Graphical Abstract

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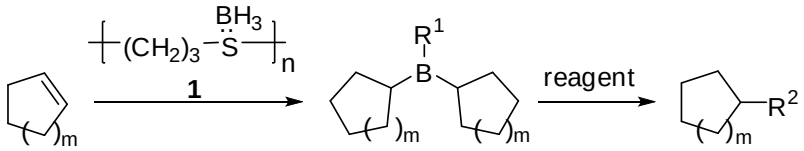

Poly(propylene sulfide)–borane: convenient and versatile reagent for organic synthesis

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ABSTRACT: Poly(trimethylene sulfide)–borane adduct has been used as an efficient borane reagent in hydroboration reactions to produce various organoboranes, which have then been used without isolation in further reactions that involve single, double and triple migrations of alkyl groups. The presence of the polymer causes no problems, but there are practical advantages associated with its use, including lack of odour and easy recoverability.

Keywords: borane tetrahydrofuran complex, poly(trimethylene sulfide), borane adduct, hydroboration, organoboranes, organic synthesis

1. Introduction

Organoboranes have multifarious applications for organic syntheses.[1,2] Their importance arises from the fact that they can be transformed into many different product types containing useful functional groups (aldehydes, ketones, amines, alkenes, alkynes, alcohols, *etc*.), often in a highly stereoselective manner.[3,4] Such intermediates are usually produced by hydroboration[1] and the starting material for such reactions is a complexed form of borane (BH_3). Accordingly, the borane adducts that are used to produce the organoboranes are very important reagents.

Borane-dimethyl sulfide (BH_3–SMe_2, BMS) and borane–tetrahydrofuran (BH_3–THF) are the most commonly used borane adducts.[5] Nevertheless, both of these reagents have significant disadvantages. For example, BH_3–THF is commercially available only as a dilute solution, 1.0 *M* in BH_3, and it is unstable over long periods of time. It is therefore not suitable for bulk commercial use. Although BMS is available as a neat complex, 10.0 *M* in BH_3, and is stable and soluble in a wide range of solvents, it liberates dimethyl sulfide, which is insoluble in water, highly volatile and flammable and has an obnoxious odour, thereby causing environmental and safety problems. Over the years researchers have therefore endeavoured to develop borane adducts that are free of these disadvantages.

Several alternative borane reagents have been reported, including borane-1,4-thioxane,[6] *N*-ethyl-*N*-*iso*-propylaniline-borane,[7] *tert*-butyldialkylamine–borane adducts such as *tert*-butylisopropylmethylamine–borane and *tert*-butylisopropylethylamine–borane,[8] *N*,*N*-dialkylamine–boranes,[9] borane-2-(perfluorooctyl)ethyl methyl sulfide,[10] borane–dodecyl methyl sulfide (DMS) and borane-methyl 6-morpholinohexyl sulfide (MMS),[11] but none of

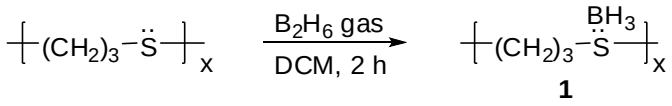
them have been sufficiently advantageous to rival the two simple adducts of borane with THF and dimethyl sulfide.

A number of polymeric borane reagents have also been reported; these are easy to handle, have minimal odour, and the polymeric carrier is easily recoverable.[12-16] In principle, they should be very attractive alternatives to the simple borane complexes. However, several disadvantages are associated with use of the reported reagents, such as low borane content, the requirement for an acid catalyst in the reduction of aldehydes and ketones, the need for use of excess of the polymeric reagent, or limited solubility of the complexes. Perhaps because of these reasons, such reagents have only ever been used in simple hydroboration-oxidation reactions and reductions of carbonyl compounds and have never been used in more sophisticated applications in organic synthesis. They have also not been applied at commercial scale. To be attractive as an alternative borane source, a borane complex needs to involve a carrier that is cheap, non-volatile, virtually odourless and easily removed or recovered from reaction mixtures, have a borane content approaching that of BMS, and be capable of replacing BMS across a whole range of organoboron reactions with different reagents and leading to different products.

Reduction and hydroboration–oxidation reactions place minimal demands on the borane source (which can be used in excess) or on any organoboron intermediates produced, since the organic groups are simply individually cleaved and it does not matter if the boron intermediates produced are monosubstituted, disubstituted or trisubstituted with alkyl or alkoxy groups. Furthermore, these reactions involve relatively mild reagents/conditions and give products with a relatively unreactive functional group. By contrast, many useful reactions of organoboranes involve more demanding reagents, give products with more reactive functionalities (*e.g.* amines, ketones), or involve combination of two or more different groups on the same boron atom into a single product. Such reactions, typically carried out in an ether solvent such as THF with either borane–THF or borane–SMe_2 as the borane source, require the clean formation of individual organoboron intermediates. While formation of such intermediates by hydroboration reactions involving borane–THF or BMS is well studied, it is not clear that the presence of a non-volatile sulfide in a reaction mixture will be innocuous or that borane supported on a polymer will lend itself readily to clean formation and reactions of unsymmetrical organoboranes, which are needed for many reactions. Alternative borane carriers have not been tested in such reactions.

