Heteroatom Chemistry
Volume 5, Number 5/6, 1994

(Trialkylstannyl)cuprates: A Spectroscopic and Chemical Investigation

Sunaina Sharma* and Robin A. Martin

Department of Chemistry, The University of Western Ontario, London, ON, Canada N6A 5B7

Received 10 June 1994

ABSTRACT

Low-temperature ^1H, ^{13}C, and ^{119}Sn NMR spectroscopic techniques were used to probe the nature of cuprates derived from Me_3SnLi, CuCN, or $CuBr \cdot Me_2S$. In THF, addition of Me_3SnLi and CuX (X = Br or CN) gives aggregated $[Me_3SnCu \cdot LiX]_n$. When the ratio of stannyl anion to cuprous cation is 2:1, mixtures of $(Me_3Sn)_3Cu_2Li$, $(Me_3Sn)_2CuLi \cdot LiX$, and $(Me_3Sn)_3CuLi_2$ are formed. This behavior is unlike either homo trialkylsilylcyanocuprates, which form $(R_3Si)_2Cu(CN)Li_2$ at 2:1 ratios of silyl anion to cuprous ion, or mixed trialkylstannyl- or trialkylsilylcuprates, which exist as $(R_3M)Cu(R')(CN)Li_2$ (M = Si or Sn and R' = Me or Bu). $(R_3Sn)_3CuLi_2$ is the major species when the stannyl anion to cuprous cation ratio reaches 3:1. On the other hand, the analogous magnesium cuprates are discrete species in solution and possess differential reactivity.

In the mid-1970s; Hudec disclosed that addition of 2.0 equivalents of Me_3SnLi to CuI leads to the formation of trialkylstannylcuprates [2]. Although these were formulated as $(Me_3Sn)_2CuLi$, implying a Cu(I) monoanionic species, the solution structure of these extensively used organometallics [3–7] has remained an enigma. Indeed, they often possess considerably different stability [8] and afford variable regiochemistry [3–8] when compared to other commonly used metallocuprates, e.g., $(R_3Si)_nCuLi_{n-1} \cdot LiX$, n = 1 or 2; X = Br or CN [9,10]. We now describe, using spectroscopic studies, *prima facie* evidence for the formation of hitherto unknown higher order Cu(I) dianionic species of the general formula $(R_3Sn)_3CuLi_2$. We also present evidence that, unlike either homo trialkylsilylcyanocuprates, $(R_3Si)_2Cu(CN)Li_2$ [10a], or mixed trialkylstannyl- or trialkylsilylcuprates. $(R_3M)Cu(R')(CN)Li_2$ (M = Si or Sn and R' = Me or Bu) [11], which exist as discrete species in solution, higher order homo trialkylstannylcuprates, $[(R_3Sn)_2Cu(CN)Li_2]$, are present in solutions as equilibrium mixtures of three species. We also present evidence that the analogous magnesium, aluminum, or boron species are discrete in solution and possess differential reactivity.

RESULTS AND DISCUSSION

Low-temperature ^1H NMR spectroscopic studies were initially conducted on THF solutions containing 1, 2, or 3 equivalents of trimethylstannyl lithium (**1**) and 1 equivalent of $CuCN \cdot 2LiCl$ in the region between δ 1.0 and −2.0 with the specific goal of observing the resonances due to the various methyl groups on tin. Me_3SnLi (**1**) in THF was prepared by the reaction of $(Me_3Sn)_2$ (**2**) and MeLi at −45°C and therefore contains equimolar amounts of Me_4Sn (δ = 0) [12]. These preparations gave a broad ^1H signal at δ −0.42 (Figure 1a) [13]. As previously reported, no $^1J(^{119}Sn-^1H)$ coupling was observed [13a].

The ^{119}Sn NMR spectrum of solutions resulting from the reaction of **2** (Figure 2a) with MeLi revealed a broad signal for **1** at δ −187.9 (Figure 2b) [14].

The hydrogen-decoupled ^{13}C NMR spectrum of solutions of **1** (Figure 3a) in THF exhibited a broad signal at δ −3.7. Contrary to what might be expected, no $^{13}C-^{119}Sn$ coupling was observed for **1** in THF. At least two mechanisms can account for this absence of observable Sn–C coupling. First, rapid exchange of methyl groups between Me_3SnLi

Dedicated to Prof. Adrian Gibbs Brook on the occasion of his seventieth birthday.

*To whom correspondence should be addressed.

