

β-Diketone Derivatives of Methylmercury

P. CLARE and F. GLOCKLING

Department of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG N. Ireland

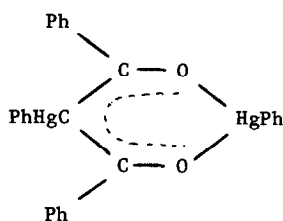
Received August 7, 1975

Compounds of the types $\text{MeHg}(\text{diketonate})$, $(\text{MeHg})_2(\text{diketonate})$ and $\text{MeHg}(\text{amine})(\text{diketonate})$ have been isolated either by direct reaction between dimethylmercury and the diketone or from the diketone and $\text{MeHgN}(\text{SiMe}_3)_2$.¹ Pyrolysis of $(\text{MeHg})_2(\text{C}_5\text{H}_6\text{O}_2)$ gives Me_2Hg and $(\text{MeHgC}_5\text{H}_6\text{O}_2)_2\text{Hg}$. Complexes are mixtures of $\text{MeHg}-\text{C}$ and $\text{MeHg}-\text{O}$ bonded forms having complex ^1H nmr spectra. Complexation of methylmercury with β-diketones does not result in a facile demethylation reaction.

Introduction

This paper is concerned with attempts to bring about the irreversible cleavage of methylmercury bonds using potentially chelating β-diketones.

Inorganic mercury(II) compounds have previously been shown to form β-diketonates with mercury bonded to the γ-carbon atom and ^1H n.m.r. studies have indicated an equilibrium between C–Hg and O–Hg bonded structures:^{2,3} $\text{Hg}[\text{CH}(\text{COR})_2]_2 \rightleftharpoons (\text{RCO})_2\text{CHHgOCR}:\text{CHCOR}$, with the C-bonded forms predominating in the solid state.^{2,4} In a preliminary note⁵ it has been claimed on the basis of carbonyl stretching frequencies that phenylmercuric halides combine with dibenzoylmethane forming (A) whereas the C-bonded structure $(\text{RCO})_2\text{C}(\text{HgPh})_2$ had previously been proposed.



(A)

In this work we have studied the formation, structure and reactivity of β-diketone complexes of methylmercury. Compounds were prepared either by direct reaction of the β-diketone with dimethylmercury at

reflux temperature or from the β-diketone and methylmercurysilazide, $\text{Hg}(\text{Me})\text{N}(\text{SiMe}_3)_2$ at -80°C , and three types of compounds were isolated corresponding to $\text{MeHg}(\text{diketonate})$, $(\text{MeHg})_2(\text{diketonate})$ and $\text{MeHg}(\text{amine})(\text{diketonate})$.

Experimental

All operations were carried out in the absence of air and water. Mercury analyses were conducted by pyrolysis at 600°C in an atmosphere of CO_2 with subsequent amalgamation on pre-weighed gold foil. Chemical shifts, δ , are in ppm from internal TMS and coupling constants, J, in Hertz.

Acetylacetonatomonomethylmercury(II), $\text{MeHg}(\text{C}_5\text{H}_7\text{O}_2)$

$\text{MeHgN}(\text{SiMe}_3)_2$ (1.5 g) in ether (10 ml) was added at -78°C to acetylacetone (0.83 g) in ether (10 ml). The complex separated rapidly as a white precipitate, $\nu(\text{CO})$, 1620 cm^{-1} . After 12 h at -78°C it was filtered and washed with dry ether. Yield 0.75 g, 60%, m.p. $70\text{--}73^\circ\text{C}$. Found: C, 22.7; H, 3.2; Hg, 63.5. $\text{C}_6\text{H}_{10}\text{HgO}_2$ requires C, 22.9; H, 3.2; Hg, 63.7%. Its mass spectrum contained a strong parent ion at m/e 316 for ^{202}Hg . Dimethylmercury did not react with acetylacetone at 140°C .

