

Article

The Use of a Tin Nucleophile for the Preparation of a Novel Sn₅ Organotin Cluster

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Um novo método para a obtenção de nucleófilos do tipo R₃Sn⁻ é aqui apresentado, em comparação com outros métodos existentes na literatura. Este novo processo, utilizando um bronze de sódio em amônia líquida, permite a redução do estanho a partir de espécies do tipo R₃SnCl de forma limpa e com alto rendimento. A partir do nucleófilo Ph₃Sn⁻ foi preparado um novo cluster organometálico de fórmula bipy.Sn(SnPh₃)₄, fortemente colorido e extremamente reativo. A natureza do cluster foi elucidada por uma combinação de espectroscopia Mössbauer e RMN de ¹¹⁹Sn.

A new method for obtaining tin nucleophiles of the type R₃Sn⁻ is presented here, in comparison with other existing methods from the literature. This new process, using a sodium bronze in liquid ammonia, allows the reduction of tin from species such as R₃SnCl in a clean way and with a high yield. From the nucleophile Ph₃Sn⁻ a new organometallic cluster was prepared, having the formula bipy.Sn(SnPh₃)₄, and being strongly colored and extremely reactive. The nature of the cluster was elucidated by a combination of ¹¹⁹Sn Mössbauer and ¹¹⁹Sn NMR spectroscopies.

Keywords: Sn₅ cluster, tin nucleophiles, organotin cluster

Introduction

Tin is remarkable in its ability to change its coordination number upon complexation, and in the variety of complexes it can form^{1,2}. The metal can be part of either an electrophilic species or a nucleophilic ligand. This work shows the metal behaving in both capacities and forming a five-atom tin cluster in which the species Ph₃Sn⁻ replaced all Cl⁻ ligands in the adduct bipy.SnCl₄. A new and more efficient method for producing R₃Sn⁻ nucleophiles has previously been briefly reported and is discussed here at length³. The combination of ¹¹⁹Sn Mössbauer and ¹¹⁹Sn NMR spectroscopy was essential for the establishment of the nature of the cluster.

Experimental

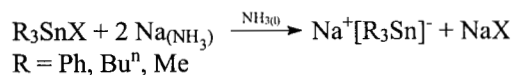
All manipulations of air-sensitive materials were performed using either standard Schlenk-line techniques un-

der pure dry N₂ or an N₂-filled glovebag. Solvents were purified by standard methods⁴. I.R. spectra were obtained from a 283 B Perkin-Elmer instrument using nujol mulls between CsI windows. The Mössbauer spectrum was obtained from a constant acceleration spectrometer moving a CaSnO₃ source at room temperature. The sample was analyzed at 85K with respect to that source, and the spectrum was computer-fitted assuming Lorentzian single lines. ¹¹⁹Sn NMR spectra were run in THF in an ARX-400, 9.4 T Bruker instrument (400 MHz for proton frequency) using Me₄Sn as an external reference. The highest possible concentration was on the order of 3.5 x 10⁻² molL⁻¹.

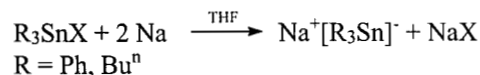
The preparation of Na⁺[Ph₃Sn]⁻

Different techniques have been used for the preparation of Na⁺[R₃Sn]⁻:

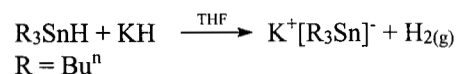
a) 1927 - reduction of organotin halides with sodium in liquid ammonia (blue solution)⁵:



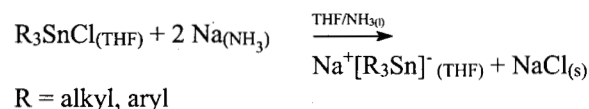
b) 1962 - reduction of organotin halides with sodium in aprotic solvents⁶:



c) 1989 - reaction of organotin hydrides with KH in aprotic solvents⁷:



Comparison of the methods eventually led us to an improved procedure for the preparation of Na⁺[Ph₃Sn]⁻ with the use of a two-phase liquid system formed by a bronze dispersion of Na in liquid ammonia over a solution of organotin chloride in THF. This process was previously briefly described³ and is given here in detail. The bronze dispersion was very efficient in forming the nucleophile, which remained dissolved in THF. After completion of the reaction, the solution of the nucleophile in THF was separated by filtration under N₂, and was ready for use. The process can be summarized by:



Experimental Procedure

A large excess of freshly cut sodium (washed with THF) was added to a Schlenk tube containing a solution of R₃SnCl in dry and peroxide-free THF. The tube was then saturated with NH_{3(g)} and put in a dewar with liquid N₂, keeping the flow of NH_{3(g)} for another 30 s. After this time the Schlenk tube was removed from the Dewar, and its contents magnetically stirred. After some minutes the bronze dispersion began to form and floated in the tube. At this point the reduction of R₃SnCl began to take place, indicated by the yellow color which started to develop in the solution. After about 15 min the reaction was completed, the NH₃ was given off (all excess removed under vacuum), and the solution was filtered under N₂. The solution of Na⁺[Ph₃Sn]⁻ in THF does not last long, even under N₂. It must be used within a few hours after being prepared.

