Communications

Fine Tuning the Si–Sn Bond: Transmetalations Forming Either Trialkylstannyl or Trialkylsilyl Higher Order Cyanocuprates

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Summary: Depending upon the nature of the alkyl groups attached to silicon and tin in $R_3Sn-SiR'R_2''$, compounds of this type undergo ligand exchange upon treatment with a higher order cuprate to afford trialkylstannyl or trialkylsilyl mixed cuprates which participate in substitution, conjugate addition, and metalcupration reactions.

Sir: Organic synthesis based on organotin reagents is rapidly becoming a highly valued, visible area of current research.[1] The facility with which tin hydrides[2a,b] and vinylstannanes[2c] undergo transmetalations with higher order (HO) cyanocuprates led us to consider the possibility of converting readily available silylstannanes ($R_3Sn-SiR'_3$, 1) directly to stannylcuprates using $R_2Cu(CN)Li_2$, therefore eliminating the need for prior formation of precursor stannyllithiums (e.g., R_3SnLi).[3] Alternatively, if the cuprate could be influenced to attack at tin rather than at silicon, (trialkylsilyl)cuprates would be formed from the same one-pot operation. We now report that by simply adjusting the steric environment around each metal, ligand exchange can be fully controlled to arrive at either stannyl- or silylcuprates in a rapid, quantitative manner. The reagents so formed can then be employed to effect coupling reactions, thereby introducing either the trialkylstannyl or the trialkylsilyl moiety into a variety of substrate types.
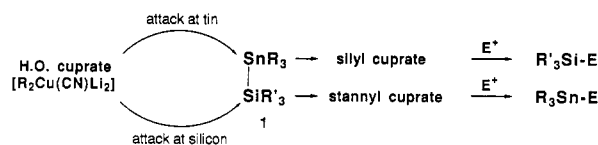
(Tributylstannyl)cuprates are readily prepared using the (trimethylsilyl)stannane $n-Bu_3Sn-SiMe_3$ (2).[4,5] Attack by $n-Bu_2Cu(CN)Li_2$ (3a) or $Me_2Cu(CN)Li_2$ (3b) was anticipated to occur exclusively at silicon in 2, judging from earlier studies by Chenard[5] where naked cyanide ion catalysis led to Michael donor $n-Bu_3Sn^-$. Exposure of 2 to 3b in THF at 0 °C for 30 min presumably generates, in addition to Me_4Si, mixed HO cyanocuprate ($n-Bu_3Sn$)-$MeCu(CN)Li_2$ (4). Recooling to −78 °C followed by addition of a substrate leads to selective delivery of the tributylstannyl group. Table I (entries 1–6) lists some examples indicative of the various modes of cuprate reactivity.

To alter the regiospecificity of this transmetalation, the steric bulk around tin was reduced, while that surrounding silicon was increased. Thus, both $Me_3SnSiMe_2(t-Bu)$ (5)[4a,6a] and $Me_3SnSiMe_2(thexyl)$ (6)[6] were prepared from Me_3SnLi[7] and the corresponding silyl chlorides. Treatment of 5 or 6 (at room temperature) with $n-Bu_2Cu(CN)Li_2$

(1) Organotin Compounds in Organic Synthesis; Tetrahedron Symposia-in-Print Number 36; Yamamoto, Y., Ed.; 1989. Pereyre, M.; Quintard, J.-P.; Rahm, A. In Tin in Organic Synthesis; Butterworths: London, 1987.

(2) (a) Lipshutz, B. H.; Reuter, D. C. Tetrahedron Lett., in press. (b) Lipshutz, B. H.; Ellsworth, E. L.; Dimock, S. H.; Reuter, D. C. Ibid. 1989, 30, 2065. (c) Behling, J. R.; Babiak, K. A.; Ng, J. S.; Campbell, A. L.; Moretti, R.; Koerner, M.; Lipshutz, B. H. J. Am. Chem. Soc. 1988, 110, 2641.

(3) Piers, E.; Tillyer, R. D. J. Org. Chem. 1988, 53, 5366. Gilbertson, S. R.; Challlener, C. A.; Bos, M. E.; Wulff, W. D. Tetrahedron Lett. 1988, 29, 4795.

(4) (a) Chernard, B. L.; Van Zyl, C. M. J. Org. Chem. 1986, 51, 3561. (b) Tamborski, P. C.; Ford, F. E.; Soloski, E. J. Ibid. 1963, 28, 237. (c) The purity of 2, prepared from addition of $n-Bu_3SnH$ to LDA which contained excess TMS-Cl at −78 °C, is highly variable with $n-Bu_4Sn$ being the major contaminant. Thus, excess 2 was used to form 4, the amount being determined by GC analysis of 2. For the recent preparation of $Bu_3SnSiMe_2Ph$ and $Me_3SnSiMe_2Ph$, see: Ritter, K. Synthesis 1989, 218.

