Synthesis of a Novel Ate Tin Hydride Complex Bearing a Nucleophilic Iodide Substituent and 1,4-Regioselective Reduction of α,*β*-Unsaturated Aldehydes

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*Summary: A novel ate tin hydride complex, $Li^+[n\text{-}Bu_2SnI_2H]^-$ (**I**), was synthesized and characterized on the basis of its ^{119}Sn NMR spectrum as a trigonal bipyramid (TBP) structure, in which two iodine atoms and one hydrogen atom occupy the apical and the equatorial positions, respectively. The apical iodine has much greater nucleophilicity than the hydrogen, so that the attack by iodide precedes the reduction by hydrogen, achieving regioselective 1,4-reduction of α,β-unsaturated aldehydes.*

Recently, pentacoordinated organotin ate complexes have received much attention.[1] Although the formation of organotin ate complexes bearing five Sn−C bonds has been postulated in the transmetalation of organolithiums with tetraalkyltins[2,3] or in the ring opening of stannacyclobutane by a Grignard reagent,[4] only in several cases have ^{119}Sn NMR data supported the formation of such species. Polar tin compounds, such as tin alkoxides, form stable pentacoordinated ate complexes, and their structures have been investigated.[5] However, neither the formation nor the synthetic utility of ate complexes containing tin−hydrogen bonds has been reported thus far. We report here the first clear formation of a pentacoordinated tin hydride, $Li^+[n\text{-}Bu_2SnI_2H]^-$ (**I**), as a stable ate complex. This finding resulted from our recent investigations of various tin halide hydride·hexamethylphosphoric triamide (HMPA) complexes ($n\text{-}Bu_2SnXH\cdot HMPA$; X = F, Cl, I).[6] Because these tin hydrides were found to promote characteristic chemoselective reductions of epoxides,[7a] imines,[7b] and enones[7c] even in the presence of normally reducible carbonyl functions, we believed that further development of new tin hydride complexes would lead to other useful chemoselective reductions.

The ate complex **I** could be readily prepared from $n\text{-}Bu_2SnIH$ and LiI in THF at room temperature, and their structures were confirmed by their ^{119}Sn NMR spectra as illustrated in Figure 1 and Table 1.[8] When an equimolar amount of LiI was added to a THF solution of $n\text{-}Bu_2SnIH$ prepared by redistribution of $n\text{-}Bu_2SnI_2$ with $n\text{-}Bu_2SnH_2$,[7a] a homogeneous solution was formed and a new peak appeared at −177.9 ppm with concomitant disappearance of the peak corresponding to $n\text{-}Bu_2SnIH$ (−76.3 ppm) (Figure 1). The observed upfield chemical shift strongly indicates the formation of a pentacoordinated tin complex.[1b,9] Moreover, the spin−spin coupling constants, $^1J(^{119}Sn-^1H)$ and $^1J(^{119}Sn-^{13}C)$, both increased, from 2060 and 408 Hz to 2318 and 498 Hz, respectively (Table 1). These coupling constant changes indicate an increase in the s character of the Sn−C and Sn−H bonds.[9] Thus, the anion in $Li^+[n\text{-}Bu_2SnI_2H]^-$ is assumed to have a TBP structure in which two iodine atoms occupy apical positions and the hydrogen atom and butyl groups are located in equatorial positions. Next, we investigated the relationship between the ^{119}Sn chemical shift and the amount of added LiI. As shown in Figure 3, the chemical shift gradually changed as the amount of LiI was increased, up to 1 molar equiv. Further addition of 2 or 3 equiv of LiI gave only a small increase in chemical shift. Similar phenomena were observed in the case of the coupling constants.[10] These results indicate that a statistical average between $n\text{-}Bu_2SnIH$ and $Li^+[n\text{-}Bu_2SnI_2H]^-$ was observed in a rapid equilibrium and that

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[1] For example: (a) Davis. A. G. *Organotin Chemistry*; VCH: New York, 1997; p 236. (b) Harrison, P. G. *Chemistry of Tin*; Blackie: London, 1989; p 282.

[2] (a) Reich, H. J.; Borst, J. P.; Coplien, M. B.; Phillips, N. H. *J. Am. Chem. Soc.* **1992**, *114*, 6577−6579. (b) Reich, H. J.; Philips, N. H. *J. Am. Chem. Soc.* **1986**, *108*, 2102−2103. (c) Meyer, N.; Seebach, D. *Chem. Ber.* **1980**, *113*, 1290−1303.

