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Organoboration of Alkynylstannanes. 13.¹ Synthesis of a 2.5-Distannyl-3-borolene, a Precursor of the Pentaalkylborol Dianion

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The attempted synthesis of a 1,4-bis(trimethylstannyl)-3-bora-1,4-pentadiene derivative gave the title compound instead. This is shown by ¹H, ¹¹B, ¹³C, and ¹¹⁹Sn NMR studies at variable temperature which also showed that at room temperature both Me₃Sn groups migrate around the ring. From this it appears that the title compound (2,5-bis(trimethylstannyl)-1,2,5-triethyl-3,4-dimethyl-3-borolene) should permit the synthesis of a pentaalkylborol dianion.

Introduction

Heterocyclic dienes containing the R₂Sn moiety adjacent to the C=C double bonds are of great importance in the synthesis of other heterocyclic compounds.²⁻⁸ It occurred to us that 1,5-distannyl-1,4-pentadienes (1) should also be of considerable interest for this purpose.



Although there is a wealth of information on heterocyclic dienes,²⁻⁸ there is only a single report on the synthesis of

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the thermally unstable (1E, 4E)-1.5-bis(trimethylstannyl)-1.4-pentadiene⁹ and there is no mention of the preparation of 3-hetero analogues like 1. There are several reports in the literature on reactions that should lead to compounds similar to 1, at least as intermediates. However, the reaction failed¹⁰ or rearranged products^{11,12} are observed instead of the substituted 3-hetero-1,4-pentadienes.

The present work concerns the attempted synthesis of a 1,5-bis(trimethylstannyl)-3-bora-1,4-pentadiene (2) via the organoboration of alkynylstannanes.¹³ The stability of the final products (no halogen atoms on boron or tin are involved) should allow conclusive evidence for the structure of 2 or of any rearrangement product to be obtained.

Results and Discussion

(A) Attempted Synthesis of 2. The $Sn-C \equiv$ bond in alkynylstannanes (3) is cleaved by trialkylboranes (4) to

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⁽⁹⁾ Jutzi, P.; Baumgärtner, J. J. Organomet. Chem. 1978, 148, 257. (10) In ref 4f it is reported that 1,1,4,4-tetramethyl-1,4-distanna-2,5cyclohexadiene reacts with the bulky ferrocenylboron dibromide to give the corresponding 1,4-dibora-2,5-cyclohexadiene whereas the reaction with simple boron halides such as BCl₃, BBr₃, MeBBr₂, and PhBCl₂ is not successful. This may be explained by a rearrangement of the substituted 3-hetero-1,4-pentadiene once the ring has been opened by electrophilic attack.

⁽¹¹⁾ In ref 5 it is reported that the reaction between 1,1,2,4,6-pentamethyl-1-stanna-4-boracyclohexadiene and MeBBr₂ proceeds exclusively in 1:2 stoichiometry, leading to Me₂SnBr₂ and a 2,5-diboryl-3-borolene. The 1,5-diboryl-3-bora-1,4-pentadiene that is expected when Me₂SnBr₂ is formed is not observed at all.

⁽¹²⁾ In ref 2f the intermediacy of a 1,5-diboryl-3-stanna-1,4-pentadiene is proposed on the basis of NMR data. Above 0 °C quantitative rearrangement to a 2,5-diboryl-3-stannolene takes place.

give an alkynylborate-like intermediate (5). The alkene derivative 6 is formed stereoselectivity in essentially quantitative yield, 1,13,14 as shown in eq 1. The reaction

$$\begin{array}{c} (CH_3)_3 \operatorname{Sn} - C \equiv C - CH_3 \\ \bullet \\ (C_2H_5)_3 B \end{array} \left[\begin{array}{c} C_2H_5 \\ C_2H_5 - B - C \equiv C - CH_3 \\ C_2H_5 \\ C_2H_5 \end{array} \right] \xrightarrow{C_2H_5} C = C \\ Sn(CH_3)_3 \end{array} \right]$$
(1)

