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PAPER

Radical reductions of alkyl halides bearing electron withdrawing groups with *N*-heterocyclic carbene boranes†‡

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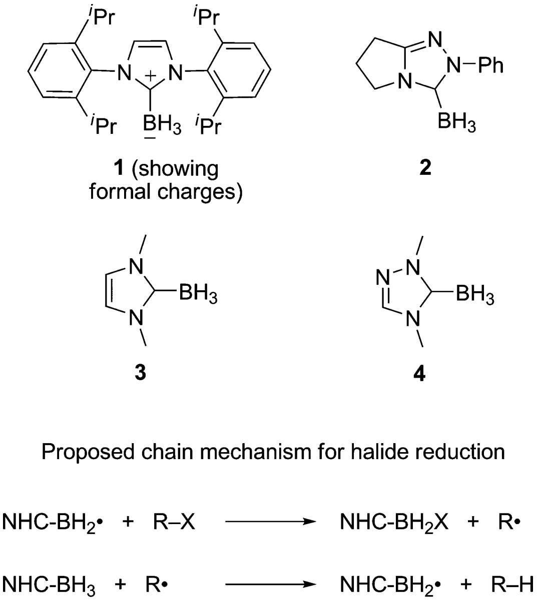
1,3-Dimethylimidazol-2-ylidene borane and 2,4-dimethyl-1,2,4-triazol-3-ylidene borane are found to be useful reagents for the reduction of alkyl iodides and bromides bearing nearby electron withdrawing substituents. Signatures of radical chain reactions are seen in many cases, but ionic reductions may also be occurring with some substrates. The reagents are attractive because of their low molecular weight, their availability from inexpensive precursors, and their stability. Separation of the borane products from the target products is readily accomplished either with or without prior regeneration of the borane for later reuse. 2,4-Dimethyl-1,2,4-triazol-3-ylidene borane is versatile because both starting borane and its derived products can be removed by extraction with water.

Introduction

Based on calculated bond dissociation energies, we recently predicted that *N*-heterocyclic carbene boranes (hereafter, NHC-boranes or NHC-BH_3) could serve as radical hydrogen atom donors.[1a] This prediction was then verified by the reductive deoxygenation of secondary xanthates with 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene borane **1** and 2-phenyl-1,2,4-triazol-3-ylidene borane **2** (Fig. 1).[1b] Subsequent rate constant measurements suggested that smaller and less expensive 1,3-dimethylimidazol-2-ylidene borane **3** and 2,4-dimethyl-1,2,4-triazol-3-ylidene borane **4** would be better reagents than **1** and **2**,[2] and indeed xanthate reductions with these reagents proceeded more rapidly and in higher yields.[3] Proposed radical chain mechanisms for the xanthate reductions have been supported by EPR spectra of intermediate NHC-boryl radicals (NHC-$BH_2\cdot$) and other experiments.[4]

In other radical chemistry, several NHC-boranes (including those in Fig. 1) show promise as co-initiators in radical photopolymerizations.[5] Preliminary EPR[4] and laser flash photolysis[5] experiments showed that NHC-boryl radicals abstract halogen atoms from alkyl halides. This in turn suggests that alkyl halides can be reduced by NHC-boranes by the radical chain mechanism shown in Fig. 1. However, we found that chain propagation was not very efficient in radical reduction of unfunctionalized alkyl iodides and bromides with **1** and **2**.[6] Instead, ionic reductions took place with suitable substrates (for example, 1°-alkyl halides) by heating at high temperatures (>100 °C) without any initiator.[7]



$$\text{NHC-BH}_2\cdot + \text{R–X} \longrightarrow \text{NHC-BH}_2\text{X} + \text{R}\cdot$$

$$\text{NHC-BH}_3 + \text{R}\cdot \longrightarrow \text{NHC-BH}_2\cdot + \text{R–H}$$

Fig. 1 Structures of *N*-heterocyclic carbene boranes used in reductive deoxygenation of xanthates and halides and a proposed radical chain mechanism for reduction of halides.