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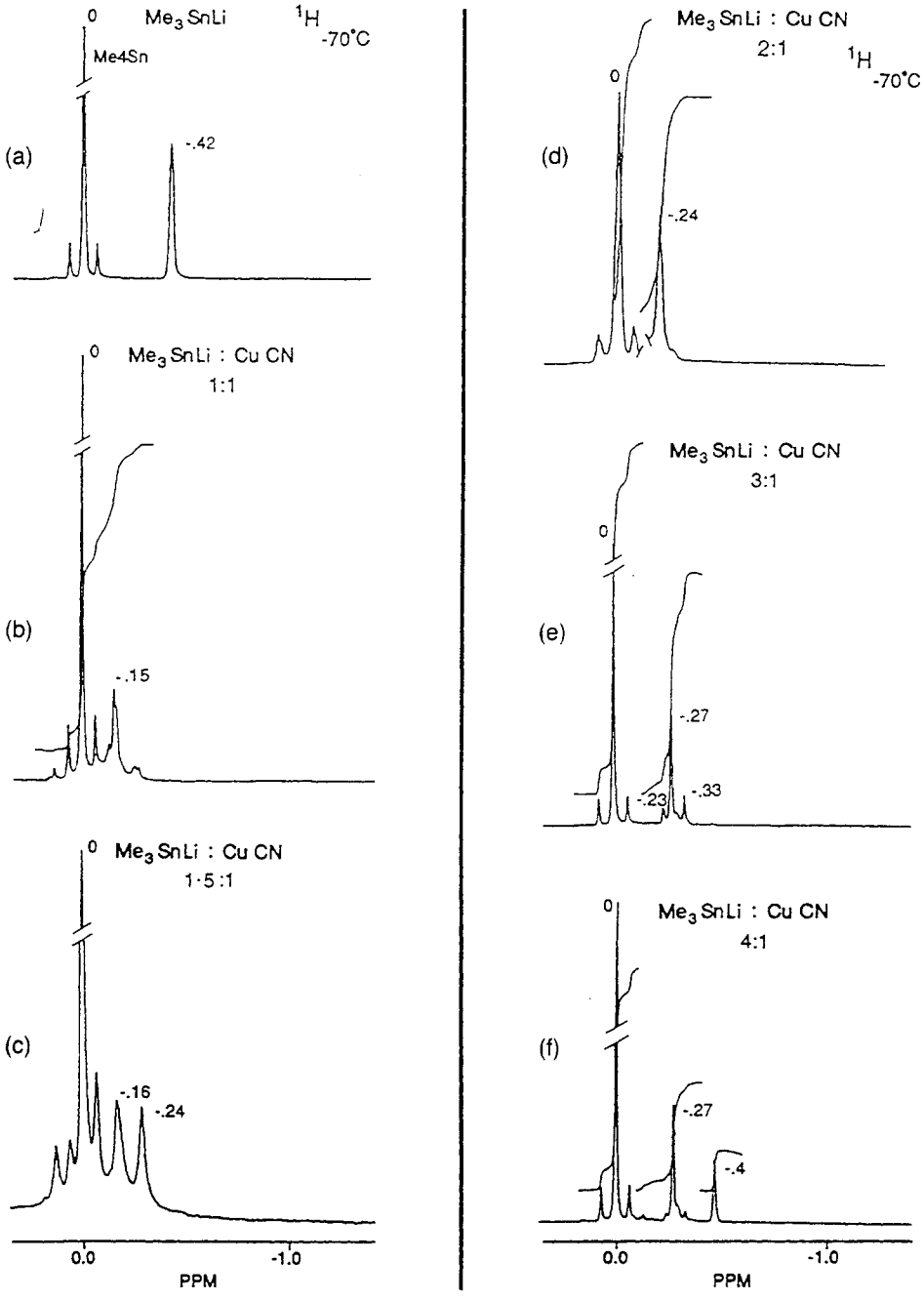


FIGURE 1 ^{1}H NMR spectra of (a) Me_3SnLi, (b) 1.0 Me_3SnLi + CuCN, (c) 1.5 Me_3SnLi + CuCN, (d) 2.0 Me_3SnLi + CuCN, (e) 3.0 Me_3SnLi + CuCN, and (f) 4.0 Me_3SnLi + CuCN; the spectra were run at −70°C.

and $(Me_3Sn)_2$ would destroy the correlation between the ^{13}C and ^{119}Sn spin states [15a]. Second, association with THF to give $[Me_3Sn \cdot (THF)_x]^-$ solvated anions would lower the symmetry of the anion, and quadrupolar relaxation effects would average out the coupling. At present, we cannot distinguish these two possibilities, although the lack of coupling even at −85°C, where methyl exchange rates are apt to be slow, suggests that solvation of the anion is a more likely rationale [15b]. This explanation is consistent with the observation that the ^{1}H and ^{13}C NMR chemical shifts of this reagent are concentration dependent [15c].

Solutions of stannylcuprates [3,8a] were generated by addition of CuCN · LiCl to THF solutions of **1** at −78°C. Combination of equimolar ratios of **1** and CuCN · 2LiCl resulted in an orange solution, which showed several ^{1}H NMR signals in the range of δ −0.1 to −0.3 with a major signal centered near −0.15 (Figure 1b) [15d]. This signal is assigned to $Me_3SnCu(CN)Li$ (**3**). Evidence that cyanide is bound to copper comes from infrared analysis, which

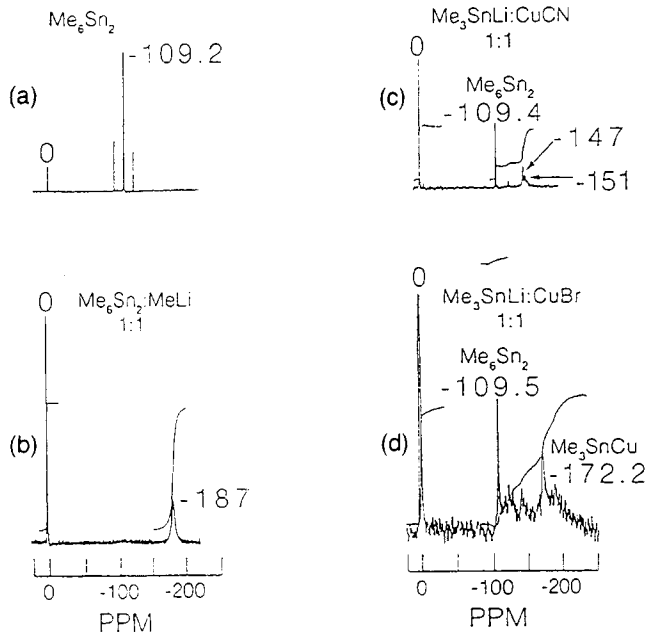


FIGURE 2 ^{119}Sn NMR spectra of (a) Me_6Sn_2, (b) Me_3SnLi, (c) 1.0 Me_3SnLi + CuCN, and (d) Me_3SnLi + $CuBr \cdot Me_2S$; the spectra were run at −70°C.

