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A PREPARATIVE AND ^1H AND ^{13}C NMR SPECTROSCOPIC STUDY OF MERCURY(II)—ARENE COMPLEXES *

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Summary

A wide range of new arene complexes of mercury(II) have been isolated from the appropriate arene and a strong acid salt of mercury ($Hg(SbF_6)_2$, $HgF(AsF_6)$ or $Hg(O_2CCF_3)_2$) in liquid SO_2. Low-temperature, slow-exchange (except when Arene = C_6H_6), ^1H and ^{13}C NMR spectra of the systems $Hg(SbF_6)_2$—Arene—SO_2 have provided evidence for very stable $Hg(Arene)^{2+}$ and $Hg(Arene)_2{}^{2+}$ complexes. Intramolecular exchange is rapid at the lowest accessible temperatures: the intramolecular exchange-averaged couplings to ^{199}Hg suggest strongly that the arenes are bound to mercury in an η^1-manner.

Introduction

In earlier work it has been shown that arene complexes of $Hg_2{}^{2+}$ [1], Zn^{2+} [2] and Cd^{2+} [2] can be prepared in, and often isolated from, SO_2 solutions containing the arene and a strong acid ($AsF_6{}^-$ and/or $SbF_6{}^-$) salt of the required cation. We have now extended these studies of Group IIB—arene complexes to include complexes of mercury(II). We find that combination of $Hg(SbF_6)_2$ and the appropriate arene in liquid SO_2 allows isolation of a range of mercuric—arene complexes. In addition we show, using ^1H and ^{13}C NMR spectroscopy, that, depending on the Arene/Hg^{2+} ratio used, 1/1 and/or 2/1 Arene/Hg^{2+} complexes exist in liquid SO_2, that these species are of high stability in this solvent, and that, at reduced temperatures in the absence of excess arene, intermolecular exchange processes are often slow while intramolecular exchange processes are not.

Mercury(II)—arene complexes are the postulated intermediates in mercuration of aromatic substrates, an electrophilic substitution process [3], but the struc-

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* Dedicated to Professor Joseph Chatt on the occasion of his 65th birthday.

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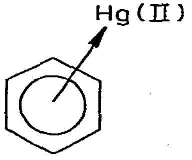
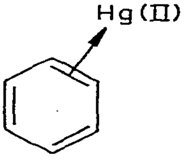
ture (or structures) of these intermediates is (are) unknown. *A priori*, structures I, II, and III seem plausible.



(I)



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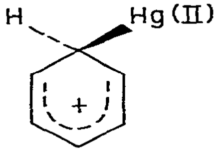

(III)

A weak interaction of type I may occur in the solid state structure of $Ph_2SO \cdot HgCl_2$, but the relative orientations of $HgCl_2$ and a phenyl "tail" may be a consequence of packing requirements [4]. The structures of a series of solid molecular complexes of mercuric halides and aromatic hydrocarbons * are as yet unknown, though hydrocarbon—halogen interactions may be at least part of the cohesive force [6]. From a ^1H NMR study, intramolecular mercury—phenyl interaction is thought to occur in a series of 3-arylpropylmercury compounds, and by analogy with the known structures of Group IB cation—arene complexes, bonding of type II has been suggested [7]. Kinetic evidence favours III as the structure of the intermediate in mercuration [3], but previous NMR studies of the interaction of arenes with the mercurating agent $Hg(O_2CCF_3)_2$ in CF_3CO_2H [8] and in FSO_3H [9] have yielded equivocal results: exchange-averaged spectra were observed but because no coupling to ^{199}Hg ($I = 1/2$; 16.84% natural abundance) was detected, it did not prove possible to distinguish between rapid intermolecular exchange and rapid intramolecular exchange as the cause of exchange averaging. However Olah et al. [9] suggested that the direction ** of the exchange-averaged shifts in the system $Hg(O_2CCF_3)_2$ — FSO_3H was inconsistent with structure I, and concluded that the best description of the complexes studied was in terms of structures II and III in rapid exchange, though the possibility of II occurring only as a transition state in an equilibrating system of complexes of structure III could not be excluded.

In the present study we have observed intramolecular exchange-averaged coupling to ^{199}Hg in both ^{13}C and ^1H NMR spectra in many cases, and our data suggest that III is the predominant species under our experimental conditions.

A preliminary account of this work has been published [10].

Results and discussion

Preparation of the complexes

The most satisfactory route to the complexes is from the reaction of the

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* A variety of evidence suggests specific solvation of mercuric halides in aromatic solvents. For a recent review, see ref. 5.

** Presumably inadvertently, Olah et al. [9] suggested that uniform downfield shifts relative to the free arene should occur in structure I. However as we have discussed earlier [1], shielding, i.e. upfield shifts, is the consequence of central bonding by transition metals.

SO_2-soluble $Hg(SbF_6)_2$ with the appropriate arene in liquid sulfur dioxide:

$$Hg(SbF_6)_2 + n \text{ Arene} \xrightarrow{SO_2} Hg(\text{Arene})_n(SbF_6)_2$$

The complexes with $n = 2$ were generally isolated by removal of all volatiles from solutions containing excess arene. However the bis(biphenyl) complex was insoluble and isolable by filtration. The insoluble 1/1 complexes of biphenyl, naphthalene and phenanthrene precipitated from mixtures containing excess $Hg(SbF_6)_2$. Under the same conditions, anthracene gave the insoluble reduction product $Hg_2(SbF_6)_2 \cdot$ Anthracene, a mercurous complex described earlier [1]. We were unable to isolate soluble 1/1 complexes because they occur in equilibrium mixtures with $Hg(SbF_6)_2$ and the 1/2 complex (see below).

Other routes to the arene complexes which were tried but which were not as useful or convenient as the preceding include the reaction of the arene in SO_2 with $HgF(AsF_6)$, $HgF(SbF_6)$, HgF_2/BF_3, HgF_2/PF_5, HgF_2/AsF_5, or $HgCl_2/Ag(SbF_6)$. Details of these less general routes are provided in the Experimental Section.