As a part of our own interest in the synthesis of sulfur-containing compounds,[17] the use of solids in green methodologies[18] and boron chemistry[19] we have recently developed a

convenient procedure for the synthesis of various polymeric sulfides from reactions of dihaloalkanes with sodium sulfide nonahydrate[20] and have converted them into new polymeric sulfide-borane complexes (*e.g*. adduct **1**; Scheme 1). Adduct **1** is cheap to make, has high molarity in BH_3, is convenient to handle, and has minimal odour and low volatility.[21] We have also successfully used it in simple hydroboration-oxidation and reduction reactions.



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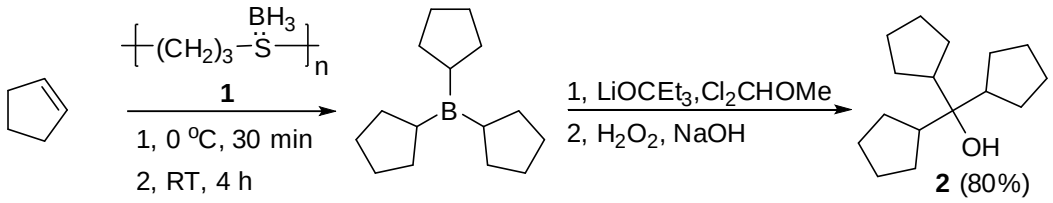
Scheme 1. Synthesis of poly(propylene sulfide)–borane adduct **1**.

It was of interest to see whether this reagent would allow extension of the utility of a polymer-supported borane for the first time to a range of more sophisticated applications. In order to test the wider applications of the new borane adduct **1**, we decided to use it in various synthetic pathways leading to a varied set of compound types, namely a tertiary alcohol, an alkyne, a primary amine, a ketone, and a (*Z*)-alkene, and we now report that it can indeed be used in such applications. It is also easy to recover the poly(propylene sulfide), which can therefore be recycled.

2. Results and discussion

We first wanted to test whether it was possible to prepare a single trialkylborane using the polymer adduct. In order to do so we decided to carry out a reaction in which all three alkyl groups would migrate from the boron atom to a single carbon atom, so that subsequent oxidation would give a tertiary alcohol possessing all the essential features of the original organoborane, thereby verifying the organoborane structure. There are several ways to achieve such a transformation, including carbonylation,[19e] cyanidation[19f] and reaction with the anion of α,α-dichloromethyl methyl ether (DCME).[22] We decided to use the DCME reaction and conducted an *in situ* preparation of tricyclopentylborane from cyclopentene (28.0 mmol) and adduct **1** (*ca.* 9.40 mmol), which on reaction with DCME and lithium triethylcarboxide gave tricyclopentylmethanol (**2**, Scheme 2) in 80% isolated yield.

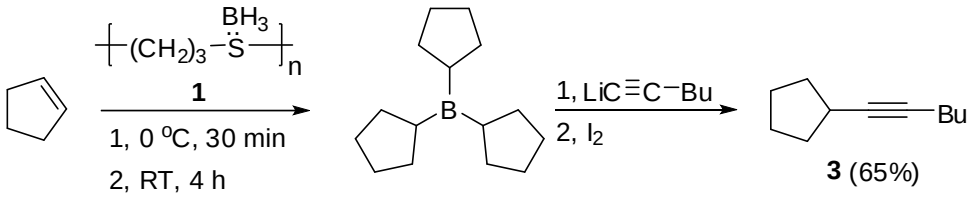


Scheme 2. Synthesis of Tricyclopentylmethanol (**2**).

Isolation of **2** verified that tricyclopentylborane had indeed been formed in substantial yield. However, Brown and Carlson[22] had reported the synthesis of **2** in 91% yield starting with a standard (1 *M*) solution of tricyclopentylborane in THF on a 50 mmol scale. It was not clear whether the lower yield obtained in the present experiment with the polymer-borane complex was an inherent issue associated with the reagent or whether it was merely a problem of the experimental procedure, caused by the use of a smaller scale or preparation of the organoborane *in situ* or some other difference. In order better to understand the situation, we repeated the reaction represented in Scheme 2 but with BH_3–Me_2S instead of the polymer-borane adduct **1**. Compound **2** was obtained in 80% yield, which is the same as that produced using **1**. Clearly, the differences in yields between the reported literature value and that obtained using **1** do not result from any inherent problems associated with the reagent.

