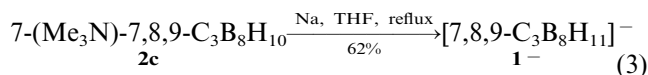


As seen from Eqs. (1) and (2), the principal problem of the synthesis of ligand derivatives **2** are the low total yields of the Me_3N -derivative **2c** which has so far been a single precursor of the parent anion **1**[−] [1,2]:



Here we report on simple and high-yield procedures leading to a new 7-(H_3N)-*nido*-7,8,9- $\text{C}_3\text{B}_8\text{H}_{10}$ derivative along with improved routes to other 7-*L-nido*-7,8,9- $\text{C}_3\text{B}_8\text{H}_{10}$ (where $\text{L} = \text{Bu}'\text{H}_2\text{N}$, Me_3N , and Me_2NH) compounds previously reported [1,2], which have become essential starting materials for the development of tricarbollide [1,2] and metallatricarbollide [5] chemistry. Numbering schemes for the 10- and 11-vertex *nido* cages used in this work are in Scheme 1.

2. Experimental

2.1. General

All reactions were carried out using standard vacuum or inert-atmosphere techniques as described by Shriver [6], although some operations, such as column chromatography, were carried out in air. The starting $\text{Bu}'\text{NC}$ [7] and 5,6- $\text{C}_2\text{B}_8\text{H}_{12}$ [4] were prepared according to the literature. The Aldrich hexane, benzene, and dichloromethane were dried over CaH_2 and freshly distilled before use. Other chemicals were reagent or analytical grade and were used as purchased. Column chromatography was carried out on silica gel (Aldrich 200–400 mesh) and the purity of individual chromatographic fractions was checked by analytical TLC on Silufol (silica gel on aluminum foil; detection by di-

iodine vapor, followed by spraying with aqueous 2% AgNO_3 solution).

2.2. Physical measurements

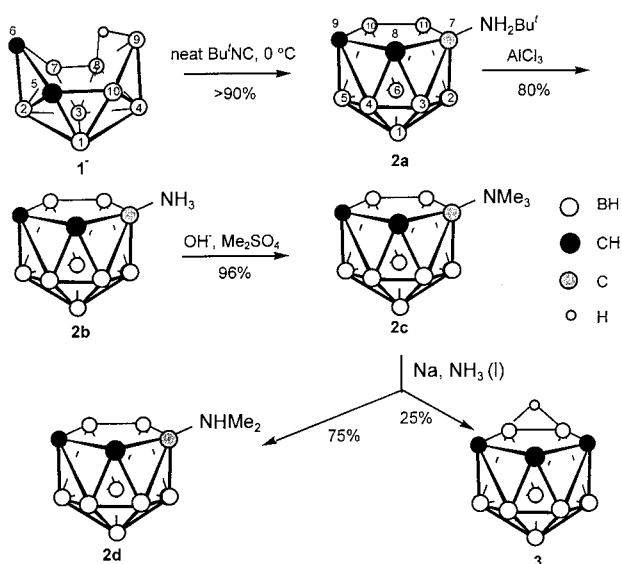
Low resolution mass spectra were obtained using a Finnigan MAT MAGNUM ion trap quadrupole mass spectrometer equipped with a heated inlet option, as developed by Spectronex AG, Basle, Switzerland (70 eV, EI ionisation). Proton (^1H) and boron (^{11}B) NMR spectroscopy was performed at 7.05 and 11.75 T on Bruker ARX 300 and Varian XL-500 instruments, respectively, and the spectra were compared to those obtained for compounds previously reported [1,2].

2.3. Preparation of 7-($\text{Bu}'\text{H}_2\text{N}$)-*nido*-7,8,9- $\text{C}_3\text{B}_8\text{H}_{10}$ (**2a**)

Upon cooling to 0°C and stirring, a solution of 5,6- $\text{C}_2\text{B}_8\text{H}_{12}$ (3.0 g, 25 mmol) in 15 ml of Et_2O was added dropwise to a suspension of NaH (ca. 720 mg, 30 mmol) in 15 ml of Et_2O during 30 min (dihydrogen evolution). The Et_2O was then evaporated and the oily residue dried at room temperature (r.t.) for ca. 2 h. The solid light yellow $\text{Na}^+ [5,6\text{-C}_2\text{B}_8\text{H}_{11}]^-$ thus obtained was dissolved in 20 ml of $\text{Bu}'\text{NC}$ under intensive shaking and cooling to 0°C . After the dissolution was achieved, the excess $\text{Bu}'\text{NC}$ was immediately evaporated on a vacuum line and recovered in a -78°C trap. The oily residue was dried at ambient temperature for 1 h and treated with a mixture of 50 ml of CH_2Cl_2 and 5 ml of MeCN . Upon cooling in a 0°C bath and intensive shaking, the mixture was then treated carefully with 50 ml of water and acidified to pH 1 with 5% HCl (exothermic reaction, dihydrogen evolution). The bottom layer was separated and the aqueous layer re-extracted with a mixture of 50 ml of CH_2Cl_2 and 5 ml of MeCN . The combined organic layers were evaporated in vacuo and the residual solid subjected to column (5×25 cm) chromatography using CH_2Cl_2 as the liquid phase to collect the main fraction of R_f (anal.) ca. 0.25. This was evaporated to dryness and repeatedly sublimed in vacuo at $120\text{--}150^\circ\text{C}$ (bath) to obtain typically 4.5 g (90%) of a white solid, which was identified as compound **2a** by NMR spectroscopy as reported earlier [1].