Like amine-boranes,[8] NHC-boranes have a formal negative charge on boron (see **1**) and are presumably best paired in reactions with radicals having electron withdrawing substituents due to polar effects.[9] Depending on location, such substituents may

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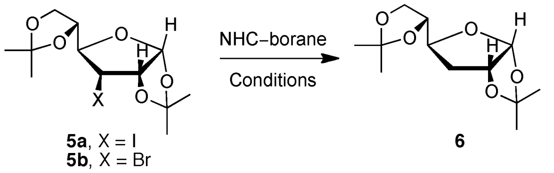
† Dedicated to the memory of Professor Athelstan L. J. Beckwith, 1930–2010

‡ Electronic supplementary information (ESI) available: Contains a table of experiments with admantyl iodide, experimental procedures for halide precursors **5a**, **5b**, **9**, **15a**, **17**, and **20**, timecourse data of ^{11}B NMR experiments for recovery of borane **3** and copies of spectra of precursors and products. See DOI: 10.1039/c0ob01075h

Table 1 Radical reductions of di-*O*-isopropylidene-3-halo-glucofuranoses **5a** and **5b**



Entry	Substrate	NHC borane	Conditions[a]	Yield **6**[b]
1	**5a**	**3**	A	77%
2	**5a**	**1**	A	35%[c]
3	**5a**	Š	A	23%[d]
4	**5b**	**3**	A	79%
5	**5b**	**1**	A	S.M.
6	**5a**	**3**	B	63%
7	**5b**	**3**	B	77%
8	**5a**	**3**	C	50%
9	**5b**	**3**	C	73%
10	**5a**	**4**	C	41%
11	**5a**	**4**	C	57%[e]
12	**5b**	**4**	C	72%
13	**5b**	**4**	C	63%[e]

[a] Conditions, A: Et_3B (1 equiv.), PhH, rt, 2 h. B: AIBN (1 equiv.), PhH, 80 °C, 2 h. C: $(t\mathrm{BuO})_2$ (1 equiv.), hν, 60 °C, 1 h. [b] Isolated by flash chromatography unless otherwise indicated. [c] Based on a 62% isolated yield of a 1.3/1 mixture of **6** and **5a**. [d] Reaction time extended to 18 h. [e] Isolated by washing with water and solvent evaporation only.

also discourage ionic reactions of the boranes with the halide precursors. Herein we show that NHC-borane reductions of alkyl halides with nearby electron withdrawing groups are both possible and potentially useful. However, the conditions needed to obtain good yields suggest that the radical chains are relatively short. Smaller boranes **3** and **4** are the preferred reagents, and the boron-derived products in reductions of **4** can be removed simply by water extraction. The recycling of reagent **3** is also demonstrated. These reagents are white solids that are stable to air and water.

Results and Discussion

We selected 3-iodo- (**5a**) and 3-bromo- (**5b**) di-*O*-isopropylidene glucofuranoses as representative hindered secondary halides that would resist ionic reduction but might be sensitive to radical reductions with carbene boranes. Both features follow because the halides are surrounded by electron withdrawing groups. The two halides were reduced at room temperature with triethylborane/air[10] (Conditions A), by heating at 80 °C with AIBN (Conditions B) and by photolysis at about 60 °C with di-*tert*-butyl peroxide (Conditions C). All reactions were conducted in benzene at 0.1 M substrate concentration. The results of this series of experiments are summarized in Table 1.

In a typical experiment under Conditions A, a flask containing a benzene solution of borane **3** (1 equiv.), iodide **5a** (1 equiv.), and Et_3B (1 equiv.) was sealed and the stopper was pierced with a needle to admit ambient air. After 2 h at room temperature, the solvent was evaporated and the crude product was purified by flash chromatography to provide **6** in 77% yield (Table 1, entry 1). A similar reduction with borane **1** provided 62% of a mixture of product **6** and starting iodide **5a** in a ratio of 1.3/1 (entry 2, 35% corrected yield of **6**).[11] To control for background reduction by triethylborane (alone or with residual water),[12] we conducted a similar experiment without adding **3** and by extending the reaction time from 2 h to 18 h. However, **6** was observed by ^{1}H NMR spectroscopy in only 23% yield (entry 3), and most of the remaining balance was starting iodide **5a** and other unidentified products. Reduction of bromide **5b** with **3** under Conditions A also occurred smoothly to provide **6** in 79% yield (entry 4). In contrast, **5b** was not reduced by **1** (entries 4 and 5).

