evaporation gave 4.75 g of a colorless oil. The colorless oil is purified by vacuum distillation at 34-35 °C (13 Torr) or 20-21 °C (0.6 Torr) via short-path vacuum distillation to provide 5 as a pure sample. A Kugelrohr bulb to bulb distillation at 65-68 °C (13 Torr) provides 1.66 g of 5 (64.0% overall yield) on a 14.3 mmol scale reaction of 1 and 2. Compound 5: ^{1}H NMR (dd, 6.42 with J_{H-H} = 7 Hz, 1 H), (d, 4.72 with J_{vic-HF} = 16 Hz, 2 H), (m, 4.36, 2 H); IR (neat film) cm^{-1} 3130, 3060 (=CH), 3000, 2940, 2900 (sat. CH), 1645 (C=C), 1600, 1300 (NO_2); mass spectrum m/e 181 (1.2) M + 1, 180 (19.3) M$^+$, 134 (5.6), 88 (16.4), 62 (24.9), 46 (33.4), 45 (79.8), 44 (27.5), 43 (21.2), 42 (30.9), 30 (100) base. Isolated acetaldehyde byproduct 11: ^{1}H NMR (quart, 9.74, 1 H), (d, 2.15, 3 H); IR (CCl_4 solution) cm^{-1} 3052, 2986 (CH and CH_3), 1730 (C=O); mass spectrum m/e 44 (45.5) M$^+$, 43 (29.1), 29 (100) base, 28 (44.0).

Synthesis of 2,2-Dinitropropyl Vinyl Ether (Product 6). A 250-mL single-necked round-bottom flask was charged with 3.50 g (50.0 mmol) of 1, 100 mL of CH_2Cl_2, 7.50 g (50.0 mmol) of 3, and a Teflon-coated magnetic stirring bar. To the stirred solution was added 0.50 g of HgO followed by 500 μL of TFAA. The reaction flask was fitted with a water-cooled reflux condenser topped with a Drierite-filled drying tube. The reaction was stirred at reflux temperature 17.5 h. The CH_2Cl_2 solvent was removed by rotary evaporation leaving a slightly yellow oil. The oil was placed onto a short column prepared by packing 15.0 g of neutral aluminum oxide (pH 6.9) slurried in CCl_4 into a 30-mL "coarse" glass-sintered Buchner funnel. Elution with 40 mL of CCl_4 and solvent removal by rotary evaporation gave 7.52 g of a slightly yellow oil. The crude oil is purified by vacuum distillation at 38.2-40.0 °C (0.2 Torr) giving 5.64 g (64.2%) of 6 as a colorless oil: ^{1}H NMR (dd, 6.42 with J_{H-H} = 7 Hz, 1 H), (s, 4.51, 2 H), (m, 4.27, 2 H), (s, 2.23, 3 H); IR (neat film) cm^{-1} 3110, 3060 (=CH), 2980, 2940, 2880 (sat. CH), 1640, 1625 (C=C), 1570, 1320 (NO_2); mass spectrum m/e 177 (0.8) M$^+$, 133 (7.2), 84 (68.6), 57 (46.2), 44 (35.5), 43 (57.1), 41 (100) base, 39 (83.4), 30 (75.7). Anal. Calcd for $C_5H_8N_2O_5$: C, 34.1; H, 4.54; N 15.9; O 45.5. Found: C, 33.8; H, 4.70; N, 16.0; O by difference, 45.4.

Synthesis of 2,2,2-Trinitroethyl Vinyl Ether (Compound 7). A 100-mL single-necked, round-bottom flask was charged with 1.50 g (21.4 mmol) of 1, 50 mL of CH_2Cl_2, 3.62 g (20.1 mmol) of 4, and a Teflon-coated magnetic stirring bar. To the stirred solution was added 0.10 g of HgO followed by 500 μL of TFAA. The reaction flask was fitted with a water-cooled reflux condenser topped with a Drierite-filled drying tube. The reaction was stirred at reflux temperature for 16.25 h.[13] The CH_2Cl_2 solvent was removed by rotary evaporation leaving an orange oil. The oil was placed onto a short column prepared by packing aluminum oxide (pH 7.3) slurried in CCl_4 in the manner already described. The unreacted alcohol 4, however, remained upon CCl_4 solvent removal. Hexane elution of the crude product oil through a 1.5- × 34.0-cm SiO_2 (60/200-mesh) chromatographic column followed. Hexane removal via rotary evaporation gave 1.59 g (25.9%) of 7 as a slightly yellow oil: ^{1}H NMR (dd, 6.44 with J_{H-H} = 8 Hz, 2 H), (s, 4.98, 2 H), (m, 4.43, 2 H); IR (neat film) cm^{-1} 3140, 3060 (=CH), 3000, 2940, 2900 (sat. CH), 1645 (C=C), 1600, 1300 (NO_2).

