Carbon-13 Nuclear Magnetic Resonance Study of Methyl- and Phenylmercury(II) Compounds

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The ^{13}C chemical shifts of the methyl carbon in a wide range of compounds of methylmercury(II) and of the phenyl-ring carbons in several phenylmercury(II) compounds (HgRX) have been observed and rationalised. Direct carbon-13–mercury-199 couplings, $^1J(C-Hg)$, have also been observed in most of the compounds and are strongly dependent on the solvent as well as on the nature of the unidentate ligand X, as are the corresponding two-bond proton–mercury couplings, $^2J(H-Hg)$. Some very large values of $^1J(C-Hg)$ have been observed, {*e.g.* 2 661.1 Hz for phenylmercury(II) acetate in [$^2H_6$]dimethyl sulphoxide}. The observed variations of coupling constant are explicable either by a rehybridisation scheme or by a departure from strict molecular linearity in nucleophilic solvents.

THE proton shifts and proton–mercury couplings, $^2J(H-Hg)$, in a wide range of methylmercury(II) compounds of the type HgMeX (X = unidentate ligand) have been studied previously[1-3] as also have the ^{13}C n.m.r. spectra of dimethylmercury(II)[4] and diphenylmercury(II).[5] Scheffold[1] noted a strong dependence of $^2J(H-Hg)$ on X, and correlated these couplings with various characteristics of X, such as its (logarithmic) nucleophilicity and the stability of the Hg–X bond. Also, a strong solvent dependence of $^2J(H-M)$ couplings in metal alkyls has been observed with dimethylthallium(III)[6] and dimethyl-lead(IV) complexes[7,8] and with some neopentylmercury(II) compounds[9,10] in which at least one co-ordination position is presumed to be available for solvent molecules. In all the cases studied so far, including the present work, $^2J(H-M)$ increases with an increase in the co-ordinating ability or nucleophilicity of the solvent. The couplings can change by up to 30% with change of solvent, which is more than ten times the normal range of solvent dependence of direct coupling constants.

In the present study, the effect of varying X in HgRX (R = Me or Ph) on the ^{13}C chemical shifts and metal–carbon coupling constants were investigated for a wide range of ligands containing N, P, O, S, and Se donor atoms and halide-ion donors.

EXPERIMENTAL

Methyl- and phenyl-mercury(II) compounds were either obtained from Pfaltz and Bauer Inc. or prepared from related compounds by standard methods.[11] It was necessary to enrich the methyl group with ^{13}C in order to observe the couplings to ^{199}Hg in the less-soluble complexes. This was carried out by a published method[12] using 90 atom % $^{13}CH_3I$ obtained from Prochem Ltd. Selenomethionine was obtained from the Sigma Chemical Company, and other compounds used were reagent grade. Carbon-13 and ^1H n.m.r. spectra were observed on a Bruker WH 90 Fourier-transform spectrometer using standard conditions.[13]

RESULTS AND DISCUSSION

Observed shifts (p.p.m. from $SiMe_4$) and couplings (Hz) at 305 K (unless otherwise noted) are presented in the Table.

Shifts.—The observed shifts may be explained using existing theory.[14] Mason showed that the ^{13}C chemical

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shifts of substituted methanes may be divided into a diamagnetic contribution, capable of independent calculation but important only for directly bound atoms, and a paramagnetic contribution proportional to a mean reciprocal excitation energy of the molecules, $1/\Delta E$, as in the usual theory of temperature-independent paramagnetism. The quantity ΔE may be approximately identified, in simple monosubstituted methanes, with the $\sigma^* \leftarrow \sigma$ excitation energy of that bond to the heteroatom. It is thus directly related to the energy of that bond, so that a decrease in bond energy leads to a downfield shift. The total paramagnetic contribution in $HgMe_2$ is *ca.* +340 p.p.m.,[14] which implies a 7% increase in ΔE between $HgMe_2$ and $[HgMe]^+$. This increase is consistent with the observed *ca.* 30% increase in the C–Hg bond dissociation energy; for HgMeX literature values for the C-Hg bond dissociation energies are 215 (X = Me), 244 (I), 256 (Br), and 267 kJ mol^{-1} (Cl).[1] Presumably a strong covalent interaction of X with $[HgMe]^+$ transfers charge to the mercury atom and hence increases the electron–electron repulsion in the C–Hg bond, and to a lesser extent in the σ^* orbital involved in the notional excitation of energy ΔE.

