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(Trimethylstannyl)- and (Tributylstannyllithium): Solution Structure in Ether, THF, and HMPA

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Summary: (Tributylstannyl)- and (trimethylstannyl)-lithium are momomeric in ether and THF solution; coordination between Sn and Li is indicated by the observation of large Li–Sn couplings. The addition of HMPA in ether produces an unusual dimeric structure, $(Bu_3SnLi)_2(HMPA)_3$, in which each tin is coordinated by one lithium and the two lithiums are bridged by three molecules of HMPA. In both ether and THF, more than 2 equiv of HMPA produces separated ion pairs.

(Trialkylstannyl)lithium reagents are easily prepared and show a number of useful and interesting reactions.[2] Their extraordinary nucleophilicity makes them valuable reagents for introducing trialkylstannyl groups into molecules.[2,3] We report here NMR studies of the solution structure of (trimethylstannyl)- and (tributylstannyl)-lithium. Previous NMR studies have shown that (triorganostannyl)lithiums form separated ion pairs in polar solvents,[4] that (trimethylstannyl)lithium and hexamethyldistannane are in rapid dynamic equilibium,[5] and that (triphenylstannyl)lithium[6] is monomeric in benzene with a large ^7Li–^{119}Sn coupling (412 Hz). NMR studies of (triorganosilyl)lithiums in THF[4,7] and X-ray crystal studies of (triphenylstannyl)-[6] and (triphenylplumbyl)lithium[8] have shown that these also have monomeric structures.

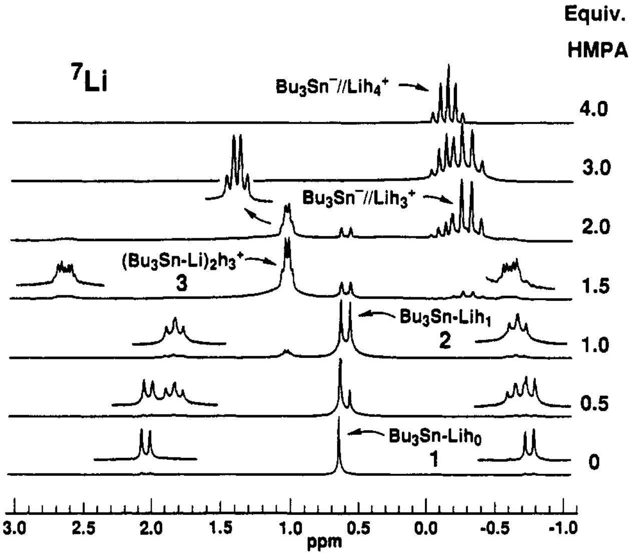

Figure 1. ^7Li NMR spectra of an HMPA titration of (tributylstannyl)lithium in ether at −124 °C. Insets show ^{117}Sn and ^{119}Sn satellites; h = HMPA.

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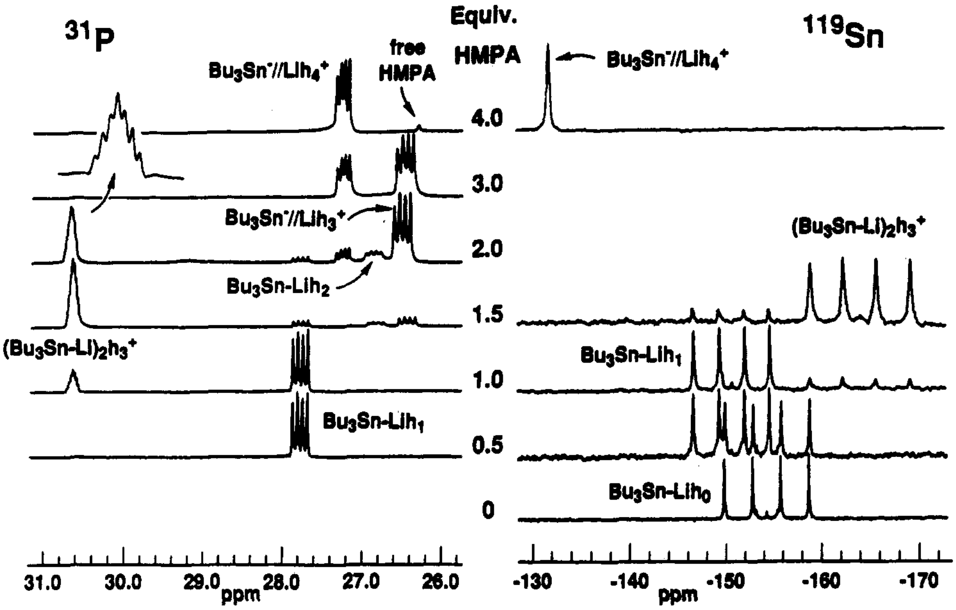
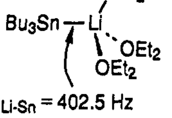


Figure 2. ^{31}P and ^{119}Sn NMR of HMPA titration of (tributylstannyl)lithium in ether at −119 °C (h = HMPA).