The preparation of the precursor bipy.SnCl₄

A solution of 0.50 mL (1.13 g, 4.33 mmole) of SnCl₄ in CH₂Cl₂ (5 mL) was slowly added, under stirring, to a solution of 0.678 g (4.33 mmole) of 2,2'-bipyridine (bipy) in CH₂Cl₂ (15 mL). A light orange precipitate was immediately formed, giving 1.55 g of product (86% yield). This solid decomposed at 200 °C and its analysis agreed with the expression bipy.SnCl₄. Found: C, 28.67; H, 1.46; N,

6.55%. Calcd. for C₁₀H₈N₂SnCl₄: C, 28.82; H, 1.94; N, 6.72%.

The preparation of the cluster bipy.Sn(SnPh₃)₄

By means of a transfer needle the solution of the nucleophile Na⁺[Ph₃Sn]⁻ in THF, obtained from 0.390 g (1.00 mmole) of Ph₃SnCl, was slowly added to a slurry of 0.100 g (0.240 mmole) of bipy.SnCl₄ in dry THF (5 mL). The solution immediately became yellow and gradually darkened to a deep brown color. This solution was transferred to another Schlenk tube and evaporated under vacuum. A loose brown powder was obtained (over 80% yield), which must be kept under N₂. Analysis of the product gave the results below.

Found: C, 60.11; H, 4.05; N, 1.61%. Calcd. for C₈₂H₆₈N₂Sn₅: C, 58.80; H, 4.09; N, 1.67%.

A similar reaction was performed using Na⁺[Ph₃Sn]⁻ and the adduct prepared from ethylenediamine and SnCl₄. The presumed homologous cluster produced was highly pyrophoric upon exposure to air and extremely difficult to characterize.

Results and Discussion

The cluster bipy.Sn(SnPh₃)₄, **1**, prepared from the adduct bipy.SnCl₄ by reaction with Na⁺[SnPh₃]⁻, is highly sensitive to oxygen, but can be conveniently handled under N₂ either in the solid state or in purified THF. The cluster is brown, but upon oxidation it changes to yellow and then to a yellowish white. The analytical data for **1** are consistent with the replacement of all four Cl⁻ ligands by the Ph₃Sn⁻ nucleophiles. Bipy.SnCl₄ presented a very strong absorption at 290 cm⁻¹ in its I.R. spectrum, characteristic of the Sn-Cl stretching frequency. This band was absent in the spectrum of the cluster.

The older literature describes a different method for the preparation of the neopentane analogue Sn(SnPh₃)₄^{8,9}, but this compound is clearly different from our cluster. Sn(SnPh₃)₄ is reported as a very stable white solid, in marked contrast with **1**, and its preparation was not repeated here.

Straight-chain and discrete branched-chain polytins are usually colorless¹⁰. The deep color of **1** is probably due to a ligand-to-metal charge transfer effect. Presumably, reaction with oxygen eliminates or drastically reduces this charge transfer, resulting in the change in color described above.

The ¹¹⁹Sn Mössbauer spectrum of **1**, presented in Fig. 1, showed an absorption band which did not conform to a Lorentzian curve. A better statistical adjustment, taking into account two Lorentzian curves, led to two different Sn sites which are also chemically different: the most abundant site (79%) had an isomer shift, σ = 1.53 mms⁻¹,

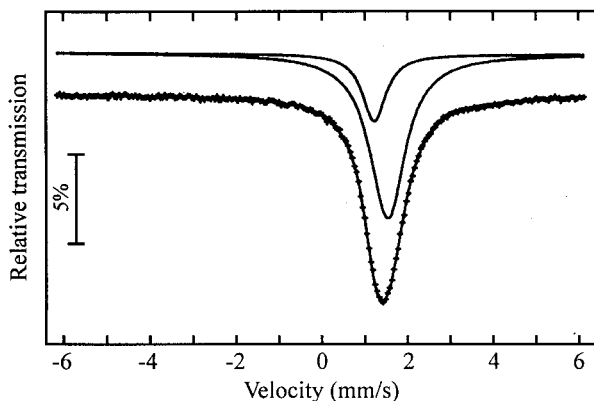


Figure 1. ^{119}Sn Mössbauer spectrum of $\text{bipy}\cdot\text{Sn}(\text{SnPh}_3)_4$.

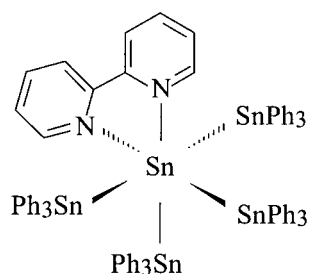


Figure 2. Proposed structure of the cluster $\text{bipy}\cdot\text{Sn}(\text{SnPh}_3)_4$.

whereas the least abundant site (21%) corresponded to $\sigma = 1.22 \text{ mms}^{-1}$.

The Mössbauer results are in agreement with a formulation such as that shown in Fig. 2.