Shifts (p.p.m.) and couplings (Hz) in HgMeX and HgPhX compounds

(*a*) HgMeX

X	Solvent	$\delta(^{13}C)$	^1J(C–Hg)	^2J(H–Hg)	Ref. and comment
dmso	$[^2H_6]$dmso acidified with CF_3SO_3H	1.4	1 936.9	260.6	
Me	pure liquid	23.7	692	101	1
	$[^2H_6]$dmso	23.1	725.6	105.1	
	$[^2H]$chloroform	23.4	688.5	101	
Water–$[OH]^-$	water, pH < 0	0.3	1 764	260	see also ref. 3
	water, pH 1.0	−0.8	1 750		
	water, pH 11.5	−0.8	1 309	204	see also ref. 3
$MeCO_2^-$	80% $MeCO_2H$	−1.3	1 624		
	water, pH 5.4	−0.5	1 629		
	$[^2H_6]$dmso	0.8	1 695.3		
	pyridine			220.8	1
Cl^-	$[^2H_6]$dmso	8.4	1 673.8	221.5	
	$[^2H]$chloroform	8.6	1 430.7	203.6	
	pyridine			215.2	1
	dioxan			209	1
Br^-	$[^2H_6]$dmso	11.7	1 630.9	217.7	
	$[^2H]$chloroform	12.8	1 393.6	196.9	
	pyridine			212.9	1
	dioxan			205	1
I^-	$[^2H_6]$dmso	17.1	1 540	208	see also ref. 2; broad satellites (315 K)
	$[^2H]$chloroform	18.8	1 301.3	184	
	pyridine			200	1
CN^-	$[^2H_6]$dmso	4.7			^{13}C coupling not observable
NCS^-	$[^2H_6]$dmso	0.0	1 710		bound $N^{13}CS^-$ at δ 128.4
Tetrahydrothiophen	$[^2H_6]$dmso	0.7	1 690		both ring ^{13}C resonances shift by 1.2 p.p.m. on co-ordination
PPh_3	$[^2H_6]$dmso	1.2	1 710		
Glycine	water, pH 7.05	−1.3	1 588.4	216	at 270 K; see ref. 3 for ^1H
L-2-Phenylalanine	water, pH 6.5	−2.7	1 582.5	220	at 265 K; see ref. 3 for ^1H
DL-Tyrosine	water, pH 3.66	−3.0	1 591.3		at 270 K
DL-Methionine	water, pH 0.29	5.8	1 601.0		at 280 K; S-bound at this pH
Seleno-DL-methionine	water, pH 0.47	8.6	1 510.2		at 280 K; Se-bound at this pH
DL-Cysteine	water, pH 7.8	9.8	1 256.8	174	at 280 K; S-bound at this pH; see ref. 3 for ^1H
Thioglycolic acid	water, pH 6.8	9.6	1 270.0		at 280 K; S-bound
DL-Penicillamine	water, pH 9.2	8.4	1 335.9		at 280 K; S-bound
$Hg(CH_2Ph)_2$	fused solid		638		at 390 K; ring couplings not reliably detected

(*b*) HgPhX

X	Solvent	$\delta(^{13}C)$	^nJ(C–Hg)	Ring carbon number (n)	Ref. and comment
Ph	fused solid (?)	unknown	1 186, 88 101.6, 17.8	1, 2, 3, 4	
	$[^2H_6]$dmso	172.5, 139.7 129.4, 128.7	1 275, 85.3 101.5, 10(?)		
$MeCO_2^-$	$[^2H_6]$dmso	147.1, 138.6 129.9, 129.7	2 661.1, 119.6 210.0, 36.6	1, 2, 3, 4	
	80% $MeCO_2H$	143.0, 137.5 129.6, 129.9	127, 218, 36	1, 2, 3, 4	C^1 resonance too weak to observe coupling
	$[^2H]$chloroform	144.0, 137.7 130.7, 130.4	122 203, 37	1, 2, 3, 4	
Br^-	$[^2H_6]$dmso	156.4, 138.2 129.9, 129.6	122 206, 38	1, 2, 3, 4	

The shifts were not very dependent on solvent. This is evidence that the shift mechanism (unlike the coupling mechanism) is not highly dependent on structure.

The largest shifts, other than for X = Me or halogen, are for X = $[SR]^-$ (cysteine, thioglycolic acid, and penicillamine), followed in order by SeRR′ (selenomethionine) and then SRR′ (methionine). This is also the order of the known binding constants.[3] Thus the ^{13}C shift of methylmercury(II) is a useful indicator both of the nature of X and of the covalent X–Hg bond strength. This has been of use in studying the interaction of methylmercury(II) with the enzyme Papain.[15]

