Preparation and use of sterically hindered organobis(2,4,6-triisopropylphenyl)hydroborates and their polystyrene derivatives for the diastereoselective reduction of ketones

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Preparations of benzyl and phenylbis(2,4,6-triisopropylphenyl)hydroborates [organoditripylhydroborates] are outlined. The lithium and potassium benzylditripylhydroborates reduce substituted cyclohexanones with diastereoselectivities comparable to those obtained with the most selective reagents known (*e.g.* 99% *cis*-4-methylcyclohexanol from 4-methylcyclohexanone). Lithium phenylditripylhydroborate also reduces ketones with significant selectivity. For example, 4-methylcyclohexanone is reduced to *cis*-4-methylcyclohexanol in 88% isomeric purity. Unlike with most other highly selective reagents the reactions take place at room temperature and have the additional advantage that the boron reagent can be recovered quantitatively. Coupling of Merrifield's resin with ditripylfluoroborane in the presence of lithium naphthalenide affords (ditripylborylmethyl)polystyrene. Similarly, coupling of bromopolystyrene with ditripylfluoroborane in the presence of *n*-BuLi affords (ditripylboryl)polystyrene. Reactions of these polymeric organoboranes with *t*-BuLi give the corresponding polymer-supported lithium hydroborates. Lithium ditripylhydroboratylmethylpolystyrene reduces cyclic ketones in identical fashion to its non-polymeric counterpart, giving the corresponding thermodynamically less stable alcohols in 99% or better isomeric purity. Similarly, lithium ditripylhydroboratylpolystyrene behaves like its non-polymeric counterpart and reduces 4-methylcyclohexanone to *cis*-4-methylcyclohexanol in 89% isomeric purity. Recovery and reuse of the organoboranes are even easier for the polymeric reagents.

Introduction

Highly hindered organoborohydides are very useful reagents for the diastereoselective reduction of ketones.[1] Unhindered reductants such as sodium tetrahydroborate[2–4] and borane–THF[5] tend to reduce cycloalkanones to yield the more stable alcohol by attack from the more hindered face of the molecule. As the reductant becomes more hindered[6] there is increasing attack from the less hindered face to give the less stable alcohol. The most selective reagents reported for this latter process are lithium tri-*sec*-butylhydroborate,[7] lithium tris(1,2-dimethylpropyl)hydroborate (lithium trisiamylhydroborate)[8] and lithium ethylbis(2,4,6-triisopropylphenyl)hydroborate [lithium ethylditripylhydroborate].[9]

There are advantages associated with the use of lithium ethylditripylhydroborate, because it works at room temperature and the parent organoborane is stable in solution, stable to water and air, and can be recovered quantitatively after the reduction. By contrast, the procedures used for other boron reagents, such as tri-*sec*-butylhydroborates,[7] require low temperature (−78 °C) to provide a high selectivity for some cyclic ketones, and result in complete degradation of the organoborane during work up. Therefore, we have sought to build on the advantages of the alkylditripylborane derivative by generating more hindered organoboranes, *e.g.* benzyl and phenylditripylboranes and their polymeric analogues. Moreover, it was anticipated that the polymeric analogues would have the additional advantage of ease of recovery by filtration, without the need for column chromatography.

The most easily accessible polymeric analogue appeared to be one derived from the Merrifield resin, which would be a direct analogue of benzylditripylborane, or one derived from bromopolystyrene, which would be a direct analogue of phenylditripylborane. In the present work, therefore, we have investigated the preparations of benzylditripylborane, phenylditripylborane, (ditripylborylmethyl)polystyrene and (ditripylboryl)polystyrene. We also report hydride transfers from various sources of hydride to these hindered ditripylborane derivatives and the use of the hydroborates obtained in highly stereoselective reductions.

Results and discussion

Benzylditripylborane (**1**) was prepared in 71% purified yield by reaction of ditripylfluoroborane[10] and benzylmagnesium chloride in THF under reflux for 3 h, in a manner similar to that used previously for the preparation of ethylditripylborane. Moreover, formation of benzyllithium by treatment of benzyl chloride with lithium naphthalenide in diethyl ether–tetrahydrofuran–light petroleum (bp 30–40 °C) (4:3:1),[11] followed by reaction with ditripylfluoroborane, gave benzylditripylborane (**1**) in 67% yield. However, when a mixture of benzyl chloride and ditripylfluoroborane was treated *in situ* with lithium naphthalenide in THF, this one step procedure afforded benzylditripylborane (**1**) in even better yield (81%). The one step procedure is therefore recommended for the synthesis of **1**, since it is both simpler and provides a higher yield.

