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LETTERS

A NOVEL CYCLIZATION IN THE HYDROBORATION OF DIVINYLSTANNANES

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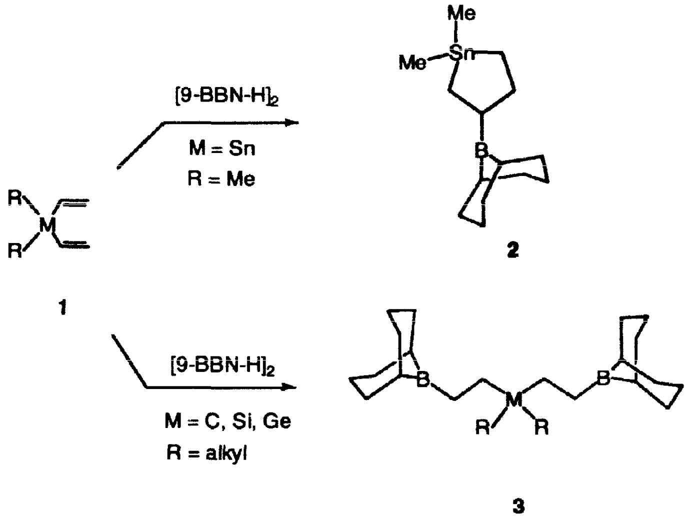
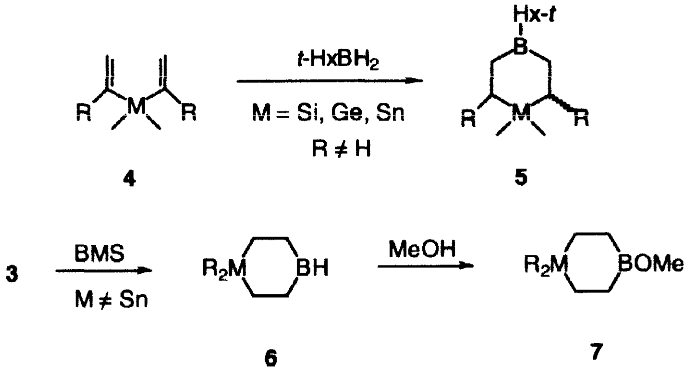
Abstract: *The clean formation of the 3-boryl-1-stannacyclopentane* **(2)** *is observed from the monohydroboration of divinyldimethyltin with 9-BBN-H, a previously unknown process. This heterocyclic system undergoes expected organoborane reactions with the notable exception of the Suzuki-Miyaura coupling where, with bromobenzene, 3-butenyl(dimethyl)phenyltin* **(16)** *is the exclusive coupling product, evidently forming through an unprecedented "stanna-Heck" process.*

Scheme 1



We wish to report an unusual cyclization which occurs in the hydroboration of divinyltin derivatives (**1**, M = Sn) with 9-borabicyclo-[3.3.1]nonane (9-BBN-H) resulting in 3-(9-BBN)-1,1-dimethyl-1-stannacyclopentane (**2**) as the exclusive reaction product. This unusual behavior contrasts markedly to that of other divinyl derivatives of Group 14 metalloids (*i.e.* Si, Ge), which undergo normal dihydroboration leading to 1,5-diboryl adducts (**3**) (Scheme 1).[2]

As an integral part of our continuing studies on the preparation and reactions of functionalized Group 14 heterocycles, we initially accessed these systems through the cyclic hydroboration of divinylmetalloids (**4**).[3] Employing α-substitution on the vinylic moieties, we were able to obtain the desired metallaborinanes, including the tin derivatives (**5**). However, with unsubstituted divinyl systems, **1** (M = Si) leads to borolane rather than borinane products. To obtain **6**, we fixed the desired 1,5-diboryl placement with 9-BBN-H, exchanging **3** with borane-dimethyl sulfide (BMS), ultimately isolating these heterocycles as their *B*-methoxy derivatives (**7**).[2a,b]