[3] Ashe, A. J.; Lohr, L. L.; Al-Tawee, S. M. *Organometallics* **1991**, *10*, 2424−2431.

[4] Seetz, J. W. F. L.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1983**, *105*, 3336−3337.

[5] (a) Akiba, K.; Ito, Y.; Kondo, F.; Ohashi, N.; Sakaguchi, A.; Kojima, S.; Yamamoto, Y. *Chem. Lett.* **1992**, 1563−1566. (b) Kawashima, T.; Iwama, N.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 2507−2508. (c) Yamamoto, Y.; Sakaguchi, A.; Ohashi, N.; Akiba, K. *J. Organomet. Chem.* **1996**, *506*, 259−263.

[6] (a) Kawakami, T.; Shibata, I.; Baba, A.; Matsuda, H. *J. Org. Chem.* **1993**, *58*, 7608−7609. (b) Kawakami, T.; Sugimoto, T.; Shibata, I.; Baba, A.; Matsuda, H.; Sonoda, N. *J. Org. Chem.* **1995**, *60*, 2677−2682.

[7] (a) Kawakami, T.; Shibata, I.; Baba, A. *J. Org. Chem.* **1996**, *61*, 82−87. (b) Shibata, I.; Suwa, T.; Moriuchi-Kawakami, T.; Tanizawa, D.; Sugiyama, E.; Matsuda, H.; Baba, A. *J. Org. Chem.* **1998**, *63*, 383−385. (c) Kawakami, T.; Miyatake, M.; Shibata, I.; Baba, A.; Matsuda, H. *J. Org. Chem.* **1996**, *61*, 376−379.

[8] Synthesis of $n\text{-}Bu_2SnIH$ and $Li^+[n\text{-}Bu_2SnI_2H]^-$ for the measurement of ^{119}Sn NMR. $n\text{-}Bu_2SnIH$: To 0.5 mL of dry THF-d_8 in a 10 mL round-bottomed flask were added di-*n*-butyltin dihydride ($n\text{-}Bu_2SnH_2$, 2 mmol) and di-*n*-butyltin diiodide ($n\text{-}Bu_2SnI_2$, 2 mmol). After stirring at room temperature for 10 min, di-*n*-butyliodotin hydride ($n\text{-}Bu_2SnIH$, 4 mmol) was formed in situ, which was confirmed by the shift of IR absorption band (ν(Sn−H)) from 1837 to 1846 cm^{-1}; see ref 7a. $Li^+[n\text{-}Bu_2SnI_2H]^-$: To the in situ formed $n\text{-}Bu_2SnIH$ was added LiI (4 mmol). After stirring the mixture at room temperature for 10 min, a homogeneous solution of $Li^+[n\text{-}Bu_2SnI_2H]^-$ was formed. IR absorption was observed at 1846 cm^{-1}.

[9] For example: (a) Holecek, J.; Nádvorník, M.; Handlír, K.; Lycka, A. *J. Organomet. Chem.* **1983**, *241*, 177−184. (b) Nádvorník, M.; Holecek, J.; Handlír, K.; Lycka, A. *J. Organomet. Chem.* **1984**, *275*, 43−51.

[10] When 0.5 equiv of LiI was added, the value of the coupling constant, $^1J(^{119}Sn-^1H) = 2238$ Hz, was smaller than 2318 Hz (equimolar addition). Whereas, the addition of 3 equiv of LiI gave a similar value, $^1J(^{119}Sn-^1H) = 2336$ Hz.

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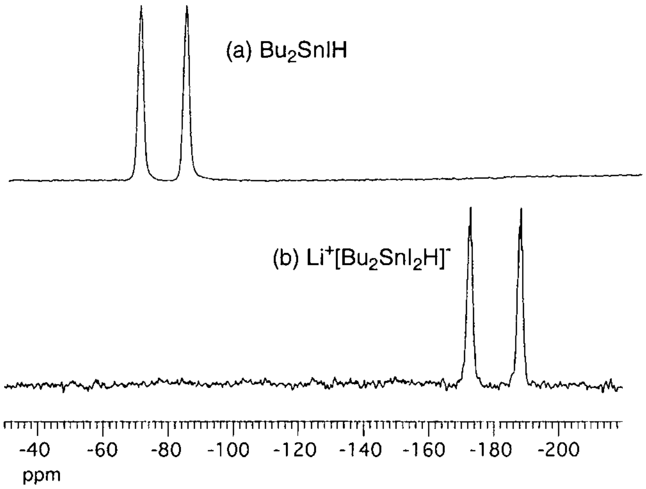


Figure 1. ^{1}H–coupled ^{119}Sn NMR spectra (THF-d_8 solution): (a) Bu_2SnIH, (b) $Li^+ [Bu_2SnI_2H]^-$.

