

# Hydrozirconation/transmetalation of acetylenic stannanes. New 1,1-dimetallo reagents

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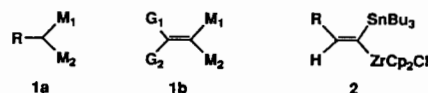
## Abstract

Treatment of 1-tributylstannylalkynes with  $\text{Cp}_2\text{Zr(H)Cl}$  affords olefinic intermediates substituted by both  $\text{Bu}_3\text{Sn}$  and  $\text{Cp}_2\text{ZrCl}$  groups on the terminal  $\text{sp}^2$ -like carbon. These stereodefined reagents can be selectively transmetalated at zirconium to afford cuprates which deliver product vinyl stannanes in both substitution and Michael addition reactions.

**Key words:** Hydrozirconation; Transmetalation; Zirconium complexes; Hydride complexes; Tin alkyne complexes

## Introduction

1,1-Dimetallo reagents **1** offer unique opportunities to effect sequential multiple carbon–carbon and/or carbon–heteroatom bonds [1]. Those which are  $\text{sp}^2$  carbon-based (**1b**) are particularly attractive in that they provide access to polysubstituted alkenes of defined stereochemistry ( $G_1 \neq G_2$ ) [2], assuming that clean chemodifferentiation of the metals attached can be achieved.

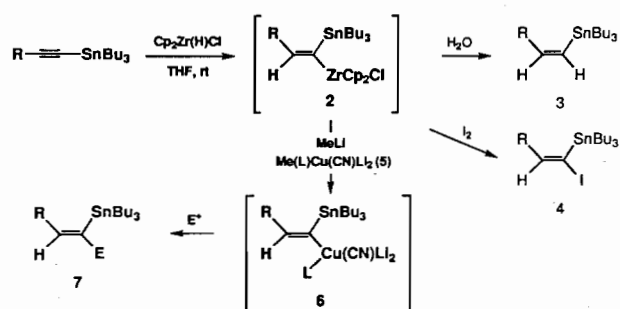


Previously, we had noted that acetylenic stannanes could be converted to *Z*-vinyl stannanes (**3**) via a trivial hydrozirconation-proton quenching scheme [3]. The intermediacy of a 1,1-dimetallo species (**2**) was demonstrated by selective treatment of **2** with  $\text{I}_2$  to afford isomerically pure iodostannane (**4**). More useful, however, would be the selective transmetalations of **2** to reactive organometallics, including cuprate reagents capable of efficient C–C bond forming reactions [4]. Realization of such a procedure would complement well established prior art as a means of preparing polysubstituted alkenes (e.g. via carbometallation of alkynes [5]). In this report, we describe chemospecific ligand exchange reactions of 1,1-dimetallo species (**2**),

induced by higher order cyanocuprates (**5**), to various trisubstituted alkenes (**7**) (Scheme 1).

## Experimental

A representative procedure for the preparation of diene (**13**) (see Table 2) is as follows. A 10 ml round bottom flask was charged with 45 mg (0.17 mmol) zirconocene chloride hydride and 3 ml of THF. To the stirred suspension were added 50 mg (0.15 mmol) of 1-tributylstannylpropyne. The solution was stirred until it became clear and colorless (10 min). The flask was cooled to  $-78^\circ\text{C}$  at which point 0.63 ml (0.17 mmol, 0.27 M in THF) of 2-thienyl cyanocuprate and 0.23 ml (0.34 mmol, 1.45 M in ether) of methyllithium were added. The solution was stirred for 10 min before 23



Scheme 1.

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TABLE 1. Conjugate addition reactions of cuprate **6a**

Stannane	Enone	Product <sup>a</sup>	Yield (%) <sup>b,c</sup>
			79
			93
			77
			71
			74

<sup>a</sup>Fully characterized by IR, NMR, MS and HRMS data. <sup>b</sup>Isolated, chromatographically purified materials. <sup>c</sup>Based on enone.

TABLE 2. Alkylation reactions of cuprate **6b**

Stannane	Alkylating agent <sup>a</sup>	Product <sup>b</sup>	Yield (%) <sup>c,d</sup>
			75
			88
			87
			78
			86
			73

<sup>a</sup>Used in slight excess (1.3–1.8 equiv.). <sup>b</sup>Fully characterized by IR, NMR, MS and HRMS data. <sup>c</sup>Isolated, chromatographically purified materials. <sup>d</sup>Based on acetylenic stannane.