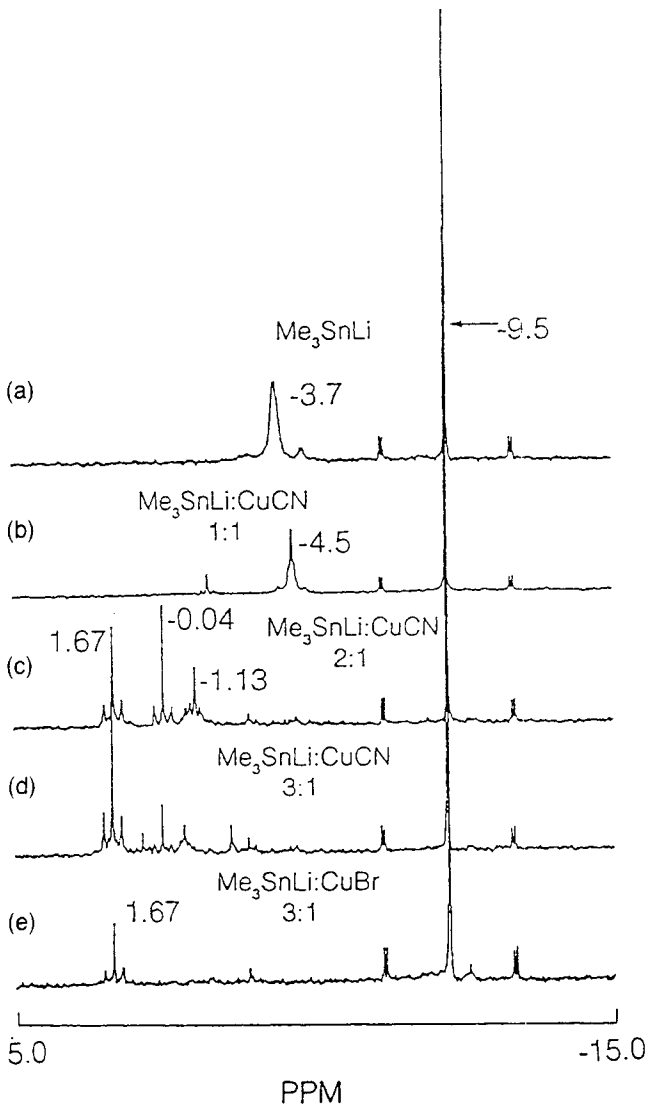


FIGURE 3 ^{13}C NMR spectra of (a) Me_3SnLi, (b) 1.0 Me_3SnLi + CuCN, (c) 2.0 Me_3SnLi + CuCN, (d) 3.0 Me_3SnLi + CuCN, and (e) 3.0 Me_3SnLi + CuBr; the spectra were run at −70°C.

shows a major absorption at 2111 cm^{-1} due to bound nitrile accompanied by a less intense absorption at 2082 cm^{-1} due to free LiCN [16,17]. This observation, coupled with the ^{13}C NMR (*vide infra*), which revealed a bound nitrile at δ 148.0, provides strong evidence for the composition of **3**.

The ^{119}Sn spectrum of the 1:1 combination of **1** and CuCN exhibited a multitude of ^{119}Sn signals in the region of δ −140.0 to −160.0, again suggesting the aggregated nature of this reagent (Figure 2c). These signals are accompanied by a minor signal at −109.0 due to **2**, suggesting thermal decomposition of **3** [8]. Appearance of signals for **2** in the ^{119}Sn NMR spectrum but not in the ^{1}H or ^{13}C spectra is attributed to the decomposition of **3** during the longer time required to acquire the ^{119}Sn spectrum.

To rule out the presence of Me_3SnCu (**4**) in solutions of **3**, we mixed equimolar amounts of **1** and $CuBr \cdot Me_2S$. The resulting solutions exhibited several ^{119}Sn signals centered near δ −179.0, again suggesting an aggregated species (Figure 2d). These signals were clearly absent in preparations of **3**. Lower order cuprates containing 1 equivalent of RLi to each equivalent of cuprous ion, such as $PhMe_2SiCu(CN)Li$ [10a], "$PhMe_2SiCu$" [10b], and CH_3Cu [18], are also aggregated in nature.

The ^{13}C NMR spectrum of **3** exhibited a triplet at δ −4.5 (Figure 3b). The possibility that the multiplicity of this signal is due to $^2J(^6Li-^{13}C)$ coupling (^{6}Li–^{13}C coupling has been observed in Me_2CuLi) [19] is ruled out because the observed satellites (total intensity of 16.5%) are more intense than calculated (7.42% of ^{6}Li), and the coupling is significantly larger than expected [20]. The satellites of this signal are attributed to $^1J(^{119}Sn-^{13}C)$ coupling, in agreement with the natural abundance of ^{119}Sn [21]. The very low coupling constant of J = 63.0 Hz is indicative of a trimethyltin group bonded to a weakly electron-attracting moiety, as in the case of Me_3SnLi [$^1J(^{119}Sn-^{13}C)$ = 120.0 Hz] [14,22].

