Synthesis and Solution Stoicheiometries and Stabilities of Mercury(II)–Arene Complexes

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Summary Addition of arenes to $Hg(SbF_6)_2$ or $HgF(AsF_6)$ in liquid sulphur dioxide produces readily isolable 2:1 arene–mercury(II) complexes of high stability.

Mercury(II)-arene complexes have long been proposed as intermediates in aromatic mercuration, but have not yet been isolated. The most direct support for the existence of the ions is of very recent origin: Olah *et al.*[1] found ^{13}C and ^1H n.m.r. complexation shifts of arenes to occur when the arenes were treated with $Hg(O_2CCF_3)_2$–FSO_3H or CH_3CO_2-HgMe–FSO_3H in SO_2 at 197 K. We now present evidence, previously lacking, regarding the stoicheiometries and stabilities of these interesting species in SO_2 solution, and also describe a straightforward route to the compounds in the solid state.

Arene complexes of mercury(II) are readily synthesised from $Hg(SbF_6)_2$† or $HgF(AsF_6)$† (prepared from HgF_2 and SbF_5 or AsF_5, respectively, in SO_2) and excess of arene in liquid SO_2 according to the general equations (1) and (2).

$$\mathrm{Hg(SbF_6)_2 + 2\ Arene \xrightarrow{SO_2} Hg(SbF_6)_2{\cdot}2\ Arene} \qquad (1)$$

$$\mathrm{2HgF(AsF_6) + 2\ Arene \xrightarrow{SO_2} Hg(AsF_6)_2{\cdot}2\ Arene + HgF_2 \downarrow} \qquad (2)$$

Lyophilization of the solutions, followed by removal of all volatile material *in vacuo* yields the SO_2-soluble complexes in pure form. Typical compounds isolated in this way include $Hg(SbF_6)_2{\cdot}2$ arene† [arene = pentamethylbenzene (yellow), durene (yellow), mesitylene (yellow), *p*-xylene (pale yellow), toluene (colourless), benzene (colourless), or naphthalene (orange)] and $Hg(AsF_6)_2{\cdot}2$ arene† [arene = pentamethylbenzene (yellow) or durene (yellow)]. The complexes are stable to short exposure to moist air but are solvolysed (decolourised) on long exposure or in common donor solvents; their i.r. spectra (4000—500 cm^{-1}) are unexceptional.

The ^1H and ^{13}C-{^1H} n.m.r. spectra of the complexes in SO_2 confirm that, remarkably, no mercuration has occurred. (Mercuration would presumably require a reasonable proton-acceptor, and none is present in the system used.) Except for the C_6Me_6 complex (*vide infra*), rapid exchange of bound arene with excess of free arene occurs at all temperatures down to the freezing point of the solutions. Use of the program LISA[2] allows analysis of curves of exchanged-averaged shift *vs.* arene–Hg^{2+} ratio, yielding stability constants and shifts of bound arene. For example, results for the system C_6H_6–$Hg(SbF_6)_2$ at 308 K are consistent‡ with the occurrence of the two labile equilibria (3) and (4) with $K_1 = ca.\ 5 \times 10^8$ l mol^{-1} and $K_1/K_2 = 120$. The complexation shifts of the 1:1 and 2:1 benzene complexes are 5·7 and 3·8 p.p.m., respectively. The stabilities of the Hg^{2+}–C_6H_6 complexes are somewhat larger than those of similar Hg_2^{2+} complexes,[3] but quite different from the stability of $Cd(C_6H_6)^{2+}$ in SO_2, for which $K_1 = 0{\cdot}48$ l mol^{-1} at 308 K.[4]

$$\mathrm{Hg^{2+} + C_6H_6 \overset{K_1}{\rightleftharpoons} Hg(C_6H_6)^{2+}} \qquad (3)$$

$$\mathrm{Hg(C_6H_6)^{2+} + C_6H_6 \overset{K_2}{\rightleftharpoons} Hg(C_6H_6)_2{}^{2+}} \qquad (4)$$

$Hg(C_6Me_6)_2{}^{2+}$ decomposes slowly in SO_2 at room temperature§ but is stable in solution at *ca.* 253 K or below. From 253 K to the freezing point, no evidence for exchange of bound with excess of free C_6Me_6 is found in the ^{13}C n.m.r. spectrum. In the aromatic region, the ion gives rise to a singlet, deshielded by 6·9 p.p.m. from free C_6Me_6, while the methyl signal is deshielded by 1·5 p.p.m. Shoulders on the aromatic signal suggest $^1J(^{199}Hg-^{13}C)_{av.} = ca.$ 30 Hz.

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† Satisfactory elemental analyses were obtained for all new compounds.

‡ Standard deviation of fit = 0·10 p.p.m.

§ Electron-rich arenes in SO_2 solution typically char in the presence of strong acid salts of metal cations.[3,4] In the present case neither the ^1H nor the ^{13}C n.m.r. spectra provided evidence for mercurated species among the decomposition products.

Within experimental error the complex is completely formed.

It seems improbable that the simple ^{13}C n.m.r. spectrum observed for $Hg(C_6Me_6)_2^{2+}$ is the limiting spectrum, for this would imply a centrally bound mercury, whereas the pattern of upfield and downfield ^{13}C n.m.r. complexation shifts and downfield aromatic proton complexation shifts observed[1] for a series of methylated benzenes is typical of more localised bonding.[3,4] It is more likely that rapid intramolecular exchange is occurring in an η^2 or η^1 type species. An *X*-ray crystallographic analysis of $[Hg(durene)_2](SbF_6)_2$, presently in progress, should help clarify the bonding geometry.

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