Inorg. Chem. **2000,** *39,* 2577−2580 **2577**

Unusual 9 → 10 Rearrangement of the Substituted Cage Carbon in the Ferratricarbollide Series. Synthesis of the Isomeric Complexes [2-η^5-(C_5H_5)-10-X-*closo*-2,1,7,10-$FeC_3B_8H_{10}$] (Where X = H_2N, MeHN, Me_2N, and Bu^{t}HN)

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Received November 29, 1999

Treatment of the zwitterionic amine tricarbollides of general formula 7-L-*nido*-7,8,9-$C_3B_8H_{10}$ (**1**) (where L = Me_2HN (**1c**) and Bu^tH_2N (**1d**)) with [(η^5-C_5H_5)Fe(CO)$_2$]$_2$ in refluxing mesitylene resulted in the formation of a mixture of the known compounds [2-(η^5-C_5H_5)-9-X-*closo*-2,1,7,9-$FeC_3B_8H_{10}$] (**2**) (where X = H_2N (**2a**), Me_2N (**2c**), and Bu^{t}HN (**2d**)) and a series of new, isomeric ferratricarbollylamines [2-(η^5-C_5H_5)-10-X-*closo*-2,1,7,10-$FeC_3B_8H_{10}$] (**3**) (where X = H_2N (**3a**), Me_2N (**3c**), and Bu^{t}HN (**3d**)) in moderate yields. Complexes of type **3** (where X = H_2N (**3a**), MeHN (**3b**), Me_2N (**3c**), and Bu^{t}HN (**3d**)) were also obtained readily by heating complexes of type **2** (where X = H_2N (**2a**), MeHN (**2b**), Me_2N (**2c**), Bu^{t}HN (**2d**), and Bu^t(Me)N (**2e**)) at ca. 300 °C for 10 min. All the complexes of type **3** contain reactive amine functions in meta positions with respect to the metal center. The observed 9 → 10 rearrangement of the substituted cluster carbon is quite unexpected and is believed to result from higher thermodynamic stability of the 10-substituted isomers. The structures of all compounds of type **3** were established by high-field NMR spectroscopy and mass spectrometry, and that of **3d** was determined by an X-ray diffraction study.

Introduction

The synthesis of the zwitterionic 11-vertex ligand tricarbaboranes[1] of general formula 7-L-*nido*-7,8,9-$C_3B_8H_{10}$ (where L = amines) (**1**), along with that of the parent tricarbollide anion[2] [*nido*-7,8,9-$C_3B_8H_{11}$]$^-$, allowed for the synthesis of the first types of metallatricarbollides. These have so far been represented by the unsubstituted complex [2-(η^5-C_5H_5)-*closo*-2,1,7,10-$FeC_3B_8H_{11}$][3] and the recently isolated series of amino derivatives [2-(η^5-C_5H_5)-9-X-*closo*-2,1,7,9-$FeC_3B_8H_{10}$] (**2**) (where X = amino substituents).[4] Both types of these cage-isomeric compounds are characterized by maximum space separation of the cluster carbons over the cluster area. Nevertheless, in view of the distance of the amino substituent from the metal center, the 9-substituted (para) complexes of type **2** were supposed to be more stable than their 10-substituted (meta) counterparts. We have, however, found that the opposite is true and that compounds of type **2** surprisingly undergo rearrangement into 10-substituted complexes under relatively mild conditions. We now present an initial study of this rearrangement resulting in the isolation of a series of new amino-substituted ferratricarbollides [2-(η^5-C_5H_5)-10-X-*closo*-2,1,7,10-$FeC_3B_8H_{10}$] that contain reactive amino substituents in the meta position with respect to the metal center.

Experimental Section

General Procedures. All reactions were carried out with use of standard vacuum or inert-atmosphere techniques as described by Shriver,[5] although some operations, such as preparative thin-layer chromatography (TLC), were carried out in air. The starting compounds of types **1** and **2** were prepared according to the literature.[1,2,4] The Fluka hexane, benzene, toluene, and dichloromethane were dried over CaH_2 and freshly distilled before use. Other chemicals were reagent or analytical grade and were used as purchased. Preparative TLC was carried out using silica gel G with a fluorescent indicator (Aldrich, type UV 254) as the stationary phase on plates of dimensions 200 mm × 200 mm × 1 mm, made on glass formers from aqueous slurries followed by drying in air at 80 °C. The purity of individual chromatographic fractions was checked by analytical TLC on Silufol (silica gel on aluminum foil; detection by diiodine vapor followed by 2% aqueous $AgNO_3$ spray). Melting points were measured in sealed capillaries under nitrogen and are uncorrected. 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, electron impact (EI)

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(1) Štíbr, B.; Holub, J.; Teixidor, F.; Viñas, C. *J. Chem. Soc., Chem. Commun.* **1995**, 795−796. (b) Štíbr, B.; Holub, J.; Císařová, I.; Teixidor, F.; Viñas, C.; Fusek, J.; Plzák, Z. *Inorg. Chem.* **1996**, *35*, 3635−3642. (c) Štíbr, B.; Holub, J.; Teixidor, F. In *Advances in Boron Chemistry*; Siebert, W., Ed.; Royal Society: London, 1997; pp 333−340.