Synthesis of 3-Hydroxy-2,2-dinitropropyl Vinyl Ether (Compound 8).[14] A 250-mL three-necked, round-bottom flask was charged with 1.59 g (7.67 mmol) of 7, 20 mL of methanol, and 6 mL of 30% H_2O_2. One side neck was fitted with a 30-mL pressure-equalized addition funnel and the other side neck with a ground-glass thermometer assembly. The center neck was fitted with an overhead mechanical stirring motor and assembly. The stirred solution was cooled to -15 °C, and then a solution containing 3.50 g of NaOH in 7 mL of 1:1 H_2O/methanol was added dropwise to the stirred solution at a rate to keep the reaction temperature at -4 °C or lower. After addition was complete, the cold bath was removed and the reaction came to room temperature. Next, enough water was added to dissolve all solids and two layers formed.[15] Six mL of 37% formaldehyde solution was added dropwise to the stirred solution such that the reaction temperature remained at 33 °C or lower. The heterogeneous slurry homogenized into an orange solution which then was warmed gently to 40 °C. Enough concd HCl (37%) was added to effect pH 2 (pH Hydrion paper), and a lemon yellow solution appeared. The reaction solution was placed into a freezer (ca. -10 °C) over the weekend, and oil droplets formed in the reaction mixture. Most of the methanol was removed by rotary evaporation, and a CH_2Cl_2 extraction followed. The CH_2Cl_2 extract was dried over anhyd $MgSO_4$. Gravity filtration and CH_2Cl_2 removed by rotary evaporation produced 0.70 g of a yellow oil. The yellow oil was eluted through a 1.5- × 20.0-cm 60/200-mesh SiO_2 column packed with hexane. Elution was begun with hexane followed by incremental 10, 15, 20, 50, and 75% CH_2Cl_2-hexane enrichments. Early fractions produced 0.29 g (19.2%) of nearly pure 8. Compound 8 could be vacuum distilled with a molecular still at 55 °C (0.3 Torr): ^{1}H NMR (dd, 6.42 with J_{H-H} = 7 Hz, 1 H), (s, 4.64, 4 H),[16] (m, 4.44, 2 H), (broad t, 2.78, 1 H); IR (neat film) cm^{-1} 3500 (OH), 3060 (=CH), 2960, 2900 (sat. CH), 1640 (C=C), 1575, 1320 (NO_2); mass spectrum m/e 192 (M$^+$).

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(13) Aliquots taken during this reaction indicate it apparently proceeds much more slowly than the analogous reactions with alcohols 2 and 3.

(14) The denitrosation/formalation of 7 to form 8 was based upon a procedure described in: Hall, T. N.; Shipp, K. G. *NOLTR 61-2*, 21 Mar 1961, 10.

(15) Because H_2O_2 can react violently with aqueous formaldehyde solution, enough water is added to achieve complete solubility at room temperature (ref 9).

(16) The singlet at δ 4.64 has some overlap with the split multiplet at δ 4.44; however, the total integration of both spectral sets is the correct 6 H (Figure 1).

A New Class of Enantioselective Organoboron Reducing Agents. BH_3 Complexes with Chiral Terpenic 1,2-Azaboracyclohexanes†