The second reaction planned was the synthesis of an internal acetylene from an alkene and a terminal alkyne. In such reactions a trialkylborane is reacted with a 1-lithioalkyne to form the corresponding lithium (1-alkynyl)trialkylborate, which is then reacted with iodine at low temperature to give the corresponding internal acetylene.[23] The reaction involves a single alkyl migration from boron to the carbon atom to form a new carbon-carbon bond. We prepared tricyclopentylborane *in situ* from adduct **1** as described for the previous reaction and then reacted it with 1-lithiohexyne and then iodine as described in the literature, though on a smaller scale. 1-Cyclopentylhexyne (**3**, Scheme 3) was isolated in 65% isolated yield based on 1-hexyne. This is a clear indication that the presence of the polymeric sulfide in the reaction mixture causes no significant problems. Suzuki *et al.*[23] reported the synthesis of **3** in quantitative yield, but for a reaction conducted on a larger scale (30.8 mmol R_3B), using a standard solution of preformed organoborane rather than organoborane prepared *in situ*, and used GC estimation rather than isolation of the product for determination of the yield. It is clear, therefore, that there is no significant disadvantage of using the adduct **1** for *in situ* preparation of the trialkylborane instead of preparing the organoborane using the traditional reagents for this kind of reaction. The polymeric sulfide was recovered (75%) by precipitation with diethyl ether and was investigated by ^{1}H NMR spectroscopy, which showed

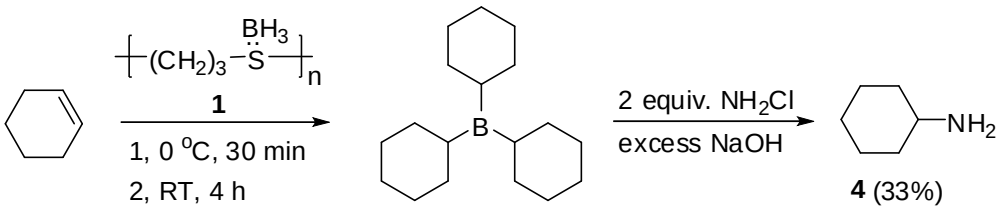
that the recovered polymer had an almost identical spectrum to that of the polymer originally used to produce the borane complex **1**.



Scheme 3. Synthesis of 1-cyclopentylhexyne (**3**).

The next reaction to be tested was the synthesis of a primary amine *via* reaction of a trialkylborane with freshly prepared chloramine. Reactions of this type are reported to involve coordination of chloramine to the boron atom, followed by migration of an alkyl group with displacement of chloride; a maximum of two of the three alkyl groups migrate from boron to nitrogen, thereby limiting the yield based on alkyl groups to 67%.[24] The reactions are usually conducted with organoboranes prepared using borane–THF.

The use of chloramine could provide a possible complication for the use of the polymeric sulfide adduct, since the reagent might oxidize the sulfide groups in the polymer. We also decided to use tricyclohexylborane, generated *in-situ* from cyclohexene and **1** (Scheme 4), because this would introduce a further potential complication to use of the polymeric adduct, which produces a turbid reaction mixture. Hydroboration of cyclohexene with a simple borane complex results in initial precipitation of dicyclohexylborane dimer, which then slowly dissolves on reaction with further cyclohexene to give tricyclohexylborane.[25] The reaction is normally self-indicating, therefore, and can be considered complete when no solid remains. By use of **1**, however, it would not be possible to monitor the dissolution of the dicyclohexylborane dimer very clearly and the hydroboration reaction time would have to be based on literature precedent for a simple complex. A reaction time of 4 h at room temperature was chosen by analogy with the standard procedure reported for the *in situ* preparation of trialkylboranes used in the original report of the generalized chloramine reaction.[24] Cyclohexene (36.5 mmol) and **1** (*ca.* 12.8 mmol BH_3) were stirred in THF for 4 hours and then freshly prepared chloramine (two mole equivalents) and sodium hydroxide solution were added (Scheme 4). Cyclohexylamine was isolated in 33% yield (based on cyclohexene) by solvent extraction followed by distillation. Again, 75% of the polymeric sulfide was recovered.



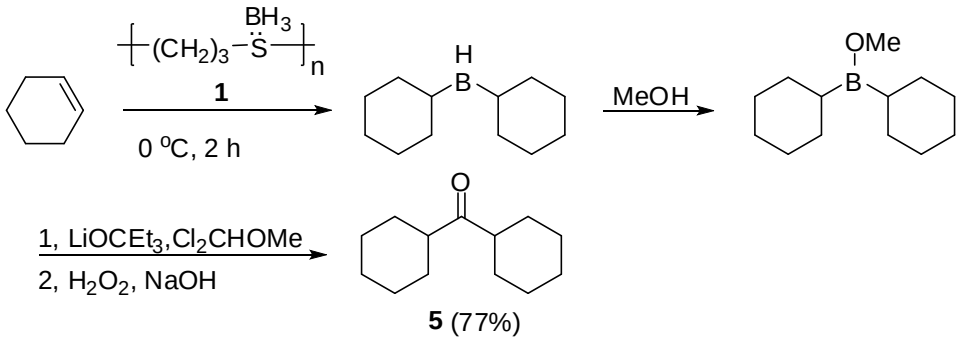
Scheme 4. Synthesis of cyclohexylamine (**4**).

