

Lithium pentaalkyl/aryl stannate complexes as intermediates in the lithium-tin exchange reaction

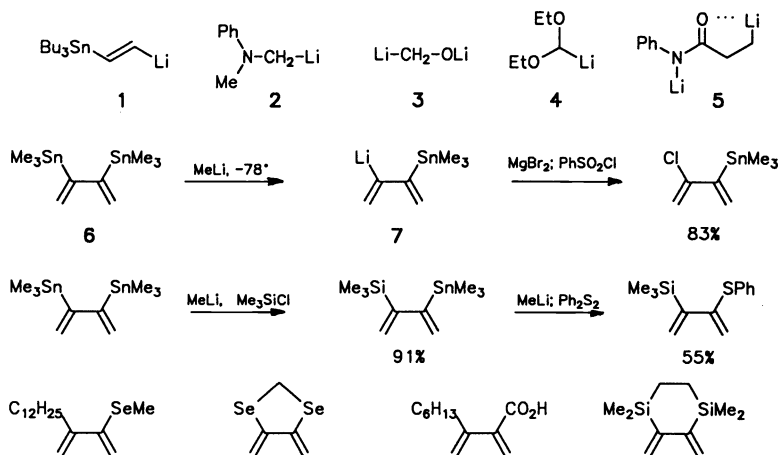
Hans J. Reich and Nancy H. Phillips

McElvain Laboratories of Organic Chemistry, Department of Chemistry,
 University of Wisconsin, Madison, Wisconsin 53706

Abstract - The lithium-tin exchange, a metathesis reaction used for the preparation of organolithium reagents, proceeds by way of intermediate pentorgano "ate" complexes. Under suitable conditions these complexes can be observed spectroscopically. The formation constants of the complexes are dramatically increased by polar coordinating solvents such as THF and HMPA. The "ate" complexes have trigonal bipyramidal structures, and undergo rapid pseudorotation even at very low temperatures.

INTRODUCTION

The lithium-tin exchange reaction is one of the premier methods for the preparation of organolithium reagents in situations where other less expensive methods such as metallation or the reduction of halides are not selective or mild enough to be effective (ref. 1,2,3). Aryl, vinyl (1, ref. 1c,2a), and several kinds of functionalized alkyl lithium reagents such as α -amino (2, ref. 2b), α -alkoxy (3, 4, ref. 2c) and those bearing electrophilic substituents (5, ref. 2d) are frequently made this way. The bistrimethylstannyl butadiene 6 can be converted to either the monolithium reagent 7 or a dilithium reagent (ref. 1c). Derivatization of 7 gives a new trimethylstannylbutadiene, which can be exchanged a second time to provide efficient syntheses of a series of 2,3-disubstituted butadienes.



Examples of Lithium Reagents Prepared Using Li/Sn Exchange

Although some kinetic work has been done (ref. 3), the mechanism of this interesting transformation has not been established securely, but has generally been assumed to proceed through a four-centered transition state. An alternative mechanism involving intermediate "ate" complexes has been proposed (ref. 1a, 1b, 2c, 4).



The formation of pentacoordinate tin compounds is a common occurrence when there are several electronegative groups bonded to tin. A small number of pentacoordinate tin compounds with four alkyl and one electronegative group are known (ref. 5), but none with five organic groups have been characterized prior to our work. The earliest evidence for a pentaorganostannate that we have been able to find is a 1954 report by Beermann and Hartmann (ref. 6) which describes the reaction of triphenyltin chloride with sodium acetylidyde in liquid ammonia. The first-formed insoluble triphenylethynyltin dissolved on addition of a second equivalent of the acetylidyde, a process ascribed (without direct structural evidence) to the formation of sodium triphenyldiethynylstannate.

Recent spectroscopic and chemical studies of α -alkoxyalkyltin systems directed at the question of stable tin "ate" complexes have given negative or indefinite results (ref. 2c).

We have experimentally addressed the question of whether such previously undetected intermediates may actually be present in finite concentrations and offer here convincing kinetic and spectroscopic evidence that this is the case.