In a typical AIBN experiment (Conditions B), a benzene solution of borane **3** (1 equiv), iodide **5a** (1 equiv.), and AIBN (1 equiv.) was heated at 80 °C for 2 h. The product **6** was isolated by flash chromatography in 63% yield. Likewise, bromide **5b** was reduced in 77% yield (entries 6 and 7). In a typical ^{t}BuOO^{t}Bu experiment (Conditions C), a benzene solution of borane **3** (1 equiv.), iodide **5a** (1 equiv.), and di-*tert*-butyl peroxide (1 equiv.) was placed in a tube and irradiated with a sunlamp for 1 h. The lamp warmed the solution to an estimated temperature of 60 °C. After cooling and solvent evaporation, standard flash chromatographic isolation provided **6** in 50% yield from iodide **5a** and 73% yield from bromide **5b** (entries 8 and 9).

Triazol-3-ylidene borane **4** is itself soluble in both benzene and water. So we speculated that it might be possible to conduct reactions in benzene and then to remove the borane-derived products by water extraction. We chose the ^{t}BuOO^{t}Bu Conditions (C) for these experiments because there are no non-volatile organic products generated from the initiator (di-*tert*-butyl peroxide). Pairs of experiments were conducted with iodide **5a** and bromide **5b** with standard purification by flash chromatography (entries 10 and 12) or with purification only by water extraction and solvent evaporation (entries 11 and 13). The yields of **6** were comparable (from **5a**, 41% and 57%; from **5b**, 72% and 63%), as were the purities.

The success of the water extraction procedure for removal of starting borane **4** and reagent-derived products is pleasing, especially since we are not completely sure what the reagent byproducts are. Speculation on what may occur is shown in Fig. 2.

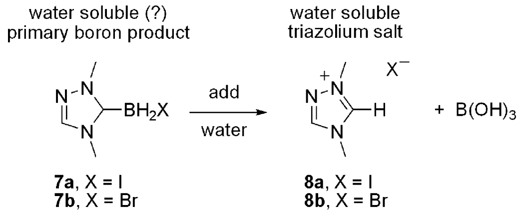
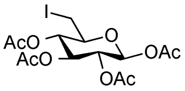
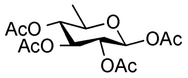
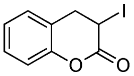
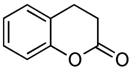
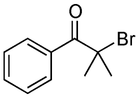
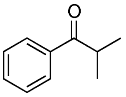
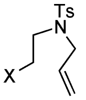
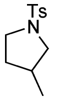
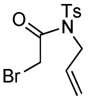
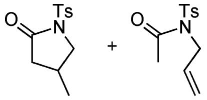
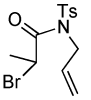
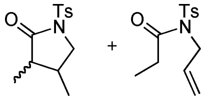


Fig. 2 Understanding the successful water workup procedure with **4**; possible fates of the borane-derived by-products.

Based on experiments with **1**[13a] (also see below), we expect that the boron halide **7a** or **7b** is the primary reaction product. It is not clear whether these halides are soluble in water or not. However, they may decompose when water is added to generate the *N*,*N*-dimethyltriazolium salt **8** and inorganic boron.[13b] Whatever is formed during the reductions from triazolylidene borane **4**, it is evidently more soluble in water than benzene.

We next selected NHC-borane **3** to survey the scope of reductions with a series of substrates, and the results of these reactions are summarized in Table 2.

Table 2 Reductions of iodides and bromides bearing electron withdrawing substituents with NHC-borane **3**

Entry	Substrate	Cond.^{a}	Equiv. **3**	Products, yields^b	
					
1	**9**	B	2	**10**, 67%	
2	**9**	C	1	**10**, 71%	
					
3	**11**	D	1	**12**, 70%^{c}	
					
4	**13**	A	2	**14**, 83%^{d,e}	
5	**13**	B	1	**14**, 76%^{d,f}	
					
6	**15a**, X = I	B	2	**16**, 61%	
7	**15a**, X = I	C	2	**16**, 60%	
8	**15b**, X = Br	B	2	**16**, 63%	
9	**15b**, X = Br	C	2	**16**, 77%	
					
10	**17**	B	1	**18**, 11%	**19**, 58%
11	**17**	B^g	1	**18**, 39%	**19**, 36%
12	**17**	C^h	1	**18**, 42%	**19**, 27%
					
