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BIS[TRIS(TRIMETHYLSILYLMETHYL)STANNYL]MERCURY—A STABLE STANNYLMERCURY COMPOUND

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SUMMARY

The compounds $[(Me_3SiCH_2)_3Sn]_2M$, where M = Hg and Cd, are essentially more thermally stable than the compounds prepared earlier with Sn–M–Sn groupings. Apparently this is a result of the stabilizing effect of the Me_3SiCH_2 substituents. The reactivity of the stannylmercury compound does not differ considerably from that of bis(triethylgermyl)mercury and related compounds.

INTRODUCTION

It is known that the thermal stability of symmetric silyl- and germyl-mercurials of the type $(R_3E)_2Hg$ (where R = alkyl or aryl, E = Si, Ge) is quite high[1]. In contrast, bis(trialkylstannyl)mercury compounds are unstable at temperatures above -10 to $-5°$ [2,3]. Bis(triphenylstannyl)mercury is more stable than its alkyl analogues. However this mercurial also readily precipitates metallic mercury especially from solutions in visible light[4].

It could be suggested that the stability of the compounds $(R_3E)_2Hg$ should depend not only upon the nature of the E atoms but also on the properties of the adjacent R substituents. For example, it is known that the compounds $(HMe_2Si)_2Hg$ and $(H_2MeSi)_2Hg$ are unstable in contrast to bis(trimethylsilyl)mercury[5]. It has been shown recently that transition metal compounds with Me_3SiCH_2 and related ligands (*e.g.* $Me_3SiCH_2W(CO)_3C_5H_5$-π) possess a greater thermal stability than the corresponding σ-alkyl (C_nH_{2n+1}, $n > 1$) transition metal complexes[6]. In order to obtain more information on steric and other effects of the trimethylsilylmethyl group, we have commenced a study of the synthesis and reactions of bis[tris(trimethylsilylmethyl)stannyl]mercury.

RESULTS AND DISCUSSION

Bis[tris(trimethylsilylmethyl)stannyl]mercury (I) has been obtained according to the reactions*:

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* Short communication, see Ref. 7.

$$RMgCl \xrightarrow[(a)]{SnCl_4} R_4Sn \xrightarrow[(b)]{SnCl_4} R_3SnCl \xrightarrow[(c)]{LiAlH_4} R_3SnH \xrightarrow[(d)]{Et_2Hg} \underset{(I)}{(R_3Sn)_2Hg} \qquad (1)$$

where $R = Me_3SiCH_2$.

The reaction (1a) was carried out in diethyl ether using a 6/1 molar ratio of Grignard reagent to stannic chloride. These conditions lead to the formation of tetrakis(trimethylsilylmethyl)tin (75.6%) and hexakis(trimethylsilylmethyl)ditin (8.2%).

Such a product composition is not surprising. Reactions of stannic chloride proceed in a similar fashion with other Grignard reagents, RMgX, containing bulky R substituents such as isopropyl[8], t-butyl[9,10], neopentyl[11] and cyclohexyl[12].

It is assumed that the formation of derivatives with Sn–Sn bonds in such reactions is preceded by the formation of stannylmagnesium compounds

$$R_3SnCl + RMgCl \rightarrow R_3SnMgCl + RCl \qquad (2)$$

$$R_3SnMgCl + R_3SnCl \rightarrow R_3SnSnR_3 + MgCl_2 \qquad (3)$$

It is interesting to note that the reaction of trimethylsilylmethylmagnesium chloride with stannic chloride in tetrahydrofuran (THF) is reported[13] to give only tetrakis(trimethylsilylmethyl)tin in high yield. Dealkylation of tetrakis(trimethylsilylmethyl)tin by the Kocheshkov method [reaction (1b)] may be completed only after prolonged heating (16 h) at 200–210°. It is probable that steric effects also operate to limit the reactivity at the trimethylsilylmethyl–tin bond. In contrast, the reaction of tris(trimethylsilylmethyl)tin hydride with diethylmercury [reaction (1d)] at a reagent ratio 2/1 proceeds at room temperature in the absence of a solvent. The stannylmercurial (I) is produced (81.7% yield) along with ethane (97.5%). Apparently the replacement of the ethyl groups in diethylmercury occurs in a stepwise manner