KINETIC EVIDENCE FOR LITHIUM PENTAALKYL(ARYL)STANNATE INTERMEDIATES

The reactivity of solutions of phenyllithium in THF is practically unaffected by the presence of varying concentrations of tetramethyltin and phenyltrimethyltin (Fig. 1). However, when higher phenyl analogues were used in the same experiment, there were pronounced effects on the reactivity which we have ascribed to the formation of pentaorganotin "ate" complexes $\underline{\delta}$ (Eq. 1). Direct spectroscopic studies of solutions containing methylithium or phenyllithium and various tin compounds have provided more direct evidence for such species. Some of our results are detailed below.

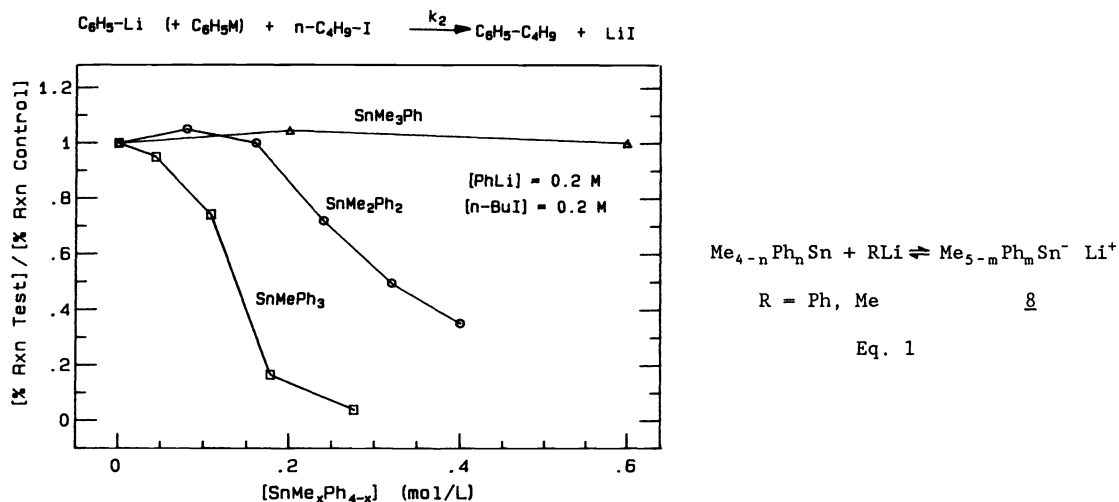


Fig. 1. Rates of reaction of phenyllithium with n-butyl iodide in the presence of various tetraorganotins.

SPECTROSCOPIC CHARACTERIZATION OF LITHIUM PENTAALKYL(ARYL)STANNATE COMPLEXES

NMR spectra of solutions of tetramethyltin and methylithium in THF show only these two species. However, when HMPA was added (Fig. 2), a new species appeared, which we have identified as lithium pentamethylstannate. The ^{119}Sn NMR signal at -277 ppm is in a region characteristic of penta and hexacoordinate tin compounds (ref. 7), and its multiplet structure is consistent only with the calculated line intensities for a tin split equally by 15 protons. The stabilizing effect of HMPA on the "ate" complex compared to its constituents can be ascribed to the greater solvation demands of the "ate" complex lithium cation, versus the more covalent methylithium. This effect is quite general, and is also observed for iodine, tellurium, antimony and bismuth "ate" complexes (ref. 1e).

Solutions of tetramethyltin and methylithium in THF/HMPA show dynamic NMR behavior in the ^1H , ^{13}C and ^{119}Sn spectra. Figure 3 shows a series of ^1H spectra at temperatures between -78° and 5°C which serve to demonstrate that the three species (MeLi , Me_4Sn and $\text{Li}^+\text{Me}_5\text{Sn}^-$) are interconverted by an exchange process.