Acetylacetonatobis(methylmercury(II)), $(\text{MeHg})_2(\text{C}_5\text{H}_6\text{O}_2)$

$\text{MeHg}(\text{C}_5\text{H}_7\text{O}_2)$ (0.484 g) was heated at 50°C and 10^{-4} mm for 24 h. Acetylacetone was evolved leaving the pure complex as a white solid (0.401 g), dec. ca. 180°C . Found: C, 15.8; H, 2.4; Hg, 75.8. $\text{C}_7\text{H}_{12}\text{Hg}_2\text{O}_2$ requires C, 15.9; H, 2.3; Hg, 75.8%. It showed two carbonyl bands at 1620 and 1580 cm^{-1} . The same complex was obtained in 90% yield by carrying out the reaction between acetylacetone and a slight excess of $\text{MeHgN}(\text{SiMe}_3)_2$ at room temperature. Its mass spectrum for ions with $m/e \geq 200$ is given in Table I.

The assignment of initial methyl loss to the acetyl group is supported by comparison of the spectrum with those from $\text{MeHg}(\text{CF}_3\text{CO})_2\text{CH}$ and $\text{MeHg}(\text{CH}_3$

TABLE I. Mass Spectrum of $(\text{MeHg})_2(\text{C}_5\text{H}_6\text{O}_2)$, ca. 110°C .

Fragment	m/e ^a	% Base Peak
$(\text{MeHg})_2\text{C}_5\text{H}_6\text{O}_2^+$	530	17.8
$(\text{MeHg})_2\text{C}_4\text{H}_3\text{O}_2^+$	515	17.8
$(\text{MeHg})_2\text{C}_2\text{HO}^+$	473	11.5
HgHgCHO^+	431	23.1
MeHgHg^+	417	0.6
HgHg^+	402	0.7
$\text{MeHgC}_5\text{H}_7\text{O}_2^+$	316	6.5
$\text{MeHgC}_5\text{H}_6\text{O}_2^+$	315	9.7
$\text{MeHgC}_4\text{H}_4\text{O}_2^+$	301	5.4
$\text{MeHgC}_4\text{H}_4\text{O}^+$	285	0.4
Me_2Hg^+	232	8.7
MeHg^+	217	100.0
Hg^+	202	54.8

^a ^{202}Hg or $^{202}\text{Hg}^{200}\text{Hg}$.

COCHCOCF_3) where the latter shows loss of methyl but the former does not.

Thermal Decomposition of $(\text{MeHg})_2(\text{C}_5\text{H}_6\text{O}_2)$

$(\text{MeHg})_2(\text{C}_5\text{H}_6\text{O}_2)$ (0.165 g) was heated in an evacuated sealed tube at 105°C for 9 h. HgMe_2 was distilled off leaving $[\text{MeHg}(\text{C}_5\text{H}_6\text{O}_2)]_2\text{Hg}$ as a white solid (0.127 g). Found: C, 17.1; H, 2.1; Hg, 72.7. $\text{C}_{12}\text{H}_{18}\text{Hg}_3\text{O}_4$ requires C, 17.4; H, 2.2; Hg, 72.7%. Its i.r. spectrum contained a strong $\nu(\text{C}=\text{O})$ band at 1610 cm^{-1} .

Benzoylacetone monomethylmercury(II)

$\text{MeHg}(\text{C}_{10}\text{H}_9\text{O}_2)$ was prepared from $\text{MeHgN}(\text{SiMe}_3)_2$ and benzoylacetone as a white solid. Found: C, 35.8; H, 3.5. $\text{C}_{11}\text{H}_{12}\text{HgO}_2$ requires C, 35.1; H, 3.2%. Its mass spectrum at 70°C showed a parent ion centred on 378; at 150°C the parent ion corresponding to $(\text{MeHg})_2(\text{C}_{10}\text{H}_8\text{O}_2)$ was present. Its ^1H n.m.r. spectrum in CDCl_3 showed two coincident HgMe signals (δ , 0.87; $^2\text{J}(\text{HgH})$, 154 and 178); two CH_3CO signals (δ , 2.15 and 2.25), $\gamma\text{-CH}$ signal (δ , 5.45); aromatic signals centred at δ , 7.57. After three days at 140°C Me_2Hg and benzoylacetone produced only a trace of methane.