As the ratio of **1** to CuCN was increased from 1:1 to 1.5:1, a new peak at δ −0.24 in the ^{1}H NMR spectrum appeared and increased in intensity at the expense of the signal at −0.16 (Figure 1c). When the ratio of **1** to CuCN reached 2:1, minor signals due to **3** (δ −0.16) and $(Me_3Sn)_3CuLi_2$ (**5**, δ −0.27)

and a major signal at δ −0.24 (Figure 1d) appeared. The latter signal is attributed to a species containing a Me_3Sn/Cu ratio between 1:1 and 3:1.

The ^{13}C NMR spectra of solutions prepared from 2.0 equivalents of **1** and 1 equivalent of CuCN contained three signals (δ 1.67, −0.04, and −1.13, Figure 3c). Each signal is accompanied by a set of satellites attributed to coupling of the two tin nuclides of spin 1/2 to carbon. The observation of spin coupling allows the establishment of Cu–Sn stoichiometry in solution based on the relative intensities [14a,15b]. Thus, the signal centered at δ 1.67 exhibited $^{119}Sn-^{13}C$ coupling of 44.3 Hz and satellites of 45.0% intensity indicating ^{13}C coupling to three tin nuclei, while that at δ −0.04 was accompanied by satellites revealing a $^{119}Sn-^{13}C$ coupling of 46.8 Hz to two tin nuclei (26.0%) and the signal at δ −1.13 exhibited $^{119}Sn-^{13}C$ couplings of 46.8 and 23.8 Hz due to two different tin nuclei in the ratio of 3:2.

The signal at δ 1.67 is assigned to **5** based on the observation that this signal grows at the expense of the signals at −0.04 and −1.13 as the Sn/Cu ratio is increased from 2:1 to 3:1 and beyond (Figure 3d). The presence of signals corresponding to **5** requires the presence of species containing a 1.5:1 ratio of Me_3Sn/Cu to maintain the copper-tin balance in these solutions. The ^{13}C NMR spectrum of a solution generated by mixing 1.5 equivalents of **1** with 1 equivalent of $CuBr \cdot Me_2S$ exhibits a broad peak at δ −1.13. Hence, $(Me_3Sn)_3Cu_2Li$ (**6**) is assigned to the latter signal. The ^{13}C NMR spectrum of a solution generated from the combination of 2 equivalents of **1** and 1 equivalent of $CuBr \cdot Me_2S$ exhibits a broad signal at δ −1.35 assigned to $(Me_3Sn)_2CuLi$ (**7**). This signal is absent in solutions generated from a 2:1 combination of **1** and CuCN. Thus, the stannylcuprate giving rise to the signal centered at δ −0.04 may be attributed to $(Me_3Sn)_2Cu(CN)Li_2$ (**8**, Scheme 1).

It is significant that both the ^1H and ^{13}C NMR spectra revealed the absence of **1** in these solutions. This limits consideration of the composition of the stannylcuprates possessing Me_3Sn/Cu ratios between 1:1 and 3:1 to **5** (δ 1.67), **6** (δ −1.13), and **8** (δ −0.04, Scheme 2). This interpretation is in agreement with the ^{13}C NMR and low-temperature infrared analyses of these solutions, which revealed both bound nitrile at δ 156.0 and 2123 cm^{-1}, respectively, and free LiCN at δ 163.0 and 2083 cm^{-1}.

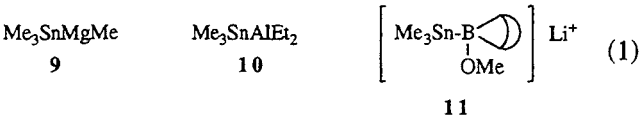
Sequential addition of **1** to solutions containing a Me_3SnLi:CuCN ratio of 2:1 (<0.5 equivalent) resulted in the appearance of a new signal at δ −0.27 in the ^1H NMR spectrum. When the ratio of **1** to CuCN was 3:1 (Figure 1e), the major ^1H signal was at δ −0.27 accompanied by a minor signal due to **8** (δ −0.23). The peak at δ −0.27 was attributed to $(Me_3Sn)_3CuLi_2$ (**5**) by analogy with our earlier observations on the trialkylsilylcuprates [10].

In support of our interpretation of the ^1H NMR spectral data, the ^{13}C NMR spectrum of this solution showed a major signal at δ 1.67 (Figure 3d). Moreover, solutions of Me_3SnLi:$CuBr \cdot Me_2S$ (3:1) exhibited ^{13}C NMR spectra with a signal at δ 1.67 (Figure 3e).

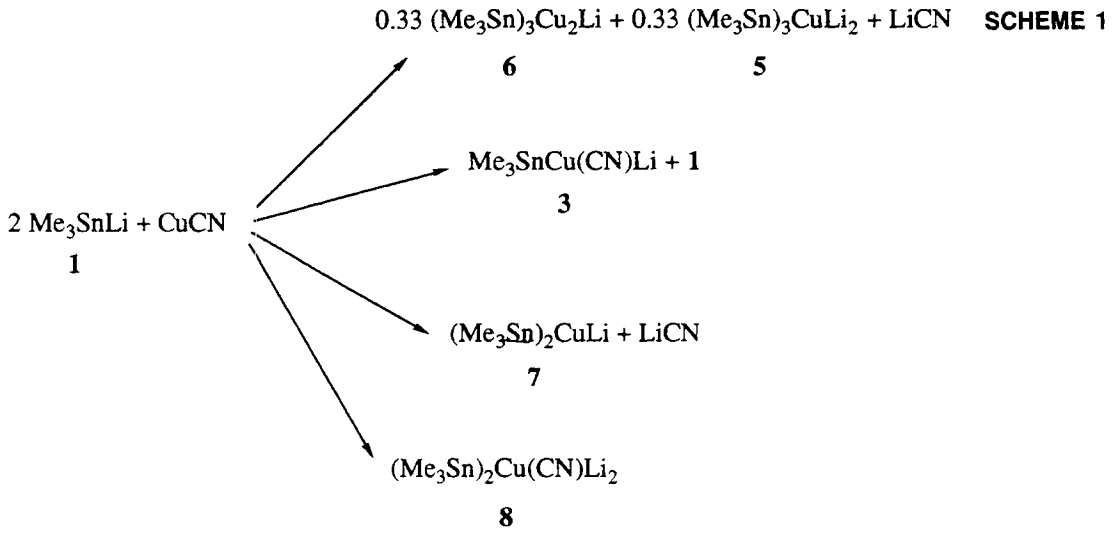
Substantial amounts of Me_3SnLi were detected by ^1H NMR analysis (Figure 1f) only in solutions containing more than 3.0 equivalents of **1** to each equivalent of CuCN.