Couplings.—The ligands X which give rise to substantial shifts also give rise to strongly solvent-dependent C–Hg couplings (except with $HgMe_2$). Almost parallel changes are apparent in the ^2J(H–Hg) methyl proton–mercury couplings (see Figure 1). In relatively non-co-ordinating solvents such as chloroform the ligand X reduces the coupling in much the same way as it increases the chemical shift δ, although by larger proportions. This link may be explained by standard theory, which predicts[16,17] that $^1J(\text{C–Hg}) \propto \alpha_C^2\alpha_{Hg}^2|\psi_{C(2s)}|^2|\psi_{Hg(6s)}|^2$ where α^2 is the *s* character of the (hybrid) atomic orbital used by each atom in the C–Hg bond and $|\psi_{(s)}|$ is the electron density at the nucleus of the *s* orbital involved in that hybrid. The increased negative charge on Hg which reduces ΔE and thus increases δ will also reduce $|\psi_{Hg(6s)}|^2$ by causing an expansion of the orbital. However, the changes in ^1J(C–Hg) (up to 64%) are much too large to be explained by this mechanism alone, and therefore must also involve changes in α_{Hg}^2, the only other likely variable.

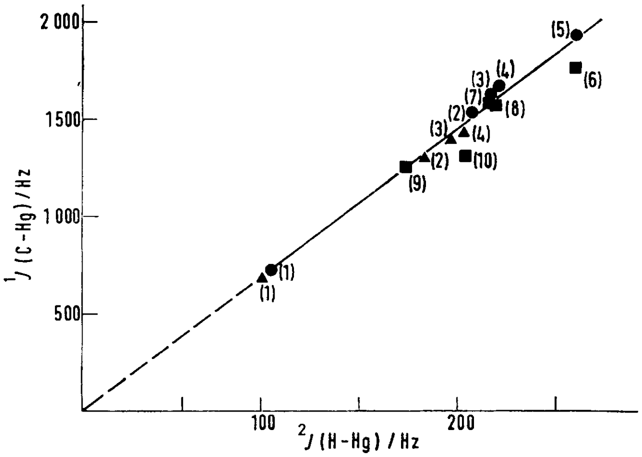

FIGURE 1 Correlation of ^1J(C–Hg) and ^2J(H–Hg) coupling constants in HgMeX compounds. X = Me (1), I (2), Br (3), Cl (4), dmso (5), H_2O (6), glycinate (7), L-2-phenylalaninate (8), cysteinate (9), and hydroxide (10). Solvents are $S(CD_3)_2O$ (●), $CDCl_3$ (▲), and $H_2O–D_2O$ (■)

With this theory, the decrease in ^1J(C–Hg) from 1 937 to 689 Hz between $[HgMe]^+$ and $HgMe_2$ reflects not only a loss of bond strength but also a reduction of the *s* character by a factor of up to one half, for in the latter compound the mercury 6*s* orbital must be symmetrically shared between the two C–Hg bonds. An exact halving would lower ^1J(C–Hg) to 968 Hz; the remaining 29% reduction actually observed would then be due to changes in $|\psi_{Hg(6s)}|^2$. This fits well with the observed reductions in bond dissociation energy.

The case of X = $[OH]^-$ is rather anomalous because ^1J(C–Hg) is strongly reduced, whereas δ (and hence presumably $|\psi_{Hg(6s)}|^2$) is barely affected. It appears that a very hard negative ion such as $[OH]^-$ does not transfer any charge to mercury, but does change that atom's hybridisation.

Solvent Effects.—The Table shows that nucleophilic solvents have the opposite effect to $[OH]^-$, tending always to increase ^1J(C–Hg). Three theories may be advanced for this. The first, due to Kawasaki and Majima,[7] is that nucleophilic solvents increase $|\psi_{Hg(6s)}|^2$. This explanation is hard to reconcile with the insensitivity of shifts to solvent or with simple electrostatics. The second theory is due to Shier and Drago;[6] in essence it is proposed that the mercury atom in $HgMe_2$ forms three $5d_{z^2}$–$6s$–$6p_z$ hybrid orbitals, namely two $d^{\frac{1}{2}}s^{\frac{1}{2}}p$ bonding hybrid orbitals and an *s–d* toroidal lone pair. In the $[HgMe]^+$ ion the p_z contribution to the bonding would no longer be necessary, so that the *s* character would double and the bond strength increase. In HgMeX, solvation would disfavour the *s–d* hybridisation and hence once again increase the *s* character of the C–Hg bond. The main objection to this theory is that, whilst it may hold for compounds of Pb^{IV} and Tl^{III}, it predicts rather smaller ^1J(C–Hg) couplings than are in fact observed, by limiting the C–Hg bond in the $[HgMe]^+$ ion to *ca.* 50% *s* character.

The third possibility is that co-ordination of nucleophilic solvents causes bending of the molecule, thus altering the hybridisation pattern and concentrating *s* character in the strongest bond, *i.e.* C–Hg. This proposal is consistent with the small solvent effect in $HgMe_2$ where such asymmetric rehybridisation cannot occur. It also explains the relatively large coupling constants, but has the drawback of being structurally abnormal.