Alkenyltin compounds are reported to undergo smooth hydroboration with 9-BBN-

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H,[4] suggesting that **3** (M = Sn) should be readily available from the hydroboration of **1** with this reagent. We carried out the hydroboration of vinyltrimethyltin, which gives **8**, cleanly. However, the attempted hydroboration of **1** (R$_2$M = Me$_2$Sn) with 2 equiv of 9-BBN-H consumes only 1 equiv of the reagent. ^{11}B NMR revealed that the mixture consisted of a 1:1 mixture of **2** (δ 78.1) and unreacted [9-BBN-H]$_2$ (δ 28). With the 1:1 stoichiometry in pentane, **2** is formed quantitatively in 24 h at room temperature. Its 3-borylstannacyclopentane structure is wholly consistent with the NMR data (Figure 1).

This novel cyclization appears to be quite general. Thus, tetravinyltin gives diastereomeric 9-stannaspirobicyclo[4.4]nonanes (**2a**) with 9-BBN-H. Moreover, when 9-BBN-H is replaced by dicyclohexylborane, **2b** is cleanly formed from **1**.[5]

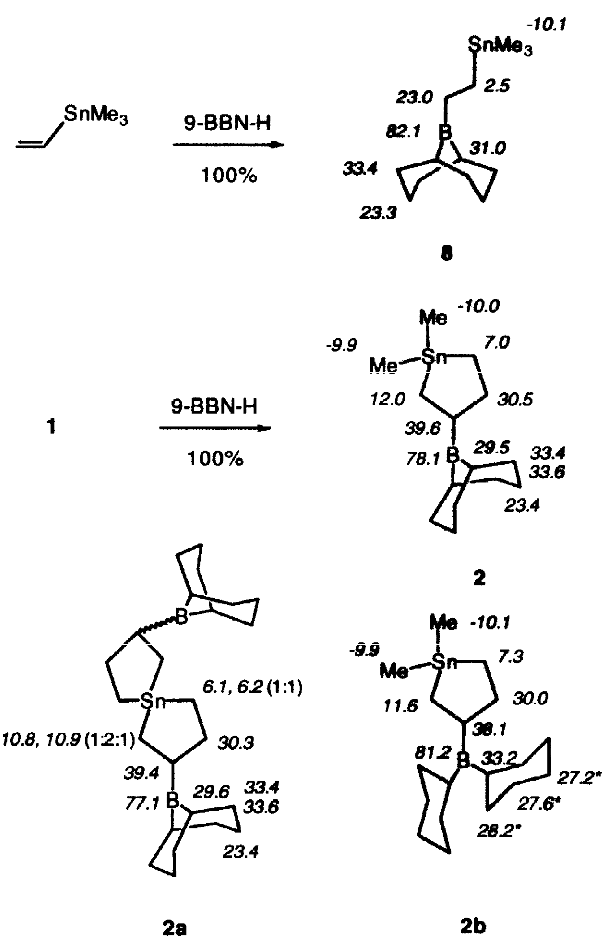
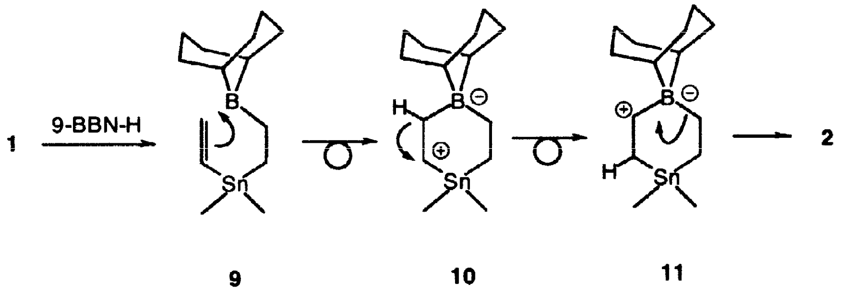


Figure 1. ^{13}C and ^{11}B NMR data for the products of the hydroboration of vinyltins. * May be interchanged.