Hexafluoroacetylacetone monomethylmercury(II), $\text{MeHg}(\text{C}_5\text{HF}_6\text{O}_2)$

Hexafluoroacetylacetone (6.4 g) and dimethylmercury (9.3 g) were refluxed for 65 h yielding a yellow solution and a yellow solid containing a trace of elemental mercury. Vacuum distillation gave some unreacted materials followed by the complex, b.p. $46\text{--}54^\circ\text{C}/2 \times 10^{-2}\text{ mm}$ (7.03 g), $\nu(\text{CO})$ in CCl_4 at 1675 cm^{-1} . Found: C, 16.9; H, 0.9; Hg, 47.3; parent ion at m/e, 424. $\text{C}_6\text{H}_4\text{F}_6\text{HgO}_2$ requires C, 17.05; H, 1.0; Hg, 47.5%. $\text{CH}_3\text{HgOCOCF}_3$ was also isolated

as a white sublimate. The yellow solid (1.3 g) was not identified. Found: C, 4.95; H, 0.69; Hg, 77.82%; it was insoluble in organic solvents and water and its mass spectrum showed the ions Hg^+ , MeHg^+ , Me_2Hg^+ and CF_3^+ . The ^1H n.m.r. spectrum of $\text{MeHg}(\text{C}_5\text{HF}_6\text{O}_2)$ in CDCl_3 showed CH_3Hg , δ , 1.36 $^2\text{J}(\text{HgH})$, 246; CH, δ , 6.03; $^4\text{J}(\text{HF})$, 0.45 (septet).

A further reaction using Me_2Hg (3.00 g) and hexafluoroacetylacetone (1.49 g) gave, after 80 days irradiation in a pyrex tube with a mercury vapour lamp, mercury (1.30 g), unreacted materials, CH_4 , C_2H_6 and traces of fluorocarbons together with $\text{MeHg}(\text{C}_5\text{HF}_6\text{O}_2)$.

Ammonia Adduct of $\text{MeHg}(\text{C}_5\text{HF}_6\text{O}_2)$

Ammonia (0.818 mmol) was condensed onto $\text{MeHg}(\text{C}_5\text{HF}_6\text{O}_2)$ (0.387 mmol) and after 1 h at 20°C the excess ammonia (0.424 mmol) was separated leaving the adduct as a pale yellow solid, m.p. $90\text{--}93^\circ\text{C}$, $\nu(\text{CO})$ in CCl_4 at 1670 cm^{-1} . Found: C, 16.4; H, 1.6; N, 3.2; Hg, 45.5. $\text{C}_6\text{H}_7\text{F}_6\text{HgO}_2\text{N}$ requires C, 16.4; H, 1.6; N, 3.2; Hg, 45.6%. The ^1H n.m.r. spectrum in deuteroacetone gave two MeHg signals (δ , 0.53, $^2\text{J}(\text{HgH})$, 193; δ , 0.74, $^2\text{J}(\text{HgH})$, 211) and a CH septet at δ , 5.51, $^4\text{J}(\text{HF})$, 0.7. The same ammonia adduct was isolated in 28% yield when hexafluoroacetylacetone and $\text{MeHgN}(\text{SiMe}_3)_2$ were mixed in dry pentane at -78°C .