Table 1. Spectral Data of Bu_2SnIH and $Li^+[Bu_2SnI_2H]^-$ in THF-d_8

	Bu_2SnIH^a	$Li^+[Bu_2SnI_2H]^{-b}$
FT-IR (neat) ν(Sn–H) (cm^{-1})	1846.1	1846.1
^{1}H NMR δ(^{119}Sn–^{1}H) (ppm)	6.41	7.10
^{13}C NMR ^1J(^{119}Sn–^{13}C) (Hz)	408	498
^{119}Sn NMR		
δ(^{119}Sn) (ppm)	−76.3	−177.9
^1J(^{119}Sn–^{1}H) (Hz)	2060	2318

[a] 8.0 M. [b] 1.0 M.

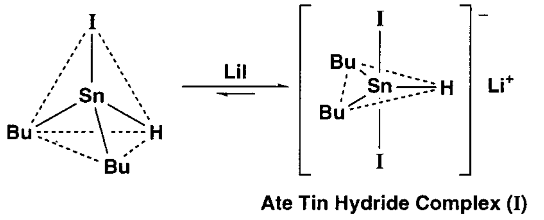


Figure 2. Assumed structure of the ate tin hydride complex.

addition of an equimolar amount of LiI resulted in formation of a high concentration of the ate complex.

Since the apical iodines were expected to show high nucleophilicity, complex **I**, $Li^+[n\text{-}Bu_2SnI_2H]^-$, was treated with 2,3-epoxypropylbenzene (**1**) at room temperature for 15 min. The iodohydrine **2** was formed in 62% yield together with a 24% yield of alcohol **3**.[11] When the reaction was quenched at 0 °C after 5 min, **2** was obtained in 83% yield together with a small amount of **3**. This suggests that preferential attack of the nucleophilic iodine substituent on the epoxide gives the tin alkoxide (**II**). The subsequent intramolecular reduction of the C–I bond thus formed provides the pathway to **3** (Scheme 1).[12] Thus, this novel ate tin hydride may be expected to show a unique reducing ability, because no conventional metal hydride reagents also contain a substituent that is more nucleophilic than hydrides.

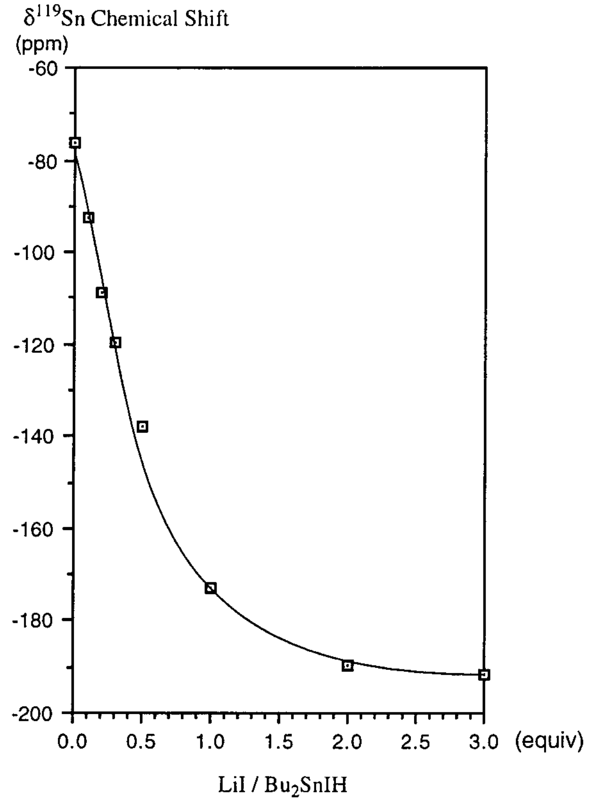
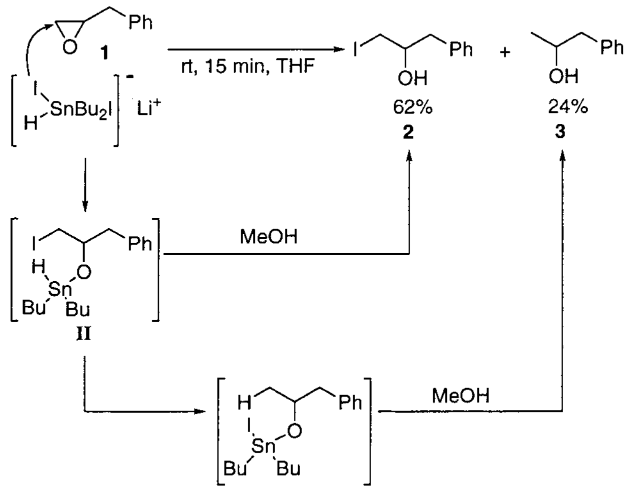


