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TRANSMETALATION REACTIONS OF HIGHER ORDER CYANOCUPRATES: DIRECT FORMATION OF TRIALKYLTIN CUPRATES FROM TIN HYDRIDES WHICH BYPASSES ORGANOLITHIUM INTERMEDIATES

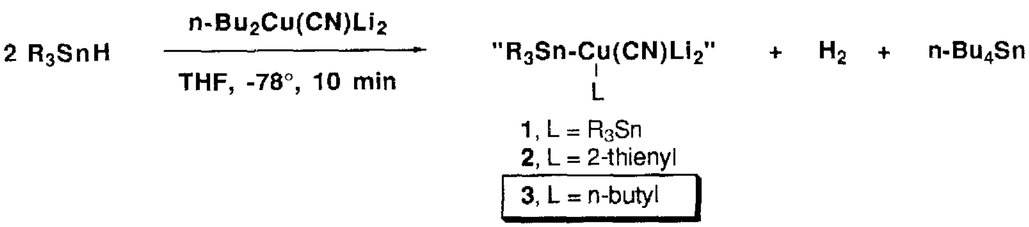
Bruce H. Lipshutz,*[1] Edmund L. Ellsworth, Stuart H. Dimock, and Deborah C. Reuter

Department of Chemistry
University of California, Santa Barbara, CA 93106

Summary: Simple exposure of n-Bu_3SnH to $Bu_2Cu(CN)Li_2$ in THF at low temperatures leads directly to the presumed mixed higher order trialkyltin cuprate, the reactions of which selectively transfer the trialkylstannyl group to a variety of substrates.

The continuing popularity of organotin intermediates in organic synthesis has recently been highlighted by an excellent monograph on this subject.[2] New, efficient, and mild methods for preparing compounds which contain the trialkylstannyl moiety would facilitate arrival at the desired arrays, and indeed two such reports have just appeared on the formation and tin-carbon couplings of higher order (H.O.) trialkylstannylcuprates, 1[3] and 2.[4] Reagents of this and related types are attractive in that they are less basic[5,6] than the corresponding lithio species, and effect many reactions characteristic of organocopper complexes not to be expected with R_3SnLi.[7] In this Letter, we now describe a remarkably straightforward, indeed unprecedented route to mixed H.O. organotin cuprates which relies on in situ cuprate technology[8] and thereby completely bypasses prior formation of an organolithium precursor.

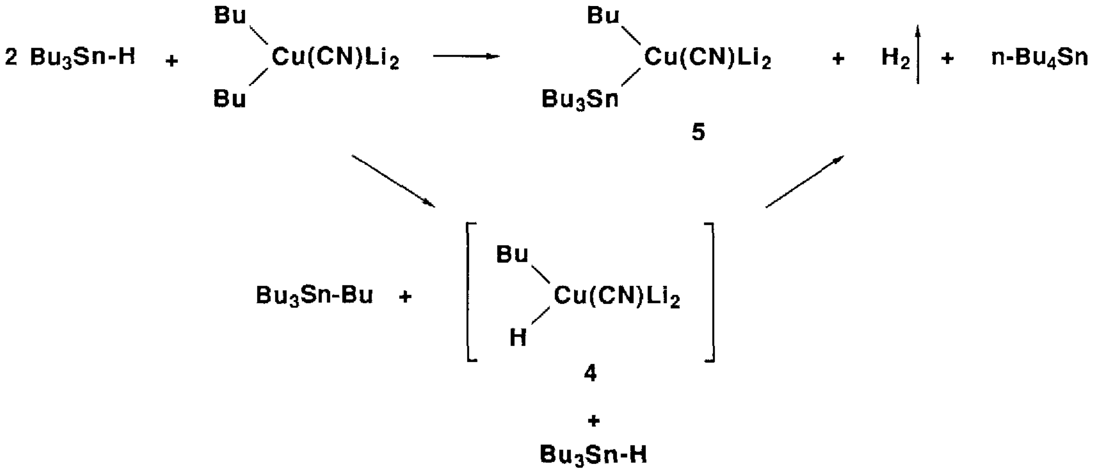
Treatment of Bu_3SnH (2 equiv) with $Bu_2Cu(CN)Li_2$[9] in THF at -78° leads to the immediate release of gas producing a yellowish, homogeneous solution. Following gas evolution (ca. 10 minutes), introduction of the substrate may commence, with reaction times dependent upon the educt. Table I illustrates the diversity of substrates which, upon exposure to the presumed mixed reagent 3, L = n-Bu, afford good isolated yields of trialkyltin-containing adducts. As best we can tell, the Bu_3Sn ligand is transferred exclusively.



$$2\,R_3SnH \xrightarrow[\text{THF, -78°, 10 min}]{n\text{-}Bu_2Cu(CN)Li_2} \text{"}\underset{\displaystyle L}{R_3Sn\text{-}Cu(CN)Li_2}\text{"} + H_2 + n\text{-}Bu_4Sn$$

1, L = R_3Sn
2, L = 2-thienyl
3, L = n-butyl

Although the precise nature of the reagent involved is not known with certainty, the identities of both the gas evolved and tin-containing by-product have been established. Apparently, a rapid exchange of a butyl-for-hydride ligand occurs giving rise to Bu_4Sn (identified by VPC) and hydrido cuprate 4, followed by a second bimolecular reaction to liberate H_2 (trapped and used for a catalytic hydrogenation) and the (likely) H.O. mixed reagent 5. This is all the more fascinating, since not only do these events happen virtually upon mixing at -78°, but Normant has shown[10] that the lower order magnesio cuprate $Me_2CuMgBr \cdot 2LiCl$ reacts with Bu_3SnH to give the proposed dihydrido reagent $H_2CuMgBr$ rather than a lower order stannylcuprate. Irrespective of the organocopper species formed in this ligand exchange process, the trialkyltin group can be introduced quickly under mild conditions and in good yields.