The published yield for the case of cyclohexylamine from tricyclohexylborane prepared using borane–THF was actually 49%.[24] However, the process involved use of chloramine of known concentration (whereas in the present reaction its concentration was assumed based on estimated concentration of the bleach used in its preparation) and the reaction had been applied on a significantly larger scale (100 mmol of alkene). It is also likely that the hydroboration reaction to produce the organoborane had been left for a longer period in view of the authors' experience with such systems. In the present case, everything was carried out in one pot without isolation of any intermediates, but synthesis of the intermediate tricyclohexylborane was clearly achieved successfully, even if in somewhat lower yield as a result of the short period for the hydroboration step. The lower yield of cyclohexylamine than by use of borane–THF was not a major concern since there were many separate steps involved and none of them were individually optimized for the specific case. It is clear that the adduct **1** can be used as a borane source even for a reaction involving chloramine as a reagent and producing a primary amine as product.

The above examples (Schemes 2–4) showed successful production of symmetrical trialkylboranes as intermediates by the use of borane adduct **1**. However, many reactions require either unsymmetrical trialkylboranes or organoboranes that contain a mixture of alkyl groups and other types of substituents. Inevitably, this involves an initial hydroboration that must stop cleanly at a monoalkylborane or dialkylborane stage prior to addition of a different alkene or an alternative type of reagent. Although conditions have been worked out for achieving this in many cases in homogeneous solution, it was by no means obvious that the same conditions would be appropriate for a polymeric borane complex, where relative rates of reaction might be different and intermediates might have different solubilities from the starting complex, potentially resulting in heterogeneous reaction mixtures and leading to mixtures of alkylboron compounds. The final two examples were therefore designed to explore the possibility of production of unsymmetrical organoboron compounds as well as testing out other further reactions. In each case dicyclohexylborane was selected as the initial target. As stated above, when prepared with borane–THF this normally precipitates out as a

dimer, which assists in gaining selectivity, but it was not known whether the same would apply with adduct **1**.

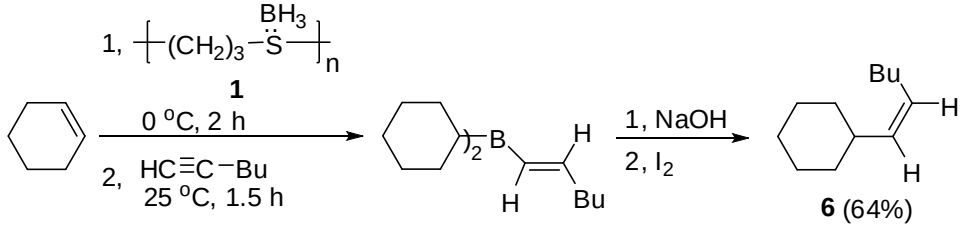
The fourth test reaction was the synthesis of a ketone *via* reaction of a dialkylmethoxyborane with the anion from DCME.[26] This is a general reaction that involves migration of both alkyl groups from boron to carbon, followed by oxidation with alkaline hydrogen peroxide to give the dialkyl ketone. Adduct **1** (*ca.* 8.00 mmol BH_3) in THF was stirred with cyclohexene (15.8 mmol) at 0 ^oC for 2 hours and then methanol (7.80 mmol) was added. The mixture was then further treated with DCME in the presence of lithium triethylcarboxide (prepared *in situ*) followed by oxidation with alkaline hydrogen peroxide (Scheme 5). Dicyclohexyl ketone (dicyclohexylmethanone, **5**) was isolated in 78% yield by distillation. The published procedure for this compound gave **5** in 85% isolated yield from a 50 mmol scale reaction of dicyclohexylmethoxyborane.[26] The modest diminution in yield for the present reaction is entirely understandable given the much smaller scale used and our limited practical experience with the particular type of reaction, so it may safely be concluded that the adduct **1** can be used without problem to produce dicyclohexylmethoxyborane.



Scheme 5. Synthesis of dicyclohexylmethanone (**5**).