$$\begin{tikzcd}
(Me_3SiCH_2)_3SnH + Et_2Hg \arrow[r, "(a)"] & C_2H_6 + (Me_3SiCH_2)_3SnHgEt \arrow[d, "(b)"', "(Me_3SiCH_2)_3SnH"] \\
 & \underset{(I)}{[(Me_3SiCH_2)_3Sn]_2Hg} + C_2H_6
\end{tikzcd} \qquad (4)$$

However, even when the $(Me_3SiCH_2)_3SnH/Et_2Hg$ ratio was unity, only the symmetrical mercurial (I) was isolated. Two possible explanations appear to be available for the production of this compound: (i) The rate of replacement of the second ethyl group [eqn. (4b)] may to be faster than that of the first [eqn. (4a)]. (ii) If the mixed species, $(Me_3SiCH_2)_3SnHgEt$, is unstable under the reaction conditions, it might be expected to undergo disproportionation to diethylmercury and (I).

It is interesting to note that $Et_3SiHgEt$, $Et_3GeHgEt$ and related compounds are stable[1] and can be readily prepared by a similar scheme to (4a)[14,15].

The stannylmercurial (I) is quite stable both as the solid (m.p. 101–103°) and in THF or n-hexane solutions. Pyrolysis at ca. 150° for 10 h gives an almost quantitative yield of mercury, together with metallic tin (76.2%) and tetrakis(trimethylsilylmethyl)tin (65.0%). The reaction appears to involve the formation of hexakis(trimethylsilylmethyl)ditin as an intermediate followed by its disproportionation according to eqn. (5).

$$2\,(\mathrm{Me_3SiCH_2})_6\mathrm{Sn_2} \rightarrow 3\,(\mathrm{Me_3SiCH_2})_4\mathrm{Sn} + \mathrm{Sn} \qquad (5)$$

The chemical properties of (I) do not differ significantly from those of compounds with Si–Hg–Si and Ge–Hg–Ge groups[16,17]. Thus, reaction with molecular oxygen in THF yields the corresponding distannoxane, $[(\mathrm{Me_3SiCH_2})_3\mathrm{Sn}]_2\mathrm{O}$, together with metallic mercury. The mercurial (I) reacts with 1,2-dibromoethane at room temperature to give a high yield of mercury and ethylene, along with tris(trimethylsilylmethyl)tin bromide. Similar results have been reported for mercurials of the type $(\mathrm{R_3E})_2\mathrm{Hg}$, where R = Me, Et, Ph; E = Si or Ge[18–21].

Sunlight filtered through molybdenum glass is capable of initiating the reaction of (I) with ethyl bromide in benzene solution

$$[(\mathrm{Me_3SiCH_2})_3\mathrm{Sn}]_2\mathrm{Hg} + 2\,\mathrm{EtBr} \rightarrow \mathrm{Et_2Hg} + 2\,(\mathrm{Me_3SiCH_2})_3\mathrm{SnBr} \qquad (6)$$

The yield of diethylmercury and tris(trimethylsilylmethyl)tin bromide is high indicating that the reaction does not proceed via the addition of Et radicals at metallic mercury. The reaction apparently involves a four-centre molecular mechanism. A similar photochemical reaction mechanism has been observed with bis(triethylgermyl)mercury[14,22].

Bis[tris(trimethylsilylmethyl)stannyl]mercury has been shown to undergo a transmetallation reaction with lithium in THF solution

$$[(\mathrm{Me_3SiCH_2})_3\mathrm{Sn}]_2\mathrm{Hg} + 2\,\mathrm{Li} \xrightarrow[\sim 20^\circ]{\mathrm{THF}} \mathrm{Hg} + 2\,(\mathrm{Me_3SiCH_2})_3\mathrm{SnLi} \qquad (7)$$

Such reactions are also specific to the mercurials $(\mathrm{R_3E})_2\mathrm{Hg}$, where R = Me, Et, i-Pr, Ph; E = Si or Ge[1,23,24].