^1H and ^{13}C NMR spectra and structure of Hg^{2+}—Arene complexes

The ^1H and ^{13}C NMR spectra of the soluble complexes were obtained from SO_2 solutions of $Hg(SbF_6)_2$ and various amounts of the appropriate arene. In all the systems studied, except those containing benzene, it was possible to obtain spectra, complete with ^{199}Hg satellites, under conditions of slow intermolecular exchange. The ^1H spectral data are given in Table 1, the corresponding ^{13}C data in Table 2. Figure 1 shows representative ^{13}C and ^1H NMR spectra, those of an equilibrium mixture of $Hg(C_6H_5Me)^{2+}$ and $Hg(C_6H_5Me)_2{}^{2+}$ in SO_2 at ca. 200 K.

Overall, three different types of behaviour were found among the cases studied. When the substrate is benzene, intermolecular exchange of free and bound ligands is rapid at all accessible temperatures and with all $C_6H_6/Hg(SbF_6)_2$ ratios. The intermolecular exchange-averaged ^{13}C NMR spectra have been analyzed in terms of the two labile equilibria:

$$\text{Arene} + Hg^{2+} \overset{K_1}{\rightleftharpoons} Hg(\text{Arene})^{2+}$$

$$\text{Arene} + Hg(\text{Arene})^{2+} \overset{K_2}{\rightleftharpoons} Hg(\text{Arene})_2{}^{2+}$$

to yield the bound shifts of both $Hg(C_6H_6)^{2+}$ and $Hg(C_6H_6)_2{}^{2+}$ (Table 2), as well as approximate values for the formation constants K_1 and K_2 (see later).

In extreme contrast, $Hg(C_6Me_6)_2{}^{2+}$ does not undergo rapid intermolecular exchange with excess free ligand: at 260 K or below, sharp separate signals from the 1/2 complex and free ligand can be seen in both ^1H and ^{13}C NMR spectra of solutions in which $C_6Me_6/Hg(SbF_6)_2 > 2$. (The samples are not stable for extended periods of time at temperatures above 260 K.) The free ligand resonances disappear at $C_6Me_6/Hg(SbF_6)_2 \approx 2$, and as L/M is reduced further, fresh lines due to a second, 1/1, complex appear. When $L/M \approx 0.75$ (see the following section), the signals from the 2/1 complex are no longer evident.

In all the other systems investigated, intermolecular exchange-averaged ^1H and ^{13}C NMR spectra are observed at all accessible temperatures when Arene/Hg-

TABLE 1

^{1}H NMR COMPLEXATION SHIFTS [a], $\Delta\delta$(H), AND AVERAGE ^{199}Hg—^{1}H COUPLING CONSTANTS [b] (parentheses) FOR SOME ARENE COMPLEXES OF Hg$(SbF_6)_2$ IN LIQUID SO_2

Substrate	in Hg-(Arene)$_n$$^{2+}$ n =	T(K)	Phenyl	Methyl
Hexamenthylbenzene	1	198		0.46 (120)
	2	198		0.34 (62)
Pentamethylbenzene	1	198	−0.10 (485)	0.63 [d], 0.61 [e], 0.32 [f] (231) (121) (8)
	2 [c]	253	−0.25 (242)	0.60 [d], 0.40 [e], 0.28 [f,g] (121) (74)
1,2,4,5-Tetramethyl-benzene [h]	1	213	0.75 (268)	0.44 (63)
	2	213	0.49 (137)	0.30 (39)
1,3,5-Trimethyl-benzene	1	198	0.59 (154)	0.52 (151)
	2	198	0.49 (80)	0.39 (89)
1,4-Dimethyl-benzene	1	198	0.97 (139)	0.46 (57)
	2	198	0.73 (86)	0.34 (34)
Toluene	1 [i]	198	0.32 [j], 0.98 [k], 1.38 [l]	0.54 (198)
	2 [i]	198	−0.05 [j], 0.87 [k], 1.12 [l]	0.52 (122)

[a] $\Delta\delta(H) = \delta(H)_{obsd} - \delta(H)_{free\ arene}$ in ppm. Estimated error ±0.005 ppm. [b] Coupling constants in Hz. Estimated error ±1 Hz. [c] The bis(arene) complex is insoluble in liquid SO_2 at 198 K. [d] Me(3). [e] Me(1,5). [f] Me(2,4). [g] ^{199}Hg satellites not observed. [h] For Hg$(BF_4)_2$ · (durene) $\Delta\delta$(H) 0.71 ppm (phenyl) and 0.39 ppm (methyl), and $J(^{199}Hg—^{1}H)$ 265 Hz (phenyl) and 61 Hz (methyl). [i] ^{3}J(H(2)—H(3)) 7 Hz; ^{3}J(H3)—H(4)) 6 Hz; ^{199}Hg satellites could not be observed for the phenyl protons. [j] H(4)(triplet). [k] H(2,6)(doublet). [l] H(3,5)(doublet of doublets).

$(SbF_6)_2$ exceeds 2/1. However, when no excess arene is present, the low temperature spectra show separate signals from Hg(Arene)$_2$$^{2+}$ and/or Hg(Arene)$^{2+}$ under conditions of slow intermolecular exchange (indicated by the observation of coupling to ^{199}Hg), as exemplified in Fig. 1. The occurrence of fast- and slow-exchange regions in these cases is of considerable utility in making and confirming signal assignments, since in the fast-exchange regions the weighted-averaged resonances observed can be traced back to the free arene.