Dimethylamine Adduct of $\text{MeHg}(\text{C}_5\text{HF}_6\text{O}_2)$

Excess dry Me_2NH and $\text{MeHg}(\text{C}_5\text{HF}_6\text{O}_2)$ (0.610 g) were kept at 20°C for 1 h. The excess Me_2NH was pumped off leaving the adduct as a yellow solid (0.675 g), with $\nu(\text{CO})$ in CCl_4 at 1665 cm^{-1} . Found: C, 20.4; H, 2.3; N, 3.1; Hg, 42.8. $\text{C}_8\text{H}_{11}\text{F}_6\text{HgO}_2\text{N}$ requires C, 20.5; H, 2.4; N, 3.0; Hg, 42.9%. Its ^1H n.m.r. spectrum at 35°C in CDCl_3 immediately after preparation gave MeHg (δ , 0.93, $^2\text{J}(\text{HgH})$, 212), a septet at δ , 5.72, $^4\text{J}(\text{HF})$, 0.7, and a broad signal at δ , 6.39 which moved progressively to low field with time.

Pyridine Adducts of $\text{MeHg}(\text{C}_5\text{HF}_6\text{O}_2)$

Excess pyridine and $\text{MeHg}(\text{C}_5\text{HF}_6\text{O}_2)$ (0.666 g) were allowed to react for 1 h at 20°C . The weight increase after removal of excess pyridine at $25^\circ\text{C}/10^{-3}\text{ mm}$ corresponded (0.213 g) to the adduct $\text{MeHg}(\text{C}_5\text{HF}_6\text{O}_2)\text{py}_2$, obtained as a yellow liquid. Its ^1H n.m.r. spectrum gave the ratio $\text{Me}:\text{CH}:\text{C}_5\text{H}_5\text{N}$ as 3.0:1.0:9.6 with the following parameters (MeHg , δ , 0.86, $^2\text{J}(\text{HgH})$, 233; CH, δ , 5.58, $^4\text{J}(\text{HF})$, 0.70; $\text{C}_5\text{H}_5\text{N}$, δ , 7.63, 8.03 and 8.80). Sublimation of this adduct at 45°C and 0.05 mm removed one mol of pyridine giving $\text{MeHg}(\text{C}_5\text{HF}_6\text{O}_2)\text{py}$ as a white solid with $\nu(\text{CO})$ in CCl_4 at 1670 cm^{-1} . Found: C, 26.3; H, 1.7; N, 3.0; Hg, 39.7. $\text{C}_{11}\text{H}_9\text{F}_6\text{HgO}_2\text{N}$ requires C, 26.3; H, 1.8; N, 2.8; Hg, 40.0%. Its ^1H n.m.r. spectrum in deuteroacetone gave the ratio $\text{Me}:\text{CH}:\text{C}_5\text{H}_5\text{N}$ as

3.2:1.0:5.0 (MeHg, δ , 1.07, $^2J(\text{HgH})$, 234; CH, δ , 5.70, $^4J(\text{HF})$, 0.6).

Ammonia Adduct of $\text{MeHg}(\text{CF}_3\text{COCHCOCH}_3)$

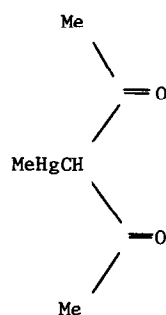
$\text{MeHgN}(\text{SiMe}_3)_2$ (1.49 g) and trifluoroacetylacetone (1.20 g) combined at -78°C to yield the adduct, m.p. $87-89.5^\circ\text{C}$ (0.68 g, 38%). Found: C, 18.5; H, 2.5; N, 3.5. $\text{C}_6\text{H}_{10}\text{F}_3\text{HgO}_2\text{N}$ requires C, 18.7; H, 2.6; N, 3.6. Its mass spectrum contained an ion at m/e , 370 corresponding to (parent $-\text{NH}_3$). Dimethylmercury did react with trifluoroacetylacetone but much less readily than with $(\text{CF}_3\text{CO})_2\text{CH}_2$ and at 135°C extensive decomposition occurred with deposition of mercury and formation of methane.

