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The stannylenes, R_2Sn : [R = bis(trimethylsilyl)methyl and 2,4,6-triisopropylphenyl], react with 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne to give the corresponding stannacyclopropene derivatives. Full characterization, including crystallographic analysis, reveals some insight into the nature of bonding in stannacyclopropenes and the structural and electronic requirements for the reactivity of stannylenes with acetylenes. Keywords: Tin Compounds, Cyclic Compounds, Organometallic Compounds, (AW).

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INVESTIGATION OF THE FACTORS INFLUENCING THE STRUCTURE AND
STABILITY OF STANNACYCLOPROPENES: THE SYNTHESIS AND MOLECULAR
STRUCTURE OF TWO DERIVATIVES

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Abstract The stannylenes, R_2Sn : [R = bis(trimethylsilyl)-methyl and 2,4,6-triisopropylphenyl], react with 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne to give the corresponding stannacyclopentene derivatives. Full characterization, including crystallographic analysis, reveals some insight into the nature of bonding in stannacyclopentenes.

INTRODUCTION

The chemical consequences of reactions of stannylenes, R_2Sn : (1), with carbon-carbon multiple bonds is still poorly understood. This is largely due to the very successful competing polymerization reaction, $n R_2Sn \rightarrow (R_2Sn)_n$, which can occur below $0^\circ C$. By employing sterically demanding ligands on the tin atom, however, one can slow down, or even completely eliminate, this unfavorable polymerization process, and in this way, Neumann and co-workers¹ were able to make a detailed investigation of the addition of the known kinetically stabilized stannylene derivative, bis[bis(trimethylsilyl)methyl]tin (1a)², with a series of substituted dienes to produce 1-stannacyclopent-3-enes. Herein, we describe the reaction of sterically hindered stannylenes, 1a and 1b [R = bis(trimethylsilyl)methyl and 2,4,6-triisopropylphenyl, respectively], with the cyclic acetylene, 2³, to provide the first known examples of stannacyclopentenes, 3a and 3b (Scheme 1).⁴ Full characterization of these derivatives, including the crystal structures, reveals some insight into the nature of bonding of stannacyclopentenes.

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SYNTHESIS OF STANNACYCLOPROPENES

The synthesis of 3a from the cyclic acetylene 2 has been presented elsewhere.⁴ For the synthesis of 3b, the stannylene 1b was generated, in the presence of an excess of 2, from the cyclotristannane 4 in methylcyclohexane at either room temperature under thermal conditions or at -78°C upon photolysis with a Hanovia high-pressure lamp (quartz) (Scheme 1).⁵ In the latter process, repetitive photolysis, followed by warming to room temperature each time, was required to produce a high yield of 3b which, upon removal of methylcyclohexane and excess acetylene under reduced pressure, was recrystallized from pentane at -40°C .

CHARACTERIZATION AND PROPERTIES

A notable feature of the stannacyclopropenes, 3a and 3b, which are air- and moisture-sensitive in the solid state, is that both were found to be in rapid equilibrium with the cyclic acetylene 2 in solution at room temperature. Accordingly, all the spectroscopic data of these compounds were recorded at either low temperature in solution (-25°C) or in the solid state. Both 3a and 3b show a characteristic resonance in the ^{13}C NMR (75 MHz, methylcyclohexane- d_{14}) for the stannacyclopropene carbon atoms at 163.9 ppm for 3a and 161.9 ppm for 3b. Surprisingly, by solid state ^{13}C CP-MAS NMR (75 MHz), compound 3a exhibits two resonances at 166.2 ppm [$^1J(^{117/119}\text{Sn}-^{13}\text{C}) = 140\text{ Hz}$] and 164.7 ppm [$^1J(^{117/119}\text{Sn}-^{13}\text{C}) = 120\text{ Hz}$], respectively.⁶ The tin-carbon coupling constants observed for these resonances are over half that commonly encountered for organotin compounds, which are typically in the range of 300-400 Hz⁷, and this may be indicative of an unusual bonding situation within the stannacyclopropene ring system. The ^{119}Sn NMR (112 MHz, methylcyclohexane- d_{14}) data for 3a and 3b is uncommon in that the chemical shifts of -536.8 ppm for the former and -690.5 ppm for the latter are more than 100 ppm

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upfield from the chemical shifts of the highly strained
cyclotristannanes.^{5,8} IR (Nujol) data show ν_{C-C} at 1587 cm^{-1} for
3a and at 1605 cm^{-1} for 3b.