Figure 3. Relation between the ^{119}Sn chemical shift and the amount of LiI added (in THF-d_8).

Scheme 1



To explore this idea, we investigated the possibility of a selective 1,4-reduction of α,β-unsaturated aldehydes by ate complex **I**. Although numerous reductions of α,β-unsaturated aldehydes by metal hydrides including our tin hydrides have been reported, most of them resulted in 1,2-reduction because of the high reactivity of the aldehyde function.[13] For the 1,4-reduction, it is necessary to use transition metal complexes such as those of Pd,[14] Rh,[15] and Cu[16] or bulky Lewis acids such as

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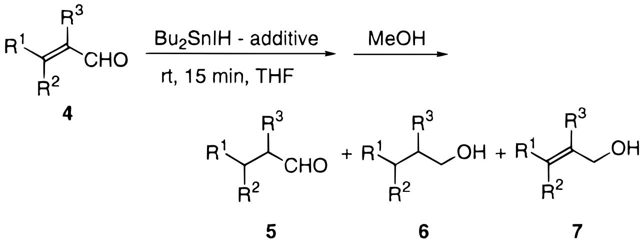
[11] To a THF solution of the tin ate complex **I** (1 mmol) prepared according to ref 8 was added 2,3-epoxypropylbenzene (**1**) (1 mmol), and the mixture was stirred at room temperature for 15 min. After quenching with MeOH (5 mL), volatiles were removed under reduced pressure. The residue was subjected to silica gel column chlomatgraphy, eluting with hexanes–EtOAc (9:1) to give the products **2** and **3**. Further purification was performed by silica gel TLC eluting with hexanes–EtOAc (9:1).

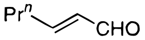
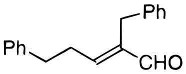
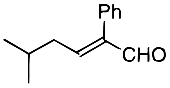
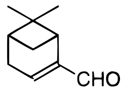
[12] Although the yield of **3** was not increased after a longer reaction time perhaps because of side reactions, the reaction of the epoxide with 3 equiv of $Li^+[n\text{-}Bu_2SnI_2H]^-$ at room temperature for 15 min gave **3** in a quantitative yield.

[13] Greeves, N. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 8, Chapter 1.1, pp 1–24.

Table 2. Selective 1,4-Reduction of Various Enals by *n*-Bu$_2$SnIH−Additive Systems



4 5 6 7

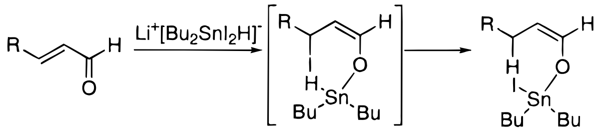
entry	enal		additive	yield/ %		
				5	6	7
1		4a	LiI[a]	80	9	trace
2			none	12	6	15
3			HMPA	18	18	10
4			Bu$_4$NI	37	14	10
5			NaI	38	19	trace
6		4b	LiI[a]	57	0	0
7		4c	LiI[a]	98	0	0
8		4d	LiI[a]	55	0	0

[a] Enal/Bu$_2$SnIH/LiI = 1.5:2:2 mmol, THF 4 mL.

aluminum tris(2,6-diphenylphenoxide) (ATPH) as formyl protectors.[17] Our new tin reagent allowed the 1,4-reduction of α,β-unsaturated aldehydes under mild and neutral conditions and did not require the assistance of transition metal catalysts.

