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The preparation and variable temperature ^{1}H NMR characterization of 1-(tri-*n*-butylstannyl)indene, 1-(Bu_3Sn)C_9H_7†

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Abstract—The synthesis of 1-(tri-*n*-butylstannyl)indene, **1**, was carried out by the reacting lithium indenide with tributylstannyl chloride. The pale yellow product was collected by distillation in 65% yield, and the procedure is scalable to large quantities. Examination of the room-temperature ^{1}H NMR spectrum of **1** revealed a fluxional process in which the tributylstannyl group was rapidly interchanging between the 1 and 3 positions on indene. A variable-temperature ^{1}H NMR study was performed on **1** from -60°C to $+40$°C and the free energy of activation for the 1,3-interchange was calculated as 15.4 kcal mol^{-1} at 60°C, using the Eyring equation. This result is compared to previous studies of the 1,3 migrations of trimethylsilyl and trimethylstannyl groups on indene. © 1997 Elsevier Science Ltd

Keywords: indene; NMR; fluxional; activation; tributylstannylindene.

Organotin reagents have been shown to be valuable cyclopentadienyl transfer reagents by Abel and Moorhouse who used tin reagents to transfer cyclopentadienyl, indenyl, and fluorenyl to a wide range of metal carbonyls [1]. Green *et al.* used Bu_3SnCp to transfer Cp to niobium(V) and tantalum(V) without reducing the metal center [2], and Teuben *et al.* independently accomplished the same task using Me_3SnCp or $MgCp_2$ [3]. Finally, Sanner *et al.* used *n*-Bu_3SnCp^* to transfer Cp* to $TaCl_5$ without reduction of the metal center to give Cp^*TaCl_4 [4].

New synthetic routes to transition metal Cp complexes using organosilanes were discovered by Clark *et al.* who were able to use Me_3SiCp to prepare $CpMX_3$ complexes of titanium, niobium, and tantalum halides (M = Ti, X = Cl, Br, I; M = Nb and Ta, X = Cl) [5]. Similarly, Llinás *et al.* used Me_3SiCp^* to transfer Cp* to the Group 4 metal halides to give (η^5-C_5Me_5)MX_3 (M = Ti, X = Cl, Br, I; M = Zr and Hf, X = Cl) [6]. These new synthetic routes were predominantly one step, and they had the added advantage of allowing easy isolation of the product by loss of volatile and/or soluble Me_3SiCl or Me_3SnCl.

Reaction of trialkyltin and trialkylsilicon halides with Group 1 or Group 2 salts of cyclopentadiene has been the most widely used method for preparing R_3ECp' (R_3E = trialkyltin or trialkylsilicon) [1–4]. Another method has involved reacting $R_3SnNR'_2$ with the acidic proton of cyclopentadiene to give the trialkyltin cyclopentadienyl product by displacing the free amine [7,8].

Some organotin compounds have been shown to be fluxional. For example, Fritz and Krieter have demonstrated that 1-trimethylsilylcyclopentadiene has a temperature-dependent ^{1}H NMR spectrum [9]. Their data are consistent with a series of 1,2 and/or 1,3-trimethylsilyl shifts at such a rate that proton equivalence results. Characterization of the fluxional behavior by variable-temperature ^{1}H NMR studies has been extended to the analogous Group 14 indenyl compounds [10–15].

To date, all NMR studies of trialkylsilyl- or trialkylstannylindene compounds have been performed on compounds containing tri*methyl*tin or tri*methyl*silicon groups. The synthesis of tri-*n*-butylstannylindene appears in a couple of footnotes and in

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† This paper is dedicated to the memory of Professor Paul Harris.

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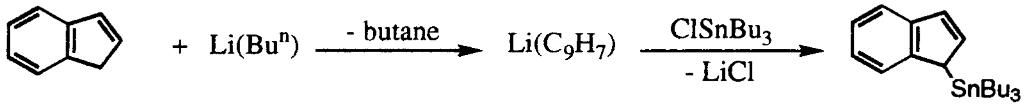
the patent literature without details of its preparation, characterization, or reactivity [16–20].