Attempted preparation of sodium benzylditripylhydroborate by reaction of **1** with sodium hydride or sodium borohydride was not successful due to incomplete hydride transfer to the borane reagent. Lithium aluminium hydride was more successful, but the ^{11}B NMR spectrum of the resultant mixture showed that ditripyldihydroborate was formed as well as benzylditripylhydroborate, apparently as a result of debenzylation of **1** or its hydroborate derivative under the reaction conditions.

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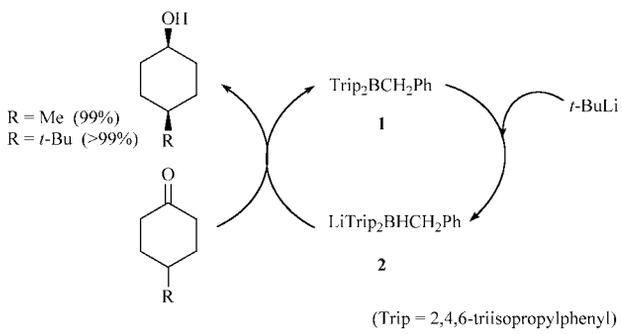
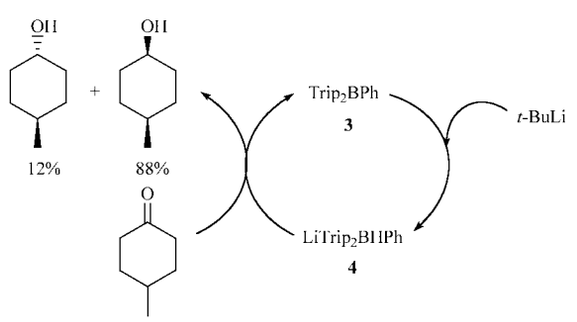
Our attention was turned next to the use of potassium triisopropoxyborohydride and tetrabutylammonium borohydride as hydride sources. ^{11}B NMR showed that hydride transfer was successful in these cases, the corresponding benzylditripylhydroborates being formed in essentially quantitative yields. However, when solutions of the hydroborates generated *in situ* in this way were used for reduction of cyclohexanones, although the reactions gave excellent yields of the corresponding alcohols the stereoselectivity was low, presumably due to competitive reduction by potassium triisopropoxyborohydride[12] or tetrabutylammonium borohydride[13] present in equilibrium with the benzylditripylhydroborate.

Our attention was therefore turned next to the use of *t*-BuLi as a hydride source.[1b] Indeed, addition of *t*-BuLi to **1** gave lithium benzylditripylhydroborate (**2**), which reduced 4-methylcyclohexanone and 4-*tert*-butylcyclohexanone to *cis*-4-methylcyclohexanol and *cis*-4-*tert*-butylcyclohexanol in 99% and >99% isomeric purity, respectively (Scheme 1).



Scheme 1

Our success in the stereoselective reduction of ketones using **2** prompted us to prepare other hindered organoboranes. Phenylditripylborane (**3**) was prepared in 80% yield after crystallisation by reaction of ditripylfluoroborane[10] and phenyllithium in light petroleum (bp 30–40 °C) for 26 h at room temperature. In a manner similar to that used previously for the preparation of **2**, lithium phenylditripylhydroborate (**4**) was prepared by addition of *t*-BuLi to **3**. Reduction of 4-methylcyclohexanone using **4** gave *cis*-4-methylcyclohexanol in 88% isomeric purity (Scheme 2). The selectivity of this reagent is



Scheme 2

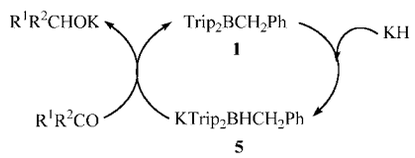
therefore rather lower than that of lithium ethylditripylhydroborate[9] or lithium benzylditripylhydroborate (see above). A possible reason is that triarylboranes tend to form radical anions, which may lower the stereoselectivity.[14]

Our attention was turned next to the use of KH as a hydride source in the hope of obtaining potassium benzylditripylhydroborate (**5**) for use in selective reductions. Indeed, addition of a THF solution of **1** to a THF suspension of activated KH afforded potassium benzylditripylhydroborate (**5**) within less than five minutes. Addition of a THF solution of a substituted cyclohexanone into the THF solution of **5** at room temperature (Scheme 3), followed by stirring overnight at room temperature

Table 1 Diastereoselectivities in reduction of cyclic ketones with potassium ditripylbenzylhydroborate (**5**)

Ketone	Alcohol	% of less stable alcohol[a]	Yield (%)[b]
2-Methylcyclopentanone	*cis*	>99	85
2-Methylcyclohexanone	*cis*	>99	90
3-Methylcyclohexanone	*trans*	>99	87
4-Methylcyclohexanone	*cis*	99	93
4-*tert*-Butylcyclohexanone	*cis*	>99	97

[a] GC indicated that the reactions were all essentially quantitative. [b] Yield of isolated, purified product.