That the formation of **3** and **5** is reversible was shown by addition of 0.5 equivalents of CuCN to the solution whose ^1H NMR spectrum is shown in Figure 1e. This results in the regeneration of the spectrum shown in Figure 1d. Further introduction of CuCN (1.0 equivalent) to the latter solution results in the regeneration of the spectrum shown in Figure 1b.

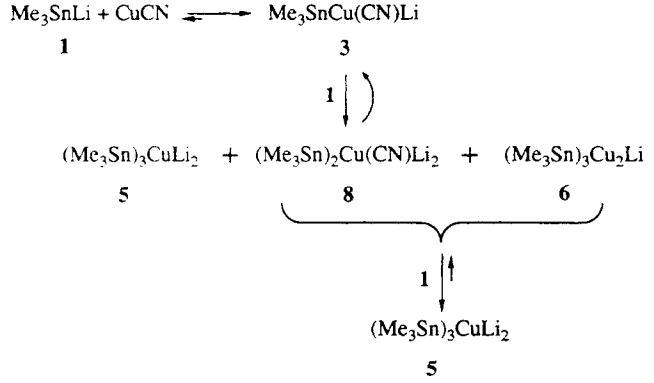
The observed $^1J(^{119}Sn-^{13}C)$ coupling decreases as one proceeds from lower order to higher order stannylcuprates, i.e., $^1J(^{119}Sn-^{13}C$, 63.0 Hz) of $Me_3SnCu(CN)Li$ (**3**, δ −4.5) > $^1J(^{119}Sn-^{13}C$, 46.8 Hz) of $(Me_3Sn)_2Cu(CN)Li_2$ (**8**, δ −0.04) > $^1J(^{119}Sn-^{13}C$, 44.3 Hz) of $(Me_3Sn)_3CuLi_2$ (**5**, δ 1.67). The small $^{119}Sn-^{13}C$ coupling observed in higher order homo trialkylstannylcuprates as compared to lower order homo trialkylstannylcuprates is consistent with a greater electron density on the tin atom in the former [13b,14]. According to this rationale, a greater negative charge on the tin atom would lead to a greater *s*-character in the orbital containing the lone pair bound to copper [13b]. An increase in the fractional *s*-character of the bond should lead to a decrease in *s*-character of the remaining tin–carbon bonds and result in a lower $^{119}Sn-^{13}C$ coupling as observed [13,14]. We have observed the same phenomenon for stannylmetalloids such as $Me_3SnMgMe$ (**9**), $Me_3SnAlEt_2$ (**10**), and $[(Me_3Sn\text{-}9\text{-}BBN \cdot OMe)^-]Li^+$ (**11**). The small couplings in **9** [$^1J(^{119}Sn-^{13}C$, 29.0 Hz], **10** [$^1J(^{119}Sn-^{13}C$, 40.0 Hz], and **11** [$^1J(^{119}Sn-^{13}C$, 56.0 Hz] are close to those observed for the stannylcuprates discussed previously [23].



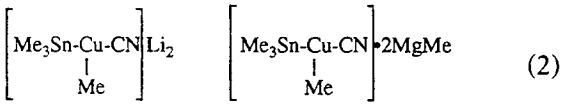
We also studied the effect of counterion on the solution properties of trialkylstannylcuprates. Thus, the reaction of $Me_3Sn(Me)Cu(CN)Li_2$ (**12**) with 2.0 equivalents of MeMgI resulted in the formation of new species that exhibited ^{13}C NMR signals at δ −16.5, −6.9, and 1.18 due to the CH_3 on magnesium, CH_3 on copper, and CH_3 on tin, respectively, indicating the presence of discrete species in solution.



SCHEME 1



SCHEME 2

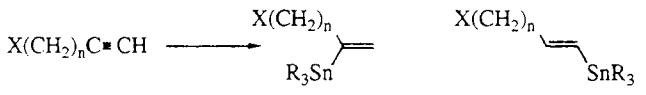


(2)

We studied the addition of $R_3SnCu(CN)Li$ (**3**), R_3SnCu (**4**), $(R_3Sn)_2Cu(CN)Li_2$ (**8**), $R_3Sn(Cu)R(CN)Li_2$ (**12**), and $R_3Sn(Cu)R(CN)\cdot 2MgMe$ (**13**) to 1-alkynes. In agreement with existing reports [3–8], we found that homo lithio[trialkylstannylcuprates] derived from Me_3SnLi and Bu_3SnLi added to 1-alkynes to yield a mixture of **14** and **15** in which the former predominated (Table 1). This trend of the trialkylstannyl group to migrate preferentially to the more substituted carbon has been assumed to be due to the polarity of the transition state wherein this group bears a negative charge relative to the copper [8c].