We wish to report the synthesis and variable-temperature ^{1}H NMR study of 1-(tri-*n*-butyl) stannylindene.

RESULTS AND DISCUSSION

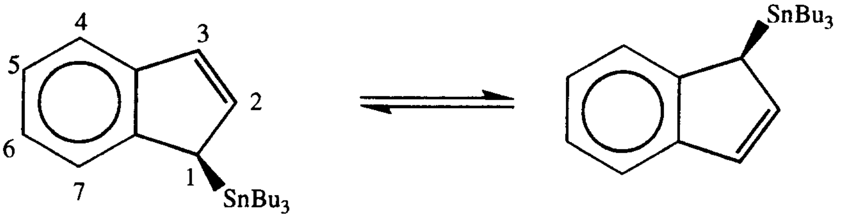
The reaction of *n*-butyllithium with an equimolar amount of indene in pentane produces lithium indenide, which when treated with equimolar amounts of tri-*n*-butylstannylchloride in pentane produces tri-*n*-butylstannylindene in good yield (Eq. 1). Tri-*n*-butylstannylindene, is a distillable pale-yellow liquid which is slightly light sensitive.



(1)

^{1}*H NMR spectral data for tri-*n*-butylstannylindene*

At room temperature the tri-*n*-butylstannyl group is apparently migrating rapidly between the 1- and 3-positions (Eq. 2), since the 1-proton appears as a very broad signal centered at δ 4.24 and the 3-proton is unobservable at this temperature. This fluxional behavior was studied through the use of variable temperature ^{1}H NMR, in toluene-d_8.



(2)

The stacked spectra for 1-(tri-*n*-butylstannyl)indene (Fig. 1) indicate the fluxional behavior by showing the growth of the 1- and 3-position proton peaks as the temperature is lowered from +40°C to −60°C. The butyl and indenyl ^{1}H NMR resonances at 40°C (Fig. 2) and at −60°C (Fig. 3) are compared and discussed below.

40°C spectrum

At +40°C the Bu$_3$Sn group appears to be undergoing a rapid 1,3 shift with its time-averaged position midway between carbons 1 and 3. This fluxional behavior affects the ^{1}H NMR spectrum in three ways: (1) all 3 *n*-butyl groups are equivalent and appear as a group of sharp multiplets ($\delta = 0.6$–1.6); (2) the resonances for the 1 and 3 protons on indene are broadened while the signal for the 2-proton remains a sharp triplet; (3) the six-membered ring protons (4/7 and 5/6) exhibit the expected AA′BB′ pattern.

−60°C spectrum

At −60°C the 1,3 migration of the *n*-Bu$_3$Sn group is significantly slower than the ^{1}H NMR time scale. This gives rise to a chiral (*) carbon atom at the (1) position and the loss of any time-averaged mirror plane for the molecule. In addition, rotation about the C—Sn bond appears to be slowed so that the three *n*-butyl groups are no longer equivalent. The combination of these two factors could explain the broad peaks ($\delta = 0.6$–1.6) observed for the *n*-butyl groups at low temperatures even though the remaining resonances remain narrow.

Also, at this low temperature, the resonance for the 1-proton appears as a large singlet with two small satellites. The large singlet ($\delta = 4.10$) arises from the protons at position 1 which are adjacent to NMR silent isotopes of tin (82.7% abundant). The low intensity satellites surrounding the singlet at $\delta = 4.10$ are due to the smaller number of position 1 protons that are coupled to NMR active ^{117}Sn or ^{119}Sn isotopes (16.3% abundant). The ^{119}Sn–H coupling constant in Bu$_3$SnInd, measured at −60°C, is 82 Hz. By way of comparison, Rakita *et al.* reported ^{119}Sn–H coupling constants of 91 Hz at −60°C for Me$_3$SnInd [11]. Coupling constants between tin and hydrogen are usually reported as $J(^{119}\text{Sn–H})$ values since $^nJ(^{119}\text{Sn, X})/^nJ(^{117}\text{Sn, X}) = \gamma^{119}\text{Sn}/\gamma^{117}\text{Sn} \approx 1.0$.