(2) Holub, J.; Štíbr, B.; Hnyk, D.; Fusek, J.; Císařová, I.; Teixidor, F.; Viñas, C.; Plzák, Z.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1997**, *119*, 7750−7759.

(3) Štíbr, B.; Holub, J.; Teixidor, F.; Viñas, C. *Collect. Czech. Chem. Commun.* **1995**, *60*, 2023−2027.

(4) Holub, J.; Grüner, B.; Císařová, I.; Teixidor, F.; Viñas, C.; Štíbr, B. *Inorg. Chem.* **1999**, *38*, 2775−2780.

(5) Shriver, D. F.; Drezdon, M. A. *Manipulation of Air Sensitive Compounds*; Wiley: New York, 1986.

10.1021/ic991375s CCC: \$19.00 © 2000 American Chemical Society
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ionization). Proton (^{1}H) 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. The [$^{11}B-^{11}B$] correlation spectroscopy (COSY)[6] and $^{1}H-\{^{11}B(selective)\}$[7] NMR experiments were essentially as described in other related papers from our laboratories.[8] Chemical shifts are given in ppm to high frequency (low field) of $\Xi = 32.083\,971$ MHz (nominally $F_3B{\cdot}OEt_2$ in $CDCl_3$) for ^{11}B (quoted to ±0.5 ppm) and $\Xi = 100$ MHz ($SiMe_4$) for ^{1}H (quoted to ±0.05 ppm), Ξ being defined as in ref 9. Solvent resonances were used as internal secondary standards. Coupling constants $^{1}J(^{11}B-^{1}H)$ are taken from resolution-enhanced ^{11}B spectra with digital resolution of ±8 Hz and are given in hertz. IR spectra were obtained on a EU 9512 Pye-Unicam Fourier transform spectrometer.

