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NOTE

REACTIONS OF BIS(TRIMETHYLSILYL)MERCURY WITH MERCURIC COMPOUNDS

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Dimethylmercury readily undergoes redistribution reactions with mercury dihalides to give the stable methylmercury halides. The equilibrium constants for these reactions greatly favour the mixed species[1]:

$$Me_2Hg + HgX_2 \rightarrow 2\ MeHgX \qquad (X = Cl, Br, I)$$

Similarly in exchange between mercury dihalides and mercury–transition-metal compounds of the type $[\pi\text{-}C_5H_5(CO)_n]_2Hg$ ($M = Mo$ or W, $n = 3$; $M = Fe$, $n = 2$) the mixed species is greatly favoured. Equilibrium is established more rapidly in the latter case than for the corresponding reactions of organomercury compounds, the reactions being instantaneous at room temperature in acetone solvent[2].

We find that bis(trimethylsilyl)mercury reacts with a variety of mercuric compounds not to give the expected trimethylsilyl–mercury derivative, but rather mercury and the corresponding trimethylsilyl derivative:

$$(Me_3Si)_2Hg + HgX_2 \rightarrow 2\ Me_3SiX + 2\ Hg \qquad [X = Cl, Br, I, CN, Co(CO)_4]$$

The reactions are instantaneous at room temperature in cyclopentane solution. No evidence for the mixed species Me_3SiHgX was found in any of these reactions.

Bis(trimethylsilyl)mercury has been shown to react with mercuric chloride in benzene solution to give mercury and trimethylsilyl chloride[3].

The reaction with mercuric cyanide is of interest in view of the fact[2] that no mixed species could be isolated from the reaction between mercuric cyanide and mercury–transition-metal compounds. The reaction between bis(trimethylsilyl)mercury and mercury cobalt tetracarbonyl occurs in both chloroform and cyclopentane solutions, and provides a very convenient new route to trimethylsilyl cobalt tetracarbonyl. Further, the reaction could be extended to prepare many new trimethylsilyl–transition-metal compounds as a wide variety of transition-metal–mercury compounds are available (ref. 2, and references therein).

Other reactions which might have been expected to produce the trimethylsilylmercury cation also failed to do so. Thus, the reaction between bis(trimethylsilyl)mercury and hydrogen chloride has been reported[4] to give mercury, trimethylsilane and trimethylsilyl chloride:

$$(Me_3Si)_2Hg + HX \rightarrow Me_3SiH + Hg + Me_3SiX \qquad (X=Cl,I)$$

Similarly, we find that it reacts with hydrogen iodide to give mercury, trimethylsilane and trimethylsilyl iodide. With hydrogen cyanide, there is no reaction even after half an hour at room temperature, although the reactions with hydrogen halides are instantaneous at room temperature.

If the trimethylsilylmercury cation is first formed in any of the above reactions then it must be very unstable. Little is known about cationic trimethylsilyl species. Adducts of trimethylsilyl halides have been formulated as cationic species[5]. Bis(trimethylsilyl)thallium chloride has been prepared from the reaction between tris(trimethylsilyl)thallium and chloroform, but the bis(trimethylsilyl)thallium cation would seem to be less stable than the corresponding dimethylthallium cations[6].

The compound ethyl(triethylsilyl)mercury has been prepared by the reaction of triethylsilane and diethylmercury[7]. There is no reaction between bis(trimethylsilyl)-mercury and dimethylmercury in dichloromethane solvent at room temperature. Dimethylmercury has been reported not to readily participate in reactions in which methyl groups are exchanged from one metal to another[8,9], and exchange of methyl groups on dimethylmercury is slow at room temperature. Proton magnetic resonance parameters of bis(trimethylsilyl)mercury are as follows: in carbon disulphide solvent, τ(CH) 9.74 ppm, $J(^{29}SiCH)$ 6.6 Hz, $J(^{199}HgSiCH)$ 40.4 Hz, and $J(^{13}CH)$ 120.5 Hz; in dichloromethane solvent, τ(CH) 9.83 ppm, $J(^{29}SiCH)$ 6.2 Hz, $J(^{199}HgSiCH)$ 41.1 Hz, and $J(^{13}CH)$ 120.2 Hz. The observation of ^{199}Hg satellites in these solvents at room temperature shows that any exchange of trimethylsilyl groups must be slow. The ^{199}Hg–H coupling constant is only slightly solvent dependent: in a trimethylamine/dichloromethane mixture as solvent it has the value 40.9 Hz, suggesting that no adduct formation occurs between trimethylamine and bis(trimethylsilyl)mercury. This was confirmed by a tensiometric titration, in which formation of neither a 1/1 not a 2/1 adduct could be detected. In this it is similar to organomercury compounds, which also show little tendency to complex formation[11].

EXPERIMENTAL

Bis(trimethylsilyl)mercury

This was prepared from trimethylsilyl chloride and sodium amalgam[4] as follows. Sodium amalgam (0.5%, 14 ml) was shaken for several days with trimethylsilyl chloride (5.5 ml) in cyclopentane (20 ml) in an evacuated flask (100 ml). The resulting yellow solution was then filtered under vacuum into a tap ampule[12] from which portions were removed, under vacuum, as required.

NMR spectra were recorded on a Varian Associates HA 100 Spectrometer operating at 100 MHz for protons fitted with the standard variable temperature probe (-60 to $+120°$). With carbon disulphide as solvent, internal tetramethylsilane was used as standard, and with dichloromethane, the solvent itself. A frequency meter was used in determining chemical shifts from the standard.

All reactions of bis(trimethylsilyl)mercury were carried out *in vacuo.*

Reaction with mercuric halides

In a typical experiment, mercuric bromide (excess) reacted with bis(trimethylsilyl)mercury (1.2 mmoles) to give mercury and trimethylsilyl bromide (2.5 mmoles, confirmed by vapour pressure and infra-red and NMR spectroscopy).

Reaction with $Hg[Co(CO)_4]_2$

$Hg[Co(CO)_4]_2$ (0.05 mmoles) and excess bis(trimethylsilyl)mercury in cyclopentane were mixed *in vacuo* and left at room temperature for five minutes. The mixture was then cooled to 0°, and all the volatiles at this temperature were pumped away, then, with the mixture at room temperature, the (trimethylsilyl)cobalt tetracarbonyl was condensed out into a trap at −196°. Yield 0.08 mmoles, as a very pale pink solid, involatile at 0°, but volatile at 20°. In cyclohexane solution, τ(CH) 9.39 ppm[13].

Reaction with hydrogen iodide

Hydrogen iodide was prepared by the action of iodine on boiling tetralin. Excess bis(trimethylsilyl)mercury (0.22 mmoles) reacted with hydrogen iodide (0.10 mmoles) to give mercury, trimethylsilane (0.10 mmoles) and trimethylsilyl iodide (0.11 mmoles).

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