Bending of methylmercury(II) compounds has previously been proposed,[18] but has only been clearly established for (2,2′-bipyridyl)methylmercury(II)[19] for which a 16° deviation from linearity leads to an increase of 9 Hz in ^2J(Hg–H).

Phenylmercury(II) *Compounds.*—Because of low solubilities, the data obtained for HgPhX compounds are more limited. In particular, the important one-bond coupling constant is hard to measure because of the lack of relaxation and nuclear-Overhauser enhancement from an attached proton. Nevertheless, the ^1J(C–Hg) coupling constants of 1 186 Hz ($HgPh_2$) and 2 661.1 Hz ($[HgPh(O_2CMe)]$) are respectively 171 and 157% of those in the corresponding methylmercury(II) compounds, indicating the importance of both the 33% increase in *s* character between an sp^3 and an sp^2 hybrid carbon orbital, and also an increase in $|\psi_{Hg(6s)}|^2$. This latter

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increase is attributable to the phenyl group being less electropositive than methyl, which is why the fractional increase above 133% is nearly twice as great in the diphenyl compound.

Although the direct ${}^{1}J$(C–Hg) coupling is not readily observable in most cases, it seems likely, judging from the two compounds in which it is available, that it is proportional to the more easily measured ${}^{n}J$(C–Hg) couplings ($n = 2$—4). If this is the case, then it would appear that bromide ion has a similar effect on the C–Hg coupling in phenylmercury(II) bromide in dimethyl sulphoxide (dmso) as in methylmercury(II) bromide in dmso. Also, in HgBrPh the downfield shift of C^1 (relative to the acetato-compound) is 13.4 p.p.m., which is very close to the value in the methyl compounds of 13.0 p.p.m. The other carbons are almost constant in shift, which suggests that any π interaction of the phenyl ring with the mercury atom is small.

Amino-acid Compounds.—Unusually low shifts of the methyl carbon are observed with the nitrogen-bound phenylalanine and tyrosine compounds of methylmercury(II).[15] These are consistent with the low ^{1}H shifts in the phenylalanine compound observed by Rabenstein and his co-workers[3] and support his contention of a hydrophobic interaction between the phenyl ring and the methyl group of the methylmercury(II) moiety. The figures quoted in the Table are for the major nitrogen-bound species. Other carboxylate-bound species are also observable in this system, and give rise to separate ^{13}C resonances under appropriate conditions of temperature and pH.[20] One of the most clearly separated of these resonances is that of C^4 on the phenyl ring, which is further strong confirmation of Rabenstein's hydrophobic-interaction hypothesis.

Dibenzylmercury(II).—The alkylcarbon–mercury coupling of 638 Hz is somewhat less than the 692 Hz observed for $HgMe_2$. However, the coupling is still far larger than would be predicted if the alkyl carbon were substantially sp^2 hybridised, using a p orbital to bind to mercury, as suggested on theoretical grounds by Scherr *et al.*[21] for benzylmercury(II) bromide.

Methylmercury(II) *Iodide.*—Broad ^{199}Hg satellites were observed in the ^{13}C spectrum (Figure 2) as in the ^{1}H spectrum.[2] The widths of the satellite peaks (*ca.* 20 Hz) were the same, within experimental error, as those observed in the proton spectrum. This supports the proposed relaxation-broadening mechanism.[2]

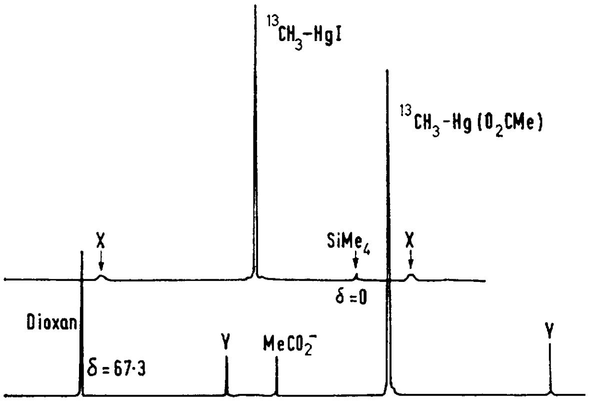

FIGURE 2 Hydrogen-1 decoupled ^{13}C N.m.r. spectra of *ca.* 10% ^{13}C-enriched methylmercury(II) compounds showing broad ^{13}C-^{199}Hg satellite resonances (X) in the iodo-compound (solvent $CDCl_3$ with $SiMe_4$ as standard), and sharp satellites (Y) in the acetato-compound (solvent D_2O with dioxan as standard)

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