

A versatile synthesis of 9-BBN derivatives from organometallic reagents and 9-(triisopropylsilyl)thio-9-borabicyclo[3.3.1]nonane

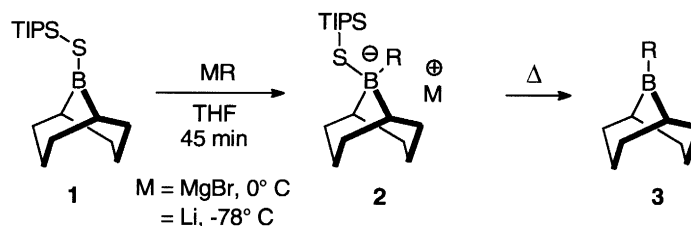
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Abstract

Representative B-substituted-9-BBNs (**3**) are efficiently prepared from either organolithium or Grignard reagents through their addition to (TIPS)S-9-BBN (**1**) which is readily available from TIPSSH and 9-BBN-H. The thermally induced collapse of the intermediate ‘ate’ complexes (**2**) produces **3** which is easily isolated in good yield and high purity. © 2000 Elsevier Science Ltd. All rights reserved.



For many important organoborane conversions (e.g. Suzuki–Miyaura coupling),¹ the greater Lewis acidity of trialkylboranes compared to more oxygenated counterparts (e.g. RB(OR')_2) can be advantageous. Among these reagents, 9-BBN derivatives (**3**) are often the reagents of choice because of the robust nature of the 9-BBN moiety which functions efficiently as spectator ligation in many such transformations.² Hydroboration provides many of these derivatives, but for those which cannot be prepared by this method, several organometallic routes exist, the most straightforward being the addition of organolithium reagents to B-MeO-9-BBN in hydrocarbon solvents.^{3a} In some cases (e.g. R=alkynyl), the intermediate ‘ate’ complex, Li[R(MeO)-9-BBN] is very stable and the addition of Lewis acids is required to produce **3**.⁴ Unfortunately, with the exception of MeMgX , the analogous Grignard process is unworkable because the intermediate complex (M=MgX) decomposes too easily leading to di-addition (e.g. $\text{M[R}_2\text{-9-BBN]}$) and unreacted B-MeO-9-BBN.^{3a} These complications and others^{3b–d} limit the generality of the method and for a number of applications of **3**, it is preferable to either prepare

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3 from 9-BBN-H and organocuprate reagents, or to generate **3** in situ from the exchange of *B*-Cl-9-BBN with RSnR'_3 .^{2,5}

We wish to report that (TIPS)S-9-BBN (**1**), which is easily prepared from 9-BBN-H and (TIPS)SH (1:1, 135–150°C (12 h), 85%, bp 143–146°C, 0.3 torr, ^{11}B NMR 81.7 (C_6D_6)),⁷ provides a simple entry to **3** through both organolithium and Grignard procedures (Table 1).⁸ With the exception of ViMgBr , the 1:1 adducts **2** are generally formed cleanly. Simply heating **2** under vacuum liberates **3**, which distills in pure form from the mixture (Table 1).⁸ Acidification of the residue (HCl (aq.)) gives (TIPS)SH with a minor amount (~3%) of its hydrolysis product, TIPSOH.

Table 1
Representative *B*-R-9-BBNs (**3**) from **1**

Entry	M	R	Yield (2) ^a	δ ^{11}B NMR(2) ^b	Yield (3) ^c	Temperature ^d (°C, Torr)
1	MgBr	Me (a)	>98	-18.0	73	105, 15
2	MgBr	Et (b)	>98	-19.2	57	35-40, 3
3	MgBr	Ph (c)	>98	-16.7	90	100, 0.5
4	MgBr	cyclopropyl (d)	>98	-16.6	68	100-105, 3
5	MgBr	allyl (e)	>90	-24.4	60	85-90, 3
6	MgBr	vinyl (f)	^e	^e	25 ^e	125, 3
7	MgBr	<i>n</i> -Bu (g)	>98	-15.3	82	105-110, 3
8	Li	<i>n</i> -Bu (g)	>98	-22.1	72	100, 0.3
9	Li	<i>t</i> -Bu (h)	>98	-16.8	71	52-60, 3
10	MgBr	1-hexynyl (i)	>85	-21.8	60	110-115, 0.1

^a ^{11}B NMR yield based on conversion to **2**. ^b 96.3 MHz ^{11}B NMR in C_6D_6 , referenced to $\text{BF}_3\cdot\text{EE}$ (δ 0.00 ppm). ^c Isolated yield of >98% pure material. ^d Distillation head temperature during thermal decomposition. ^e The low solubility of **2** in this case prevented its observation by ^{11}B NMR. Other species observed were **1** and the di-addition adduct.

In contrast to the behavior of **1**, the addition of BuMgBr to *B*-(*n*-PrS)-9-BBN (76.7)⁶ at 0°C, from ^{11}B NMR analysis, gives a 1:1 mixture of unreacted *B*-(*n*-PrS)-9-BBN and $\text{MgBr}[\text{Bu}_2\text{-(9-BBN)}]$ (−18.9). This reagent with *B*-(TIPSO)-9-BBN (57.1) produces ~1:1:1 mixture of this borate complex (−18.3), starting borane, and an intermediate complex assigned to the adduct ($\text{MgBr}[(\text{TIPSO})(\text{Bu})\text{-(9-BBN)}]$ −17.9), which is converted to *B*-Bu-9-BBN (87.7) upon treatment with Me_3SiCl . Thus, the unique ability of the STIPS group to stabilize **2** is critical to the success of this new route to **3**.

Acknowledgements

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8. Representative procedures: (RLi) To a solution of **1** (1.24 g, 4.0 mmol) in dry ethyl ether (10 mL) at –78°C was added *t*-BuLi (3.4 mL, 1.6 M). After 45 min, concentration and distillation (head temp. 52–55°C, 3 torr) gave 0.50 g (72%) of **1h**. (RMgX) To a solution of **1** (1.52 g, 4.8 mmol) in dry THF (10 mL) at 0°C was added *n*-BuMgBr (2.75 mL, 2.0 M in THF) dropwise. After 45 min, the system was allowed to reach 25°C, the solvents were removed in vacuo, and heating as above (92–95°C at 5 torr) gave 0.72 g (84%) of pure **1g**.