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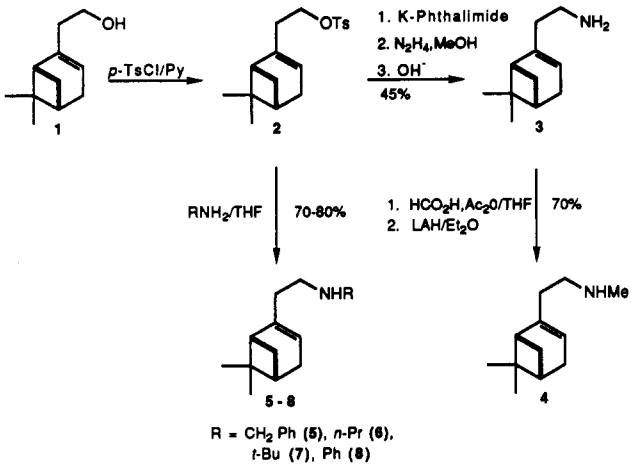
In the last few years, remarkable achievements have been made in the area of enantioselective boron reducing agents.[1,2] For example, chiral oxazaborolidines may be used as catalysts in the BH_3 reduction of ketones.[2] Herein we describe a new class of enantioselective boron reducing agents, BH_3 complexes of *N*-alkyl-10,10-dimethyl-5-aza-6-boratricyclo[7.1.1.0^{2,7}]undecanes.

It was found that various secondary nopylamines (4-8), easily prepared according to Scheme I from nopol (1)

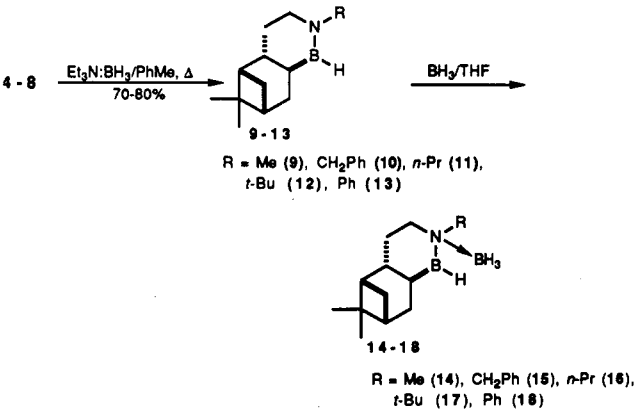
† We dedicate this paper to Professor H. C. Brown on the occasion of his 80th birthday.

0022-3263/92/1957-2953$03.00/0

Scheme I



Scheme II



through nopyl tosylate (**2**), could be hydroborated with borane–triethylamine complex in refluxing toluene to produce cyclic *N*-alkylazaboranes **9–13** in high yields. The stereochemistry of **9–13** is assumed to be the same as that observed in the hydroboration of α-pinene.

Cyclic azaborane derivatives of this type are very poor reducing agents toward ketones.[3] For example, reduction of acetophenone with *N*-propylazaborane **11** proceeds very slowly at room temperature and after 72 h gives (*S*)-(−)-1-phenylethanol in 25% yield and 15% ee. On the other hand, lithium, sodium, and potassium aminoborohydrides prepared by reactions of azaborane derivatives **11** and **12** with *t*-BuLi, NaH, and KH reduce acetophenone at room temperature in 10–20% ee.[3]

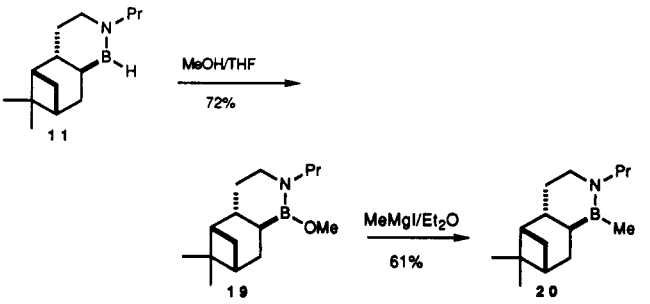
We next examined the BH_3 complexes of the azabora derivatives and found that ketone reductions occur much faster and with much higher enantioselectivities. It is well-known[4] that aliphatic amine boranes usually do not reduce ketones at room temperature in THF without the presence of a Lewis acid. The increased reactivity of the borane complexes may be explained in the same manner as proposed by Corey for reductions with chiral oxazaborolidine–BH_3 complexes.[2] Thus, the boron of the cyclic azaborane compound presumably complexes the carbonyl oxygen and activates it toward reduction.

Table I. Reductions with Borane Complexes[a]

run	reagent	ketone	yield (%)	ee (%)
1[b]	14	PhCOMe	67	76
2[c]	15	PhCOMe	91	64
3[b]	16	PhCOMe	87	77
4[d]	16	PhCOMe	80	35
5[c]	16	HexCOMe	76	64
6[c]	16	*t*-BuCOMe	61	82
7[b]	19	PhCOMe	69	74
8[c]	20	PhCOMe	70	31

[a] All reductions were carried out in THF at room temperature, ratio of reagent:BMS:ketone = 1.6:1.3:1. [b] 1 h at room temperature. [c] Overnight at room temperature. [d] 1 equiv excess of BH_3 was used, reaction time 5 min at room temperature.