The final reaction was the synthesis of a (*Z*)-alkene by the Zweifel reaction, which has normally been accomplished with an alkenyldialkylborane obtained *via* hydroboration using BH_3–THF or BMS.[27] Such an alkenyldialkylborane is treated with a mixture of sodium hydroxide (converts the borane into a hydroxyborate) and iodine (attacks the alkenyl group and induces rearrangement) to give an unstable (2-iodoalkyl)boron compound, which eliminates an iodoboron species to give the final product, a (*Z*)-alkene. The particular geometrical isomer results from the stereospecific nature of all of the intermediate steps. The use of **1** in such a reaction would therefore test its ability to hydroborate alkynes as well as alkenes and its ability to form an all-carbon unsymmetrical organoborane cleanly, as well as testing its performance under the conditions of the Zweifel reaction. Adduct **1** (*ca.* 8.00 mmol

BH_3) was therefore treated successively with cyclohexene (15.8 mmol) and 1-hexyne (7.80 mmol) in the hope of producing dicyclohexyl-1-hexenylborane, which was then subjected to alkaline iodination to produce **6** (Scheme 6). Product **6** was isolated by column chromatography in 64% yield, based on hex-1-yne (7.80 mmol). The reported synthesis of (*Z*)-1-cyclohexylhex-1-ene **6** using BH_3–THF was accomplished in 75% yield for a reaction on a three times larger scale (25.0 mmol 1-hexyne).[27] The modest diminution in yield achieved with **1** on a smaller scale and without individual optimization of reaction conditions is not of significance and it can safely be concluded that the use of **1** is entirely appropriate for such reactions.



Scheme 6. Synthesis of (*Z*)-1-cyclohexylhex-1-ene (**6**).

At this point we had shown that adduct **1** could be used to produce various different types of organoboranes and that a variety of further reactions could be conducted with the poly(trimethylene sulfide) present. In two cases we had also recovered samples of the polymer by precipitation following addition of diethyl ether and methanol, and their proton NMR spectra showed that both recovered samples were very similar to the original polymer. This suggested that it should be easy to reuse the polymer to prepare a fresh batch of adduct **1** from the recovered polymer or to precipitate the polymer from a reaction mixture prior to subsequent reaction of the organoborane, which might in some cases be advantageous if the presence of the polymer is problematical. Therefore, we decided to investigate the recovery and reuse of the polymer in more detail. In order to do so we used reduction of benzaldehyde with adduct **1**[21] as a convenient reaction to study. To a sample of adduct **1** (2.40 g, *ca.* 20.0 mmol borane) in THF (57 mL) was added benzaldehyde (5.30 g, 50.0 mmol) and the mixture was stirred for 30 min at 0 °C, then for 4 hours under reflux conditions, followed by the addition of methanol (15 mL) to quench the reaction. The polymeric material was precipitated as a white solid by the addition of diethyl ether (100 mL) during the work up process and was removed by filtration. The polymeric sulfide was washed with aqueous sodium hydroxide (3 *M*) to remove any boric acid, then washed with water and dried under vacuum. A sample was withdrawn for analysis and the rest was treated with diborane gas to

reform adduct **1**. The new adduct was then analyzed for borane content and used in a further reaction with benzaldehyde in a manner that was identical except for being on a slightly smaller scale. The whole process of recovery and reuse was then repeated once more. The benzyl alcohol was produced quantitatively each time. The amount of polymer recovered and the properties of the recovered polymer are recorded in Table 1.

Table 1
The borane content and GPC results for the recovered polymeric sulfide

Polymer	Recovery (%)	Mn (Daltons)[a]	Mw (Daltons)[a]	PDI [a]	BH_3 in **1** (mmol/g)
1st use	—	4,178	09,415	2.253	8.5
2nd use	70	6,746	12,451	1.845	8.3
3rd use	90	7,736	13,049	1.687	7.7

[a] Mn = number average molecular weight; Mw = weight average molecular weight; PDI = poly dispersity index.

The results showed that recovery of polymer from the first run was around 70%, but the second recovery was significantly better (*ca*. 90%). The ^{1}H NMR spectrum of the polymer recovered from the first run was broadly similar to that of the initial polymer, but the average molecular weight of the polymer had increased, suggesting that the process of recovery of the polymer resulted in loss primarily of short chain polymeric material, which was probably more soluble in the ether used to precipitate the polymer. The polymeric sample recovered from the third use was quite similar to that recovered from the second use, in terms of both NMR spectrum and molecular weight, and the yields of benzyl alcohol were consistently high. It therefore seems that the initial polymer contains a small amount of relatively short chain oligomers that are lost during the first recovery. Thereafter, the recovered polymer is less polydisperse and has a somewhat higher average molecular weight, but forms a borane complex that behaves in a manner similar to that of the initial polymer as a reducing agent.

The ability to recover the polymer increases the attractiveness of the adduct **1** as a reagent. Its recycling would reduce the cost of the reagent, while precipitation of the polymer after organoborane formation but before further reaction would allow such reactions to be conducted in the absence of the polymeric sulfide where this was appropriate.

