Journal of Organometallic Chemistry, 204 (1981) 1—12
Elsevier Sequoia S.A., Lausanne —Printed in The Netherlands

NMR INVESTIGATION OF ARYL- AND BENZYL-MERCURIC COMPOUNDS; EXPERIMENTAL EVIDENCE FOR σ—π CONJUGATION INVOLVING THE CARBON—MERCURY BOND

ELIE MICHEL

E.R. 84, Universite P. et M. Curie, 4, place Jussieu, 75230-Paris Cedex 05 (France)

JACQUES PERIE * and ARMAND LATTES

ERA 264, Laboratoire des Composes Azotes Polyfonctionnels. UER-PCA, Université Paul Sabatier, 118, route de Narbonne 31077-Toulouse Cedex (France)

(Received June 12th, 1980)

Summary

^{199}Hg and ^{13}C NMR spectra of a large number of aryl- and benzyl-mercuric compounds ($ArHgX$ and $ArCH_2HgX$) have been obtained, in order to throw more light on the relationship between the coordination state of the mercury atom and its NMR parameters. For the aryl series ArHgCl there is a good correlation between the ^{199}Hg chemical shift and σ^+, with electron releasing substituents in Ar resulting in an upfield chemical shift. This correlation arises from the contribution of the paramagnetic term to the chemical shift. Comparison of the NMR parameters in ArHgCl and $ArCH_2HgCl$ provides unambiguous evidence for conjugation between the C—Hg bond in $ArCH_2HgCl$ and the aromatic ring, the C—Hg system behaving as a strongly donating group. This is explained in terms of vertical stabilization, as proposed by Traylor.

In our investigation of the reactivity of organomercuric compounds [1], we have made use of the magnetic properties of the ^{199}Hg isotope, which has spin 1/2, and natural abundance 16.8%. Our initial studies involved satellite peaks in ^{1}H NMR spectra due to ^{199}Hg—H coupling [2]. Recently, we have turned to direct measurement of the ^{199}Hg NMR spectra. Examination of the literature shows that although certain features of ^{199}Hg NMR spectra have been investigated [3], more results need to be obtained before there is a thorough understanding of the correlation between ^{199}Hg chemical shift and the structure and

---

* To whom inquiries should be addressed.

coordination about the mercury atom. Such a correlation would be particularly useful in the study of biological processes of environmental importance.

We have therefore measured the ^{199}Hg chemical shift and the ^{199}Hg coupling with ^{1}H and ^{13}C atoms for compounds of the type RHgX, R = aryl or benzyl. Relatively little NMR investigation has been carried out on such compounds, as compared to that devoted to the molecules of the R_2Hg type, perhaps because of the generally low solubility of RHgX. The RHgX molecules however offer more scope for the study of concentration and solvent effects, because of their greater tendency for self association and complexation [4]. We have chosen aromatic mercuric compounds to investigate through Hammett correlations electronic effects on the ^{199}Hg resonances. It has been suggested that the paramagnetic term makes the predominant contribution to the chemical shift [3d]. The existence of a contrary proposal [5], however, convinced us that further investigation was necessary.

We have compared aryl and benzyl compounds. On the simplest picture this should allow a comparison of the change in the ^{199}Hg resonance produced by the same electronic effect as the distance to the ^{199}Hg atom is varied. There is moreover considerable evidence for some form of unusual behavior in unsaturated compounds bearing a C—Hg bond. This has been seen previously in photoelectron spectroscopy [6,7] and in reactivity variations [8,9]. The special behavior has been rationalized in terms of a conjugation between the C—Hg bond and the π system, a conjugation which has been ascribed to "*d* orbital participation" [10], σ—π conjugation [9a], or vertical stabilization [9b], and this special effect is not present in neopentylmercuric compounds [11]. The effect accounts for certain reactivity effects in organometallic compounds; for example, there is a recently reported case of stereoelectronic control by the C—Hg bond on substitution reactions [12]. We therefore thought if of interest to see if this conjugation effect also shows up in the NMR spectra.

Results and discussion

Concentration effects

Table 1 lists values of the ^{199}Hg chemical shift for C_6H_5HgX and $C_6H_5CH_2$-HgX in DMSO and $CDCl_3$. The data show that there is not dependence on concentration for RHgCl in either solvent, or for RHgOAc in DMSO. The latter compounds, however, do show some dependence on concentration in $CDCl_3$. This behavior can be ascribed to the tendency of RHgOAc to dimerize in this weakly complexing solvent [4], while the strongly donating DMSO inhibits dimerization. In the case of R_2Hg, where there is known to be little self association, no concentration effect is observed in either solvent. In the light of these results, on further discussions will usually be restricted to spectra obtained in DMSO.