The formation of this stannyl lithium derivative was confirmed by the coupling reaction involving bromotriethylgermane which afforded $(\mathrm{Me_3SiCH_2})_3\mathrm{SnGeEt}$ (63.4% yield). The latter compound was also prepared by treating tris(trimethylsilylmethyl)tin chloride with one equivalent of bis(trimethylgermyl)mercury in THF solution. This reaction must involve the initial formation of a compound with a Sn–Hg–Ge grouping*

$$\begin{array}{rr} (\mathrm{Me_3SiCH_2})_3\mathrm{SnCl} + (\mathrm{Et_3Ge})_2\mathrm{Hg} \rightarrow \mathrm{Et_3GeCl} + (\mathrm{Me_3SiCH_2})_3\mathrm{SnHgGeEt_3} & \\ \downarrow \qquad\qquad & \\ \mathrm{Hg} + (\mathrm{Me_3SiCH_2})_3\mathrm{SnGeEt_3} & (8) \\ (51.6\%) \qquad\qquad & \end{array}$$

Other compounds with the Ge–Sn bond were obtained earlier in the same fashion[25,26].

It is well known that silyl- and germyl-mercurials containing Si–Hg–Si or Ge–Hg–Ge groupings react readily with $\mathrm{HgX_2}$, where X is an electron-withdrawing atom or radical. These exchange reactions are a potential source of new types of organometallic compounds[1,25,27]. We have found that compound (I) also undergoes such reactions [X = Cl, $\mathrm{CH_2COOMe}$, PhC≡C, $\mathrm{Co(CO)_4}$].

$$\begin{array}{rr} [(\mathrm{Me_3SiCH_2})_3\mathrm{Sn}]_2\mathrm{Hg} + \mathrm{HgX_2} \xrightarrow[\sim 20^\circ]{\mathrm{THF}} 2\,(\mathrm{Me_3SiCH_2})_3\mathrm{SnHgX} \rightarrow & \\ 2\,\mathrm{Hg} + 2\,(\mathrm{Me_3SiCH_2})_3\mathrm{SnX} & (9) \end{array}$$

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* *Note added in proof*: A paper appeared recently on use of NMR spectroscopy for investigating similar reactions. Treatment of a series of compounds, $\mathrm{R_3SnOMe}$, with $(\mathrm{Me_3Si})_2\mathrm{Hg}$ or $(\mathrm{Me_3Ge})_2\mathrm{Hg}$ was shown to yield the corresponding symmetrical mercurials: $\mathrm{Me_3M{-}Hg{-}SnR_3} \rightleftharpoons 0.5\,(\mathrm{Me_3M})_2\mathrm{Hg} + 0.5\,(\mathrm{R_3Sn})_2\mathrm{Hg}$ (M = Si, Ge)[3,31].

Compounds of the type $(Me_3SiCH_2)_3SnX$ have been obtained in high yield from such reactions in addition to quantitative amounts of mercury.

We have also found that the mercurial (I) reacts under mild conditions with bis(perfluoro-t-butyl)mercury, to give mercury, tris(trimethylsilylmethyl)tin fluoride and perfluoroisobutylene

$$\underset{(I)}{[(Me_3SiCH_2)_3Sn]_2Hg} + Hg[C(CF_3)_3]_2 \xrightarrow{THF} 2\,(Me_3SiCH_2)_3SnHgC(CF_3)_3 \rightarrow$$
$$2\,Hg + 2\,(Me_3SiCH_2)_3SnF + 2\,(CF_3)_2C{=}CF_2 \quad (10)$$

On the other hand, compound (I) does not react with HgR_2 where $R=CF_3$ or $CF(CF_3)_2$. This difference in behaviour is probably due to the greater electron-withdrawing effect of the $C(CF_3)_3$ group in comparison with that of the CF_3 or $CF(CF_3)_2$ group and cannot be due to steric hindrance. It is known that nucleophilic coordination of a fluoride ion with the Hg atom of bis(perfluoroalkyl)mercurials HgR_2 substantially enhances the carbanion character of R groups[27]. In agreement with this viewpoint we have found that caesium fluoride catalyses the exchange reaction of (I) with HgR_2 $[R=CF_3$ or $CF(CF_3)_2]$ in THF. Thus, in the case of $Hg[CF(CF_3)_2]_2$, the reaction takes several minutes at room temperature to give an almost quantitative yield of mercury along with tris(trimethylsilylmethyl)tin fluoride and perfluoropropylene [*cf.* eqn. (10)].

