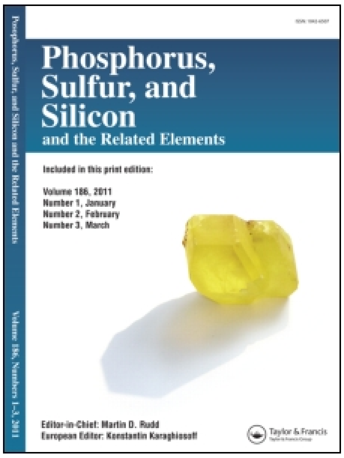

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Communication

FORMATION OF $(Me_3M)_3Sb$ (M = Ge, Sn, Pb) AND $(Me_3M)_4Sb_2$ (M = Pb) BY REACTION OF $(Me_3Si)_3Sb$ WITH Me_3MCl

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Reaction of $(Me_3Si)_3Sb$ (**1**) with Me_3MCl gives $(Me_3M)_3Sb$ [M = Ge (**2**), Sn (**3**), Pb(**4**)]. The lead stibine **4** decomposes readily with formation of Me_4Pb and $(Me_3Pb)_4Sb_2$ (**5**).

Key words: Tris(trimethylgermyl)stibine, tris(trimethylstannyl)stibine, tris(trimethylplumbyl)stibine, tetrakis(trimethylplumbyl)distibane.

INTRODUCTION

Tris(trimethylmetal)stibines of the type $(Me_3M)_3Sb$ with M = Si (**1**), Ge (**2**), or Sn (**3**) are known for many years.[1] They have been used as ligands in transition metal complexes[2,3] and as starting materials for the preparation of antimonides,[4] distibanes[5] or cluster compounds.[6] Their syntheses have been performed by the reactions of M_3Sb (M = Li, Na) with Me_3MCl in diethyl ether or liqu. ammonia. Earlier attempts to synthesize the lead analogue $(Me_3Pb)_3Sb$ (**4**) have not been successful.[7] We report here on exchange reactions of **1** with Me_3MCl leading to **2**, **3**, or **4** and $(Me_3Pb)_4Sb_2$ (**5**).

RESULTS AND DISCUSSION

The reactions of **1** with Me_3MCl (M = Ge, Sn) in absence of solvent at ambient temperature give **2**, or **3** (Equation 1).

$$\underset{\mathbf{1}}{(Me_3Si)_3Sb} + 3\,Me_3MCl \rightarrow \underset{\mathbf{2}:\ M\,=\,Ge,\ \mathbf{3}:\ M\,=\,Sn}{(Me_3M)_3Sb} + 3\,Me_3SiCl \qquad (1)$$

Me_3SiCl is removed by distillation in order to complete the reactions and to isolate the products which are obtained in almost quantitative yield. These new syntheses are very easy to do and minimize the use and the handling of the expensive and poisonous reagents Me_3MCl.

The reaction of **1** with Me_3PbCl is best performed at −50°C. Stirring of the heterogeneous mixture of the reagents results in the formation of Me_3SiCl and a red solid material consisting of two products, $(Me_3Pb)_3Sb$ (**4**) and $(Me_3Pb)_4Sb_2$ (**5**). The presence of **4** is demonstrated by the mass spectrum showing the molecular ion at highest mass and an intensive signal in the ^{1}H-NMR spectrum. **4** is unstable in the product mixture and in solution. Decomposition leads to Me_4Pb [δ (C_6D_6) = 0.71, ^2J (^{207}Pb, ^{1}H) = 62 Hz (Reference 8 identical data)] and black solid materials. The distibane **5** is isolated when the initial product is washed with toluene. It is a red solid that is stable at room temperature in an open atmosphere for several days. Solutions of **5** in hydrocarbon are yellow. They decompose rapidly with formation of Me_4Pb. The identity of **5** is confirmed by elemental analyses and by the ^{1}H-NMR spectrum. In the UV-VIS spectrum of solid **5** in $BaSO_4$ there is a plateau of absorption from 320–520 nm with a slope ending at 580 nm. Maxima are at 380 nm and 490 nm. Mass spectra of **4** and **5** are similar. A molecular ion of **5** is not observed. The formation of **4** is described in Equation (2). Equation (3) shows a possible path for the formation of **5**. Hexamethyldilead has been detected by mass spectrometry. The dilead compound decomposes with formation of tetramethyllead and elemental lead.

$$(Me_3Si)_3Sb + 3\ Me_3PbCl \rightarrow \underset{\mathbf{4}}{(Me_3Pb)_3Sb} + 3\ Me_3SiCl \qquad (2)$$

$$2\ (Me_3Pb)_3Sb \rightarrow \underset{\mathbf{5}}{[(Me_3Pb)_2Sb]_2} + (Me_3Pb)_2 \qquad (3)$$