(5) Chenard, B. L.; Laganis, E. D.; Davidson, F.; Rajan Babu, T. V. J. Org. Chem. 1985, 50, 3666.

(6) Prepared as described by Chenard[4a] using $ClSiMe_2(thexyl)$ in place of $ClSiMe_2(t-Bu)$; bp 110 °C (23 mmHg).

(7) Still, W. C. J. Am. Chem. Soc. 1977, 99, 4836. See also ref 4b.

Table I. Reactions of (Trialkylstannyl)- and (Trialkylsilyl)cuprates Formed from Transmetalations of $R_3Sn-SiR'R''_2$ Using Cuprate 3a or 3b in THF at 0 °C for 30 min

entry	substrate	$R_3Sn-SiR'R''_2$	product(s)[a]	yield,[b] %
1	X = Br; X = Cl	$Bu_3Sn-SiMe_3$		quant 85
2		$Bu_3Sn-SiMe_3$		58
3		$Bu_3Sn-SiMe_3$		94[c]
4		$Bu_3Sn-SiMe_3$		87[d]
5		$Bu_3Sn-SiMe_3$[e]		82
6		$Bu_3Sn-SiMe_3$		93
7		$Me_3Sn-SiMe_2(t\text{-}Bu)$		99
8		$Me_3Sn-SiMe_2(thexyl)$		98
9		$Me_3Sn-SiMe_2(thexyl)$		94
10		$Me_3Sn-SiMe_2(thexyl)$		71
11		$Me_3Sn-SiMe_2(t\text{-}Bu)$		74[f]
12		$Me_3Sn-SiMe_2(thexyl)$		82
13		$Me_3Sn-SiMe_2(t\text{-}Bu)$		97
14		$Me_3Sn-SiMe_2(t\text{-}Bu)$		98

[a] All products were fully characterized by IR, NMR, MS, and HRMS analyses. [b] Isolated chromatographically pure. [c] A 1:2 mix of E to terminal olefinic materials. [d] MeOH (20 equiv) was necessary for consumption of the educt. [e] This transmetalation was performed using $n\text{-}Bu(Th)Cu(CN)Li_2$.[9] [f] A 9:1 mix of E to Z isomers.

now leads to silyl cuprates $t\text{-}BuMe_2Si(n\text{-}Bu)Cu(CN)Li_2$ (7) or $(thexyl)Me_2Si(n\text{-}Bu)Cu(CN)Li_2$ (8), both of which can be utilized to selectively transfer a trialkylsilyl ligand.[8] Entries 7–14 in Table I demonstrate the effectiveness of this method. Particularly noteworthy are the cases involving silylcupration (entries 7–9) which occur not only in a regiospecific manner[8] but in the absence of hydroxyl protecting groups. A vinylsilane is also the outcome from silylcuprate coupling with an unprotected hydroxy vinyl iodide (entry 10).

In conclusion, (tributylstannyl)- and (trialkylsilyl)-cuprates are now available from common precursor silylstannanes 1 following transmetalations with trivial HO cuprates derived from CuCN. In effect, the silyl or stannyl

group in 1 can be viewed as a proton analogue (toward LDA), a halide surrogate (toward Li[0]), or as a hydride equivalent (toward 3)[2a,b] to give 4 or 7/8. Once these reagents have formed, they are well-behaved yet highly reactive, giving rise to products containg the R_3Si or R_3Sn appendage.[10]

(8) Previously observed with $PhMe_2Si(Me)Cu(CN)Li_2$; cf. Fleming, I.; Newton, T. W. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1805.

(9) Lipshutz, B. H. *Synthesis* **1987**, 325 and references therein.

(10) A typical procedure is as follows (Table I, entry 6): To $n\text{-}Bu_2Cu(CN)Li_2$ (0.52 mmol) in THF at −78 °C is added (thexyldimethylsilyl)trimethylstannane (0.13 mL, 0.527 mmol). The bath is removed, and the solution is warmed to and stirred at room temperature for 1.5 h, after which it is recooled to −78 °C and 3-methylcyclopentenone (0.04 mL, 0.40 mmol) is added neat via syringe. After 5 min, the mixture is quenched at −78 °C (10% NH_4OH/saturated aqueous NH_4Cl) and worked up in the usual way. Chromatography on SiO_2 (3:1 hexanes–Et_2O) gave the product in quantitative yield (96 mg): IR (neat, cm^{-1}) 1740; NMR (500 MHz, $CDCl_3$) δ (relative to $CHCl_3$) 2.3–2.25 (m, 1 H), 2.22–2.19 (d, 1 H, J = 18), 2.16–2.10 (m, 1 H), 2.05–1.99 (m, 1 H), 1.97–1.93 (d, 1 H, J = 18), 1.79–1.72 (m, 2 H), 1.11 (s, 3 H), 0.90–0.85 (m, 12 H), 0.20 (s, 3 H), 0.05 (s, 3 H); MS (EI) m/z 155 (M^+ − 85); HRMS calcd for $C_{14}H_{28}OSi$ (M^+ − H) 239.1831; found 239.1814.

