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THE SOLID STATE STRUCTURE OF ARENE-MERCURY(II) COMPLEXES FROM MAGIC-ANGLE SPINNING CARBON-13 NMR AND THE SOLUTION CARBON-13 NMR OF SOME COMPLEXES OF MERCURY(II) WITH ARENES HAVING BULKY ALIPHATIC SUBSTITUENTS

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Summary

The cross-polarization magic angle spinning ^{13}C NMR spectra of $Hg(SbF_6)_2 \cdot 2$ Arene (Arene = C_6HMe_5, 1,2,4,5-$C_6H_2Me_4$, 1,2,3,4-$C_6H_2Me_4$, or C_6H_6) have been measured. The spectra of the complexes of C_6HMe_5 and 1,2,4,5-$C_6H_2Me_4$ are consistent with static η^1-bonding of the mercury to the arene at an unsubstituted carbon atom, while the spectra of the 1,2,3,4-$C_6H_2Me_4$ and C_6H_6 complexes show the arene to have time-averaged C_s or C_2, and C_6 symmetry respectively, at the temperature of measurement (300 K).

The reduced temperature ^{13}C NMR spectra of $Hg(Arene)_n^{2+}$ (n = 1 or 2; Arene = 1,3,5-$C_6H_3R_3$ (R = Me, i-Pr, or t-Bu)) in SO_2 solution are also reported and affirm that in these intramolecularly mobile species the mercury bonds in an η^1-manner, with unsubstituted aryl carbon atoms being the strongly preferred point of mercury attachment. This site preference is further demonstrated by the solution ^{13}C NMR spectra of $Hg(Arene)_n^{2+}$ (Arene = 1,2,3,4-$C_6H_2Me_4$, n = 1 or 2; Arene = 1,4-$C_6H_4R_2$, R = Me or t-Bu, n = 1). The spectra of the 1,4-$C_6H_4R_2$ complexes and $Hg(p\text{-}C_6H_4\text{-t-BuMe})^{2+}$ provide clear evidence for steric influence of the binding site.

Like $Hg(C_6Me_6)_2^{2+}$, but unlike most of the complexes of substituted benzenes which have been studied, $Hg(1,3,5\text{-}C_6H_3\text{-i-}Pr_3)_2^{2+}$ exchanges only slowly with excess free ligand.

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Introduction

In recent work from one of our laboratories [1], 1/1 and 1/2 complexes of mercury(II) with arenes have been studied in SO_2 solution by low temperature ^{13}C and ^1H NMR, and many of the 1/2 complexes have been isolated in the solid state.

The NMR spectra showed that when the arene is one of a range of methylated benzenes intermolecular ligand exchange could be stopped at reduced temperature, though intermolecular exchange of benzene itself was rapid at all accessible temperatures. The spectra obtained when intermolecular exchange was slow were consistent with localized bonding of Hg^{2+} to the arene, but it was evident that, except possibly with C_6HMe_5 as arene, intramolecular exchange was rapid at all points within the accessible temperature range. The intramolecular exchange averaged data appeared most consistent with η^1-coordination of the mercury, i.e. onium ion formation, but η^2-coordination, as is known for many arene-silver(I) complexes in the solid state (see, for example, ref. 2), could not be ruled out with complete certainty. Since, as has already been pointed out [1], these arene-mercury(II) complexes may be models for the normally unisolable intermediates of aromatic mercuration, it seemed desirable to obtain details of the structure(s) of some key complexes in the solid state. Accordingly we have measured the CP/MAS * ^{13}C NMR spectra of solid $Hg(SbF_6)_2 \cdot 2$ Arene (Arene = C_6HMe_5, 1,2,4,5-$C_6H_2Me_4$, 1,2,3,4-$C_6H_2Me_4$, or C_6H_6). CP/MAS ^{13}C NMR has proved a useful alternate or complement to X-ray analysis in favourable instances [3–6].

In extension of the present solid state study and our previous solution studies, we have also obtained the solution spectra of several complexes having arenes with bulky aliphatic substituents. These spectra provide supporting information regarding the structure and have allowed us to assess further the extent to which the localization of mercury at unsubstituted aryl carbons occurs, and the cause of this localization.

