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STRUCTURAL STUDIES OF INDENYLMERCURY SYSTEMS

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SUMMARY

The compounds indenylmercury chloride, (1,3-dideuteroindenyl)mercury chloride and (3-methylindenyl)mercury chloride have been synthesised, and shown to possess the *monohapto*-1-indenyl structure. Employing ^1H and D nuclear magnetic resonance spectroscopy, (PMR and DMR), complete chemical shift assignments have been made, and ^{199}Hg–D and ^{199}Hg–^1H coupling constants determined. Some relative signs of coupling constants are deduced, and the relevance of the parameters determined to cyclopentadienylmercury systems is demonstrated. Superficially odd features in the vibrational and electronic spectra of these mercury systems are accounted for.

INTRODUCTION

There has been considerable recent interest in the structures and spectral properties of cyclopentadienyl mercurials, and it is now known from proton magnetic resonance studies that indenylmercury chloride[1] and diindenylmercury[2] have *monohapto*-1-indenyl structures. However, PMR studies of C_5H_5 mercurials have not been as rewarding in favoring the h^1 or h^5 formulations[3,4], since in general a single proton resonance at τ *ca.* 4 ppm has been observed[2], and this is consistent with a fluxional h^1 structure as well as the centro-symmetric h^5 mode of attachment***. Although vibrational spectra[4], which constitute a faster camera than NMR, strongly favor the h^1 structure, Russian workers[5] have argued against this proposal. In the present report, we have employed the special properties of the indenyl group[6] to determine accurately certain NMR parameters, and have applied these to cyclopentadienyl systems.

EXPERIMENTAL

monohapto-1-Indenylmercury chloride was prepared by the addition of the calculated amount of $HgCl_2$ to a solution of indenyllithium in THF/hexane (1/1

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*** *Note added in proof.* See, however, the recent definitive low temperature PMR studies on cyclopentadienylmercury systems. (P. West, M. C. Woodville and M. D. Rausch, *J. Amer. Chem. Soc.*, 91 (1969) 5649).

molar ratio). The lithium compound was prepared by the addition of n-butyllithium in hexane (1 molar equivalent) to indene (distilled) in THF. The slightly yellowish mercurial was recrystallised from methanol/THF, m.p. 139°. (Found: C, 30.32; H, 2.20. C_9H_7HgCl calcd.: C, 30.76; H, 2.0%.)

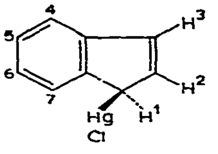
monohapto-1-(3-*Methylindenyl*)*mercury chloride* was prepared by a similar procedure employing 3-methylindene. The recrystallised mercurial (ethanol) had m.p. 132°. (Found: C, 32.76; H, 2.82. $C_{10}H_9HgCl$ calcd.: C, 32.9; H, 2.44%.)

1,1,3-*Trideuteroindene* was prepared by quenching indenyllithium with D_2O. The extent of deuterium incorporation was monitored by PMR spectra.

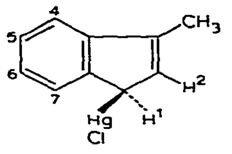
60 MHz spectra were recorded on a Varian-A-60 machine with variable temperature accessory. 100 MHz spectra were recorded on the HA-100 instrument at the Department of Chemistry, Indiana University.

RESULTS AND DISCUSSION

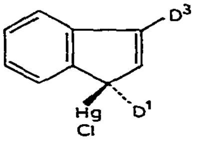
1-Indenyl- and 1-(3-methylindenyl)mercury chloride, (I) and (II), were synthesised and observed to be quite stable. Employing 1,1,3-trideuteroindene as the precursor of the lithium reagent, (III) was also prepared.



(I)



(II)



(III)

1-*Indenylmercury chloride* (*I*)

The 100 MHz proton spectrum of C_9H_7HgCl (Fig. 1a) immediately establishes the correctness of portrait (I) and we can imagine no other structure which accounts for the spectral features★.

The complex resonance, of relative intensity four, in the 2.45 to 2.89 τ region is assignable to the aromatic group H^4–H^7. Two of these protons are somewhat separated from the others and are probably H^4 and H^7, while H^5 and H^6 resonate at essentially the same field strength. The protons H^2 and H^3 arise at τ 3.28 and 3.15 ppm (or the reverse at this stage, but see later) as is appropriate for such protons. H^2 and H^3 are coupled [$J(H^2\text{–}H^3) \sim 5\text{–}6$ Hz], but not strongly with H^1 [$J(H^1\text{–}H^2), J(H^1\text{–}H^3) <$ 2 Hz] which is located at τ 5.58 ppm as a broadened singlet. Examination of the PMR spectrum of (III) (in which deuterium incorporation of C^2 is prohibited by the mild conditions of exchange) in the presence of *ca.* 25% of (I), showed that the lower field component of the vinylic AB pattern was of reduced intensity (Fig. 1b). This then identifies the τ 3.15 resonance as H^3.