Scheme 3

and then work up, gave the corresponding cyclic alcohol with a very high *cis*- to *trans*- ratio (Table 1).

As shown in Table 1, potassium benzylditripylhydroborate (**5**) completely reduces 2-methylcyclopentanone, 2-methylcyclohexanone, 3-methylcyclohexanone, 4-methylcyclohexanone and 4-*tert*-butylcyclohexanone with very high stereoselectivities, comparable with those obtained using the most selective reagents known, but without the requirement for low temperatures needed by several other systems.[6,7]

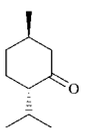
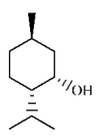
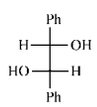
In view of the ease of conversion of **1** into its potassium hydroborate derivative and the ease of reduction of ketones by the latter reagent, it appeared possible that **1** could be used to catalyse the direct KH reduction of cyclic ketones. A series of experiments was therefore conducted in which a catalytic amount of **1** and excess potassium hydride were used in attempts to reduce 4-substituted cyclohexanones directly. Indeed, the 4-substituted cyclohexanones were reduced in excellent yields to the corresponding alcohols, but the diastereoselectivities were low, presumably due to formation of ditripylborane as a result of debenzylation of **1** under the influence of the excess KH present. Similar observations were made in the case of ethylditripylborane.[9]

Our investigations thus far had shown that both lithium and potassium benzylditripylhydroborates **2** and **5** are amongst the most selective reagents known for reduction of cyclohexanones, and that the corresponding organoborane, **1**, can be recovered quantitatively after reduction. However, because of their high molecular weights large quantities of reagent are required for such reductions. Moreover, separation of product and organoborane reagent by column chromatography after reaction would be a major problem for large-scale use. By contrast, polymer-supported reagents have the advantage of allowing separation of insoluble polymeric by-products from the reaction mixtures by filtration.[15] In some cases the polymeric reagents can be regenerated. It was therefore of interest to investigate the use of polymer-supported analogues of the boron reagents **1** and **3** for selective reductions.

Chloromethylpolystyrene (Merrifield's resin) and bromopolystyrene are readily available commercial polymers and we decided to use these to generate functionalised polymers. A convenient method for the preparation of organylditripylboranes involves the reaction of ditripylfluoroborane with a reactive organometallic reagent such as an organolithium or organomagnesium reagent.[9] Therefore, we proposed to try to functionalise the commercial resins by this route.

There is no report in the literature concerning preparation of the lithium derivative of Merrifield's resin, although the mag-

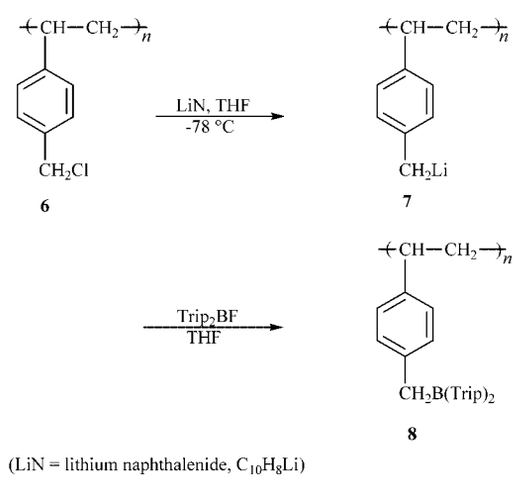
Table 2 Diastereoselectivities in reduction of cyclic ketones with lithium ditripylhydroboratylmethylpolystyrene (**9**)

Ketone	Alcohol	% of less stable alcohol[a]	Yield (%)[b]
2-Methylcyclopentanone	*cis*	>99	85
2-Methylcyclohexanone	*cis*	>99	90
3-Methylcyclohexanone	*trans*	>99	89
4-Methylcyclohexanone	*cis*	99	91
4-*tert*-Butylcyclohexanone	*cis*	>99	96
		>99	92
		>99	88

[a] GC indicated that the reactions were all essentially quantitative. [b] Yield of isolated, purified product.

nesium derivative has been prepared.[16] Our successful generation of benzyllithium from benzyl chloride[11] prompted us to attempt preparation of ditripylborylmethylpolystyrene (**8**) under similar conditions.