3. Conclusions

In conclusion, poly(propylene sulfide)–borane adduct **1** has proved to be a versatile, efficient and convenient reagent for *in situ* generation of a range of organoboron types

(trialkylboranes, alkenyldialkylboranes, dialkylalkoxyboranes) and their subsequent conversion into a range of organic compound classes [tertiary alcohol, alkyne, (*Z*)-alkene, primary amine, ketone] by use of several potentially problematical reagents (hydrogen peroxide, chloramine, iodine, strong bases). All of the reactions proceeded without problem and yields of isolated products were only marginally lower than those reported in the literature for reactions involving organoboranes prepared using borane–THF or borane–dimethyl sulfide (BMS), even though the current reactions were generally conducted on a much smaller scale and were not individually optimized. The new polymeric-borane adduct contains around 8-8.5 mmol of borane per gram of reagent, which is much greater than that of borane–THF solutions and around two thirds of that of BMS. However, compared to BMS it is much more stable in air and the liberated sulfide is much less volatile, does not have an obnoxious odour and is much less flammable. The polymeric sulfide, which is not very expensive to produce at the outset, can be easily recovered after reactions of the borane complex, and by recycling the material it could further mitigate any differences in cost compared to BMS. Adduct **1** could replace BH_3–THF and BH_3–SMe_2 complexes in all cases tried and might well be suitable for large scale industrial application.

4. Experimental section

4.1. General experimental details

All reactions were performed under a nitrogen atmosphere. Glassware was oven dried, assembled hot and allowed to cool under a stream of nitrogen gas. All chemicals and reagents were purchased from commercial sources and used without further purification. THF was distilled from sodium benzophenone ketyl and other solvents were purified by standard procedures.[28] ^{1}H and ^{13}C NMR spectra were recorded on a spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C measurements, respectively. Chemical shifts δ are reported in parts per million (ppm) relative to TMS. ^{13}C Signals corresponding to CH, CH_2, or CH_3 are assigned from DEPT–90 and 135 spectra and all others carbons are quaternary (C). Low and high–resolution mass spectra were recorded on a time-of-fight mass spectrometer using electron impact (EI). IR spectra were recorded on a FT–IR spectrometer by applying droplets of the material on a NaCl plate.

The borane adduct **1** was prepared by passing diborane gas into a solution of the polymeric sulfide in DCM and the borane content was measured by gas analysis.[21]

4.3. Synthesis of tricyclopentylmethanol (2)

Cyclopentene (1.90 g; 28.0 mmol) was added to a stirred cooled (0 °C) mixture of **1** (1.10 g, *ca.* 9.40 mmol BH_3) and anhydrous THF (20 mL) under nitrogen and the mixture was stirred at 0 °C for 30 min and then at room temperature for 4 h. In another dried 50 mL flask 3-ethyl-3-pentanol (1.05 g, 9.04 mmol) was added to a stirred cooled solution of *n*-BuLi in hexane (6.00 mL of 1.5 *M*, 9.00 mmol) and the mixture was stirred for 30 min at 0 °C. The tricyclopentylborane solution was cooled to 0 °C and DCME (1.20 g, 10.4 mmol) was added followed by transfer of the lithium triethylcarboxide by a double ended needle over a period of 10 min. The cooling bath was removed and the reaction mixture was stirred for 1 h. The flask was cooled to 0 °C and ethanol (10 mL, 95%) was added followed by sodium hydroxide (2.40 g, *ca*. 60.0 mmol) and slow addition of hydrogen peroxide (9 mL, 35%, *ca*. 90 mmol). The mixture was stirred for 1 h at 70 °C and then allowed to cool. Diethyl ether (20 mL) was added to precipitate the polymeric material, which was filtered, and anhydrous potassium carbonate was added to the filtrate to salt out the aqueous phase. The mixture was filtered and the solid was washed with ether (2 × 10 mL). The filtrate and washings were combined and the organic layer was separated, washed with brine (3 × 20 mL) and dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (alumina; hexane-ether; 1:1) to give **2** (1.70 g, 7.20 mmol, 80%) as a colourless oil (Lit. oil)[22]; R_f (10% Et_2O/hexane) 0.22; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.06 (appt. pentet, J = 9.5 Hz, 3H), 1.36–1.51 (m, 24H), 1.16 (s, exch., 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 77.6 (C), 47.8 (CH), 27.9 (CH_2), 25.2 (CH_2); MS (EI) *m/z* (%) 218 ($[M - H_2O]^+$, 6), 167 (90), 149 (96), 125 (19), 97 (100), 81 (52), 69 (99); HRMS (EI) calcd for $C_{16}H_{26}$ ($[M - H_2O]^+$) 218.2034, found 218.2035; IR (FT) ν_{max} 3623, 3521, 2941, 1451. The R_f value and spectroscopic data of **2** were identical in all respects with those of an authentic sample prepared according to the literature procedure.[22]