The dioxane complex of (tris(2-furyl)stannyl)lithium forms a dimeric triple-ion structure with lithium coordinated only to oxygen.[9]

Ether. (Tributylstannyl)lithium in ether (1) at low temperature shows Li–Sn coupling (J_{LiSn} = 402.5 Hz) in both the ^7Li and ^{119}Sn NMR spectra (Figures 1 and 2). In addition to the 1:1:1:1 quartet from coupling of ^{119}Sn to ^7Li, the 1:1:1 triplet of natural-abundance ^6Li is clearly visible in the ^{119}Sn spectra. The expected ^{117}Sn and ^{119}Sn satellites are well-resolved in the ^7Li spectra.[10] Thus, to the limits of detection by NMR spectroscopy, (tributylstannyl)lithium is monomeric in ether.



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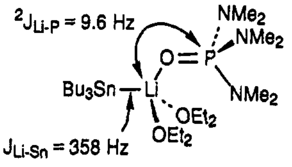

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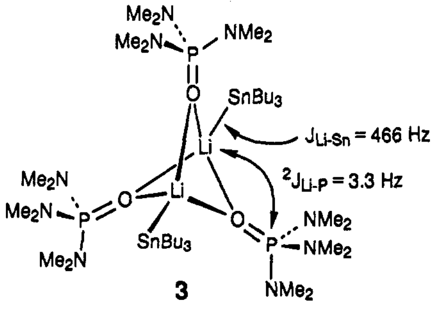

3

Addition of HMPA[1] to 1 produces first a mono-HMPA complex (2) with well-resolved ^7Li–^{119}Sn (J_{LiSn} = 358 Hz) and Li–P couplings, which describe the species $Bu_3SnLi(HMPA)$. The tin satellites in Figure 1 are especially useful here, allowing the observation of both monomeric species (1 and 2) which are superimposed in the central peak. A new species (3) appears at 1 equiv of HMPA, becoming the principal component at 1.5 equiv and declining thereafter. This species has a 1:3:3:1 quartet in the ^7Li spectrum at 1.02 ppm[10] and a 1:2:3:4:3:2:1 septet at 30.60 ppm in the ^{31}P spectrum,[10] as well as a 1:1:1:1 quartet at −163.9 ppm (J_{LiSn} = 466 Hz) in the ^{119}Sn NMR spectrum. These couplings reveal a Sn bonded to one Li, a Li bonded to one Sn and three HMPA's, and HMPA bonded to two Li atoms. They uniquely define $(Bu_3SnLi)_2(HMPA)_3$ (3), with two lithiums bridged by three HMPA's. Thus, the extraordinary coordination ability of HMPA has resulted in conversion of a monomeric species to a dimer,[11] in which all solvent molecules have probably been displaced from the lithium. This unusual dimer results from lithiums sharing a limited number of HMPA ligands, rather than the usual phenomenon of two lithiums sharing an anionic center and vice versa. Possible ^6Li–^7Li coupling in the dimer was not observed in the natural-abundance ^6Li NMR spectrum. The Sn–Li coupling constant for 3 is the largest reported coupling to lithium.[6] Snaith and co-workers have characterized a structurally analogous lithium bromide–HMPA complex $(LiBr)_2(HMPA)_3$, by single-crystal X-ray crystallography and NMR in toluene solution.[14]

Past 1.5 equiv of HMPA the signals for 2 and 3 decline, to be replaced by species which show the characteristic spectral properties of the separated ions $Bu_3Sn^-//Li(HMPA)_3^+$ and $Bu_3Sn^-//Li(HMPA)_4^+$.[1a]

The spectroscopic properties of (trimethylstannyl)lithium in ether and ether/HMPA are almost identical with those of 1, although the low solubility of $(Me_3Sn)_2(HMPA)_3$ in ether has not permitted us to resolve the Li–P coupling in the ^{31}P NMR spectra. We have also

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[10] Lithium NMR spectra were referenced to external 0.3 M LiCl in methanol and ^{31}P to external PPh_3 in THF (6.0 ppm).

[11] An increase in average aggregation on addition of HMPA has also been observed for lithium phenoxides in THF.[12] This behavior is not well-understood but does not appear to be related to the sharing of HMPA ligands as in the present case. Lithium amides in THF show little change in aggregation on addition of HMPA.[13]