Polymer **8** was indeed conveniently prepared *via* lithiomethylpolystyrene (**7**). The addition of excess of lithium naphthalenide in THF to a mixture of Merrifield's resin (**6**) and ditripylfluoroborane (molar ratio of Cl to $Trip_2BF$ 1:1.5) in THF at −78 °C afforded polymer **8** in a functional yield of 75% (Scheme 4). In view of its stability in air, polymer **8** was readily

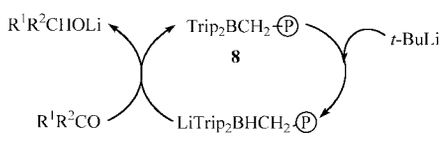


(LiN = lithium naphthalenide, $C_{10}H_8Li$)

Scheme 4

purified by simple filtration on a fritted funnel and washing with a series of solvents.

Treatment of a suspension of **8** in THF with *tert*-butyllithium at room temperature afforded the corresponding lithium hydroborate **9**, which completely reduced representative ketones (Scheme 5) in 99% or better isomeric purity. The results are shown in Table 2.

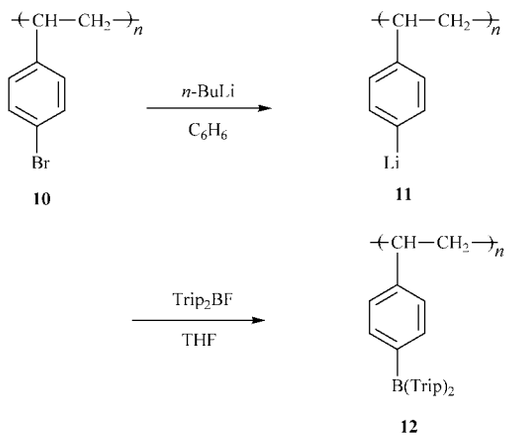


Scheme 5

As shown in Table 2, polymer **9** completely reduces 2-methylcyclopentanone, 2-methylcyclohexanone, 3-methylcyclohexanone, 4-methylcyclohexanone, 4-*tert*-butylcyclohexanone, (−)-menthone and benzoin with very high stereoselectivities, again comparable with those obtained using the most selective reagents known, but without the requirement for low temperatures needed by several other systems.[6,7]

The polymer **8** could be separated and purified from the reduction product by simple filtration on a fritted funnel and washing with THF. Recovered **8** behaved in the same way as original **8**, even when **8** was reused several times. Overall, therefore, polymer **8** acts as a mediator for the selective reduction of ketones by *tert*-butyllithium (Scheme 5).

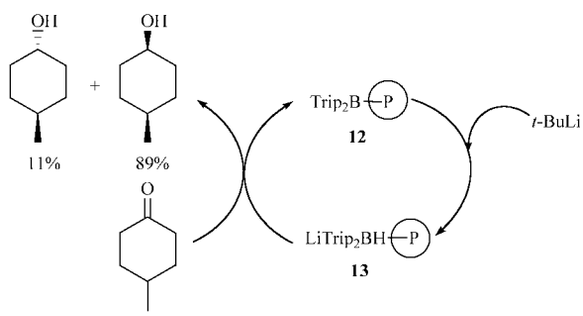
Our attention was turned next to the preparation of (ditripylboryl)polystyrene (**12**) and its use in stereoselective reductions. Lithiated polystyrene **11** is a useful intermediate in the preparation of numerous other functional polymers.[17,18] Initially, the ditripylborylpolystyrene **12** was prepared by the method shown in Scheme 6. Reaction of bromopolystyrene **10**



Scheme 6

with concentrated *n*-butyllithium (10 mol dm^{-3})[19] in benzene afforded polystyryllithium **11**, which was treated with ditripylfluoroborane[9] in THF to give **12** in a functional yield of 66%. The second step reaction from **11** to **12** worked smoothly in THF at room temperature, but the reaction gave a low yield (23%) in benzene.

Treatment of a suspension of **12** in THF with *tert*-butyllithium at room temperature afforded the corresponding lithium hydroborate **13**, which reduced 4-methylcyclohexanone to *cis*-4-methylcyclohexanol of 89% purity (Scheme 7). This



Scheme 7

result is very similar to the result from the reaction with lithium phenylditripylhydroborate (**4**).

Conclusion

Lithium and potassium benzylditripylhydroborates reduce representative ketones with high diastereoselectivities compared

with most other stereoselective reagents. Moreover, reactions are carried out at room temperature and the organoborane reagent can be recovered quantitatively.

Polymeric analogues of benzyl- and phenyl-ditripylboranes have been successfully prepared from Merrifield's resin and bromopolystyrene, respectively, and have then been converted into their hydroborates by the use of *tert*-butyllithium. The polymeric hydroborates are also very selective reagents for the diastereoselective reduction of ketones, comparable with their non-polymeric counterparts. The organoborane polymers have the additional advantage that they can be recovered easily by filtration and without the need for chromatography. They should therefore prove attractive for larger scale work. The polymer derived from Merrifield's resin should be particularly attractive in view of the very high stereoselectivities exhibited in reactions using its hydroborate derivative.

