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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 stannacyclopropene derivatives. Full characterization, including crystallographic analysis, reveals some insight into the nature of bonding in stannacyclopropenes.

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-workers[1] 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, 2[3], to provide the first known examples of stannacyclopropenes, 3a and 3b (Scheme 1).[4] Full characterization of these derivatives, including the crystal structures, reveals some insight into the nature of bonding of stannacyclopropenes.

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^{0}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^{0}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^{0}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 [$^{1}J(^{117/119}Sn-^{13}C)$ = 140 Hz] and 164.7 ppm [$^{1}J(^{117/119}Sn-^{13}C)$ = 120 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 Hz[7], 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 upfield from the chemical shifts of the highly strained cyclotristannanes.[5,8] IR (Nujol) data show $\nu_{C=C}$ at 1587 cm^{-1} for 3a and at 1605 cm^{-1} for 3b.

CRYSTALLOGRAPHIC ANALYSIS

Figures 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 elsewhere[4], 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) A, 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) A]. 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) A of 3b is similar to that of 3a [1.340 (6) A].

One of the critical features observed previously for the structure of 3a was the 356.1^0 average sum for two sets of angles (C_{1b}-Sn-C_{1a}, C_1-Sn-C_{1b}, C_1-Sn-C_{1a} and C_{1b}-Sn-C_{1a}, C_2-Sn-C_{1b}, C_2-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 355.7^0. Accordingly, when compared to the 328.5^0 value expected for an idealized tetrahedral configuration, the geometry of the tin atom 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 formulated[10] 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 stannacyclopro-penes, it can be postulated that the observed increase in $\nu_{C=C}$ in 3b (1605 cm^{-1}) over that of 3a (1587

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 stannacyclopropene with a very electronegative tin core. Further experimental and theoretical investigations are currently underway to probe this π-complex model of bonding for stannacyclopropenes.

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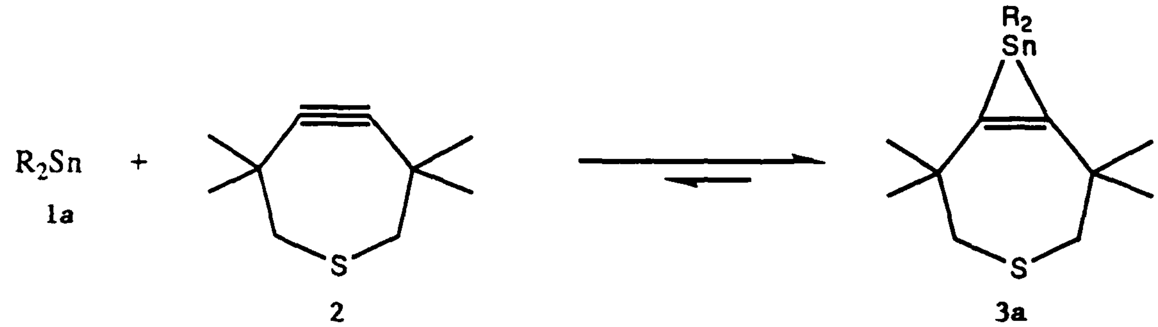
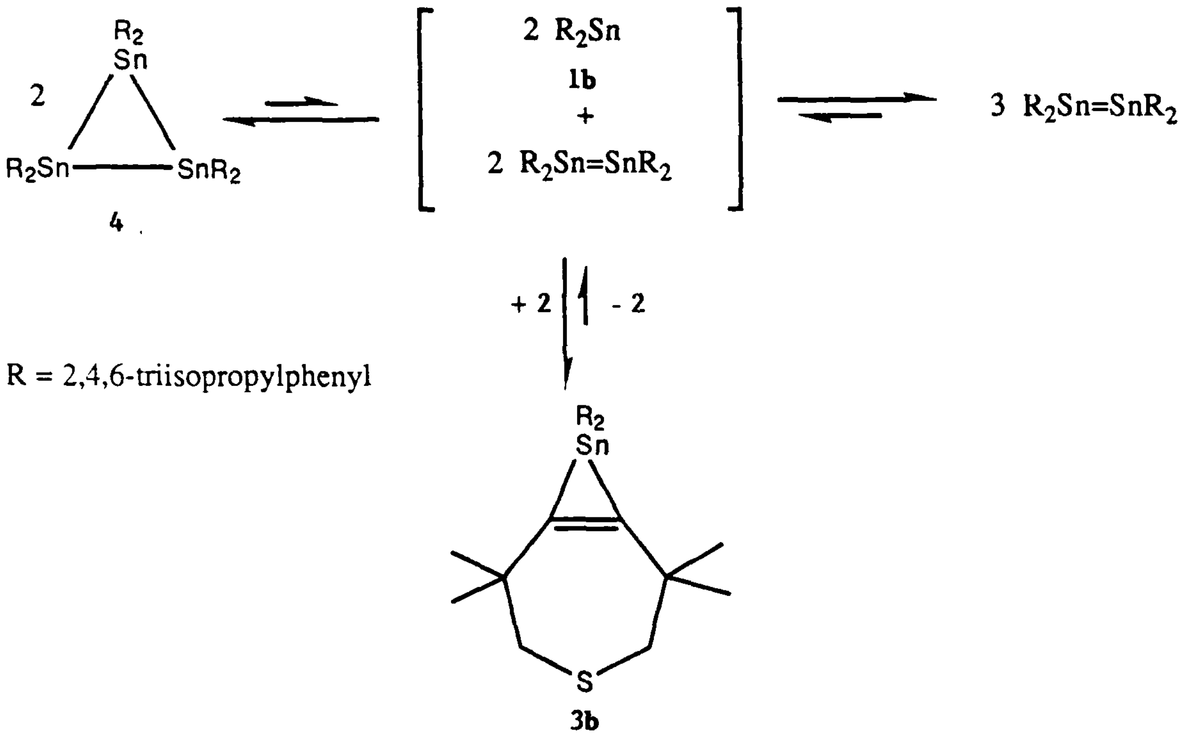
Scheme 1



R = bis(trimethylsilyl)methyl



R = 2,4,6-triisopropylphenyl

FIGURE 1