2.4. Preparation of 7-(H_3N)-*nido*-7,8,9- $\text{C}_3\text{B}_8\text{H}_{10}$ (**2b**)

Compound **2a** (6.0 g, 29.2 mmol) was heated with anhydrous AlCl_3 (8.2 g, 60 mmol) in 150 ml of benzene for 3 h. The red solution was then decomposed with 50 ml of 1% HCl under intensive stirring and cooling in a 0°C bath, and then evaporated to a sirupy consistence. The residue was extracted with three 50 ml portions of hot MeCN and the solvent was evaporated leaving a



Scheme 1.

yellow solid. This was treated with ca. 100 ml of hot water and the still hot solution was filtered to remove the insoluble yellow, oily material. The filtrate was reduced in volume to ca. 25 ml and left to crystallize at ambient temperature to obtain the first crop (1.8 g) of a white, crystalline material, which was isolated by filtration and identified as **2b** by NMR spectroscopy. The second crop (1.7 g, total yield 3.5 g, 80%) was obtained by evaporating the mother liquors to dryness and drying the residue in vacuo for 2 h. For **2b**: m.p. > 250°C. R_f (anal.) 0.07 (33% CH₂Cl₂ in MeCN). δ (¹¹B) [assignments and ¹J_{BH} (where applicable) in square brackets] –15.5 [B(6,10), –], –17.8 [B(11), –], –18.5 [B(5), –], –20.2 [B(4), ~160], –23.1 [B(2,3), –], –47.1 [B(1), 143] (assignments by ¹¹B–¹¹B-COSY spectroscopy [8]). δ (1H) [assignments in square brackets] 2.68 [H(9)], 1.78 [H(8)], 1.70 [H(4)], 1.55 [H(3)], 1.52 [H(5)], 1.24 [H(10)], 1.30 [H(11)], 1.07 [H(6)], 1.04 [H(2)], 0.20 [H(1)] (assignments by ¹H{¹¹B(selective)} NMR spectroscopy [9]). IR (KBr) 3431 (s), 3222 (s), 2959 (w), 2927 (m), 2856 (w), 2593 (m), 2362 (w), 2262 (w), 1631 (m), 1420 (s), 1195 (m), 1118 (s), 812 (m), 618 (m), 548 (w) cm⁻¹. Anal. Found: C, 23.45; H, 8.42. Calc.: C, 24.07; H, 8.75%. MS (in *m/z*, relative intensity (%)) and assignment in parentheses): Found 151 (18, [M]⁺), 148 (100, [M]⁺ – 3H).

2.5. Preparation of 7-(Me₃N)-nido-7,8,9-C₃B₈H₁₀ (**2c**)

Compound **2b** (3.0 g, 20.0 mmol) was dissolved in 60 ml of 1 M NaOH and the solution was treated dropwise with Me₂SO₄ (6.5 g, 62 mmol) under stirring at ambient temperature to precipitate a white solid. After adding 10 ml of aqueous 24% ammonia, the mixture was filtered, the solid washed with three 20 ml portions of water and vacuum dried at ambient temperature for 3 h to obtain 3.7 g (96%) of **2c** which was identified by NMR spectroscopy as reported earlier [1b].

2.6. Preparation of 7-(Me₂HN)-nido-7,8,9-C₃B₈H₁₀ (**2e**) and nido-7,8,9-C₃B₈H₁₂ (**3**)

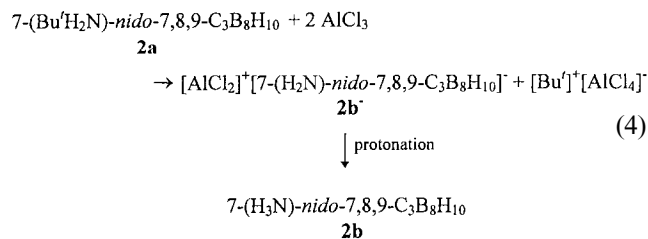
Liquid ammonia (100 ml) was condensed to a sample of **2c** (2.3 g, 11.9 mmol) and metallic sodium (1.00 g, 43.4 mmol) was added in smaller portions during 1 h. The mixture was stirred magnetically for 2 h and then treated carefully with 5 g of NH₄Cl. The ammonia was evaporated at r.t., which was followed by the addition of 50 ml of methanol and 50 ml of water. The aqueous solution was then acidified with 50 ml of dilute aqueous HCl (1:2) (dropwise) to precipitate a white solid. This was isolated by filtration, dried in vacuo, and extracted with hexane (3 × 20 ml). The combined hexane extracts were evaporated to dryness and the residue sublimed at 50°C (oil pump) to isolate 300 mg (19%) of compound

3. The remaining solid was dried in vacuo to give 1.5 g (71%) of compound **2d**. Both products were identified by NMR spectroscopy by comparison with the spectra of authentic compounds reported earlier [1,2].

