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NOVEL HYDROBORATING AGENTS FROM SILYLAMINE-BORANES

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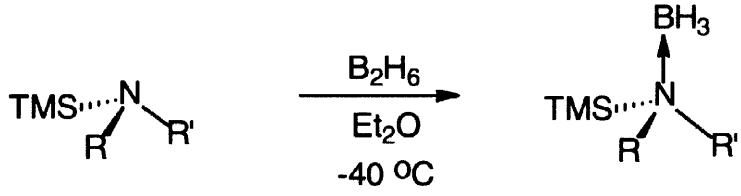
Abstract: *Exhibiting a broad spectrum of hydroboration reactivities, seven (7) new silylamine-borane complexes (1) were efficiently prepared from diborane and the corresponding silylated amines (2). Most are crystalline solids which are air-stable, concentrated borane sources. All provide convenient alternatives to other hydroborating agents, 2 undergoing complete hydrolysis to volatile and/or water soluble by-products upon aqueous work-up, thereby greatly facilitating the isolation of the borane-derived reaction products.*

Amine-boranes (BH_3-NR_3) offer the potential for attractive alternatives to the common laboratory sources of borane for hydroboration and other processes.[1] These complexes provide a stable, concentrated form of the reagent, and the high solubility of the amine by-products in an acidic aqueous medium greatly facilitates the isolation of the borane-derived products. However, they are often too stable to supply borane at ambient temperatures so that hydroboration proceeds at reasonable rates only at elevated temperatures which can be accompanied by the thermal isomerization of the organoborane.[1b,2] Both borane-THF[1a] and borane-dimethyl sulfide (BMS)[3] are effective borane sources at or below room temperature, but the former is only stable in solution (≤2.5 M) and with the latter, the dimethyl sulfide can contaminate reaction solvents and its oxidation by-products can interfere with the isolation of the borane-derived materials.[4] Using aryl or sterically demanding 3°-amines, the reactivities of the amine-boranes can be markedly enhanced,[5] but these modifications make the separation of the amine from the borane-derived product more difficult, requiring strongly acidic work-up procedures.[6] The construction of very hindered, less basic amines (*i.e.* **2**)[7] through the silylation of more water soluble 1°- or 2°-amines should also provide stable, yet highly reactive silylamine-boranes (**1**). However, the advantage in using **2** over traditional bulky amines is that they are readily hydrolyzed producing their soluble amine precursors and volatile silicon by-products, thereby greatly facilitating both product isolation and solvent recovery. Representative silylamine-borane complexes (**1**) were prepared as potential new borane sources.



2 **1**

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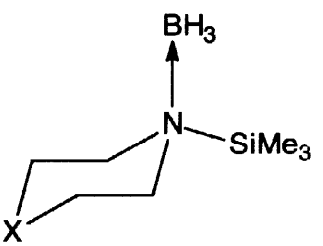
Table 1. Diborane-derived silylamine-borane complexes (**1**).

1	R	R'	^{11}B NMRδ (J_{B-H})[a]	Yield(%)[b]
a	*t*-Bu	H	-20 (99)	89
b	Et	Et	-14 (96)	89
c	*i*-Pr	H	-22 (95)	83
d	$-CH_2CH_2OCH_2CH_2-$		-18 (96)	85
e	$-CH_2CH_2CH_2CH_2CH_2-$		-17 (98)	94
f	*n*-Bu	H	-18 (94)	89
g	$-CH_2CH_2CH_2CH_2-$		-12 (98)	91

[a] Recorded at 96.5 MHZ (THF/C_5H_{12}) using C_6D_6 as an internal lock ($BF_3{\cdot}OEt_2$ δ 0.00). [b] Isolated yields of pure materials. Complexes **1a,c-e,g** are crystalline (mp 55(dec), 32-4, 83-5, 60-2 and 45-7 °C, respectively). The others melt too near to room temperature to record accurate values.

Seven (7) stable trimethylsilyl (TMS) amine-borane complexes (**1**) were readily prepared in excellent yields (83-94%) by the addition of diborane to the corresponding silylated amine (**2**) in diethyl ether at -40 °C followed by solvent removal *in vacuo* (Table 1). Each exhibited the expected upfield quartet in its ^{11}B NMR spectrum (Table 1). The single crystal X-ray structures of **1d,e** reveal that the borane moiety occupies an axial position in the chair conformation of the heterocyclic ring systems.[8] The following procedure for the preparation of **1d** is representative:



1d (X = O)
1e (X = CH_2)