Scheme III



Freshly distilled liquid azaboracyclohexanes **9–13** exist predominantly in THF solution as monomers (^{11}B NMR), but they will slowly undergo dimerization. Borane (BH_3) complexation for the *N*-methyl (**9**), *N*-benzyl (**10**), and *N*-propyl (**11**) derivatives occurs quantitatively in THF within a few minutes at room temperature according to ^{11}B NMR spectroscopy. The *N*-*tert*-butyl (**12**) and *N*-phenyl (**13**) compounds react with BH_3 very slowly. The formation of the appropriate complexes were not complete even after 2 days, despite an excess of the starting azaborane.

Complexes **14–16**, formed in situ, have been used for asymmetric reduction of acetophenone. The best results were obtained when borane–methyl sulfide (BMS) in THF was used as a source of BH_3, reductions were carried out in THF solution at room temperature, and an excess of starting azaborane derivative was used. The results are shown in Table I.

Among tested complexes, the best enantioselectivity for acetophenone reduction was achieved using the *N*-propyl–BH_3 complex **16**. It gave also rather high enantiomeric excesses when the aliphatic ketones 2-octanone and 3,3-dimethyl-2-butanone (runs 5 and 6) were reduced. Unfortunately, we have found (run 4) that this type of azaborane compound cannot be used in catalytic quantities for the asymmetric reduction of ketones.

To extend our knowledge about this type of reagent, we have also prepared two derivatives of compound **11** functionalized on boron. The *B*-methoxy (**19**) and *B*-methyl (**20**) analogues were prepared according to Scheme III and used for asymmetric reduction of acetophenone as

(1) For leading references see: Seyden-Penne, J. *Reductions by the Alumino- and Borohydrides in Organic Synthesis*; VCH Publishers: New York, 1991. Brown, H. C.; Park, W. S.; Cho, B. T.; Ramachandran, P. V. *J. Org. Chem.* **1987**, *52*, 5406. Brown, H. C.; Ramachandran, P. V. *Acc. Chem. Res.* **1992**, *25*, 16.

(2) Itsuno, S.; Sakarai, Y.; Ito, K.; Hirao, A.; Nakahama, S. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 395. Corey, E. J.; Bakshi, R. K.; Shibata, S. *J. Am. Chem. Soc.* **1987**, *109*, 5551. Corey, E. J.; Bakshi, R. K.; Shibata, S. *Ibid.* **1987**, *109*, 7925. Corey, E. J.; Shibata, S.; Bakshi, R. S. *J. Org. Chem.* **1988**, *53*, 2861. Corey, E. J.; Link, J. O. *Tetrahedron Lett.* **1988**, *30*, 6275. Corey, E. J.; Bakshi, R. K. *Ibid.* **1990**, *31*, 611. Mathre, D. J.; Jones, T. K.; Xavier, L. C.; Blacklock, T. J.; Reamer, R. A.; Mohan, J. J.; Jones, E. T. T.; Hoogsteen, K.; Baum, M. W.; Grabowski, E. J. J. *J. Org. Chem.* **1991**, *56*, 751. Jones, T. K.; Mohan, J. J.; Xavier, L. C.; Blacklock, T. J.; Mathre, D. J.; Sohar, P.; Jones, E. T. T.; Reamer, R. A.; Roberts, F. E.; Grabowski, E. J. J. *J. Org. Chem.* **1991**, *56*, 763.

(3) Kazubski, A. Unpublished results.

(4) Lane, C. F. *Aldrichimica Acta* **1973**, *6*, 51. Hutchins, R. O.; Learn, K.; Nazer, B.; Pytlewski, D. *Org. Prep. Proced. Int.* **1984**, *16*, 335. Brown, H. C.; Murray, L. T. *Inorg. Chem.* **1984**, *23*, 2746.

BH_3 complexes (Table I, runs 7, 8). While the *B*-methoxy compound exhibited good asymmetric induction, the *B*-methyl compound showed reduced selectivity. Presumably increased steric hinderance around boron and the amine prevents formation of the amine–borane complex or ketone–borane complex, and this results in a decrease in enantioselectivity.

