Communication

Towards rod-shaped molecules based on the twelve-vertex ferratricarbollides ☆

Bohumír Grüner [a,*], Jaroslav Bačkovský [a], Ivana Císařová [b], Bohumil Štíbr [a]

[a] *Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, Area of Research Institutes, Husinec-Řež 1001, 250 68 Řež, Czech Republic*
[b] *Faculty of Natural Sciences of Charles University, Hlavova 2030, 128 42, Prague 2, Czech Republic*

Abstract

The compounds with a single and double –$CH_2C_6H_4CH_2$– spacer, [$CpFeC_3B_8H_{10}$-NH-$CH_2C_6H_4CH_2$-NH-$C_3B_8H_{10}FeCp$] and [$CpFeC_3B_8H_{10}$-N-$(CH_2C_6H_4CH_2)_2$-N-$C_3B_8H_{10}FeCp$], represent the first example of designed shaping by extremely stable cyclopentadienyl-ferratricarbollide (CpFeTCB) cages into rigid molecular constructions approaching linear arrangement.
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Tailoring of oligomeric or polymeric materials based on covalent bonding of boron clusters has attracted attention during past years [1,2]. This is undoubtedly due to expected high chemical and thermal stability, rigidity of the resulting blocks, and a possibility of introducing functional groups in a space pre-defined array. However, the spectrum of boron-cluster compounds usable for designed shaping of covalently bonded materials has so far been rather limited. The same may apply to synthetic tools that would allow for building-up such systems in rational and controlled manners. More explored seems to be the area of small carboranes and metallaboranes that allow for easy in situ generation of {C_2B_3} and {C_3B_2} planar rings or pyramidal {C_2B_4} subclusters as building blocks for construction of stable multidecker shapes. Most of them emerged from the advanced work of Grimes' group [3,4]. Also

much extended has been the field of small metallaboranes featured by exoskeletal bonding to various organic substrates in C–C and B–C manners [4,5]. The area of larger borane clusters is comparatively less explored. Only few larger multidecker compounds have been reported to date [6] and there are only few compounds suitable for exo-cluster linkage of boron clusters in *para* positions. These have been recently reviewed [2] and range from *p*-carboranes 1,12-$C_2B_{10}H_{12}$, 1,10-$C_2B_8H_{10}$, to *p*-$(NH_3)_2B_{12}H_{10}$. Indeed, the first stable rod-like molecules based on C–C and C–B bonding to *p*-carborane cluster units have been reported [7] along with carboranes linked by organic spacer groups [8].

In 1999, we reported [9] on the synthesis of an extremely stable 12-vertex ferratricarbollide, [9-H_2N-2-Cp-*closo*-2,1,7,9-$FeC_3B_8H_{10}$] (**1**), the H_2N-substituent of which is conveniently attached to one of the cage carbons in a *p*-position with respect to the Fe-centre. This structural feature constitutes an ideal setting for linear molecular designs, which we would like to demonstrate in this initial study. The reaction between **1** and two equivalents of 1,4-dibromomethylbenzene in 1,2-dimethoxyethane (DME) in the presence of NaH (see Scheme 1,
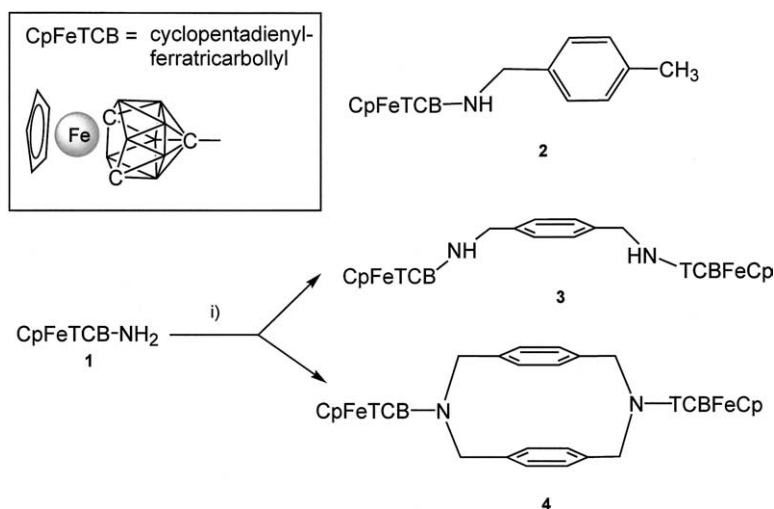
Scheme 1. Synthesis of CpFeTCB rod molecules, (i) NaH, l,4-(BrCH$_2$)$_2$-C$_6$H$_4$, NaH, DME, reflux 120 h.