Results and discussions

Details of the CP/MAS ^{13}C NMR spectra of $Hg(SbF_6)_2 \cdot 2$ Arene (Arene = C_6HMe_5, 1,2,4,5-$C_6H_2Me_4$, 1,2,3,4-$C_6H_2Me_4$, or C_6H_6) are given in Table 1, together with data from the corresponding solution spectra for comparison. Figure 1 shows the 15.1 MHz ^{13}C NMR spectra of the C_6HMe_5 and 1,2,4,5-$C_6H_2Me_4$ complexes in the solid state.

The ^{13}C NMR spectrum of solid $Hg(SbF_6)_2 \cdot 2\ C_6HMe_5$ bears a close resemblance to that of the same complex in SO_2 solution, suggesting that the structure is basically the same in both phases. As confirmed by delayed decoupling experiments (see Experimental section), all the aromatic-carbon resonances of solid $Hg(SbF_6)_2 \cdot 2\ C_6HMe_5$ between 130 and 170 ppm arise from non-protonated aromatic carbons, while the broad peak near 100 ppm arises from the protonated carbon. From the solution spectrum, η^1-bonding of mercury, mainly at C(6),

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* Cross polarization/magic-angle spinning.

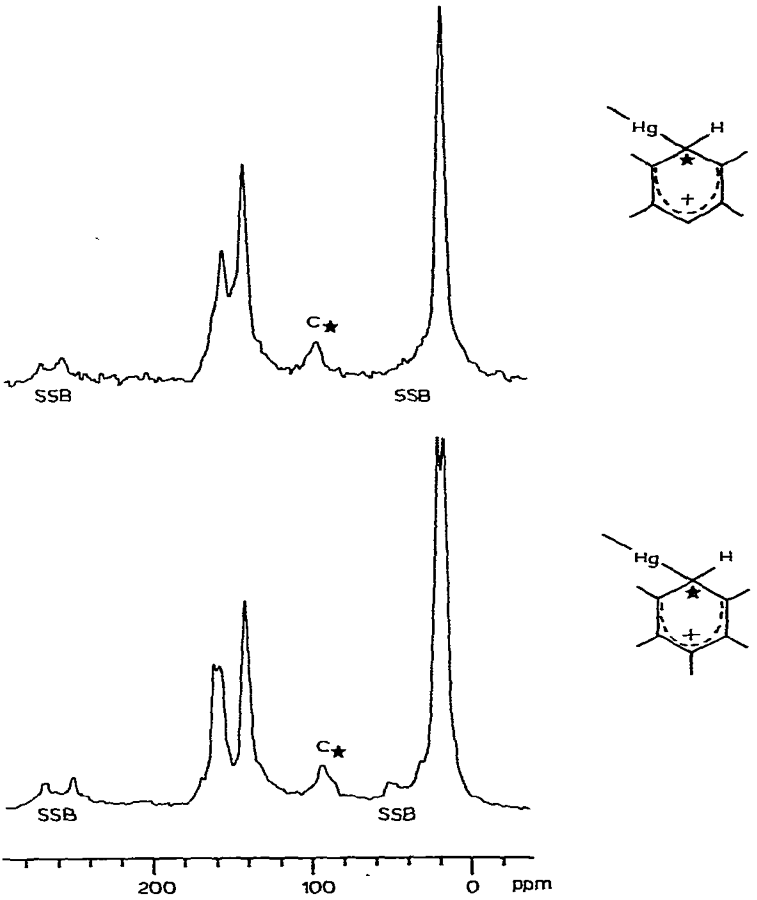


Fig. 1. The 300 K 15.1 MHz CP/MAS ^{13}C spectra of (top) $Hg(SbF_6)_2 \cdot 2(1,2,4,5\text{-}C_6H_2Me_4)$ and (bottom) $Hg(SbF_6)_2 \cdot 2(C_6HMe_5)$ under full decoupling conditions. (SSB = spinning sideband).

has been inferred, based primarily on the large magnitudes of $^1J(^{199}Hg—^{13}C(6))$ and $^2J(^{199}Hg—C(6)—^1H)$ and the extensive shielding of C(6) caused by complexation [1]. The scalar couplings to carbon are, however, not large enough to be clearly resolved in the solid state spectrum.