In conclusion, we have explored a new class of terpenic organoboron asymmetric reducing agents—BH_3 complexes of *N*-alkylazaboranes. Our preliminary results have demonstrated their use for reductions of prochiral ketones with modest to high enantioselectivity (60–82%). Aliphatic and aromatic ketones are reduced with equal efficiency. Large groups on nitrogen prevent the formation of the required borane complex while smaller groups on nitrogen tend to favor formation of a dimeric species. In order to obtain an effective reagent, the size of the groups on boron and nitrogen must be properly balanced.

Experimental Section

General Comments. All air- and moisture-sensitive materials were handled following standard procedures.[5] THF was freshly distilled from benzophenone–potassium ketyl under N_2. Nopol (Aldrich) was distilled prior to use (bp 54–55 °C (0.005 Torr), $[\alpha]^{25}_D$ −37.45° (neat, d = 0.96), 94% ee). Ketones were freshly distilled from CaH_2. ^1H and ^{13}C spectra were recorded in $CDCl_3$ on a JEOL FX200 (200-MHz) instrument. ^{11}B NMR spectra were recorded on a Nicolet 300-MHz wide-bore NMR (at 96.272 923 MHz) with BF_3·Et_2O as an external standard (0.00 ppm).

Preparation of *N*-Benzyl-, *N*-Propyl-, *N*-*tert*-Butyl-, and *N*-Phenyl-*N*-nopylamines (5–8) (General Procedure). To a solution of 48.1 g (0.15 mol) of crude nopyl tosylate in 150 mL of dry THF was added 0.45 mol of an appropriate amine, and the solution was refluxed overnight (15 h). The THF and excess of amine were distilled off under reduced pressure at 20–50 °C (in the case of aniline and benzyl amine the use of a vacuum pump was required). The residue was diluted with water and stirred for 0.5 h with a solution of 7.2 g (0.18 mol) of NaOH in 70 mL of H_2O. The product was extracted with ether, and the combined extracts were washed with water (three times) and saturated NaCl solution, and dried (K_2CO_3). After evaporation of ether, the crude amine was distilled in vacuo to give the following:

***N*-Benzyl-6,6-dimethylbicyclo[3.1.1]hept-2-ene-2-ethanamine (5):** 33.6 g (88%), bp 130–135 °C (0.025 Torr); n^{20}_D = 1.5320; $[\alpha]^{20}_D$ = −30.1° (*c* 5.32, $CHCl_3$).

***N*-Propyl-6,6-dimethylbicyclo[3.1.1]hept-2-ene-2-ethanamine (6):** 26.0 g (84%), bp 61–63 °C (0.005 Torr); n^{20}_D = 1.4796; $[\alpha]^{20}_D$ = −33.4° (*c* 5.14, $CHCl_3$).

***N*-*tert*-Butyl-6,6-dimethylbicyclo[3.1.1]hept-2-ene-2-ethanamine (7):** 24.4 g (73%), bp 69–71 °C (0.05 Torr); n^{20}_D = 1.4744; $[\alpha]^{20}_D$ = −29.6° (*c* 5.09, $CHCl_3$).

***N*-Phenyl-6,6-dimethylbicyclo[3.1.1]hept-2-ene-2-ethanamine (8):** 27 g (76%), bp 135–137 °C (0.025 Torr); n^{20}_D = 1.5540; $[\alpha]^{20}_D$ = −21.94° (*c* 5.05, $CHCl_3$).

