1,2-Dihydro-1,3-stannaboroles *via* Organoboration of Functionally Tin Substituted Alkynylstannanes

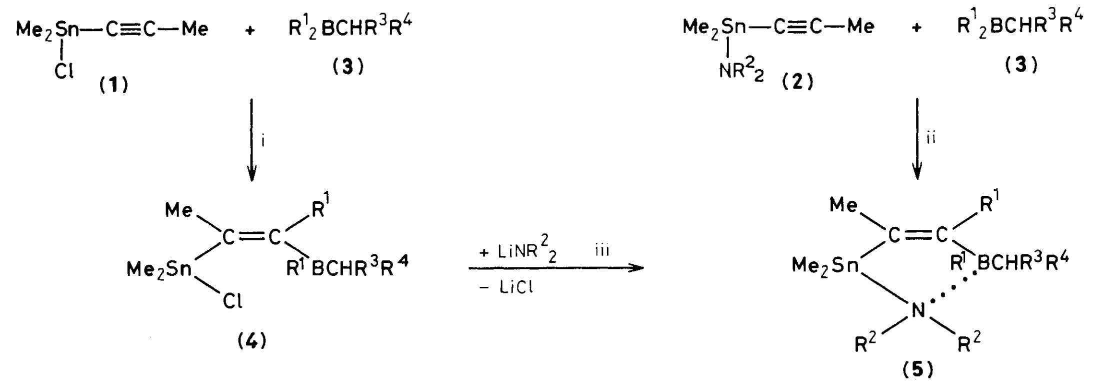
Susanna Kerschl and Bernd Wrackmeyer*

Institut für Anorganische Chemie der Universität München, Meiserstrasse 1, D-8000 München 2, Federal Republic of Germany

Organoboration of suitably substituted alkynylstannanes leads to alkenyl-diorganoboranes from which 1,2-dihydro-1,3-stannaboroles (**7**) may be obtained in high yield *via* intramolecular proton abstraction by a stannylamino group followed by amine elimination and Sn–C ring closure.

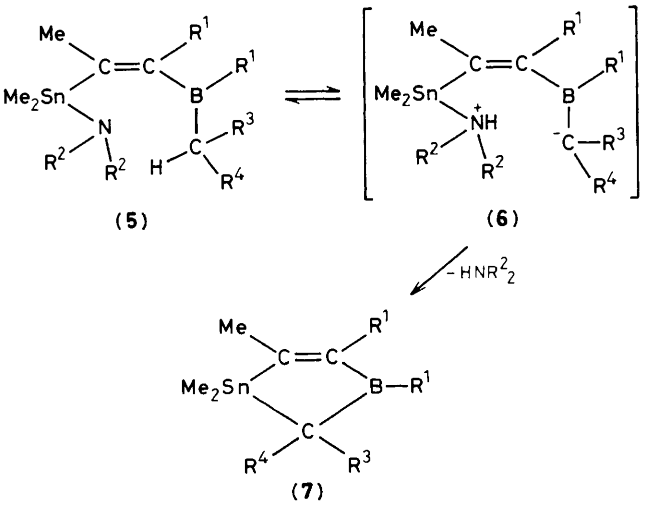
The 1,1-organoboration of alkynylstannanes[1] of the types (**1**) and (**2**) with trialkylboranes (**3**) provides a convenient stereospecific method for synthesising the useful alkenylboranes (**4**) and (**5**) in which the tin atom still carries a functional group (Cl, Br,[2] or NEt_2[3]) (Scheme 1). For the Sn–NEt_2 compound and R^1 = Me or Et, we have shown previously[3] that strong intramolecular N→B co-ordination is present. If the formation of a co-ordinatively saturated ate complex can be avoided the formation of α-carbanions is possible.[4] The stannylamino-moiety may function as an α-proton acceptor from a *B*-organyl group in (**5**) to give the intermediate (**6**) (Scheme 2). Therefore, we have now studied examples with substituents of greater steric bulk either on boron or on nitrogen.

