Preparation and Carbon-13 Nuclear Magnetic Resonance Spectra of Arene Complexes of Mercury(I)

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Summary A general route for the synthesis of mercurous ion–arene complexes is described; ^{13}C n.m.r. has been used to show, for the first time, the existence of these complexes in solution.

ORGANOMETALLIC compounds of mercury(I) are rare: only the subvalent organomercurials[1] and a benzene–mercurous tetrachloroaluminate[2] have been reported.

We report here a ready synthesis of arene complexes of mercury(I) from sulphur dioxide solutions of mercurous hexafluoroarsenate[3] and the arene according to the general equation:

$$m\mathrm{Hg_2(AsF_6)_2} + n\ \mathrm{Arene} \xrightarrow{\mathrm{SO_2}} m\mathrm{Hg_2(AsF_6)_2},\ n\mathrm{Arene}$$

In many cases the complexes are precipitated immediately upon mixing of the solutions. Some of the products obtained by this general route include the 1:1 complexes $Hg_2(AsF_6)_2$,Arene (Arene = benzene, biphenyl, naphthalene *m*-dinitrobenzene)† and with 9,10-benzophenanthrene, complexes having Hg_2^{2+}: Arene = 2:1 and 1:3. (No evidence was found for a 1:1 complex with 9,10-benzophenanthrene.) Where they could be obtained, the Raman spectra of these water-sensitive products showed a strong low frequency band (or bands) assignable to the Hg–Hg stretching frequency, thus demonstrating the integrity of the dimeric Hg_2^{2+} ion in the compounds. The position of the Raman band was arene-dependent indicating interaction of the arene and the mercurous ion, *e.g.* ν(Hg–Hg) in the solid 1:1 benzene and naphthalene complexes is 166 and 134 cm^{-1}, respectively [both significantly lower than the value reported[3] for mercurous hexafluoroarsenate (182 cm^{-1})].

When no precipitation occurs on mixing SO_2 solutions of the reactants, ^{13}C n.m.r. readily shows the presence of arene complexes in solution. Separate signals for free and complexed arene are not observed at ambient temperatures, but, instead, averaged signals, the positions of which are dependent on the Hg_2^{2+}/arene ratio and on the reactant concentrations. The Figure shows the variation of the aryl carbon shift with variation in the arene/Hg_2^{2+} ratio for the system $Hg_2(AsF_6)_2$–hexamethylbenzene (HMB).

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† All new compounds had satisfactory analyses.

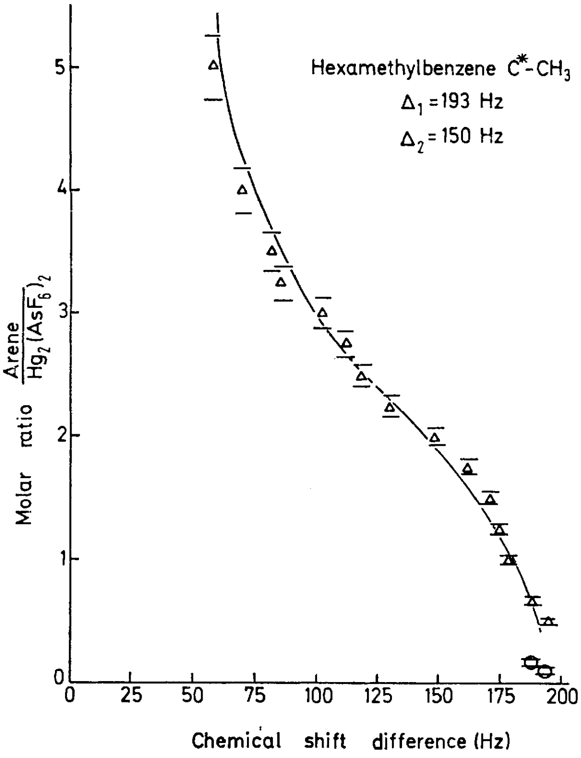

FIGURE. *Dependence of the downfield shift of the aryl carbon on the* HMB/$\mathrm{Hg_2}^{2+}$ *ratio in* $\mathrm{SO_2}$ *solutions at* 40 °C, *measured at* 25·2 MHz. *The solid line represents the best fit for a two-step process* (*see text*) *when* $[\mathrm{C_6Me_6}] = 0{\cdot}75\,\mathrm{M}$. (HMB *concentrations are*: Δ, 0·75M; ○, 0·15M.)

The quaternary carbon resonance moves to lower field as HMB/$\mathrm{Hg_2}^{2+}$ becomes smaller, but the change is not monotonic. The shape of the curve is not explicable in terms of the formation of a single complex with $\mathrm{Hg_2}^{2+}$: HMB = 1 : 1 or 1 : 2. However using the programme LISA,[4] the curve can be fitted satisfactorily in terms of the two labile equilibria‡:

$$\mathrm{Hg_2}^{2+} + \mathrm{HMB} \overset{K_1}{\rightleftharpoons} \mathrm{Hg_2(HMB)}^{2+}$$

$$\mathrm{Hg_2(HMB)}^{2+} + \mathrm{HMB} \overset{K_2}{\rightleftharpoons} \mathrm{Hg_2(HMB)_2}^{2+}$$

The best fit in this case (standard deviation = 0·15 p.p.m.) indicates $K_1 = 9{\cdot}4 \times 10^4$ and $K_1 = 27K_2$, the shifts of the aryl carbons of the 1 : 1 and 1 : 2 complexes being 7·7 and 6·0 p.p.m. downfield from the corresponding resonance of the free HMB, respectively.

Bonding geometries resembling those of transition metal–arene complexes[6], Ag$^+$–arene complexes,[7] or the bis(benzene)dipalladium chloroaluminates[8] may be envisaged[2] for mercurous ion–arene complexes. However, in both (Arene)-$\mathrm{M(CO)_3}$(M = Cr,Mo,W)[9] and Ag$^+$–HMB[10] the aryl quaternary carbon resonances shift upfield with respect to the free arene, whereas in $\mathrm{Hg_2}^{2+}$-HMB we have found a downfield shift. Our results thus seem to support a structure for the mercurous ion–arene complexes resembling that of the dipalladium complexes. We are investigating this possibility further.

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‡ The 'free' hexamethylbenzene will, according to the work of Andrews and Keefer,[5] be virtually completely specifically solvated in liquid $\mathrm{SO_2}$.

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