6,6-Dimethylbicyclo[3.1.1]hept-2-ene-2-ethanamine (3). To a suspension of 33.5 g (0.228 mol) of phthalimide in 150 mL of DMF was added 16.6 g (0.12 mol) of freshly powdered anhydrous K_2CO_3, and the resulting mixture was stirred for 2 h at 130–140 °C. The reaction mixture was cooled, and a solution of 60.9 g (0.19 mol) of crude nopyl tosylate in 50 mL of DMF was added. The mixture was stirred for 15 h at 120–130 °C. After being cooled it was quenched with ice–water and extracted with $CHCl_3$. The combined extracts were washed with water, 5% NaOH solution, saturated NaCl solution and dried over anhydrous K_2CO_3. After removal of $CHCl_3$, the residue was dissolved in 250 mL of methanol and refluxed for 10 h with 10 mL (10.32 g, 0.20 mol) of hydrazine monohydrate. Then about half of the added methanol was removed, 400 mL of 6% NaOH solution (24 g, 0.6 mol) was added, and the whole mixture was refluxed for 2 h. After extraction with ether, the combined organic extracts were concentrated under reduced pressure, treated with 200 mL of dilute (1:4) (0.4 mol) HCl, and vigorously stirred for 15 min at rt. Impurities and side products were separated from nopylamine hydrochloride by extraction (two times) with ether. The combined water layers were treated with 10% NaOH solution to pH 14 and extracted with ether. The combined extracts were washed with water and saturated NaCl solution and dried over anhydrous K_2CO_3. After evaporation of ether, the crude product was distilled under reduced pressure to give 15.8 g (50%) of nopylamine: bp 45–48 °C (0.4 Torr); n^{20}_D = 1.4913; $[\alpha]^{25}_D$ = −41.6° (*c* 5, $CHCl_3$).

***N*-Methyl-6,6-dimethylbicyclo[3.1.1]hept-2-ene-2-ethanamine (4).** To 14.2 g (13.1 mL, 0.13 mol) of acetic anhydride was added 10.3 g (8.5 mL, 0.2 mol) of 90% formic acid at 0 °C, and the resulting solution was stirred for 2 h at 60–70 °C. It was cooled, diluted with 10 mL of THF, and treated dropwise with a solution of 3.30 g (0.02 mol) of nopylamine in 10 mL of THF. After being stirred overnight, the reaction was quenched with ice–water, saturated with solid NaCl, and extracted with ether. The combined ethereal extracts were washed with water and saturated NaCl solution and dried ($MgSO_4$). After evaporation of ether, the crude *N*-formylnopylamine [^1H NMR 0.83 (s, 3 H), 1.12 (d, J = 8.8 Hz, 1 H), 1.28 (s, 3 H), 1.9–2.45 (m, 8 H), 3.21 (m, 2 H), 5.31 (bs, 1 H), 8.15 (s, 1 H)] was dissolved in 10 mL of anhydrous Et_2O and added dropwise to a well-stirred suspension of 0.80 g (0.021 mol) of $LiAlH_4$ in 40 mL of Et_2O. The mixture was refluxed for 6 h and then quenched by careful addition of 0.8 mL of H_2O, 0.8 mL of 15% NaOH solution, and 2.4 mL of H_2O. The aluminum salts were filtered and washed with ether. The ethereal filtrate was dried over a small amount of anhydrous K_2CO_3 and evaporated to give a crude product which was subjected to a Kugelrohr distillation (pot 80–85 °C (0.025 Torr)) to give 2.51 g (70%) of 4: n^{20}_D = 1.4843; $[\alpha]^{25}_D$ = 38.7° (*c* 5.21, $CHCl_3$).

Preparation of Substituted *N*-Alkyl-10,10-dimethyl-5-aza-6-boratricyclo[7.1.1.0^{2,7}]undecanes 9–13. To a solution of 50 mmol of the appropriate amine in 20 mL of dry toluene was added 5.75 g (7.40 mL, 50 mmol) of Et_3N·BH_3, and the whole mixture was refluxed for 15 h under N_2. The toluene and formed Et_3N were evaporated at a reduced pressure, and the residue was distilled in vacuo to give:

***N*-Methyl-10,10-dimethyl-5-aza-6-boratricyclo[7.1.1.0^{2,7}]-undecane (9):** 7.33 g (77%), bp 54–58 °C (0.05 Torr); ^{11}B NMR (THF) δ 42.6 (d, monomer), 8.37 (d, dimer).

***N*-Benzyl-10,10-dimethyl-5-aza-6-boratricyclo[7.1.1.0^{2,7}]-undecane (10):** 10.88 g (81%), bp 119–120 °C (0.025 Torr); ^{11}B NMR (THF) δ 43.50 (bs, monomer), 7.40 (bs, dimer).