Effect of ligand X

With both C_6H_5HgX and $C_6H_5CH_2HgX$, the ^{199}Hg chemical shift shows a dependence on the amount of ionic character in the Hg—X bond, moving increasingly downfield as the ionic character increases (Table 1). This variation is attributed to the contribution of the paramagnetic term to the chemical

TABLE 1

^{199}Hg CHEMICAL SHIFTS FOR C_6H_5HgX AND $C_6H_5CH_2HgX$ (IN ppm RELATIVE TO $(CH_3)_2Hg$)

Compound	Solvent	Conventration (M)	Chemical shift
C_6H_5HgCl	DMSO	1	1186
		0.125	1187
C_6H_5HgOAc	$CDCl_3$	1	1440
		0.5	1438
		0.125	1435
	DMSO	1	1442
		0.5	1442
		0.125	1442
	Pyridine	1	1377
C_6H_5HgCN	DMSO	1	1123
$C_6H_5HgCH_3$	DMSO	1	812
$C_6H_5HgClO_4$	DMSO		1358
$C_6H_5HgC_6H_5$	$CDCl_3$	1	752
$C_6H_5CH_2HgCl$	$CDCl_3$	1	1146
		0.5	1146
		0.125	1146
	DMSO	1	1184
		0.5	1185
		0.125	1185
	Pyridine	1	1109
$C_6H_5CH_2HgOAc$	$CDCl_3$	1	1401
		0.5	1399
		0.125	1395
		0.065	1395
	DMSO	1	1399
		0.125	1398
	Pyridine	1	1338
$C_6H_5CH_2HgCN$	$CDCl_3$	0.5	1010
		0.125	1001
	DMSO	0.5	1057
		0.125	1058
$C_6H_5CH_2HgClO_4$	DMSO	1	1247
$C_6H_5CH_2HgCH_3$	$CDCl_3$	1	692
	DMSO	1	757

shift. For the two cases for which information is available on the proportion of *s* character in the Hg—X bond, viz. $C_6H_5HgCH_3$ (67%) and C_6H_5HgCl (53%) [1], the ^{199}Hg chemical shifts show that the resonance lies further upfield the greater the *s* character.

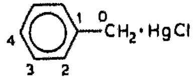
Solvent effects

Large solvent effects have previously been observed in the ^{199}Hg NMR spectra of compounds of general formula R_2Hg, both on the actual chemical shifts [3e] and on various coupling constants [14]. The shielding effect of basic solvents was interpreted in terms of a Lewis type interaction, while the variation

TABLE 2

SOLVENT EFFECTS ON ^{13}C CHEMICAL SHIFTS AND ^{13}C—^{199}Hg COUPLING CONSTANTS

Compound and solvent	C(0)		C(1)		C(2)		C(3)		C(4)	
	δ(ppm)	J(Hz)	δ(ppm)	J(Hz)	δ(ppm)	J(Hz)	δ(ppm)	J(Hz)	δ(ppm)	J(Hz)
$C_6H_5CH_2HgCl$										
$CDCl_3$	37.1	1426.7	139.2	158.7	128.5	106.8	128.7	53.4	125.5	64.1
DMSO	35.1	1632.7	141.7	155.6	128.2	112.9	127.9	53.4	124.1	64.1
pyridine	33.2	1698.3	143.1	158.7	128.6	112.9	128.6	52.4	124.4	65.6
$C_6H_5CH_2HgOAc$										
$CDCl_3$	30.0	1438.4	139.5	157.2	128.5	111.3	128.7	50.3	125.4	62.5
$C_6H_5CH_2HgCN$										
$CDCl_3$	33.5	1310.0	140.4	121	128.5	84.6	128.7	40	125.1	45.9
C_6H_5HgCl										
DMSO			151.2	2634	136.6	117.6	128.1	209.5	127.8	36.2
pyridine			151.3		137.5	115.9	129.9	410.5	128.2	24.4
C_6H_5HgOAc										
$CDCl_3$			142.6		136.4	129.5	129.1	204.5	129.4	36.6
pyridine			146.0	2660	137.8	118.3	128.8	210.8	128.3	37.0

[a] Numbering follows 

in the coupling constants was related to changing *s* character in the orbitals about the mercury atom.