4.4. Synthesis of hex-1-ynylcyclopentane (3)

Tricyclopentylborane (*ca.* 3.70 mmol) was prepared as described in the synthesis of **2** from cyclopentene (0.749 g; 11.0 mmol) and adduct **1** (0.450 g, *ca.* 3.80 mmol BH_3). A freshly prepared solution of hex-1-ynyllithium (*ca*. 3.50 mmol), prepared by addition of a solution of *n*-butyllithium in hexane (1.50 *M*, 2.40 mL) to a solution of hex-1-yne (0.290 g, 3.50 mmol) in THF (10 mL) at 0 °C, was added slowly by syringe and the mixture was stirred for 30 min at 0 °C. The reaction mixture was stirred efficiently, cooled to –78 °C, a solution of iodine (1.00 g, 3.94 mmol) in dry ether (15 mL) was added by syringe over 30 min and the mixture

was stirred for a further 45 min at –78 ^{o}C. The reaction mixture was left to warm up to room temperature and few drops of saturated aqueous sodium thiosulfate solution were added to decompose the excess iodine. Diethyl ether (20 mL) was added to precipitate the polymer, followed by filtration. The solid was washed with ether (2 × 10 mL) and the combined filtrate and washings were washed with aqueous sodium hydroxide solution (2 × 20 mL, 3 *M*). The aqueous layer was extracted with diethyl ether (2 × 20 mL) and sodium hydroxide (4.00 mL, 3 *M*, 12.0 mmol) was added to the combined organic layers, followed by dropwise addition of hydrogen peroxide (1.50 mL, 30%, *ca*. 13.0 mmol). The aqueous layer was saturated with K_2CO_3 and the organic layer was separated and then dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to give a yellow oily material, which was purified by column chromatography (silica gel, hexane) to give hex-1-ynylcyclopentane **3** (0.341 g, 2.27 mmol, 65%) as a colourless oil (Lit. oil)[23]; R_f (hexane) 0.87; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.60–2.53 (m, 1H), 2.16 (dt, J = 2.0, 6.9 Hz, 2H), 1.92–1.35 (m, 12H), 0.91 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 84.4 (C), 79.6 (C), 34.1 (CH_2), 31.3 (CH_2), 30.4 (CH), 24.9 (CH_2), 21.9 (CH_2), 18.5 (CH_2), 13.6 (CH_3); MS (EI) *m/z* (%) 150 (M^+, 53), 137 (55), 121 (57), 137 (87), 108 (85), 93 (100), 91 (97), 67 (98); HRMS (EI) calcd for $C_{11}H_{18}$ (M^+) 150.1407 found 150.1409; IR (FT) ν_{max} 2957, 2933, 2871, 2236. The R_f value and spectroscopic data of **3** were identical with those of an authentic sample prepared according to the literature procedure.[23]

4.5. Synthesis of cyclohexylamine (4)

Cyclohexene (3.00 g; 36.5 mmol) was added to a stirred cooled (0 °C) solution of **1** (1.50 g, *ca.* 12.7 mmol BH_3) in anhydrous THF (20 mL) under nitrogen and the mixture was stirred at room temperature for 4 h. An aqueous NaOH solution (3 *M*, 18 mL) was added to the mixture followed by addition of a freshly prepared solution of chloroamine [*ca.* 25.0 mmol; prepared as follows: in a 100 mL flask were placed water (25 mL) and aqueous ammonium hydroxide (5.00 mL, 5 *M*); the mixture was cooled to 0 ^{o}C after which commercial bleach (aqueous sodium hypochlorite, 50.0 mL, 0.50 *M*) was added and the mixture was stirred at 0 ^{o}C for 1 h to produce chloroamine]. The mixture was stirred at room temperature for a further 2 h and then acidified (checked by pH paper) with hydrochloric acid (2 *M*). Diethyl ether (25 mL) was added to precipitate the polymeric material, which was removed by filtration. Solid sodium hydroxide was used to make the solution strongly alkaline. The organic layer was separated and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the product was purified by distillation under reduced

pressure using an oil pump to give pure **4** (1.20 g, 12.0 mmol, 33% based on cyclohexene) as a colourless oil; b.p. 45–47 ^{o}C/35 mm Hg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.58–2.52 (m, 1H), 1.76–1.50 (m, 6H), 1.24–0.94 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 50.3 (CH), 36.7 (CH_2), 25.6 (CH_2), 25.0 (CH_2); MS (EI) *m/z* (%) 99 (M^+, 15), 82 (4), 70 (12), 67 (6), 56 (100); HRMS (EI) calcd for $C_6H_{13}N$ (M^+) 99.1045, found 99.1048; IR (FT) ν_{max} 3348, 3276, 2927, 2853. The boiling point and spectroscopic data of **4** were identical with those of an authentic sample obtained from Sigma–Aldrich.