***N*-Propyl-10,10-dimethyl-5-aza-6-boratricyclo[7.1.1.0^{2,7}]-undecane (11):** 7.93 g (72%), 82–84 °C (0.1 Torr); ^{11}B NMR (THF) δ 42.93 (bs, monomer), 8.02 (bs, dimer); ^1H NMR δ for monomer 0.71 (d, J = 9.3 Hz, 1 H), 0.84 (t, J = 7.3 Hz, 3 H), 1.12 (s, 3 H), 1.24 (s, 3 H), 1.49 (sext, J = 7.3 Hz, 2 H), 1.60–2.30 (m, 8 H), 2.45 (m, 1 H), 3.00 (m, 5 H).

***N*-*tert*-Butyl-10,10-dimethyl-5-aza-6-boratricyclo-[7.1.1.0^{2,7}]undecane (12):** 8.89 g (76%), bp 92–96 °C (0.06 Torr); ^{11}B NMR (THF) δ 40.9 (bs, monomer).

***N*-Phenyl-10,10-dimethyl-5-aza-6-boratricyclo[7.1.1.0^{2,7}]-undecane (13):** 9.98 g (79%), bp 140–142 °C (0.05 Torr); ^{11}B NMR (THF) δ 43.90 (bs, monomer).

***N*-Propyl-*B*-methoxy-10,10-dimethyl-5-aza-6-boratricyclo[7.1.1.0^{2,7}]undecane (19).** To a solution of 4.38 g (0.02 mol) of azaborane 11 in 5 mL of THF was added 0.85 mL (0.02 mol) of anhydrous methanol dropwise and the solution refluxed for 2 h. Excess THF was removed under reduced pressure, and the residue was distilled in vacuo to give 3.09 g (62%) of the desired compound: bp 138–140 °C (0.1 Torr); ^{11}B NMR (THF) δ 31.97 (bs, monomer), 7.78 (bs, dimer); ^1H NMR ($CDCl_3$) δ for monomer: 0.73 (d, J = 9 Hz, 1 H), 0.82 (t, J = 7.3 Hz, 3 H), 1.15 (s, 3 H), 1.23 (s, 3 H), 1.40 (sext, J = 7.3 Hz, 2 H), 1.50–2.30 (m, 7 H), 2.46 (m, 1 H), 2.91 (m, 5 H), 3.68 (s, 3 H).

***N*-Propyl-*B*-methyl-10,10-dimethyl-5-aza-6-boratricyclo-[7.1.1.0^{2,7}]undecane (20).** To a solution of 3.55 g (14.3 mmol) of 19 in 20 mL of dry Et_2O cooled to −78 °C was added a solution of CH_3MgI, prepared from 0.382 g (15.7 mmol) of magnesium turnings and 2.03 g (0.89 mL, 14.3 mmol) of CH_3I in 30 mL of ether. The reaction mixture was stirred for 0.5 h and then warmed slowly to rt and stirred overnight. The solution was filtered under N_2, and the ether was evaporated. The residue was dissolved in

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5 mL of dry THF and filtered once more. The solution was concentrated under reduced pressure and distilled in vacuo to give 2.4 g (61%) of 20: bp 74–76 °C (0.005 Torr); ^{11}B NMR (THF) δ 46.14 (monomer); ^{1}H NMR δ 0.27 (s, 3 H), 0.68 (d, J = 9.3 Hz, 1 H), 0.83 (t, J = 7.3 Hz, 3 H), 1.12 (s, 3 H), 1.23 (s, 3 H), 1.46 (sext, J = 7.3 Hz, 2 H), 1.6–2.08 (m, 7 H), 2.42 (m, 1 H), 2.95 (m, 5 H).

Reduction of Ketones with the BH_3 Complexes of *N*-Alkyl-10,10-dimethyl-5-aza-6-boratricyclo[7.1.1.0^{2,7}]undecanes (General Procedure). To a solution of 10 mmol of the appropriate azaborane in 20 mL of THF was added 14.5 mL of 0.58 M BH_3/THF (8.42 mmol) or 18.2 mL of 0.462 M BMS/THF (8.40 mmol) dropwise, and the resulting solution was stirred for 1 h at rt. A solution of 6.25 mmol of ketone in 12 mL of THF was added dropwise at either 0 °C or rt. The solution was stirred for 1 h or overnight depending upon the substrate. The reaction was quenched by the addition of 2 mL of MeOH–H_2O (1:1) and refluxed for 0.5 h with 4 mL of diluted HCl (1:1). The reaction mixture was subsequently saturated with solid NaCl and extracted with ether. The combined extracts were washed with water, saturated $NaHCO_3$ solution, and brine and dried (K_2CO_3). After evaporation of ether, the residue was subjected to Kugelrohr distillation to give the alcohol which was subjected to ^{1}H NMR shift studies (Eu(hfc)$_3$).