As in R_2Hg type compounds [3d], the unsymmetrical derivatives studied are sensitive to solvent effects, the chemical shift moving downfield in the sequence DMSO < $CDCl_3$ < pyridine (Table 1); effects other than the solvent basicity must be involved, since pyridine and DMSO have similar basicities on the Gutman scale [17].

A second factor which must be considered is the variation with solvent of the amount of *s* character in the orbitals around the mercury atom. As seen in Table 2, the ^{199}Hg—^{13}C coupling constant for the benzylic carbon in $C_6H_5CH_2$-HgCl increases considerably on going from $CDCl_3$ to pyridine. These coupling constants are related to the *s* character through the α^2Hg term in the equation below [15] (the α^2 term corresponds to the *s* character in the hybrid atomic orbital contributing to the C—Hg bond).

$$J(^{199}\text{Hg}—^{13}\text{C}) = \gamma_{\text{Hg}}\gamma_{^{13}\text{C}}(\alpha^2_{\text{Hg}}\,\alpha^2_{^{13}\text{C}}/\Delta E)\,|\Psi_{\text{Hg}}|^2\,|\Psi_{^{13}\text{C}}|^2$$

A third consideration involves the question of the actual form of the compound in solution, since these mercuric compounds are capable of forming stable solvates in strongly donating solvents. For example, the ^{199}Hg chemical shift of 2,2′-bipyridylmethylmercury nitrate is shifted 143 ppm compared to that of pyridylmethylmercury nitrate [16], the main difference between these two compounds being that the coordination number of mercury is 3 in the former compound and 2 in the latter. In other words there may be a sizeable contribution to the upfield shift observed in our studies on pyridine solutions due to coordination of a solvent molecule to the mercury atom. It is also known that DMSO is capable of forming solvates by coordination through its oxygen atom [18], but the effect of this on the ^{199}Hg chemical shift is unknown.

Aryl Derivatives

Table 3 lists values of the ^{199} Hg chemical shift for a series of compounds of general formula ArHgCl in DMSO. As seen in Figure 1 the shifts are reasonably

TABLE 3

^{199}Hg CHEMICAL SHIFTS RELATIVE TO $(CH_3)_2Hg$ OF ARYL- AND BENZYL-MERCURIC CHLORIDES IN DMSO (CONCENTRATION, 0.75 *M*)

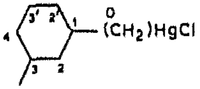
XC_6H_4HgCl X	δ ^{199}Hg (ppm)	$XC_6H_4CH_2HgCl$ X	δ ^{199}Hg (ppm)
p-CH_3	1162.1	*p*-CH_3	1172.6
p-C_2H_5COO	1212.3	*p*-Cl	1181.0
p-CH_3O	1142.3	*p*-F	1183.2
p-Br	1182.4	*p*-CH_3O	1133.2
p-NO_2	1231.7	*p*-NO_2	1210.3
H	1182.6	H	1184.4
m-CH_3	1181.9	*m*-CH_3	1172.6
m-CF_3	1222.9	*m*-Cl	1168.2
m-CH_3O	1129.3	*m*-F	1182.6
m-Br	1234.3		
m-NO_2	1238.1		
m-F	1206.2		