As shown by the data in Tables 1 and 2, the ^{1}H and ^{13}C spectra of the arenes complexed to mercury retain the symmetry of the corresponding spectra of the parent arenes. However, as Olah and coworkers have pointed out [9], the pattern of upfield and downfield complexation shifts observed for the mercury complexes is inconsistent with structure I, for which, by analogy with η^6-arene

TABLE 2

^{13}C NMR COMPLEXATION SHIFTS ^{a}, $\Delta\delta$(C), AND AVERAGE ^{199}Hg—^{13}C COUPLING CONSTANTS ^{b} (parentheses) FOR SOME ARENE COMPLEXES OF Hg(SbF$_6$)$_2$ IN LIQUID SO$_2$

Substrate	in Hg-(Arene)$_n$$^{2+}$ n =	T(K)	Aryl C(1)	Aryl C(2)	Aryl C(3)	Aryl C(4)	Aryl C(5)	Aryl C(6)	Methyl
Hexamethylbenzene	1	260	*10.09* (+30) ^{c}	*10.09* (+30)	*10.09* (+30)	*10.09* (+30)	*10.09* (+30)	*10.09* (+30)	2.05 (66)
	2	260	*7.98* (+27)	*7.98* (+27)	*7.98* (+27)	*7.98* (+27)	*7.98* (+27)	*7.98* (+27)	1.76 (34)
Pentamethylbenzene	1	260	*28.88* (−117)	*12.07* (−105)	*33.37* (−63)	*12.07* (−105)	*28.88* (−117)	−47.39 (+705)	2.60 ^{d}, 0.66 ^{e} (43), (139) 4.68 ^{f} (73)
	2	260	*21.34* (−80) ^{c}	*11.77* (−40) ^{c}	*25.10* ^{g}	*11.77* (−40)	*21.34* (−80)	−35.39 (+195)	1.65 ^{d}, 0.98 ^{e} (19), (120) ^{c} 3.49 ^{f,g}
1,2,4,5-Tetramethylbenzene	1	230	*17.05* (−92) ^{c}	*17.05* (−92)	−10.11 (+335) ^{c}	*17.05* (−92)	*17.05* (−92)	−10.11 (+335)	1.20 (30) ^{c}
	2	230	*13.53* (−68) ^{c}	*13.53* (−68)	−8.46 (+105) ^{c}	*13.53* (−68)	*13.53* (−68)	−8.46 (+105)	0.88 ^{g}
1,3,5-Trimethylbenzene	1	205	*31.56* ^{g}	−12.19 (+185)	*31.56*	−12.19 (+185)	*31.56*	−12.19 (+185)	2.95 (53)
	2	205	*25.28* ^{g}	−8.61 (+39)	*25.28*	−8.61 (+39)	*25.28*	−8.61 (+39)	2.04 (33)
1,4-Dimethylbenzene	1	205	*17.84* (−80) ^{c}	0.33 (+98)	0.33 (+98)	*17.84* (−80)	0.33 (+98)	0.33 (+98)	1.01 (21) ^{c}
	2		*15.65* (−60) ^{c}	0.25 ^{g}	0.25	*15.65* (−60)	0.25	0.25	0.73 ^{g}
Toluene	1	205	*30.07* (−160) ^{c}	5.36 (−74)	17.08 (+53)	−36.12 (+408)	17.08 (+53)	5.36 (−74)	3.46 (77)
	2	205	*26.67* (−99)	6.96 (−54)	13.75 (+51)	−30.50 (+162)	13.75 (+51)	6.96 (−54)	2.80 (46) ^{c}
Benzene ^{h}	1	310	5.7	5.7	5.7	5.7	5.7	5.7	
	2	310	3.8	3.8	3.8	3.8	3.8	3.8	

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[a] $\Delta\delta(C) = \delta(C)_{obsd} - \delta(C)_{free\ arene}$ in ppm. Estimated error ±0.06 ppm or less. Substituted carbon shifts are in italic type. [b] Coupling constants in Hz. Estimated error ±2 Hz or less except when noted. See text for discussion of signs. [c] Estimated error ±5 Hz or less. [d] Me(1,5). [e] Me(2,4). [f] Me(3). [g] Satellites not observed. [h] Rapid exchange occurred at all temperatures. Shifts calculated from the curve of exchange-averaged shift vs. Arene/Hg^{2+} (see Experimental Section).