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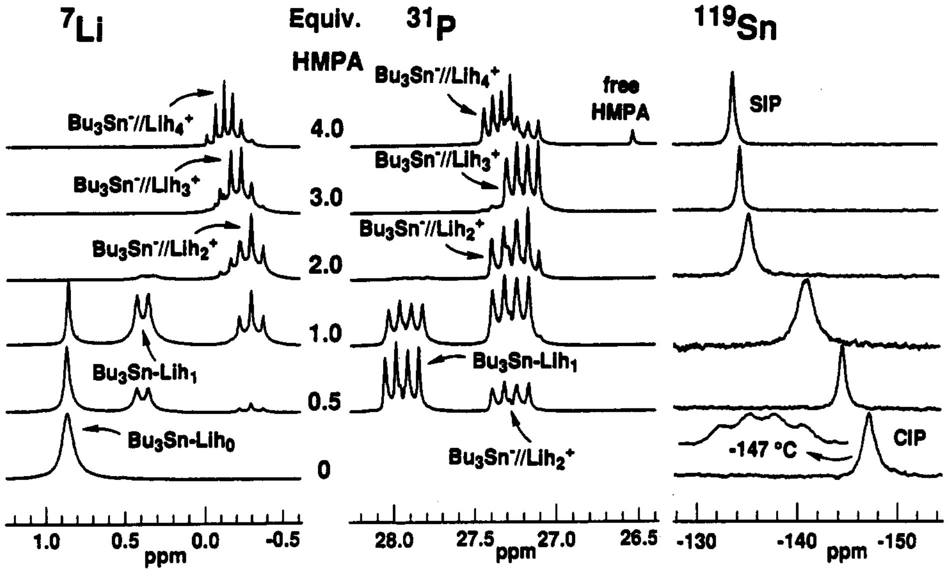
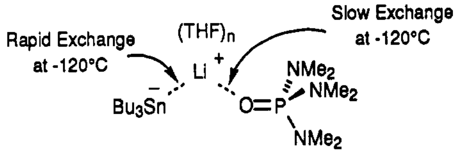


Figure 3. ^{7}Li, ^{31}P, and ^{119}Sn NMR spectra of an HMPA titration of (tributylstannyl)lithium in 5/3/2 Me_2O/Et_2O/THF at −132 °C.

examined several other lithium reagents and found that PhLi, PhSLi, and PhSeLi appear to form similar $(RLi)_2(HMPA)_3$ species in ether/HMPA. These systems show either limited solubility in ether or unresolved coupling and thus could not be as fully characterized as **3**. In each case a downfield signal near 31 ppm in the ^{31}P NMR spectrum with a characteristic triangular shape and narrow line width suggests tris-HMPA dimer structures.

Tetrahydrofuran. The HMPA titration of Bu_3SnLi in THF between 0 and 1 equiv of HMPA (Figure 3) produces the spectral fingerprint of a weakly bound contact ion pair. Such a contact ion pair is indicated by a broad singlet in the ^{7}Li NMR at 0.87 ppm,[10] a value well downfield of the position usually seen for separated $R^-//Li(THF)_4^+$ (−0.3 to −0.8 ppm).[1a–c] The ^{119}Sn NMR at −132 °C shows a broad singlet due to residual Li–Sn coupling, which can be resolved when the solution is cooled to −147 °C (J_{LiSn} = 363 Hz). With the addition of up to 1 equiv of HMPA distinct signals are observed in the ^{7}Li and ^{31}P NMR for both the one-HMPA contact ion pair (d, J_{LiP} = 10.8 Hz) and for the two-HMPA separated ion pair (t, J_{LiP} = 10.0 Hz). The chemical shift of the mono-HMPA species is particularly temperature sensitive; this, together with the fact that only an average signal is seen in the ^{119}Sn NMR, indicates that a rapid equilibrium between CIP and SIP ($Bu_3Sn{-}Lih_1 \rightleftharpoons Bu_3Sn^-//Lih_1^+$) may be operative. A rapid exchange (Figure 3) of the Bu_3Sn^- contact anion with the separated anion is verified,[1b] under conditions in which ligand exchange of HMPA is slow (i.e. Li–P coupling still observed). The tributylstannyl anion in THF, therefore, is a weak ligand for lithium since the addition of only 2 equiv of HMPA converts nearly all the contact Bu_3SnLi to separated $Bu_3Sn^-//Lih_2^+$. Except for slightly easier ion separation, Me_3SnLi showed nearly identical ion pair behavior in THF.



The formation of substantial amounts of dimer **3** during the HMPA titration of **1** in diethyl ether shows that even a shared HMPA is superior to ether as a ligand for lithium. On the other hand, the absence of any detectable amounts of **3** in THF reflects its superior solvating ability. The ease of ion separation which we observed for (trialkylstannyl)lithium reagents in THF indicates weak coordination between Sn and Li, in accord with earlier studies,[4] and provides a rationale for their characteristic high nucleophilicity.[1d,3]

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Supplementary Material Available: A table giving NMR data (δ and J_{LiX}) for (tributylstannyl)lithium, text giving a general procedure for the HMPA titration of lithium reagents (including Bu_3SnLi and Me_3SnLi), and figures showing a variable-temperature ^{7}Li and ^{31}P NMR study of 0.17 M (tributylstannyl)lithium in ether at 2.0 equiv of HMPA and the ^{7}Li, ^{31}P, and ^{119}Sn NMR spectra of an HMPA titration of (trimethylstannyl)lithium in 3/2 THF/ether (4 pages). Ordering information is given on any current masthead page.

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