J. Am. Chem. Soc. **1996,** *118,* 283−284

Titanium-Mediated Heterodehydrocoupling of Tributylstannane and Tellurium. X-ray Structure of $(C_5Me_5)_2TiTeSn(C_6H_5)_3$

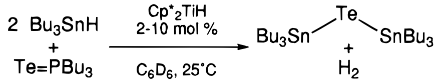
Jason M. Fischer,[†] Warren E. Piers,*
Susan D. Pearce Batchilder,[‡] and Michael J. Zaworotko[‡]

Department of Chemistry and Biochemistry
University of Guelph, Guelph, Ontario, N1G 2W1 Canada
Department of Chemistry, Saint Mary's University
Halifax, Nova Scotia, B3H 3C3 Canada

Received September 6, 1995

Emerging applications for main group metal tellurides[1] have spawned research programs aimed at developing molecular, single-source precursors to these materials.[2−5] Conventional routes for preparing precursors containing the requisite element−tellurium bonds are generally stoichiometric salt elimination reactions which have undesirable byproducts, *i.e.*, contaminated salts. Alternative, perhaps catalytic, methods for producing molecules identified as successful precursors to telluride materials are thus desirable.

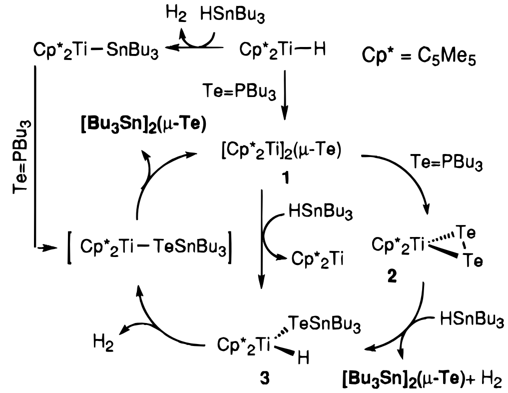
In this regard, catalytic dehydrocoupling reactions have been suggested as an attractive method for generating molecules or polymers containing element−element (E−E) bonds.[6] *Hetero*dehydrocoupling reactions,[7] in which E−E′ bonds are formed, are less well developed but would be necessary in order for this method to be applied to the synthesis of main group telluride precursors. Herein we report the titanium-mediated heterodehydrocoupling of tellurium (using Te═PBu$_3$) and tributylstannane to [Bu$_3$Sn]$_2$(μ-Te) (eq 1), a potential single-source precursor[4b] for the low-temperature synthesis of the small band gap semiconductor tin telluride (SnTe).[8]



(1)

The heterodehydrocoupling reaction in eq 1 proceeds at a rate of ∼10 turnovers h^{-1} (25 °C) when 2−10 mol % Cp*$_2$TiH is used as catalyst precursor. In a typical experiment, Cp*$_2$TiH was premixed with 10−50 equiv of Bu$_3$SnH in C$_6$D$_6$. Upon addition of 5−25 equiv of Te═PBu$_3$, dihydrogen was evolved (δ = 4.45) as the reaction began to turn over. A series of ^{119}Sn{^{1}H} NMR spectra collected during the reaction showed smooth conversion of Bu$_3$SnH to [Bu$_3$Sn]$_2$(μ-Te).[9] At higher catalyst loadings, an intermediate (δ ^{119}Sn = −57.9) was observed to build up to a constant concentration and to wane once substrate was consumed. Under identical conditions in the absence of titanium, coupling of Bu$_3$SnH and Te═PBu$_3$ was less than 2% complete over the same time frame required to complete the catalysis.[10]

Scheme 1



Several stoichiometric reactions provide insight into the general pathway by which this catalytic reaction takes place; these reactions are summarized in Scheme 1. For example, Cp*$_2$TiH is converted quantitatively to Cp*$_2$TiSnBu$_3$ upon reaction with Bu$_3$SnH.[11] Whether generated *in situ* or isolated as a viscous purple oil, Cp*$_2$TiSnBu$_3$ reacts with Te═PBu$_3$ in the absence of Bu$_3$SnH to yield the paramagnetic dimer [Cp*$_2$Ti]$_2$(μ-Te) (**1**), with concomitant production of [Bu$_3$Sn]$_2$(μ-Te). We have previously shown **1** to be converted to the diamagnetic ditelluride Cp*$_2$Ti(η^2-Te$_2$)(**2**)[12] upon treatment with Te═PBu$_3$. Both of these compounds react rapidly with Bu$_3$SnH in the *absence* of tellurium.