No other intermediate organoboranes are observed in this unusual process, which quite obviously involves a series of rapid rearrangements. This cyclization, while clearly different, is reminiscent of the stannacyclopentadienes formed from the addition of triethylborane to dialkynyltins.[6] These were rationalized through a complex series of cationic processes. With this in mind, we consider the most plausible pathway to **2** to involve the initial formation of **9** and its collapse to **10**. This is followed by a hydride shift resulting in **11** which rearranges to **2**.[7]

Because no M-C bonds were cleaved in this process, we were intrigued by the fact that only Sn, but not the analogous C, Si nor Ge systems undergo this cyclization. We performed a series of MMX calculations on these intermediates (M = C, Si, Ge, Sn) which suggest that all of the initial adducts **9** favor a *gauche* relationship between the metalloidal groups (*i.e.* B, M).



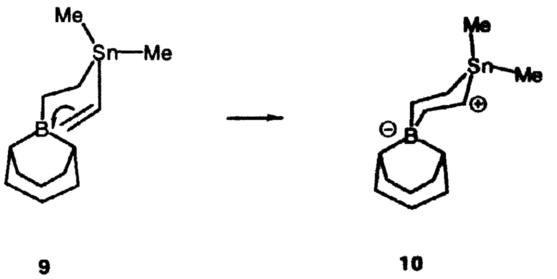


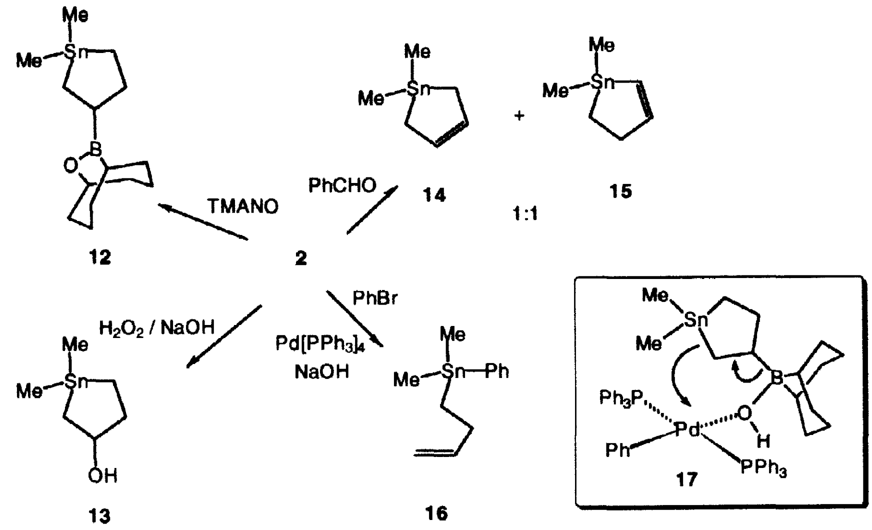
Figure 2. Proposed structures for **9** → **10**.

However, in this same series, the vinyl group is progressively oriented more inwardly making the **9** → **10** conversion for the tin derivative quite feasible. At the STO-3G level, *ab initio* calculations on the Sn *vs.* Si systems reveal that for both, **10** is a stable intermediate, with elongated B-C(3) bonds. However, the Si system must undergo considerable reorganization in the **9** → **10** conversion. This contrasts to the tin system whose greater Sn-C bond lengths (~2.1 Å) permit the vinylic group in **9** to occupy a position which can collapse easily to **10** (Figure 2). The HOMO of **10** also contains a considerable contribution from the ring Sn-C and Sn-Me (ax) bonds which may also help to account for this unusual cyclization. Similar calculations on **11** also suggest that the most favored B-C bond to migrate is the one contained in the stannacycle because it is nearly perpendicular (78°) to the plane of the carbocation in **11** in excellent position for overlap with the empty p orbital. This contrasts to the B-C 9-BBN ring bonds which are poorly aligned (*i.e.* 20 and 41° out of planarity) and do not migrate competitively.