Unlike the solution and solid state spectra of the C_6HMe_5 complex, the spectra of the $1,2,4,5\text{-}C_6H_2Me_4$ complex in the two phases are quite different from each other (Table 1). Whereas in solution the symmetry of the free ligand spectrum is retained, the spectrum of the solid complex shows two signals from substituted and two signals from unsubstituted aryl carbons. One of the latter two resonances has a chemical shift of ca. 140 ppm and is detected by its disappearance under delayed decoupling conditions: the other occurs near 100 ppm and is marked in the figure as $C_\star$.

The solution spectrum of the durene complex has been interpreted [1] in terms of rapid intramolecular (as indicated by the observation of ^{199}Hg satellites in both ^{13}C and ^1H NMR spectra) exchange of η^1-bound mercury between

TABLE 1

^{13}C COMPLEXATION SHIFTS, $\Delta\delta(C)$ [a], OF SOME COMPLEXES $Hg(SbF_6)_2 \cdot 2$ Arene IN THE SOLID STATE (S.S.) AND IN SO_2 SOLUTION [b]

Arene	Phase	T(K)	Aryl						Methyl
			C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	
C_6HMe_5	S.S.	300	22.4	7.7	24.2	7.7	22.4	−37.2	−0.3 [c], 0.8 [d], — [e,f]
	SO_2	260	21.3	11.8	25.1	11.8	21.3	−35.4	1.7 [c], 1.0 [d], 3.5 [e]
1,2,4,5-$C_6H_2Me_4$	S.S.	300	21.7	8.5	17.	8.5	21.7	−34.8 [g]	0.4 [h]
	SO_2	230	13.5	13.5	−8.5	13.5	13.5	−8.5	0.9
1,2,3,4-$C_6H_2Me_4$	S.S.	300	16.6 [i]	15.5 [i]	15.5 [i]	16.6 [i]	−9.3	−9.3	−0.4 [j], 2.7 [k]
	SO_2 [l]	230	14.9	17.9	17.9	14.9	−13.3	−13.3	0.8 [j], 2.2 [k]
C_6H_6	S.S.	300	5.7	5.7	5.7	5.7	5.7	5.7	
	SO_2	310	3.8	3.8	3.8	3.8	3.8	3.8	

[a] $\Delta\delta(C) = \delta_{complex} - \delta_{free\ arene}$ (SO_2 solution; same temperature), in ppm. Data for free arenes from refs. 1 and 11 and this work. [b] Data for SO_2 solutions from ref. 1, except where noted. [c] Me(1,5). [d] Me(2,4). [e] Me(3). [f] Not observed (obscured by Me(1,5)?). [g] Quaternized carbon with η^1-bound Hg (see text). [h] Me(2,4) and Me(1,5) were not resolved (see Fig. 1). [i] C(1,4) and C(2,3) were not resolved (see text). [j] Me(1,4); assignment from ref. 8. [k] Me(2,3); assignment from ref. 8. [l] This work; full details of the spectrum are given in Table 2.

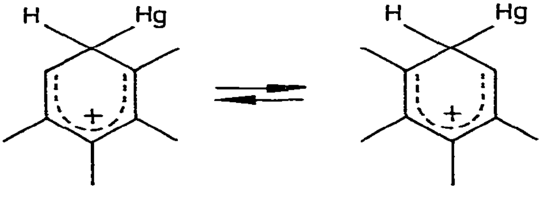
the various aryl carbons, with C(3) and C(6) being the preferred binding sites (Ia and Ib).

(Ia) (Ib)

The solid state spectrum is quite consistent with a static structure I, having the mercury localized on one unsubstituted ring carbon. From the solid state data, the predicted exchange-averaged solution chemical shifts of a mixture comprised principally of Ia and Ib are 150 ppm for C(1, 2, 4, 5) and ca. 124 ppm for C(3,6) *. These calculated values are remarkably similar to the shifts of 147.6 and 122.9 ppm observed in the 230 K solution spectrum [1].