Cp*$_2$Ti(η^2-Te$_2$) reacts with Bu$_3$SnH to eliminate [Bu$_3$Sn]$_2$(μ-Te) and produce an unstable Ti(IV) species, formulated as the stannyltelluroate hydride compound **3**.[13] A signal at 4.85 ppm in the ^{1}H NMR spectrum of **3** is characteristic of a Ti(IV) hydride ligand, but attempts to obtain infrared spectroscopic evidence in support of this assignment were inconclusive due to the compound's instability. The stannyltellurolate ligand was characterized by ^{119}Sn{^{1}H} NMR spectroscopy (−57.9 ppm, $^1J_{Sn-Te}$ = 3230 Hz). This compound is thus presumed to be the intermediate observed during the catalytic reaction of eq 1 (*vide supra*). Solutions of diamagnetic **3** lost H$_2$ at a moderate rate, yielding a mixture of μ-telluride dimer **1** and [Bu$_3$Sn]$_2$(μ-Te), thereby closing the catalytic cycle. Although not detected in this reaction sequence, the paramagnetic stannyltellurolate Cp*$_2$TiTeSnBu$_3$ is a likely intermediate on the path from **3** to [Cp*$_2$Ti]$_2$(μ-Te) (*vide infra*).

Separately isolated samples of [Cp*$_2$Ti]$_2$(μ-Te) and Cp*$_2$Ti(η^2-Te$_2$) each served as catalyst precursors for this reaction, although the role of **2** may not be important once the reaction

---

* Author to whom correspondence may be addressed. Present address: Department of Chemistry, The University of Calgary, 2500 University Drive NW, Calgary, AB, T2N 1N4 Canada. Phone: 403-220-5746. FAX: 403-289-9488. E-mail: wpiers@chem.ucalgary.ca.

[†] University of Guelph.

[‡] St. Mary's University.

(1) (a) Siemeling, U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 67. (b) O'Brien, P. *Chemtronics* **1991**, *5*, 61.

(2) Group 12: (a) Bochmann, M.; Coleman, A. P.; Webb, K. J.; Hursthouse, M. B.; Mazid, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 973. (b) Stuczynski, S. M.; Brennan, J. G.; Steigerwald, M. L. *Inorg. Chem.* **1989**, *28*, 4431. (c) Brennan, J. G.; Siegrist, T.; Carroll, P. J.; Stuczynski, S. M.; Reynders, P.; Brus, L. E.; Steigerwald, M. L. *Chem. Mater.* **1990**, *2*, 403. (d) Arnold, J.; Walker, J. M.; Yu, K. M.; Bonasia, P. J.; Seligson, A. L.; Bourret, E. D. *J. Cryst. Growth* **1992**, *124*, 674.

(3) Group 13: Rahbarnoohi, H.; Kumar, R.; Heeg, M. J.; Oliver, J. P. *Organometallics* **1995**, *14*, 502.

(4) Group 14: (a) Seligson, A. L.; Arnold, J. *J. Am. Chem. Soc.* **1993**, *115*, 8215. (b) Boudjouk, P.; Seidler, D. J.; Bahr, S. R.; McCarthy, G. J. *Chem. Mater.* **1994**, *6*, 2108. (c) Strzelecki, A. R.; Likar, C. L.; Helsel, B. A.; Utz, T.; Lin, M. C.; Bianconi, P. A. *Inorg. Chem.* **1994**, *33*, 5188.

(5) Group 15: (a) Breunig, H. J.; Ebert, K. H.; Schulz, R. E.; Wieber, M.; Sauer, I. *Z. Naturforsch.* **1995**, *50b*, 735. (b) Groshens, T. J.; Gedridge, R. W., Jr.; Lowe-Ma, C. K. *Chem. Mater.* **1994**, *6*, 727.

