

Methylene Insertion into a B–N Bond at a Cluster Surface: Crystal Structure of 1-Me₂N-2-Pr₂N(H)CH₂-*closo*-1-CB₁₁H₁₀

Francis S. Mair,*^a Avelino Martín,^a John H. Morris,^b Gavin S. Peters^b and Mark D. Spicer^b

^a University Chemical Laboratory, Lensfield Road, Cambridge, UK CB2 1EW

^b Department of Pure and Applied Chemistry, Strathclyde University, UK Glasgow G1 1XL

Insertion of Pr₂NBCl₂ into Li₂[7-Me₃N-*nido*-7-CB₁₀H₁₀] induces removal of a methyl group from the trimethylamine substituent, methylene insertion into the *exo*-polyhedral B–N bond and protonation of the diisopropylamino group to give 1-Me₂N-2-Pr₂N(H)CH₂-*closo*-1-CB₁₁H₁₀, which has been characterised by multinuclear NMR and X-ray crystallography.

The nature of interactions between *exo*-substituents and boron clusters has in recent times been studied rather less than other aspects of the varied chemistry of boranes and their derivatives.¹ The few studies that have appeared have been concerned primarily with the effect of the substituent on the cluster, notably in the field of ¹¹B NMR chemical shift rationalisation.² It was our intention in this work to investigate the structural changes that substituents may induce on clusters, but instead we have discovered a remarkable reaction suggesting an influence of the cluster upon the substituent.

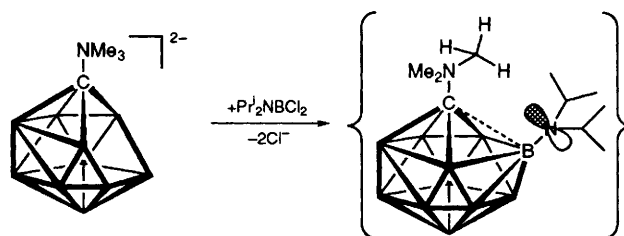
We recently reported the insertion of reagents 'RBX₂' (R = Ph, *p*-Tol, F, O(CH₂)₄Cl, NMe₂; X = Cl, F) into the [*nido*-7-CB₁₀H₁₀]³⁻ anion to yield [2-R-*closo*-1-CB₁₁H₁₁]⁻ specifically substituted icosahedral anions.³ In attempts to prepare the related neutral, zwitterionic 1-Me₃N-2-R-*closo*-1-CB₁₁H₁₀ species we have been successful in a number of cases (e.g. R = Ph, F *etc.*)⁴ but where the insertion reagent was Pr₂NBCl₂ the reaction took an unexpected course.

Reaction of Li₂[7-Me₃N-*nido*-7-CB₁₀H₁₀] with Pr₂NBCl₂ at ambient temperature for 30 min followed by chromatography produced a compound which appeared from elemental analyses to be the desired insertion product of LiCl elimination.[†] While the ¹¹B NMR was consistent with the expected eleven-boron species of C_s symmetry, the envelope of chemical shifts was narrower than that expected for a cluster with a strongly π-interacting substituent.² There were anomalies too in the ¹H NMR. The source of these anomalies was revealed by an X-ray crystal structure determination.[‡]

The distorted *closo* species shown in Scheme 1 was not isolated. Fig. 1 shows the structure of the product in which a methyl group has been lost from the trimethylamine ligand and inserted into the B–N bond producing a methylene

linkage and a quaternised nitrogen atom. This remarkable activation of C–H and B–N bonds in reasonable yield is all the more surprising in view of the very mild conditions of synthesis.