Solid $Hg(SbF_6)_2 \cdot 2(1,2,3,4\text{-}C_6H_2Me_4)$ gives a CP/MAS ^{13}C NMR spectrum having two resonances from arene carbon nuclei: one of relative intensity ca. 2.4 an 152 ppm ($\nu_{1/2} \approx$ 130 Hz), the other with unit relative intensity at 119 ppm ($\nu_{1/2} \approx$ 320 Hz). An apparent C_s or C_2 symmetry of the complexed aromatic moiety is indicated by this spectrum. This, together with the absence of a resonance at ca. 100 ppm which, by analogy with the results for the solid pentamethylbenzene and durene complexes (see above) would indicate static η^1-coordination of the mercury at one of the unsubstituted sites, is consistent with the occurrence of either static η^2-coordination of the mercury (at C(2,3) or C(5,6)) or an averaging process in the solid prehnitene complex at the temperature of our measurement (300 K).

The ^{13}C complexation shifts found for $Hg(SbF_6)_2 \cdot 2(1,2,3,4\text{-}C_6H_2Me_4)$ in SO_2 solution and in the solid state are similar (Table 1), assuming the 152 ppm resonance of the solid to be the unresolved composite of the C(1,4) and C(2,3) resonances. The results for both 1/1 and 1/2 $Hg^{2+}/1,2,3,4\text{-}C_6H_2Me_4$ complexes in solution (Tables 1 and 2) are in reasonable agreement with those expected ** for rapid intramolecular equilibration of, mainly, structures IIa and IIb, so it



(IIa) (IIb)

seems that some fluxional motion must occur in the solid state also, again with

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* The calculated shifts of C(1,2,4,5) and C(3,6) in the solution spectrum correspond to the averages (δ(C(1,5) + δ(C(2,4))/2 and (δ(C(3) + δ(C(6))/2, respectively, of the solid state data.

** With the assumption that localization of the mercury at C(6) is complete in $Hg(C_6HMe_5)_n^{2+}$, transferring the data from the C_6HMe_5 complexes to the IIa, IIb equilibrium, (ref. 1 outlines the method in detail) yields expected values of —18.5 and —14.6 ppm and 249 and 58 Hz for Δδ(C(5,6)) and $^1J(^{199}Hg—^{13}C(5,6))$ in the 1/1 and 1/2 prehnitene complexes, respectively.

TABLE 2

^{13}C NMR COMPLEXATION SHIFTS, $\Delta\delta(C)$ [a] AND AVERAGE ^{199}Hg—^{13}C COUPLING CONSTANTS [b] (parentheses) FOR SOME COMPLEXES OF $Hg(SbF_6)_2$ WITH ALKYL-SUBSTITUTED ARENES IN LIQUID SO_2

Arene	n in $Hg(SbF_6)_2 \cdot n$ (Arene)	T (K)	Aryl						Aliphatic	
			C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(1)	C(2)
1,4-$C_6H_4Me_2$	1 [c]	205	17.8 (−80)	0.3 (+98)	0.3 (+98)	17.8 (−80)	0.3 (+98)	0.3 (+98)	1.0 (21)	
1,4-C_6H_4-t-Bu_2	1 [d]	205	18.7 (65)	1.1 (95)	1.1 (95)	18.7 (65)	1.1 (95)	1.1 (95)	2.4	−1.2
1,4-C_6H_4-t-BuMe	1	205	16.6 [e]	11.1	−16.1 (155)	21.1 (106)	−16.1 (155)	11.1	1.4 [f] 2.5 [h] (62)	−1.1 [g]
1,3,5-$C_6H_3Me_3$	1 [c]	205	31.6	−12.2 (+185)	31.6	−12.2 (+185)	31.6	−12.2 (+185)	3.0 (53)	
	2 [c]	205	25.3	−8.6 (+39)	25.3	−8.6 (+39)	25.3	−8.6 (+39)	2.0 (33)	
1,3,5-C_6H_3-i-Pr_3	1	205	31.1	−11.5 (176)	31.1	−11.5 (176)	31.1	−11.5 (176)	2.6 (44)	−0.8 (61)
	2	205	26.4	−7.8	26.4	−7.8	26.4	−7.8	1.9	−0.04
1,3,5-C_6H_2-t-Bu_3 [d]	1	220	31.2	−10.2 (152)	31.2	−10.2 (152)	31.2	−10.2 (152)	4.1	−1.0
	2	220	28.5	−6.9 (~35)	28.5	−6.9 (~35)	28.5	−6.9 (~35)	3.4	−0.5
1,2,3,4-$C_6H_2Me_4$	1	230	17.9 (91) [i]	20.8 (52) [i]	20.8 (52) [i]	17.9 (91) [i]	−15.4 (218) [i]	−15.4 (218) [i]	1.3 [j] (23) [i]	2.6 [k] (43) [i]
	2	230	14.9 (66) [l]	17.9 (31) [l]	17.9 (31) [l]	14.9 (66) [l]	−13.3 (38) [l]	−13.3 (38) [l]	0.8 [j]	2.2 [k]

