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PRELIMINARY COMMUNICATION

CONCERNING THE STRUCTURES OF CYCLOPENTADIENYL MERCURIALS

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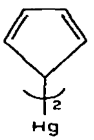
Dicyclopentadienylmercury, $(C_5H_5)_2Hg$, was reported[1] some years ago, and on the basis of its infrared spectrum, chemical behaviour, and valence consideration, was considered to have the σ-structure (I), rather than the π-bonded (II). Di(π-allyl) bonding as in (III), has been considered more recently[2].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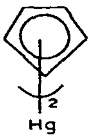
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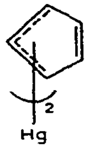
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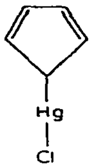
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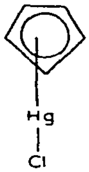

(V)

The observation of a single proton resonance at *ca.* 4τ was rationalised[3] in terms of (I) by postulating a rapid re-orientation of the Hg—C σ-bonds amongst the thermally accessible degenerate configurations. The observation of ^{199}Hg—^{1}H satellites[4,5] (which we have confirmed), with $J \sim 66$ Hz, established that this process, if the correct explanation, must be intramolecular[★]. A single proton resonance and ^{199}Hg satellites are consistent with (II) and fluxional[2,6] (III). In principle, fluxional (I) and (III), and (II) are operationally distinguishable, since (I) and (III) should exhibit temperature dependent NMR spectra[★★], while the resonance due to (II) should be temperature independent, if there is always essentially free rotation about the five-fold axis. However, at temperatures as low as -70°, in a number of solvents[7,8], no significant changes in the proton spectrum of $(C_5H_5)_2Hg$

[★] This point has recently been emphasised by Davison (A. Davison and P.E. Rakita, *J. Amer. Chem. Soc.*, 90 (1968) 4479 concerning intramolecular rearrangements of certain cyclopentadienyltin compounds. However, certain authors (*e.g.* see ref.5) have misunderstood the significance of metal—^{1}H satellites, and have concluded that even rapid *intra*molecular migration of a Hg—C σ-bond leading to equivalent molecular configurations should result in the non-appearance of satellites.

[★★] In practice, however, this might be difficult to demonstrate, depending on the height of the potential barrier for rearrangement. A low barrier might require spectral observations at very low temperatures in solvents which are poor for the mercurials.

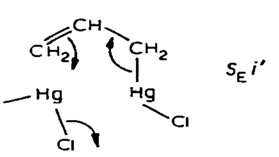
and C_5H_5HgCl apparently occur (except in the case* of $(C_5H_5)_2Hg$ in liquid SO_2) and Russian workers have argued[5,7,8] strongly for structures (II) and (V). We now present new data that confirm the σ-cyclopentadienyl structure for indenylmercuric chloride and heavily implicate (I) (or III) and (IV) for the C_5H_5 mercurials.

We considered that cyclopentadienylmercuric halides, if having structure (IV) should behave as allylic mercuric halides[11] *e.g.* (VI), but perhaps with altered reactivity.

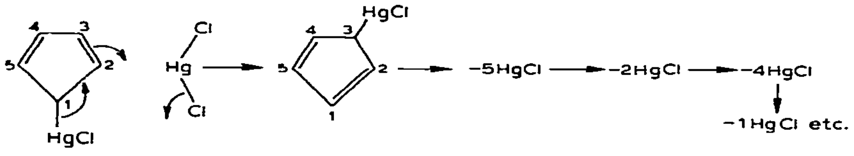
$CH_2{=}CH{-}CH_2HgCl$ (VI)

$CH_2{=}CH{-}CH_2HgOAc$ (VII)

Allylmercuric acetate[12] (VII) has the σ-allyl structure (100 MHz spectrum) as does allylmercuric chloride[11] (60 MHz) and the assignments are located in Table 1. The addition of very small quantities of $HgCl_2$ to an acetone-d_6 solution of (VI) changes the spectrum dramatically[11] to that expected for the AX_4 situation and ^{199}Hg satellites are no longer visible, suggesting an intermolecular exchange mechanism. Mercury exchange between radio-$HgCl_2$ (^{203}Hg) and (VI) occurs very rapidly[13] (*e.g.* statistical exchange < 25 sec at *ca.* 20°) and a catalytic mechanism of the following type apparently operates.



The same situation appears to obtain with $C_5H_5HgCl^{7,8}$, (prepared from C_5H_5Tl and $HgCl_2$ in 1:1 ratio), since the rather broad resonance at 3.85–3.90 τ (width at half-height 11 Hz) is markedly sharpened by the addition of small quantities of $HgCl_2$ (width at half-height 2.0 Hz) and ^{199}Hg satellites are not visible. We have not been able to demonstrate unambiguously the presence of ^{199}Hg satellites about the resonance of C_5H_5HgCl, as recently claimed[5], where $J \sim 115$ Hz. It should be pointed out that both $(C_5H_5)_2Hg$ and C_5H_5HgCl (to a lesser degree) are both photo and thermally sensitive and care must be taken to avoid the presence of potentially catalysing impurities. A catalytic but analytically indetectable amount of $HgCl_2$ would, in our opinion, suffice to partially collapse and broaden (with the disappearance of ^{199}Hg satellites) the spectrum. It has been claimed[5] that the satellites about the $(C_5H_5)_2Hg$ resonance actually sharpen with decreasing temperature, which suggests partial arrest of a rate process and not a