of 6 with a further equivalent of alkynylstannane may proceed either by transfer of the alkenyl group, leading primarily to a butadiene derivative, or by transfer of the ethyl group to give the target compound (eq 2). We have



shown that compounds of type 8 rearrange irreversibly (eq 3) to allenes 10 when there are more bulky substituents than the methyl group at the $C \equiv C$ triple bond in 3. Bulky

$$\begin{array}{c} C_{2}H_{5} \\ C_{2}H_{5}$$

substituents will favor the trans conformation, 9, of the butadiene which is one requirement for the allylic rearrangement.^{1,13,15a-d} However, no allenes are observed in reactions with R = Me. The reaction according to eq 2, therefore, proceeds to form 2. If 8 is formed at all, it will be in equilibrium with 6 and 3 via the deorganoboration reaction which is known to take place readily.^{1,13,15}

Similarly, compound 2 may be in equilibrium with 6 and 3 (via the intermediate 7). Thus, the final product of the reaction between 3 and 6 (eq 2) may have the elemental composition of 2 but a different structure. This was shown subsequently by chemical analysis and by a multinuclear NMR study in solution between -50 and +50 °C.

We propose a mechanism as shown in eq 4 in order to account for our failure to obtain compound 2. This mechanism takes into account the possibility of an electrophilic attack at the olefinic carbon adjacent to boron in 7 followed by transfer of an ethyl group from boron to the alkynyl carbon and ring closure to form compounds 11 or 13. These should be in equilibrium with compound 12. Indeed, the mobility of the Me₃Sn groups is readily



shown by NMR spectroscopy. From this we predict that compound 12 is a likely precursor for the pentaalkylborol dianion $14.^{16}$



(B) NMR Study of the 3-Borolene 12 (Table I). ¹H NMR. At ambient temperature a rapid intramolecular exchange of the Me₃Sn groups in 12 is evident. The intensities of ^{117/119}Sn satellites of the ¹H resonances of the ring substituents in 2-, 3-, 4-, and 5-positions (CH₂, CH₃, CH₃, and CH₂, respectively) indicate coupling with two equivalent tin atoms. Furthermore, we expect a complex pattern for the ¹H resonances of the CH₂ groups since the protons are diastereotopic. However, at room temperature and above only a broadened quartet is visible (Figure 1B). Upon cooling coalescense is observed at 7 °C, and at lower temperature the expected complex pattern emerges (Figure 1A). Homodecoupling reduces the complex pattern to an AB system (Figure 1A) or to a singlet (Figure 1B). Comparison of Figure 1A,B also shows that the ¹H resonances of the CH₃ groups (3- and 4-positions) are accompanied by two sets of ^{117/119}Sn satellites (30.9 and 13.3 Hz) according to ${}^{4}J(\text{SnH})$ (±) and ${}^{5}J(\text{SnH})$ (+), leading to the mean value of 8.8 Hz for rapid exchange.

 13 C NMR. At room temperature the 13 C NMR spectrum displays similar features as observed in the ¹H NMR spectrum. The intensities of the $^{117/119}$ Sn satellites of the 13 C resonances of the ring substituents are correct for the interaction with two equivalent tin atoms. The 13 C resonances of all ring carbon atoms are broad (which is not affected by 11 B decoupling), and $^{117/119}$ Sn satellites are not observed.

At -40 °C the ¹³C NMR spectrum shows one sharp resonance for the olefinic carbon atoms with two sets of ^{117/119}Sn satellites ($|^{2,3}J(^{119}Sn^{13}C)|$ 51.0, 62.2 Hz) and a broadened resonance for the ring carbon atoms attached to boron. The relatively small coupling constant $|^{1}J(^{119}Sn^{13}C)|$ (89 Hz) is in agreement with the $|^{1}J(^{119}Sn^{13}C)|$ data obtained in the fragment Me₃Sn-C-B< for other compounds.¹ The coupling constants $|^{2}J(^{119}Sn^{13}CH_{2})|$ and $|^{3}J(^{119}SnCH_{2}{}^{13}CH_{3})|$ are almost doubled, indicating very small contributions of $|^{4,5}J(^{119}Sn^{13}C)|$ to the mean value in case of rapid exchange. A fairly small coupling $|^{3}J(^{119}SnCC^{13}CH_{3})|$ (13.0 Hz) is observed. This is in agree-