Experimental

^{1}H and ^{11}B NMR spectra were recorded on a Bruker spectrometer operating at 400 MHz for ^{1}H, 100 MHz for ^{13}C and 128 MHz for ^{11}B measurements. Low resolution mass spectra were recorded on a VG 12-253 spectrometer, electron impact (EI) at 70 eV and chemical ionization (CI) by use of ammonia as ionizing gas. Accurate mass data were obtained on a VG ZAB-E instrument. Column chromatography was carried out using Merck Kieselgel 60 (230–400 mesh). *tert*-Butyllithium and cyclic ketones were obtained from Aldrich Chemical Company and *t*-BuLi was estimated prior to use by the method of Watson and Eastham.[20] Bromopolystyrene and chloromethylpolystyrene (Merrifield resin) were obtained from Fluka Chemical Company. THF was distilled from sodium benzophenone ketyl. Other chemicals were obtained from Aldrich Chemical Company and used without further purification. Solvents were purified by standard procedures.[21,22]

Preparation of benzylbis(2,4,6-triisopropylphenyl)borane (1) *via* benzylmagnesium chloride

A dry 100 cm^3, two-necked round-bottomed flask equipped with a reflux condenser and magnetic follower was charged with bis(2,4,6-triisopropylphenyl)fluoroborane (2.05 g, 4.7 mmol). The flask was purged with nitrogen and warmed for several minutes with a hair dryer. THF (10 cm^3) was added and the resulting solution cooled in an ice bath. A solution of benzylmagnesium chloride (8 cm^3, 14.1 mmol) was added using a syringe. Once addition was complete the coolant was removed and the mixture was stirred at room temperature for 30 min, then under reflux for 3 h, then for 16 h at room temperature. The mixture was quenched with saturated ammonium chloride solution (5 cm^3); diethyl ether (30 cm^3) was added, and the layers were separated. The organic layer was washed with brine (2 × 30 cm^3) and the combined aqueous layers were extracted with a portion of fresh ether (20 cm^3). The combined ether portions were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residue obtained was recrystallised from methanol to give **1** (1.70 g, 3.35 mmol, 71%) as white crystals. Mp 95–96 °C; $\delta_H(CDCl_3)$ 7.10–7.03 (m, 5 H, Ph), 6.94 (s, 4 H, ArH), 3.47 (br s, 2 H, CH_2), 2.85 [m, 6 H, 6 × C*H*$(CH_3)_2$], 1.23 [d, *J* 6.9 Hz, 12 H, 2 × CH(C*H*$_3)_2$] and 0.98 [br d, 24 H, 4 × CH(C*H*$_3)_2$]; $\delta_C(CDCl_3)$ 150.10 (s, C-2), 149.67 (s, C-4), 142.30 (s, C-1), 140.31 (s, C-1 of Ph), 129.65 (d, C-2 of Ph), 127.91 (d, C-3 of Ph), 124.72 (d, C-4 of Ph), 121.13 (d, C-3), 42.26 (t, CH_2), 34.16 [d, 2 × *C*H$(CH_3)_2$], 33.72 [d, 4 × *C*H$(CH_3)_2$], 24.53 [q, 2 × CH(*C*H$_3)_2$] and 23.92 [q, 4 × CH(*C*H$_3)_2$]; $\delta_B(CDCl_3)$ 83.83; *m*/*z* (EI) 508 (M^+, 0.4%), 416 (30), 213 (18), 203 (13), 189 (8), 169 (10), 91 (95) and 43 (100); *m*/*z* (CI) 526 ($M + NH_4^+$, 100%), 417 (35), 322 (44), 305 (27), 203 (8) and 91 (5) (Found: $M + NH_4^+$, 526.4584. Calc. for $C_{37}H_{57}NB$: 526.4584).

Preparation of benzylbis(2,4,6-triisopropylphenyl)borane (1) *via* benzyl chloride (in two steps)

A solution of benzyl chloride (0.324 g, 2.56 mmol) in diethyl ether (8 cm^3), THF (6 cm^3) and light petroleum (bp 30–40 °C) (2 cm^3) was added *via* a double ended needle to a stirred solution of lithium naphthalenide (1.0 mol dm^{-3}; 6.78 cm^3, 6.78 mmol) in THF over a period of 15 minutes (lithium naphthalenide was prepared by stirring a solution of naphthalene in THF with lithium metal at 0 °C for 6 h). The resultant mixture was stirred for a further 15 min at −95 °C, after which bis(2,4,6-triisopropylphenyl)fluoroborane (2.4 g, 5.5 mmol) in diethyl ether (6 cm^3) was added dropwise at −78 °C. The mixture was stirred at −78 °C for 20 min, then stirred overnight at room temperature. Crystallisation of the crude product from methanol after work up afforded **1** (1.87 g, 3.68 mmol, 67%) as white crystals.

