Organometallics 1988, *7*, 245–246

Application of Phosphine Tellurides to the Preparation of Group II–VI (2–16[†]) Semiconductor Materials

M. L. Steigerwald* and C. R. Sprinkle

AT&T Bell Laboratories
Murray Hill, New Jersey 07974

Received September 8, 1987

Summary: In order to find low-temperature routes to metal tellurides, we have investigated some of the reactions of phosphine tellurides. Via the phosphine telluride, tellurium is chemically transported by PMe_3 under very mild conditions ($T \approx 150$ °C). Triethylphosphine telluride reacts with Hg at room temperature and with HgR_2 (R = Et, Ph) at 115 °C, in each case giving HgTe as the sole solid-state product. We studied the reaction with $HgPh_2$ in greater detail, showing that Ph_2Te and Ph_2Te_2 are the major organic products.

A chemical impediment to the synthesis of group II–VI (2–16) materials such as HgTe and $Hg_xCd_{1-x}Te$ by organometallic vapor phase epitaxy (OMVPE) is the stability of the organometallic precursors that have commonly been used. In the simplest description of OMVPE, pyrolysis of the organometallic precursors gives metal atoms (or their equivalents) that combine to give the polydiatomic solid. Conventional tellurium sources ($TeMe_2$, $TeEt_2$) are too stable to generate a significant amount of atomic tellurium at temperatures as low as 200 °C. At the higher temperatures that are required for pyrolysis of the dialkyl tellurides, the high surface mobility and high vapor pressure of mercury hamper growth of the the technologically important mercury containing compounds.[1]

One solution to the organotellurium source problem is in the use of phosphine tellurides. Phosphine tellurides (R_3PTe) are not new compounds, but remarkably little is known about their chemistry. We were led to study phosphine tellurides by the report[2] of the equilibrium in eq 1. This suggests that (1) tellurium may be chemically

$$R_3P + Te \rightleftharpoons R_3PTe \qquad (1)$$

transported[3] by sufficiently volatile phosphines and (2) phosphine tellurides may be good sources of atomic tellurium in OMVPE synthesis.[4]

The ability of phosphines to transport tellurium is demonstrated by the following experiment. A tube containing Te (310 mg, 2.4 mmol) and Me_3P (5 μL, 0.05 mmol) was sealed and placed in a temperature gradient (160–180 °C) in a tube furance. After an hour, transport and crystallization of Te in the cooler zone was observed. Use of more Me_3P hastened this process. A similar tube containing only Te was sealed under vacuum and placed in the same gradient. No transport or crystallization was seen in this tube.

The utility of phosphine tellurides in the OMVPE process was assayed by allowing Et_3PTe to react with elemental mercury. A solution of 7.9 mmol of Et_3PTe in toluene (0.5 M) was added to 4.9 mmol of Hg at room temperature. An immediate reaction to form HgTe was observed. After vigorous stirring of this mixture under argon for 20 h filtration gave a black solid. Washing with toluene/PEt_3 (4/1) removed any excess Te. Differential scanning calorimetry (DSC) showed no free Hg, and X-ray powder diffraction showed only HgTe. The yield of the dry powder was quantitative (based on Hg). The ease of this process may be rationalized by viewing the phosphine telluride as a single-coordinate complex of Te(0).[5]

Since volatile metal alkyls are routinely used in OMVPE, we checked the reaction of Et_3PTe with $HgEt_2$. The phosphine telluride (3.85 g, 15.7 mmol) and triethylphosphine (1.7 g, 14.2 mmol) were dissolved in 25 mL of toluene and treated with $HgEt_2$ (2.04 g, 7.9 mmol), and the mixture was heated to reflux. Within 10 min HgTe began to form. After continued heating for 24 h the black solid was isolated, washed, and dried. This gave 1.65 g of solid, the X-ray powder diffraction pattern of which showed only HgTe. GC analysis[6] of the filtrate showed unreacted $HgEt_2$ (30%); therefore, this reaction produced HgTe in practically quantitative yield at 70% conversion. Further heating continued to produce HgTe.