Results and Discussion

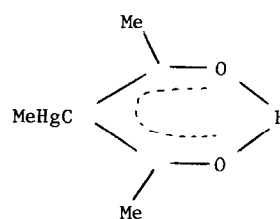
Whereas the fluorinated β -diketones $(\text{CF}_3\text{CO})_2\text{CH}_2$ and $\text{CF}_3\text{COCH}_2\text{COCH}_3$ eliminate methane with dimethylmercury forming $\text{MeHg}(\text{diketonate})$ complexes, acetylacetone and benzoylacetone are unreactive at temperatures up to 140°C . Complete demethylation with the formation of elemental mercury was only observed for the two fluoro complexes under forcing conditions.

The complex $\text{MeHg}(\text{C}_5\text{H}_7\text{O}_2)$, a white crystalline solid, produced in CDCl_3 a temperature dependent ^1H n.m.r. spectrum (Table II) which provides good evidence for the presence in solution of two $\text{MeHg}-\text{C}$ bonded structures (B) and (C), and some evidence (based on the integration data in Table II) for the *cis* and *trans* $\text{MeHg}-\text{O}$ bonded forms (D) and (E),

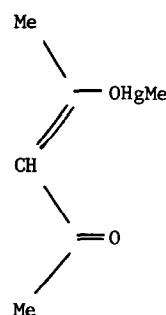
analogous to structures reported for silicon acetylacetonates:⁶



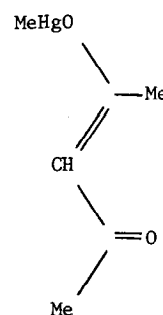
(B)



(C)



(D)



(E)

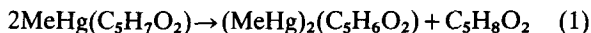
TABLE II. Low Temperature ^1H n.m.r. Spectra of $(\text{MeHg})(\text{C}_5\text{H}_7\text{O}_2)$ and $(\text{MeHg})_2(\text{C}_5\text{H}_6\text{O}_2)$.

Assignment	$\delta(\text{ppm})$	$^2J_{\text{HgH}}$	Rel. Int ^b	% Distribution in ^b Environments
$(\text{MeHg})(\text{C}_5\text{H}_7\text{O}_2)$ at -60°C				
CH_3Hg	0.82	<i>ca.</i> 144 ^c	3	36
CH_3Hg	0.91	<i>ca.</i> 154		64
CH_3CO	2.14	—	5.97 ^d	22
CH_3CO	2.36 ^a	—		78
$>\text{CH}(\text{HgMe})$	4.28	135	1.2	54
$-\text{CH}=\text{c}$	5.62	—		19
OH	15.71	—		27
$(\text{MeHg})_2(\text{C}_5\text{H}_6\text{O}_2)^e$ at -20°C				
CH_3Hg	0.74 ^a	140	6	35
CH_3Hg	0.85	162		35
CH_3Hg	0.94	144		30
CH_3CO	2.23	—	5.75	56
CH_3CO	2.29 ^a	—		44

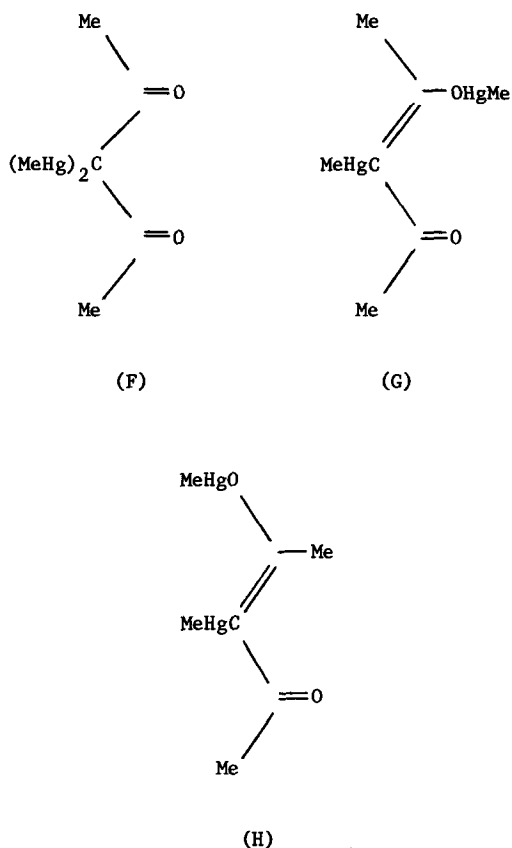
^aFurther splittings observed for these signals. ^bRelative intensities and % in each environment not necessarily calculated from the same integrations. ^cIn deuteroacetone at 35°C , 3 coupling constants observed at 129, 142 and 160 Hz, even though only one MeHg resonance resolved. ^dOn cooling, these signals both shift, but in opposite directions, being coincident at ca. -30°C . ^eThis n.m.r. spectrum shows variable proportions of the keto and enol forms, depending on the mode of purification.

