

FACILE FORMATION AND REACTIONS OF MIXED TRIMETHYLSTANNYLMETHYL CUPRATES

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Summary: Solutions comprised of equimolar concentrations of methyllithium, trimethylstannyl lithium and cuprous cyanide as well as reaction of $\text{Me}_2\text{Cu}(\text{CN})\text{Li}_2$ with one equivalent of hexamethylditin give $\text{Me}_3\text{Sn}(\text{Me})\text{Cu}(\text{CN})\text{Li}_2$ which selectively delivers the R_3Sn moiety to a variety of substrates.

During the evolution of trialkylstannylcuprate chemistry one aspect that has remained invariant has been their method of preparation. These cuprates have historically been synthesized by combination of trialkylstannyl lithiums with cuprous salts.¹ The trialkylstannyl anions are traditionally generated by reaction of a trialkylstannyl hydride with LDA or by cleavage of a hexaalkyldistannane with an alkyl lithium.² Reactions of organic substrates with trialkylstannylcuprates containing one, two or three trialkylstannyl groups per copper cation result in incorporation of the organostannyl moiety into the organic molecule¹.

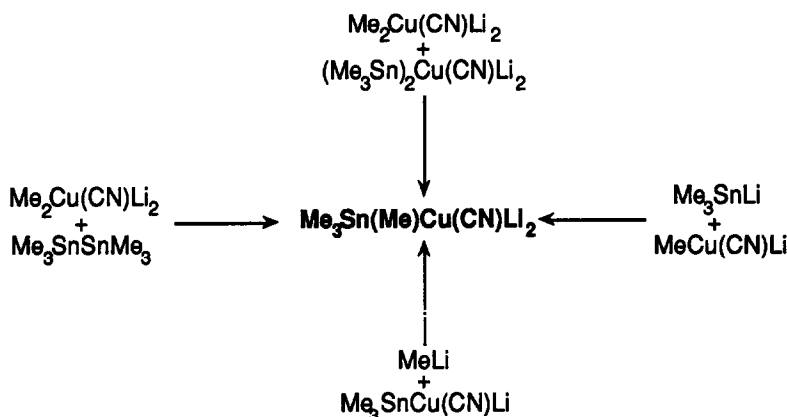
In spite of the synthetic utility of this methodology, these reactions are beset with difficulties of product purification. This complication stems from the presence of unconsumed trialkylstannyl anions which are converted to tin by-products upon work-up. Unless the desired product contains a polar functional group removal of tin impurities by column chromatography is virtually impossible.

A remedy to this type of problem was first reported by Fleming and Newton who found that the mixed cuprate, $\text{PhMe}_2\text{Si}(\text{Me})\text{Cu}(\text{CN})\text{Li}_2$, reacted with organic substrates by exclusive donation of the trialkylsilyl group leaving the methyl group as the non-transferred ligand.³ Lipshutz *et al.* has recently shown that a similar strategy can be applied with $\text{Bu}_3\text{Sn}(\text{Bu})\text{Cu}(\text{CN})\text{Li}_2$.⁴ This reagent selectively transferred a tributylstannyl group to organic substrates leaving the hydrocarbon bonded to copper. The obvious advantage of using such mixed cuprates is that the remaining alkyl is eventually converted into an easily removable volatile hydrocarbon.

Since preparation of $\text{Bu}_3\text{Sn}(\text{Bu})\text{Cu}(\text{CN})\text{Li}_2$ proceeded from reaction of $\text{Bu}_2\text{CuCNLi}_2$ with two equivalents of Bu_3SnH and generated one equivalent of Bu_4Sn it provides only a partial solution to the complications of product isolation. This problem could be circumvented by use of $\text{Me}_3\text{Sn}(\text{Me})\text{Cu}(\text{CN})\text{Li}_2$ (1) since the Me_4Sn by-product is easily removed by distillation. While it

was recognized that **1** would provide definite advantages over previous cuprate reagents, its preparation by the strategy outlined above did not seem practical due to the toxicity and volatility of trimethyltin hydride.⁵

We wish to report that solutions containing one equivalent each of methyl lithium, trimethylstannyl lithium⁶ and cuprous cyanide produce **1**. For example, reaction of $\text{Me}_2\text{Cu}(\text{CN})\text{Li}_2$ (Me , ^{13}C $\delta = -9.5$) with $(\text{Me}_3\text{Sn})_2\text{Cu}(\text{CN})\text{Li}_2$ (MeSn , ^{13}C $\delta = -0.04$) or reaction of MeLi (Me , ^{13}C $\delta = -12.6$) with $\text{Me}_3\text{SnCu}(\text{CN})\text{Li}$ (MeSn , ^{13}C $\delta = -4.5$) gave solutions exhibiting identical ^{13}C , ^1H and ^{119}Sn spectra attributable to $\text{Me}_3\text{Sn}(\text{Me})\text{Cu}(\text{CN})\text{Li}_2$ (MeSn , ^{13}C $\delta = -2.0$; Me , ^{13}C $\delta = -9.2$).⁷ In addition, the preparation of **1** can be achieved without the preformation of Me_3SnLi by direct reaction of $\text{Me}_3\text{SnSnMe}_3$ with $\text{Me}_2\text{Cu}(\text{CN})\text{Li}_2$ in THF at -40°C .^{8,9}