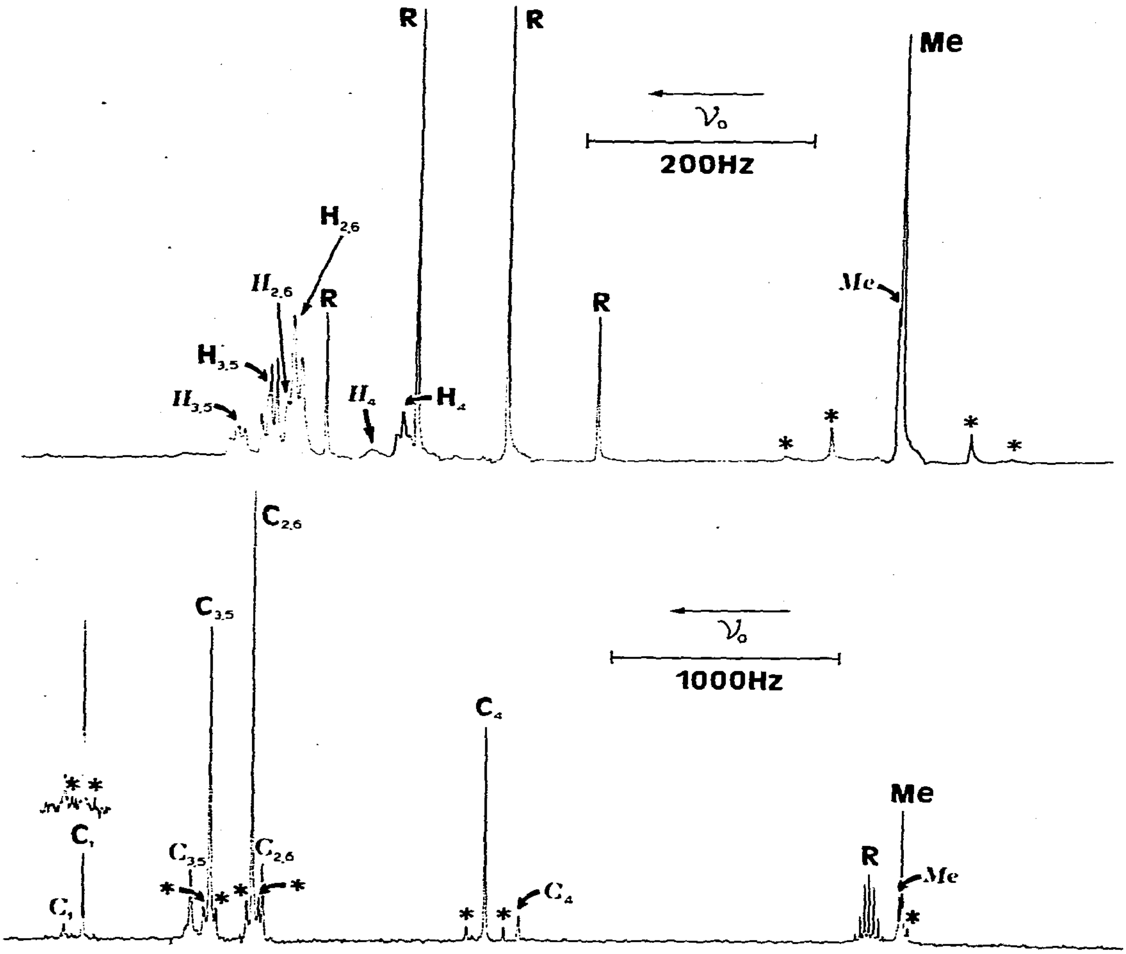

Fig. 1. 198 K 100 MHz ^{1}H NMR spectrum (top) and 205 K 25.2 MHz ^{13}C NMR spectrum (bottom) of an SO$_2$ solution where toluene/Hg(SbF$_6$)$_2$ ≈ 1.4/1. Bold lettering indicates signals from (C$_6$H$_5$Me)$_2$Hg^{2+} italics signals from (C$_6$H$_5$Me)Hg^{2+}, and asterisks ^{199}Hg satellites. Bold R signifies reference lines.

complexes of diamagnetic transition metals, upfield shifts only are anticipated *. Considerable further support is lent to this suggestion by the conspicuously large variation in ^{199}Hg—^{13}C and ^{199}Hg—^{1}H couplings in the present study **, e.g. from +705 for $J(^{199}\text{Hg}—^{13}\text{C}(6))$ to −117 Hz for $J(^{199}\text{Hg}—^{13}\text{C}(1,4))$ in Hg(C$_6$Me$_5$H)$^{2+}$. (See below for a discussion of the signs of these couplings.) It seems unlikely that such great variation would occur in an η^6-structure and therefore we rule out structure I with some confidence.

The simplicity of the patterns of chemical shifts, with the simultaneous observation of coupling to ^{199}Hg, is consistent with localized mercury—arene

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* For a detailed discussion of the complexation shifts expected for different types of coordination of arenes, see ref. 1.

** ^{199}H—^{1}H coupling to the methyl protons of m-C$_6$H$_4$Me$_2$ is very clear in Fig. 2 of ref. 9, but was not mentioned in that work.

bonding (structures II and III) only if rapid intramolecular exchange of mercury between sites is occurring. The data in Table 2, particularly, provide compelling evidence for such exchange. Provided that the different complexes have the same type of mercury-arene bonding and that the coupling between ^{199}Hg and an aryl carbon depends primarily on the relative positions of the coupled nuclei, the average value of $J(^{199}\text{Hg}—^{13}\text{C}_{\text{aryl}})$ should be the same whether rapid intramolecular averaging of all sites is complete or not *. With the signs indicated in Table 2, there is near-constancy of

$$J(^{199}\text{Hg}—^{13}\text{C}_{\text{aryl}})_{\text{ave}}\left(=\frac{1}{6}\sum_{n=1}^{n=6}J(^{199}\text{Hg}—^{13}\text{C}_{n})\right).$$

For the most complete series, the 1/1 complexes, J_{ave} = 30, 33, 31, 50, 39 and 39 Hz for the hexamethylbenzene (at 260 K), pentamethylbenzene (at 260 K), durene (at 230 K), mesitylene (at 205 K), *p*-xylene (at 205 K) and toluene (at 205 K) complexes, compared with a total range of some 820 Hz for the individual couplings. Clearly the complexes do have the same structure and the intramolecular exchange of mercury is rapid. Also our assignments of relative signs are supported by the small variation in the average coupling.

Distinction between structures II and III using the intramolecular exchange-averaged spectra is difficult. However, we favour structure III for the reasons which follow **: (i) In both Hg(Mesitylene)$^{2+}$ and Hg(Mesitylene)$_2{}^{2+}$ both the ^{13}C complexation shifts and the ^{199}Hg—^{13}C couplings of the substituted and unsubstituted aryl carbons are quite different, a result expected for III, but not for II with anything like symmetrical coordination of the mercury to one of the chemically equivalent aromatic C—C bonds. (A very unsymmetrical coordination would be equivalent to III.) (ii) The largest ^{199}Hg—^{13}C coupling in the pentamethylbenzene complexes is that to C(6), the unsubstituted carbon. Either C(6) (in structure III) or the equivalent C(1)—C(6) and C(5)—C(6) bonds (in structure II), being least hindered, should be the preferred coordination site(s) in the C_6Me_5H complexes. For either structure, $J(^{199}\text{Hg}—^{13}\text{C}(6))$ should probably be the largest coupling, but in structure II, because C(1)—C(6) and C(5)—C(6) coordinations are equally preferred on average, $J(^{199}\text{Hg}—^{13}\text{C}(1,5))$ should be *ca.* $\frac{1}{2}J(^{199}\text{Hg}—^{13}\text{C}(6))$ and most likely of the same sign. A much greater difference in magnitude and an apparent difference in sign (see above) is found (see Table 2), so that structure III is indicated. (iii) The magnitudes of $J(^{199}\text{Hg}—^{13}\text{C}(4))$ and $J(^{199}\text{Hg}—^{1}\text{H}(6))$ in Hg(C_6Me_5H)$^{2+}$ and Hg(C_6Me_5H)$_2{}^{2+}$ place them in the approximate range expected for mercury bound to *sp*^{3} hybridized carbons [12]. Again structure II is implicated. Indeed, it appears likely that in the pentamethylbenzene complexes the mercury is localized mainly on C(6), so that the observed $J(^{199}\text{Hg}—^{13}\text{C}(6))$ is essentially a one-bond coupling, and so should have

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* In ref. 1, this argument is made in detail for averaging of chemical shifts.