13	**20**	B^g	1	**21**, 44%^{i}	**22**, 28%
14	**20**	C^g	1	**21**, 56%^{i}	**22**, 17%

^{a} Conditions, A: Et_3B (1 equiv.), PhH, rt, 2 h. B: AIBN (1 equiv.), PhH, 80 °C, 2 h. C: $(t\mathrm{BuO})_2$ (1 equiv.), hν, 60 °C, 1 h Δ, PhH, rt, 1 h. ^{b} Isolated by flash chromatography unless otherwise indicated. ^{c} Yield was determined by ^{1}H NMR analysis, the isolated yield was 60%. ^{d} Yield was determined by GC analysis. ^{e} Reduction without the NHC-borane gave **14** in 21% yield. ^{f} Reduction without AIBN gave **14** in 23% yield. ^{g} 0.02 M. ^{h} 0.01 M. ^{i} 4.5/1 *trans/cis*.

The substrates were selected to have one or more electron withdrawing groups, sometimes conjugated to the radical precursor (**11**, **13**, **17**, **20**), other times operating only by inductive effects (**9**, **15a,b**). Conditions were the same as A–C above (benzene, 0.1 M) unless otherwise indicated. In several cases, higher yields were obtained with 2 equiv. of borane **3**, so this variable is also featured in Table 2. Reported yields are again isolated unless otherwise indicated.

Reduction of tetra-*O*-acetyl-6-iodo-β-D-glucopyranose **9** under Conditions B (AIBN, heat) and C (^{t}BuOO^{t}Bu, photolysis) provided **10** in 67% and 71% yield, respectively. In the first experiment with 3-iodo-3,4-dihydrocoumarin **11**, we observed that reduction was occurring at rt even before any initiator was added. The reduction was complete after 1 h (Conditions D), and 3,4-dihydrocoumarin **12** was formed in 70% according to NMR spectroscopic analysis (entry 3). Flash chromatography provided pure **12** in 60% yield.

Reduction of 2-bromo-2-methyl-1-phenyl-1-propanone **13** provided 2-methyl-1-phenyl-1- propanone **14** in 83% yield under Et_3B initiation (A, entry 4) and 76% yield under AIBN initiation (B, entry 5). Complementary control experiments were conducted for each of these two experiments (see Table footnotes). When the NHC-borane was omitted from entry 4, the yield of **14** was reduced to 21%. And when the AIBN was omitted from entry 5, the yield of **14** was reduced to 23%.

Reduction of *N*-allyl-*N*-(2-haloethyl)-4-methyl-benzene-sulfonamide as either the iodide **15a** or the bromide **15b** provided good yields of cyclized product **16** under either AIBN (B) or ^{t}BuOO^{t}Bu (C) conditions (entries 6–9, yields 60–77%). There was no evidence for formation of the directly reduced product (*N*-allyl-*N*-ethyl-4-methylbenzene-sulfonamide) in any of these experiments. In contrast, reductions of *N*-allyl-*N*-(2-bromoethanoyl)-4-methylbenzene-sulfonamide **17** and the propanoyl analog **20**[14] gave mixtures of directly reduced and cyclized/reduced products under all conditions studied. Reduction of **17** under AIBN conditions (B) provided 11% of **18** and 58% of **19** at 0.1 M and 39% of **18** and 36% of **19** at 0.02 M. A ^{t}BuOO^{t}Bu (C) experiment at 0.01 M provided 42% of **18** and 27% of **19**. Reduction of **20** with AIBN (B) at 0.02 M gave 44% of **21** and 28% of **22** while a ^{t}BuOO^{t}Bu (C) reduction at the same concentration gave the same two products in 56% and 17% yield.

The results in Table 2 confirm that radical reductions of halides bearing electron withdrawing groups can indeed be practical. The control experiments with **13** and the exclusive (from **15a,b**) or partial (from **17** and **20**) formation of cyclized products support a radical chain mechanism. However, it is not clear that a radical chain mechanism can account for all of the results in Table 2. For example, iodocoumarin **11** is reduced without initiator, but in all other cases relatively large amounts of initiator are needed to consume the precursors. And directly reduced products **19** and **22** were isolated from the reductions of **17** and **20**, even though NHC-borane **3** is a relatively modest hydrogen atom donor (at least towards 2°-alkyl radicals).[2] So some of the products from these experiments could originate from ionic reductions. If so, then NHC-borane **3** must be much more reactive in such reactions than previously studied **1**.[7]

To close the study, we briefly investigated the prospects for recovery of the NHC-borane **3** after halide reduction. This is possible in principle because **3** is a robust white solid, stable under ambient laboratory conditions, flash chromatography, moisture, *etc.* The results of these experiments are summarized in Fig. 3.