The stench of the lower alkyls of tellurium made further study of this reaction inconvenient. Fortunately, the reaction of the less volatile $HgPh_2$ with Et_3PTe also produces HgTe. A solution of Ph_2Hg (4.00 g, 11.6 mmol) and Et_3P (3.6 g, 30.5 mmol) in 20 mL of toluene was added to a solution of Et_3PTe (5.77 g, 23.5 mmol) and Et_3P (0.83 g, 7.0 mmol) in 25 mL of toluene, and the mixture was heated at reflux for 20 h. This resulted in disappearance of Ph_2Hg and precipitation of HgTe. Filtration gave 3.63 g (11.1 mmol, 95%) of pure HgTe as analyzed by X-ray powder diffraction.

In addition to HgTe, the reaction of Ph_2Hg with Et_3PTe gave Ph_2Te. GC analysis[7] of the organic products of the above reaction showed only Ph_2Te and Ph_2Te_2 in a 97:2 molar ratio, and fractional distillation gave 2.61 g (9.3 mmol, 82%) of pure Ph_2Te. Interestingly the telluride/ditelluride ratio is a direct function of the Ph_2Hg/Et_3PTe ratio. When the latter is less than 2, very little ditelluride is formed. When it is greater than 2.5, 20% of the observed organotellurium product is ditelluride (shown by GC analysis of the crude reaction mixture). It is known that monotellurides can be prepared from organomercurials and Te powder at elevated temperatures.[8] The present work demonstrates a milder route.

The nature and distribution of products from this reaction leads to speculation on its mechanism. Both $HgEt_2$ and $HgPh_2$ are stable in refluxing toluene so thermolysis to give elemental Hg which reacts as above is not likely. We have previously shown[9] that compounds of the form

---

[†] In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13-18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

(1) Irvine, S. J. C.; Geiss, J.; Gough, J. S.; Blackmore, G. W.; Royle, A.; Mullin, J. B.; Chew, N. G.; Cullis, A. G. *J. Cryst. Growth* **1986**, *77*, 437–51.

(2) Zingaro, R. A.; Stevens, B. H.; Irgolic, K. *J. Organomet. Chem.* **1965**, *4*, 320–3.

(3) Schäfer, H. *Chemical Transport Reactions*; Academic: New York, 1964.

(4) Tributylphosphine telluride has been used as the source of Te in the electrochemical synthesis of thin films of CdTe: Darkowski, A.; Cocivera, M. *J. Electrochem. Soc.* **1985**, *132*, 2768–71.

(5) (a) Austad, T.; Rod, T.; Ase, K.; Songstad, J.; Norbury, A. H. *Acta Chem. Scand.* **1973**, *27*, 1939–49. (b) duMont, W.-W.; Kroth, H.-J. *J. Organomet. Chem.* **1976**, *113*, C35–C37.

(6) Analysis was done with a 6-ft OV-101 column on a HP-5880 GC (FID detection, isothermal oven, $T = 75$ °C).

(7) Analysis as in ref 6, but with temperature programming 175 → 225 °C.

(8) (a) Krafft, F.; Lyons, R. E. *Chem. Ber.* **1894**, *27*, 1768–73. (b) Adloff, M.; Adloff, J. P. *Bull. Chim. Soc. Fr.* **1966**, 3304.

0276-7333/88/2307-0245$01.50/0

$Hg(TeR)_2$ thermolyze to give HgTe and organotelluriums (both TeR_2 and Te_2R_2). The pathway shown in eq 2 rationalizes the observed products. The reversibility of the reaction between Hg and Te_2R_2 accounts for the increasing yield of ditellurides with increasing initial Te/Hg ratio. Mercury, when expelled from the $Hg(TeR)_2$ complex, is immediately scavenged by the excess Et_3PTe.

$$Ph_2Hg + Et_3PTe \rightarrow \{PhHgTePh\} \xrightarrow{Et_3PTe} Hg(TePh)_2 \rightarrow Ph_2Te + HgTe \quad (2)$$

The critical feature of this proposal is the insertion of Te atoms into the Hg–C bonds of Ph_2Hg. This process has precedent in the literature. Grignard[10] and organolithium[11] reagents are known to react with elemental Te to give RTeM compounds in a heterogeneous reaction. In an example perhaps more relevant to the present discussion, the reaction of t-Bu_3PTe with t-Bu_2PSiMe_3 results in insertion of Te into the P–Si bond in a homogeneous process.[12]

In this communication we have shown a very mild route to the semimetal HgTe. The ability to prepare such solid-state compounds at low temperatures highlights one aspect of the utility of organometallic reactions in material synthesis.