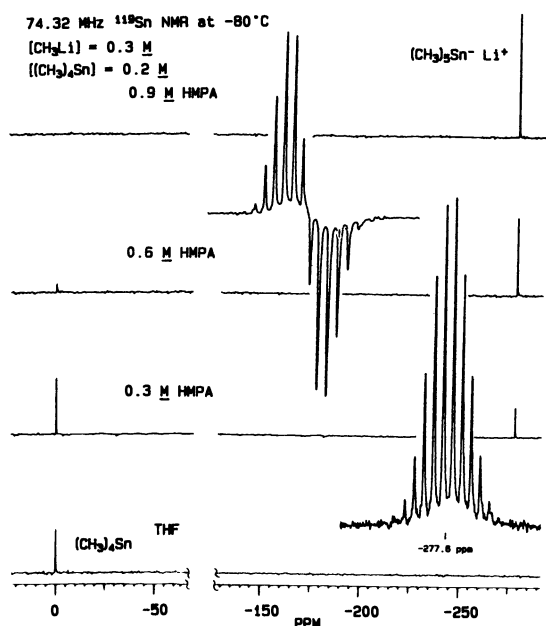


Figure 2. ^{119}Sn NMR spectra of MeLi and Me_4Sn with 0, 1, 2, and 3 equiv of HMPA per MeLi. The inset shows ^1H coupled expansions of the signal at -277 ppm using a normal and INEPT pulse sequence. $^2J_{\text{Sn-H}}$ is 39 Hz.

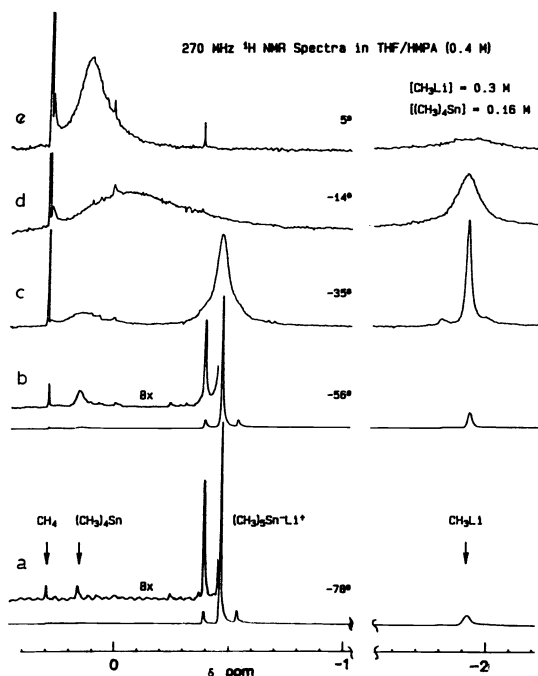


Figure 3. Variable temperature ^1H NMR spectra of a solution of MeLi (0.3 M), $(\text{Me}_3)_4\text{Sn}$ (0.16 M) and HMPA (0.4 M) in THF. The insets of the first two spectra (a and b) are 8x vertical expansions.

Solutions of mixed phenyl methyl complexes were analogously prepared by the addition of the organostannane to methyl- or phenyllithium in THF/HMPA. All of the mixed complexes disproportionated easily; pure solutions were obtained only when all operations were carried out at low temperature. Again, the ^{119}Sn and ^{13}C NMR signal multiplicities and intensities were fully consistent with the structures expected from 1:1 complexation of organolithium reagent and organostannane.

Tetragonal pyramid geometries are occasionally observed for pentacoordinate tin compounds (ref. 8), but trigonal bipyramidal structures are far more common (ref. 9). We believe that our organotin ate complexes have trigonal bipyramidal structures. Each compound showed only a single set of phenyl and methyl resonances in the ^{13}C spectra at temperatures down to -80°C , but at lower temperatures some broadening was observed for $\text{Li}^+\text{Ph}_3\text{Me}_2\text{Sn}^-$ (Fig. 4) indicating