In conclusion it should also be noted that diethylcadmium reacts with two equivalents of tris(trimethylsilylmethyl)tin hydride at room temperature to give ethane (ca. 100%) and bis[tris(trimethylsilylmethyl)stannyl]cadmium (82.6%) [*cf.* eqn. (4)]. The latter compound melts at 96–99° without decomposition and as with the germylmercury analogue it gives stable solutions in both polar and non-polar solvents. It should be noted that compounds with the Sn–Cd bond (*e.g.* $Ph_3SnCdCl$ and $Ph_3SnCdSnPh_3$) described earlier are apparently stable only as complexes with bidentate ligands[28,29]. Thus the presence of Sn–M–Sn linkages (M = Hg or Cd) must contribute considerable stability to the compounds especially when the tin atoms are bonded to Me_3SiCH_2 groups.

The reaction of tris(trimethylsilylmethyl)tin hydride with diethylzinc proceeds in a different manner, however; ethane, zinc and ethyltris(trimethylsilylmethyl)tin were isolated, but no $[(Me_3SiCH_2)_3Sn]_2Zn$ was apparently formed.

EXPERIMENTAL

All reactions were carried out in degassed sealed glass ampoules following the technique described ref. 30. All melting points were measured in evacuated capillary tubes. Gaseous products were analyzed by GLC.

Tetrakis(trimethylsilylmethyl)tin

30.2 g (0.12 mole) of stannic chloride was added dropwise with stirring (20 min) to a cooled Grignard reagent prepared under argon from 16.7 g (0.69 g-atom) of magnesium, 81.5 g (0.66 mole) of chloromethyltrimethylsilane and 500 ml of ether. To the reaction mixture was added 300 ml of benzene and the former was refluxed for 3 h. The mixture was then allowed to cool and was hydrolyzed with water and saturated aqueous ammonium chloride solution. The organic layer was dried over

$CaCl_2$ and the solvent evaporated. Distillation of the residue gave the desired product (41.0 g, 75.6%), b.p. 107–111°/1 mm, n_D^{20} 1.4850 (lit.[13] b.p. 94°/0.2 mm, n_D^{25} 1.4839). (Found: C, 41.27; H, 9.35; Si, 23.46; Sn, 24.71. $C_{16}H_{44}Si_4Sn$ calcd.: C, 41.10; H, 9.48; Si, 24.03; Sn, 25.39%.) In addition, 3.6 g (8.2%) of hexakis(trimethylsilylmethyl)ditin was isolated, m.p. 110–112°. (Found: C, 38.08; H, 8.94; Si, 21.75; Sn, 30.63. $C_{24}H_{66}Si_6Sn_2$ calcd.: C, 37.90; H, 8.74; Si, 22.15; Sn, 31.21%.) (Mol.wt. Found: 795, calcd.: 761).

Tris(trimethylsilylmethyl)tin chloride

A mixture of 44.2 g (94.5 mmole) of $(Me_3SiCH_2)_4Sn$ and 8.2 g (31.5 mmole) of stannic chloride was heated for 45 min on a water bath and for 16 h at 200–210° on an oil bath. The resulting crystalline product was distilled at 106–114°/1.5 mm, washed with cold pentane (ca. −35°) and dried at reduced pressure. The desired product was obtained (39.5 g, 79.0%) m.p. 94–96°. (Found: C, 34.02; H, 8.18; Cl, 8.30; Si, 20.14; Sn, 28.37. $C_{12}H_{33}ClSi_3Sn$ calcd.: C, 34.66; H, 8.00; Cl, 8.53; Si, 20.26; Sn, 28.55%.)