We believe that steric factors are superimposed on this electronic bias. Thus, in the preceding reactions, there is a higher preference for the formation of 2-trialkylstannyl-1-alkenes (**14** vs. **15**) for trimethylstannyl reagents [3,6,7] than for those carrying the tributylstannyl group (Table 1, compare entries 2 and 3). Likewise, the higher preference for formation of 2-trialkylstannyl-1-alkenes (**14** vs. **15**) by the aggregated lower order lithio[trialkylstannylcuprates] [3] prepared from 1.0 equivalents of R_3SnLi and Cu(I)X salts could also be attributed to the larger steric requirements for copper center in these reagents (Table 1, compare entries 7 and 5). On the other hand, the magnesium derived trialkylstannylcuprates prefer the

TABLE 1 Reaction of Stannylcuprates with 1-Alkynes



14 15

Reagent Used	**14**	**15**	*Yield*
a, X = OH, *n* = 1			
1 $Me_3SnCu(CN)Li$	95	5	82%
2 $(Me_3Sn)_2Cu(CN)Li_2$	90	10	83%
3 $(Bu_3Sn)(Bu)Cu(CN)Li_2$	66	34	78%
4 $(Bu_3Sn)(Bu)Cu(CN)\cdot MgMe$	34	66	75%
b, X = OTHP, *n* = 4			
5 Bu_3SnCu	87	13	81%
c, X = H, *n* = 6			
6 $Me_3Sn(Me)Cu(CN)\cdot 2MgMe$	66	34	80%
7 $Bu_3Sn(Bu)Cu(CN)Li_2$	60	40	62%
8 $Bu_3Sn(Bu)Cu(CN)\cdot 2MgMe$	20	80	88%
9 $Bu_3SnMgMe\cdot 0.1CuCN$	6	94	75%

formation of 1-trialkylstannyl-1-alkene (**15**) over 2-trialkylstannyl-1-alkene (**14**, Table 1, compare entries 4, 6, and 8).

Hence, regioselectivity in stannylcuprations is not only dictated by the polarity of the Sn–Cu bond but is also influenced by the steric bulk of the alkyl groups on the tin as well as copper center in the stannylcopper reagent.

Further corroboration of these results was obtained by the reaction of $Bu_3SnMgMe \cdot 0.1$ CuCN with 1-octyne. As expected, 1-trialkylstannyl-1-alkene (**15**) was produced in a ~15:1 ratio over 2-trialkylstannyl-1-alkene (**14**, Table 1, entry 9).

EXPERIMENTAL

All glassware and syringes were dried in an oven overnight at 120°C, and glassware was flame dried under vacuum and flushed with argon immediately prior to use. Syringes were flushed with argon and kept under positive argon pressure until use. Transfer of reagents was performed by syringes equipped with stainless steel needles. Reactions were carried out in three necked round-bottom flasks equipped with filtration units and Teflon-coated magnetic stirring bars.

Transfer of CuCN and CuX took place in a glove bag. All alkyllithiums were freshly titrated before use [24].

Tetrahydrofuran was freshly distilled over potassium benzophenone-ketyl. Unless otherwise stated, other chemicals obtained from commercial sources were used without further purification.

Preparative TLC was performed using Merck precoated silica gel 60 F_{254}, 20 × 20 cm, 0.25-mm thick glass-backed analytical plates. Analytical TLC analysis was carried out using Merck precoated silica gel 60 F_{254}, 0.2-mm thick aluminum-backed sheets cut to the desired size. All ^1H NMR, ^{13}C NMR, and special experiments were recorded on a Varian Gemini 300 spectrometer (300 MHz ^1H and 75 MHz ^{13}C). Mass spectra were recorded on a Finnegan-MAT 8230 mass spectrometer. Infrared spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrophotometer.

Low-temperature ^{119}Sn NMR experiments were conducted on a Bruker WM-400 spectrometer with an operating frequency of 149.197 MHz. A typical set of parameters utilized a spectral width of 50,000 Hz, 8 K of memory, 11 Hz/data point, an acquisition time of 0.09 seconds, and a 55° pulse of 35 μs. The decoupler was turned on during acquisition and off during the relaxation delay (4 seconds) in order to suppress the negative nOe of ^{119}Sn. A line broadening of 20 Hz was applied to all spectra. Spectra were recorded in THF that contained Me_4Sn as internal reference.

Low-temperature ^{13}C NMR spectra were obtained on a Varian XL-300 spectrometer with an operating frequency of 75.46 MHz. Parameters for the ^{13}C spectral acquisition typically involved a spectral width of 15,000 Hz, 32 K of memory, an acquisition time of 0.4 seconds, and a 60° pulse of 12 μs. The spectra were recorded on THF solutions unless otherwise specified and were referenced to THF, $\alpha = 25.3$, $\beta = 67.41$.

Low-temperature ^1H NMR spectra were recorded on a Varian XL-300 spectrometer in THF-d_8. The peaks are referenced to Me_4Sn (δ 0) as internal reference.

A vacuum-jacketed, glass dewar measuring 7.5 × 16.0 cm (i.d. 5.5 cm) was designed with tapering bottom to fit in the cup of the vortex mixer. All NMR samples were stirred while cooling at the indicated temperatures in this dewar.

Preparation of CuCN · 2LiCl. THF (11.0 mL) was added to a mixture of CuCN (0.98 g, 11.0 mmol) and LiCl (0.95 g, 22.0 mmol) in a round-bottomed flask under argon. A clear, faint yellow solution was obtained after 0.5 hours of stirring. This solution was used as the CuCN source for all the ^{13}C and ^1H NMR sample preparations unless otherwise specified.