The absorption for the number 3 proton is also observable in the ^{1}H NMR spectrum at this temperature ($\delta = 7.25$). It is now strictly in an olefinic environment and appears as a doublet due to coupling to the number 2 proton. The resonance for the number

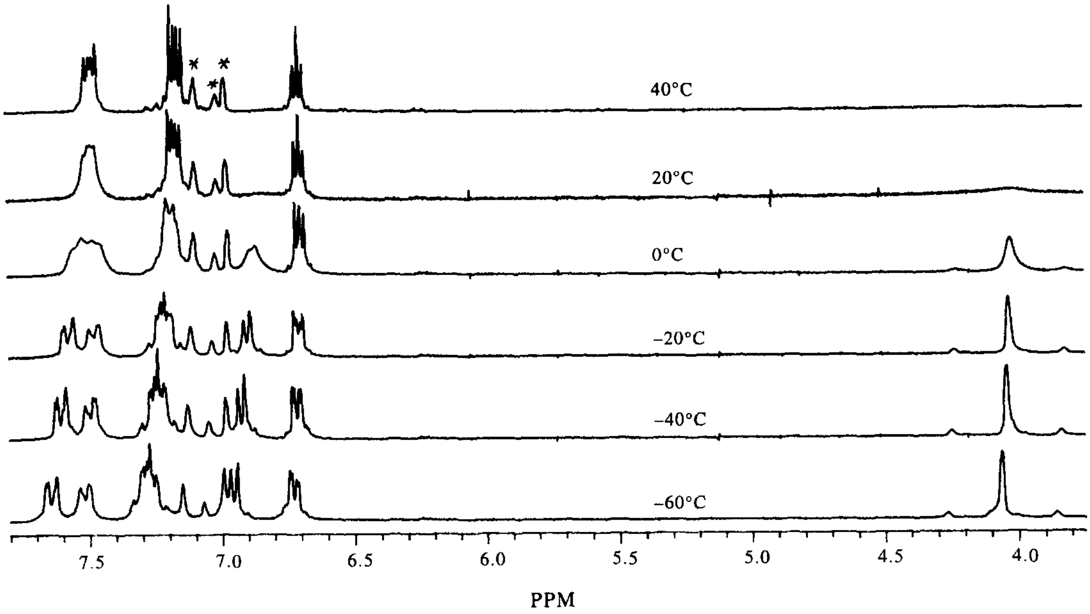


Fig. 1. 200 MHz ^{1}H NMR stacked spectra of 1-(Bu_3Sn)C_9H_7 from −60°C to 40°C showing the indenyl resonances. Peaks due to residual toluene are marked with an *.

