

Ferratricarbollide design for molecular assemblies: complexes [9,9'-(Bu'HN)₂-*commo*-2,2'-M-*closo*-1,7,9-(C₃B₈H₁₀)-1',7',9'-(C₃B₈H₁₀)] (where M = Fe or Ru), the first examples of double-cluster metallatricarbollides †

Bohumír Grüner,^{ab} Francesc Teixidor,^b Clara Viñas,^b Reijo Sillanpää,^c Raikko Kivekäs^d and Bohumil Štíbr^{*a}

^a Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 25068 Řež, Czech Republic

^b Institute of Material Sciences, Campus UAB, 08193 Bellaterra, Spain

^c Department of Chemistry, University of Turku, FIN-20500, Turku, Finland

^d Department of Chemistry, University of Helsinki, FIN-00014, Helsinki, Finland

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The first types of double-cluster metallatricarbollides, compounds of general structure [9,9'-(Bu'HN)₂-*commo*-2,2'-M-*closo*-1,7,9-(C₃B₈H₁₀)-1',7',9'-(C₃B₈H₁₀)] (for M = Fe or Ru), were synthesised from reactions between 7-(Bu'H₂N)-7,8,9-C₃B₈H₁₀ and FeCl₂ or [RuCl₂(DMSO)₄] in the presence of excess NaH at high temperature; the complexes contain two amino groups conveniently attached in *para*-positions to the metal centres, which is a convenient feature for designed constructions of linear molecular assemblies.

We are currently interested in the chemistry of the 11-vertex *nido*-tricarboranes (tricarbollides)¹ and metallatricarbollides. The latter compounds have so far been represented by mixed-sandwich cyclopentadienyl analogues of ferrocene, the *closo* ferratricarbollides [10-X-2-(η⁵-C₅H₅)-2,1,7,10-FeC₃B₈H₁₀] (where X = H, H₂N, MeNH, Me₂N and Bu'HN)² and [9-X-2-(η⁵-C₅H₅)-*closo*-2,1,7,9-FeC₃B₈H₁₀] (where X = H₂N, MeNH, Me₂N, Bu'HN and Bu'(Me)N).³ Although double-cluster metal sandwiches are quite common in metalladecarbollide chemistry,⁴ we have found that the corresponding metallatricarbollide counterparts cannot be prepared under comparable conditions. Finally we have recognized that the latter complexes can be synthesized only under forcing reaction conditions and we report here our preliminary results on the isolation of the first representatives of double-cluster Fe(II) and Ru(II) complexes containing two tricarbollide ligands. Moreover, these compounds contain two reactive amino substituents conveniently attached to the tricarbollide subclusters in *para* positions with respect to the metal centre and thus constitute novel building blocks for constructing linearly shaped molecular assemblies of high stability.

Prolonged treatment of 7-(Bu'H₂N)-7,8,9-C₃B₈H₁₀ **1** with excess NaH and FeCl₂ or [RuCl₂(DMSO)₄]⁵ (reaction scale 2.4 and 1.2 mmol of **1**, respectively; path *i* in Scheme 1) ‡ in refluxing diglyme [(MeOCH₂CH₂)₂O], followed by chromatographic separation, led to the isolation of a mixture of compounds. Of these the most significant were the light red and pale yellow compounds which were identified as [9,9'-(Bu'HN)₂-*commo*-2,2'-M-*closo*-1,7,9-(C₃B₈H₁₀)-1',7',9'-(C₃B₈H₁₀)] (**2** for M = Fe and **3** for M = Ru) (unoptimized yields 4 and 10%, respectively). Other products from these reactions, of which most interesting are the isomeric *closo* complexes [9,10'-(Bu'HN)₂-*commo*-2,2'-M-1,7,9-(C₃B₈H₁₀)-1',7',10'-(C₃B₈H₁₀)] and [10,10'-(Bu'HN)₂-*commo*-2,2'-M-1,7,9-(C₃B₈H₁₀)-1',7',10'-(C₃B₈H₁₀)] (where M = Fe and Ru), will be discussed in a full paper.