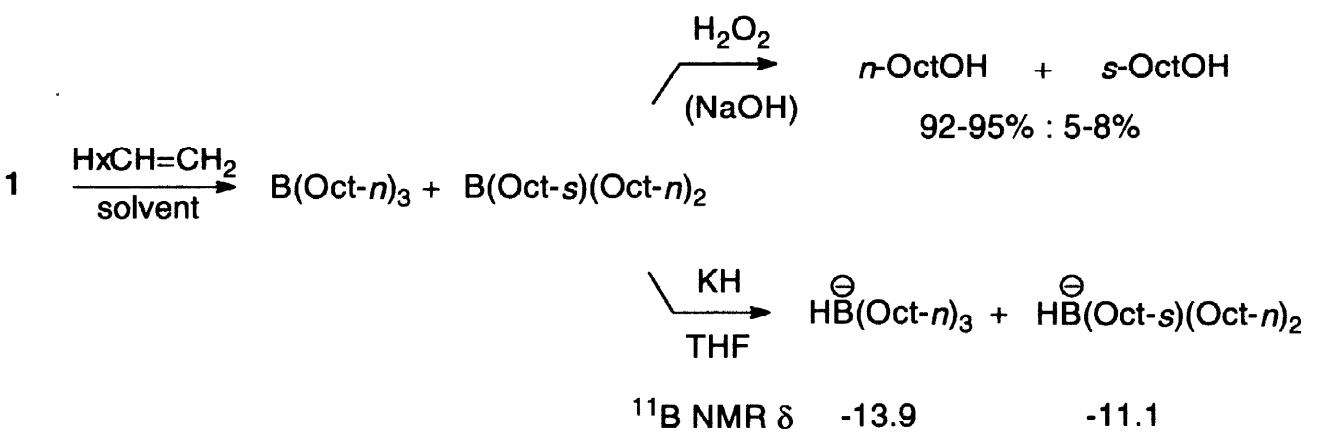
To a stirred solution of *N*-(trimethylsilyl)morpholine (16.0 g, 101 mmol) of in diethyl ether (160 mL) at -40 °C, contained in a glass pressure reactor equipped with an air-driven stirrer, reflux condenser, pressure inlet and exhaust safety valve, was added gaseous diborane (1.5 g, 54 mmol) carefully measuring the rate of addition employing an in-line calibrated flowmeter. After the addition was completed, the reaction mixture was transferred at -40 °C under positive nitrogen pressure to a second flask fitted with a solvent stripper. The solvents were removed *in vacuo* (0.25 Torr) employing a vacuum system equipped with dual vacuum traps, each containing methanol (~30 mL) to destroy any excess of diborane present in the reaction mixture. The residual material is essentially pure **1d** (14.8 g , 85%) obtained a crystalline white solid (mp 83-85 °C). ^{1}H NMR ($CDCl_3$) δ 4.42 (dt, *J* = 11.8, 1.9 Hz, 2 H), 3.60 (dd, *J* = 12.0, 3.7 Hz, 2 H), 2.95 (dt, *J* = 11.7, 3.4 Hz, 2 H), 2.63 (d, *J* = 12.0 Hz, 2 H), 0.38 (s, 9H) ; ^{13}C NMR ($CDCl_3$) δ 60.7, 49.9, -3.0; ^{11}B NMR ($CDCl_3$) δ -18 (q, *J* = 96 Hz);IR (CCl_4) 2970, 2942, 2883, 2393, 2297, 1449, 1280, 1193, 1120 cm^{-1}.

To determine their relative reactivities in the hydroboration process, each was examined in THF solution employing 3 equiv of 1-octene monitoring the reaction progress by ^{11}B NMR. This revealed a wide range of reactivities for **1**, with the *t*-butylamine derivative (**1a**) requiring only minutes at 25 °C while its pyrrolidine counterpart required heating to reach completion (65 °C, 2 h). However, all proved to be useful hydroborating

Table 2: Summary of the hydroboration-oxidation of 1-octene with **1**.

Complex	Temperature (°C)	Reaction Time	Regioselectivity External/Internal	GC Yield[a] without NaOH	GC Yield[a,b] with NaOH
1a	25	10 min	94:6	88	99(87)
1b	25	2 h	94:6	87	95(85)
1c	32	4 h	92:8	95	95(84)
1d	25	22 h	95:5	84	98(82)
1e	25	72 h	93:7	99	100(88)
1f	32	90 h	94:6	64	71(63)
1g	65	2 h	94:6	97	99(83)

[a] GC yield with internal hydrocarbon standard. [b] Isolated yield given in parentheses.



agents giving good-excellent yields of the 1- and 2-octanol (~94:6) products, often without requiring added base to facilitate the oxidation process (Table 2).[9] In each case, the hydrolysis of the silylamine **2** was complete after the oxidation of the organoboranes as evidenced by its absence in the reaction mixtures. Moreover, the GC analysis of the organic material prior to its concentration reveals the presence of the non-silylated amine, trimethylsilanol and hexamethyldisiloxane.