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⁽¹⁶⁾ Reaction of 12 in THF with an excess of potassium for 4 h at 60 °C gave first a bright red solution ($\delta(^{11}B)$ -6.7) and finally a dark brown solution ($\delta(^{11}B)$ +27.0). The latter $\delta(^{11}B)$ value agrees with that reported for [Ph₅BC₄]²-;^{3a} Wrackmeyer, B., manuscription preparation.

Table I. NMR Data ^a for Compound 12						
	$\delta(^{13}C)(^{n}J(^{119}Sn^{13}C))$		$\delta({}^{1}\mathrm{H})({}^{n}J({}^{119}\mathrm{Sn}{}^{1}\mathrm{H}))$			
	28 °C	−50 °C	50 °C	-40 °C	δ(¹¹ B)	δ(¹¹⁹ Sn)
$\begin{array}{c} C (2,5) \\ C (3,4) \\ CH_3 (2,5) \\ CH_3 (3,4) \\ CH_2CH_3 (2,5) \\ BCH_2 (1) \\ BCH_2CH_3 (1) \\ SnCH_3 (2,5) \end{array}$	71.8b134.6b24.8 (17.0c)12.717.7 (40.0c)13.9b10.2-6.5 (288.0)	$\begin{array}{c} 69.3^{b} (89.0) \\ 134.8 (62.2, 51.0) \\ 24.7 (33.3) \\ 12.5 (13.0^{c,d}) \\ 18.1 (84.4) \\ 13.7^{b} \\ 10.1 \\ -6.7 (288.5) \end{array}$	2.10 (q) (22.0 ^c) 1.71 (s) (8.8 ^c) 0.73 (t) 1.45-1.25 (m) 1.14 (m) 0.05 (s) (48.8)	2.13 (q, d) ^e 1.70 (s) (30.9, 13.3) 0.67 (t) 1.45-1.0 (m ^{f}) 1.45-1.0 (m ^{f}) 0.05 (s) (48.8)	64.0 ^g	34.0 ^{<i>h</i>}

^a Solution of 12 in CDCl₃ (ca. 15% w/v); $\delta({}^{1}\text{H})$, $\delta({}^{13}\text{C})$, and $\delta({}^{19}\text{Sn})$ relative to $(\text{CH}_{3})_4$ Si (internal), BF₃-O(C₂H₅)₂ (external), (CH₃)₄Si (internal), and (CH₃)₄Sn (external), respectively; plus signs denote shifts to higher frequencies. ^b Broad signals. ^c Intensities of the ^{117/119}Sn satellites indicate coupling with two equivalent tin atoms. ^d ³J(¹¹⁹Sn¹³C) \approx ⁵J(¹¹⁹Sn¹³C). ^e ^{117/119}Sn satellites of the AB system (by homodecoupling of the CH₃ protons) are not clearly defined. ^f The appearance of the multiplet due to an A_2B_3 system at 50 °C changes on cooling, indicating the even more complex pattern of an ABC_3 system. ^g Width of the ¹¹B resonance at half-height: 400 ± 20 Hz (40 °C), 1200 ± 100 Hz (-30 °C). ^h ^gJ(¹¹⁹Sn¹¹⁷Sn)|= 52.0 Hz.