1-(3-*Methylindenyl*)*mercury chloride* (*II*)

The 100 MHz spectrum ($CDCl_3$/TDF) (Fig. 2) shows aromatic resonance in

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★ This spectrum resembles in form the low temperature spectrum reported by Cotton and Marks[2] for diindenylmercury.

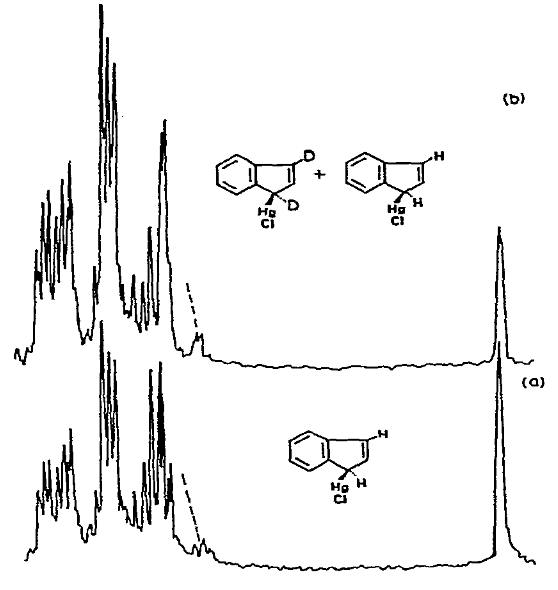


Fig. 1(a). 100 MHz spectrum of indenylmercury chloride in TDF. 1(b). 100 MHz spectrum of indenylmercury chloride and (1,3-dideuteroindenyl)mercury chloride, illustrating reduction in intensity of lower field resonance on deuteration.

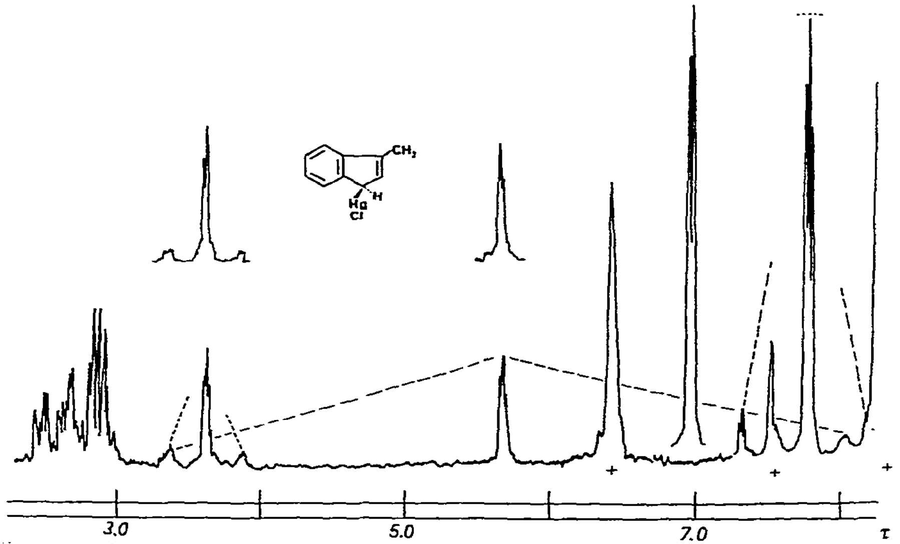
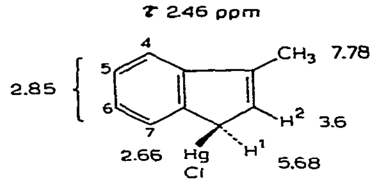
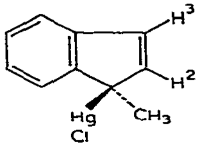


Fig. 2. 100 MHz spectrum of (3-methylindenyl)mercury chloride ($CDCl_3$/TDF), showing ^{199}Hg satellites. Insets are associated with decoupling experiments, and are discussed in the text. + signifies solvent or impurity resonances.



(IV)



(V)

the form of a 1/1/2 intensity pattern at τ 2.46, 2.66 and 2.85 ppm. Vinylic proton resonance (relative intensity 1) at τ 3.6, a one-proton resonance at 5.68 and methyl group absorption at τ 7.78 complete the pattern. Of the two conceivable *monohapto*-indenyl structures drawn above, the first is accommodated uniquely by the data. The exclusive occurrence of (IV) is consistent with greater thermodynamic stability of the secondary over the tertiary allylic structure (V).

