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The First Phosphine-Catalyzed Insertion of Tellurium into Sn−Sn and Pb−Pb Bonds: A Simple and Efficient Route to R_3MTeMR_3 (M = Sn, Pb)

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Summary: In the presence of a catalytic amount of a phosphine, elemental tellurium efficiently inserts into Sn−Sn and Pb−Pb bonds under mild conditions to give the corresponding tellurides R_3MTeMR_3 (M = Sn, Pb) in quantitative yield. Mechanistic study shows that first a phosphine telluride $R'_3P{=}Te$ is formed via the reaction of R'_3P with tellurium, which subsequently reacts with $(R_3M)_2$ to produce $(R_3M)_2Te$ and concomitantly regenerates R'_3P to restart another cycle of the catalytic insertion.

Technology to use tellurium-containing materials as structurally defined single-source precursors in electronic, optic, and optoelectronic applications is rapidly emerging.[1] Accordingly, development of clean methods for the synthesis of these materials starting with readily available organotelluriums[2] is a subject of current scrutiny.[3] The use of phosphine tellurides ($R'_3P{=}Te$)[4] as tellurium delivery agents in insertion reactions to a variety of metal−metal and metal−carbon bonds has attracted attention, and some novel tellurium compounds have been prepared.[5] However, all hitherto known reactions require a stoichiometric quantity of $R'_3P{=}Te$, and hence an equimolar amount of PR'_3 is inevitably formed, which can be another drawback to the purification of the resulting products.[5c] Moreover, $R'_3P{=}Te$ usually are difficult to prepare and handle because of their thermal instability and high air sensitivity.[4] Herein we disclose the first examples of the *phosphine-catalyzed* insertion of elemental tellurium into Sn−Sn and Pb−Pb bonds.[6] The products, $(R_3M)_2Te$ (M = Sn, Pb), formed in quantitative yield, are known as efficient low-temperature single-source precursors to structurally defined narrow-band-gap semiconductors.[7]

Great efficacy of phosphines is exemplified by the following experiments. In a control experiment, an equimolar mixture of $(Me_3Sn)_2$ (1 mmol, 328 mg) and finely powdered tellurium (1 mmol, 128 mg) suspended in benzene (10 mL) was stirred at room temperature for 3 h. GC and ^1H NMR analyses showed that no detectable product had been formed and the starting materials remaining unchanged. When a trace amount of t-Bu_3P (10 mg, 5 mol %) was added to the suspension, however, the tellurium powder completely disappeared within 3 h to afford $(Me_3Sn)_2Te$ (**1a**) as sole product in quantitative yield (eq 1).[8,9] Although heating was needed, other distannanes such as $(n\text{-}Bu_3Sn)_2$ and $(Ph_3Sn)_2$ behaved similarly using either n-Bu_3P or t-Bu_3P as the

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(8) In the absence of a phosphine, the reaction of tellurium with $(Me_3Sn)_2$ proceeded, albeit very sluggishly even at 80 °C, to give $(Me_3Sn)_2Te$ in 34% yield after 24 h.

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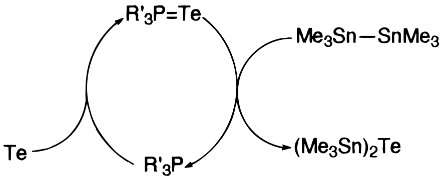
Table 1. Phosphine-Catalyzed Insertion of Tellurium into Sn−Sn Bonds[a]

phosphine	$(R_3Sn)_2$	conditions	% yield[b]
$(4\text{-ClC}_6H_4)_3P$	$(Me_3Sn)_2$	80 °C, 3 h, 1 M	34
Ph_3P	$(Me_3Sn)_2$	80 °C, 3 h, 1 M	45
$(n\text{-Bu})_3P$	$(Me_3Sn)_2$	80 °C, 0.5 h, 1 M	100
$(n\text{-Bu})_3P$	$(Me_3Sn)_2$	25 °C, 18 h, 1 M	9
$(n\text{-Bu})_3P$	$(n\text{-Bu}_3Sn)_2$	80 °C, 3 h, 1 M	100
$(n\text{-Bu})_3P$	$(Ph_3Sn)_2$	80 °C, 3 h, 0.1 M	73
		80 °C, 5 h, 0.1 M	100
$(t\text{-Bu})_3P$	$(Me_3Sn)_2$	25 °C, 3 h, 0.1 M	100
$(t\text{-Bu})_3P$	$(Ph_3Sn)_2$	80 °C, 2 h, 0.1 M	100

