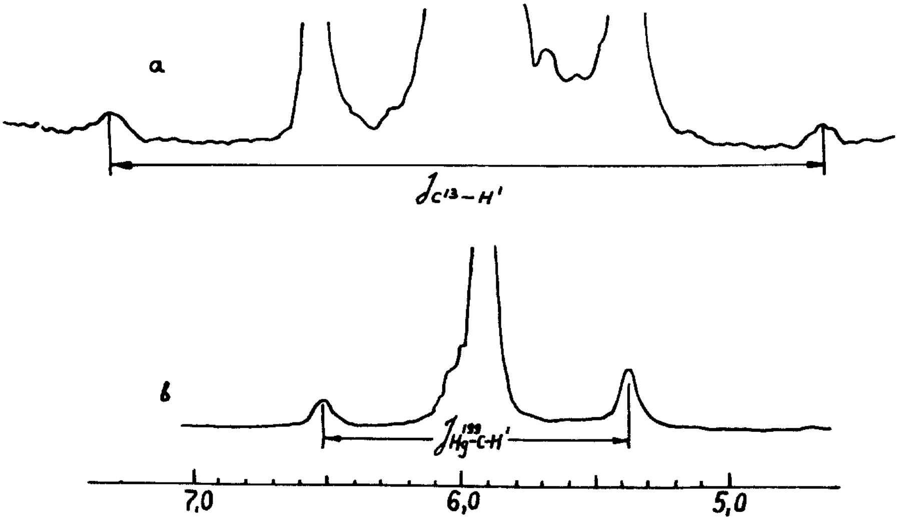


Fig. 1

PMR spectrum of $(C_5H_5)_2Hg$ in acetone was taken using an accumulator of weak signals (100 passages)

We have also studied the PMR spectra of $PhHgCH_3$ (IV) and

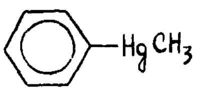
Table I

PMR spectral parameters of some compounds

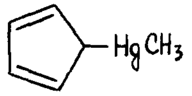
Compound	Solvent	t°C	$J_{Hg^{199}-C-H}$ (c/s)	$J_{C^{13}-H}$ (c/s)	Width of the main signal of the C_5H_5 group (c/s)
$(C_5H_5)_2Hg$	$CDCl_3$	34	66.0	-	1.9
Idem	acetone	34	68.9	159±1	1.7
Idem	THF	34	66.7	161±1 *	2.6
Idem	Idem	0	69.2	-	1.9
Idem	Idem	-40	71.1	-	1.5
C_5H_5HgCl	THF	0	115.2	-	2.4
Idem	Idem	-30	119.0	-	1.5

* One satellite was observed only - in the low field (from the main signal)

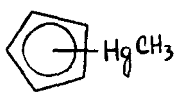
$CpHgCH_3$ (V or VI) **



IV



V



VI

and obtained the following results: R = Ph: δ_{CH_3} 0.60 p.p.m., $J_{Hg^{199}-C-H}$ = 109 c/s (cf.16: δ_{CH_3} 0.55 p.p.m., $J_{Hg^{199}-C-H}$ = 109 c/s); R = Cp: δ_{CH_3} - 0.35 p.p.m. at 34° in $CHCl_3$ (cf.16: $(CH_3)_2Hg$ δ_{CH_3} 0.27 p.p.m.)

It will be seen from Fig.2 below that the resulting data favour structures IV and VI. The spectrum of the second compound revealed next to the CH_3 signal (in the high field) a less intensive broad signal assigned to the Hg^{199}-C-H coupling in CH_3HgI molecules. An approximate calculation (17,18) gave the following values for the CH_3 proton shift for IV and VI respectively: 0.33 p.p.m. to the low field and 0.42 p.p.m. to the high field. With structure

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** These compounds were prepared directly in sample tube of the NMR-spectrometer Hitachi-H-60 through the reaction of $R_2Hg + CH_3HgI \rightleftharpoons RHgCH_3 + RHgI$, the above accumulator being used to reveal the CH_3 -signal from $CpHgCH_3$.

V one would expect a shift to the low field because the effects of Cp- and Ph-substituents on the shielding of CH_3 protons are similar under these conditions (19,20).

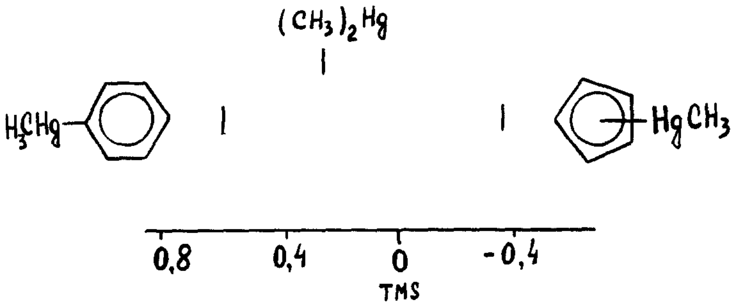

Fig.2

Shielding of CH_3-protons in $RHgCH_3$

The same tendencies in chemical shifts of CH_3-protons were found to take place in asymmetric methyl-phenyl and methyl-cyclopentadienyl compounds of Sn^{IV} and Pb^{IV} (21,22,23,24).

The comparison of spin-spin coupling constants J_{M-C-H} in methyl and cyclopentadienyl compounds of Hg^{II} and Sn^{IV} (Table II) shows a considerable decrease in J_{M-C-H} for the case of cyclopentadienyl derivatives.

We suppose that this fact also favours a sandwich structure for these Cp - compounds. It indicates some decrease in the overlapping of either the Hg^{II}-sp-orbital or the Sn^{IV}-sp^3-orbital with the p-orbitals of each C-atom as compared with ordinary localised two-centered σ -bonding $C_{(sp^3)}$ - $M_{(sp,sp^3)}$. The possibility of overlapping of the metal valent orbital with the five C-p-orbitals simultaneously appears however to lead to a gain in

Table II

Comparison of spin-spin coupling constants J_{M-C-H} in methyl and cyclopentadienyl compounds of Hg and Sn.

Compound	Metal hybridisation	R = CH_3		R = C_5H_5	
		Solvent	J_{M-C-H} (c/s)	Solvent	J_{M-C-H} (c/s)
R_2Hg^{199}	sp	$CDCl_3$	101 *	$CDCl_3$	66,0
R_4Sn^{119}	sp^3	$CDCl_3$	54,3 **	CS_2	26,9 ***

* see 16; ** see 25; *** see 22.

energy because of the "aromatisation" of the whole molecule. The size of valent electron orbitals of the metals of periods V and VI is large enough to improve the chance of such " π -overlapping" and seems to favour the exclusion of the σ -structure I in the solvents under investigation over a wide range of temperatures, whereas the smaller size of these orbitals for the II - IV period metals enable $\sigma - \pi$ - rearrangements of the σ - Cp-M $\rightleftharpoons$ π-Cp-M type to take place with a small change in temperature (26,27).

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