Like BMS, **1** is an effective hydroborating agent in a wide variety of solvents. We carried out the hydroboration of 1-octene with **1a** in representative solvents at 25 °C. Complete hydroboration occurs in < 10 min for THF, DME and ether, but is slower in benzene (2 h), hexane (0.5 h) and methylene chloride (2.5 h). In each case, an aliquot from the hydroboration mixtures was added to a slurry of KH in THF at 0 °C to form the borohydrides as a ~3:1 mixture of $KHB(Oct\text{-}n)_3$ and $KHB(Oct\text{-}s)(Oct\text{-}n)_2$, consistent with the observed regioselectivity of the hydroboration process.[10]

In summary, we have demonstrated that stable borane complexes (**1**) are readily prepared through the simple addition of diborane to **2**. These compounds provide new highly convenient borane sources for hydroboration, ranging in reactivity from minutes at room temperature (*e.g.* **1a**) to requiring elevated temperatures (*e.g.* **1g**) to complete the hydroboration of 1-octene. The reagents **1** can be used in many solvents, analogous to other common borane complexes such as BMS. However, unlike dimethyl sulfide, the amine by-products are easily removed from the organic solvents by aqueous extraction, a feature of these reagents attributable to the facile hydrolysis of **2** to its non-silylated 1°- or 2°-amine counterpart. Since the bulky 3°-amines normally required to obtain highly reactive amine-borane complexes are separable from the borane-derived product only through multiple acidic extractions, this useful feature of **2** greatly facilitates product isolation compared to these traditional alternatives.

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REFERENCES AND NOTES

1. (a) Brown, H. C. *Organic Syntheses via Boranes*, Wiley-Interscience: New York, 1975. (b) Soderquist, J. A. in *Encyclopedia of Inorganic Chemistry*, R. B. King (ed.), J. Wiley & Sons, Ltd.: London, UK , **1994**, *2*, 401.
2. Ashby, E. C. *J. Am. Chem. Soc.* **1959**, *81*, 4791.
3. Burg, A.; Wagner, R. I. *J. Am. Chem. Soc.* **1954**, *76*, 3307.
4. Brown, H. C.; Mandal, A. K. *J. Org. Chem.* **1980**, *45*, 916.
5. Brown, H. C.; Chandrasekharan, J. *J. Am. Chem. Soc.* **1984**, *106*, 1863.
6. Salunkhe, A. M.; Burkhardt, E. R.; *Tetrahedron Lett.* **1997**, *38*, 1519.
7. Fessenden, R.; Fessenden, J. S. *Chem. Rev.* **1961**, *61*, 361.
8. (a) Huang, S. D.; Medina, J. R.; Huertas, R.; Soderquist, J. A. *Acta. Cryst., in press.* (b) Huang, S. D.; Huertas, R.; Medina, J. R.; Soderquist, J. A. *J. Chem. Cryst., in press.*
9. General Procedure for the Hydroboration of 1-Octene: To a solution of **1a** (1.84g, 11.6 mmol) in THF (12 mL) at 25 °C was added 1-octene (4.7 mL, 30 mmol) dropwise. After 0.5 h, NaOH (0.5 mL, 3 M) was added cautiously (H_2 evolution) followed by H_2O_2 (5 mL, 30%) dropwise (exothermic!). The reaction mixture was heated at reflux temperature for 1h. After cooling to 25 °C, EE (25 mL) was added and the aqueous phase was saturated with NaCl (or K_2CO_3). The organic layer was separated and washed with saturated $NaHCO_3$ (3 x 15 mL) and water (2 x 15 mL), dried over K_2CO_3, filtered, concentrated and distilled to give 3.3 g (85%) of 1-octanol and 2-octanol. For the GC analyses, tetradecane was added as an internal standard, and after oxidation, K_2CO_3 is added to the reaction mixture, an aliquot was withdrawn from the organic phase, treated with MSTFA and analyzed.
10. Determination of Reaction Times and KH Analysis: As above, the reactions were monitored by ^{11}B NMR until the ratio of trialkylborane and **1** remained constant. After completion, an aliquot (0.5 mL) of the reaction mixture was added via syringe to a small vial containing KH (~0.1 g) and THF (~0.2 mL) at 0 °C. Centrifugation provides a clear supernatant which was analyzed by ^{11}B NMR.