** In earlier work it has been argued that structure III should lead to a reduction in $^{1}J(^{13}\text{C}—^{1}\text{H})_{\text{ave}}$ since quaternization should cause a reduction at the site of complexation [9]. Experimentally an increase in $^{1}J(^{13}\text{C}—^{1}\text{H})_{\text{ave}}$ was observed, leading to the suggestion that II and III might be present in equilibrium [9]. However, transferring the one-bond couplings predicted for the benzenium ion [11] to (η^1-C_6H_6)Hg^{2+} and averaging shows a slight increase in $^{1}J(^{13}\text{C}—^{1}\text{H})_{\text{ave}}$ on complexation (160 Hz for (η^1-C_6H_6)Hg^{2+} vs. 158 Hz for benzene under approximately the same conditions).

the absolute positive sign known [13] for such couplings. With the assumptions of localization of mercury on the unsubstituted carbon and of the transferability of analogous couplings from $Hg(C_5Me_5H)^{2+}$ to $Hg(C_6Me_4H_2)^{2+}$, the predicted values of $J(^{199}Hg—^{13}C(3,6))$ and $J(^{199}Hg—^{13}C(1,2,4,5))$ for the 1/1 durene complex are +321 and —111 Hz, respectively. These are in reasonable agreement with the +335 and —92 Hz found, thus lending further support to a model involving localized bonding. Predictions for the less-substituted benzenes are not as satisfactory probably because these contain different, less hindered, and therefore more accessible, sites.

Two further questions regarding the structure of the mercuric complexes must be answered. Firstly, there is the possibility that the coordination of the arene to mercury is not direct, but rather occurs via an SO_2 molecule coordinated to the mercury. The magnitudes of the couplings to ^{199}Hg make it unlikely that such SO_2-inserted species occur in solution *, and neither the elemental analysis nor the infrared spectra of the solid complexes provide any evidence for this type of coordination. Secondly, it must be established, if possible, what part anion coordination and/or solvation play in the complexes. Here only a partial answer is possible. Comparison of our data with those of Olah et al. [9] makes it clear that these earlier workers studied the 1/1 complexes. (Neither the stoichiometry nor the stabilities of the mercury complexes was established in this prior work.) Our ^{13}C and ^{1}H chemical shift data for the 1/1 complexes are virtually identical with the earlier data; it is not clear why no coupling to ^{199}Hg was observed previously, even at —78°C (see however footnote page 6). The anion in Olah's investigation must have been either $CF_3CO_2^-$ or SO_3F^-, whereas it is SbF_6^- in our study. We conclude either that the ^{13}C and ^{1}H NMR spectra of the 1/1 complexes are insensitive to a coordinated anion, an unprecedented situation for RHgX molecules, or, more likely, that the anions are not coordinated. With regard to solvation, the extent of solvation at the mercury is unclear, but the white or yellow colour of the solid complexes changes on dissolution in SO_2 (e.g., $Hg(C_6Me_6)_2(SbF_6)_2$ is yellow in the solid state, deep red in solution) and we attribute this change to charge-transfer interaction between SO_2 and the coordinated arene. (A similar interaction is thought to occur in cadmium(II)—Arene complexes [2].)

Stabilities of the Hg^{2+}—Arene complexes

The slow-exchange low-temperature spectra of the methyl-substituted benzene complexes make it evident that the complexes are not significantly dissociated to free arene. Further confirmation of the great stability of this type of complex was provided by a detailed study of the system $C_6H_6—Hg(SbF_6)_2—SO_2$. As noted above, it was not possible to stop intermolecular exchange in this case. However, using the program LISA [16], the curve of exchange-averaged ^{13}C complexation shift vs. Arene/Hg^{2+} ratio was analyzed to yield the approximate values $K_1 = 5 \times 10^8\ M^{-1}$ and $K_1/K_2 = 120$ at 308 K. For comparison, K_1 for the formation of $Cd(C_6H_6)^{2+} \approx 0.48\ M^{-1}$ under the same conditions [2]. The

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* Though the exact reason is not certain [14], $^2J(^{199}Hg—^1H)$ is reduced to zero when $Hg—CH_2$ is converted to $Hg—O—S(O)—CH_2$ [14,15]. The corresponding ^{13}C data have not been reported but an accompanying reduction in $^1J(^{199}Hg—^{13}C)$ seems very likely.

enormous difference between the stabilities of the Cd^{2+} and Hg^{2+} complexes must be a manifestation of the well-known [17] high affinity of mercury for carbon.

K_1/K_2 is the equilibrium constant for the redistribution

$$Hg(Arene)_2{}^{2+} + Hg^{2+} \rightleftharpoons 2Hg(Arene)^{2+}$$

The value found for benzene implies that when $C_6H_6/Hg^{2+} = 1$, appreciable concentrations of $Hg(C_6H_6)_2{}^{2+}$ will occur along with the predominant $Hg(C_6H_6)^{2+}$. Our qualitative observations suggest that the above equilibrium does not lie completely to the right for the other systems studied either: both $Hg(Arene)_2{}^{2+}$ and $Hg(Arene)^{2+}$ coexist until $Arene/Hg(SbF_6)_2 \approx 0.75$, when only the 1/1 species is evident by NMR spectroscopy.

Evidence for a C_6Me_6 complex of $Hg(O_2CCF_3)_2$ in SO_2 solution and in the solid state

In accord with earlier work [3,8] in which other solvents were used, we find that pentamethylbenzene and durene are mercurated rapidly by $Hg(O_2CCF_3)_2$ in SO_2 at room temperature, as evidenced by the expected changes in the ^1H and ^{13}C NMR spectra of the substrates. Benzene is mercurated more slowly at room temperature (and not at all at 260 K) but there is no significant ^{13}C NMR complexation shift of the unreacted C_6H_6. C_6Me_6 cannot be mercurated readily, but a significant ^{13}C complexation shift of the aryl carbons of this substrate does occur. A downfield shift of 1.9 ppm occurs in a solution where $Hg(O_2CCF_3)_2/C_6Me_6$ is 5/1, this shift presumably approximating the bound shift. Sokolov et al. [8] have shown previously that a C_6Me_6—$Hg(O_2CCF_3)_2$ species of undetermined stoichiometry and structure occurs in CF_3CO_2H as solvent, but did not isolate the complex. We find that removal of all volatiles from a solution of $Hg(O_2CCF_3)_2$ in SO_2 containing excess C_6Me_6 yields colourless $Hg(O_2CCF_3)_2 \cdot C_6Me_6$. In view of the deshielding of the aryl carbon nuclei observed for this species, a localized, as opposed to and η^6-, structure seems likely, but at present we have no basis for choice between a structure like II and one like III.