(6) (a) Harrod, J. F.; Mu, Y.; Samuel, E. *Polyhedron* **1991**, *10*, 1239. (b) Harrod, J. F. *Stud. Surf. Sci. Catal.* **1992**, *73*, 147. (c) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22.

(7) (a) Blum, Y.; Laine, R. M. *Organometallics* **1986**, *5*, 2081. (b) Liu, H. Q.; Harrod, J. F. *Can. J. Chem.* **1990**, *68*, 1100. (c) Liu, H. Q.; Harrod, J. F. *Organometallics* **1992**, *11*, 822. (d) Procipio, L. J.; Berry, D. H. *J. Am. Chem. Soc.* **1991**, *113*, 4039.

(8) George, J.; Palson, T. I. *Thin Solid Films* **1985**, *127*, 233.

(9) Identified via separate synthesis (^{119}Sn{^{1}H} NMR −21.1 ppm) according to the following: Segi, M.; Koyama, T.; Takata, Y.; Nakajima, T.; Suga, S. *J. Am. Chem. Soc.* **1989**, *111*, 8749.

(10) (a) Other control experiments ruled out a pathway involving homodehydrocoupling of tributylstannane[10b] followed by tellurium insertion into the tin−tin bond of hexabutylditin. (b) Imori, T.; Lu, V.; Cai, H.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 9931.

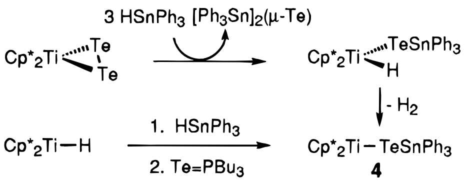
(11) Formed by σ-bond metathesis, cf.: Woo, H.-G.; Freeman, W. P.; Tilley, T. D. *Organometallics* **1992**, *11*, 2198.

(12) Fischer, J.; Piers, W. E.; MacGillivray, L. R.; Zaworotko, M. J. *Inorg. Chem.* **1995**, *34*, 2499.

(13) For data on all new compounds, see supporting information.

0002-7863/96/1518-0283$12.00/0

Scheme 2



is initiated. Independent experiments showed dimer **1** to react directly with Bu_3SnH to produce hydride **3** and permethyltitanocene (Cp^*_2Ti),[14] which we have also shown separately to be an effective catalyst precursor. Thus, an alternate pathway which does not involve **2** may be operative. Based on the observed accumulation of $Cp^*_2Ti(H)TeSnBu_3$ during the dehydrocoupling reaction, it is clear that elimination of H_2 from this species is rate limiting. The relative rates of reaction between dimer **1** and Bu_3SnH or $Te{=}PBu_3$ therefore likely dictate which path is prevalent.

Further mechanistic information was obtained from reactions involving Ph_3SnH instead of Bu_3SnH (Scheme 2). Treatment of $Cp^*_2Ti(\eta^2\text{-}Te_2)$ with Ph_3SnH led to formation of a Ti(IV) stannyltellurolate hydride analogous to **3** that was similarly unstable toward loss of dihydrogen. The product isolated, however, was not dimer **1** but a green paramagnetic ($\mu_{\text{eff}} = 2.11\ \mu_B$[15]) solid identified as the Ti(III) stannyltellurolate $Cp^*_2TiTeSnPh_3$ (**4**). This compound was synthesized via another route involving insertion of tellurium into the Ti−Sn bond of $Cp^*_2TiSnPh_3$, illustrating how the tri*butyl*stannyl complex participates in the chemistry depicted in Scheme 1. However, whereas elimination of $[Bu_3Sn]_2(\mu\text{-}Te)$ from "$Cp^*_2TiTeSnBu_3$" is apparently quite facile, heating solutions of $Cp^*_2TiTeSnPh_3$ at 120 °C resulted only in slow formation of $[Ph_3Sn]_2(\mu\text{-}Te)$[16] ($t_{1/2} \approx 4$ days), along with significant decomposition.