[a] All reactions were run in a Schlenk flask using equimolar Te powder and $(R_3Sn)_2$ in C_6D_6 in the presence of 5 mol % phosphine catalyst with stirring. [b] Yields refer to NMR yields; since no other product was found by NMR spectroscopy, the yield was evaluated based on the integration of the signals arising from the product and the starting distannane.

Scheme 1. Proposed Mechanism for the Phosphine-Catalyzed Insertion of Tellurium into Sn−Sn Bonds

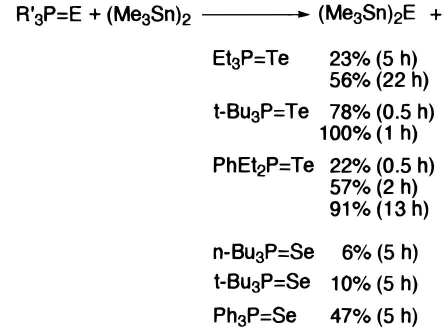


catalyst, and quantitative yields of the corresponding distannyl tellurides were obtained (Table 1). Aromatic phosphines such as Ph_3P and $(4\text{-ClC}_6H_4)_3P$ also catalyzed the reaction with somewhat low activity as compared with n-Bu_3P and t-Bu_3P. For example, a 45% yield of **1a** was formed after 3 h heating when Ph_3P was employed as the catalyst. Among the phosphines screened, t-Bu_3P showed the highest catalytic activity, followed by n-Bu_3P, Ph_3P, and $(4\text{-ClC}_6H_4)_3P$, which parallels their basicities.[10]

$$(R_3Sn)_2 + Te \xrightarrow[\text{benzene}]{5\text{ mol\% }PR'_3} (R_3Sn)_2Te \qquad (1)$$

This phosphine-catalyzed insertion of tellurium could be successfully extended to diplumbanes, efficiently producing diplumbyl tellurides. As shown in eq 2, air and moisture sensitive $(Ph_3Pb)_2Te$, which had been prepared only in moderate yield via the reaction of $Ph_3PbTeLi$ with Ph_3PbCl,[11] was obtained in high yield simply by heating an equimolar mixture of $(Ph_3Pb)_2$ and tellurium powder in benzene in the presence of 5 mol % of t-Bu_3P at 50 °C for 5 h.[12,13]

Scheme 2. Reaction of Me_6Sn_2 with $R'_3P{=}E$ in Benzene-d_6 (0.4 M): 25 °C for E = Te and 80 °C for E = Se



$$(Ph_3Pb)_2 + Te \xrightarrow[\substack{\text{benzene}\\ 50\ ^\circ\text{C, 5 h}}]{5\text{ mol\% }t\text{-Bu}_3P} \underset{96\%\text{ yield}}{(Ph_3Pb)_2Te} \qquad (2)$$

Monitoring the progress of the Et_3P-catalyzed reaction of $(Me_3Sn)_2$ with tellurium by ^1H NMR spectroscopy clearly revealed that the catalysis involved two processes, generation of $Et_3P{=}Te$ and its reaction with $(Me_3Sn)_2$, with the second step being rate-determining as far as trialkylphosphines are concerned (Scheme 1). Thus, stirring a mixture of $(Me_3Sn)_2$ (0.1 mmol), Te powder (0.1 mmol), and Et_3P (0.05 mmol) in C_6D_6 (1 mL) at room temperature for 5.5 h resulted in complete consumption of Et_3P to form $Et_3P{=}Te$ in quantitative yield (based on Et_3P) along with a trace of $(Me_3Sn)_2Te$ (11% based on the distannane). Upon heating the reaction mixture at 80 °C for 3 h, a pale yellow transparent solution was obtained, in which only $(Me_3Sn)_2Te$ (∼0.1 mmol, ∼100% yield) and Et_3P (∼100% recovery) were detected, while $Et_3P{=}Te$ and $(Me_3Sn)_2$ had completely disappeared.