Preparation of benzylbis(2,4,6-triisopropylphenyl)borane (1) *via* benzyl chloride (in one step)

To a cooled solution (−78 °C) of lithium naphthalenide (1.0 mol dm^{-3}; 12.5 cm^3, 12.5 mmol) in THF under nitrogen, a solution of bis(2,4,6-triisopropylphenyl)fluoroborane (1.95 g, 4.47 mmol) and benzyl chloride (0.354 g, 2.79 mmol) in THF (50 cm^3) was added dropwise. The mixture was stirred at −78 °C for 6 h and at room temperature for 16 h. The mixture was diluted with diethyl ether (60 cm^3) then quenched with water (5 cm^3). The organic layer was separated and washed with NH_4Cl (3 × 6 cm^3). The extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue obtained was purified by crystallisation from methanol to give **1** (1.84 g, 3.62 mmol, 81%) as white crystals.

Preparation of lithium benzylbis(2,4,6-triisopropylphenyl)hydroborate (2) using *t*-BuLi, and its use for selective reduction of 4-substituted cyclohexanones

A dry 100 cm^3 round-bottomed flask connected to a bubbler was charged with **1** (1.02 g, 2.0 mmol) and then flushed for 5 min with nitrogen. Tetrahydrofuran (20 cm^3) was added and the solution was stirred whilst *tert*-butyllithium (1.7 mol dm^{-3}; 1.2 cm^3, 2.0 mmol) was added slowly by syringe. The resulting solution was stirred for 10 min at room temperature, after which it showed a doublet in its ^{11}B NMR spectrum at $\delta = -13.94$ (d, $J = 77.9$ Hz), which collapsed to a singlet on decoupling the proton signals. A solution of 4-substituted cyclohexanone (1.0 mmol) in THF (5 cm^3) was added and the mixture was stirred overnight at room temperature. The reaction mixture was quenched with a mixture of water (10 cm^3) and diethyl ether (10 cm^3) and the separated organic layer was washed further with brine (3 × 20 cm^3). The aqueous layers were combined and then washed with ether (20 cm^3). The organic layers were combined, dried ($MgSO_4$), and filtered and the solvent was then removed under reduced pressure. The residue was transferred to a dry silica gel column and eluted with light petroleum (30–40 °C) to give recovered benzylbis(2,4,6-triisopropylphenyl)borane (**1**) (~0.94–0.96 g, ~94–96%). The column was then eluted with light petroleum (bp 30–40 °C)–diethyl ether mixture (50:50→0:100) until the product had completely eluted to give the corresponding alcohol. The GC results are given in Scheme 1. The recovered benzylbis(2,4,6-triisopropylphenyl)borane was used for a repeat of the same reaction and gave the same results.

Preparation of phenylbis(2,4,6-triisopropylphenyl)borane (3)

A dry 100 cm^3, two-necked round-bottomed flask equipped with a reflux condenser and magnetic follower was charged with bis(2,4,6-triisopropylphenyl)fluoroborane (2.09 g, 4.8 mmol). The flask was purged with nitrogen and warmed for several minutes with a hair dryer. Light petroleum (bp 30–40 °C)

(10 cm^3) was added and the resultant solution was cooled in an ice bath. A solution of phenyllithium (1.0 mol dm^{-3}; 9.6 cm^3, 9.6 mmol) was added using a syringe and the mixture was then allowed to warm up and stirred for 26 h at room temperature. The reaction was carefully quenched by the addition of a mixture of diethyl ether (20 cm^3) and water (20 cm^3). The organic layer was washed with water (2 × 10 cm^3), dried ($MgSO_4$), and filtered and the solvent was removed under reduced pressure. The crude product obtained was recrystallised from methanol to give **3** (1.83 g, 3.70 mmol, 80%) as white crystals. Mp 117–118 °C; $\delta_H(CDCl_3)$ 7.46–7.30 (m, 5 H, Ph), 6.96 (s, 4 H, ArH), 2.98–2.84, 2.50–2.35 [2 m, 6 H, 6 × C*H*$(CH_3)_2$], 1.25 [d, *J* 6.9 Hz, 12 H, 2 × CH(C*H*$_3)_2$] and 1.15, 0.68 [2 br s, 24 H, 4 × CH(C*H*$_3)_2$]; $\delta_C(CDCl_3)$ 151.39 (s, C-4), 149.58 (s, C-2), 149.05 (s, C-1 of Ph), 141.60 (s, C-1), 135.42 (d, C-2 of Ph), 131.00 (d, C-4 of Ph), 127.26 (d, C-3 of Ph), 121.71, 119.99 (2 d, C-3), 34.47, 34.18, 33.48 [3 d, 3 × *C*H$(CH_3)_2$] and 24.89, 23.93, 23.69 [3 q, 3 × CH(*C*H$_3)_2$]; $\delta_B(CDCl_3)$ 77.55; *m*/*z* (EI) 290 (20%), 247 (100) and 169 (30); *m*/*z* (CI) 512 (M + NH_4^+, 16%), 495 (MH^+, 3) and 308 (100) (Found: M + NH_4^+, 512.4427. Calc. for $C_{36}H_{55}NB$: 512.4427).