Experimental

Materials

Sulphur dioxide (Matheson Anhydrous Grade) was stored in the gas phase over Linde 3A Molecular Sieves at least 12 h before use. All arenes were obtained commercially; solids were purified by sublimation and liquids by distillation from calcium hydride under a dry nitrogen atmosphere. Mercuric fluoride (Alfa Anhydrous Grade, 98.5%), silver powder (Alfa, 99.999%), arsenic pentafluoride (PCR), boron trifluoride (Matheson, 99.5%), and phosphorus pentafluoride (Matheson, 99.0%) were used without further purification. Antimony pentafluoride (PCR) was purified by double distillation under a dry nitrogen atmosphere.

General preparative procedure

All of the products are exceedingly moisture-sensitive. Reactions were carried out in baked out (140°C) glass vessels as previously described [1], and all manipulations of solid reagents and liquid SbF_5 were performed in a nitrogen-filled glove box, the atmosphere of which was circulated through liquid nitrogen traps. SbF_5 was dispensed from an all-glass syringe. Liquid arenes were added outside the glove box either by syringe using standard N_2-vacuum line techniques or *in vacuo* from a calibrated Teflon and glass vacuum line. AsF_5 was added from the calibrated vacuum line.

Preparation of mercuric salts

$Hg(SbF_6)_2$ and $HgF(SbF_6) \cdot SO_2$ were obtained by reaction of slightly less than two moles of SbF_5 with one mole of HgF_2 in liquid SO_2 at room temperature in a sealed glass H-tube of a type described previously [18]. After about one hour of stirring, all the HgF_2 dissolved giving a colourless solution. Gradually over a period of several hours, a colourless material was deposited from solution. The insoluble material was filtered off, washed with SO_2, and dried in vacuo. It proved to be $HgF(SbF_6) \cdot SO_2$. Anal. Found: F, 25.89; Hg, 39.1 ± 0.3. F_7HgO_2SSb calcd.: F, 25.61; Hg, 38.61%. (infrared spectrum (Nujol/halocarbon mulls): 1337vs; 1319vs; 1303m; 1158m; 1147s; 650s(br) (ν_3, SbF_6^-); 525s.) The solvent was removed from the filtrate yielding $Hg(SbF_6)_2$ which was dried in vacuo. Anal. Found: F, 33.69, Hg, 30.2 ± 0.5. $F_{12}HgSb_2$ calcd.: F, 33.92, Hg, 29.85%.

$HgF(BF_4)$ and $HgF(AsF_6)$ were prepared as above but using excess of the volatile fluorides. Colourless insoluble $HgF(BF_4)$ was the sole product of the HgF_2—BF_3 reaction. Anal. Found: Hg, 64.9 ± 0.5. BF_5Hg calcd.: Hg, 65.47%. The HgF_2—AsF_5 reaction gave soluble and insoluble products, both colourless. After removal of the insoluble material by filtration, all volatiles were removed from the soluble portion yielding $HgF(AsF_6)$, which was then insoluble in SO_2. Anal. Found: F, 32.57, Hg, 48.5 ± 0.5. AsF_7Hg calcd.: F, 32.56, Hg, 49.10%.

The solubility of $HgF(AsF_6)$ in SO_2 can be restored by addition of AsF_5. Presumably $Hg(AsF_6)_2$ exists in solution but loses AsF_5 on pumping. Similar behaviour is known for several other divalent metal fluorides [18,19].

Attempts to prepare $Hg(PF_6)_2$ and $HgF(PF_6)$ by the preceding method were unsuccessful. Some HgF_2 dissolves in SO_2 in the presence of PF_5, but the solution gives only HgF_2 on pumping.

Mercuric trifluoroacetate was obtained by the literature method [20].

It should be noted that HgF_2 reacts with liquid SO_2 at room temperature over several days yielding colourless insoluble $2\,HgF_2 \cdot SO_2$. Anal. Found: F, 13.71, Hg, 73.5 ± 0.5. $F_4Hg_2O_2S$ calcd.: F, 14.04, Hg, 74.92%. (Infrared spectrum (Nujol/halocarbon mulls): 1240s(br); 1180s(br); 1050s(br); 950s(br); 790s; 720m; 650m; 620m; 590m; 575s; 558m.)

Preparation of arene complexes

(a) From $Hg(SbF_6)_2$. Complexes of the type $Hg(SbF_6)_2(Arene)_2$ were generally prepared by reaction of excess arene with the mercuric salt in SO_2 in a sealed H-tube at room temperature. The complexes are formed upon mixing, but those of the more highly methylated benzenes decompose in solution over a period of hours. Therefore, the product-containing solutions were filtered as soon as possible and the solvent removed by lyophilization. The remaining volatiles were pumped from the solid residues with slight warming (318 K, 10^{-2} mmHg). In this manner were prepared the 1/2 Hg^{2+}/Arene complexes of benzene, toluene,

p-xylene, mesitylene, durene, pentamethylbenzene, hexamethylbenzene and naphthalene.

The complex $Hg(SbF_6)_2(biphenyl)_2$, prepared as above, was poorly soluble. It was isolated by filtration, washed several times with fresh SO_2, and pumped dry.

1/1 complexes with biphenyl, naphthalene and phenanthrene precipitated from SO_2 solutions of the arene and excess $Hg(SbF_6)_2$. Like the bis(biphenyl) compound they were isolated by filtration.