---

[9] Steigerwald, M. L.; Sprinkle, C. R. *J. Am. Chem. Soc.* **1987**, *109*, 7200–1.

[10] Haller, A. S.; Irgolic, K. J. *J. Organomet. Chem.* **1972**, *38*, 97–103.

[11] Engman, L.; Cava, M. P. *Synth. Commun.* **1982**, *12*, 163–5.

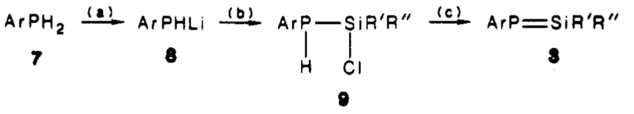
[12] du Mont, W.-W. *Angew Chem., Int. Ed. Engl.* **1980**, *19*, 554–5.

Additions and Corrections

Cornelis N. Smit and Friedrich Bickelhaupt*: Phosphasilenes: Synthesis and Spectroscopic Characterization. **1987**, *6*, 1156.

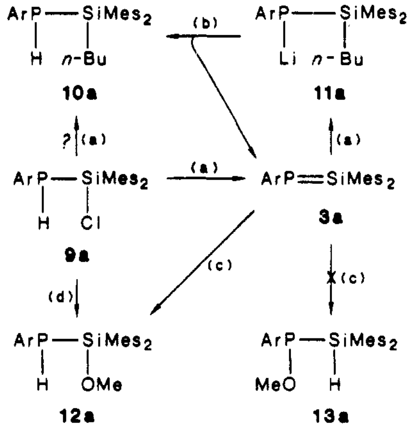
Schemes I and II should appear as follows.

Scheme I



(a) n-BuLi, THF, ca. −60 °C. (b) $R'R''SiCl_2$ (4), −60 °C. (c) n-BuLi, −60 °C, then slowly warming to room temperature. In some reactions, steps a and b were combined to one step.

Scheme II



(a) n-BuLi, THF, −60 → +25 °C. (b) **9a**. (c) MeOH. (d) MeONa/MeOH in THF.

Alberto R. Dias,* Palmira B. Dias, Hermínio P. Diogo, Adelino M. Galvão, Manuel E. Minas da Piedade, and José A. Martinho Simões: Energetics of Molybdenum–Azobenzene, Titanium–Azobenzene, Titanium–Iodide, and Titanium–Carbonyl Bonds in Bis(cyclopentadienyl) Complexes. **1987**, *6*, 1427.

The E(M–L) values for the complexes $M(Cp)_2(PhN{=}NPh)$ (M = Ti, Mo) in Table V, 49 and 144 kJ mol^{-1}, are incorrectly calculated from the remaining data in the same table. They should be replaced by 195 and 290 kJ mol^{-1}, respectively. The conclusions are not affected, except that a disagreement with literature ab initio values is now apparent. However, the theoretical prediction that titanium-azobenzene bond is "weak" is still supported by the corrected bond enthalpy terms.

H. H. Murray, David A. Briggs, Guillermo Garzón, Raphael G. Raptis, Leigh C. Porter, and John P. Fackler, Jr.*: Structural Characterization of a Linear [Au···Pt···Au] Complex, $Au_2Pt(CH_2P(S)Ph_2)_4$, and Its Oxidized Linear Metal–Metal Bonded [Au–Pt–Au] Product, $Au_2Pt(CH_2P(S)Ph_2)_4Cl_2$. **1987**, *6*, 1992–1995.

In the summary, the space group for complex 2 should be "$I\bar{4}$" and not "$I4$". In ref 5j, "Mays, A. J." should be "Mayar, A. J.".