The methyl resonance appears as a "triplet" ($J \sim 2.0$–2.5 Hz) resulting from approximately equal coupling to two other protons, one of which could be conceivably $H^{4(7)}$. H^1 and H^2 appear as "quintets" with line separations of ~2 Hz. Irradiation at the methyl resonance frequency collapsed H^1 and H^2 to doublets [$J(H^1$–$H^2) \sim 2.5$ Hz], so that the "triplet" signal for the methyl group is due to equal coupling to H^1 and H^2. Furthermore irradiation in the region of H^2 produced a doublet for the methyl resonance, showing $J(H^1$–$CH_3) \sim 2.5$ Hz. Thus there exists an interesting five bond coupling H^1–CH_3. Coupling to $H^{4(7)}$ is shown to be negligibly small. Again fluxional behaviour is not observed over a limited (+70°) temperature range[1].

Mercury(^{199}*Hg*)*-proton spin coupling*

One of the aims of this work was to establish the magnitudes of ^{199}Hg ($I = \frac{1}{2}$; 16.8% natural abundance) spin coupling to H^1, H^2 and H^3. In our initial report[1] we indicated that for indenylmercuric chloride, $J(Hg$–$H^1)$ was ~470 Hz, positive identification of the satellites being thwarted by coincidence with other resonances (on the downfield side). Coupling to H^2 and H^3 was observable, but again only the higher field satellites declared themselves, the lower ones being lost beneath aromatic absorption. Thus it was not clear which satellite was related to which vinyl proton. On the high-field side of H^1 a signal of intensity appropriate for a ^{199}Hg satellite was observed *ca.* 238 Hz removed from H^1, leading to $J(Hg$–$H^1) \sim 476$ Hz, if its origin was indeed Hg–H^1 coupling. We can now describe a more fruitful situation.

In the spectrum of (IV) (Fig. 2) ^{199}Hg spin coupling to H^1, H^2 and CH_3 are clearly evident in the form of satellites about the main proton resonances (*i.e.* for molecules containing other Hg isotopes). These values are $J(Hg$–$H^1) = |466$ Hz$|$; $J(Hg$–$H^2) = |50$ Hz$|$; $J(Hg$–$CH_3) = |86$ Hz$|$, without reference to relative signs at this stage. In the proton spectrum of partially (~75%) deuterated (I) (Fig. 1b), H^2 is more intense than H^3, so that the most intense satellite must be associated with H^2, leading to $J(Hg$–$H^2) = 50$ Hz. On this basis from the spectrum of (I) it is now possible to assign the high-field satellites, about H^2 and H^3 leading to $J(Hg$–$H^3) = 78$ Hz. Although in Fig. 1b, H^1 is of necessarily reduced intensity (*cf.* H^3), a signal appropriate for a Hg satellite is again observed on the high field side, giving $J(Hg$–$H^1) \sim 476$ Hz (*vide supra*).

Having made 1-(1,3-dideuteroindenyl)mercury chloride, it seemed likely that the deuteron magnetic resonance spectrum (DMR) of this compound would be especially useful in indirectly determining ^{199}Hg–H coupling, via observation of ^{199}Hg–D coupling. The DMR spectrum was obtained at 15.351 MHz (Fig. 3) and