Tris(trimethylsilylmethyl)tin hydride

A solution of 48.0 g (115 mmole) of $(Me_3SiCH_2)_3SnCl$ in 400 ml of ether was added dropwise under argon with vigorous stirring and cooling to a suspension of 6.6 g (174 mmole) of $LiAlH_4$ in 200 ml of ether. The mixture was stirred at room temperature for 12 h and filtered, the solvent being removed at reduced pressure. Distillation of the residual liquid gave 35.4 g (80.5%) of $(Me_3SiCH_2)_3SnH$, b.p. 81–83°/1 mm, n_D^{20} 1.4750. (Found: C, 38.00; H, 9.31; Si, 21.73; Sn, 30.61. $C_{12}H_{34}Si_3Sn$ calcd.: C, 37.80; H, 8.99; Si, 22.09; Sn, 31.12%.)

Bis[tris(trimethylsilylmethyl)stannyl]mercury (I)

A mixture of 1.06 g (4.1 mmole) of freshly distilled diethylmercury and 3.15 g (8.3 mmole) of $(Me_3SiCH_2)_3SnH$ was left to stand at room temperature for 2 h. Following this the mixture was heated to 30–40° for 1.5–2 h when 180 ml (97.5%) of ethane was evolved. The residue was dissolved in n-hexane (~10 ml), the solution decanted from the remaining traces of mercury and kept at −60° overnight. The pale-yellow crystalline solid which precipitated was recrystallized twice from hexane at the same temperature to give 3.22 g (81.7%) of compound (I), m.p. 101–103°. (Found: C, 30.16; H, 7.12; Hg, 20.48; Si, 17.55; Sn, 24.72. $C_{24}H_{66}HgSi_6Sn_2$ calcd.: C, 29.99; H, 6.92; Hg, 20.87; Si, 17.53; Sn, 24.69%).

Thermal decomposition of compound (I)

3.34 g of (I) was heated at 150° for 10 h. The reaction mixture was extracted with hexane. Distillation of the extract gave 1.58 g (65.0%) of tetrakis(trimethylsilylmethyl)tin, b.p. 108–110°/1 mm, n_D^{20} 1.4855. The product was identified by GLC. In addition, 0.68 g (97.1%) of mercury and 0.16 g (76.2%) of metallic tin were obtained.

Oxidation of compound (I)

A solution consisting of 1.73 g of (I) in 10 ml of THF was discoloured upon exposure to molecular oxygen at room temperature for 1 h. Metallic mercury (0.35 g, 97.3%) was precipitated. The solvent was evaporated and the colourless crystalline residue recrystallized three times from a THF/hexane mixture (3/1) at −40°. The yield of hexakis(trimethylsilylmethyl)distannoxane was 1.03 g (73.6%), m.p. 59–61°. (Found: C, 36.99; H, 8.53; Si, 21.40; Sn, 30.18. $C_{24}H_{66}OSi_6Sn_2$ calcd.: C, 37.11; H, 8.57; Si, 21.70; Sn, 30.56%.)

Reaction of (I) with 1,2-*dibromoethane*

To an anhydrous solution of 2.2 g (11.7 mmole) of 1,2-dibromoethane in 5 ml benzene, frozen at liquid nitrogen temperature, was added 1.5 g (1.6 mmole) of (I). The mixture was warmed to room temperature when the reaction was complete in 10–15 min leading to the formation of 0.29 g (93.7%) of mercury and 30 ml (85.8%) of ethylene.

The solvent was removed in vacuo. The residue was recrystallized three times from hexane at −10° to give 0.81 g (56.6%) of $(Me_3SiCH_2)_3SnBr$, m.p. 36–37°. (Found: Br, 17.62. $C_{12}H_{33}BrSi_3Sn$ calcd.: Br, 17.36%.)