Figure 1. 200-MHz ¹H NMR spectra of 12: A, at -30 °C, ${}^{1}H_{CH_{2}} = {}^{1}H_{CH_{3}}$ double-resonance experiment is shown on top; B, at 25 °C, ${}^{1}H_{CH_{2}} = {}^{1}H_{CH_{3}}$ double-resonance experiment is shown on top.

ment with a dihedral angle close to 90° for the relevant Sn-C and C-C bonds.¹⁷

¹¹B NMR. The ¹¹B resonance of 12 does not change with temperature (except for severe broadening owing to the increase in the quadrupolar relaxation rate of the ¹¹B nucleus at low temperature). The δ ⁽¹¹B) value is found in the expected range¹⁸ if the high-frequency shift of the ¹¹B resonance (ca. 3-5 ppm) of boron as part of a five-membered ring^{18a} (with respect to analogous noncyclic compounds or six-membered rings) is taken into account.

¹¹⁹Sn NMR. At room temperature the ¹¹⁹Sn spectrum of 12 shows a single, slightly broadened resonance +34 ppm (to high frequency vs. Me₄Sn).¹⁹ Under these conditions the ¹¹⁷Sn satellites are very broad and poorly resolved. They are no longer resolved upon heating the sample to 50 °C. The δ ⁽¹¹⁹Sn) value does not change significantly with temperature. However, the ¹¹⁷Sn satellites become sharp at lower temperature. Evaluation of the free energy of activation at coalescense (ΔG_c^*) agrees fairly well with the ¹H NMR results. For both methods $\Delta G_c^* = 58 \pm 1$ kJ/M is obtained.

Experimental Section

All reactions and transfers were carried out under a dry nitrogen atmosphere. Triethylborane (4),²⁰ 1-propynyltrimethylstannane (3),²¹ and (E)-3-(diethylboryl)-2-(trimethylstannyl)pent-2-ene (6)^{11a} were prepared by literature procedures.

NMR spectra were recorded on a Bruker WP 200 FT spectrometer in 5-mm tubes (¹H) or 10-mm tubes (¹¹B, ¹³C, ¹¹⁹Sn) from ca. 15% (w/v) solutions in dry CDCl₃. The temperature control of the sample was achieved by using the standard Bruker VT unit with a thermocouple element placed directly underneath the tube. The ¹³C resonances were assigned by selective ¹H off-resonance experiments.²² The ¹¹⁹Sn NMR spectra at room temperature were run with normal ¹H broad-band decoupling, since the suppression of the NOE gave no signal enhancement, suggesting a negligible contribution of the dipole-dipole interaction to the relaxation rate. However, at -40 °C the suppression of the negative NOE becomes more important, because the relaxation mechanism due to spinrotation interaction is less efficient at lower temperatures in contrast to dipolar interaction.

IR spectra were recorded on a Perkin-Elmer 325 spectrometer. Mass spectra were recorded on a Varian CH 7 spectrometer. Elemental analyses were obtained in the institute's Analytical Laboratory.

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2,5-Bis(trimethylstannyl)-1,2,5-triethyl-3,4-dimethyl-3borolene (12). To a solution of 6 (4.5 g, 15 mmol) in 40 mL of hexane was added 3 (3.0 g, 15 mmol). This mixture was heated at 60 °C for 12 h. The clear solution was cooled to -78 °C and kept at this temperature for 6 h. The colorless crystalline 12 was filtered off and washed twice with pentane at -78 °C: yield 4.75 g (63%); mp 45–48 °C. Anal. Calcd for C₁₈H₃₉BSn₂: C, 42.9; H, 7.8. Found: C, 42.5; H, 7.7.

Alternatively, fractional distillation of the reaction mixture after the hexane had been evaporated gave a yellowish oil (5.8 g), bp 95–115 °C (10^{-3} torr) which crystallized after 5 days. ¹H NMR showed ca. 90% pure 12 to be present. Recrystallization from pentane at -78 °C yielded 3.8 g (50.4%) of pure 12: mp 45-48 °C; IR (in hexane) ν_{C-C} 1682 (w), 1695 (w, sh), 1705 (w) cm⁻¹; mol wt in C₆H₆, 510 (calcd 503.7); MS (70 eV, 25 °C), m/e (relative intensities) 506 (M, 1.1), 491 (M – Me, 0.3), 341 (M – Me₃Sn, 41), 165 (Me₃Sn, 100).