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Supplementary Material Available: ^{1}H and ^{13}C NMR data for compounds 3–8 and ^{1}H and ^{13}C NMR spectra of compounds described in the Experimental Section (20 pages). Ordering information is given on any current masthead page.

Charge-Transfer Activation of Aromatic Hydrocarbons with Stannic Chloride

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Stannic chloride ($SnCl_4$) is a versatile Lewis acid that is especially useful for various types of electrophilic aromatic substitutions, including Friedel–Crafts alkylations with alkyl chlorides, chlorinations with chlorine, etc.[1-3] The catalytic activity of stannic chloride is usually attributed to its ability to activate the electrophile (RCl, Cl_2, etc.) by ligand (chloride) coordination.[4] It is thus noteworthy that there are varied reports of charge-transfer absorption bands when different aromatic hydrocarbons ArH are exposed to stannic chloride (that are not present with either $SnCl_4$ or the aromatic compound alone).[5,6] Spectrophotometric analyses have established (with the aid of Job's plots) the 1:1 stoichiometry for ArH–$SnCl_4$ in the formation of electron donor–acceptor or EDA complexes,[7] i.e.

$$\mathrm{ArH} + \mathrm{SnCl_4} \overset{K_{EDA}}{\rightleftharpoons} [\mathrm{ArH}, \mathrm{SnCl_4}] \qquad (1)$$

The formation of [ArH, $SnCl_4$] in eq 1 is reminiscent of the series of 1:1 complexes observed between aromatic hydrocarbons and titanium tetrachloride.[8] Since both metal halides share catalytic properties in common,[9] the delineation of their behavior toward the same (aromatic) substrates would provide the comparative basis for chemical reactivity. Indeed, our recent spectroscopic and structural study of the charge-transfer (CT) structures of aromatic complexes between titanium tetrachloride[10] offers a ready format for the direct comparison of this related series of EDA complexes. Accordingly, we focus in this study on the chemical consequences of the charge-transfer excitation of aromatic EDA complexes with stannic chloride in the comparative light of the $TiCl_4$ analogues.[8]

Table I. Charge-Transfer Spectra of Aromatic EDA Complexes with Stannic Chloride[a]

aromatic donor	IP[b] (eV)	λ_{max} (nm)	$h\nu_{CT}$ (eV)
1. mesitylene	8.42	299	4.15
2. naphthalene	8.12	326	3.80
3. pentamethylbenzene	7.92	322	3.85
4. hexamethylbenzene	7.85	340	3.65
5. 1,4-dimethylnaphthalene	7.78	348	3.56
6. 1-methoxynaphthalene	7.72	352	3.52
7. 9-bromoanthracene	7.47	408	3.04
8. anthracene	7.43	400	3.10
9. 2-*tert*-butylanthracene	~7.3	408	3.04
10. 9-methylanthracene	7.25	414	3.00
11. 9,10-dimethylanthracene	7.11	434	2.86

[a] In cyclohexane solution containing 0.01 M arene and 0.05 M $SnCl_4$ at 23 °C. [b] Ionization potential from ref 11.

Results

Charge-Transfer Spectra of Aromatic EDA Complexes with Stannic Chloride. The addition of $SnCl_4$ (dissolved in cyclohexane) to mesitylene immediately resulted in a bright yellow solution. With naphthalene an orange coloration developed, and the quantitative effects of these dramatic color changes are illustrated in Figure 1. The systematic spectral shifts of the new absorption bands for the various benzene and naphthalene donors, as listed in Table I, define the linear relationship $h\nu_{max}$ = 1.0IP – 4.62 when the absorption maximum (ν_{max}) and the aromatic ionization potential (IP) are both expressed in eV.[11] Such a spectral behavior accords with Mulliken's prediction for charge-transfer excitation ($h\nu_{CT}$) in weak intermolecular complexes[12], i.e.

$$h\nu_{CT} = \mathrm{IP} - \mathrm{EA} - \omega \qquad (2)$$

Since stannic chloride is the acceptor in common, EA (electron affinity) is constant in eq 2, as is the electrostatic

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