ChemComm
www.rsc.org/chemcomm

# Novel organocycloborates *via* Grignard reagents†

**Holger Braunschweig,*[a] Giovanni D'Andola,[ab] Tom Welton[b] and Andrew J. P. White‡[b]**
[a] *Institute of Inorganic Chemistry, Am Hubland, 97074 Würzburg, Germany.*
*E-mail: h.braunschweig@mail.uni-wuerzburg.de; Fax: +499318884623; Tel: +499318885260*
[b] *Department of Chemistry, Imperial College London, Exhibition Road, South Kensington, London, UK SW7 2AZ*

***Received (in Cambridge, UK) 1st April 2004, Accepted 27th May 2004***
***First published as an Advance Article on the web 25th June 2004***

DOI: 10.1039/b404864d

**An unprecedented cyclisation reaction of α,ω-borylbromoalkanes is seen upon treatment with magnesium turnings, forming organocycloborates in high yield. The novel boratacyclopentanes and -hexanes have been characterised by X-ray crystallography.**

The chemistry of tetraorganoborates has received considerable attention,[1] due to their importance for the preparation of organic and organometallic compounds and as analytical reagents.[2] Tetraaryl- or mixed alkylarylborates have been widely used as non-coordinating anions for organometallic compounds, and as sources for nucleophilic organyl groups.[3,4] In contrast, relatively little is known about non-cyclic tetraalkylborates, which can be obtained in several ways,[5] *e.g.* from reaction of alkaline metal organyls with $BR_3$ (R = alkyl)[6,7] or from reaction of $Na[HBR_3]$ with alkenes.[8] In the case of sterically demanding trialkylboranes, however, there is a strong tendency to form trialkylborohydrides $M[HBR_3]$.[9] The chemistry of cyclic tetraalkylborates is even less well developed, and none of the aforementioned methods can be applied to their synthesis.

To the best of our knowledge, only one very specific formation of a single spirocyclic tetraalkylborate at elevated temperature has been reported, by Koster in 1969.[10] In addition, only a few 9-BBN (where 9-BBN = 9-borabicyclo[3.3.1]nonane) derivatives of the type $C_8H_{14}BRR'$[9] (R = $CH_3$, R′ = $^t$Bu) or $C_8H_{14}BArPh$[11] (Ar = $C_6H_4$-*o*-$CH_2NMe_2$) are known.

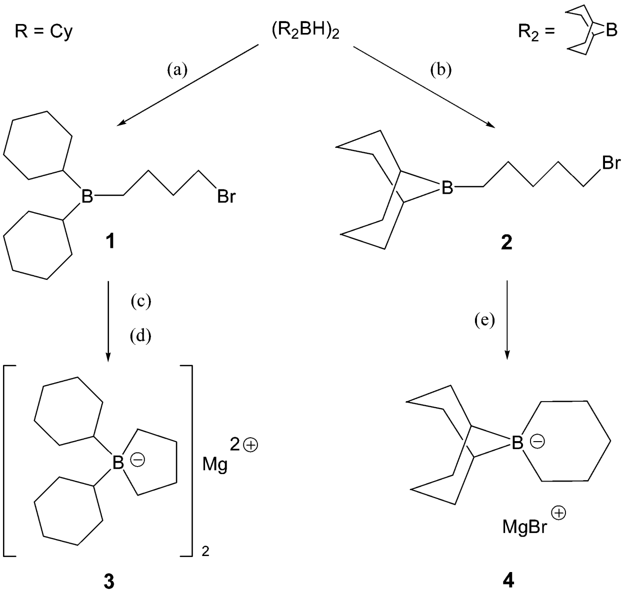
A boron-centred cyclisation reaction appeared to us to be a preferable method for the synthesis of tetraalkylcycloborates. This approach has been, so far, restricted to cyclic boranes with three coordinate boron centres, obtained *via* hydroboration of dienes,[12] or dialkylation of $R_2NBCl_2$.[13]

As summarized in Scheme 1, 4-bromo-1-butene and 5-bromo-1-pentene were treated with suitable diboranes(6) $\{(R_2BH)_2\}$ to give the ω-bromoalkyl(diorgano)boranes **1** and **2** in high yield as colourless oils. Subsequent reaction of **1** with activated Mg-turnings and then 1,4-dioxane furnished the boratacyclopentane **3** with elimination of $MgBr_2$. Similarly, the 9-BBN derivative **2** was treated with magnesium to give the boratacyclohexane **4**. In contrast to the former reaction, no 1,4-dioxane was employed here, and hence, **4** was isolated as a $MgBr^-$ salt.