path i) resulted in the isolation of three products. The first was identified as orange [9-H$_3$CC$_6$H$_4$CH$_2$NH-2-Cp-*closo*-2,l,7,9-FeC$_3$B$_8$H$_{10}$] (**2**) (yield 11%), a non-rod molecule. Other two orange products, [CpFeC$_3$B$_8$H$_{10}$-NH-CH$_2$C$_6$H$_4$CH$_2$-NH-C$_3$B$_8$H$_{10}$FeCp] (**3**) (yield 24%) and [CpFeC$_3$B$_8$H$_{10}$-N-(CH$_2$C$_6$H$_4$CH$_2$)$_2$-N-C$_3$B$_8$H$_{10}$-FeCp] (**4**) (yield 16%), are the desired single- and double-spacer dimeric molecules. It must be noted, however, that the reaction is very slow, most probably due to combination of both steric shielding of the amino group by the cage and low nucleophilicity of the H$_2$N-moiety

in **1**. Nevertheless, assumed products resulted upon a prolonged reaction period [10].

As shown in Fig. 1, the structure of **3** was determined crystallographically [11] and the constitution of compounds **2** and **4** is fully consistent with the NMR data and the results of mass spectrometry [10].

We can conclude that, single- and double-spacer molecules with defined linear geometry, based on extremely stable ferratricarbollide cages, are now, in principle, available. Therefore, there may also be a good chance for the synthesis of analogous L-shaped molecules from
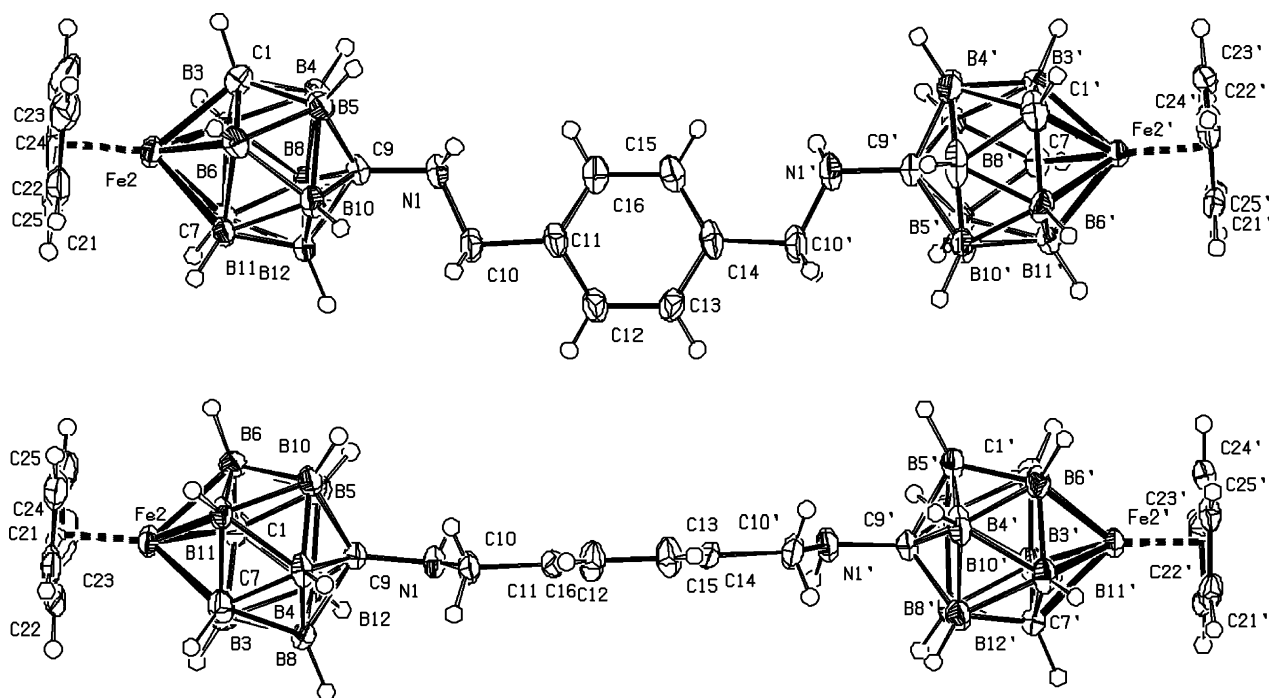