TABLE 4

^{13}C NMR CHEMICAL SHIFTS AND ^{199}Hg—^{13}C COUPLING CONSTANTS FOR ArHgCl AND ArCH$_2$HgCl IN DMSO

	C(0)		C(1)			C(2)			C(3)			C(4)		
	δ(ppm)	J(Hz)	δ(ppm)		J(Hz)	δ(ppm)		J(Hz)	δ(ppm)		J(Hz)	δ(ppm)		J(Hz)
$ClC_6H_4CH_2HgCl$	33.7	1669.3	141.1		160.2	129.9		111.4	127.7		54.9	128.4		67.1
p-$FC_6H_4CH_2HgCl$	33.8	1670.1	137.9		157.2	129.7	Hg F	102 5.5	114.6	F	21.1	159.6	F	240.5
m-$CH_3C_6H_4CH_2HgCl$	34.7	1641.8	141.6		155.6	C(2) 125.3 C(2′) 128.9		113.7 116.1	C(3) 136.9 C(3′) 127.9		54.6 52	124.8		54.9
m-$ClC_6H_4CH_2HgCl$	34.8	1638.8	141.5		152.6	C(2) 125.3 C(2′) 128.9		104 110	C(3) 136.9 C(3′) 127.9		54.9 52	124.8		61
m-$FC_6H_4CH_2HgCl$	34.1	1678.5	145.3	Hg F	158 7.6	C(2) 114.7	Hg F	109.9 21.4	C(3) 162.0	Hg F	41.1 242.6	111.8	Hg F	64.5 21.4
						C(2′) 124.6	Hg F	109.9 0	C(3′) 129.6	Hg F	54.8 9.2			
$C_6H_5CH_2HgCH_3$	46.6	634.7	139.5		155.6	127.61			127.8			125.3		61
p-$EtOOCC_6H_4HgCl$			158.3			136.3		120.7	128.2		210.5	129.1		
p-$CH_3C_6H_4HgCl$			143.9			122.3		140.4	98.7		224.3	127.1		
p-BrC_6H_4HgCl			150.3			138.4		132.7	130.6		218.2	121.4		
m-$CH_3OC_6H_4HgCl$			158.6		1920	C(2) 122.2 C(2′) 128.5		122 79	C(3) 152.5 C(3′) 128.9		 247.8	113.2		53.7
m-$CF_3C_6H_4HgCl$			153.4			C(2) 140.9 C(2′) 132.2	 F Hg	119 3 141.9	C(3′) 128.5		207.5	124.2	F Hg	3 36.6
m-$NO_2C_6H_4HgCl$			147.1			C(2) 131.0 C(2′) 143.6		157 119	C(3) 154.3 C(3′) 128.3	 Hg	 219.7	122.3		35.1
$C_6H_5HgCH_3$			170.8		1272.4	127.7		104	138.0		168	127.0		28
m-FC_6H_4HgCl			153.7	JF	1.5	C(2) 123.0	F Hg	19.8 122	C(3) 161.6	F Hg	246 304	114.4	F Hg	19.8 35.4
						C(2′) 132.8	F Hg	3.0 107	C(3′) 129.3	F Hg	6.1 247			

Numbering follows



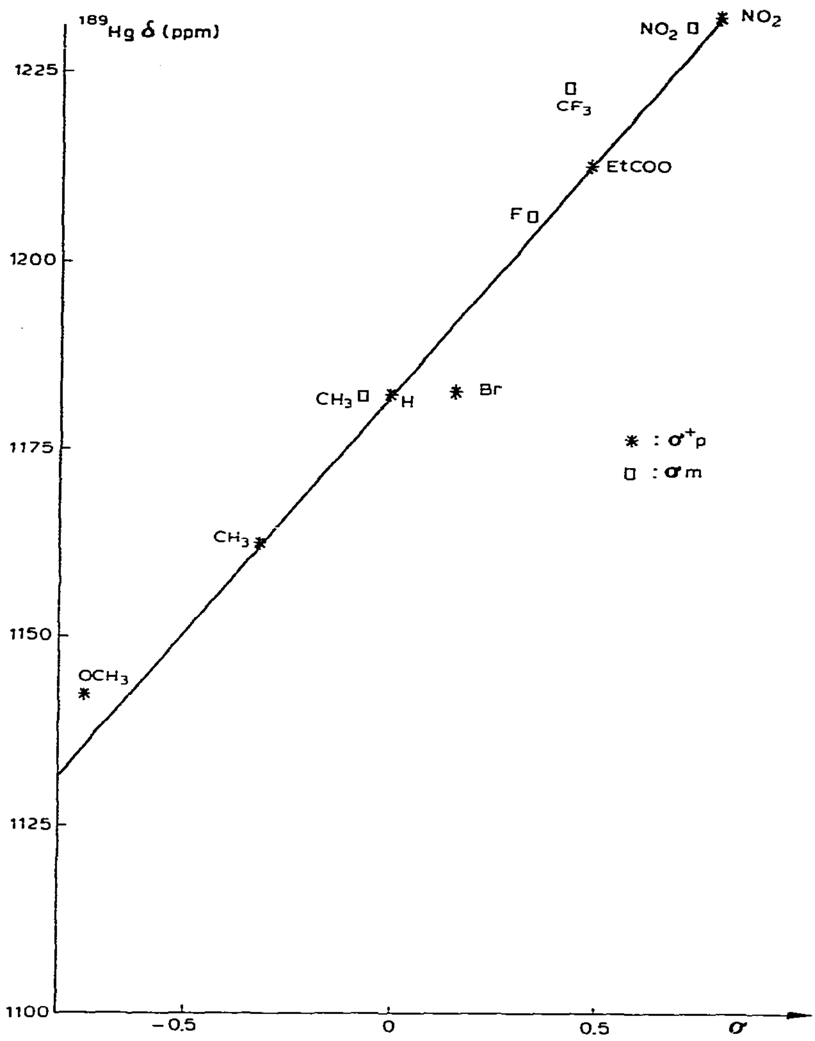


Fig. 1. Substituent effects on the ^{199}Hg chemical shifts of arylmercury compounds.

