

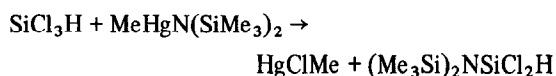
Methyl(hexamethyldisilylamino)mercury: Reaction with Phenols and Oximes

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The title compound, $\text{MeHgN}(\text{SiMe}_3)_2$, first prepared in 1971, is highly sensitive to protic reagents and may be used to prepare a wide range of methylmercury compounds [1]. For example the NH groups of porphyrins react at room temperature forming $>\text{NHgMe}$ derivatives [2]. Organo-silanes and -germanes will also cleave Hg–N bonds, but only under forcing conditions [3] (e.g. $2\text{R}_3\text{SiH} + \text{Hg}[\text{N}(\text{SiMe}_3)_2]_2 \rightarrow \text{Hg}(\text{SiR}_3)_2 + 2(\text{Me}_3\text{Si})_2\text{NH}$), and in silicon chlorohydrides it is the Si–Cl rather than the Si–H bond which is cleaved [4], reflecting the high heat of formation of Hg–Cl bonds.

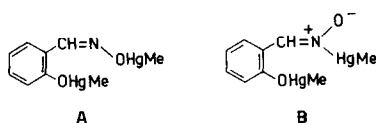


In this paper we report the reaction of $\text{MeHgN}(\text{SiMe}_3)_2$ with a number of phenols and oximes, chosen to allow the possibility of forming 3-coordinate mercury derivatives. The stability of the complexes towards symmetrization or decomposition to mercury was examined together with their spectroscopic properties.

Results and Discussion

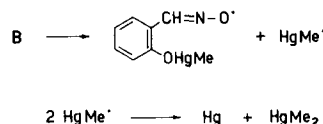
Each of the ligands (Table I) combined rapidly with $\text{MeHgN}(\text{SiMe}_3)_2$ (present in excess) at room temperature in benzene or ether solution, to yield either mono- or di-HgMe complexes, both the OH and NOH hydrogens being sufficiently acidic to react.

For the oxime complexes there is uncertainty as to whether one of the HgMe groups is O- or N-bonded. For example the salicylaldoxime complex (2) might have structure (A) or the nitrone structure (B), and on general chemical grounds structure (B) is probably the more likely.



The complexes, isolated as powders, were stable in air but decomposed slowly in chloroform solution at

room temperature with deposition of mercury. This instability in solution is unexpected and might be accounted for by the high stability of aromatic nitrone radicals [5] so that solution or thermal decomposition may proceed by the following radical reactions



Thermal decomposition of (3) began at 76 °C and extremely rapid weight loss occurred at 126 °C, approximately corresponding to evolution of dimethylmercury. T.G.A. indicated two further overlapping decomposition processes at higher temperature and, with a heating rate of 20 °C/minute, 85% weight loss occurred by 250 °C. Using a differential scanning calorimeter with graphite crucibles in a nitrogen atmosphere revealed a strongly exothermic decomposition between 127–147 °C with a heating rate of 1.25 °C/minute. No endothermic melting was observed since thermal decomposition occurs in the solid phase. The higher temperature decomposition processes detected by T.G.A. must be essentially thermo-neutral. When complexes (3) and (5) were heated above their melting points in evacuated sealed tubes mercury, dimethylmercury and tarry materials were formed together with trace amounts of methane. For the oxime complex (5) decomposition commenced about 85 °C and at 162 °C 61% weight loss occurred corresponding to loss of HgMe, possibly as $\text{Hg} + \text{HgMe}_2$. Hydrolysis of complex (1) in aqueous acetone proceeded to completion over 24 h at room temperature: the initial HgMg proton resonance at 1.00 ppm diminished progressively with time and a new signal appeared at 0.56 ppm with $^2J(\text{HgH}) = 124 \text{ Hz}$. Treatment of complex (1) with aniline in an n.m.r. tube gave a deep yellow solution of the corresponding azomethine [$\delta(\text{CH})$, 8.01; $\delta(\text{CH}_3)$, 0.3 ppm; $^2J(\text{HgH})$, 187 Hz].