Preparation of the [2-(η^5-C_5H_5)-10-X-*closo*-2,1,7,10-$FeC_3B_8H_{10}$] (3) Complexes (Where X = H_2N (3a), MeHN (3b), Me_2N (3c), and Bu^{t}HN(3d)). Method A. From 7-L-nido-7,8,9-$C_3B_8H_{10}$ (1) Compounds (Where L = Me_2HN (1c) and Bu^tH_2N (1d)). Compounds of type **1** (reaction scale of 1.5 mmol) were heated with [(η^5-C_5H_5)Fe-(CO)$_2$]$_2$ (266 mg, 0.75 mmol) in 20 mL of mesitylene at reflux for 8 h. The bulk of the solvent was evaporated at reduced pressure, and the resulting mixtures were separated by preparative TLC to develop orange (compounds of type **2**) and light-orange (compounds of type **3**) bands. The corresponding complexes were isolated by extraction with CH_2Cl_2 followed by evaporation and vacuum sublimation at ca. 200 °C (bath) as orange, air-stable compounds. By elution with toluene, from **1c** were isolated 103 mg (23%) of **2c** ($R_f = 0.56$) and 9 mg (2%) of **3c** ($R_f = 0.38$), whereas from **1d**, **2d** ($R_f = 0.73$) (134 mg, 31%) and **3d** ($R_f = 0.60$) (118 mg, 24%) were isolated, together with a mixture of **2a** and **3a**. This mixture was separated by a 3-fold elution with 40% CH_2Cl_2 in hexane to isolate 57 mg (14%) of **2a** ($R_f = 0.30$) and 7 mg (2%) of **3a** ($R_f = 0.25$). All compounds of type **2** were identified by ^{11}B NMR spectroscopy as reported previously.[4] For **3a**. Mp 89−91 °C. NMR, $\delta(^{11}B)$ (160.4 MHz, $CDCl_3$, 293K) [assignment, $^{1}J_{BH}$ in Hz]: −8.3 [B(6,11), 161], −10.6 [B(9), 162], −16.1 [B(3), ~150], −17.2 [B(5,12), ~168], −25.5 [B(4,8), 155] (all signals are doublets), all theoretical $^{11}B-^{11}B$ cross-peaks observed except for B(6,11)−B(5,12). NMR, $\delta(^{1}H)$ (500 MHz, $CDCl_3$, 293K) (assignments for individual cluster {BH} protons by $^{1}H\{^{11}B(selective)\}$ measurements): 4.68 [C_5H_5], 3.70 [H(3)], 3.01 [H(6,11)], 2.74 [H(9)], 2.22 [H(5,12)], 2.16 [H(1,7)], 1.79 [H_2N, d, $^{1}J_{H-H} = 202$ Hz], 1.31 [H(4,8)]. IR (KBr): 3380 (w), 3320 (w), 2956 (w), 2920 (w), 2862 (w), 2568 (s), 1726 (w), 1606 (w), 1416 (w), 1106 (m), 1034 (w), 994 (m), 972 (m), 920 (w), 830 (s), 728 (m), 640 (m), 436 (s) cm^{-1}. MS (70 eV, EI), *m/z* (%): 271 (55) [M^+], 270 (100) [$M^+ - H$]. Anal. Calcd for $C_8H_{17}FeB_8N$ (269.6): C, 35.63; H, 6.36. Found: C, 35.21; H, 6.40. For **3c**. Mp < 70 °C. NMR, $\delta(^{11}B)$: −9.8 [B(6,11), 164], −14.3 [B(3,9), ~162], −18.8 [B(5,12), 217], −25.8 [B(4,8), 159], all $^{11}B-^{11}B$ cross-peaks observed except for B(6,11)−B(5,12). NMR, $\delta(^{1}H)$: 4.67 [C_5H_5], 3.86 [H(3)], 3.11 [H(6,11)], 2.71 [H(9)], 2.35 [Me_2N], 2.23 [H(5,12)], 2.02 [H(1,7)], 1.29 [H(4,8)]. IR (KBr): 3426 (m), 2984 (w), 2948 (w), 2868 (w), 2832 (w), 2788 (w), 2592 (sh), 2568 (s), 2548 (s), 2524 (s), 1468 (m), 1450 (m), 1410 (m), 1274 (m), 1220 (w), 1100 (m), 1048 (m), 1000 (s), 976 (sh), 840 (s), 734 (w), 450 (m), 432 (m) cm^{-1}. MS (70 eV, EI), *m/z* (%): 299 (50) [M^+], 298 (100) [$M^+ - H$]. Anal. Calcd for $C_{10}H_{21}FeB_8N$ (297.7): C, 40.35; H, 7.11. Found: C, 40.52; H, 7.28. For **3d**. Mp 81 °C. NMR, $\delta(^{11}B)$: −8.0 [B(6,11), 132], −11.4 [B(9), 156], −15.0 [B(3), 162], −17.3 [B(5,12), 171], −25.8 [B(4,8), 159], all $^{11}B-^{11}B$ cross-peaks observed except for B(6,11)−B(5,12). NMR, $\delta(^{1}H)$ 4.67 [C_5H_5], 3.78 [H(3)], 3.15 [H(6,11)], 2.90 [H(9)], 2.28 [H(5,12)], 2.08 [H(1,7)], 1.30 [H(4,8)], 1.12 (*Bu^t*HN). IR (KBr): 3348 (w), 2992 (w), 2956 (m), 2920 (w), 2860 (w), 2620 (s), 2584 (s), 2568 (s), 2548 (s), 1728 (w), 1446 (w), 1388 (m), 1362 (m), 1218 (s), 1106 (m), 1034 (w), 1004 (s), 858 (m), 830 (s), 592 (w), 446 (s) cm^{-1}. MS (70 eV, EI), *m/z* (%): 327 (10) [M^+], 326 (20) [$M^+ - H$]. Anal. Calcd for $C_{12}H_{25}FeB_8N$ (325.7): C, 44.24; H, 7.74. Found: C, 44.60; H, 7.82.