The structure of the product, 1-dimethylamino-2-diisopropylammoniomethyl-decahydro-1-carba-*closo*-dodecaborane, displays similarities to previously determined 1-Me₂N-2-Q-*closo*-1-CB₁₁H₁₀ (Q = H⁻,⁵ SMe₂⁶) structures. Both nitrogens display slightly flattened tetrahedral geometry [sum of C–N–C angles for N(1) = 336.8; for N(2) = 339.7]. The crystallographic location of the hydrogen exclusively on N(2), confirmed in solution from the NMR data, is perhaps surprising in view of the marginally greater flattening of the tetrahedral geometry at N(2). However, a preference for the quaternary charge away from the carborane-bound amino group has been noted in the only other 1,2-disubstituted monocarbon carborane, 1-Me₂N-2-Me₂S-*closo*-1-CB₁₁H₁₀, prepared by methylation of a thiol precursor.⁶ The [N(2)]H⋯N(1) distance of 2.10 Å is consistent with a hydrogen-bonded interaction fixing the most stable conformation of the two substituent groups in the final product.



Scheme 1

[†] A tetrahydrofuran (10 cm³) solution of 7-Me₃N-*nido*-7-CB₁₀H₁₂ (0.23 g, 1.22 mmol), was deprotonated with butyllithium (2 equiv.) and treated with an excess of Pr₂NBCl₂ at 0 °C to room temp. over 30 mins. Volatiles were removed by evacuation. Chromatography of the residue on silica gel in dichloromethane produced 0.07 g (0.234 mmol, 19.3%) 1-Me₂N-2-Pr₂N(H)CH₂-*closo*-1-CB₁₁H₁₀, m.p. 191–191.5 °C. Satisfactory elemental analysis were obtained (C, H, N). ¹H NMR (CDCl₃, 400 MHz, 20 °C) δ 6.02 (1H, br t, disappears after D₂O shake, HNPr₂), 3.92 {2H, sep of doublets, collapses to sep after D₂O shake, HN[C(H)Me₂]}, 2.38 (6H, s, Me₂N), 1.32 [12H, two doublets, (CH₃)₂CH], boron-bound methylene not observed due to quadrupolar broadening and superposition of many small couplings; ¹¹B NMR (CDCl₃, 128.4 MHz, 20 °C) δ -7.91 (1B, singlet), -9.88 (1B, doublet), -15.06 (1 + 2 + 2 + 2 + 2B, br multiplet).

[‡] Crystal data: *M* = 300.29, colourless crystals from CH₂Cl₂; space group P $\bar{1}$, *a* = 8.71(3), *b* = 9.02(3), *c* = 12.86(4) Å, α = 98.54(3), β = 89.62(1), γ = 108.56(1)°, *Z* = 2, *D*_c = 1052 g cm⁻³, μ(Mo-Kα) = 0.27 cm⁻¹, *T* = 293 K, *F*(000) = 324. Direct methods yielded the positions of all non-hydrogen atoms. Of the 4314 unique reflections, 2012 with *F* > 4σ(*F*) were used in the refinement using SHELXTL 76. All hydrogens were located on a difference map. Boron-bound hydrogens were refined with common isotropic *U*. Final *R* = 0.060, *R*_w = 0.063. Largest difference peak and hole = ± 0.23 e Å⁻³. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

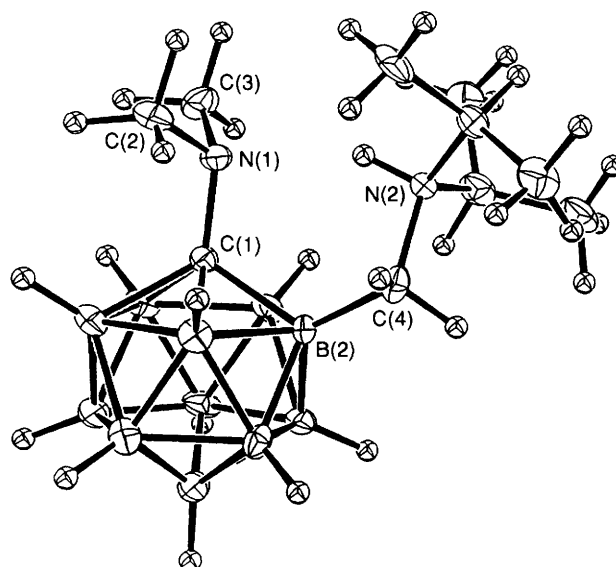


Fig. 1 Molecular structure of 1-Me₂N-2-Pr₂N(H)CH₂-*closo*-1-CB₁₁H₁₀. Thermal ellipsoids drawn at 40% probability.