The stability of **4** allowed us to characterize it crystallographically (Figure 1). The Ti−Te distance of 2.8681(18) Å is similar to distances of ~2.90 Å reported for independent molecules of $Cp_2Ti(TeSi(SiMe_3)_3)PMe_3$.[17] Steric crowding in the molecule distorts the geometries at titanium, tin, and most notably tellurium and may explain the compound's thermal stability compared to that of $Cp^*_2TiSnBu_3$ if the $[R_3Sn]_2(\mu\text{-}Te)$ elimination is bimolecular.[18]

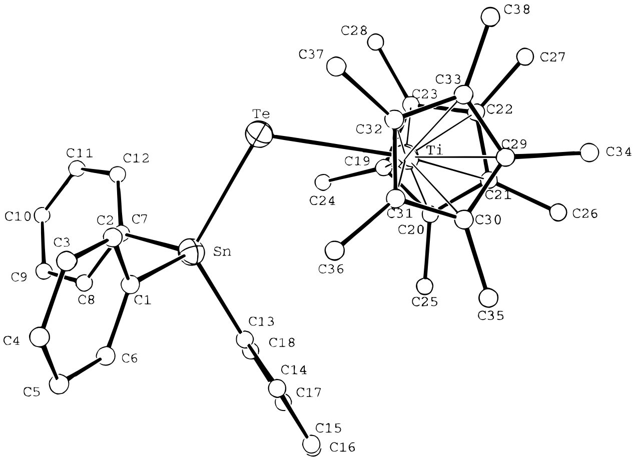


Figure 1. ORTEP diagram of **4**. Selected distances (Å): Ti−Te, 2.8681(18); Te−Sn, 2.6824(10). Selected angles (deg): Sn−Te−Ti, 110.98(6); Te−Sn−C1, 109.6(3); Te−Sn−C7, 107.9(3); Te−Sn−C13, 120.9(3).

Studies aimed at determining the relative importance of the pathways available, the screening of other Ti(III) catalysts, and probing the application of this type of dehydrocoupling reaction to the synthesis of other main group element telluride precursors[19] are continuing.

Acknowledgment. Funding from NSERC (Canada) in the form of Research Grants to W.E.P. and M.J.Z. is gratefully acknowledged. W.E.P. thanks Prof. Sandro Gambarotta (Ottawa) for magnetic moment measurements.

Supporting Information Available: Experimental details, ^{119}Sn{^{1}H} NMR spectra and listings of crystallographic data, atomic parameters, hydrogen parameters, anisotropic thermal parameters, and complete bond distances and angles for **4** (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA953081L

---

[14] Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5087.

[15] (a) The μ_{eff} value for **4** was reproducible on two separate samples. While rare, high susceptibilities have been observed for other first row, d^1 complexes.[15b] It is unlikely that the explanation proffered in that instance is applicable here, and in the absence of variable temperature susceptibility data, we have no satisfactory interpretation of this result. (b) Berno, P.; Gambarotta, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2419.

[16] Einstein, F. W. B.; Jones, C. H. W.; Jones, T.; Sharma, R. D. *Can. J. Chem.* **1983**, *61*, 2611.

[17] Christou, V.; Wuller, S. P.; Arnold, J. *J. Am. Chem. Soc.* **1993**, *115*, 10545.

[18] Piers, W. E.; Parks, D. J.; MacGillivray, L. R.; Zaworotko, M. J. *Organometallics* **1994**, *13*, 4547.

[19] (a) Titanium-mediated heterodehydrocoupling of dibutylstannane and $Te{=}PBu_3$ to a single product has also been observed, although it should be noted that the rate is only about 3−4 times faster than that of the uncatalyzed reaction in this instance. The ^{119}Sn NMR data ($\delta = -118.3$, $^{2}J_{^{119}Sn-^{119}Sn} = 216$ Hz) suggest the product is the cyclic trimer $[Bu_2SnTe]_3$.[19b] (b) Lockhart, T. P.; Puff, H.; Schuh, W.; Reuter, H.; Mitchell, T. N. *J. Organomet. Chem.* **1989**, *366*, 61.