The two cyclic tetraalkylborates were isolated as colourless, modestly air- and moisture-sensitive crystals in yields above 85%. Their structure in solution was derived from multinuclear NMR spectroscopic data. The $^{11}B$ NMR spectra exhibit expected signals at $\delta = -12.5$ (**3**) and $-20.5$ (**4**), which are high field shifted by approximately 95 ppm with respect to the triorganyl boranes **1** and **2**, indicating boron in coordination number four. The formation of the borates **3** and **4** must proceed *via* Grignard species of the type $R_2B(CH_2)_nMgBr$ ($n$ = 4, 5) with intramolecular attack of the nucleophilic carbon atom at the Lewis-acidic boron centre.

The cyclisation reaction, which yields the thermodynamically favoured 5- and 6-membered boratacycles, occurs instantaneously upon treatment of **1** and **2** with magnesium. So far, it has proven difficult to isolate the proposed intermediate. However, in the case of related compounds with shorter alkanediyl spacers, and hence, a less pronounced tendency for cyclisation, we were able to spectroscopically characterise Grignard species of the type $R_2B(CH_2)_3MgBr$.[14]

The X-ray structure§ determination of crystals of **3** showed it to contain the expected tetraalkylborate anion (Fig. 1). The five-membered $BC_4$ ring adopts a typical twisted geometry with C(2) and C(3) lying *ca.* 0.36 and 0.30 Å "above" and "below" the {B,C(1),C(4)} plane respectively. Except for the restricted bite



**Scheme 1** Synthetic pathway for the synthesis of tetraalkylcycloborates. (a) 4-bromo-1-butene, THF; (b) 5-bromo-1-pentene, THF; (c) $Et_2O$, Mg turnings; (d) 1,4-dioxane, $-MgBr_2\cdot(\text{dioxane})_n$; (e) THF, Mg turnings.

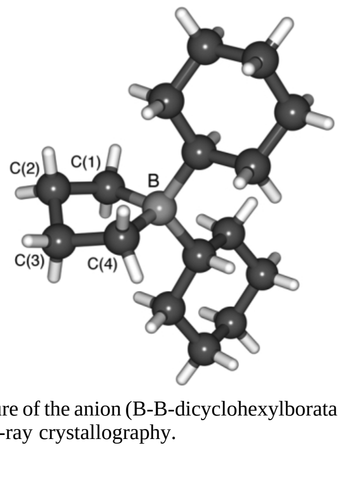


**Fig. 1** The structure of the anion (B-B-dicyclohexylboratacyclopentane) (**3**), determined by X-ray crystallography.

---

† Electronic supplementary information (ESI) available: experimental details and $^1H$, $^{13}C$ and $^{11}B$ NMR data for **1**, **2**, **3**and **4**, single crystal X-ray data and additional figures for **3**and **4**. See http://www.rsc.org/suppdata/cc/b4/b404864d/

‡ This paper is dedicated to Prof. Dr. Wolfdieter Schenk on the occasion of his 60th birthday.

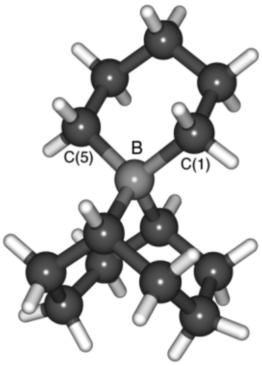


**Fig. 2** The structure of the anion 1,5-pentadiyl-9-borabicyclo[3.3.1]nonane (**4**), determined by X-ray crystallography.

angle within the $BC_4$ ring [C(1)–B–C(4) 100.9(3)°] the angles at the boron centre are close to ideal tetrahedral, being in the range 109.9(3) to 112.0(3)°. Within statistical significance, all four B–C bond lengths are the same [1.655(5) to 1.668(5) Å].