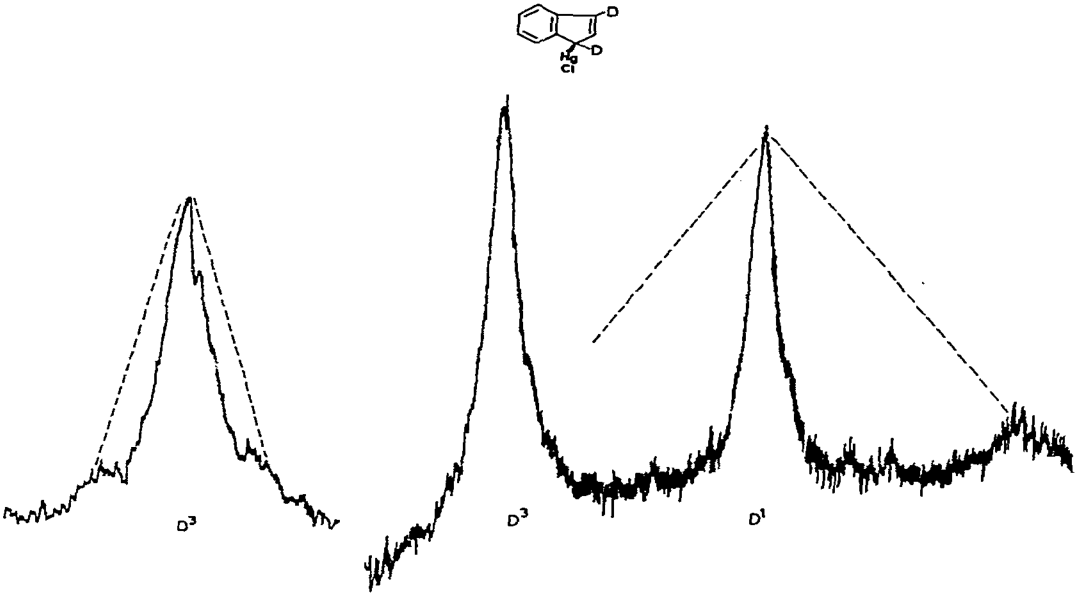
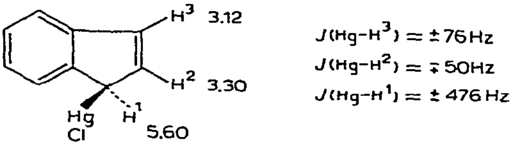


Fig. 3. 15.3 MHz Deuterium magnetic resonance spectrum (DMR) of (1,3-dideuteroindenyl)mercury chloride. Higher field is to the right and shows the higher field satellite about D^1, and the lower field satellite lies beneath the D^3 signal. The left hand inset shows D^3 (reduced sweep width) with the associated ^{199}Hg satellites. The spectra are discussed in the text. Spectra were accumulated with the Varian C-1024 Computer.

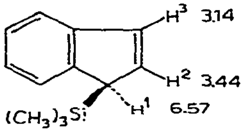
two areas of absorption, equi-intense, are located at +6.7 and +4.5 ppm from external D_2SO_4. The higher field resonance must be D^1. Located about each resonance are satellites which lead to J(Hg–D^1) = 72.8 Hz and J(Hg–D^3) = 11.6 Hz. Since γ(H)/γ(D) [γ = magnetogyric ratio = $2\pi \cdot \mu/(I \cdot h)$] = 6.5, it follows that J(Hg–H^1) = 474 ± 3 Hz and J(Hg–H^3) = 76 ± 3 Hz, in excellent agreement with those observed in the proton spectrum.

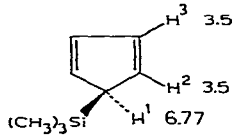
It is of considerable importance to consider the relative signs of Hg–H coupling constants, since these will seriously regulate the "averaged" observed coupling for a fluxional (*i.e.* intramolecular) system. In almost all ethyl derivatives (A_3B_2M) of metals J(M–A) and J(M–B) have opposite signs. This has been established with certainty for tin and mercury[7]. If this is applicable to indenylmetal systems J(Hg–H^1) and J(Hg–H^2) are also opposite. We can establish, by observing the temperature dependence of the satellites in the spectrum of indenyltrimethylstannane that J(Sn–H^1) and J(Sn–H^3) have the same sign[8,9], and we believe this is likely to be true for mercury also. Thus, on this basis, J(M–H^1) and J(M–H^3) are of like sign, while J(M–H^2) is opposite. In indene itself[10] (M = H), J(M–H^2) and J(M–H^3) are also of opposite sign, and this alternation of sign is quite expected.

We can condense the chemical shift and coupling constant data as below and see how valid is extrapolation to C_5H_5–Hg systems. Before calculating an averaged



chemical shift for C_5H_5HgCl from the above data, it is necessary to consider possible diamagnetic anisotropic effects emanating from the aromatic fragment, not possible in the C_5H_5 derivatives. Although model systems are scarce, comparison of resonances H^1, H^2, H^3 for indenyl- and cyclopentadienyltrimethylsilanes[11,12] does indicate the operation of a deshielding effect in the former, more serious for H^1 and H^3 as expected.





Compared with other metal substituents (particularly those of the transition series bearing carbonyl, nitrosyl or cyano groups), complicating effects due to silicon and mercury are expected to be small, particularly in the regions of H^2 and H^3.

Thus compared with C_5H_5HgCl, resonance values for each of H^1, H^2 and H^3 in (I) would be too low by *ca.* 0.2–0.3 ppm. If we then select values of τ 5.8, 3.40 and 3.42 ppm for H^1, H^2 and H^3 in C_5H_5HgCl, on this basis, the calculated average resonance position is 3.8–3.9 ppm, in excellent agreement with that observed for C_5H_5HgCl (3.8).