The evidence for structure (B) is that at -60°C one of the two resonances associated with the γ -CH proton shows ^{199}Hg satellites with $^2J(\text{HgH}) = 135$. The appearance of an OH resonance, broad at -40°C , but sharp at -60°C indicates structure (C).

When $\text{HgMe}(\text{C}_5\text{H}_7\text{O}_2)$ is heated thermogravimetrically it does not lose methane but undergoes reaction (1) at its melting point of 70 – 72°C .



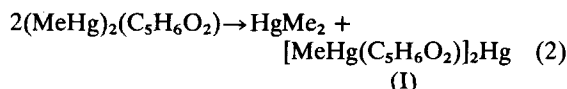
The bis-complex $(\text{MeHg})_2(\text{C}_5\text{H}_6\text{O}_2)$, a white crystalline solid, also shows a temperature dependent ^1H n.m.r. spectrum which provides evidence for structures (F), (G) and (H), with three distinct methyl mercury environments at 40°C which were better resolved at -20°C :



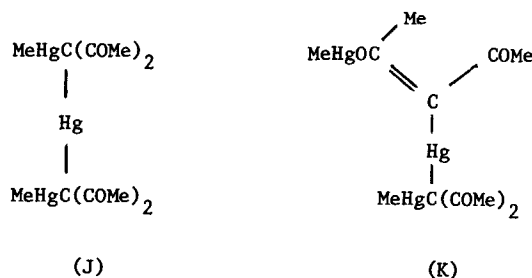
Two of the HgMe signals have similar ^{199}Hg -H coupling constants and are assigned to the $\text{MeHg}-\text{C}$ bonded forms, (F) at δ , 0.94 and (G) + (H) at δ , 0.74. The signals due to (G) and (H) are broader than those due to (F) in both the acetyl and methylmercury regions. A signal at δ , 0.85 is assigned to the O-bonded HgMe in (G) and (H). Structure (F) does not appear to equilibrate rapidly with (G) and (H) even at

50 – 60°C , since its signals remain sharp whereas those due to the methylmercury protons in (G) and (H) coalesce at this temperature. Moreover by fractional crystallisation it is possible to reduce the proportion of (F) to less than 10%. For structures (G) and (H) there must be accidental equivalence of the acetyl protons, possibly due to rapid exchange via a chelated intermediate.

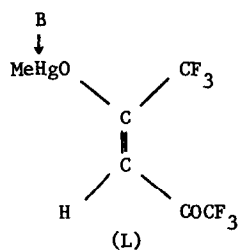
In addition to reaction (1) thermogravimetric studies (100 – 160°C) provided evidence for the clean decomposition of the bis-complex (reaction 2).