Synthetically, the reaction was successful in that it shows a route to hetero-1,2-disubstituted monocarbon carboranes, further exemplifying functionalised boron insertion as a general method for synthesis of regiospecifically substituted boron clusters.³ However, the unexpected path that the system chose subsequent to (or possibly during) boron insertion is more significant. It was hoped that the steric crowding about the diisopropylamino substituent would induce planarity at nitrogen. The resultant maximisation of 'p'-character in the lone pair was intended to facilitate interaction with the surface orbitals of the carborane cluster which semi-empirical molecular orbital calculations have suggested would result in the distortion shown in Scheme 1.⁴ Similar distortions have been observed before in icosahedral clusters, with a carbonyl group in place of the aminoboryl group.⁷ It is tempting to invoke participation of such a partially opened cluster in proposing a mechanism for this rearrangement, but care must be taken to base speculation on precedent where available. Loss of a methyl group has been seen before in the insertion of Et_3NBH_3 into 7-Me₃N-7-nido-CB₁₀H₁₂, but only after prolonged reflux at 200 °C.⁸ In that case the methyl group was transferred to the triethylamine,⁹ but here at much lower temperatures it inserts into the *exo*-polyhedral B-N bond. In both cases the quaternary charge is removed to a remote site, giving some thermodynamic advantage, but here further stabilisation is gained by relieving the considerable steric strain induced by having trimethylamine and diisopropylamino groups in *ortho* positions on the cluster. Indeed, we postulate that the first step of the rearrangement is a sterically induced C-H activation: transfer of hydrogen from the methyl group to the diisopropylamino group producing an unstable $\text{Me}_2(\text{cluster})\text{N}^+\text{CH}_2^-$ ylide which disproportionates to generate an amine and a carbene. This mode of carbene generation is rare, but has some precedent.¹⁰ Carbene insertion into a B-N bond is to our knowledge without precedent and therefore mechanistic

speculations become groundless at this point. All that may be said with certainty is that the very unusual reaction or set of reactions occurring at the cluster surface merits further study. We are currently exploring the effects of variation of the substituents, and will report the results in a forthcoming full paper.⁴

We thank Professor M. B. Hursthouse and Dr M. Harman of the SERC crystallographic service for collection and partial solution of the crystallographic data, the SERC for a postgraduate studentship (G. S. P.) and the Associated Octel Co. Ltd./Queens' College, Cambridge for a Research Fellowship (F. S. M.).

Received, 24th March 1993; Com. 3101715J

References

- 1 N. N. Greenwood, *Chem. Soc. Rev.*, 1992, **21**, 49.
- 2 F. Teixidor, C. Vinas and R. W. Rudolph, *Inorg. Chem.*, 1986, **25**, 3339 and references therein.
- 3 F. S. Mair, J. H. Morris, D. F. Gaines and D. Powell, *J. Chem. Soc., Dalton Trans.*, 1993, 135.
- 4 F. S. Mair, J. H. Morris, G. S. Peters and M. D. Spicer, manuscript in preparation.
- 5 C. Novák, V. Šubrtová, V. Petříček, L. Hummel and J. Hašek, *Collect. Czech. Chem. Commun.*, 1990, **55**, 653.
- 6 S. A. Khan, J. H. Morris, M. Harman and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1992, 119.
- 7 D. A. Brown, W. Clegg, H. M. Colquhoun, J. A. Daniels, I. A. Stephenson and K. Wade, *J. Chem. Soc., Chem. Commun.*, 1987, 859.
- 8 J. Plešek, T. Jelínek, E. Dráková, S. Heřmánek and B. Štíbr, *Collect. Czech. Chem. Commun.*, 1984, **49**, 1559.
- 9 S. A. Khan, J. H. Morris and S. Siddiqui, *J. Chem. Soc., Dalton Trans.*, 1990, 2053.
- 10 W. Kirmse, *Carbene Chemistry*, Academic Press, New York, 2nd edn., 1971, pp. 69-70 and references therein.