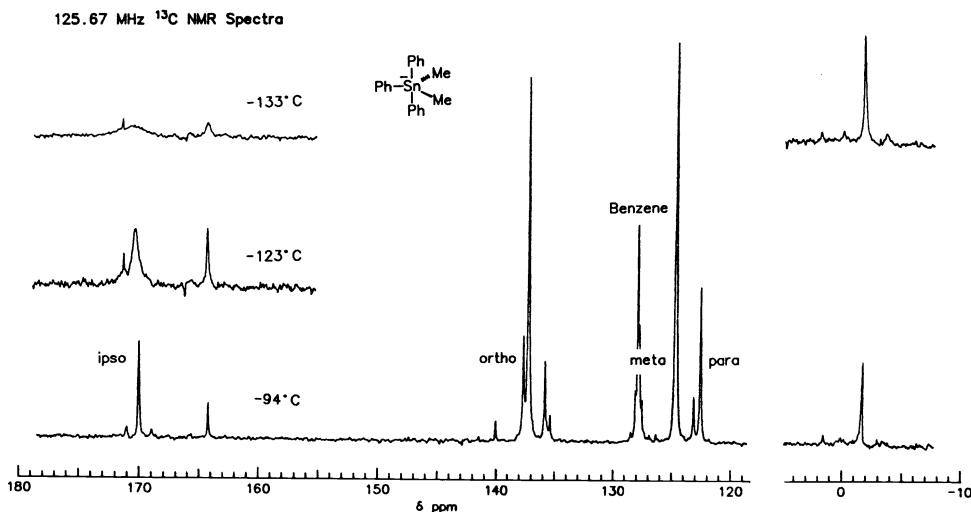


Figure 4. Variable Temperature ^{13}C NMR spectra of $\text{Li}^+\text{Ph}_3\text{Me}_2\text{Sn}^-$.

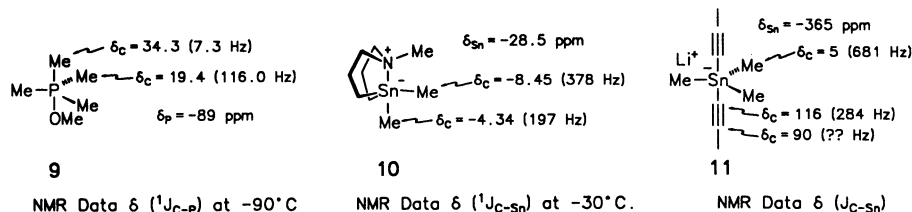
that pseudorotation was slowing on the NMR time scale (ref. 10). Dimethyl ether was added to the solutions to lower the freezing point, but decoalescence was not observed even at -133°C . The small peak at 164.5 ppm is the ipso-C signal of $\text{Li}^+\text{Ph}_4\text{MeSn}^-$, which apparently has a lower barrier to pseudorotation.

Table 1 presents the NMR parameters for the complete series of methyl phenyl "ate" complexes. The $^1\text{J}_{\text{CSn}}$ values and ipso phenyl chemical shifts can best be interpreted in terms of trigonal bipyramidal structures, in which the phenyl groups are apical (ref. 11). Values of $^1\text{J}_{\text{CSn}}$ and δ were calculated by assigning optimal J and δ values to apical and equatorial groups and averaging the appropriate number of each type of ligand. This simple model provided predictions which agreed remarkably well with the experimental values of $^1\text{J}_{\text{CSn}}$ for methyl and ipso phenyl as well as the ^{13}C chemical shifts of the ipso, ortho and para carbons. Table 1 lists some of these experimental parameters, along with their calculated values. A tetragonal pyramid model did not fit the observed data.

Table 1. NMR Chemical Shifts (ppm) and Coupling Constants (Hz) for $\text{Li}^+\text{R}_5\text{Sn}^-$.