(b) From $HgF(AsF_6)$. The more electron-rich arenes react with SO_2-insoluble $HgF(AsF_6)$ in SO_2 according to the equation:

$$2\ HgF(AsF_6) + 2\ \text{Arene} \rightarrow Hg(AsF_6)_2(\text{Arene})_2 + HgF_2\downarrow$$

Removal of the insoluble HgF_2, and excess $HgF(AsF_6)$, if present, by filtration, and removal of the solvent and excess arene from the filtrate as for the $Hg(SbF_6)_2$ complexes above, yields the solid 1/2 complexes. This method was satisfactory for pentamethylbenzene, durene and naphthalene as aromatic substrates. HgF_2 was precipitated as expected when mesitylene and *p*-xylene were the hydrocarbons used. However, the first gave an oily product while only $HgF(AsF_6)$ was isolated from the filtrate of the second. (Presumably $Hg(AsF_6)_2(p\text{-xylene})_2$ exists but loses *p*-xylene and AsF_5 on pumping in vacuo.) No HgF_2 was formed upon treatment of $HgF(AsF_6)$ with either toluene or benzene and $HgF(AsF_6)$ was recovered on removal of volatiles. The behaviour of $HgF(SbF_6) \cdot SO_2$ is identical to that of $HgF(AsF_6)$.

(c) From $Hg(O_2CCF_3)_2$. Removal of solvent and volatiles from an SO_2 solution of $Hg(O_2CCF_3)_2$ and excess C_6Me_6 at room temperature yielded the colourless 1/1 complex $Hg(O_2CCF_3)_2 \cdot C_6Me_6$. However, less substituted arenes are mercurated (see text). Evidently $Hg(O_2CCF_3)_2$ is too reactive to be of general use in synthesizing mercury(II)—Arene complexes.

(d) By other routes. Several other synthetic methods for the arene complexes were tried briefly but none proved as satisfactory as those preceding. SO_2-insoluble $HgCl_2$ reacts over a matter of hours with $AgAsF_6$ or $AgSbF_6$ in the presence of the arenes in SO_2:

$$HgCl_2 + 2\ \text{Arene} + 2\ AgMF_6 \rightarrow Hg(MF_6)_2(\text{Arene})_2 + 2\ AgCl$$

Evidence for the complexes in solution was obtained from ^{13}C NMR. However, products isolated were usually contaminated by small amounts of AgCl, the method is not applicable to 1/1 complexes, and the lengthy reaction times led to some decomposition when more electron-rich arenes were used.

HgF_2 and $HgF(BF_4)$ dissolve in SO_2 solutions containing excess of both arene and BF_3:

$$HgF_2 + BF_3 \rightarrow HgF(BF_4)$$

$$HgF(BF_4) + 2\ \text{Arene} + BF_3 \rightarrow Hg(BF_4)_2(\text{Arene})_2$$

Again NMR (^{13}C and (see Table 1) ^1H) provided evidence for the complexes in solution but attempts at isolation led to loss of BF_3 and/or volatile arenes on pumping. Similar experiments showed PF_5 to be even less satisfactory as a fluoride acceptor in the system HgF_2—excess PF_5—excess arene: dissolution of the HgF_2 was incomplete, though evidence was found for the complexes in solution; again isolation was not possible.

The arene complexes isolated, and their analyses, are given in Table 3.

Fourier transform ^1H and ^{13}C-$\{^1H\}$ NMR spectra

All NMR spectra were obtained using a Varian XL-100-12 spectrometer system equipped with the Gyrocode Observe Accessory and operating at 100.10 MHz for ^1H and 25.16 MHz for ^{13}C.

For proton spectroscopy, samples of complexes (usually prepared in situ) and free arenes (for comparison) were prepared in sealed 5 mm o.d. medium-walled NMR tubes, the arene concentration being ca. 0.25 *M* in the SO_2, and were referenced with internal CHF_3 *. The choice of reference was dictated by the need for inertness: more conventional references were not inert. Spectra were recorded using a single 90° pulse (20 μs) without field/frequency lock (the last condition resulting from the reactivity of possible ^2D lock substances). The lowest temperature compatible with reasonable solubility was generally employed.

Assignment of the proton spectra of both the free ligands (Table 4) and the complexes (Table 1) was normally straightforward because of the real or effective symmetry of the substrates. The phenyl protons of complexed toluene could be assigned from the splitting pattern. Assignment of the C(1,5)—Me and C(2,4)—Me proton signals of the pentamethylbenzene complexes (and hence, from intermolecular exchange-averaged spectra with excess arene, the parent hydrocarbon) was made to be consistent with the perturbation of the ^{13}C spectrum of the Hg^{2+}-complexed ligand (C(1,5) more greatly affected than C(2,4) by complexation: Table 2) and with the greater deshielding of the *o*-methyls than the *m*-methyls when one aryl carbon of C_6Me_6 or C_6Me_5H is quaternized by protonation [21,22] or (for C_6Me_6) by addition of NO_2^+ [22].

Carbon-13 NMR samples were usually prepared in situ, as reported earlier [1,2], the hydrocarbon concentration being up to 0.52 *M*, depending on solubility. The spectra were obtained using external $(CD_3)_2CO$ as both a lock and reference substance **. Most of the spectra were recorded using a 20°C pulse (10 μs), a 7500 Hz spectral window, a 1 s acquisition time and a 3 s cycle time. Approximately 12 000 transients were required to produce acceptable spectra of the least symmetrical aromatic substrates, whereas 100 transients gave acceptable spectra for the benzene-containing systems.

The ^{13}C NMR spectra of most of the substrates in SO_2 at ambient probe temperature have been reported earlier [1]. The chemical shifts for other temperatures used in this work are presented in Table 5. Assignment of the spectra of the complexes $Hg(SbF_6)_2(Arene)_2$ was made from those of the free arenes using the intermolecular exchange-averaged spectra observed when $Arene/Hg^{2+} > 2$. The assignments for $Hg(SbF_6)_2(Arene)$ and other complexes were made by analogy with $Hg(SbF_6)_2(Arene)_2$.

For the low temperature ^{13}C NMR spectra, the temperatures for various settings of the temperature regulator were determined using a Doric Trendicator Type

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* Shifts were converted to a TMS reference scale using $\delta(H)(TMS, int) = \delta(H)(CHF_3, int) + 6.666$ ppm.