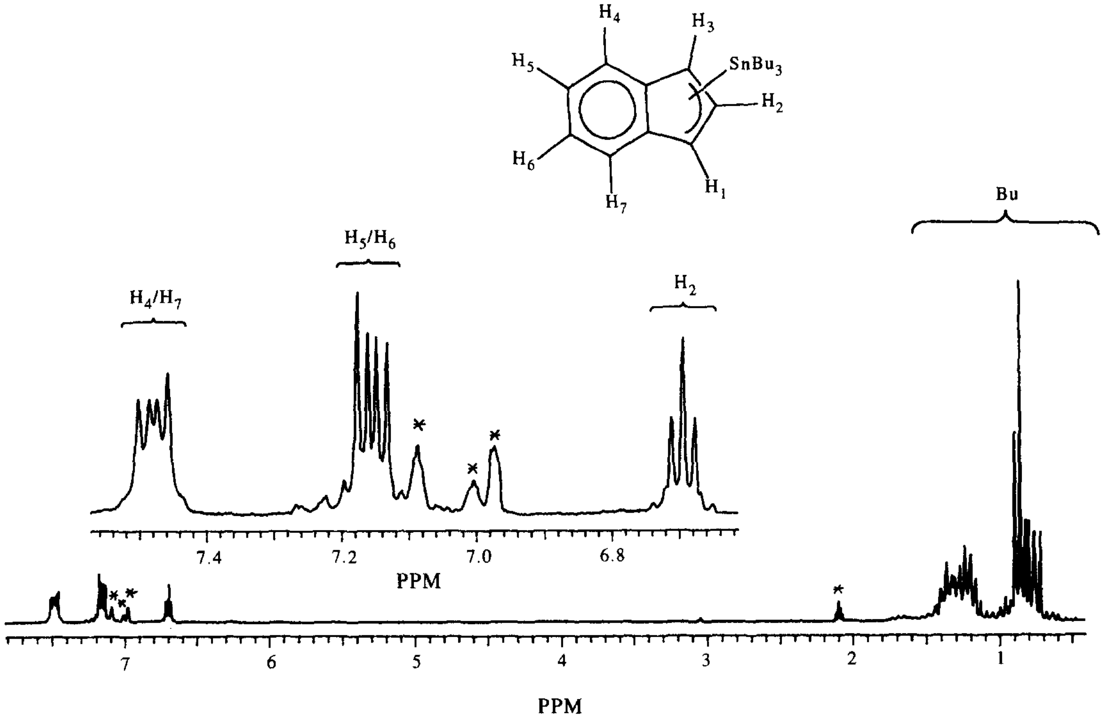


Fig. 2. 200 MHz ^{1}H NMR spectrum of 1-(Bu_3Sn)C_9H_7 at 40°C. Peaks due to residual toluene are marked with an *.

2 proton appears as a multiplet due to coupling with the 1 and 3 protons. The aromatic protons are non-equivalent at this temperature with the resonances for protons 4 and 7 appearing as doublets (δ 7.46–7.72) and the absorptions for protons 5 and 6 appearing as a complex multiplet (δ 7.20–7.40).

Other workers have reported evidence for the 1,3 migration of trimethylstannyl and trimethylsilyl

