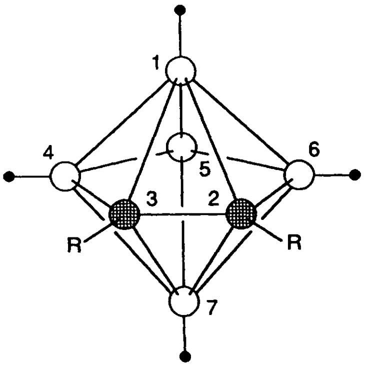
Letters

The true identity of the 'bare-carbon' cluster, *closo*-$C_3B_5H_7$

In 1971 Thompson and Grimes[1] reported the isolation and characterisation of a compound which was thought to be the first tricarba-*closo*-octaborane, $C_3B_5H_7$ **1**. The compound was generated in the thermolysis of either μ- or 4-silyl-2,3-dicarba-*nido*-hexaborane(8), $H_3SiC_2B_4H_7$, at 250 °C, and was thought to contain a 'bare' carbon atom, *i.e.* one carrying an unshared electron pair rather than a hydrogen atom, in the polyhedral framework. It was assumed to be isoelectronic and isostructural with $[B_8H_8]^{2-}$, and its solution NMR spectra were interpreted in terms of a time-averaged square antiprismatic geometry. No further work was reported on **1** until very recently when Bausch *et al.*[2] carried out an *ab initio*/IGLO/NMR treatment, the results of which cast considerable doubt on the unusual *closo* structure proposed for this molecule. Treatments at even higher levels of *ab initio* and IGLO (individual gauge for localized orbitals) theory, taking into account various 'static' and 'fluxional' candidates, were said to be in progress and an experimental re-investigation of the compound to generate more accurate NMR data was proposed. We now show that none of these undertakings is necessary, and clarify some potential sources of confusion in the literature.

During the course of our recent studies of reactions of binary boranes with unsaturated hydrocarbons[3,4] it has become apparent to us that the compound reported as **1** is in fact the parent dicarba-*closo*-heptaborane, 2,3-$C_2B_5H_7$ **2**. The 2,3-dimethyl (**3**) and 2,3-diethyl (**4**) derivatives of **2** were reported by Schaeffer[5] and Sneddon[6] and their respective co-workers, but the parent carbaborane seemed to remain elusive until very recently when Bausch *et al.*[7] isolated it in 60% yield from the thermolysis of *nido*-4,5-$C_2B_6H_{10}$ and characterised it for the first time by NMR spectroscopy in conjunction with *ab initio* and IGLO chemical shift calculations. However, from a comparison of the NMR data in Table 1 there can be little doubt that *closo*-$C_3B_5H_7$ **1** and *closo*-2,3-$C_2B_5H_7$ **2** are one and the same compound.



2 R = H
3 R = Me
4 R = Et

Table 1 NMR data of '*closo*-$C_3B_5H_7$' **1**,[1] 2,3-$C_2B_5H_7$ **2**,[7] 2,3-Me_2-2,3-$C_2B_5H_5$ **3**[5b] and 2,3-Et_2-2,3-$C_2B_5H_5$ **4**[6b]

	$^{11}B\ \delta^a(J_{BH}{}^b)$		
Compound	B(4,6)	B(5)	B(1,7)
1[c]	7.0 (169)	3.5 (146)	−17.1 (174)
2[d]	7.1	3.6	−17.9
3[e]	10.6 (150)	5.2 (150)	−12.1 (170)
4[f]	7.0 (170)	2.5 (150)	−14.2 (170)

	$^1H\ \delta^g$			
	BH(4,6)	BH(5)	BH(1,7)	CH
1[h]	3.90	3.56	−0.45	6.54[i]
3[j]	*k*	*k*	*k*	0.67[l]
4[m]	4.5	4.5	0.2	2.13,[n] 0.94[o]