The colour changes and the relative stability of **5** compare well with the properties of the analogues $[(Me_3M)_2Sb]_2$ (M = Si, Ge, Sn).[9] These distibanes are also red as solids and yellow in solution and have similar UV-VIS spectra. The bathochromic shift on crystallization is a result of the formation of chains through short intermolecular Sb···Sb contacts. Similar structural features may be responsible for the deep colour of **5**. The novel lead stibanes **4** and **5** are among the first molecular compounds with covalent Sb—Pb bonds. Earlier reports consider the syntheses of $(Ph_3Pb)_3Sb$[7] and $Ph_2SbPbPh_3$.[10] The As and P homologues of **4** are also known.[7]

EXPERIMENTAL

All the operations are carried out in an argon atmosphere in carefully dried solvents. The NMR spectra were recorded on a Bruker WH 360 spectrometer at 360 MHz. For the mass spectra a Varian MAT CH 7A spectrometer was used. $(Me_3Si)_3Sb$ (**1**) was prepared following the procedure described in the literature[1] or in a modified way, using tetrahydrofuran instead of diethylether as solvent.

Tris(trimethylgermyl)stibine (**2**): 4.0 g (26.4 mmol) Me_3GeCl are added to 3.0 g (8.8 mmol) **1**. The mixture is stirred at room temperature for 2 hours. Raising the bath temperature to 70°C results in the distillation of Me_3SiCl. The remaining liquid consists of 3.1 g (91.2%) of **2**. NMR and MS data are as reported in the literature.[1,3]

Tris(trimethylstannyl)stibine (**3**): 5.0 g (17.6 mmol) Me_3SnCl are added to 2.0 g (5.8 mmol) **1**. The mixture is stirred at room temperature for 2 hours. Raising the bath temperature to 70°C results in the distillation of Me_3SiCl. Distillation of the remaining liquid gives 6.0 g (85.7%) of **3** (b.p. 136°C/0.1 mm Hg). NMR and MS data are as reported in the literature.[1,3]

Tris(trimethylplumbyl)stibine (**4**) and Tetrakis(trimethylplumbyl)distibine (**5**): 2.7 g (9.4 mmol) Me_3PbCl are added to 1.07 g (3.1 mmol) **1**. At first the mixture becomes yellow and later the colour turns red. After stirring the mixture at −50°C in the dark for 15 minutes Me_3SiCl is removed at reduced pressure. The remaining red solid consists of **4** and **5**. **4**: ^{1}H-NMR: $\delta(C_6D_6)$ 1.11, ^2J (^{207}Pb, ^{1}H) = 46 Hz, MS (70 eV, 30°C) m/z (%): 878 (1) M^+, 863 (2) M^+-Me, 773 (1) Me_2Pb_3Sb, 758 (1) $MePb_3Sb$, 743 (2) Pb_3Sb, 642 (1) Me_7Pb_2Sb, 627 (3) Me_6Pb_2Sb, 597 (1) Me_4Pb_2Sb, 582 (1) Me_3Pb_2Sb, 567 (1) Me_2Pb_2Sb, 552 (1) $MePb_2Sb$, 537 (2) Pb_2Sb, 506 (1) Me_6Pb_2, 491 (5) Me_5Pb_2, 389 (15) Me_4PbSb, 374 (1) Me_3PbSb, 359 (7) Me_2PbSb, 329 (3) PbSb, 253 (100) Me_3Pb, 223 (70), MePb, 208 (50) Pb, 151 (5) MeSb. The solid is washed with 12 ml toluene at −15°C. The remaining solid is **5** (yield: 0.73 g, 37.2%; m.p. dec. 85–87°C). **5**: ^{1}H-NMR: $\delta(C_6D_6)$ 1.19, ^2J (^{207}Pb, ^{1}H) = 44 Hz, MS (DCI, neg., NH_3) m/z (%): 627 (30) Me_6Pb_2Sb, 253 (100) Me_3Pb.

CH-analysis: found. (%): C (11.00), H (2.70); calc. (%): C (11.49) H (2.90).

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LITERATURE

1. E. Amberger and R. W. Salazar G., *J. Organometal. Chem.*, **8,** 111 (1967).
2. H. Schumann, H. J. Breunig and U. Frank, *J. Organometal. Chem.*, **60,** 279 (1973).
3. H. J. Breunig and W. Fichtner, *J. Organometal. Chem.*, **222,** 97 (1981).
4. G. Becker, A. Münch and C. Witthauer, *Z. anorg. allg. Chem.*, **492,** 15 (1982).
5. S. Roller, M. Dräger, H. J. Breunig, M. Ates and S. Gülec, *J. Organometal. Chem.*, **378,** 327 (1989).
6. D. Fenske and C. Persan, *Z. anorg. allg. Chem.*, **593,** 61 (1991).
7. H. Schumann, A. Roth, O. Stelzer and M. Schmidt, *Inorg. Nucl. Chem. Letters*, **2,** 311 (1966).
8. H. P. Fritz, *J. Organometal. Chem.*, **1,** 297 (1964).
9. H. J. Breunig in S. Patai, ed., "The Chemistry of Organic Arsenic, Antimony and Bismuth Compounds," John Wiley & Sons, Chichester, 1994, p. 441.
10. H. Schumann and M. Schmidt, *Inorg. Nucl. Chem. Letters*, **1,** 1 (1965).