Preparation of lithium phenylbis(2,4,6-triisopropylphenyl)hydroborate (4) using *t*-BuLi, and its use for selective reduction of 4-methylcyclohexanone

With the same procedure as for lithium benzylbis(2,4,6-triisopropylphenyl)hydroborate **2**, a brown solution of lithium phenylbis(2,4,6-triisopropylphenyl)hydroborate (**4**) (0.99 g, 2.0 mmol) was prepared. 4-Methylcyclohexanone (0.11 g, 1.0 mmol) was added and reduced to *cis*-4-methylcyclohexanol in 88% isomeric purity (*i.e.* a ratio of *cis*- to *trans*- isomers 88 : 12). The recovered yield of phenylbis(2,4,6-triisopropylphenyl)-borane (**3**) was 89% and the isolated yield of 4-methylcyclohexanol was 83%.

General procedure for the preparation of potassium benzylbis-(2,4,6-triisopropylphenyl)hydroborate (5) using potassium hydride, and its selective reduction of cyclic ketones

An oven-dried 100 cm^3 round-bottomed flask equipped with a nitrogen inlet and a glass-coated magnetic bar was charged with potassium hydride (0.30 g of a 35% oil dispersion, 2.62 mmol) and flushed with nitrogen. Light petroleum (30–40 °C, 3 × 15 cm^3) was added and the mixture was stirred for 20 minutes. The suspension was allowed to settle, and then the solvent was removed through a double-ended needle. A solution of $LiAlH_4$ was prepared by stirring the solid (2.5 g) in THF (100 cm^3) for 16 h. A sample of the supernatant (10 cm^3, containing about 2.94 mmol of $LiAlH_4$) was added to the KH, the suspension was stirred for 30 min, and the supernatant was then removed. The solid residue was washed with THF (10 cm^3) and then suspended in THF (10 cm^3). Benzylbis(2,4,6-triisopropylphenyl)borane (**1**) (1.0 g, 2.0 mmol) in THF (10 cm^3) was added. There was a gently exothermic reaction, and the mixture was stirred for 10 min at room temperature. The resultant solution showed a doublet in the ^{11}B NMR spectrum at $\delta = -13.91$ (d, $J = 78.9$ Hz), which collapsed to a singlet on decoupling the proton signals. The solution so prepared was transferred by a double-ended needle to a stirred solution of cyclic ketone (1.0 mmol) in THF (5 cm^3) and the mixture was stirred overnight at room temperature. The reaction mixture was quenched with a mixture of water (5 cm^3) and diethyl ether (5 cm^3) and the separated organic layer washed further with brine (2 × 10 cm^3). The combined aqueous extracts were washed with ether (20 cm^3), the combined organic layers were dried ($MgSO_4$) and filtered, and the solvent was removed under reduced pressure. The residue was transferred to a dry silica gel column and eluted with light petroleum (bp 30–40 °C) to give benzylbis(2,4,6-triisopropylphenyl)borane (~0.94–0.97 g, ~94–97%) and then with light petroleum (bp 30–40 °C)–diethyl ether mixture (50 : 50→0 : 100) until the product alcohol had completely eluted (85–97% isolated yields). Isomer proportions were estimated by GC. The results are given in Table 1.

Preparation of bis(2,4,6-triisopropylphenyl)borylmethyl-polystyrene (8)

To a suspension of 1% cross-linked chloromethylpolystyrene (**6**) (0.80 g, 1.36 mmol Cl) and bis(2,4,6-triisopropylphenyl)fluoroborane (0.86 g, 2.06 mmol) in THF (25 cm^3) under nitrogen at −78 °C was added lithium naphthalenide (1.0 mol dm^{-3}; 5.8 cm^3, 5.8 mmol) rapidly. The mixture was stirred at −78 °C for 6 h then at room temperature for 15 h. The reaction was quenched with aqueous saturated ammonium chloride solution (5 cm^3), then filtered. The polymer was washed with H_2O, Et_2O, THF–H_2O (2 : 1), H_2O, THF and Et_2O three times and dried at 50 °C under vacuum for 8 h to give the boron polymer **8** (1.12 g).