† Supplementary data available: rotatable 3-D crystal structure diagram in CHIME format. See <http://www.rsc.org/suppdata/dt/1999/3337/>

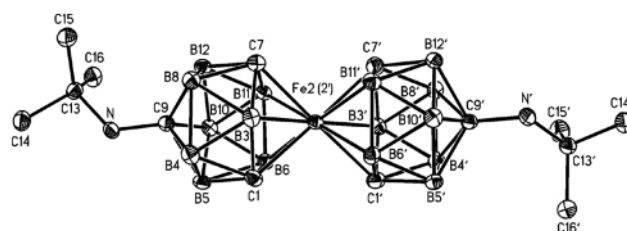
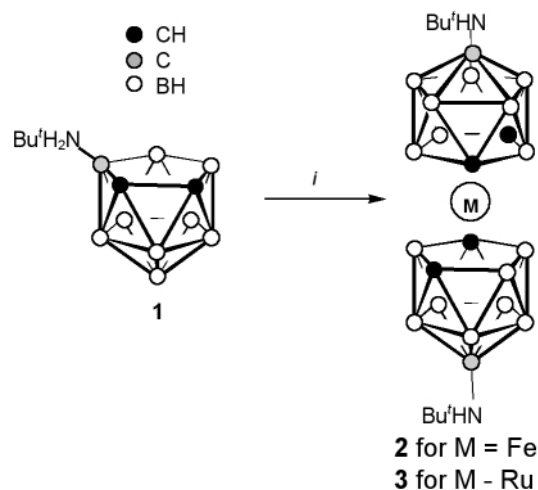


Fig. 1 Molecular structure of **2** with selected bond distances (Å): Fe–C(1) 2.067(5), Fe–C(7) 2.052(5), Fe–B(3) 2.047(5), Fe–B(6) 2.053(5), Fe–B(11) 2.061(6), Fe–C(1') 2.079(5), Fe–C(7') 2.074(5), Fe–B(3') 2.096(6), Fe–B(6') 2.069(5), Fe–B(11') 2.090(6). Hydrogen atoms omitted for clarity.



Scheme 1

The structures of both 9,9'-(Bu'HN)₂-derivatives **2** and **3** were determined by X-ray diffraction studies§ and are depicted in Figs. 1 and 2. The tricarbollide subclusters in compound **2** are somewhat different, showing several statistically significant differences in bond parameters, and the mutual configuration of the C₂B₃ pentagons is essentially staggered. On the other hand, the tricarbollide subunits in compound **3** are essentially identical with mutual orientation of the C₂B₃ pentagons closer to eclipsed than staggered. The mean C₂B₃ pentagonal planes flanking the metal centre both in **2** and **3** are essentially parallel, the dihedral angles being 0.96(11) and 1.1(3)°, respectively. The disposition of atoms C(9), Fe(2) and C(9') is effectively linear, as shown by the C(9)–M(2)–C(9') angles 179.27(11) and

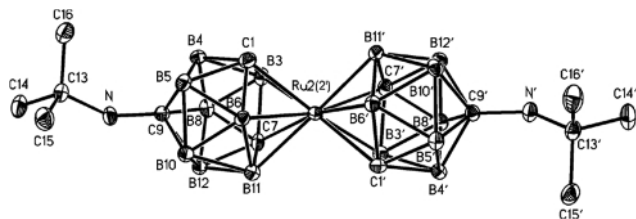


Fig. 2 Molecular structure of **3** with selected bond distances (Å): Ru–C(1) 2.183(5), Ru–C(7) 2.208(5), Ru–B(3) 2.163(5), Ru–B(6) 2.179(5), Ru–B(11) 2.181(5), Ru–C(1′) 2.199(5), Ru–C(7′) 2.202(5), Ru–B(3′) 2.165(6), Ru–B(6′) 2.164(6), Ru–B(11′) 2.185(5). Hydrogen atoms omitted for clarity.

179.35(9)°, respectively. The structures show that both amino groups are *para*-positioned with respect to the metal centre and that the tricarborane subclusters underwent extensive rearrangement of the cluster carbons during the complexation as in the case of the [9-*X*-2-(η^5 -C₅H₅)-*closo*-2,1,7,9-FeC₃B₈H₁₀] complexes reported previously.³

The spectroscopic data are also consistent with the crystallographically determined structures. The ¹¹B NMR spectra§ of both complexes **2** and **3** consist of 2 : 1 : 2 : 1 : 2 patterns of doublets as do the spectra of the corresponding [9-*X*-2-(η^5 -C₅H₅)-*closo*-2,1,7,9-FeC₃B₈H₁₀] compounds³ and the observed [¹¹B–¹H] COSY cross-peaks do not permit any other than the {2,1,7,9-FeC₃B₈H₁₀} structural variation. Similar intensity patterns apply to the corresponding {BH} resonances in the ¹H NMR spectra in which singlet resonances of intensity 4 for the {CH} cage units were also clearly found. Mass spectra¶ of both compounds **2** and **3** show theoretical cut-offs in their molecular-ion envelopes.