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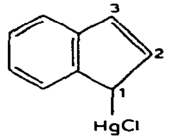
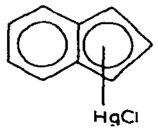
*These observations are of much importance and warrant deeper study, particularly since allylmercuric acetate reacts with SO_2 to yield an unstable insertion product[10]. However lack of SO_2 insertion into $(C_5H_5)_2Hg$ at −10° (as evidenced by the single proton resonance) would strongly support the interpretations of Maslowsky and Nakamoto[9], since it appears doubtful, although not impossible, that SO_2 insertion would be reversible with temperature under such conditions (liquid SO_2). Positive identification or absence of ^{199}Hg satellites would establish whether the Hg–C bond was intact.

symmetrical π-structure, for which lower temperatures should have no consequences. (*e.g.* see ref.6). See also ref.2 p.221 (comment by M.D. Rausch). A mechanism of the following type resulting in a series of 1,3 shifts may be in action[★].
Such a spectral change hardly seems consistent with (V).

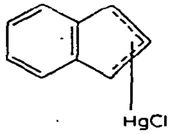
Indenylmercuric chloride[★★] (from indenyllithium and $HgCl_2$ in THF–hexane), m.p. 139° (Found: C, 30.32; H, 2.20, Calcd.: C, 30.76; H, 2.0) is soluble in THF and its 100 MHz spectrum (details in Table 1) is particularly important since it shows unambiguously that this cyclopentadienylmercurial has the σ-structure (VIII).



(VIII)



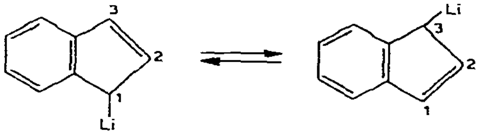
(IX)



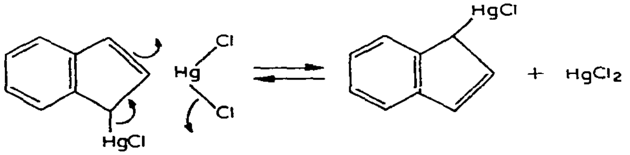
(X)

In addition to aromatic resonance (a perturbed AA'BB' system), H_2 and H_3 constitute an AB system centered at 3.26τ and 3.12τ, while H_1 appears as a broadened singlet at 5.56τ. The higher field lines in the AB pattern are coupled to H_1, and these probably correspond to H_2. Structures (IX) and (X) can be eliminated.

Indenyllithium has an NMR spectrum (Table 1) in which H_1 and H_3 are magnetically equivalent (4.07τ; doublet, J 3.5 Hz). Rapid rearrangement in the sense below is one likely explanation for the spectrum[★★★]. The addition of $HgCl_2$ to a THF solution of



(VIII) would be expected to collapse the spectrum in the limiting case to that observed for indenyllithium by the following mechanism. The results of adding $HgCl_2$ and heating



(90–100°) are summarised in Table 1. The main features are that one vinylic proton and the allylic proton (H_1 and H_3 in (VIII)) have disappeared and the remaining vinylic proton is approaching the triplet pattern, while a broad resonance appears between the original positions of H_1 and H_3. Also the aromatic resonance adopts a symmetrical pattern

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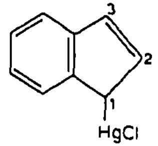
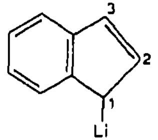
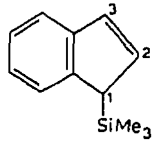
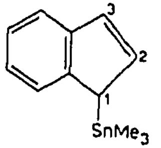
[★] Jensen has suggested 1,3 migrations might occur generally amongst the metals, by proceeding through the π-allyl system. See ref.2 p.234.

[★★] Zimmer (J. D'Ans, H. Zimmer and V. Brauchitsch, *Ber.*, 88 (1955) 1510) has reported the reaction between indenyllithium and -mercuric halides, but it was not clear whether indenylmercuric chloride or the bromide had been formed. The analytical data are consistent with the bromide, but no spectral characterisation was reported.

[★★★] Other explanations could involve an ionic structure, (*cf.* evidence on allyllithium[14], and even π-indenyl or π-allyl formulations. Only the "static" σ-indenyl structure has a unique NMR spectrum.