δ_{Sn}	-277	-291	-311	-300	-292	-303	-29.7
$\delta_{\text{C}}(\text{Me})$	6.3	3.3	-1.0	-0.7	-2.3	-	10.4
$^1\text{J}_{\text{Sn-Me}}$	258	375	450	450	436	-	351
Calc: $\text{J}_{\text{ap}} = -17$, $\text{J}_{\text{eq}} = 441$	258	327	441	441	441	-	
$\delta_{\text{C}}(\text{p-Ph})$	-	122.1	122.5	123.2	124.0	124.2	128.0
Calc: $\delta_{\text{ap}} = 122.3$, $\delta_{\text{eq}} = 125.4$		122.3	122.3	123.3	123.9	124.2	
$\delta_{\text{C}}(\text{i-Ph})$	-	182.2	180.0	170.6	165	161.9	141.6
Calc: $\delta_{\text{ap}} = 180$, $\delta_{\text{eq}} = 151$		180	180	170	163	161	
$^1\text{J}_{\text{Sn-Ph}}$	-	80	60	250	376	427	473
Calc: $^1\text{J}_{\text{ap}} = 80$, $\text{J}_{\text{eq}} = 640$		80	80	267	360	416	

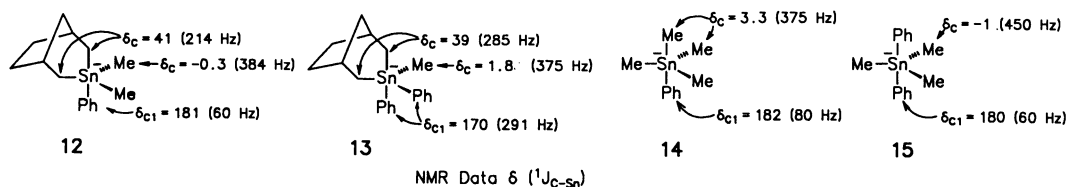
The calculated $^1\text{J}_{\text{CSn}}$ values for both methyl and phenyl carbons were as expected: small coupling to apical (low s character) and large coupling to equatorial carbons (ref. 12). The phenyl ipso carbon shifts were also interesting: the equatorial shifts were unexceptional (150 ppm, cf. 142 ppm for trimethylphenyltin), while the apical phenyls were strongly downfield (180 ppm, close to the value for phenyllithium (ref. 13)). This effect, which is also observed for a number of other "ate" complexes involving iodine and tellurium as central atoms, is probably a consequence of the weak hypervalent apical bonds and the development of extra negative charge on the apical ligands, as predicted by the molecular orbital theory of trigonal bipyramidal structures (ref. 14). Para carbons are especially diagnostic of charge delocalization. We calculate a δ_{para} of 122.1 for apical and 125.6 ppm for equatorial phenyl (versus 121 and 128 for PhLi and PhSnMe_3). The pattern of coupling constants and chemical shifts observed here is also seen in phosphorane 9 (ref. 12) and to some extent in the stannatane 10 (ref. 5b).



We have also prepared a family of methyl/phenyl bicyclic "ate" complexes. The NMR parameters support a trigonal bipyramidal structure, but they require that the ring be equatorial-apical, even though this means placing a phenyl equatorial instead of in the preferred apical position, apparently a consequence of the same ring strain effects seen in phosphoranes (ref. 15). Thus the ring CH_2 signals of 12 and 13 are identical, but the phenyl parameters change dramatically. This is in contrast to the acyclic analogues 14 and 15, in which the phenyl parameters are almost identical, but the methyl parameters change.

The exchange rates of methyl and phenyl groups in the "ate" complexes discussed above were slow on the NMR time scale at temperatures below -70°C (i.e. separate sharp signals were observed for R_4Sn and R_5SnLi). This was not the case for the trimethyldipropynylstannate complex 11 in which the corresponding signals were averaged at low temperature while there

was excess trimethylpropynyltin present. However, when excess propynyllithium was present, separate signals for the lithium reagent and "ate" complex were observed (Fig. 5). This is not explicable by a simple exchange mechanism, but requires the intervention of an



organolithium species kinetically distinct from the observed one. The most economical explanation we have been able to devise is that the actual exchanging species is a lower aggregate (or perhaps a lesser solvated form) of the lithium reagent than the one being detected, and that the rate of exchange among the lithium aggregates is slower than exchange among the tin species. Thus the rate determining step for exchange of excess lithium reagent with "ate" complex is aggregate dissociation, whereas the rate determining step for exchange of the "ate" complex with excess R_4Sn is the rate of its reaction with the lower lithium aggregate.