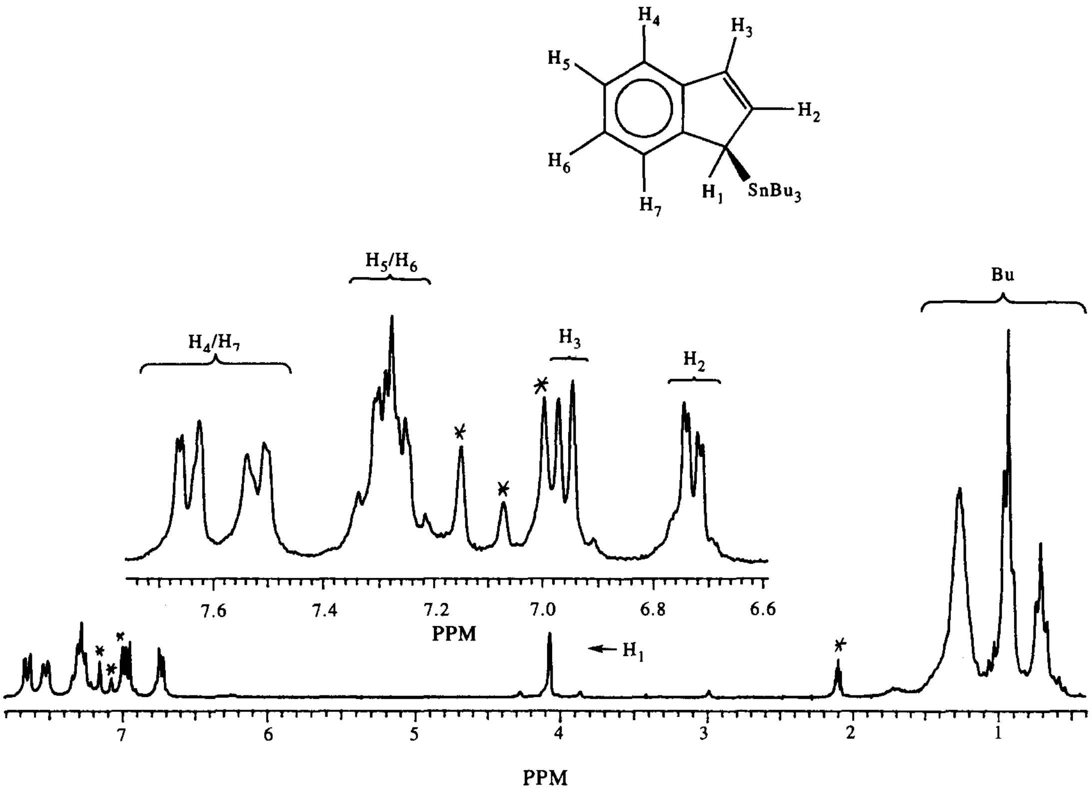


Fig. 3. 200 MHz ^{1}H NMR spectrum of 1-$(Bu_3Sn)C_9H_7$ at −60°C. Peaks due to residual toluene are marked with an *.

groups on indene. The spectral data for Me_3SnInd are consistent with intramolecular exchange *via* 1,3 trimethylstannyl shifts [11]. Similar data were observed for Me_3SiInd, although they do not begin to occur until about +180°C, so that the complete range of limiting low- to limiting high-temperature spectra were not obtained [11,12].

Trimethylsilyl- and trimethylstannylindene compounds bearing substituents at various positions on the indene ring have demonstrated similar fluxional behavior when studied by variable temperature ^{1}H NMR methods [13–15]. For example, Rakita *et al.* was able to show that the rate of metal migration could be accelerated or retarded on the positions of the methyl substituents [14].

Free energy of activation for the 1,3 *migration of the* Bu_3Sn *group in* $Bu_3Sn(C_9H_7)$

The Eyring equation, $k = (k_BT_c/h)\,e^{(-\Delta G\ddagger/RT_c)}$, was used to analyze the spectra data of tri-*n*-butylstannylindene (where $k = (\pi\Delta\nu/\sqrt{2})$) near the coalescent temperature. Using $\Delta\nu = 581$ s^{-1} and $T_c = 333$ K, the free energy of activation ($\Delta G\ddagger$) for the migration of the Bu_3Sn in 1-(tri-*n*-butylstannyl)indene was found to be 64.2 kJ mol^{-1} (15.4 kcal mol^{-1}). Instrument limitations prevented the collection of the limiting high-temperature spectrum, so our calculation by using the spectrum collected at the highest available temperature (60°C) represents a low estimate of the energy of activation for the 1,3 migration. The 60°C spectrum is not presented in Fig. 1 as it is indistinguishable from the 40°C spectrum.

A summary of the free energies of activation for representative indene compounds as calculated by line shape analysis of the variable-temperature ^{1}H NMR data using the Eyring equation is presented in Table 1. Direct comparisons of free energies of activation are only proper if the data are collected at similar temperatures. Since each fluxional compound in Table 1 has a different coalescence temperature, exact comparisons cannot be made; however, the following conclusions seem appropriate. While the free energy of

Table 1. Summary of $\Delta G\ddagger$ for fluxional R_3MInd complexes (M = Si, Sn) in kcal/mol

Compound	$\Delta G\ddagger$
Me_3Si-2-MeInd	26.5
Me_3SiInd	23.8
Me_3Si-4,7-Me_2Ind	21.8
Me_3Sn-2-MeInd	18.6
Bu_3SnInd	15.4[a]
Me_3SnInd	15.0
Me_3Sn-4,7-Me_2IInd	14.0

[a] This work.

activation is consistently higher for the silane derivatives than that for the stannane derivatives, methyl substitution on the number 2 carbon results in the highest activation energy, since that position sterically hinders the fluxional 1,3-trimethylsilyl or 1,3-trimethylstannyl migration. Substitution on the six-membered ring lowers the free energy of activation below that of the unsubstituted indenyl ring. This may in part be due to redistribution of the π-electron densities of the five-membered ring. The free energy of activation value of 15.4 kcal mol^{-1} for the 1,3 migration of the Bu_3Sn group in 1-(tri-*n*-butylstannyl)indene is lower than the corresponding value for the *trimethylsilyl* analogs, as would be expected by comparing the mean bond dissociation energy of 230 kJ/mol for C—Sn bonds to 300 kJ/mol for C—Si bonds. The $\Delta G\ddagger$ value is slightly larger than for the *trimethylstannyl* analog due to the steric effects of the larger *n*-butyl groups [21,22].