The mass spectrum of (5), like other metal oxime complexes [6] produced an abundant parent ion. Its subsequent fragmentation involved first loss of $\text{OH}^\bullet$ giving presumably an N-bonded mercury ion which decomposed further by the processes indicated in Scheme 1. Each of the other complexes showed clear evidence of thermal decomposition since HgMe_2^{++} was present together with a number of mercury-containing ions that could not have been formed by direct bond cleavage reactions of the parent. For these compounds parent ions were either not observed or were of very low abundance.

The infrared spectra of complexes 1–5 showed few differences from those of the free ligands and no clear

TABLE I. Methylmercury Complexes.

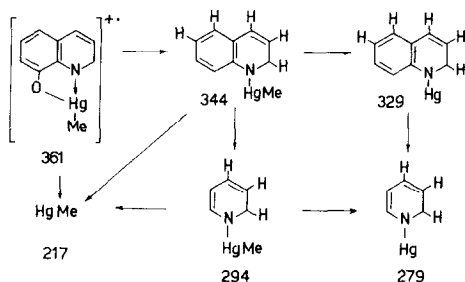
Ligand	Complex	Colour	Mp °C	Analysis [% Found/(Calc.)]			
				C	H	N	Hg
1. Salicylaldehyde	C ₈ H ₈ HgO ₂	colourless	89–91	28.67 (28.61)	2.67 (2.4)	—	60.21 (59.60)
2. Salicylaldoxime	C ₉ H ₁₁ Hg ₂ NO ₂	colourless	115–119(d)	19.37 (19.11)	1.91 (1.94)	2.53 (2.47)	70.29 (70.84)
3. 2-Hydroxyacetophenoneoxime	C ₁₀ H ₁₃ Hg ₂ NO ₂	colourless	118–20(d)	20.92 (20.69)	2.38 (2.25)	2.23 (2.41)	69.76 (69.12)
4. α-Benzoinoxime	C ₁₆ H ₁₇ Hg ₂ NO ₂	colourless	140–142	29.51 (29.31)	2.51 (2.59)	2.06 (2.13)	60.65 (61.12)
5. 8-Hydroxyquinoline	C ₁₀ H ₉ HgNO	pale yellow	90–91	33.16 (33.38)	2.54 (2.52)	3.75 (3.89)	55.68 (55.75)

TABLE II. N.m.r. Spectra.

Complex	¹ H N.m.r. Spectra			
	δ(HgCH ₃)	δ(phenyl)	δCH ₃ /CH	² J(¹⁹⁹ Hg– ¹ H)
C ₈ H ₈ HgO ₂	1.0(s)	6.8–7.56(m)	9.76(s) CH	212, 218 ^a , 216 ^b
C ₉ H ₁₁ Hg ₂ NO ₂	0.998(s) 1.025(s)	6.93–7.36(m)	8.26(s) CH	148, —
C ₁₀ H ₁₃ Hg ₂ NO ₂	0.96(s) 1.03(s)	6.76–7.53(m)	2.33(s) CH ₃	144, —
C ₁₆ H ₁₇ Hg ₂ NO ₂	0.913(s) 1.00(s)	7.24	5.98(s) CH	—
C ₁₀ H ₉ HgNO [8]	1.05(s)	6.90–8.60(m)	—	217, 216 ^a , 212 ^b
Complex	¹³ C n.m.r. Spectra			
	δ(Hg– ¹³ CH ₃)	δ ¹³ C _{phenyl}	δ ¹³ C=O	J(¹⁹⁹ Hg– ¹³ C)
C ₈ H ₈ HgO ₂	–2.144	121.985, 126.470 139.598, 140.637	199.064	1559
C ₁₀ H ₉ HgNO	–3.899	112.367, 115.032 120.296, 129.590 137.649, 145.122 130.370, 139.468 162.345	—	1690

^aIn C₆D₆.^bIn CCl₄.

δ values in ppm. J. values in Hz. s, singlet. m, multiplet.



Scheme 1. Mass spectrum of complex 5.

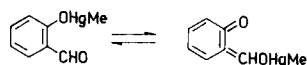
distinction could be drawn between structures such as (A) and (B). In the free ligands $\nu(\text{OH})$ appears as a broad band in the region 3450–3100 cm^{-1} whereas

in the complexes a fine series of bands is observed in the $\nu(\text{CH})$ region (3070–2900 cm^{-1}). In complex (1) $\nu(\text{CH})$ for the methine hydrogen is at 2760 cm^{-1} , and the strong carbonyl absorption at 1670 cm^{-1} is not appreciably changed from the value for the free ligand, hence its coordination to MeHg is unlikely. In chloroform solution complex (1) retains $\nu(\text{CO})$ at 1670 cm^{-1} with shoulders at 1650 and 1622 cm^{-1} , and the spectrum was unchanged over 4 days. Each complex showed several bands in the $\nu(\text{Hg}-\text{CH}_3)$ region around 500 cm^{-1} but unique assignments could not be made because of other ligand vibrations in this region. For similar reasons $\nu(\text{Hg}-\text{O})$ could not be identified.