[a] In ppm, $BF_3{\cdot}Et_2O$ reference (δ 0.00). [b] In Hz. [c] 32.2 MHz, in CS_2. [d] The chemical shifts of B(4,6) and B(5) were interchanged in the original report (ref. 7), but, considering the excellent agreement between the values for **2**, as presented here, and those reported for **1**, **3** and **4**, this is thought to be an error. The assignments for the latter three compounds are backed up by the relative intensity data. [e] 70.6 MHz, neat liquid. [f] 64.2 MHz, in C_6D_6. [g] In ppm, reference $SiMe_4$ (δ 0.00). [h] 100 MHz, in CS_2. [i] CH(2,3). [j] 100 MHz, neat liquid. [k] Not reported. [l] Singlet CH_3. [m] 200.1 MHz, in C_6D_6. [n] Quartet CH_2. [o] Triplet CH_3.

The electron ionization mass spectrum of **1** showed no evidence for the presence of the three-carbon species, and it was concluded that decomposition to the 'carbons-apart' isomer *closo*-2,4-$C_2B_5H_7$ was occurring. It was also proposed that this conversion occurred in the pyrolysis of **1** at 400 °C, a rearrangement which is now seen to parallel the reported conversion of 2,3-Et_2-2,3-$C_2B_5H_5$ **4** to 2,4-Et_2-2,4-$C_2B_5H_5$ at 320 °C.[6b] Interestingly, *closo*-2,4-$C_2B_5H_7$ is the principal product from the pyrolysis of *nido*-2,3-$C_2B_4H_8$ at temperatures in the range 290–300 °C, and the alkyl derivatives show similar behaviour.[8] It would seem that silylation of *nido*-2,3-$C_2B_4H_8$ facilitates the transformation to the *closo* system, and that *closo*-2,3-$C_2B_5H_7$ is in fact an intermediate in the conversion of *nido*-2,3-$C_2B_4H_8$ to *closo*-2,4-$C_2B_5H_7$.

Note added at proof: Professor P. von R. Schleyer has informed us that his group also computed various structures of $C_3B_5H_7$ without finding one which fitted the experimental data. Professor L. G. Sneddon and Dr. J. W. Bausch have confirmed that there is indeed an error in ref. 7 (see above, Table 1, footnote *d*).

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Mark A. Fox and Robert Greatrex*
School of Chemistry
University of Leeds
Leeds LS2 9JT, UK

References

1 M. L. Thompson and R. N. Grimes, *J. Am. Chem. Soc.*, 1971, **93**, 6677.

2 J. W. Bausch, G. K. Surya Prakash and R. E. Williams, *Inorg. Chem.*, 1992, **31**, 3763.

3 M. A. Fox, R. Greatrex, N. N. Greenwood and M. Kirk, *Polyhedron*, 1993, **12**, 1849.

4 M. A. Fox, R. Greatrex, M. Hofmann and P. von R. Schleyer, *Angew. Chem.*, in the press.

5 (*a*) R. R. Rietz and R. Schaeffer, *J. Am. Chem. Soc.*, 1971, **93**, 1263; (*b*) R. R. Rietz and R. Schaeffer, *J. Am. Chem. Soc.*, 1973, **95**, 6254.

6 (*a*) J. S. Beck, A. P. Kahn and L. G. Sneddon, *Organometallics*, 1986, **5**, 2552; (*b*) J. S. Beck and L. G. Sneddon, *Inorg. Chem.*, 1990, **29**, 295.

7 J. W. Bausch, P. J. Carroll and L. G. Sneddon, *Current Topics in the Chemistry of Boron*, ed. G. W. Kabalka, Royal Society of Chemistry, Cambridge, 1994, pp. 224–227.

8 T. P. Onak, F. J. Gerhart and R. E. Williams, *J. Am. Chem. Soc.*, 1963, **85**, 3378; T. P. Onak, R. P. Drake and G. B. Dunks, *Inorg. Chem.*, 1964, **3**, 1686.

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