The solid state structure§ of **4** was shown to be $[(thf)_5MgBr][C_{13}H_{24}B]\cdot thf$, confirming the presence of a magnesium bromide cation and the anion shown in Fig. 2. The geometry at the boron is distorted tetrahedral with angles in the range 102.7(3)–113.2(3)°, the greater flexibility of the six-membered ring causing less strain at the boron centre than is seen in **3**, the C(1)–B–C(5) angle being 104.8(3)° for the intra-ring boron angle in **4** *cf.* 100.9(3)° in **3**. The six-membered $(CH_2)_5B$ ring adopts a chair conformation, as do both of the $C_5B$ portions of the 9-BBN ring. The B–C bond lengths are in the narrow range 1.643(5)–1.649(5) Å, at the high end of those seen for trialkyl boron centres with either a $(CH_2)_5B$ or 9-BBN ring system (*ca.* 1.60–1.64).[15]

Though a few examples of $BC_4H_8$ and $BC_5H_{10}$ rings have been previously reported, we believe these to be the first examples of such rings at a tetraalkyl boron centre.[16] The most closely related analogues are trialkylborohydride moieties $\{(H)(PhCH_2)BC_4H_8\}$ and $\{(H)(PhCH_2)BC_5H_{10}\}$ in $Cp_2Zr\{(\mu\text{-}H)B(X)CH_2Ph\}\{(\mu\text{-}H)_2BX\}$ (X = $C_5H_{10}$, $C_4H_8$), which are linked to the zirconium centre *via* a B–H–Zr bridge.[17] All other examples involving a $(H)_2BC_4H_8$ or $(H)_2BC_5H_{10}$ unit are linked to a metal centre by two B–H–M bridges.

In conclusion, this unprecedented ring closure reaction at the boron centre represents a facile and versatile synthesis for tetraalkylborates, which will be further exploited.

## Notes and references

§ *Crystal data for* **3**: $[(C_4H_8O)_6Mg](C_{16}H_{30}B)_2\cdot 4C_4H_8O$, $M$ = 1211.77, monoclinic, $P21/n$ (no. 14), $a$ = 13.8628(19), $b$ = 17.177(3), $c$ = 15.580(2) Å, β = 96.390(11)° $V$ = 3686.9(9) Å$^3$, $Z$ = 2 ($C_i$ symmetry), $D_c$ = 1.092 g cm$^{-3}$, μ(Cu–Kα) = 0.613 mm$^{-1}$, $T$ = 203 K, colourless plates; 4964 independent measured reflections, F2 refinement, R1 = 0.073, wR2 = 0.204, 3417 independent observed reflections [|Fo| > 4σ(|Fo|), 2θmax = 120°], 426 parameters. CCDC 236834.

*Crystal data for* **4**: $[(C_4H_8O)_5MgBr](C_{13}H_{24}B)\cdot C_4H_8O$, $M$ = 727.98, monoclinic, $P21/c$ (no. 14), $a$ = 10.953(2), $b$ = 14.4213(16), $c$ = 25.584(3) Å, β = 93.597(15)° $V$ = 4033.4(11) Å$^3$, $Z$ = 4, $D_c$ = 1.199 g cm$^{-3}$, μ(Mo–Kα) = 1.075 mm$^{-1}$, $T$ = 203 K, colourless blocks; 7040 independent measured reflections, F2 refinement, R1 = 0.046, wR2 = 0.095, 4555 independent observed absorption corrected reflections [|Fo| > 4σ(|Fo|), 2θmax = 50°], 513 parameters. CCDC 236835. See http://www.rsc.org/suppdata/cc/b4/b404864d/ for crystallographic data in .cif or other electronic format.

1 A. Pelter, K. Smith and H. C. Brown, *Borane reagents*, Academic Press, 1988; M. F. Lappert, *Chem. Rev.*, 1956, **56**, 1035.

2 M. F. Lappert and E. L. Muetterties, *The Chemistry of Boron and its Compounds*, Wiley, New York, 1967.

3 E. Negishi, *J. Organomet. Chem.*, 1976, **108**, 281; E. Negishi, K. W. Chin and T. Yoshida, *J. Org. Chem.*, 1975, **40**, 1676; E. Negishi, A. Abramovitch and R. E. Merrill, *J. Chem. Soc., Chem. Commun.*, 1975, 138; R. Hunter, J. P. Michael and G. D. Tomlinson, *Tetrahedron*, 1994, **50**, 871.