^1H n.m.r. spectra (Table II) were recorded in CDCl_3 with TMS as internal reference. For complexes (1) and (5) CCl_4 and C_6D_6 were also used as solvents. Solubility limitations restricted ^{13}C n.m.r. studies to complexes (1) and (5) in CDCl_3 with TMS as reference. In common with other methylmercury compounds $^2\text{J}(\text{HgH})$ was solvent dependent but whereas for (5) the expected trend was observed for (1) the value in CDCl_3 was lower than in the non-polar solvents CCl_4 and C_6D_6 . Although for (2) and (3) two HgMe resonances were detected only one pair of satellites were observed: limited solubility restricted further nmr investigation. Complex (4) was too insoluble for satellites to be detected. A striking, but unexplained feature of the spectra is the large difference between $^2\text{J}(\text{HgH})$ in the oxime derivatives and those of (1) and (5).

The proton spectrum of (1) in CDCl_3 solution changed with time, possibly due to a slow reaction with the solvent. This might account for the anomalous value of $^2\text{J}(\text{HgH})$ in CDCl_3 solution. Over 1 week the original HgMe signal weakens and its associated satellites broaden and finally disappear. Simultaneously a new HgMe signal appears $\sim 4\text{Hz}$ upfield from the original together with mercury satellites ($^2\text{J}(\text{HgH})$, 144 Hz). The methine resonance remains unchanged. Double irradiation at the methine, phenyl, and original methyl frequencies did not affect the "new" methyl resonance. The ^{13}C n.m.r. spectra (Table II) showed unusually high values for the shift of the methyl carbon and, like $^2\text{J}(\text{HgH})$, $^1\text{J}(\text{Hg}^{13}\text{C})$ is large compared to the methylmercury halides [7].

An earlier report [9], based on U.V. spectra in polar solvents, suggested the existence of benzenoid-quinonoid structures of the type:



However, under our conditions neither U.V., or nmr data support the existence of tautomers.

Experimental

A slight excess of each ligand, dissolved in the minimum amount of ether, benzene or n-hexane was treated with $\text{MeHgN}(\text{SiMe}_3)_2$ at room temperature or at 0°C for complex (5). Reaction mixtures were stirred for 1 hour when the complexes were filtered, washed several times with the solvent and dried *in vacuo*. λ_{max} -log ϵ values for complex (1) in cyclohexane showed no change with time (259, 3.89; 331, 3.38). Complex (5) gave 4 bands in the U.V. (250sh, 4.22; 258; 4.30; 338sh, 3.23; 374, 3.10).

References

- 1 J. Lorberth and F. Weller, *J. Organometal. Chem.*, **32**, 145 (1971).
- 2 P. Clare and F. Glockling, *Inorg. Chim. Acta*, **17**, 229 (1976).
- 3 F. Glockling and J. J. Sweeney, *J. Chem. Res.*, (S)35, (M) 615 (1977).
- 4 G. S. Kalinina, B. I. Petrov, O. A. Kruglaya and N. S. Voyazankin, *Zh. Obshch. Khim.*, **42**, 148 (1972).
- 5 J. S. Vincent and E. S. Grubbs, *J. Am. Chem. Soc.*, **91**, 2022 (1969).
- 6 J. Charalambous, M. H. Jori, L. C. Thiang and S. Rocca, *Inorg. Chim. Acta*, **22**, 93 (1977).
- 7 A. J. Brown, O. W. Howarth and P. Moore, *J. Chem. Soc. Dalton*, 1589 (1976).
- 8 L. F. Sytsma and R. J. Klime, *J. Organometal. Chem.*, **54**, 15 (1973).
- 9 V. I. Minkin, L. P. Olekhmovich, M. I. Knyazhanskii, I. E. Mikhailov and A. E. Lyubarskaya, *Zh. Org. Khim.*, **10**, 817 (1974).