Reaction of (I) with ethyl bromide

A solution consisting of 3.07 g (3.2 mmole) of (I) and 1.40 g (12.8 mmole) of ethyl bromide in 5 ml of benzene was exposed to sunlight at ~20°. The mixture was discoloured after 2 h when benzene and other volatiles were removed from the reaction mixture by recondensation in vacuo. 2.79 g (94.9%) of $(Me_3SiCH_2)_3SnBr$ was isolated from the crystalline residue by the procedure described above; m.p. 35–37° (mixed m.p.). Diethylmercury was identified as ethylmercuric chloride by treatment of the volatiles with $HgCl_2$ in benzene solution. The mixture was heated at 100° for 2 h in a sealed ampoule. 1.55 g (95.1%) of EtHgCl was obtained, m.p. 189–190° (mixed m.p.).

Reaction of (I) with lithium

To 0.36 g (51.9 mg-atom) of lithium, in the form of small pieces of thin foil, in 8 ml of THF, frozen at liquid nitrogen temperature, was added 2.44 g (2.5 mmole) of (I). Initially the reaction was exothermic and was complete after 2.5 h at ~20°. The resulting dark-brown solution was decanted from the metallic mercury (0.35 g, 68.7%) and excess lithium. To the solution obtained was added 1.22 g (5.1 mmole) of bromotriethylgermane and the mixture was allowed to stand overnight at room temperature. The resulting mixture was filtered and the usual work-up gave 1.73 g (63.4%) of triethylgermyl[tris(trimethylsilylmethyl)]tin, b.p. 138–140°/1.5 mm, n_D^{20} 1.5135. (Found: C, 40.30; H, 9.06; Ge, 13.08; Si, 15.17; Sn, 21.38. $C_{18}H_{48}GeSi_3Sn$ calcd.: C, 40.03; H, 8.96; Ge, 13.44; Si, 15.60; Sn, 21.97%.) IR spectrum: 1460 w, 1410 w, 1360 w, 1240 vs, 1015 s, 960 w, 840 vs, 760 s, 720 s, 690 s, 595 m, 580 m, 565 m, 530 w, 510 m.

Reaction of $(Me_3SiCH_2)_3SnCl$ *with bis(triethylgermyl)mercury*

A mixture of 3.92 g (9.4 mmole) of $(Me_3SiCH_2)_3SnCl$ and 4.90 g (9.4 mmole) of bis(triethylgermyl)mercury in 14 ml of THF was heated at 100° for 23 h and in addition irradiated with visible light from an electric lamp (150 W) until the colour disappeared (27 h). Metallic mercury (1.84 g, 96.8%) was precipitated from the solution. Distillation of the organic layer gave 2.62 g (51.6%) of $(Me_3SiCH_2)_3SnGeEt$, b.p. 130–132°/1 mm, n_D^{20} 1.5140.

Its IR spectrum was similar to that described above.

The volatiles were analyzed by GLC. Chlorotriethylgermane (1.2 g, 65.2%) and hexaethyldigermane (0.5 g, ~18%) were identified. In addition, 0.6 g (~17%)

of hexakis(trimethylsilylmethyl)ditin was isolated; m.p. 109–111° (mixed m.p.).

Reaction of (I) with mercury(II) chloride

A solution of 0.43 g (1.6 mmole) of $HgCl_2$ in 7 ml of THF was added to 1.54 g (1.6 mmole) of (I). The exothermal reaction was complete after 10–15 min when the organic layer was decanted from the metallic mercury (0.64 g, 100 %). 1.21 g (91.1 %) of tris(trimethylsilylmethyl)tin chloride was isolated from the organic layer by the usual procedure; m.p. 93–95° (mixed m.p.).

Reaction of (I) with bis(phenylethynyl)mercury

A mixture of 1.39 g (1.4 mmole) of (I) and 0.57 g (1.4 mmole) of bis(phenylethynyl)mercury in 4 ml of THF was heated for 3 h at 100°. 0.58 g (100 %) of mercury was isolated. Distillation of the organic layer gave 0.92 g (66.2 %) of $(Me_3SiCH_2)_3SnC{\equiv}CPh$, b.p. 135–136/1.5 mm n_D^{20} 1.5245. (Found: C, 50.20; H, 7.83; Si, 17.10; Sn, 24.05. $C_{20}H_{38}Si_3Sn$ calcd.: C, 49.89; H, 7.96; Si, 17.50; Sn, 24.65 %.)