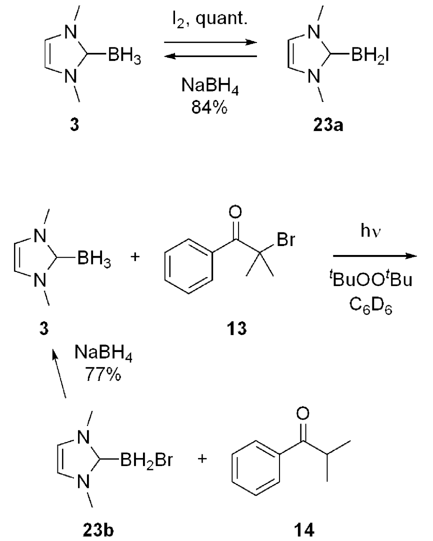


Fig. 3 Characterizing and recycling boron halides **23a,b**.

First, a solution of NHC-borane **3** in C_6D_6 in an NMR tube was treated with 0.5 equiv. of diiodine (I_2). Bubbling ceased after 10 min, and both ^{1}H and ^{11}B NMR spectroscopic analysis showed rapid and essentially quantitative formation of a new product assigned as boron iodide **23a** (δ −32.7, triplet in ^{11}B NMR spectrum), see Supporting Information‡. To the solution containing **23a** was added 2 equiv. of a 2 M solution of $NaBH_4$ in triethyleneglycol dimethyl ether. After 30 min, the resonance for **23a** had disappeared and that for **3** (δ −36.4, quartet) had reappeared along with another small resonance of an unknown boron product at (δ −23.7, broad). Standard workup and flash chromatography returned **3** in pure form in 84% yield.

To extend this proof-of-principle to an actual reduction, we irradiated a solution of **13**, **3** and ^{t}BuOO^{t}Bu in an NMR tube in C_6D_6 (Conditions C). After 15 min, **13** was consumed and the only observable products were **14** (from the ^{1}H NMR spectrum), boron bromide **23b** (from the ^{11}B NMR spectrum, δ −22.5, triplet), and few excess of NHC-borane **3**. A solution of $NaBH_4$ (2 equiv.) was added gradually. After 3 h, the reaction mixture was worked up and the crude product was purified by flash chromatography to return **3** in 77% yield. These results suggest that it should be generally possible to recover borane **3** from preparative halide reductions.

Conclusions

This study begins to establish the scope and utility of radical reductions of halides by NHC-boranes. Unlike xanthates, unfunctionalized alkyl halides are not reduced very efficiently by existing NHC-borane reagents under radical chain conditions. However, ionic reductions can be expected for suitably reactive substrates.[7] In contrast, halides bearing electron withdrawing groups can be reduced in good yields by reagents **3** and **4** by initiation with Et_3B/air, with AIBN/heat or with ^{t}BuOO^{t}Bu/photolysis.

Compared to related reductions with current standard reagents like tributyltin hydride[15] and *tris*-trimethylsilyl silicon hydride,[16] the new reagents have both advantages and disadvantages. On the down side, the scope of halide reductions with **3** and **4** does not begin to approach that of Bu_3SnH or even $(TMS)_3SiH$.[6] These reagents reduce all sorts of halides (diverse alkyl, aryl, alkenyl, *etc.*) rapidly and in high yields. Typically, large amounts of initiator are not needed. In contrast, the scope of radical reductions with **3** and **4** seems limited to alkyl halides with electron withdrawing substituents. And even with such substrates, large amounts of initiator (1 equiv.) and sometimes even excess borane (up to 2 equiv.) speed the reaction and improve the yields. These observations suggest that the chains with **3** and **4** are relatively short.