CRYSTALLOGRAPHIC ANALYSIS

Figure 1 depicts the molecular structures of 3b as derived from
crystallographic analysis.⁹ Since the molecular structure and
salient features of the structure of 3a have already been
presented elsewhere⁴, they will only be mentioned here as they
pertain to comparisons with the structure of 3b.

Unlike 3a, the stannacyclopropene ring of 3b is skewed and
this is reflected in unequal Sn-C_{sp^2} bond lengths of 2.17 (1) and
2.13 (1) Å, respectively, with the longer of these two bond
lengths falling slightly outside the Sn-C_{sp^2} bond values
encountered previously for 3a [cf. 2.134 - 2.136 (5) Å]. With
regard to steric interactions of the bulky substituents at tin, it
is interesting to note that a common feature in the structures of
both 3a and 3b is that the substituents serve to place a methyl
group over each face of the stannacyclopropene ring. These methyl
groups, which are in close proximity to the geminal dimethyl
groups of the seven-membered ring fragment, serve to form a steric
shield which undoubtedly helps to kinetically stabilize the
stannacyclopropene ring system. In addition, the carbon-carbon
bond length of 1.33 (2) Å of 3b is similar to that of 3a [1.340
(6) Å].

One of the critical features observed previously for the
structure of 3a was the 356.1° average sum for two sets of angles
($\text{C}_{1b}\text{-Sn-C}_{1a}$, $\text{C}_1\text{-Sn-C}_{1b}$, $\text{C}_1\text{-Sn-C}_{1a}$ and $\text{C}_{1b}\text{-Sn-C}_{1a}$, $\text{C}_2\text{-Sn-C}_{1b}$, $\text{C}_2\text{-Sn-C}_{1a}$) at tin. This feature is once again repeated in 3b with
the average value for the same two sets of angles being 355.7° .
Accordingly, when compared to the 328.5° value expected for an
idealized tetrahedral configuration, the geometry of the tin atom

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in both stannacyclopropene derivatives can best be considered
nearly trigonal coplanar.

From the crystallographic comparison of the structures of 3a
and 3b, it can be concluded that apart from the skewing of 3b,
which can be accounted for in terms of crystal packing
interactions, the choice of using either bis(trimethylsilyl)methyl
or 2,4,6-triisopropylphenyl groups as ligands has little effect on
the stannacyclopropene ring structure with regard to steric
interactions. However, the electronic contributions of these
ligands to the tin atom are not identical and this should manifest
itself in a difference in the physical properties of 3a and 3b
which might then be correlated with a model of bonding for
stannacyclopropenes.