Fig. 1. Two different views the molecular structure of **3**. ORTEP representation drawn with 50% probability level. Selected interatomic distances (Å) and bond angles (°): C(1)–Fe(2) 2.030(5), C(7)–Fe(2) 2.044(5), C(1)–B(3) 1.694(6), B(3)–C(7) 1.707(6), C(9)–B(4) 1.725(6), B(6)–B(11) 1.769(6), C(9)–N(1) 1.435(6), [C(21)–C(25) centroid]-[C(21′)-C(25′) centroid] 20.726(17) Å; C(9)–N(1)–C(10) 115.8(4), B(11)–Fe(2)–C(1) 86.70(18), C(1)–B(3)–C(7) 106.0(3).

the isomeric complex [10-H_2N-2-Cp-2,l,7,10-FeC_3B_8-H_{10}] [12]. Oligomeric or polymeric linear arrays might be also obtainable via the full-sandwich *closo* complexes of general [Fe($C_3B_8H_{10}NH_2$)$_2$] constitution [13,14] that contain two H_2N substituents in positions suitable for chemical shaping.

Acknowledgements

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[10] In a typical experiment, a solution of **1** (500 mg, 1.89 mmol) in DME (40 ml) was treated with solid NaH (96%, 95 mg, 3.8 mmol) and the slurry was stirred for 3 h. A solution of 1,4-dibromomethyl benzene (490 mg, 1.85 mmol) in DME (10 ml) was then syringed dropwise over a 1 h-period, followed by addition of solid