Although yet unoptimized, the synthesis of the neutral, highly stable, 26-cluster-electron *closo* complexes **2** and **3**, perfect cluster analogues of ferrocene and ruthenocene, clearly shows that metal sandwiches with two tricarborane cages are generally available. The interesting feature of the present synthesis is the straightforward, one-step generation of the reactive amino group in both *para*-positions with respect to the metal centre, which is not easily achievable in the area of cluster–boron chemistry.^{4,6} Upon improving the yields and selectivity of this type of complexation reaction this feature will be of significance for designed constructions of highly stable, metalla-carborane-based polymers or other molecular assemblies with linear space orientations of individual building blocks (rigid rods, *etc.*). Preliminary experiments point to facile debutylation and conversion to H₂N-derivatives, from which a broad spectrum of structurally designed compounds will be available *via* analogies from organic chemistry. Also anticipated is reaction chemistry on the amino groups, which should lead to extended derivatization of the cages, as is also the chemistry derived from isomerization and substitution reactions of both subclusters.

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Notes and references

† A slurry of **1** (500 mg, 2.43 mmol) in 15 cm³ of diglyme was treated with NaH (320 mg, 8 mmol) and the mixture was then stirred under vacuum at room temperature for 1 h and 30 min at 80 °C. After adding anhydrous FeCl₂ (0.65 g, 5.12 mmol), the mixture was heated at 160 °C (bath) for 48 h. The diglyme was then evaporated and the residue treated with 20 cm³ of Et₂O and 40 cm³ of aqueous 1 M HCl. After re-extracting the aqueous layer with an additional 20 cm³ of Et₂O, the combined Et₂O extracts were evaporated and mounted onto a silica gel

column (2 × 20 cm). Elution with CH₂Cl₂ gave, among other fractions, a red front component. This was purified by extraction with hexane, followed by preparative liquid chromatography on a silica gel column (25 × 1.5 cm), using 25% CH₂Cl₂ in hexane as the mobile phase to separate a red band of R_f (anal.) 0.25 (25% CH₂Cl₂ in hexane). Complex **2** (22 mg, 4%) was then isolated therefrom and purified by crystallization from a concentrated light petroleum (bp *ca.* 45–60 °C) solution at *ca.* 0 °C. In another experiment, a slurry of **1** (247 mg, 1.20 mmol) in diglyme (15 cm³) was treated with NaH (144 mg, 60% in light mineral oil, *ca.* 3.60 mmol) and the resulting mixture stirred at ambient temperature for 30 min and then under vacuum for 3 h. Heating of the mixture at 160 °C upon addition of [RuCl₂(DMSO)₄] (740 mg, 1.52 mmol) and stirring for 3 h was followed by removing the diglyme *in vacuo*. The dark residue was treated with 30 cm³ of benzene and 20 cm³ of water and the insoluble materials were filtered off and washed with 20 cm³ of benzene. The benzene layer was then separated and the aqueous layer acidified with 10 cm³ of 3 M HCl, and re-extracted with benzene. The combined benzene fractions were evaporated to dryness and subjected to a twofold preparative TLC separation (silica gel plates), using 33% benzene in hexane as the mobile phase. Complex **3** then separated as a third yellow band of R_F (prep.) 0.28, from which the pure product was obtained as yellow crystals (29 mg, 10%) upon crystallization from light petroleum at *ca.* 0 °C.

§ Crystallographic data for **2** [**3**]: C₁₄H₄₀B₁₆N₂Fe [C₁₄H₄₀B₁₆N₂Ru], *M* = 465.29 [510.51], orthorhombic [orthorhombic], space group *Pna*2₁ [*P*2₁2₁2₁], *a* = 11.197(2) [11.846(2)], *b* = 12.727(2) [19.816(2)], *c* = 18.012(3) [11.089(2) Å], *U* = 2566.8(7) [2603.0(7) Å³], *Z* = 4 [4], *D*_c = 1.204 [1.303 Mg m⁻³], *F*(000) 976 [1048], λ(Mo–Kα) = 0.71069 Å, μ = 0.595 [0.610 mm⁻¹]. Data were collected at 294 K on a Rigaku AFC5S diffractometer, in the ω–2θ mode for the range of 1.96 [2.00] < θ < 25.00 [25.01]. The structures were solved by direct methods (SHELXS86) and refined with full-matrix least squares on *F*² (SHELXL97). Final residuals for 2339 [2608] independent reflections were *R*₁ = 0.0478 [0.0396], *wR*₂ = 0.1013 [0.0813] and for the 2043 [2335] reflections with *I* > 2σ(*I*), *R*₁ = 0.0347 [0.0302], *wR*₂ = 0.0943 [0.0762]. In contrast to complex **3**, carbon and boron atoms at the Fe-coordinated C₂B₃ faces in compound **2** could not be reliably distinguished. CCDC reference number 186/1619. See <http://www.rsc.org/suppdata/dt/1999/3337/> for crystallographic files in .cif format.