PREPARATION OF TRIALKYLSTANNYLCUPRATES

^{13}C and ^1H NMR Sample Preparation

Preparation of Me_3SnLi (**1**). Me_3SnLi was prepared in accordance with Ref. [12], as described in Ref. [11].

Preparation of Me_3SnCu (**4**). $CuBr \cdot Me_2S$ (0.205 g, 1.0 mmol) was placed in a 5 mL round-bottomed flask, equipped with an argon inlet. The flask was repeatedly (3 times) evacuated and purged with argon. It was then cooled to −78°C and trimethyltin lithium in THF (2.0 mL, 1.0 mmol) was added dropwise.

Preparation of $(Me_3Sn)_2CuLi$ (**7**). A THF solution of Me_3SnLi (2.0 mL, 1.0 mmol) was added to a 5 mL round-bottomed flask containing a THF solution of Me_3SnCu (**4**) (1.0 mmol, *vide supra*) at −78°C. The resultant deep red colored solution was stirred prior to examination by NMR spectroscopy.

Preparation of $(Me_3Sn)_3CuLi_2$ (**5**). To a THF solution of $(Me_3Sn)_2CuLi$ (2.0 mL, 1.0 mmol) prepared as outlined previously was added a THF solution of Me_3SnLi (2.0 mL, 1.0 mmol) at −78°C.

Preparation of $Me_3SnCu(CN)Li$ (**3**). $CuCN \cdot 2LiCl$ (1.0 mL, 1.0 mmol) was placed in a 5 mL round-bottomed flask, equipped with an argon inlet. The flask was repeatedly (3 times) evacuated and purged

with argon. The solution was cooled to −78°C and trimethyltin lithium in THF (2.0 mL, 1.0 mmol) was added dropwise. An orange suspension was obtained.

Preparation of $(Me_3Sn)_2Cu(CN)Li_2$ (**8**). A THF solution of Me_3SnLi (2.0 mL, 1.0 mmol) was added to a flask containing a THF solution of $Me_3SnCu(CN)Li$, **3** (1.0 mmol, *vide supra*), at −78°C. The NMR spectrum was recorded for the resultant yellow colored solution.

Preparation of $(Me_3Sn)_3CuLi_2$ (**5**). To a THF solution of **8** (1.0 mmol) prepared as outlined previously was added a THF solution of Me_3SnLi (2.0 mL, 1.0 mmol) at −78°C.

Typical Procedure for Stannylcupration of 1-Alkynes

Table 1, Entry 4. BuLi (1.40 mL, 2.2 mmol, 1.6 M in hexanes) was added dropwise to a suspension of CuCN (0.10 g, 1.1 mmol) in THF (3.0 mL) at −78°C. Bu_3SnH (0.59 mL, 2.2 mmol) was added dropwise to the resultant clear yellow solution. After 30 minutes, MeMgI (0.73 mL, 2.2 mmol, 3.0 M in ether) was added dropwise at −78°C. A yellowish-white precipitate was formed immediately. After 5 minutes, a solution of propargyl alcohol (0.06 mL, 1.0 mmol) in THF (1.0 mL) pretreated with ^{t}BuMgCl (0.5 mL, 1.0 mmol, 2.0 M in ether) was added to the reaction mixture at −78°C. The reaction mixture was then allowed to warm to −20°C and stirred for 3.5 hours. The usual workup followed by column chromatography (hexanes:ethyl acetate, 10:1, containing 1% (v/v) Et_3N as eluant) yielded 34.0% of 3-hydroxy-2-tributylstannyl-1-ethene and 66.0% of 3-hydroxy-1-tributylstannyl-1-ethene, respectively. Gas chromatographic analysis revealed a purity of >97% for both isomers.

3-Hydroxy-2-tributylstannyl-1-ethene. R_f, 0.48 (hex:EtOAc, 5:1); IR (NaCl) 3317 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.86 (d, J = 2 Hz, ^3JSn–H = 130 Hz, 1H, HC=CSn), 5.22 (d, J = 2 Hz, ^3JSn–H = 62 Hz, 1H, SnC=CH), 4.26 (q, J = 2 Hz, 2H, OCH_2), 1.20–1.60 (m, 12H), 0.8–1.0 (m, 15H); $^{13}C\{^1H\}$ NMR, 155.0 ($C=CSnBu_3$), 123.3 ($C=CH_2$), 70.1 (OCH_2), 29.1, 27.3, 13.6, 9.4; MS m/z 291 (M^+ −57). Anal. calcd $C_{11}H_{23}SnO$: 291.0771; found: 291.0769.

3-Hydroxy-1-tributylstannyl-1-ethene. R_f, 0.40 (hex:EtOAc, 5:1); IR (NaCl) 3318 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.2 (d, J = 20 Hz, $^3J_{Sn-H}$ = 32 Hz, 1H, HCSn=CH), 5.9 (dt, J = 20, 6 Hz, $^3J_{Sn-H}$ = 60 Hz, 1H, SnCH=CH), 4.15 (q, J = 6 Hz, 2H, OCH_2), 1.20–1.60 (m, 12H), 0.8–1.0 (m, 15H); $^{13}C\{^1H\}$ NMR, 147.0 ($C=CSnBu_3$), 128.3 ($C=CH_2$), 66.4 (OCH_2), 29:1, 27.3, 13.7, 9.4; MS m/z 291 (M^+−57). Anal. calcd $C_{11}H_{23}SnO$: 291.0771; found: 219.0772.