Registry No. 2, 17955-46-3; **3a**, 80473-69-4; **3b**, 80473-70-7; **4**, 122539-76-8; **5**, 97877-91-3; **6**, 122539-75-7; **7**, 122539-77-9; **8**, 122539-78-0; MeOC₆H₄-p-(CH₂)₂SnBu₃, 122539-61-1; (*E*)-Bu₃SnCH=CH(CH₂)₂OH, 107399-01-9; H₂C=C(SnBu₃)-(CH₂)₂OH, 122229-78-1; (*E*)-HOCH₂CH=C(SnBu₃)CH₂OH, 103223-42-3; (*E*)-HOCH₂CH=CHSiMe₂(*t*-Bu), 122539-65-5; (*E*)-HOC(CH₃)₂CH=CHSiMe₂C(CH₃)₂CH(CH₃)₂, 122539-66-6; (*E*)-HO(CH₂)₂CH=CHSiMe₂C(CH₃)₂CH(CH₃)₂, 122539-67-7; (*E*)-HO(CH₂)₂C(CH₃)=CHSiMe₂C(CH₃)₂CH(CH₃)₂, 122539-68-8; (*E*)-(*t*-Bu)SiMe₂CH₂CH=C(CH₃)CH₂OH, 122539-69-9; (*Z*)-(*t*-Bu)SiMe₂CH₂CH=C(CH₃)CH₂OH, 122539-70-2; MeOC₆H₄-p-(CH₂)₂Br, 14425-64-0; MeOC₆H₄-p-(CH₂)₂Cl, 18217-00-0; HC≡C(CH₂)₂OH, 927-74-2; HOCH₂C≡CCH₂OH, 110-65-6; HC≡CCH₂OH, 107-19-7; HC≡CC(CH₃)₂OH, 115-19-5; (*E*)-HO(CH₂)₂C-(CH₃)=CHI, 78592-73-1; ethyl 1-(tributylstannyl)-1-cyclopentenecarboxylate, 122539-62-2; *trans*-4-isopropyl-3-(tributylstannyl)cyclohexanone, 122539-63-3; 3-methyl-3-(tributylstannyl)cyclopentanone, 122539-64-4; 3-(dimethylhexylsilyl)-3,5,5-trimethylcyclohexanone, 122539-71-3; *trans*-3-(dimethyl-*tert*-butylsilyl)-4-isopropylcyclohexanone, 122539-72-4; 3-(dimethyl-*tert*-butylsilyl)-3-methylcyclopentanone, 122539-73-5; trifluoromethyl 2-(ethoxycarbonyl)-1-cyclohexenesulfonate, 122539-74-6; 4-isopropylcyclohex-2-enone, 500-02-7; 3-methylcyclopent-2-enone, 2758-18-1; 2-methyl-2-vinyloxirane, 1838-94-4; 3,5,5-trimethylcyclohex-2-enone, 78-59-1.

Understanding Allylic Organocuprates: σ- or π-Bound Reagents?

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Summary: The nature of both lower and higher order cuprates containing allylic ligands has been investigated using variable-temperature, high-field ¹³C NMR experiments. From these studies, the σ- vs π-bound state of these reagents has been unequivocally determined.

Sir: Notwithstanding the vast array of highly valued organocuprates composed of sp²- and sp³-based ligands,² there is a noticeable lack of successful examples involving Michael transfer of a simple allylic moiety.³ Still fewer reports exist wherein carbon-substituted units (e.g., methallyl, prenyl, etc.) are effectively delivered.⁴ Frustration over the noncharacteristic lack of chemospecificity of allylic cuprates, especially in conjugate addition schemes,⁵ᵃ has lead to the proposal that π-allyl rather than σ-bound reagents (Figure 1) account for their frequent noncuprate-like behavior.⁵ᵇ We now report that by virtue of variable-temperature ¹³C NMR spectroscopy, the precise nature of allyl ligand-containing cuprates, of both the lower order (L.O.) and higher order (H.O.) variety, has been ascertained. Moreover, the insight thereby provided has

implications for synthetic uses of these reagents.⁶

Our studies began with the H.O. diallylcuprate **3**, prepared in THF from allyltributylstannane (**2**) via treatment with *n*-BuLi (1 equiv) at –78 °C followed by addition to LiCl-solubilized CuCN (0.5 equiv)⁷ at –78 °C. ¹³C NMR analysis (decoupled) of **3** at –95 °C revealed three major sharp peaks at δ 150, 91, and 23 ppm attributed to two olefinic carbons (CH and C=CH₂, respectively) and the methylene carbon attached to copper (Figure 2). The coupled spectrum showed the required multiplicities (doublet, triplet, triplet, respectively), confirming these assignments. Hence, whereas an ³η π-allyl bound cuprate would show two signals, the presence of three distinct resonances establishes the σ-bound nature of **3**. Consistent with this trend, both **4** and **5** displayed the expected three key peaks, in addition to the vinylic methyl resonances.⁸⁻¹⁰