well correlated with the σ^+ parameter of the aromatic substituent, with upfield chemical shifts for electron donating substituents. This observation confirms that the important contribution to the chemical shift is the magnetic anisotropy. Interestingly an opposite order is found for compounds of the type Ar_2Hg, for which electron-releasing substituents cause a downfield chemical shift. It is not obvious why the two series should have completely opposite orders. With the diaryl compounds it is possible that the cumulative effect of the substituents produces a large change in the electron density about the mercury atom, with a subsequent change in solvation, the combination of these effects resulting in the observed difference.

Table 4 lists ^{13}C NMR chemical shifts and ^{13}C—^{199}Hg coupling constants for ArHgCl in DMSO. ^{13}C chemical shifts have previously been reported for such

TABLE 5

^{13}C NMR PARAMETERS OF SOME REPRESENTATIVE ARYL AND BENZYL DERIVATIVES

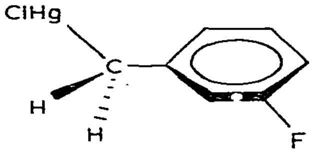
	δ(C(1)) (ppm)	J(Hg—C(1)) (Hz)	δ(C(2)) (ppm)	J(Hg—C(2)) (Hz)	δ(C(3)) (ppm)	J(Hg—C(3)) (Hz)	δ(C(4)) (ppm)	J(Hg—C(4)) (Hz)
C_6H_5HgCl	151.2	2634	136.4	118	127.9	209	137.6	37
p-$CH_3C_6H_4HgCl$	147.5	2624	136.2	124	128.6	221	136.7	35
p-$NO_2C_6H_4HgCl$	161.8	2827	137.7	139	121.9	216	147.0	48
$C_6H_5CH_2HgCl$	141.7	156	128.2	113	128.0	53	124.1	64
p-$CH_3C_6H_4CH_2HgCl$	138.5	157	128.1	116	128.6	55	133.0	69
p-$NO_2C_6H_4CH_2HgCl$	145.0	155	130.0	123	129.4	53	147.20	58

compounds [21,22] but for rather limited sets of substituents, and peak assignments were made by use of additivity relationships. Our peak assignments are based on comparison of ^{13}C chemical shifts and ^{13}C—^{199}Hg coupling constants of the compound in question with the same parameters in m-C_6H_4HgCl. Assignment of the peaks in the latter compound can be made unambiguously by using the ^{13}C coupling constants with both the ^{199}Hg atom and the F atom. Our assignments do, in fact, agree with those published previously [21,22].

Benzyl derivatives

Tables 3 and 4 also list ^{199}Hg and ^{13}C chemical shifts for a set of compounds of general formula $ArCH_2HgCl$. The ^{199}Hg chemical shifts show a similar overall dependence on the electronic nature of the substituents as is in the ArHgCl series, in that electron-releasing groups cause an upfield chemical shift. As expected, there is attenuation by the insulating benzylic carbon, so that the range of shifts observed is smaller in the benzylic series. This contrasts with the pattern observed in the ^{13}C NMR parameter (see later).

As in the ArHgCl series, ^{13}C chemical shift assignments were made on the basis of a comparison with a *meta* fluoro compound m-$FC_6H_4CH_2HgCl$. An interesting feature with this compound is that the two coupling constants between the mercury atom and the *ortho* carbons are identical. This is consistent with the conformation shown in the structure below, a conformation predicted to be an energy minimum by extended Huckel calculations [23] and rationalized in terms of σ—π conjugation.



More substantial evidence for such an interaction can be seen in comparing the NMR parameters for ArHgCl and $ArCH_2HgCl$, as is summarized in Table 5. In particular, the introduction of the CH_2 group causes a significant upfield shift in the position of the resonance for the *ortho* and *para* carbon atoms, but has very little effect for the *meta* carbon. In addition, the coupling constants between the mercury atom and the *ipso* ring carbon atom, and the mercury and the *meta* carbon decrease on introduction of the CH_2 group, from 2800 to 100 Hz, and 200 to 50 Hz, respectively. However the couplings between the mercury atom and the *ortho* and *para* carbon atoms are only slightly changed, that with the *para* carbon actually increasing. These two observations are best interpreted in terms of an increase in the electron density on the aromatic ring on replacing HgCl by CH_2HgCl, the effect being greatest at the *ortho* and *para* positions. The CHg group thus behaves as an electron-donating system.