On the basis of the proposed mechanism, and as long as the phosphine telluride is generated to a sufficient extent, one can envision that the catalytic activity of phosphines (Table 1) increases in parallel with the reactivity of their corresponding phosphine tellurides toward $(R_3Sn)_2$. Indeed, the yield of **1a** in the reaction of $Et_3P{=}Te$ with $(Me_3Sn)_2$ was only 56% even after stirring for 22 h (Scheme 2), while a quantitative formation of **1a** was observed in only 1 h when t-$Bu_3P{=}Te$ was employed.[14] Since triarylphosphines

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[9] Typical procedure for the preparation of distannyl tellurides: Hexaphenyldistannane (280 mg, 0.400 mmol), tellurium powder (54 mg, 0.423 mmol), and t-Bu_3P (4.0 mg, 0.02 mmol, 5 mol %) were placed in a Schlenk tube under nitrogen atmosphere, and 4 mL of dry benzene was added. The mixture was stirred at 80 °C for 5 h and was filtered under nitrogen to remove excess tellurium. The solvent was evaporated under reduced pressure, and the residue was washed with pentane to give a white solid of analytically pure $(Ph_3Sn)_2Te$ (331 mg, 100% yield). White crystals could be obtained by recrystallization of the solid using a CH_2Cl_2−pentane mixture (337 mg, 407 mmol, 81% yield). Mp: 157 °C (lit.[16] 149−150 °C). Anal. Calcd for $C_{36}H_{30}Sn_2Te$: C, 52.24; H, 3.65. Found: C, 52.58; H, 3.44. ^1H NMR (500 MHz, C_6D_6): δ 7.44−7.45 (m, 12H, $J_{HSn} = 55.7$ Hz), 6.98−7.06 (m, 18H). ^{13}C NMR (125 MHz, C_6D_6): δ 138.6, 137.1 ($J_{CSn} = 44.5$ Hz), 129.5 ($J_{CSn} = 12.4$ Hz), 128.9 ($J_{CSn} = 56.9$ Hz). ^{119}Sn NMR (186 MHz, C_6D_6, Me_4Sn): δ −140.2. ^{125}Te NMR (157 MHz, $CDCl_3$, Me_2Te): δ −1290.4 ($J_{^{117}SnTe} = 3085.7$ Hz, $J_{^{119}SnTe} = 3226.1$ Hz).

[10] Hudson, H. R. In *The Chemistry of Organophosphorus Compounds, Vol. 1*; Hartley, F. R., Ed.; John Wiley & Sons: New York, 1990; p 473.

[11] Schumann, H.; Thom, K.-F.; Schmidt, M. *J. Organomet. Chem.* **1965**, *4*, 28.

[12] It is important to run the reaction at lower temperatures to prevent side reactions. For example, the reaction run at 80 °C precipitated a black powder, presumably due to the formation of PbTe.