Table 1, Entry 5. $CuBr \cdot Me_2S$ (0.452 g, 2.2 mmol) was placed in a flask equipped with an argon inlet. The flask was repeatedly (3 times) evacuated and purged with argon. THF (5.0 mL) was injected, and the reaction mixture was cooled to −50°C. Tributyltin lithium in THF (4.4 mL, 2.2 mmol) was then added dropwise. The resulting deep red slurry was stirred for 0.5 hours, after which 6-tetrahydropyranyloxy-1-hexyne (0.20 g, 1.1 mmol) was added at −50°C dropwise, followed by addition of MeOH (15.0 mL). The reaction was warmed gradually to room temperature. The usual workup, followed by column chromatography on silica gel (hexane:ethyl acetate, 99:1 as eluent), gave 0.436 g (85.0%) of 6-tetrahydropyranloxy-2-tributylstannyl-1-hexene in >99.0% purity.

6-Tetrahydropyranloxy-2-tributylstannyl-1-hexene. ^1H NMR ($CDCl_3$) δ 0.88 (t, 9H, CH_3, J = 6.6 Hz), 1.32 (q, 12H, CH_2, J = 6.6 Hz), 1.5 (m, 8H, CH_2), 1.6 (t, 2H, CH_2O, J = 6.7 Hz), 2.3 (tt, 2H, $C=CCH_2$, J = 6.6 Hz, 1.9 Hz), 3.38 (ddd, 1H, OCH_2CH_2), 3.5 (tt, 1H, CH_2 on OTHP), 3.75 (ddd, 1H, OCH_2CH_2), 3.85 (tt, 1H, CH_2 on OTHP), 4.6 (tt, 1H, OCHO), 5.1 (dt, 1H, C=CH, J = 3.0, 1.2, $^3J_{Sn-H}$ = 64.0 Hz), 5.7 (dt, 1H, C=CH, J = 3.0, 1.2, $^3J_{Sn-H}$ = 140.0 Hz); $^{13}C\{^1H\}$ NMR, 155.4 ($C=CSnBu_3$), 124.8 ($C=CH_2$), 98.7 (OCHO), 67.4 (OCH_2), 62.1 (OCH_2), 41.1, 30.8, 29.5, 29.1, 27.3, 26.3, 25.5, 19.6, 13.6, 9.6; GC/MS, m/z 417 (M^+−57). Anal calcd for $C_{19}H_{37}O_2Sn$: 417.1816; found: 417.1808.

Table 1, Entry 9. A 0.3 M solution of $Bu_3SnMgMe$ was prepared at 0°C by adding BuLi (4.5 mL, 6.0 mmol, 1.33 M in hexanes) to a solution of $SnCl_2$ (0.38 g, 2.0 mmol) in THF (1.5 mL) followed by MeMgI (0.6 mL, 2.0 mmol, 3.0 M in ether). After 20 minutes, 1.7 mL (0.5 mmol) of this solution was added to a reaction tube containing 1-octyne (0.074 mL, 0.5 mmol) and a THF solution of $CuCN \cdot 2LiCl$ (0.33 mL, 0.033 mmol, 0.1 M). After 30 minutes, the reaction was quenched with 1N HCl (5.0 mL). The usual workup followed by column chromatography on silica gel (hexane containing 1% (v/v) Et_3N as eluent) gave 0.15 g (75.0%) of a mixture of 2-tributylstannyl-1-octene and *E*-tributylstannyl-1-octene in a 1:16 ratio, respectively, in >99.0% purity.

2-Tributylstannyl-1-octene. R_f *0.93, hexanes*; ^1H NMR ($CDCl_3$) δ 0.88 (t, 12H, CH_3, J = 7.5 Hz), 1.2–1.6 (m, 26H, CH_2), 2.21 (ddt, 2H, $C=CCH_2$, J = 7.0 Hz, 1.45 Hz, 1.04 Hz), 5.06 (dt, 1H, C=CH, J = 2.9 Hz, 1.04 Hz, $^3J_{Sn-H}$ = 64 Hz), 5.63 (dt, 1H, C=CH, J = 2.9 Hz, 1.45 Hz, $^3J_{Sn-H}$ = 141 Hz); $^{13}C\{^1H\}$ NMR 155.4 ($C=CSnBu_3$), 124.5 ($C=CH_2$), 41.4, 32.0, 29.7, 29.1, 27.4, 22.6, 13.7, 9.7, 8.8; ^{119}Sn NMR = −45.6; GC/MS, m/z (relative intensity), 345 (M^+ −57, 100). Anal calcd for $C_{16}H_{33}Sn$: 345.1604. Found: 345.1604.

E-Tributylstannyl-1-octene: R_f 0.93, hexanes; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 12H, CH_3, J = 7.0 Hz), 1.21–1.6 (m, 26H, CH_2), 2.1 (dq, 2H, C=CCH_2, J = 5.5 Hz, 1.2 Hz), 5.82 (dt, 1H, C=CH, J = 18.9 Hz, 1.2 Hz, $^2J_{Sn-H}$ = 60 Hz), 5.93 (dt, 1H, C=CH, J = 18.9 Hz, 5.5 Hz, $^3J_{Sn-H}$ = 47 Hz); ^{13}C {^{1}H} NMR 149.9 (C=C$SnBu_3$), 126.9 (C=CH), 37.9, 31.7, 29.3, 29.1, 27.4, 22.6, 13.7, 9.4, 8.8; ^{119}Sn NMR = −50.1; GC/MS, m/z (relative intensity), 345 (M^+ −57, 100). Anal calcd for $C_{16}H_{33}Sn$: 345.1604; found: 345.1605.

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