TABLE 1. NMR DATA FOR SOME σ-ALLYLIC AND σ-CYCLOPENTADIENYL METALLICS

System	Temp. (°C)	Solvent	Chemical shift (τ)			J(M–H)^{a}		(Hz)
			H_1	H_2	H_3	H_1	H_2	H_3
$CH_2{=}CH{-}CH_2HgOAc$	33	$CDCl_3$ (60 MHz)	7.12	4.23	5.15	286	*b*	90
$CH_2{=}CH{-}CH_2HgOAc$	33	$CDCl_3$ (100 MHz)	7.29	4.11	5.01	280	103	85
$CH_2{=}CH{-}CH_2HgCl$	33	$(CD_3)_2CO$ (60 MHz)	7.26	4.15	5.12	300	*b*	*b*
$CH_2{=}CH{-}CH_2HgCl$ + $HgCl_2$	33	$(CD_3)_2CO$ (60 MHz)	6.21	3.92	6.21	*c*	*c*	*c*
C_5H_5HgCl	33	THF (60 MHz)		3.87 (broad)			*d*	
$C_5H_5HgCl + HgCl_2$	33	THF (60 MHz)		3.90 (sharp)		*c*	*c*	*c*
	33	THF (60 MHz)	5.66	3.40	3.27	*b*	*b*	*b*
	33	TDF (100 MHz)	5.56	3.26	3.12	*f*	*b*	*b*
+ $HgCl_2$	104	THF (60 MHz)	4.38	3.40	4.38	*c*	*c*	*c*
	33	THF (60 MHz)	4.07	3.44	4.07			
	33	CCl_4 (60 MHz)	6.57	3.44	3.12			
	–45	CCl_4 (60 MHz)	6.15	3.36	3.15	91	*b*	*b*
	33	CCl_4 (60 MHz)	very broad^{e}	3.42	very broad^{e}	*b*	*b*	*b*
	+175	Neat (60 MHz)	4.67	3.42	4.67	55	*b*	55

Aromatic resonance positions, –OAc and $M(CH_3)$ resonances omitted.

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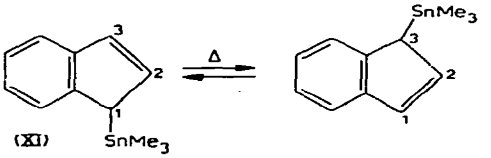
^{a}M = ^{199}Hg or ^{119}Sn whatever the case may be. ^{b}Not observable. ^{c}Considered to be absent. ^{d}Probably absent, see ref.19. ^{e}Merging into background. ^{f}This coupling is considered to be ≮470–480 Hz, but side bands etc. make identification impossible. The analogous ^{119}Sn coupling in 1-indenyltrimethylstannane is also much larger than in simple allyltin compounds.

expected for the AA'BB' case. The facility of this process is reduced in the case of (VIII) but the result shows that allylmercuric chloride (VI), C_5H_5HgCl and (VIII) behave in a consistent manner for σ-allyl mercurials. Assuming that the aromatic system has little or no effect on the resonance positions of H_1, H_2 and H_3 in (VIII), it is possible, on this basis to calculate from the 60 MHz data that the averaged resonance position for C_5H_5HgCl should be 3.80τ, in good agreement with that observed.

For comparison purposes, we studied the NMR spectra of 1-indenyl-trimethylsilane[15] and -stannane (Table 1). The latter exhibits a temperature dependent NMR spectrum, and at −40°, the spectrum corresponds to the static structure (XI), but at +33°, the resonance of H_1 and H_3 is very broad. A sharp spectrum is obtained at *ca.* +150°, indicating rapid equilibration of H_1 and H_3. These spectral changes were reversible.



(XI)

The mechanism of equilibration of H_1 and H_3 is *intra*molecular, since ^{119}Sn satellites are present about the doublet resonance of H_1 and H_3 (*i.e.* at 150°), and a 1,3-intramolecular migration of the $SnMe_3$ moiety appears to be occurring*. 1-Indenyltrimethylsilane has a room temperature spectrum which is well defined, corresponding to the static σ-indenyl structure. Very minor spectral changes occurred on heating to *ca.* 200°.

The allylic mercurials, (VI), C_5H_5HgCl and (VIII) all show an IR band in the 1610–1640 cm^{-1} region, which may be assigned to ν(C=C). The carbon–mercury stretching frequency, ν(Hg–C), is substantially lowered in the above compounds and may be due to Hg–ene interaction[16], which apparently results in low-energy shifts in the electronic spectra[1,3,7,8] of allylic and cyclopentadienylmercurials. Kreevoy[16] has also presented kinetic evidence for this phenomenon. Kreevoy demonstrates that any argument[7,8] that the low-energy bands in the electronic spectra of cyclopentadienylmercurials support a π-structure is inadmissible, since such bands are found in the spectra of simple allylmercurials. Intra- or inter-molecular Hg–ene interaction would be expected to weaken and lengthen, and generally deform the Hg–C σ-bond, resulting in a reduction in ν(Hg–C). This is seen clearly in the far infrared spectra of simple allylmercuric halides. Both indenylmercuric chloride, and indenyltrimethylstannane are yellowish in colour, and would again indicate some metallo-π type interaction. Full details of this work will be discussed at a later date.

ACKNOWLEDGEMENTS

One of the authors (W.K.) is grateful to Professor S. Winstein who in 1966 aroused interest in the similarities expected for allylic and σ-cyclopentadienyl mercurials. Mr. David Doddrell of the University of Indiana kindly recorded the 100 MHz spectra.

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*See first footnote p. P39.

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