Further evidence is provided by the data in Table 6, where relative ^{13}C chemical shifts for a series of compounds ArX : $ArCH_2X$ are listed. Except for X = HgCl, a downfield shift at the *ortho* and *para* positions is observed on going from the aryl to the benzyl compound, probably because the heteroatom is no longer conjugated in the latter case. With the mercuric compounds, however, a large upfield shift is observed, as a consequence of the increased electron den-

TABLE 6

CHEMICAL SHIFT DIFFERENCES OF AROMATIC CARBON ATOMS FOR $C_6H_5X \rightarrow C_6H_5CH_2X$ (ppm)

X	C(1)	C(2)(*ortho*)	C(3)	C(4)(*para*)
-H	+9.1	+0.3	+0.3	−2.8
-OH	−14.1	+11.4	−1.5	+6.2
$-NH_2$	−2.6	+12.2	−0.6	+7.5
-Cl	+3.2	0	−1	+2.3
-HgCl	−10	−8	0	−3.5

sity. We conclude, therefore, that the NMR spectra provide further evidence for the σ—π conjugation effect of the C—Hg bond in compounds where it can be expected to operate.

Experimental section

Arylmercuric chlorides (Table 7) were prepared by the action of finely divided copper on the diazonium chloride-mercuric chloride double salt [24]. C_6H_5HgCN was obtained by mixing stoichiometric amounts of silver cyanide and phenylmercuric chloride in dimethylformamide. $C_6H_5HgClO_4$ was prepared by reaction of an aqueous solution of sodium perchlorate with phenylmercuric acetate in chloroform. $C_6H_5HgCH_3$ was prepared by the addition at 0°C of 0.02 mole of phenylmercuric chloride to 0.04 mole of methyl iodide.

Benzylmercuric chlorides (Table 8) were usually obtained by reaction of mercuric chloride with the corresponding Grignard reagent, as previously described for the parent compound [25]; we obtained significantly better yields by using tetrahydrofuran as solvent in place of diethyl ether.

TABLE 7

ARYLMERCURIC COMPOUNDS

$X\text{-}C_6H_4HgY$	Starting material	Yield (%)	M.p. (°C)
C_6H_5HgCl	Merck		258
$p\text{-}CH_3C_6H_4HgCl$	$p\text{-}CH_3C_6H_4NH_2$	62	240(benzene)
$m\text{-}CH_3C_6H_4HgCl$	$m\text{-}CH_3C_6H_4NH_2$	68	177
$p\text{-}CH_3OC_6H_4HgCl$	$p\text{-}CH_3OC_6H_4NH_2$	46	250(EtOAc)
$m\text{-}CH_3OC_6H_4HgCl$	$m\text{-}CH_3OC_6H_4NH_2$	42	164
$p\text{-}BrC_6H_4HgCl$	$p\text{-}BrC_6H_4NH_2$	30	256(benzene)
$m\text{-}BrC_6H_4HgCl$	$m\text{-}BrV_6H_4NH_2$	40	206(ethanol)
$p\text{-}EtOOCC_6H_4HgCl$	$p\text{-}EtOOCC_6H_4NH_2$	44	218(ethanol + acetone)
$m\text{-}CF_3C_6H_4HgCl$	$m\text{-}CF_3C_6H_4NH_2$	50	148(ethanol + w.)
$p\text{-}NO_2C_6H_4HgCl$	$p\text{-}NO_2C_6H_4NH_2$	55	264
$m\text{-}NO_2C_6H_4HgCl$	$m\text{-}NO_2C_6H_4NH_2$	59	238(sublim.)
$m\text{-}FC_6H_4HgCl$	$m\text{-}FC_6H_4NH_2$	33	254(acetone)
C_6H_5HgOAc	Merck		147
$p\text{-}CH_3C_6H_4HgOAc$	$p\text{-}CH_3C_6H_4HgCl$		183
C_6H_5HgCN	$C_6H_5HgCl + AgCN$		204
$C_6H_5HgClO_4$	$C_6H_5HgOAc + NaClO_4$		250(decomp.)
$C_6H_5HgCH_3$	$C_6H_5HgCl + CH_3MgI$	80	
$C_6H_5Hg\text{—}C_6H_5$	Eastman Kodak		122