[a] $\Delta\delta(C) = \delta(C)_{(\text{obsd at } T\text{ K})} - \delta(C)_{(\text{free arene at } T\text{ K})}$ in ppm, except where noted. [b] Coupling constants in Hz. Estimated error ±5 Hz for new data except where noted. [c] Data from ref. 1. [d] $\Delta\delta(C) = \delta(C)_{(\text{obsd at } T\text{ K})} - \delta(C)_{(\text{free arene at 308 K})}$ in ppm; the free arene is poorly soluble at reduced temperature. [e] $\geq$C—Bu-t. [f] —$C(CH_3)_3$. [g] —$C(CH_3)_3$. [h] $\geq$C—CH_3. [i] ±2 Hz. [j] Me(1,4); assignment from ref. 8. [k] Me(2,3); assignment from ref. 8. [l] At 260 K; the complex is poorly soluble at 230 K; partially collapsed?

the unsubstituted aryl carbons (C(5,6)) having the highest population of bound mercury.

The benzene complex in the solid state shows a single ^{13}C resonance, deshielded by ca. 6 ppm from the resonance of free benzene, this complexation shift being similar to the value of 3.8 ppm calculated for the same complex in SO_2 solution (Table 1). In the solid complex the time-averaged symmetry is C_6, based on the axially symmetric chemical shift anistropy ($\Delta\sigma \sim$ 190 ppm) observed in non-spinning cross-polarization ^{13}C NMR experiment. The structure of the benzene complex cannot be deduced directly from these data, but all the information on alkyl-substituted benzenes (see above and below) points to η^1-bonding of mercury in the arene-mercury(II) complexes, and there is no reason to believe that the bonding of mercury to benzene will be different. Therefore we conclude that $Hg(C_6H_6)_2{}^{2+}$ too is fluxional in the solid state, like the related $Hg(\eta^1\text{-}C_5H_5)_2$ [7].

The solid state ^{13}C data, for the C_6HMe_5 and 1,2,4,5-$C_6H_2Me_4$ complexes particularly, provide strong evidence for η^1-bonding of mercury to an unsubstituted aryl carbon (see above). This evidence, combined with that presented earlier [1] for complexes of a wider variety of methylated benzenes in SO_2 solution, suggests preferential population of the unsubstituted sites in the intramolecularly-mobile solution species. We sought to assess the completeness of this preference by comparison of the ^{13}C NMR spectra of the complexes $Hg(1,3,5\text{-}C_6H_3R_3)_n{}^{2+}$ (n = 1 or 2; R = Me, i-Pr, or t-Bu) and $Hg(1,4\text{-}C_6H_4R_2)^{2+}$ (R = Me or t-Bu) which are completely formed in SO_2 solution. The intramolecularly exchange averaged complexation shifts and ^{199}Hg—^{13}C coupling constants are given in Table 2. From the striking similarity of the data for analogous complexes, it is clear that change in the aliphatic substituent has minimal effect on the ^{13}C NMR spectra *, the most plausible explanation of these results being that bonding to the unsubstituted aryl carbons is always strongly preferred. More supporting evidence for this conclusion is given by the spectra of the 1/1 and 1/2 complexes of 1,2,3,4-$C_6H_2Me_4$ (see above).