The Mössbauer data showed that the two Sn sites are in a 4:1 ratio; since the isomer shift is directly dependent on the *s* character of the Sn atom, it can be assumed that the ratio between the areas of the two curves corresponds to the ratio between the terminal and the central Sn atoms, which are sp^3 (25% *s* character) and d^2sp^3 (17% *s* character), respectively¹¹.

The linewidth for the most abundant site (0.65 mms^{-1}) was very sharp, whereas the least abundant one, corresponding to the central Sn atom, presented a wider line (1.01 mms^{-1}), indicating the presence of an unresolved quadrupole splitting for this Sn atom. The absence of any significant quadrupole splitting at the four terminal Sn atoms agrees with the generalisation that organotin species bonded to atoms devoid of lone-pair non-bonding electrons tend to give very small or no quadrupole splittings¹². The asymmetry caused by the presence of the two bipyridine nitrogens bonded to the central Sn atom widened the corresponding line, but was not sufficient to show an observable quadrupole splitting. The Mössbauer data for our cluster are quite different from those for the neopentane analogue $\text{Sn}(\text{SnPh}_3)_4$, for which all Sn atoms present identical results ($\sigma = 1.33 \pm 0.10 \text{ mms}^{-1}$, $\Delta < 0.3 \text{ mms}^{-1}$)¹³.

In this work, we also studied the product obtained by exposing our cluster to air. The Mössbauer spectrum showed that it consisted of a mixture containing different stannylated compounds, with a composition of 88% $\text{Ph}_3\text{SnSnPh}_3$ ($\sigma = 1.43 \text{ mms}^{-1}$, $\Delta \cong 0 \text{ mms}^{-1}$) and 12% SnO_2 ($\delta \cong 0 \text{ mms}^{-1}$, $\Delta = 0.43 \text{ mms}^{-1}$). These results were compared with pure samples from our laboratory and effectively showed that attack by air involved oxygen insertion into the cluster, with elimination of the products detected.

Mössbauer spectroscopy did not, however, distinguish between the two types of terminal Sn atoms, *i.e.*, those trans to Sn and those trans to N. This was possible to do by means of ^{119}Sn NMR.

Table 1 shows the ^{119}Sn NMR data for our cluster, as well as other examples from the literature.

The spectrum of **1** presented three well-defined absorptions at -58.5, -141.1 and -1212.4 ppm, all at field values higher than for Me_4Sn , our external reference. It was not possible to observe any Sn-Sn coupling in the spectrum.

The two nearest absorptions ought to correspond to the four tetracoordinate Sn atoms, whereas the signal at -1212.4 ppm is likely to be due to the hexacoordinate Sn. The latter is very shielded, much more than most examples from the literature, as seen in Table 1. Both the catenation of Sn as well as an increase in its coordination number contribute to shift its absorption to a higher field. In our case, the two effects led to an extraordinary shift to -1212.4 ppm. Chemical shifts of this magnitude have been described only for very highly coordinated Sn complexes¹⁶, or for naked tin cluster polyanions¹⁷. Examples of both cases are presented in Table 1. This table also shows that $\text{Ph}_3\text{SnSnPh}_3$ and $\text{Ph}_3\text{SnSn}(\text{Bu}^i)_2\text{SnPh}_3$ have chemical shifts for the Ph_3Sn groups of -143.6 and -138.2 ppm, respectively¹⁴. These values are very close to our value of -141.1 ppm for one of the types of Ph_3Sn groups present in our cluster. Analogy between our compound and $\text{Ph}_3\text{SnSn}(\text{Bu}^i)_2\text{SnPh}_3$ allowed

Table 1. ^{119}Sn NMR absorptions.

Compound	δ (ppm)
1. $\text{bipy}\cdot\text{Sn}(\text{SnPh}_3)_4$ ^a	-58.5, -141.1, -1212.4
2. $\text{Ph}_3\text{SnSnPh}_3$ ^b	-143.6
3. $\text{Ph}_3\text{SnSn}(\text{Bu}^i)_2\text{SnPh}_3$ ^b	-138.2, -221.0
4. SnCl_4 ^c	-150
5. SnCl_3FPT ^{d,*}	-481.5
6. $\text{Sn}(\text{NO}_3)_4$ ^e	-1033
7. Sn_4^{2-} ^f	-1895
8. Sn_9^{4-} ^f	-1230
9. $(\text{Sn}_8\text{Ti})^{5-f}$	-1167

^a in THF; ^b in CDCl_3 ¹⁴; ^c neat¹⁵; ^d in MeOH¹¹; ^e in CH_2Cl_2 or CCl_4 ¹⁶; ^f in en¹⁵.

* FPT denotes 2-formylpyridine thiosemicarbazone.

us to conclude that the absorption at -141.1 ppm corresponds to the two Ph_3Sn groups trans to each other. As a consequence, the absorption at -58.5 ppm ought to be due to the Ph_3Sn groups trans to N. The lower chemical shift can be associated with less shielding of the Sn atoms trans to the better coordinated N atoms of the chelating bipyridine ligand. Indeed, in organotin bond dissociation energies are higher for Sn-N than for Sn-Sn linkages (272-293 vs. 209-238 kJmol^{-1} , respectively¹⁸).

Acknowledgments

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