KI (50 mg). The reaction mixture was heated to reflux and stirred for 48 h. A second portion of 1,4-dibromomethyl benzene (490 mg, 1.85 mmol) in DME (20 ml) was then added, followed by addition of KI (50 mg). The reflux was continued for 4 days, the overall reaction time being 120 h. After cooling down, the reaction was quenched by aqueous ethanol (1 ml), the solvent was evaporated, and the resulting mixture was separated by flash chromatography on a silica gel column (1.5 × 20 cm), using a 4:1 hexane–benzene mixture to elute the first orange fraction containing **2** (79 mg, 11%). Benzene, followed by CH_2Cl_2, eluted compounds **3** and **4** (yields 154 mg, 24% and 119 mg, 16%, respectively). **2**: R_f (C_6H_6-hexane 1 : 1) 0.42, m.p. 72–75 °C; ^{11}B NMR (CDCl$_3$) δ = −11.4 (^1J(B,H) = 150 Hz, B6,11), −15.3 (162, B3), −18.0 (169, B5,12), −20.8 (154, B10), −25.1 (173, B4,8). ^{1}H{^{11}B} NMR (CDCl$_3$): δ = 7.16–7.09 (4H, Ar), 7.09 (br. t, 1H, NH), 4.58 (5H, Cp); 3.94 (H3); 3.84 (2H, N–CH_2); 2.83 (H6,11); 2.34 (CH_3), 2.19 (H5,12), 2.11 (2H, cage CH), 2.07 (H4,8), 1.73 (H10); MS: m/z = 375 (59%) [M]$^+$. **3**: R_f (C_6H_6-hexane 1:1) 0.17, m.p. 246–248 °C (decomp.); ^{11}B NMR (CDCl$_3$) δ = −11.4 (^1J(B,H) = 150Hz, B6,6′,11,11′), −15.3 (162, B3,3′), −17.9 (173, B5,5′,12,12′), −20.9 (154, B10,10′), −24.15 (169, B4,4′8,8′); ^{1}H{^{11}B} NMR (CDCl$_3$) : δ = 7.19 (4H, Ar), 7.09 (br. t, 2H, NH), 4.56 (10H, Cp); 3.91 (H3,3′), 3.83 (4H, CH_2), 2.8 (H6,6′,11,1′), 2.16 (H5,5′,12 12′), 2.09 (4H, cage CH), 2.04 (H4,4′,8,8′), 1.69 (H10,10′); ^{13}C{^{1}H} NMR (CDCl$_3$) δ = 138.3, 128.8, 128.5 (4C,Ar), 77.6 (Cp), 68.2 (2C, C9,9′), 54.8 (4C, cage Cl,7,1′,7′); 53.6 (2C, CH_2N); MS: m/z = 644 (25%) [M]$^+$. **4**: R_f (C_6H_6) 0.06, m.p. 126–129 °C; ^{11}B NMR (CDCl$_3$) δ = −11.4(^1J(B,H) = 150 Hz, B6,6′,11,11′), −15.3 (162, B3,3′), −17.9 (173, B5,5′12,12′), −20.9 (154, B10,10′), −24.15 (169, B4,4′8,8′); ^{1}H{^{11}B} NMR (CDCl$_3$): δ = 7.33 (4H, Ar), 7.21 (4H, Ar), 4.6 (10H, Cp), 3.98 (H3,3′), 2.94 (8H, N–CH_2). 2.88 (H6,6′,11,11′), 2.24 (H5,5′,12,12′), 2.14 (4H, cage CH), 2.12 (H4,4′,8,8′); MS: m/z = 746 (30%) [M]$^+$.
[11] Crystal data for **3**: $C_{24}H_{40}B_{16}Fe_2N_2$, M = 641.24, triclinic, $P\bar{1}$ (No. 2), a = 9.1530(4) Å, b = 11.9150(5) Å, c = 14.3330(6) Å, α = 87.378(3)°, β = 85.060(3)°, γ = 72.135(3)°, V = 1481.9(1) Å^3, Z = 2, D_x = 1.437 mg m^{-3}. An orange crystal of dimensions 0.25 × 0.12 × 0.012 mm; absorption corrections were neglected (μ = 1.002 mm^{-1}); a total of 21400 measured reflections in the range h = −11 to 11, k = −13 to 13, l = −17 to 17 (θ_{max} = 26°), from which 45722 were unique (R_{int} = 0.20) and 4151 observed according to the $I > 2\sigma(I)$ criterion. The fragility of a very thin crystal of **3** leads to splitting of diffractions, which causes large differences of the symmetrically related diffractions, however, the main geometric parameters of the compound could be resolved on a satisfactory level even from these data. All hydrogen atoms, except for those of the NH moieties, were put into idealised positions, fixed during the refinement (riding model) with assigned temperature factors H$_{iso}$(H) = 1.2 U_{eq} (pivot atom). Hydrogen of NH groups were found on a difference Fourier map and refined isotropically. The refinement converged (Δ/σ_{max} = 0.000) to R = 0.063 for observed reflections and $wR(F^2)$ = 0.127, GOF = 1.113 for 405 parameters and all 5722 reflections. The final difference map displayed no peaks of chemical significance [$\Delta\rho_{max}$ = 0.453 e Å^{-3}, $\Delta\rho_{min}$ = −0.405 e Å^{-3}]. Crystallographic data for **3** have been deposited at the Cambridge Crystallographic Data Centre as CCDC 252882. Copies may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).
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