In the 1,3,5-$C_6H_3R_3$ complexes the preference for bonding of mercury at C(2,4,6) could reflect the tendency of electron-releasing aliphatic groups to occupy *o*- and *p*-positions in the onium ion. This cannot be the case for bonding to C(2,3,5,6) in the 1,4-$C_6H_4R_2$ complexes, however; here steric influence of the preferred point of attachment is indicated. Evidence for a differential steric effect is found in the spectrum of $Hg(1,4\text{-}C_6H_4\text{-t-BuMe})^{2+}$ (Table 2), where $\Delta\delta(C)$ is larger for the methyl carbon than for the t-butyl carbon, showing that C(3,5), adjacent to the methyl, are more highly populated than C(2,6), adjacent to the t-butyl group. From this, the assignments for the aryl carbons follow. Most noteworthy, $\Delta\delta(C(3,5))$ is negative, as expected, and close to the value of ca. —17.7 ppm calculable ** from earlier data [1] for $Hg(C_6HMe_5)^{2+}$. Further, the average complexation shifts of C(1,4) and C(2,3,4,6) are very close

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* In the case of the complexes of 1,3,5-$C_6H_3R_3$, the absence of an appreciable substituent effect is additional support for η^1-bonding.

** Assuming that C(6) in the C_6HMe_5 complex and C(3,5) in the C_6H_4-t-BuMe complex are the completely preferred points of attachment for mercury, ($\Delta\delta$(C(3,5)) C_6H_4-t-BuMe complex = (($\Delta\delta$(C(6) + $\Delta\delta$(C(2,4))/2) C_6HMe_5 complex.

TABLE 3

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

Arene	T(K)	Aryl						Aliphatic	
		C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(1)	C(2)
1,4-C_6H_4-t-Bu_2	308	149.2	126.0	126.0	149.2	126.0	126.0	34.7	31.4
1,4-C_6H_4-t-BuMe	205	149.1 [b]	126.4 [c]	129.5 [c]	136.0	129.5	126.4	34.3 [d] 20.0 [f]	30.7 [e]
1,3,5-C_6H_3-i-Pr_3	205	149.3	123.4	149.4	123.4	149.4	123.4	33.8	23.5
1,3,5-C_6H_3-t-Bu_3	308	150.9	120.7	150.9	120.7	150.9	120.7	35.4	31.6
1,2,3,4-$C_6H_2Me_4$	230	135.6	136.6	136.6	135.6	128.4	128.4	20.2 [g]	15.2 [h]
1,2,3,4-$C_6H_2Me_4$	308	135.4	136.5	136.5	135.4	128.4	128.4	20.2 [g]	15.4 [h]

[a] In ppm from TMS. [b] $\succeq C$—Bu-t. [c] Assignments made by comparison with 1,4-$C_6H_4R_2$ (R = Me or t-Bu). [d] -$C(CH_3)_3$. [e] -$C(CH_3)_3$. [f] $\succeq C$—CH_3. [g] Me(1,4); assignment from ref. 8. [h] Me(2,3); assignment from ref. 8.

to those of the dimethyl and di-t-butyl complexes, showing that all the complexes of 1,4-disubstituted arenes must have the same structure. Because of the relationship between the unsubstituted sites in *p*-xylene and prehnitene, this again implies that η^1-coordination at C(5,6) occurs in the prehnitene complexes *.

One interesting difference between the species $Hg(1,3,5\text{-}C_6H_3Me_3)_2^{2+}$ and $Hg(1,3,5\text{-}C_6H_3\text{-i-}Pr_3)_2^{2+}$ ** involves their rates of exchange with free arene. In SO_2 solution the former exchanges rapidly with excess free mesitylene even at 205 K [1]. However, the spectra of excess $1,3,5\text{-}C_6H_3\text{-i-}Pr_3$ and its 2/1 complex are separate at 205 K and incompletely collapsed even at 308 K. Of the various complexes of methylated benzenes studied earlier, only C_6Me_6 exhibited similar slow bound-free exchange; in all other cases, intermolecular arene exchange was slow at some reduced temperature in the absence of excess free arene but fast at the same temperature in its presence. These data point to an associative intermolecular exchange process between $Hg(Arene)_2^{2+}$ and free arene which is fast at room temperature or below except when Arene = C_6Me_6 or $1,3,5\text{-}C_6H_3\text{-i-}Pr_3$. The slowness of the exchange in the C_6Me_6 and $1,3,5\text{-}C_6H_3\text{-i-}Pr_3$ complexes probably reflects steric crowding of the HgC_3 kernel through which the exchange most likely proceeds (cf. refs. 9 and 10).