** Shifts were converted to a TMS reference scale using $\delta(C)(TMS, int) = \delta(C)((\underline{C}D_3)_2CO, ext) +$ 10.36 ppm at 260 K (at 220 and 205 K, the difference between the two references was 10.57 and 10.69 ppm, respectively).

TABLE 3

ANALYSES OF SOME MERCURY(II)—ARENE COMPLEXES

Complex	Colour	Analysis (Found (calcd.) (%))		
		C	H	Hg
$Hg(SbF_6)_2 \cdot (Benzene)_2$	colourless	17.12 (17.40)	1.61 (1.46)	
$Hg(SbF_6)_2 \cdot (Toluene)_2$	colourless	19.36 (19.63)	2.02 (1.89)	
$Hg(SbF_6)_2 \cdot$ (*p*-Xylene)$_2$	yellow	21.46 (21.73)	2.20 (2.28)	22.92 (22.68)
$Hg(SbF_6)_2 \cdot (Mesitylene)_2$	yellow	23.40 (23.69)	2.76 (2.66)	21.86 (21.98)
$Hg(SbF_6)_2 \cdot (Durene)_2$	yellow	25.28 (25.54)	3.00 (3.01)	
$Hg(AsF_6)_2 \cdot (Durene)_2$	yellow	28.61 (28.36)	3.47 (3.34)	24.3 ± 0.5 (23.69)
$Hg(SbF_6)_2 \cdot (Pentamethylbenzene)_2$	yellow	27.12 (27.28)	3.48 (3.34)	20.98 (20.71)
$Hg(AsF_6)_2 \cdot (Pentamethylbenzene)_2$	yellow	30.02 (30.20)	3.69 (3.69)	
$Hg(SbF_6)_2 \cdot (Hexamethylbenzene)_2$	yellow	28.87 (28.92)	3.61 (3.65)	
$Hg(CF_3COO)_2 \cdot (Hexamethylbenzene)$	colourless	32.53 (32.63)	3.02 (3.09)	34.1 ± 0.5 (34.06)
$Hg(SbF_6)_2 \cdot (Naphthalene)$	yellow	14.70 (15.01)	0.99 (1.01)	25.4 ± 1 (25.07)
$Hg(SbF_6)_2 \cdot (Naphthalene)_2$	orange	25.64 (25.87)	1.93 (1.74)	21.5 ± 0.4 (21.61)
$Hg(AsF_6)_2 \cdot (Naphthalene)_2$	orange	28.48 (28.77)	2.08 (1.94)	
$Hg(SbF_6)_2 \cdot (Phenanthrene)$	orange	19.53 (19.77)	1.31 (1.19)	23.77 (23.59)
$Hg(SbF_6)_2 \cdot (Biphenyl)_2$	orange	28.81 (29.40)	2.05 (2.06)	23.8 ± 1 (24.28)
$Hg(SbF_6)_2 \cdot (Biphenyl)$	yellow	17.25 (17.44)	1.31 (1.22)	

400 Thermocouple Thermometer with the thermocouple set in a 10 mm tube of $(CD_3)_2CO$ within a stationary 12 mm tube containing $(CD_3)_2CO$. The temperatures quoted in the text will be approximate because of the heating effect of proton-decoupling. The corresponding temperatures for the ^1H spectra were

TABLE 4

^1H CHEMICAL SHIFTS OF FREE ARENES IN LIQUID SO_2 [a]

Arene	*T*(K)	Phenyl	Methyl
Hexamethylbenzene	198		2.15
Pentamethylbenzene	198	6.84	2.17 [b], 2.09 [c]
Durene	213	6.93	2.14
Mesitylene	198	6.80	2.23
p-Xylene	198	7.09	2.26
Toluene	198	7.23 [d]	2.32

[a] In ppm relative to internal TMS. [b] Me(2,4). [c] Me(3), Me(1.5), for discussion of these assignments see text. [d] Phenyl protons are not resolved.

TABLE 5

^{13}C CHEMICAL SHIFTS OF FREE ARENES IN LIQUID SO_2 [a]

Arene	T(K)	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	Methyl
Hexamethylbenzene	260	*133.0*	*133.0*	*133.0*	*133.0*	*133.0*	*133.0*	15.5
Pentamethylbenzene	260	*134.6*	*133.7*	*136.8*	*133.7*	*134.6*	130.4	20.1 [b], 15.4 [c], 15.7 [d]
1,2,4,5-Tetramethylbenzene	230	*134.1*	*134.1*	131.4	*134.1*	*134.1*	131.4	17.7
1,3,5-Trimethylbenzene	205	*138.4*	127.0	*138.4*	127.0	*138.4*	127.0	19.7
1,4-Dimethylbenzene	205	*134.8*	129.1	129.1	*134.8*	129.1	129.1	19.3
Toluene	205	*138.0*	129.0	128.3	125.3	128.3	129.0	19.8
Benzene	310	129.0	129.0	129.0	129.0	129.0	129.0	—

[a] Substituted carbons are in italic type. Chemical shifts are in ppm relative to TMS in SO_2. Assignments are those in ref. 1. [b] Me(1,5). [c] Me(2,4). [d] Me(3).

measured with the thermocouple in a stationary sample of toluene in a 5 mm tube.

Infrared spectra

Nujol and fluorocarbon oil mull spectra were recorded over the range 4000—500 cm^{-1} using a Perkin—Elmer 621 Grating Infrared Spectrophotometer. Silver chloride windows were used.

Analysis of the ^{13}C NMR chemical shift titration curve for the system Hg $Hg(SbF_6)_2$—C_6H_6—SO_2

Following measurement of $\delta(C)$ (and hence $\Delta\delta(C)$) for a series of samples of known composition, the volume of each sample was determined from the weight of an equal volume of CH_2Cl_2 (density 1.33 g cm^{-3}) in the same tube.

The exchange-averaged shifts were analyzed as previously [1,2] using the program LISA [16].

Elemental analysis

Carbon, hydrogen, fluorine and some mercury analyses were performed by the Analytische Laboratorien, Elbach, West Germany. In addition, some mercury analyses were carried out by atomic absorption using a Varian Techtron Model 1200 A.A. Spectrometer.

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