3. Results and discussion

Dissolution of Na⁺[5,6-C₂B₈H₁₁]⁻ (**1**⁻) in neat Bu'NC, immediately followed by solvent recovery and acidification, led to an average 90% yield of 7-(Bu'H₂N)-nido-7,8,9-C₃B₈H₁₀ (**2a**). In contrast to the previously reported method for the synthesis of **2a** (see Eq. (2) above) [1], the reaction is in this case was instantaneous with essentially double yields of **2a**. The reason is apparently a more intimate contact of the reactants and a large excess of the isocyanide.

A subsequent reaction between **2a** and anhydrous AlCl₃ in benzene at reflux removes the Bu' substituent and results in an average 77% yield of the H₃N-derivative **2b** upon protonation. Although no mechanistic details of this interesting cleavage of the C–N bond have so far been established, the reaction seems to be consistent with the stoichiometry of Eq. 4:



The derivative **2b**, containing a reactive H₃N group at the exohedral carbon site has become a versatile starting compound of tricarbollide chemistry. For instance, its methylation by Me₂SO₄ in an alkaline solution gives an essentially quantitative yield of 7-(Me₃N)-nido-7,8,9-C₃B₈H₁₀ (**2c**). As reported earlier [1,2], this can be converted in turn into the anion **1**⁻ via a reaction with sodium metal in boiling THF (see Eq. (2) above).

Another modification of the tricarbollide synthesis presented here is the reaction of **2c** with sodium in liquid ammonia. The main reaction mode in this case is the removal of one CH₃ substituent from the nitrogen under the formation of 7-(Me₂HN)-nido-7,8,9-C₃B₈H₁₀ (**2d**) (yield 71%). This reaction also completely removes the C-substituted Me₃N to generate the neutral tricarbaborane nido-7,8,9-C₃B₈H₁₂ (**3**) (yield 19%) upon acidification of the reaction mixture. In contrast to the previous synthesis [1,2], both the zwitterionic **2d** and the neutral **3** isolated from this procedure are very pure and can be used immediately for further syntheses.

4. Conclusions

A long-standing problem of tricarbollide chemistry have so far been the low total yields of the syntheses outlined in Eqs. (1)–(3). The present work, along with the recent modification of the 5,6-C₂B₈H₁₂ synthesis (yield up to 62%) [4c], remarkably improves the yields of tricarbollide compounds (for example, total yields of the parent anion **1**[−] and the Me₃N-derivative **2c** from *o*-carborane have been tripled) and makes them now generally feasible. Moreover, the preparation of the starting tricarbaborane **2a** at the present modification is very fast and simple. A new feature is also the AlCl₃-induced cleavage of the C–N bond resulting in removal of the Bu' substituent, which seems to be of general character and use in the areas of cluster-borane and organic chemistry. Since the discovery of the first representative of the metallatricarbaborane family, the seven-vertex [π-2-Me-C₃B₃H₅Mn(CO)₃], by Grimes' group in 1969 [10], there has been current and developing interest in the chemistry of metallatricarbaboranes [11]. In this respect, the simple and high-yield synthesis of the tricarbollides outlined above enormously facilitates the access to the highly stable cyclopentadienyl *closo* ferratricarbollides, especially to the isomeric derivatives [2-(η⁵-C₅H₅)-9-X-*closo*-2,1,7,9-FeC₃B₈H₁₀] (where X = H₂N, MeHN, Me₂N, Bu'HN, and Bu'(Me)N) [12] and [2-(η⁵-C₅H₅)-10-X-*closo*-2,1,7,9-FeC₃B₈H₁₀] (where X = H₂N, MeHN, Me₂N, and Bu'HN) [13]. These complexes, together with the recently discovered neutral *closo* metalla-bis-tricarbollides and cobaltadi/tricarbollides of types [(RHN-C₃B₈H₁₀)₂M] (where R = alkyl and M = Fe and Ru) [14] and [(RHN-C₃B₈H₁₀)Co(C₂B₉H₁₁)] [15], appear to be effective as highly stable metallacarborane building blocks for designed cluster chemistry due to the favourable space orientation of the reactive aminosubstituent.

Acknowledgements

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