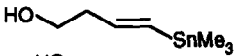
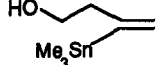
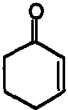
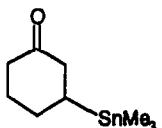
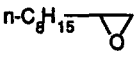
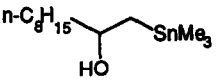
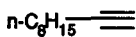
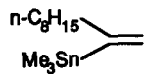
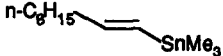
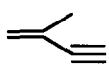
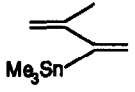
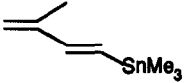
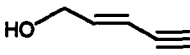
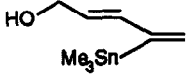
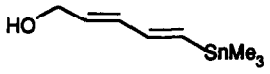
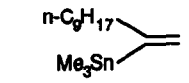
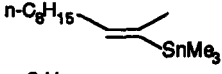
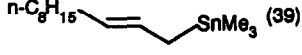


These reagents react with organic compounds with exclusive transfer of the trialkylstannyl group. This is exemplified in reactions of **1** with a variety of substrates summarized in Table 1. As was anticipated, tin by-products are easily removed under high vacuum thereby greatly facilitating product purification.

The following procedure is representative (Table 1, entry 7): To a stirred suspension of CuCN (0.225g, 2.5 mmol) in 20 mL THF cooled to -40°C and kept under an atmosphere of argon was added dropwise MeLi (4 mL, 1.4M, 5 mmol). After stirring for 15 min. injection of hexamethylditin (0.8g, 2.5 mmol) dissolved in 2 mL THF resulted in an immediate colour change of the solution from tan to deep yellow. The mixture was stirred for 1 hr and then cooled to -78°C before adding 1,2-undecadiene (0.4 mL, 2.25 mmol) via syringe as a neat liquid. The solution was allowed to warm to room temperature overnight and then quenched by pouring the contents of the flask into a separatory funnel containing ca. 10 mL saturated NH_4Cl ($\text{pH} = 8-9$) and 10 mL hexanes.

Table 1. Addition of $\text{Me}_3\text{SnCu}(\text{CN})\text{Li}_2$ to various substrates.

Me

Entry	Substrate	Product(s)	% Yield ^{a)}
1		 	84 ^{b)}
2			70
3			44
4		 	87
5		 	69
6		 	79
7	$n\text{-C}_8\text{H}_{15}\text{-CH}_2\text{=C=CH}_2$	  	73 ^{c)}

^{a)} Isolated yields. Products gave satisfactory IR, NMR, MS and micro analysis data. ^{b)} Isomer ratios change depending upon workup conditions. ^{c)} Isomers were determined by G.C. coinjection with authentic samples.

The aqueous layer was extracted with 5 x 20 mL hexanes and the combined organic extracts dried over anhyd. $MgSO_4$. Removal of the solvent in vacuo gave a crude oil from which Me_4Sn was readily removed by placing the sample under high vacuum for 2 hr at room temperature. Kugelrohr distillation ($104^\circ C @ 0.05 \text{ mmHg}$) yielded a mixture of three isomers (0.52g, 73%) which were 97% pure by G.C.

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References

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4. B. L., Lipshutz, E. L. Ellsworth, S. H. Dimrock, D. C. Reuter, *Tet. Lett.*, **30**, 2065 (1989).
5. This strategy has been adopted for the preparation of $Me_3Sn(\eta\text{-Bu})Cu(CN)Li_2$, B. H. Lipshutz and D. C. Reuter, *Tet. Lett.*, **30**, 4617 (1989).
6. Prepared by reaction of hexamethyldistannane with methyllithium in THF at $-70^\circ C$.
7. NMR data was recorded on a 400 MHz spectrometer using THF, Me_4Sn and $CDCl_3$ as internal references. For initial studies on silylcuprates see S. Sharma, A.C. Oehlschlager, *Tetrahedron*, **45**, 557 (1989). A detailed account of present spectroscopic studies is in preparation.
8. Cleavage of bis(tributyltin) with $Me_2Cu(CN)Li_2$ and $Bu_2Cu(CN)Li_2$ and reactions of organic substrates with the corresponding mixed cuprates have also been demonstrated in our laboratory.
9. The formulation of cuprates containing two equivalents of anion to each equivalent of copper cation as $R_2Cu(CN)Li_2$ has recently been questioned (Dr. S. Bertz, private communication).

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