This reaction can be followed by ^1H n.m.r. spectroscopy in perdeuterodimethylsulphoxide when the overall intensity of the various HgMe and acetyl signals remain unchanged. After 15 min at 100°C 38% of the HgMe signals was due to HgMe_2 ($^2J(\text{HgH}) = 106$) and two new HgMe signals due to (I) were present together with a single acetyl signal with the same chemical shift as $(\text{MeHg})_2(\text{C}_5\text{H}_6\text{O}_2)$. The structure of (I) has not been determined, though by analogy with compounds already discussed it probably involves structures (J) and (K); when prepared by dry thermolysis (reaction 2) it is insoluble in dimethylsulphoxide:



Unlike acetylacetone, hexafluoroacetylacetone reacted readily with dimethylmercury under reflux forming methane and $\text{MeHg}(\text{C}_5\text{HF}_6\text{O}_2)$ as a colourless liquid. Other products including the trifluoroacetate MeHg OCOCF_3 were also formed, and after a long reaction period extensive demethylation to mercury was achieved. N.m.r. examination of $\text{MeHg}(\text{C}_5\text{HF}_6\text{O}_2)$ at -60°C failed to show the presence of the $\text{MeHg}-\text{C}$ bonded form since the γ -CH proton showed no coupling to mercury; hence this compound exists entirely in the enol form. The CH_3-Hg coupling ($^2J(\text{HgH}) = 248$) is comparatively high as expected for a strongly electronegative ligand bonded to mercury. Since the Lewis acidity of the mercury is greater in $\text{HgMe}(\text{C}_5\text{HF}_6\text{O}_2)$ it is possible that the diketone is chelating, and it was found that ammonia and amines form 1:1 crystalline adducts of the type (L):



(B = NH_3 , Me_2NH , $\text{C}_5\text{H}_5\text{N}$). In the case of pyridine there was evidence for a 2:1 adduct $\text{py}_2\text{HgMe}(\text{C}_5\text{HF}_6\text{O}_2)$. In all of these adducts the value of the $\text{CH}_3\text{-Hg}$ coupling falls sharply, indicating that the base is directly bound to mercury, most probably through an empty $5p$ orbital on mercury. Arsine adducts of mercury(II) compounds have T shaped structures resulting from this bonding.⁷ In no case were coupling constants detected between MeHg and protons bonded to the nitrogen donor as expected if a pure p orbital is used in forming the N-Hg bond.

Proton n.m.r. spectra of these nitrogen adducts were complex and did not lead to definite structural assignments though they indicate a variety of isomeric forms or slow reactions following coordination of the nitrogen base. The most significant conclusion is that for the ammonia and dimethylamine adducts partial conversion to carbanolamines (N and O) is indicated.

For the ammonia adduct two HgMe signals are observed at 30°C , the larger of which (δ , 0.58) separates into two signals at -80°C (δ , 0.48 and 0.68, Table III). The $\gamma\text{-CH}$ proton remains as a singlet with no sign of coupling to mercury; hence enolization is not occurring and structure (M) is less likely than the carbanolamine (N):

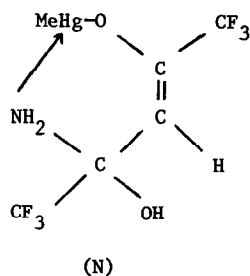
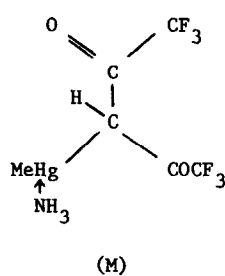


TABLE III. ^1H n.m.r. Data for $\text{MeHg}(\text{NH}_3)(\text{C}_5\text{HF}_6\text{O}_2)$ in $(\text{CD}_3)_2\text{CO}$ at -80°C .

Signal	δ (ppm)	J(Hz)	Intensity
MeHg	0.48	192	0.56
MeHg	0.68	209	1.31
MeHg	0.75	210	1.13
NH(?)	4.05		1.06
NH,OH(?)	5.26 broad		0.84
CH	5.63	0.7(HF)	0.99

The two HgMe signals (ratio 4:1 at 40°C) do not change with time, but the $\gamma\text{-CH}$ signal falls in intensity and an equivalent growth in the signal at δ , 4.05 is observed. This ammonia adduct was also prepared by the reaction of $\text{MeHgN}(\text{SiMe}_3)_2$ with $(\text{CF}_3\text{CO})_2\text{CH}_2$ in which presumably ammonia is formed by reaction between $(\text{Me}_3\text{Si})_2\text{NH}$ and the excess hexafluoroacetylacetone.