Reaction of (I) with the methyl ester of mercurybisacetic acid

A mixture of 1.44 g (1.5 mmole) of (I) and 0.52 g (1.5 mmole) of $Hg(CH_2COOMe)_2$ in 6 ml of THF was allowed to stand at room temperature for 2 days. Workup in the usual manner afforded 0.6 g (100 %) of mercury and 0.81 g (59.5 %) of $(Me_3SiCH_2)_3SnCH_2COOMe$, b.p. 126–127°/1 mm, n_D^{20} 1.4870. (Found: C, 39.33; H, 8.32; Si, 18.51; Sn, 25.81. $C_{15}H_{38}O_2Si_3Sn$ calcd.: C, 39.74; H, 8.45; Si, 18.58; Sn, 26.18 %.)

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

A mixture of 1.22 g (1.3 mmole) of (I) and 0.68 g (1.3 mmole) of $Hg[Co(CO)_4]_2$ in 4 ml of THF was left to stand at room temperature for 20–30 min when metallic mercury (0.49 g, 98.5 %) was precipitated. The solvent was evaporated and the residue recrystallized twice from n-hexane at −70°. The yield of tris(trimethylsilylmethyl)stannyltetracarbonylcobalt was 1.00 g (76.5 %), m.p. 30–32°. (Found: C, 34.36; H, 6.01. $C_{16}H_{33}CoO_4Si_3Sn$ calcd.: C, 34.87; H, 5.99 %.)

Reaction of (I) with bis(perfluoro-t-butyl)mercury

A mixture of 1.22 g (1.3 mmole) of (I) and 0.68 g (1.3 mmole) of $Hg[Co(CO)_4]_2$ in 5 ml of THF was allowed to stand for 2 h at room temperature. The organic layer was decanted from mercury (0.62 g, 98.5 %) and the THF and volatile products removed by recondensation in vacuo. The residue was recrystallized from n-hexane. 1.03 g (82.5 %) of tris(trimethylsilylmethyl)tin fluoride was obtained, m.p. 122–124°. (Found: F, 4.72. $C_{12}H_{33}FSi_3Sn$ calcd.: F, 4.76 %.) (Mol. wt. Found: 403, calcd.: 399). Perfluoroisobutylene (74.5 %) was identified by GLC analysis as being present in the volatiles.

Reaction of (I) with bis(perfluoroisopropyl)mercury catalysed by CsF

Bis(perfluoroisopropyl)mercury (1.38 g, 2.6 mmole) and (I) (2.51 g, 2.6 mmole) were dissolved in 5 ml of degassed THF and finely-dispersed, anhydrous CsF (0.38 g, 2.5 mmole) was added. The reaction was completed at room temperature after 10–15 min and metallic mercury (0.94 g, 92 %) was precipitated. The organic layer was analysed as above. The yield of tris(trimethylsilylmethyl)tin fluoride was 0.76 g (74.5 %), m.p. (mixed m.p.) 125–126°. Perfluoropropylene (74.5 %) was detected by GLC analysis as being present in the volatile products.

Bis[tris(trimethylsilylmethyl)stannyl]cadmium

A mixture of 0.90 g (5.3 mmole) of diethylcadmium and 4.01 g (10.5 mmole) of $(Me_3SiCH_2)_3SnH$ was allowed to stand for 2 h at room temperature when 230 ml (~100%) of ethane evolved. The crystalline green-yellow product obtained was dissolved in 7 ml of hexane. The solution was decanted from cadmium (traces) and kept at −70° for 6–7 h. The crystalline product precipitated was crystallized twice from hexane in the same manner. 3.79 g (82.6%) of the product was isolated, m.p. 96–99°. (Found: C, 32.87; H, 7.55; Cd, 12.90; Si, 19.33; Sn, 27.23. $C_{24}H_{66}CdSi_6Sn_2$ calcd.: C, 33.02; H, 7.62; Cd, 12.87; Si, 19.30; Sn, 27.19%.)

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