TABLE 8

BENZYLMERCURY COMPOUNDS

$XC_6H_4CH_2HgY$	Starting material	Yield (%)	M.p. (°C)
$C_6H_5CH_2HgCl$	$C_6H_5CH_2Cl$	96	105(xylene + ethanol)
p-$CH_3C_6H_4CH_2HgCl$	p-$CH_3C_6H_4CH_2Cl$	76	143
m-$CH_3C_6H_4CH_2HgCl$	m-$CH_3C_6H_4CH_2Cl$	70	109.5
p-$ClC_6H_4CH_2HgCl$	p-$ClC_6H_4CH_2Cl$	48	146
m-$ClC_6H_4CH_2HgCl$	m-$ClC_6H_4CH_2Cl$	47	110
p-$FC_6H_4CH_2HgCl$	p-$FC_6H_4CH_2Cl$	30	144
m-$FC_6H_4CH_2HgCl$	m-$FC_6H_4CH_2Cl$	72	118
p-$CH_3OC_6H_4CH_2HgCl$	p-$CH_3OC_6H_4CH_2OC_2H_5$	33	107—110
p-$NO_2C_6H_4CH_2HgCl$	p-$NO_2C_6H_4CH_2Cl$	31	152—155
$C_6H_5CH_2HgOAc$	$C_6H_5CH_2HgCl + AgOAc$	97	122
$C_6H_5CH_2HgCN$	$C_6H_5CH_2HgCl + AgCN$	95	104
$C_6H_5CH_2HgCH_3$	$C_6H_5CH_2HgCl + IMgCH_3$	80	
$C_6H_5CH_2HgClO_4$	$C_6H_5CH_2HgOAc + NaClO_4$	—	

p-Methoxybenzylmercuric chloride was prepared as follows. *p*-Methoxybenzyl ethyl ether (0.05 moles), made from p-$CH_3OC_6H_4CH_2ONa$ and ethyl bromide [25], was added to 3 g of finely divided lithium at −15°C under argon to produce p-$CH_3OC_6H_4CH_2Li$. After one hour the excess lithium was separated by decantation under argon, and 0.05 moles of $HgCl_2$ in 30 ml of anhydrous THF added. The mixture was poured into 400 ml of ice mixed with 20 ml of concentrated hydrochloric acid, the resulting solid filtered, washed with water, and recrystallized from acetone (yield, 33%; mp, 138°C).

p-Nitrobenzylmercuric chloride was made as above from the reaction of $HgCl_2$ and p-$NO_2C_6H_4CH_2Li$, the latter prepared from 2 g of finely divided lithium and 0.03 mole of p-$NO_2C_6H_4CH_2Cl$ in anhydrous ether. p-$NO_2C_6H_4$-HgCl was crystallized from 1 : 1 xylene : ethanol (yield, 31%; mp, 155°C). This compound was also prepared by nitration of $C_6H_5CH_2HgCl$ (0.18 mole) dissolved in glacial acetic acid, and addition at 0°C of a mixture of 5 ml of concentrated sulfuric acid ($d = 1.83$) and 5 ml of nitric acid ($d = 1.4$). The mixture was stirred at 20°C for 2 h before work-up (yield, 29%; mp, 158°C).

$C_6H_5CH_2HgOAc$ was obtained by adding a stoichiometric amount of silver acetate to a solution of $C_6H_5CH_2HgCl$ in methanol. $C_6H_5CH_2HgCN$ was obtained similarly by use of silver cyanide. $C_6H_5CH_2HgCH_3$ was obtained as described above for $C_6H_5HgCH_3$. $C_6H_5CH_2HgClO_4$ was obtained by treating a solution of $C_6H_5CH_2HgCl$ in benzene with aqueous sodium perchlorate, using triethylbenzylammonium chloride as a phase transfer agent. This procedure gave a 60 : 40 mixture of $C_6H_5CH_2HgClO_4$ and $C_6H_5CH_2HgCl$.

^{13}C NMR spectra were recorded on a Cameca 250 MHz spectrometer, with Fourier transform: frequency for ^{13}C, 62.82 MHz; pulse, 7 μs: acquisition time 0.65 sec; delay, 3.4 sec; 5000 to 15000 scans.