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Electrochemical, Chemical, and Spectroscopic Characterization of the *trans*-[Tetracarbonylbis(triphenylphosphine)chromium]^{+/0} Redox Couple

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Electrochemical oxidation of trans-Cr(CO)₄(PPh₃)₂ at mercury, silver, or platinum electrodes or chemical oxidation with AgClO₄, NOPF₆ or NOBF₄ produces trans-[Cr(CO)₄(PPh₃)₂]⁺. The 17-electron monomeric cation has been characterized by analysis and a wide variety of electrochemical (polarographic, voltammetric, and controlled potential electrolysis) and spectroscopic (infrared, electron spin resonance) techniques. trans-[Cr(CO)₄(PPh₃)₂]⁺ is light and moisture sensitive and unlike trans-Cr(CO)₄(PPh₃)₂ reacts relatively rapidly with acetonitrile, acetone, iodide, and bromide as well as water. All reactions studied produce trans-Cr(CO)₄(PPh₃)₂]⁺ + L \rightarrow trans-[Cr(CO)₄(PPh₃)₂]⁺ + L \rightarrow trans-[Cr(CO)₄(PPh₃)₂]⁺ + L \rightarrow trans-[Cr(CO)₄(PPh₃)₂]⁺ to be favored, although the observation of Cr(CO)₅PPh₃ as a reaction product with CO in the presence of light suggests that this step may be light catalyzed. This reaction, if it occurs, is a slow step relative to other pathways, and the [Cr(CO)₄(PPh₃)₂]^{+/0} redox couple is not a good candidate for electron-transfer catalysis.

Introduction

Recently, much interest has been shown in the area of inorganic electron-transfer and catalysis.³⁻¹⁰ Metal carbonyl complexes have attracted considerable attention in these studies. An example of a basis for catalysis is thought to be as follows: oxidation of a monomeric 18-electron carbonyl produces a relatively reactive 17-electron species (the catalyst). This species may react with the solvent or a deliberately added ligand to produce a new 17-electron complex that thermodynamically, at least, can react with the starting material in a homogeneous redox reaction to

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generate the final desired substituted 18-electron carbonyl complex and regenerate the catalyst. Equations 1-3 give

$$\mathbf{M}(\mathbf{CO})_4 \mathbf{P}_2 \rightleftharpoons [\mathbf{M}(\mathbf{CO})_4 \mathbf{P}_2]^+ + \mathbf{e} \tag{1}$$

$$[\mathbf{M}(\mathbf{CO})_4\mathbf{P}_2]^+ + \mathbf{L} \rightleftharpoons [\mathbf{M}(\mathbf{CO})_4\mathbf{PL}]^+ + \mathbf{P} \qquad (2)$$

$$[M(CO)_4PL]^+ + M(CO)_4P_2 \rightarrow M(CO)_4PL + [M(CO)_4P_2]^+ (3)$$

a typical scheme for a tetracarbonyl bis(phosphine) complex in a catalytic system (L = ligand, P = phosphine, M = metal). The thermodynamic requirement for this cycle to operate is that E° for the $[M(CO)_4P_2]^{+/0}$ redox couple must be less positive than the E° of the $[M(CO)_4PL]^{+/0}$ couple.

In the reported catalytic studies on carbonyl compounds it has been rare for the seventeen electron intermediate to be isolated and fully characterized, but for a detailed understanding of electron-transfer catalysis it is essential that the chemistry of the catalyst be known. In particular, detailed knowledge of alternative reaction pathways and methods for systematically minimizing their influence is a necessary prerequisite to achieving high catalytic activity.

Hershberger et al.⁷ in a survey of carbonyl complexes briefly mentioned that the compound trans-Cr(CO)₄-(PPh₃)₂ shows a chemically reversible oxidation cyclic