The dimethylamine adduct $(\text{Me}_2\text{NH})\text{MeHg}(\text{CF}_3\text{CO})_2\text{CH}_2$, a yellow solid, was slowly converted into a viscous liquid on storing in a nitrogen atmosphere. Its ^1H n.m.r. spectrum at $+40^\circ\text{C}$ and -90°C in deuterioacetone is summarized in Table IV.

Two MeHg environments are observed even at 40°C and the very low value of $^2\text{J}(\text{HgH})$, 130 suggests a C-bonded MeHg group. On standing, the $\gamma\text{-CH}$ signal decreased in intensity as signals ascribed to NH and OH protons increased in intensity. This suggests the presence of the carbanolamine (O), possibly in equilibrium with structures (P) and (Q):

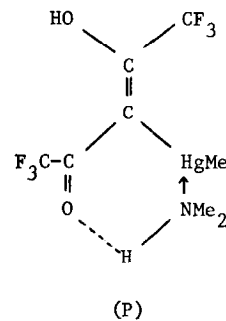
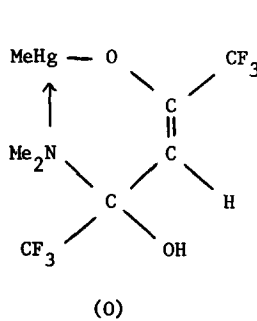
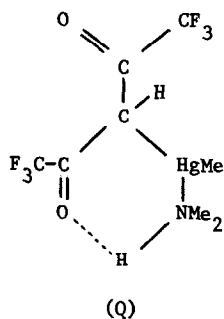


TABLE IV. ^1H n.m.r. data for $\text{MeHg}(\text{NHMe}_2)(\text{C}_5\text{HF}_6\text{O}_2)$ in $(\text{CD}_3)_2\text{CO}$

Signal	Temp $+40^\circ\text{C}$			Temp -80°C		
	δ (ppm)	J(Hz)	I	δ (ppm)	J(Hz)	I
MeHg	0.42	130	2.9	0.38	134	3.1
MeHg	0.60	193		0.56	194	
Me_2N	2.72		6.0	2.77		6.0
NH(?)	3.52		1.0	3.65		1.1
OH(?)	3.60		0.2	3.88 (broad)		
CH	5.56	0.8(HF)	0.8	5.69		0.5



For the pyridine adduct $\text{pyHgMe}(\text{C}_5\text{HF}_6\text{O}_2)$ formation of a carbanolamine is not possible but keto-enol tautomerism is indicated since the γ -CH signal intensity decreases with time and a new signal at δ , 3.70 is observed in deuterioacetone.

The extensive structural isomerism indicated by ^1H n.m.r. spectroscopy for all of the complexes described in this paper is more varied than earlier work on β -diketonates of mercury has suggested. The prevalence

of Hg-O bonded structures is somewhat at variance with the view of Fish and co-workers⁴ on the effect of possible σ - π conjugation between the Hg-C σ bond and the π -carbonyl bond.

References

- 1 J. Lorberth and F. Weller, *J. Organometal. Chem.*, **32**, 145 (1971).
- 2 R. Allmann, K. Flatau and H. Musso, *Chem. Ber.*, **105**, 3067 (1972).
- 3 F. Bonati and G. Minghetti, *J. Organometal. Chem.*, **22**, 5 (1970).
- 4 R.H. Fish, R.E. Lundin and C.G. Salentine, *J. Organometal. Chem.*, **84**, 281 (1975).
- 5 R.J. Bertino and G.B. Deacon, *J. Organometal. Chem.*, **67**, C61 (1974).
- 6 T.J. Pinnavaia, W.T. Collins, J.J. Howe, *J. Am. Chem. Soc.*, **92**, 4544 (1970).
- 7 A.J. Carty and B.M. Gatehouse, *J.C.S. Dalton.*, 511 (1972).