Experimental

Materials

1,2,3,4-Tetramethylbenzene and 4-t-butyltoluene, both from Aldrich, showed no significant impurity by $^{13}C/^1H$ NMR and were used as received after storing over 3A molecular sieves for at least 24 h. $1,3,5\text{-}C_3H_3\text{-i-}Pr_3$, a gift from Dr. J.B. Stothers, was distilled and stored over molecular sieves. $1,3,5\text{-}C_6H_3\text{-t-}Bu_3$ (Alfa) and $1,4\text{-}C_6H_4\text{-t-}Bu_2$ (Eastman Kodak) were pure by NMR and were used as received.

Mercuric hexafluoroantimonate, and $Hg(SbF_6)_2 \cdot 2$ Arene (Arene = C_6H_6, C_6HMe_5, and $1,2,3,4\text{-}C_6H_2Me_4$) were prepared as previously reported [1]. The analogous complex of $1,2,3,4\text{-}C_6H_2Me_4$ can be prepared similarly.

$Hg(SbF_6)_2 \cdot 2(1,2,3,4\text{-}C_6H_2Me_4)$ was synthesized from $Hg(SbF_6)_2$ and excess arene in liquid SO_2, in the manner described earlier [1]. Removal of all volatiles in vacuo at ca. 50°C leaves the product as a bright yellow powder. Anal. Found: C, 25.74; H, 3.06. $C_{20}H_{28}F_{12}HgSb_2$ calcd.: C, 25.54; H, 3.01%.

FT ^{13}C-$\{^1H\}$ NMR spectra of solutions

Samples in solution were, with one exception, prepared, and their 25.16 MHz ^{13}C NMR spectra obtained exactly as described earlier [1] ***. The exception, the sample of $Hg(1,4\text{-}C_6H_4\text{-t-}BuMe)^{2+}$ was prepared by slowly adding an SO_2 solution of the arene to a stirred SO_2 solution of excess $Hg(SbF_6)_2$ in a

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* As expected on this basis, $\Delta\delta(C(1,4))$ and $(\Delta\delta(C(2,3) + \Delta\delta(C(5,6))/2$ are similar for analogous *p*-xylene and prehnitene complexes (Table 2 and ref. 1).

** Extensive side reactions occur in the systems $Hg(SbF_6)_2\text{-}1,3,5\text{-}C_6H_3\text{-t-}Bu_3$ at high L/M.

*** The footnote on p. 12 of ref. 1 inadvertently gives $\delta(C)_{((CD_3)_2CO)}$ as 10.36, 10.57, and 10.69 ppm at 260, 220 and 205 K, respectively. The shifts should be 29.4, 29.2 and 29.1 ppm.

sealed H-tube with an NMR tube attached via a sidearm. This complex and the others with t-butylated aromatic substrates had a great tendency to undergo side reactions if L/M > 1; these reactions were not investigated further in this work.

The ^{13}C spectra of most of the arenes in SO_2 have been given earlier [1,11]. New data are given in Table 3.

Magic-angle spinning ^{13}C-{^{1}H} NMR spectra of solids

Cross polarization 15.1 MHz ^{13}C NMR spectra were obtained from powdered samples loaded, under dry nitrogen, into a Beams-Andrew design hollow Kel-F rotor (0.7 ml internal volume) and spun at the magic angle at 1800 Hz [3,6]. Assignments of protonated and quaternary carbon resonances were confirmed by delayed decoupling experiments in which the proton resonant decoupling field was held off for 100 μs following the cross-polarisation contact and before data acquisition; protonated carbon signals are lost during this period [12]. Other assignments were made by comparison with the known [1] solution spectra.

Elemental microanalyses

Carbon and hydrogen microanalyses were performed by the Analytische Laboratorien, Elbach, W. Germany.

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