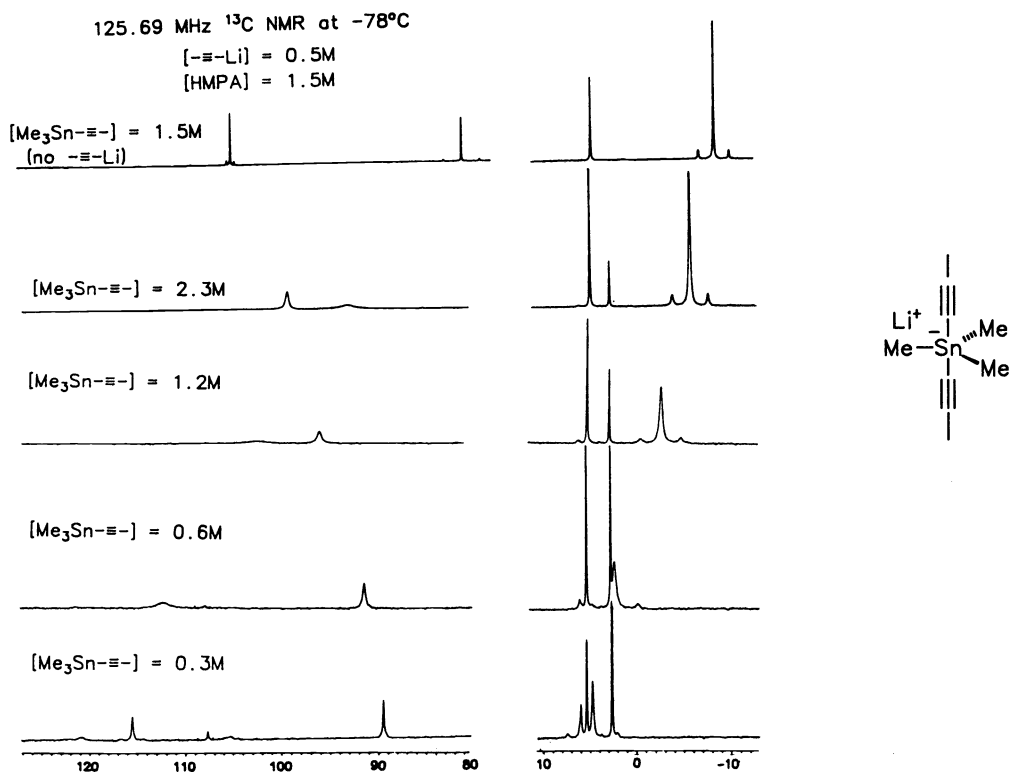


Figure 5. ^{13}C NMR spectra of trimethylpropynyltin and reaction products of it with propynyllithium. The small signals at 105 and 121 ppm in the bottom spectrum are those of propynyllithium, those at 89.5 and 115.7 ppm of lithium dipropynyltrimethylstannate **11**. The constant signal at 2.5 ppm is the methyl of propyne.

Equilibrium constants between the various "ate" complexes and their dissociated species have not been measured accurately, but some interesting qualitative observations have been made. The relative concentration of "ate" complex increases as the number of phenyl ligands is increased: the relative concentration of higher phenyl homologs is substantial even in pure THF solution, but the lower phenyl homologs need HMPA to form (ref. 1a,1b). The latter do not form in appreciable amounts in THF, but instead disproportionate to higher phenyl "ate" complexes.

Our studies provide solid evidence for the existence of hypervalent pentaorgano tin "ate" complexes and implicate them as intermediates in the Li/Sn exchange. We cannot, as yet answer the question of whether these complexes or the lithium reagents in equilibrium with them are the actual reactive species (ref. 2c), but both qualitative and quantitative reactivity tests indicate that the "ate" complexes are substantially less reactive than

lithium reagents toward electrophiles such as trimethylsilyl chloride, n-butyl iodide, and dimethyl disulfide.

Acknowledgements We would like to thank the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation and PPG Industries for support of our work. Dr. Bruce Adams provided valuable assistance in the design and execution of NMR experiments.

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