Table 2 shows the results of the reduction of various unsaturated aldehydes by the complex **I** in THF. In the case of **4a**, the complex gave the desired product **5a** in 80% yield (entry 1),[18] while *n*-Bu$_2$SnIH alone gave a mixture of **5a**, the saturated alcohol **6a**, and the allylic alcohol **7a** (entry 2). The aldehyde **5a** and alcohol **7a** were derived from **4a** via 1,4- and 1,2-reduction, respectively. The alcohol **6a** was found to be formed from aldehyde **5a**, since excess amounts of the tin hydride complex **I** decreased the yield of **5a** with increase of the yield of **6a**, irrespective of **7a**. The use of a neutral complex of pentacoordinated tin iodide hydride, *n*-Bu$_2$SnIH·HMPA,[7a] resulted in poor selectivity (entry 3). Instead of LiI, the addition of *n*-Bu$_4$NI or NaI gave only around 40% yields of **5a** (entries 4 and 5). However, the fact that both additives (entries 4 and 5) gave higher yields than *n*-Bu$_2$SnIH alone (entry 2) may suggest the formation of the respective ate complexes.[19] As in the case of **4a**, 2,3-disubstituted aldehydes **4b**−**4d** also were reduced to the saturated aldehydes **5b**−**5d** in good to excellent selectivities (entries 6−8).

Scheme 2



In conclusion, the combination of *n*-Bu$_2$SnIH and LiI forms an ate complex which can effect the selective 1,4-reduction of α,β-unsaturated aldehydes. As in the case of epoxide reductions, we suggest that the attack of the iodine group at the β-carbon of **4** takes place prior to hydride attack, giving initially the β-iodo intermediate. The latter could not be isolated from the reaction mixture.[20] Presumably, rapid intramolecular reduction of the C−I bond by tin hydride results in formation of the saturated aldehydes **5** (Scheme 2).

Further application of this novel tin hydride complex are being investigated.

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Supporting Information Available: Experimental procedures and 15 NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] (a) Keinan, E.; Gleize, P. A. *Tetrahedron Lett.* **1982**, *23*, 477−480. (b) Sommovigo, M.; Alper, H. *Tetrahedron Lett.* **1993**, *34*, 59−62.

[15] Grushin, V. V.; Alper, H. *Organometallics* **1991**, *10*, 831−833.

[16] (a) Lipshutz, B. H.; Ung, C. S.; Sengupta, S. *Synlett* **1989**, 64−65. (b) Brestensky, D. M.; Stryker, J. M. *Tetrahedron Lett.* **1989**, *30*, 5677−5680.

[17] Saito, S.; Yamamoto, H. *J. Org. Chem.* **1996**, *61*, 2928−2929.

[18] To a THF solution of the tin ate complex **I** (1.5 mmol) prepared according to ref 8 was added *n*-hexenal (**4a**) (2 mmol), and the mixutre was stirred at room temperature for 15 min. After quenching with MeOH (5 mL), volatiles were removed under reduced pressure. The residue was subjected to silica gel column chlomatgraphy, eluting with hexanes−EtOAc (9:1) to give the products **5a**. Further purification was performed by silica gel TLC eluting with hexanes−EtOAc (9:1).

[19] In the case of the combination of *n*-Bu$_2$SnIH (1 mmol) and NaI (1 mmol), which did not result in a homogeneous solution, the ^{119}Sn NMR spectrum also shows the upfield shifts, $\delta(^{119}\mathrm{Sn}) = -136.0$ ppm and increases in the coupling constant, $^1J(^{119}\mathrm{Sn}-^1\mathrm{H}) = 2218$ Hz. This system is not a clear solution as compared with the case of LiI. The smaller increase than the case of LiI may indicate a little formation of the ate complex Na$^+$[Bu$_2$SnI$_2$H]$^-$.

[20] It seems that the direct hydride attack on the β-carbon of **4** is excluded because of its poor hydridic character. In fact, the reduction of cyclopropyl methyl ketone with Li$^+$[*n*-Bu$_2$SnI$_2$H]$^-$ furnished 1-cyclopropylethanol in only 13% yield at room temperature for 2 days (80% of the ketone was recovered), whereas *n*-Bu$_3$SnH·*n*-Bu$_4$NF, which bears a higher hydride character, gave the 1-cyclopropylethanol in 78% yield at room temperature for 4 h; see: Shibata, I.; Yoshida, T.; Baba, A.; Matsuda, H. *Chem. Lett.* **1991**, 307−310. We consider that the combination of *n*-Bu$_3$SnH·*n*-Bu$_4$NF also forms a pentacoordinated ate complex, although its spectra evidence is not obtained; see ref 7a. In *n*-Bu$_4$N$^+$[*n*-Bu$_3$SnFH]$^-$ complex, it is assumed that the Sn−H bond occupies the axial position, increasing the hydridic character.