In summary, a novel and especially facile protocol for trialkyltin cuprate generation has been discovered which obviates the normally accepted prior commitment towards metalation of Bu_3SnH with LDA.[11] Direct tin cuprate formation is now realizable under extremely mild conditions using perhaps the most readily available and inexpensive H.O. cuprate (i.e., 2 n-BuLi + CuCN → $Bu_2Cu(CN)Li_2$) via a transmetalation scheme.[12] Further examples of the utility of ligand exchange phenomena involving H.O. cuprates will be forthcoming from these laboratories.

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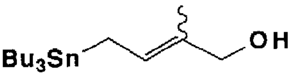
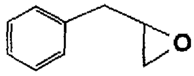
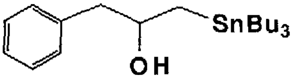
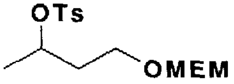
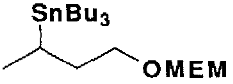
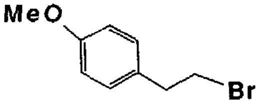
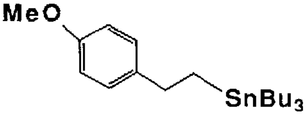
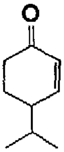
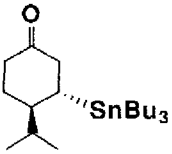
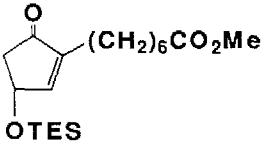
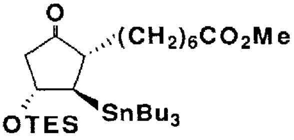
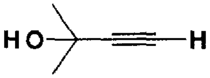
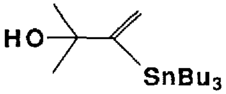
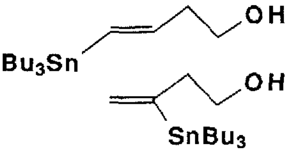
Table I. Reactions of Higher Order Tributyltin Cuprate 5 with various substrates in THF

Entry	Educt	Conditions	Product(s)	Yield(%)[a]
1		-78°, 2.5h	 [91:9 E:Z]	89
2		-40°, 1h		81
3		0°, 6h		quant
4		-78°, 10 min		83
5		-78°, 0.5h		*quant*[b]
6		-78°, 0.3h		78(87)[c]
7		-78°, 2 min		87
8		-78°, 5 min	 (50) (50)	90[d]

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[a] Isolated, chromatographically pure products which gave satisfactory IR, NMR, MS, and HRMS data. [b] A single diastereomer was obtained. [c] Yield based on recovered starting material. [d] Ratio determined by isolation of both regioisomers.

References and Notes

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11. For a typical procedure to form Bu_3SnLi, see reference 4.
12. A typical procedure is as follows (Table I, entry 7):

    CuCN (0.0672 g, 0.75 mmol) was added to a dry 10 mL round-bottom flask equipped with a stir bar and rubber septum. The flask was evacuated with a vacuum pump, and purged with argon. This process was repeated three times. THF (2 mL) was injected and the slurry cooled to -78°C where n-BuLi (0.63 mL, 1.50 mmol) was added dropwise. The mixture was allowed to warm slightly to yield a colorless, homogeneous solution which was recooled to -78°C where n-Bu_3SnH (0.40 mL, 1.5 mmol) was added *via* syringe. Stirring was continued and over *ca*. 10 min, the solution yellowed and H_2 gas was liberated. 2-Methyl-3-butyn-2-ol (0.066 mL, 0.68 mmol) was added neat *via* syringe and the reaction mixture stirred for 5 min before being quenched into a 10 mL bath of 10% NH_4OH/90% saturated NH_4Cl. Extraction with 3x20 mL ether was followed by combining the extracts and drying over Na_2SO_4. The solvent was removed *in vacuo* and the residue chromatographed on silica gel. Elution with Skelly Solve-ethyl acetate (95:5) + 1% Et_3N gave 2-methyl-3(tri-n-butylstannyl)-3-buten-2-ol (221 mg, 87%) as a colorless oil; TLC [10% EtOAc in Skelly Solve] R_f 0.38; ^1H NMR, δ 6.089-6.085 (d,2H, J_{gem} = 2 Hz), 2.151 (s,1H), 1.530-1.425 (m,124), 1.348-1.227 (m,12H), 0.898-0.846 (t,9H); ^{13}C NMR ($CDCl_3$) 155.56 (s), 122.35 (t), 30.60 (s), 29.40 (q), 29.03 (t), 27.20 (t), 13.65 (q), 9.39 (t); IR (neat) cm^{-1} 3360, 2930, 1600, 1460, 1380, 990; mass spectrum (EI), m/z (rel. intensity) 319 (M^+-57, 100), 318 (36.7), 317 (75.5), 316 (30.6), 315 (42.9), 263 (42.9), 261 (33.7), 207 (42.9), 205 (36.7), 177 (22.4), 136 (25.5), 120 (25.5), 119 (10.2), 118 (12.2), 117 (10.2), 116 (10.2), 85 (17.3), 69 (10.2), 59 (11.2); high-resolution MS (CI) m/z (M^+-17) calcd for $C_{17}H_{36}Sn$ 360.1839, found 360.1812.

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