With **2** in hand, we were interested in exploring some of its chemistry (Scheme 2). We examined its oxidation with trimethylamine *N*-oxide (TMANO, 1.0 equiv) which cleanly produces the 9-oxa-10-borabicyclo[3.3.2]decane (OBBD) derivative (**12**).[8] This borinate resists further oxidation (TMANO (1.0 equiv), CH_2Cl_2, 12 h, 25 °C) and is stable to an aqueous work-up. The conversion of **2** to the alcohol (**13**) is accomplished under the standard conditions with alkaline hydrogen peroxide (48%, ether, 3 M NaOH (1 equiv), 30% H_2O_2 (3.3 equiv)).

We also carried out the dehydroborylation[9] of **2** with benzaldehyde at 25 °C which occurs cleanly (2 h, neat), but produces a 1:1 mixture of the allyl (**14**) and vinyl (**15**) stannacycles. MMX calculations support this lack of selectivity because both of adjacent carbons (C-2, C-4) in **2** have pseudo axial hydrogens which are similarly disposed to participate in this electrocyclic process. Attempts to increase the selectivity of this process with changes in the aldehyde or to equilibrate (DBU) the product mixture to favor either product were unsuccessful.

Scheme 2



Derivatives such as **8** had previously been demonstrated to undergo selective B (Suzuki-Miyaura) rather than Sn (Stille) coupling.[4] Indeed, the Pd-catalyzed (3 mol %) coupling of **8** with PhBr under basic conditions gives the expected $PhCH_2CH_2SnMe_3$ (60%). We expected the coupling of **2** to be less efficient because competitive reduction occurs when 2°-alkylboranes are employed.[10] Surprisingly, we did not observe any of the expected 3-phenyl-1-stannacyclopentane, but rather, only a low yield (28%) of the ring-opened 3-butenyl(phenyl)stannane (**16**).[11] We confirmed that **2** is stable to base alone, and view the formation of **16** as arising from a "stanna-Heck" type process[12] where the tin is selectively transferred instead of hydrogen, followed by the reductive elimination of **16** (Scheme 2).[12] We have recently carried out a detailed study on alkyl group coupling in the Suzuki-Miyaura process which implicates the intermediacy of hydroxo μ-bridged complexes (*i.e.* **17**).[13] MMX calculations suggest that the most stable conformation of **17** nicely positions the ring Sn-C bond which is *antiperiplanar* to the HO-9-BBN over the square-planar Pd where the tin transfer can easily take place with the concomitant fragmentation of the ring.

In summary, this study reports the unusual formation of a 3-boryl-1-stannacyclopentane (**2**) from the hydroboration of divinyltins with 9-BBN-H. While **2** exhibits normal oxidative and dehydroborylation behavior, unique reactivity is observed in its Pd-catalyzed coupling to bromobenzene where ring-opening is accompanied by the formation of a Sn-Ph bond.

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1. Graduate support provided by the NIH-MBRS program (S06-GM08102).
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11. To a stirred solution of PhBr (0.38 g, 2.42 mmol) and $Pd[PPh_3]_4$ (0.09 g, 0.08 mmol) in THF (5 mL), after 0.5 h, was added a mixture of **2** (0.81 g, 2.49 mmol) in THF (5 mL) and aqueous NaOH (0.9 mL of 3.0 M, 2.7 mmol). After 18 h at room temperature, pentane (20 mL) was added and the mixture was extracted with water (5 X 20 mL), concentrated and filtered through silica with pentane and reconcentrated to obtain 0.20 g of **16** (28%). Anal. Calcd for $C_{12}H_{18}Sn$: C, 51.30; H, 6.46: Found C, 51.55; H, 6.57.
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