Titration of bis(2,4,6-triisopropylphenyl)borylmethylpolystyrene (8)

An oven-dried 50 cm^3 round-bottomed flask equipped with a nitrogen inlet and a glass-coated magnetic bar was flushed with nitrogen and charged with bis(2,4,6-triisopropylphenyl)borylmethylpolystyrene (**8**) (1.12 g) in THF (10 cm^3). A solution of *tert*-butyllithium (1.7 mol dm^{-3}; 1.0 cm^3, 1.7 mmol) in pentane was added. There was a gently exothermic reaction and the mixture was stirred for 30 min at room temperature. After removal of the liquid phase with a double-ended needle, the polymer was washed with dry THF (3 × 10 cm^3). The combined THF washing was titrated against 0.2 M HCl. The titration showed that 0.2 M HCl (3.4 cm^3, 0.68 mmol) was used. This showed that 1.02 mmol of *tert*-butyllithium (1.70 − 0.68 = 1.02 mmol) had reacted with the polymer indicating that the polymer contained 0.91 mmol g^{-1} of boron and that the functional yield was 75% (1.02 mmol from 1.36 mmol).

Preparation of lithium bis(2,4,6-triisopropylphenyl)hydroboratylmethylpolystyrene (9) and its use for selective reduction of ketones

An oven-dried 50 cm^3 round-bottomed flask equipped with a nitrogen inlet and a glass-coated magnetic bar was charged with bis(2,4,6-triisopropylphenyl)borylmethylpolystyrene (**8**) (1.12 g) in THF (10 cm^3) and flushed with nitrogen. A solution of *tert*-butyllithium (1.7 mol dm^{-3}; 1.0 cm^3, 1.7 mmol) in pentane was added slowly by syringe. There was a gently exothermic reaction and the mixture was stirred for 30 min at room temperature. After removal of the liquid phase with a double-ended needle, the polymer was washed with dry THF (3 × 10 cm^3) and suspended in dry THF (10 cm^3). A solution of the appropriate ketone (0.78 mmol) in THF (5 cm^3) was added and the mixture was stirred overnight at room temperature and then filtered. The solid was washed with THF (3 × 10 cm^3) and dried, ready to be reused for other reductions. The filtrate and washings were combined and a mixture of water (5 cm^3) and diethyl ether (5 cm^3) was added. After separation, the organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The GC results are shown in Table 2. Simple removal of the solvent gave the corresponding alcohol in 85–96% isolated yield.

Preparation of bis(2,4,6-triisopropylphenyl)borylpolystyrene (12)

A dry 50 cm^3, round-bottomed flask equipped with a magnetic follower was charged with bromopolystyrene **10** (0.66 g, 2.64 mmol Br) then flushed with nitrogen. Benzene (15 cm^3) was added and the suspension was stirred at room temperature for 30 min then *n*-butyllithium (10 mol dm^{-3}; 0.8 cm^3, 8.0 mmol) was slowly added by syringe. The mixture was stirred at room

temperature for 30 min and then stirred at 65–69 °C for 4 h. After removal of the liquid phase and washing with dry THF (3×10 cm^3), dry THF (7 cm^3) was added to the lithiated polystyrene **11**, the mixture was cooled to 0 °C and a solution of bis(2,4,6-triisopropylphenyl)fluoroborane (1.15 g, 2.64 mmol) in THF (7 cm^3) was added. The mixture was allowed to warm to room temperature and stirred for 15 h, and then stirred for 5.5 h at 50–56 °C. The resin was collected on a filter and washed successively with THF, Et_2O, THF–H_2O (2:1), H_2O, THF and finally MeOH. After drying under reduced pressure, polymer **12** (1.16 g) was obtained in 66% functional yield as measured by titration.

Preparation of lithium bis(2,4,6-triisopropylphenyl)hydroboratylpolystyrene (13) and its use for selective reduction of 4-methylcyclohexanone

With the same procedure as for polymer **9**, polymer **13** was prepared as a deep red coloured solid by treatment of bis(2,4,6-triisopropylphenyl)borylpolystyrene (**12**) (1.16 g) in THF with *tert*-butyllithium (1.7 mol dm^{-3}; 1.0 cm^3, 1.7 mmol) at room temperature. Polymer **13** reduced 4-methylcyclohexanone to *cis*-4-methylcyclohexanol in 89% stereoselectivity. The GC yield of 4-methylcyclohexanol was 96% and the isolated yield was 90%.

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