[13] Typical procedure for the preparation of diplumbyl tellurides: Hexaphenyldiplumbane (2.631 g, 3 mmol), tellurium powder (396 mg, 3.1 mmol), and t-Bu_3P (30 mg, 0.15 mmol, 5 mol %) were placed in a Schlenk tube under nitrogen atmosphere, and 15 mL of dry benzene was added. The mixture was stirred at 50 °C for 5 h and was filtered (under nitrogen) to remove excess tellurium. Solvent was evaporated under reduced pressure, and the residue was washed with pentane to give a yellow solid of spectroscopically pure $(Ph_3Pb)_2Te$ (2.893 g, 96% yield), as confirmed by ^1H and ^{13}C NMR spectroscopies. Bright yellow crystals of $(Ph_3Pb)_2Te$ were obtained by recrystallization from a CH_2Cl_2−pentane mixture, 2.20 g, 73% yield. Mp: 137 °C (lit.[11] 128−129 °C). Anal. Calcd for $C_{36}H_{30}Pb_2Te$: C, 43.04; H, 3.01. Found: C, 43.37; H, 2.80. ^1H NMR (500 MHz, C_6D_6): δ 7.06−7.08 (m, 12H, $J_{HPb} = 93.5$ Hz), 6.67−6.59 (m, 18H). ^{13}C NMR (125 MHz, C_6D_6): δ 150.8 ($J_{CPb} = 396.2$ Hz), 137.3 ($J_{CPb} = 77.6$ Hz), 129.8 ($J_{CPb} = 85.8$ Hz), 128.9 ($J_{CPb} = 19.6$ Hz). ^{125}Te NMR (157 MHz, C_6D_6, Me_2Te): δ −1079.3 ($J_{PbTe} = 4100$ Hz).

do not form isolable phosphine tellurides, we are unable to examine their reactivities toward the distannane. However, an attempted experiment using phenyldiethylphosphine telluride as an alternate revealed that its apparent reactivity in a similar treatment was higher than that of $Et_3P{=}Te$, but lower than that of t-$Bu_3P{=}Te$. To gain more reliable information related to the second step of the catalytic cycle, we examined the reactivity of phosphine selenides, which are thermally stable and nondissociative analogues of the tellurides. Similar treatment with $(Me_3Sn)_2$ showed that the reactivity decreased in the order $Ph_3P{=}Se > t\text{-}Bu_3P{=}Se > n\text{-}Bu_3P{=}Se$; the trend is the reverse of the P=Se bond strength.[15] If we consider a similar reactivity trend in the catalytic reaction between distannanes and tellurium (eq 1), we must accept that the foregoing statement about the rate-determining step is not applicable to triarylphosphines. The relatively low catalytic activity of the triarylphosphines may not be associated with the reactivity of the phosphine telluride toward the distannane, but simply because of the unfavorable equilibrium for the generation of the triarylphosphine telluride.

Extensive study on the phosphine-catalyzed insertion of chalcogen elements is now in progress.

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(14) Despite increasing number of reactions that use $R'_3P{=}Te$ as tellurium transfer reagent, the experimental data relevant to the transfer mechanism are sorely lacking. Although dependent on the structure of R′, phosphine tellurides $R'_3P{=}Te$ are known to be in equilibrium with Te and R'_3P in solution (refs 4 and 5). However, a recent study of the bond strength of n-$Bu_3P{=}Te$ (52 kcal mol^{-1}) has doubted the importance of the equilibrium in reactions: Capps, K. B.; Wixmerten, B.; Bauer, A.; Hoff, C. D. *Inorg. Chem.* **1998**, *37*, 2861. It is interesting in this context to note that the stoichiometric reaction between $Et_3P{=}Te$ and $(Me_3Sn)_2$ was not affected by an addition of free PEt_3 (2−10 equiv).

(15) The P=Se bond dissociation energy of t-$Bu_3P{=}Se$ is not available. However, P=X (X = O, Te) bonds in analogous t-$Bu_3P{=}X$ are known to be exceptionally longer than the P=X bonds with linear alkyl groups bound to the phosphorus. Therefore, the P=Se bond strength is envisaged to be $n\text{-}Bu_3P{=}Se > t\text{-}Bu_3P{=}Se$. (a) Rankin, D. W. H.; Robertson, H. E.; Seip, R.; Schmidbaur, H.; Blaschke, G. *J. Chem. Soc., Dalton Trans.* **1985**, 827. (b) Kuhn, N.; Schumann, H.; Wolmershäuser, G. *Z. Naturforsch. B* **1987**, *42*, 674.

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