As is evident from Scheme 2, the formation of a strong ate complex prevents proton abstraction in the *B*-ethyl compound (**5a**) which remains unchanged below 130 °C. In contrast, there is no evidence at all for the formation of the *B*-isopropyl analogue (**5b**). Heating to 60—70 °C in hexane is necessary to induce reaction between (**2**) (R^2 = Et) and (**3b**; R^1 = Pr^i, R^3 = R^4 = Me). Instead of (**5b**), compound (**7b**) and $HNEt_2$ are obtained in essentially quantitative yield. Compound (**5c**) is observed in a mixture together with (**7c**). The n.m.r. data for (**5c**) (absence of ^1H or ^{13}C resonances for diastereotopic



	R^1	R^2	R^3	R^4
a;	Et	Et	H	Me
b;	Pr^i	Et	Me	Me
c;	Bu^i	Et	H	Pr^i
d;	Et	Pr^i	H	Me
e;	Et	$SiMe_3$	H	Me

Scheme 1. *Reagents and conditions:* i, hexane, reflux, 2 h; ii, hexane, reflux, 2 h, for (**5a**) and (**5c**); iii, toluene, room temp., for (**5a**), (**5d**), and (**5e**). [(**5b**) could not be obtained].



Scheme 2. **a**—**e** as in Scheme 1. Results for loss of HNR^2_2 (in hexane):
(**5a**), no reaction below 130 °C.
(**5b**), reacts spontaneously at room temp.
(**5c**), slow reaction; 50—70 °C for 12 h for completion.
(**5d**), slow reaction; complete after ~12 h at room temp.
(**5e**), no reaction after 12 h at 80 °C.

methyl groups) suggest that the cleavage of the B–N bond in (**5c**) is rapid on the n.m.r. time-scale [in contrast to (**5a**)[3]]. Therefore, proton abstraction is only moderately hindered. Steric crowding at the nitrogen atom in (**5d**) (R^2 = Pr^i) also prevents strong ate complex formation and proton abstraction is the preferred course to give (**7a**). An alternative route to (**7a**) uses the transamination reaction of HNPr$^i_2$ with (**5a**) at elevated temperatures (80 °C in benzene). This leads to (**5d**) being in equilibrium with (**5a**) and the former, under these conditions, readily gives (**7a**). In the bis(trimethylsilyl)amino derivative (**7a**) the basicity of the nitrogen appears to be too low for proton abstraction.

The heterocycles (**7a**—**c**) can be purified by fractional distillation [(**7a**): b.p. 71 °C at 1.33 Pa; (**7b**): b.p. 75 °C at 1.33 Pa; (**7c**): b.p. 83 °C at 0.013 Pa]. They are colourless, oily, air- and moisture-sensitive liquids which are most conveniently characterized by their ^{1}H, ^{11}B, ^{13}C, and ^{119}Sn n.m.r. data.†

The title compounds belong to the class of geminal dimetallic compounds which are increasingly used in organic and organometallic syntheses.[5] Substituents in the 2-, 3-, 4-, or 5-positions in (**7**) can be varied widely. Therefore, a large variety of new heterocycles should be available, and there should be numerous synthetic applications of compounds (**7**) owing to the reactive Sn–C and B–C bonds.

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† Representative n.m.r. data (Bruker WP 200) for (**7a**—**c**) in C_6D_6 at 28 °C; δ-values (p.p.m.) are referred to internal Me_4Si (^{1}H), external BF_3–OEt_2 (^{11}B), external Me_4Si [^{13}C, $\delta^{13}C(C_6D_6)$ 128.0], and external Me_4Sn; coupling constants $|^nJ(^{119}Sn–^1H)|$ and $|^nJ(^{119}Sn–^{13}C)|$ in Hz are given in parentheses. (**7a**), δ(^{1}H): 0.10 [s] (53.1), 0.26 [s] (53.1) ($SnCH_3$); 0.8—1.3 [m] (BCH_2CH_3); 0.94 [t, *J* 7.3] (CH_2CH_3); 1.42 [d, *J* 6.7] (65.0) ($CHCH_3$), 1.64 [m] (CH); 2.00 [s] (56.0) (CH_3); 2.32 [d, *J* 11.9; q, *J* 7.3] (CH_2); 2.44 [d, *J* 11.9; q, *J* 7.3] (CH_2); δ(^{11}B): 75.2; δ(^{13}C): 158.9 (453.3) (SnC=); 168.5 (br.) (=CB); 29.5 (152.0) (br.) (SnCB); −8.1 (274.7), −10.2 (301.4) ($SnCH_3$); 19.9 (61.0) (=CCH_3); 23.3 (83.9) (=CCH_2); 15.1 (=CCH_2CH_3); 13.7 (br.) (BCH_2); 8.6 (BCH_2CH_3); 12.0, ($CHCH_3$); δ(^{119}Sn): 7.4; (**7b**), δ(^{11}B): 72.4; δ(^{119}Sn): 8.6; (**7c**), δ(^{11}B): 74.5; δ(^{119}Sn): −4.2.