$\mu\text{l}$  (21 mg, 0.23 mmol) of methallyl chloride were added. After 2 h at  $-78\text{ }^{\circ}\text{C}$ , the solution was poured into 15 ml of 10% aqueous sodium bicarbonate and 10 ml of diethyl ether, and the organic layer was separated. Following extraction with ether and washing with brine, the combined organic layers were dried over magnesium sulfate, filtered through a bed of Celite, and finally concentrated *in vacuo*. The resulting oil was chromatographed using reverse phase silica gel [6] to yield

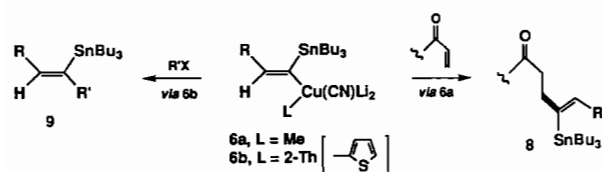
52 mg (87%) of *Z*-3-tributylstannyl-5-methylhexa-2,5-diene. IR (neat) ( $\text{cm}^{-1}$ ): 2900, 1650, 1455.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.09–6.03 (1H, q,  $J=10.5$  Hz), 4.72 (1H, d,  $J=1.5$  Hz), 4.61 (1H, d,  $J=1.5$  Hz), 2.83 (2H, s), 1.73–1.71 (3H, d,  $J=10.5$  Hz), 1.66 (3H, s), 1.45–1.41 (6H, m), 1.3–1.26 (6H, m), 0.89–0.87 (9H, t,  $J=8$  Hz), 0.80–0.77 (6H, t). EIMS  $m/z$  (rel. int.) 329 (100), 328 (32), 327 (76), 177 (45); HREIMS calc. for  $\text{C}_{15}\text{H}_{29}^{120}\text{Sn}$  ( $-\text{C}_4\text{H}_9$ ): 329.1291; found 329.1291.

## Results and discussion

The dimetallo reagent **2** can be viewed as both a vinyl stannane, as well as a vinyl zirconocene, each portion of which is a candidate for transmetalation to the corresponding mixed vinyl cuprate. Since Behling *et al.* [7] showed that while the former is subject to ligand exchange with  $R_2Cu(CN)Li_2$  in THF, ambient temperatures over the course of 1–2 h are usually needed. By contrast, vinyl zirconocenes participate in identical processes, but do so at  $-78\text{ }^\circ\text{C}$  in minutes [8]. Hence, the selective conversion of 1,1-dimetallo intermediates (**2**) to cuprates (**6**) was found to take place quite smoothly at these colder temperatures.

A variety of acetylenic stannanes [9] was converted to **2** using Schwartz' reagent [10] in THF at room temperature. Simply cooling the resulting solution of **2** to  $-78\text{ }^\circ\text{C}$  followed by the addition of MeLi (1 equiv.) and  $Me_2Cu(CN)Li_2$  (**5**, L = Me, 1 equiv.) (premixed using 3MeLi + 1CuCN) induces transmetalation to **6a** (Scheme 2). Introduction of an  $\alpha,\beta$ -unsaturated ketone leads, upon work-up and isolation, to vinyl stannane-containing product ketones (**8**) reflecting the essentially regio- and stereospecific nature of the hydrozirconation/transmetalation sequence (based on TLC, NMR and VPC analyses of reaction mixtures). Several representative cases are illustrated in Table 1. Although unhindered enones readily participate, more sterically demanding educts such as mesityl oxide and isophorone give low yields of desired 1,4-adducts, as do nitroolefins. The presence of additives (e.g.  $BF_3 \cdot Et_2O$  [4, 11] or TMS-Cl [4, 12]) did not improve the process.

Transmetalations of **2** with the mixed thienyl methyl cuprate (**5**, L = 2-thienyl [13]) lead to **6b**, which undergo alkylations to trisubstituted olefins (**9**) using either allylic or benzylic halides as electrophiles. Unactivated iodides or bromides were not acceptable partners in these couplings, as anticipated from earlier studies [14]. Primary, unactivated triflates, however, may be used to effect alkylations of **6b**. Examples of these couplings are shown in Table 2. Noteworthy cases include the use of acetylenic stannane (**11**) which contains an ester moiety\*, and the trapping of **6b** with 2,3-dibromopropene to give the vinyl bromo, vinyl stannyl 1,4-diene

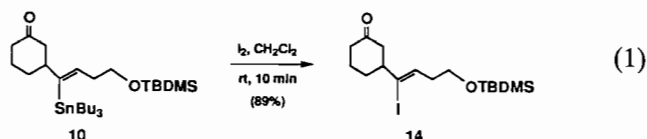


Scheme 2.

\*For cuprate couplings wherein an ester, among other electrophilic groups, is present within the reagent, see ref. 15.

(**12**) of defined olefinic geometry. Unfortunately, neither unactivated epoxides nor silyl halides reacted with cuprates **6b** even upon warming the reaction mixture to  $-30\text{ }^\circ\text{C}$ .

Products of these couplings, by virtue of the vinylstannane residue now present, have the potential for further manipulation at the carbon-bearing tin site to non-organometallic-containing trisubstituted olefins. For example, a cuprate-mediated transmetalation/coupling could be envisioned [7]. Alternatively, conversion to a halide derivative [16], as in the transformation of **10** to iodide **14** (eqn. (1)), inverts the polarity of an olefin from that of a nucleophilic to an electrophilic partner in Stille-type couplings based on palladium chemistry [17].



In summary, a new 1,1-dimetallo reagent has been developed which allows for the controlled conversion of acetylenic stannanes to trisubstituted olefins of strictly defined geometries. Further methodological advances which take advantage of vinyl zirconocene intermediates will be reported in due course.

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