NATURE OF BONDING

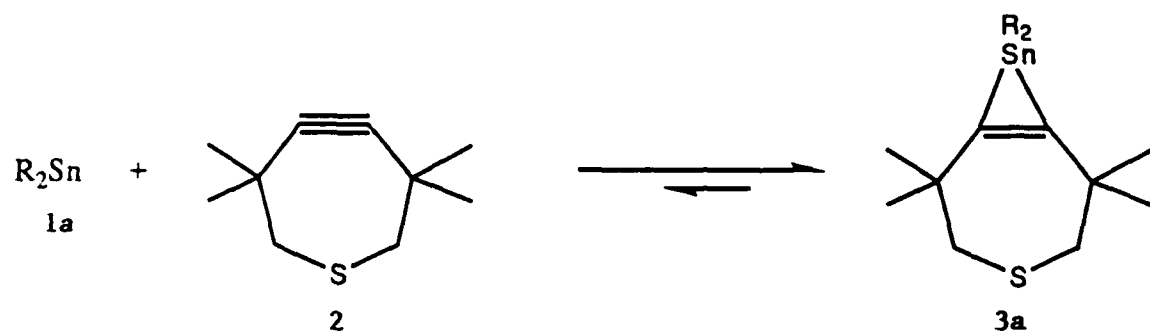
For Main Group three-membered rings, such as heteroatom-
substituted cyclopropanes, a π -complex model of bonding has been
formulated¹⁰ which is, in essence, identical to that of the Dewar-
Chatt-Duncanson π -complex model for bonding in transition metal
olefin and acetylene compounds.¹¹ In both models, two basic
donor-acceptor orbital interactions are recognized. The first
interaction represents donation from a π orbital of the organic
fragment to a valence orbital of a_1 symmetry on the heteroatom
while the second interaction involves back-donation of electron
density from an orbital of b_2 symmetry on the heteroatom into the
 π^* orbital of the organic fragment. As the electronegativity of
the heteroatom fragment increases, the first interaction will
dominate with a corresponding increase in the π -complex character
of the three-membered ring.^{10d} For heteroatom-substituted
cyclopropenes, an increase in π -complex character should be
reflected in a corresponding increase in $\nu_{C=C}$. With regard to
bonding in stannacyclopropenes, it can be postulated that the
observed increase in $\nu_{C=C}$ in 3b (1605 cm^{-1}) over that of 3a (1587

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 cm^{-1}) is a reflection of the poorer electron-donating ability of the 2,4,6-triisopropylphenyl ligand relative to the bis(trimethylsilyl)methyl group which increases the π -complex character of 3b relative to 3a. It is interesting to point out that for exocyclic ligands that are extremely electron-withdrawing, the minimum amount of back-donation that is required for a stable complex to exist may no longer be present. Indeed, this may explain the apparent inertness of tin (II) dichloride towards the cyclic acetylene which would produce a stannacyclopentene with a very electronegative tin core. Further experimental and theoretical investigations are currently underway to probe this π -complex model of bonding for stannacyclopentenes.

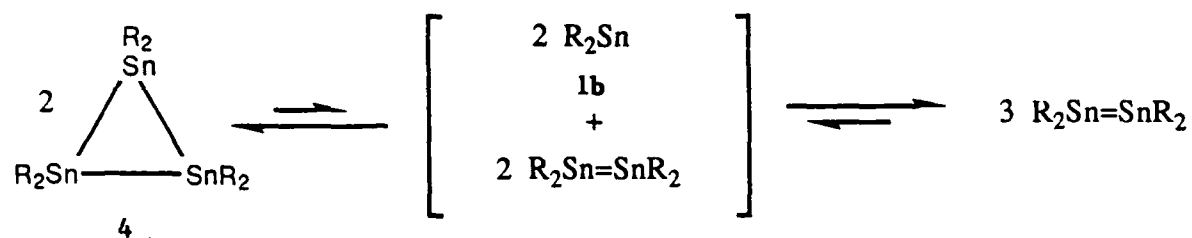
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Scheme 1



R = bis(trimethylsilyl)methyl



R = 2,4,6-triisopropylphenyl

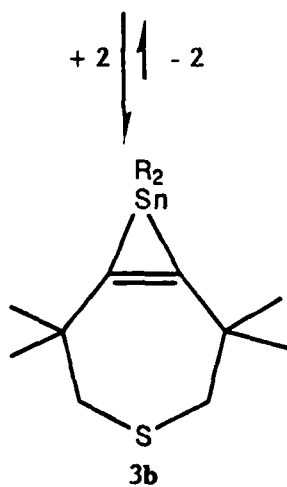


FIGURE 1