On the up side, for those substrates that do work, NHC-boranes **3** and **4** have a lot of practical advantages. Having only second row elements, these reagents have low molecular weights (110 and 111 amu, respectively) and lack the toxicity detractions of tin. They are stable solids that are easy to handle, react, separate from target products, and recover for reuse. And they are made in simple processes from inexpensive precursors. This goes especially for **3**, which has recently been made from the common, inexpensive ingredients *N*-methyl imidazole, dimethyl carbonate and borane-dimethyl sulfide.[17] Because of these attractive features, further study of the scope of radical reductions with existing NHC-boranes and study of new and potentially improved boranes are worthwhile objectives.

Experimental

General Remarks

The following compounds were prepared by previously published procedures: carbene-borane complexes **1**, **3**, **4**;[1–4] and halide precursors **11**,[18] and **15b**.[19,20]

Conditions A, General procedure for triethylborane initiated free radical reactions

Triethylborane (1 M solution in hexane, 0.1 mmol) was added to a solution of the borane (0.1 mmol) and the substrate (0.1 mmol) in benzene (1 mL). The septum was pierced with a needle to admit ambient air. The colorless solution was stirred for 2 h. Then the solvent was evaporated and the crude product was purified by flash column chromatography.

Conditions B, General procedure for AIBN initiated free radical reactions

AIBN (0.1 mmol) was added to a solution of the borane (0.1 mmol) and the substrate (0.1 mmol) in deoxygenated benzene (1 mL). The colorless solution was refluxed for 2 h. After cooling to room temperature, the solvent was removed and the residue was purified by flash column chromatography.

Conditions C, General procedure for di-*tert*-butylperoxide initiated free radical reactions

Di-*tert*-butylperoxide (0.1 mmol) was added to a solution of the borane (0.1 mmol) and the substrate (0.1 mmol) in deoxygenated benzene (1 mL). The colorless solution was charged in a quartz NMR tube and irradiated with a sunlamp for 1 h. The air temperature around the NMR tube was measured as 60 °C. After 1 h, the mixture was cooled, the solvent was evaporated, and the crude product was purified by flash column chromatography.

Water extraction procedure: After irradiation of the reaction solution with a sunlamp for 1 h, the reaction solution was diluted with 30 mL of pentane and washed with 30 mL of water (×3). The organic layer was dried ($MgSO_4$), and concentrated to give the desired product.

Borane recovery after the reaction with iodine

A mixture of iodine (12.7 mg, 0.05 mmol) and dimethylimidazol-2-ylidene borane **3** (11.0 mg, 0.1 mmol) in 1 mL of benzene-d_6 was charged in a quartz NMR tube and kept at room temperature for 10 min until the generation of bubbles ceased. The reaction progress was monitored by ^1H and ^{11}B NMR spectroscopy and 100% conversion was observed (Figure S1, Supporting Information‡). To the reaction mixture was added 0.1 mL of the solution of $NaBH_4$ (2 M in triethyleneglycol dimethylether), and the conversion of BH_2I to borane was complete after 30 min. The reaction mixture was loaded onto a silica gel column for flash chromatography (elution with $CH_2Cl_2 : MeOH = 99 : 1$) to give the starting borane complex **3** as a white solid (9.2 mg, 84%).

Procedure for recovery of starting borane 3 after halide reduction

A mixture of 2-bromoisobutyrophenone **13** (22.7 mg, 0.1 mmol) and dimethylimidazolylidene borane **3** (11.0 mg, 0.1 mmol) in 1 mL of benzene-d_6 was charged in a quartz NMR tube and irradiated by a sunlamp for 15 min. The air temperature around the NMR tube increased to 60 °C. The reaction progress was monitored by ^1H and ^{11}B NMR spectroscopy and 100% conversion was observed after 15 min irradiation. To the reaction mixture was added 0.05 mL of the solution of $NaBH_4$ (2 M in triethyleneglycol dimethylether), and the conversion was monitored by ^{11}B NMR spectroscopy (Figure S2, Supporting Information‡). To the reaction solution was added 0.1 mL of the solution of $NaBH_4$ (2 M in triethyleneglycol dimethylether), and then another 0.05 mL of the solution of $NaBH_4$ (2 M in triethyleneglycol dimethylether). The NMR tube was kept at room temperature for 3 h, and the conversion was complete. The reaction mixture was loaded to a silica gel column for flash chromatography (elution with $CH_2Cl_2 : MeOH = 99 : 1$) to give the starting borane complex **3** as a white solid (8.5 mg, 77%).

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Notes and references

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