EXPERIMENTAL

All reactions and manipulations were performed under an atmosphere of argon, either using a dry box or using standard Schlenk techniques [23]. Solvents (pentane) were distilled from sodium/benzophenone and degassed immediately prior to use. Indene was purchased from Aldrich and distilled before use. Butylithium (Aldrich) was used as received. Elemental Analyses were performed by Midwest Microlabs, Indianapolis, IN. ^{1}H NMR data were obtained on a Varian Gemini 200 NMR spectrometer at 199.975 MHz and are referenced to tetramethylsilane.

*Preparation of tri-*n*-butylstannylindene*

!Caution: Butane is vigorously evolved during the reaction and it should be vented into a fume hood.

Procedure

Degassed indene (47.0 mL/0.40 moles) is added to a 1 L 3-neck round bottomed flask containing pentane (480 mL) and equipped with a N_2 inlet, a gas outlet connected to an oil bubbler, a pressure-equalizing dropping funnel, and a large magnetic stir bar. Through the pressure-equalizing funnel, *n*-butyllithium (250 mL of 1.6 M solution, 0.40 moles) is slowly added at *ca* roughly 1 drop s^{-1} while stirring at room temperature with a mineral oil bubbler to vent the butane that evolves. The solution was stirred for 12 h and, as the reaction occurred, a white precipitate of lithium indenide formed. The supernatant was removed *via* filtration through a filter cannula using #1 Whatman™ filter paper and the precipitate is washed with pentane (2 × 300 mL); the washes are neutralized with isopropanol and discarded. Pentane (400 ml) was added to the reaction flask containing the clean lithium indenide and, using a pressure equalizing dropping funnel chlorotributylstannane (110 mL, 0.41 moles) was added dropwise at 1 drop s^{-1}. The yellow–white mixture was stirred for 5 h after the addition was complete and the reaction mixture was filtered *via* a filter cannula using #1 Whatman™ filter paper. The volatile material was removed from the supernatant under vacuum (25°C, 0.10 mmHg). The remaining yellow liquid was distilled using vacuum-jacketed distillation head (0.10 mmHg, 150 mm Vigreux column). The first fraction (unreacted tributylstannylchloride) was collected at a head temperature range of 92–95°C. The second fraction (tributylstannylindene) is collected at a head temperature range of 140–142°C. Yield: 107 g, 65%, $d = 1.070$ g mL^{-1}. Anal. calcd. for $C_{21}H_{34}Sn$: C, 62.3; H, 8.46. Found: C, 62.1; H, 8.37. ^{1}H NMR (Varian Gemini 200 NMR spectrometer at 199.975 MHz and referenced to tetramethylsilane, toluene-d_8, 20°C): δ 0.97 (m, 6H), δ 1.08 (t, $J = 6.9$ Hz, 9H), δ 1.34–1.63 (m, 12H), δ 6.92 (t, $J = 3.4$ Hz, 1H), δ 7.37–7.41 (m, 2H), δ 7.62–7.78 (br, m, 2H). Tributylstannylindene is fluxional; the tributylstannyl group migrates rapidly between the 1- and 3-positions at 20°C. While the 3-proton is unobservable at this temperature, the 1-proton is a very broad peak centered at δ 4.24.

Properties

Tributylstannylindene is a clear, pale yellow liquid with a density of 1.070 g/mL. As with 1-(trimethylsilyl)indene, 1-(tributylstannyl)indene is best stored in the dark under an atmosphere of argon (or nitrogen).

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