4 N. Miyaura, M. Itoh and A. Suzuki, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 2199; N. Miyaura, M. Itoh and A. Suzuki, *Synthesis*, 1976, 618; D. Zhu and J. K. Kochi, *Organometallics*, 1999, **18**(2), 161.

5 J. D. Odom, *Comprehensive Organometallic Chemistry*, **Vol. 1**, Ed. G. Wilkinson and F. G. A. Stone, Pergamon Press, Oxford (1982).

6 R. Damico, *J. Org. Chem.*, 1964, **29**, 1971.

7 H. C. Brown, A. B. Levy and M. M. Midland, *J. Am. Chem. Soc.*, 1975, **97**, 5017.

8 J. B. Honeycutt and J. M. Riddle, *J. Am. Chem. Soc.*, 1961, **83**, 369; P. Binger and R. Koster, *Inorg. Synth.*, 1974, **15**, 138; H. C. Brown and S.-C. Kim, *J. Org. Chem.*, 1984, **49**, 1064.

9 H. C. Brown, G. W. Kramer, J. L. Hubbard and S. Krishnamurthy, *J. Organomet. Chem.*, 1980, **188**, 1.

10 M. A. Grassberger and R. Koster, *Angew. Chem. Int. Ed.*, 1969, **8**, 275.

11 E. Kalbarczyk and S. Pasynkiewicz, *J. Organomet. Chem.*, 1985, **292**(1–2), 119–32.

12 D. Basavaiah and H. C. Brown, *J. Org. Chem.*, 1982, **47**, 1792; H. C. Brown and G. G. Pai, *J. Organomet. Chem.*, 1983, **250**, 13; H. J. Bestman, K. Suhs and T. Roders, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 1038.

13 G. E. Herberich, U. Eigendorf and C. Ganter, *J. Organomet. Chem.*, 1991, **402**, C17; S. Masamune, B. M. Kim, J. S. Petersen, T. Sato, S. J. Veenstra and T. Imai, *J. Am. Chem. Soc.*, 1985, **107**, 4549.

14 H. Braunschweig and G. D′Andola, unpublished results. For example, in the case of $R_2B(CH_2)_3MgBr$ with $R_2$ = 9-BBN or $Cy_2$, the $^1H$ NMR spectra show a highfield shifted triplet for the α-$CH_2$ methylene protons adjacent to the boron centre, and deshielded signals in the $^{11}B$ NMR spectra at approximately 80 ppm, thus proving the presence of three coordinate boron.

15 G.-M. Chen and H. C. Brown, *J. Am. Chem. Soc.*, 2000, **122**, 4217; B. Wrackmeyer, B. Schwarze and W. Milius, *J. Organomet. Chem.*, 1997, **545**, 297; M. Sigl, A. Schier and H. Schmidbaur, *Chem. Ber.*, 1997, **130**, 951; H. Schmidbaur, M. Sigl and A. Schier, *J. Organomet. Chem.*, 1997, **529**, 323; G. Erker, U. Hoffmann, R. Zwettler and C. Kruger, *J. Organomet. Chem.*, 1989, **367**, C15; H. Schumann, B. C. Wassermann, S. Schutte, B. Heymer, S. Nickel, T. D. Seuss, S. Wernik, J. Demtschuk, F. Girgsdies and R. Weimann, *Z. Anorg. Allg. Chem.*, 2000, **626**, 2081; R. Hunter, R. H. Haueisen and A. Irving, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 566; R. T. Baker, J. C. Calabrese, S. A. Westcott and T. B. Marder, *J. Am. Chem. Soc.*, 1995, **117**, 8777.

16 A search of the Jan-04 update of the Cambridge Crystallographic Database (version 5.25) revealed no examples of a tetraalkylborate centre with $BC_4H_8$ or $BC_5H_{10}$ rings.

17 F.-C. Liu, J. Liu, E. A. Meyers and S. G. Shore, *Inorg. Chem.*, 1999, **38**, 2169.