3   4   5
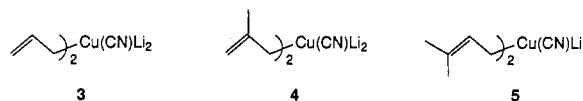
Warming **3** to –70 °C gave significant broadening of both the α- and γ-carbons almost into the base line, while the

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(1) A. P. Sloan Fellow, 1984–1988; Camille and Henry Dreyfus Teacher–Scholar, 1984–1989.

(2) Posner, G. H. *An Introduction to Synthesis Using Organocopper Reagents;* Wiley: New York, 1980. Posner, G. H. *Org. React.* **1972**, *19*, 1; **1975**, *22*, 253. Lipshutz, B. H.; Sengupta, S. *Ibid.*, in press.

(3) (a) House, H. O.; Fisher, W. F. *J. Org. Chem.* **1969**, *34*, 3615. (b) House, H. O.; Wilkins, J. M. *Ibid.* **1978**, *43*, 2443. (c) Majetich, G.; Casares, A.; Chapman, D.; Behnke, M. *Ibid.* **1986**, *51*, 1745. (d) Whitesides, G. M.; Fischer, W. F.; San Filippo, J.; Bashe, R. W.; House, H. O. *J. Am. Chem. Soc.* **1969**, *91*, 4871. (e) Majetich, G.; Casares, A. M.; Chapman, D.; Behnke, M. *Tetrahedron Lett.* **1983**, *24*, 1909. (f) Corey, E. J.; Boaz, N. W. *Ibid.* **1985**, *26*, 6019. (g) Daviaud, G.; Miginiac, Ph. *Ibid.* **1972**, 997. (h) Drouin, J.; Leyendecker, F.; Conia, J. M. *Tetrahedron* **1980**, *35*, 1203. (i) Bertz, S. H.; Dabbagh, G. *Tetrahedron* **1989**, *45*, 425.

(4) Miginiac, Ph.; Daviaud, G.; Gerard, F. *Tetrahedron Lett.* **1979**, 1811. Corriu, R. J. P.; Guerin, C.; M'Boula, J. *Ibid.* **1981**, *22*, 2985. Enda, J.; Kuwajima, I. *J. Am. Chem. Soc.* **1985**, *107*, 5495. Hutchinson, D. K.; Fuchs, P. L., *Ibid.* **1987**, *109*, 4755. Barbot, F.; Kadib-Elban, A.; Miginiac, Ph. *J. Organomet. Chem.* **1983**, *255*, 1; *Tetrahedron Lett.* **1983**, *24*, 5089.

(5) (a) See, for example: Bourgain-Commercon, M.; Foulon, J. P.; Normant, J. F. *J. Organomet. Chem.* **1982**, *228*, 321. (b) Hutchinson, D. K.; Fuchs, P. L. *Tetrahedron Lett.* **1986**, *27*, 1429.

(6) A reagent which successfully delivers a variety of allyl groups in a 1,4-sense has been developed: Lipshutz, B. H.; Ellsworth, E. L.; Dimock, S. H.; Smith, R. A. J., submitted.

(7) Knochel, P.; Yeh, M. C. P.; Berk, S. C.; Talbert, J. *J. Org. Chem.* **1988**, *53*, 2390.

(8) Methallylcuprate **4** gives four key peaks at δ 157 (C-β, vinyl), 90 (terminal CH₂), 26 (C-α, CH₂) and 24 (CH₃) ppm, while prenylcuprate **5** displays signals at δ 136 (C-β, vinyl), 103 (C-γ), 26 (*E*-CH₃), 17.4, 17.2 (*Z*-CH₃ and C-α, or vice versa).

(9) From the spectra obtained we cannot unequivocally rule out the possibility that some of the mixed (1σ, 1π) bound system is present and that it is just not being observed in these ¹³C NMR experiments. However, if such a mixed reagent was present to any appreciable degree, multiple signals would be expected for the carbons of the σ-bound allylic ligand as invariably seen with other mixed H.O.¹² and L.O.¹⁵ cuprates in both their ¹H and ¹³C spectra.

(10) For a discussion on the σ- vs π-bound nature of allylic compounds of lithium, magnesium, and potassium, see: Schlosser, M.; Stahle, M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 487.