^{199}Hg NMR spectra were obtained on a Brucker 90 MHz spectrometer, frequency for ^{199}Hg, 16.044 MHz: pulse, 4 μs; acquisition time, 0.8 sec; delay 450 μsec; 5000 to 200,000 scans. Calibration was made with dimethylmercury as reference zero, $Hg(OAc)_2$, 0.5 M in HOAc, $\delta = 2398.9$ ppm; $Hg(OAc)_2$, 0.5 M in pyridine, $\delta = 1946$ ppm; $Hg(OAc)_2$, 0.5 M in DMSO, $\delta = 2303.8$ ppm;

$Hg(NO_3)_2$, 2 *M* in HNO_3, $\delta = 2317.6$ ppm, values in agreement with those previously determined [3c,3d]. The commonly used diphenylmercury ($\delta = 211$ ppm) was employed as an external reference.

Acknowledgement

Financial support by the Centre National d'Exploitations des Oceans is fully acknowledged. The authors are grateful to Messrs. Bon and Beteille (^{13}C NMR), and Messrs. Tran and Dall'Ava (^{199}Hg NMR) for their excellent technical assistance.

References

1 M.B. Gasc, J. Perie and A. Lattes, Tetrahedron, 34 (1978) 1943.
2 J. Perie, J.P. Laval, J. Roussel and A. Lattes, Tetrahedron Lett., (1971) 4399.
3 a) G.E. Maciel, in T. Axenrod and G.A. Webb (Eds.), NMR Spectroscopy of Nuclei other than Protons, J. Wiley, New York, 1974; b) C. Schuman, H. Dreeskamp and K. Hildenbrand, J. Magn. Reson., 18 (1975) 97; c) M. Borzo and G.E. Maciel, ibid., 10 (1973) 388; d) M. Borzo and G.E. Maciel, ibid., 19 (1975) 279; e) M.A. Sens, M.K. Wilson, P.D. Ellis and J.D. Odon, ibid., 19 (1975) 322; f) A.J. Brown, O.W. Howarth and P. Moore, ibid., 28 (1977) 317.
4 I.P. Beletskaya, K.P. Butin and O.A. Reutov, Organometal. Chem. Rev., 7 (1971) 51.
5 P.R. Wells in J.J. Zuckerman (Ed.), Determination of Organic Structures by Physical Methods, vol. 4, Academic Press, New York, 1971.
6 H. Schmidt, A. Schweig and G. Manuel, J. Organometal. Chem., 51 (1973) C1.
7 A. Hosomi and T.G. Traylor, J. Amer. Chem. Soc., 97 (1975) 3682.
8 W. Hanstein and T.G. Traylor, Tetrahedron Lett., (1967) 4451.
9 a) T.G. Traylor, H.J. Berwin, J. Jerkunica and M.C. Hall, Pure and Applied Chemistry, 30 (1972) 599; b) T.G. Traylor and D.F. Eaton, J. Amer. Chem. Soc., 96 (1974) 1226.
10 G.E. Coates, M.L. Green and K. Wade, Organometallic compounds, vol. II, Ed. Methuen, London, 1968.
11 G. Singh, J. Organometal. Chem., 99 (1975) 251.
12 M. Julia and J.D. Fourneron, Tetrahedron, 32 (1976) 1113.
13 R.D. Bach and H.F. Heineike, J. Amer. Chem. Soc., 92 (1970) 5589.
14 V.S. Petrosyan and J.D. Roberts, Org. Magn. Reson., 9 (1977) 555.
15 J.B. Stothers, Carbon-13 NMR Spectroscopy, Academic Press, New York, 1972, p. 377.
16 A.J. Canty, A. Marker, P. Barrow and P. Healey, J. Organometal. Chem., 144 (1978) 371.
17 V. Gutman and A. Setininger, Monatsh. Chem., 97 (1966) 460.
18 S. Ahrland and N. Bjork, Acta. Chem. Scand. A, 28 (1974) 823.
19 H.C. Brown and Y. Okamoto, J. Amer. Chem. Soc., 80 (1958) 4979.
20 A.J. Canty and G.B. Deacon, J. Organometal. Chem., 49 (1973) 125.
21 A.J. Brown, O,W. Howarth and P, Morre, J. Chem. Soc. Dalton, (1976) 1589.
22 N.K. Wilson and R.D. Zehr, J. Magn. Reson., 21 (1976) 437.
23 P.A. Scherr, M.D. Glick, J.H. Siefert and R.D. Bach, J. Amer. Chem. Soc., 97 (1975) 1782.
24 L.G. Makarova and A.N. Nesmeyanov, The Organic Compounds of Mercury, North Holland Publishing Company, Amsterdam, 1967.
25 H. Gilman and G.L. Schwebke, J. Org. Chem., 27 (1962) 4259.