¶ Selected data for **2** [**3**]: mp 261–263 [>360 °C]; δ(¹¹B) (160.4 MHz, CDCl₃, 293 K) {assignment by [¹¹B–¹H] COSY and ¹J_{BH} in Hz} –9.1 [–9.5] {B(6,11,6′,11′)}, 149 [150], –13.0 [–13.6] {B(3,3′)}, 165 [160], –15.7 [–16.1] {B(5,12,5′,12′)}, 174 [168], –17.2 [–19.3] {B(10,10′)}, 156 [149], –22.4 [–23.4] {B(4,8,4′,8′)}, 177 [162]. δ(¹H) (500 MHz, CDCl₃, 293 K) (assignments for individual cluster {BH} protons by ¹H–¹¹B(selective)) measurements) 4.04 [2.94] {H(3,3′)}, 2.87 [2.54] {H(6,11,6′,11′)}, 2.37 [2.71] {H(5,12,5′,12′)}, 2.30 [2.51] {H(4,8,4′,8′)}, 2.23 [2.43] {Bu⁺HN}, 2.07 [2.18] {H(10,10′)}, 1.74 [2.54] {CH(1,7,1′,7′)}, 1.19 [1.28] {Bu⁺HN}. MS (70 eV, EI), *m/z* 467 [515] (M⁺, 2.5% [M⁺, 1.25]), 465 [512] (M⁺ – 4 H, 12 [M⁺ – 3 H, 5%]).

- 1 B. Štíbr, J. Holub, F. Teixidor and C. Viñas, *J. Chem. Soc., Chem. Commun.*, 1995, 795; B. Štíbr, J. Holub, I. Cisařová, F. Teixidor, C. Viñas, J. Fusek and Z. Plzák, *Inorg. Chem.*, 1996, **35**, 3635; B. Štíbr, J. Holub, I. Cisařová, F. Teixidor and C. Viñas, *Inorg. Chim. Acta*, 1996, **245**, 129; R. Rousseau, S. Lee, E. Canadell, F. Teixidor, C. Viñas and B. Štíbr, *New J. Chem.*, 1996, **20**, 277; B. Štíbr, J. Holub and F. Teixidor, in *Advances in Boron Chemistry*, ed. W. Siebert, Royal Society of Chemistry, London, 1997, pp. 333–340; J. Holub, B. Štíbr, D. Hnyk, J. Fusek, I. Cisařová, F. Teixidor, C. Viñas, Z. Plzák and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1997, **119**, 7750; B. Štíbr, J. Holub, J. Plešek, T. Jelínek, B. Grüner, F. Teixidor and C. Viñas, *J. Organomet. Chem.*, 1999, **582**, 282.
- 2 B. Štíbr, J. Holub, F. Teixidor and C. Viñas, *Collect. Czech. Chem. Commun.*, 1995, **60**, 2023; B. Grüner, A. Lehtonen, R. Kivekäs, R. Sillanpää, J. Holub, F. Teixidor, C. Viñas and B. Štíbr, *Inorg. Chem.*, submitted.
- 3 J. Holub, B. Grüner, I. Cisařová, F. Teixidor, C. Viñas and B. Štíbr, *Inorg. Chem.*, 1999, **38**, 2775.
- 4 For review see, for example, G. B. Dunks and M. F. Hawthorne, in *Boron Hydride Chemistry*, ed. E. L. Muetterties, Academic Press, New York, 1975, ch. 11, pp. 383–430; R. N. Grimes, in *Comprehensive Organometallic Chemistry, Part I*, eds. G. Wilkinson, F. G. A. Stone and E. Abel, Pergamon, Oxford, 1982, ch. 5.5, pp. 459–542.
- 5 P. Evans, A. Spencer and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1973, 204.
- 6 V. I. Bregadze, *Chem. Rev.*, 1992, **92**, 209.

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