4.6. Synthesis of dicyclohexylmethanone (5)

Cyclohexene (1.30 g; 15.8 mmol) was added to a stirred cooled (0 °C) solution of **1** (0.940 g, *ca*. 8.00 mmol BH_3) in anhydrous THF (14 mL) under nitrogen and the mixture was stirred at 0 ^{o}C for 2 h. Methanol (0.250 g, 7.80 mmol) was then added to form dicyclohexylmethoxyborane. In another 50 ml flask, 3-ethyl-3-pentanol (0.930 g, 8.00 mmol) was added to a cooled (0 ^{o}C) solution of *n*-BuLi in hexane (5.00 mL of 1.6 *M*; 8.00 mmol) and the mixture was stirred for 30 min at 0 ^{o}C to form lithium triethylcarboxide. DCME (1.06 g, 9.22 mmol) was added to the dicyclohexylmethoxyborane solution, followed by transfer of the lithium triethylcarboxide solution by a double ended needle over a period of 10 min, then the reaction mixture was allowed to warm up to room temperature and stirred for 1 h. Ethanol (3.5 mL) was added followed by NaOH (0.600 g, 15.0 mmol) then careful addition of hydrogen peroxide (2.40 mL, 30%, *ca*. 21.0 mmol). The reaction mixture was stirred for 1 h at 50 ^{o}C then left to cool down to room temperature. The reaction mixture was worked up by addition of brine (20 mL) followed by extraction with diethyl ether (2 × 50 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by distillation under reduced pressure using an oil pump to give **5** as colourless oil (1.20 g, 6.18 mmol, 77%); b.p. 96–98 ^{o}C/1.2 mm Hg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44–2.39 (m, 2H), 1.78–1.56 (m, 10H), 1.39–1.01 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.6 (C), 49.2 (CH), 28.6 (CH_2), 25.9 (CH_2), 25.7 (CH_2); MS (EI) *m/z* (%) 194 (M^+, 30), 127 (12), 111 (85), 95 (38), 84 (100), 67 (35); HRMS (EI) calcd for $C_{13}H_{22}O$ (M^+) 194.1670, found 194.1671; IR (FT) ν_{max} 2928, 2853, 1704. The boiling point and spectroscopic data of **5** were identical with those of an authentic sample obtained from Sigma–Aldrich.

4.7. Synthesis of (Z)-1-cyclohexylhex-1-ene (6)

Dicyclohexylborane (*ca.* 7.90 mmol) was prepared as described for the synthesis of **5** from cyclohexene (1.30 g; 15.8 mmol) and adduct **1** (0.940 g, *ca.* 8.00 mmol BH_3). 1-Hexyne (0.640 g, 7.79 mmol) was added while the temperature was maintained at room temperature. The mixture was stirred for 1.5 h at room temperature and then cooled to −10 ^oC and aqueous sodium hydroxide solution (6 *M*, 10 mL, 60 mmol) and iodine solution (2.50 g, 9.85 mmol) in THF (15 mL) were added by syringe dropwise over 15 min. The reaction mixture was allowed to warm up to room temperature and a small amount of saturated aqueous sodium thiosulfate solution was added to decompose the excess iodine. Diethyl ether (20 mL) was added followed by filtration to remove the polymeric sulfide. The solid was washed with ether (2 × 10 mL) and the filtrate and washings were combined. Pentane (30 mL) was added and the organic layer was separated from the aqueous layer, washed with brine (2 × 20 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica; hexane) to give pure **6** (0.83 g, 5.00 mmol, 64%) as colourless oil (Lit. oil)[27]; R_f (hexane) 0.76; ^1H NMR (400 MHz, $CDCl_3$) δ 5.31–5.19 (m, 2H), 2.32–2.23 (m, 1H), 2.06 (m, 2H), 1.76-1.61 (m, 4H), 1.36–1.05 (m, 10H), 0.93 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.0 (CH), 128.0 (CH), 36.3 (CH), 33.4 (CH_2), 32.2 (CH_2), 27.2 (CH_2), 26.1 (CH_2), 26.0 (CH_2), 22.4 (CH_2), 14.0 (CH_3); MS (EI) *m/z* (%) 166 (M^+, 56), 154 (5), 137 (5), 124 (10), 109 (84), 96 (90), 81 (96), 67 (100); HRMS (EI) calcd for $C_{12}H_{22}$ (M^+) 166.1721, found 166.1722; IR (FT) ν_{max} 2999, 2956, 2925, 2851, 1654, 1607. The R_f value and spectroscopic data of **6** were identical with those of an authentic sample prepared according to the literature procedure.[27]

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