Russian workers have recently reported that $J(Hg\text{–}H) \sim 115$ Hz in C_5H_5HgCl*. Although the Hg–H couplings in (I) will be a function of angles between C–Hg, C–H bonds and the ring plane, it seems very reasonable that the coupling constants established for (I) will be applicable without serious modification to C_5H_5HgCl. Taking into account the sign differences, $J(Hg\text{–}H)(av)$ for C_5H_5HgCl is calculated to be 106 ± 5 Hz, in good agreement with the reported value. These exceptionally good correspondences between chemical shift and coupling constant data argue strongly for similar structures, established in the C_9H_7 case as *monohapto*-1-indenyl.

Very recently Cotton and Marks[2] reported the fluxional behaviour of di(*monohapto*-1-indenyl)mercury, and although $^{199}Hg\text{–}^1H$ couplings were not identified, concentration independence of the spectra at temperatures of intermediate exchange supported an intramolecular rearrangement mechanism. However, it is possible to predict the magnitudes of $^{199}Hg\text{–}^1H$ couplings in the following way. The ratio $J(C_5H_5HgCl)/J[(C_5H_5)_2Hg] \sim 115/66 = 1.7$, and since we have shown that the averaged calculated J values for C_5H_5HgCl is *ca.* 110 Hz (on the basis of our data for indenylmercuric chloride) use of the factor 1.7 seems appropriate in scaling down the J values for indenylmercuric chloride to diindenylmercury. In this way predicted values of $J(Hg\text{–}H^1) \sim 276$ Hz, $J(Hg\text{–}H^2) \sim 29$ Hz and $J(Hg\text{–}H^3) \sim 45$ Hz are obtained. Close examination of the published data of Cotton and Marks reveals the following in the low temperature spectrum (-41°). (*a*) A signal of appropriate intensity 135 Hz downfield from H^1; (*b*) A signal of somewhat greater intensity 13–14 Hz upfield from H^2, but *ca.* 26 Hz upfield from H^3. These would lead to J values of 270 Hz, 26–28 Hz and 52 Hz respectively. As the temperature is raised and line broadening

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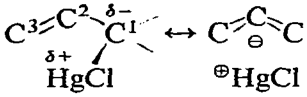
* See also third footnote page 29.

occurs, both "satellite" absorptions are affected as anticipated, but in the +28°, +49° and +68° spectra, in which H^2 is a well-resolved triplet, regions of absorption *ca.* 14–15 Hz on either side of the H^2 triplet are still apparent. Thus these agreements are almost proof of the intramolecular mechanism for fluxional behaviour in di-indenylmercury.

The low frequency of the mercury–carbon stretching frequency (*ca.* 350 cm^{-1}) and the low energy bands in the electronic spectra of cyclopentadienyl mercurials have been cited[13] as evidence against the h^1, but in favor of the h^5 structure. However, allylmercuric chloride shows ν(Hg–C) at 341 cm^{-1}, much lower than ν(Hg–C) in saturated alkyl mercuric chlorides and we suggest that the Hg–C bond is lengthened and more polar in allyl-, cyclopentadienyl- and indenylmercuric halides, leading to a reduction in ν(Hg–C). This is favored on the grounds that interaction with the 2,3-π-electrons is promoted, and allylic moieties could stabilise the incipient negative charge.



An effect of the above kind may explain partly the electronic spectra also[14], since now the chromophore is really a conjugated diene extended by the metallo interaction. Another consequence could be unusually large ^{199}Hg coupling to C^3 protons as is observed (*vide supra*). We have noted fluxional behaviour in (triphenylphosphine)cyclopentadienylgold(I)[15] and again ν(Au–C) is at *ca.* 350 cm^{-1} some 250 cm^{-1} below ν(Au–C) in alkylgold compounds[16]. We believe it will be found generally that ν(M–C) in σ-allyl and h^1-C_5H_5 metal compounds will be somewhat low, particularly for metals possessing vacant orbitals capable of interacting in the sense outlined.

These considerations raise the possibility that 1,3-migrations for certain metals are quite likely[17] [*e.g.* for Hg^{II}, Sn^{IV}, Au^{I}, Cu^{I}, which have 6*p*, 5*d*, 6*p* and 4*p* orbitals respectively available for use in the bonding sets) since migration processes in which bond formation is significant at early stages on the reaction coordinate (concurrent with bond rupture) will be more favoured. Clearly this is likely for those metals capable of increasing their coordination number. This in turn suggests solvent effects on rates of rearrangement may be important.

ACKNOWLEDGEMENTS

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