Method B. Thermal Isomerization of Complexes of Type 2. Compounds of type **2** (for X = H_2N (**2a**), MeHN (**2b**), Me_2N (**2c**), Bu^{t}HN (**2d**), and Bu^t(Me)N (**2e**)) (reaction scale of 0.2 mmol) were heated at ca. 300 °C (heating gun, outside temperature) for 10 min under nitrogen, and the mixture of compounds of types **2** and **3** thus obtained was separated by preparative TLC. Compounds **3a**, **3c**, and **3d** were isolated exactly as in the preceding experiment in yields of 15, 49, and 40%, respectively (based on compounds **2** recovered). The thermolysis of **2c** was accompanied also by the formation of **3b** ($R_f =$ 0.20 in toluene, yield 4%), and that of **2e** resulted in the formation of **2b** ($R_f = 0.34$ in toluene, yield 20%) and **3b** (yield 20%). The thermolysis of **2b** gave exclusively **3b** (yield 28%). For **3b**. Mp < 25 °C (viscous liquid). NMR, $\delta(^{11}B)$: −9.3 [B(6,11), 165], −12.7 [B(9), 161], −15.2 [B(3), 162], −18.2 [B(5,12), 171], −25.8 [B(4,8), 159]], all $^{11}B-^{11}B$ cross-peaks observed except for B(6,11)−B(5,12). NMR, $\delta(^{1}H)$: 4.61 [C_5H_5], 3.72 [H(3)], 2.97 [H(6,11)], 2.68 [H(9)], 2.27 [*Me*HN], 2.15 [H(5,12)], 2.04 [H(1,7)], 1.65 [Me*H*N], 1.25 [H(4,8)]. IR (KBr): 3352 (w), 3084 (w), 2956 (m), 2920 (w), 2800 (w), 2588 (s), 1720 (w), 1660 (w), 1470 (m), 1448 (w), 1416 (w), 1234 (w), 1166 (w), 1110 (m), 1040 (m), 1004 (m), 986 (m), 962 (w), 912 (w), 860 (m), 828 (s), 732 (m), 700 (w), 432 (m) cm^{-1}. MS (70 eV, EI), *m/z* (%): 285 (55) [M^+], 284 (90) [$M^+ - H$]. Anal. Calcd for $C_9H_{19}FeB_8N$ (283.6): C, 38.11; H, 6.75. Found: C, 37.85; H, 6.47.

Structure Analysis of 3d. ($C_{12}H_{25}B_8FeN$), $M_r = 325.66$, 0.45 mm × 0.35 mm × 0.15 mm, monoclinic, space group $P2_1/n$, $a = 13.149(4)$ Å, $b = 6.501(4)$ Å, $c = 19.421(5)$ Å, $\beta = 93.37(3)°$, $V = 1657.3(12)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.305$ g cm^{-3}, data collected at 193(2) K on a Rigaku AFC7S device with Mo Kα radiation ($\lambda = 0.710\,69$ Å), scan method $\omega/2\theta$, 2763 independent reflections with $3.10 < \theta < 24.99°$ collected, of which 2371 had $I > 2\sigma(I)$. Lorentzian polarization and absorption corrections were performed [μ(Mo Kα) = 0.897 mm^{-1}, empirical ψ scan, $T = 0.6883 - 0.8772$]. The structure was solved and refined with the SHELX97 program package.[10]The Cp ring is disordered, adopting two orientations [site occupation parameters 0.519(2) and 0.481(2)]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in the calculations at fixed distances from their host atoms and treated as riding atoms using the SHELX97 default parameters. The structure was refined against F^2 to R1 = 0.0471, wR2 = 0.1181, 202 parameters, $S = 1.040$. The min and max residual electron densities were −0.448 and 0.529 e Å^{-3}, respectively. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication CCDC 113550. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

Results and Discussion

Treatment of the zwitterionic amine tricarbollides of general formula 7-L-*nido*-7,8,9-$C_3B_8H_{10}$ (**1**) (where L = Me_2HN (**1c**) and Bu^tH_2N (**1d**)) with [(η^5-C_5H_5)Fe(CO)$_2$]$_2$ in refluxing mesitylene for 8 h (path i in Scheme 1) resulted in the formation of a mixture of the previously reported[4] compounds [2-(η^5-C_5H_5)-9-X-*closo*-2,1,7,9-$FeC_3B_8H_{10}$] (**2**) (where X = H_2N (**2a**), Me_2N (**2c**), and Bu^{t}HN (**2d**)) and a series of new, isomeric ferratricarbollides [2-(η^5-C_5H_5)-10-X-*closo*-2,1,7,10-$FeC_3B_8H_{10}$] (**3**) (where X = H_2N (**3a**), Me_2N (**3c**), and Bu^{t}HN (**3d**)). Compounds of type **3** were isolated in moderate yields as air-stable, orange complexes. The side formation of compounds **2a** and **3a**, using **1d** as the starting compound, can be clearly explained by isobutene elimination under experimental conditions employed.[4] These experiments showed that the formation of the

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(6) Kennedy, J. D. In *Multinuclear Magnetc Resonance*; Mason, J., Ed.; Plenum Press: New York, 1987; p 221. (b) Hutton, W. C.; Venable, T. L.; Grimes, R. N. *J. Am. Chem. Soc.* **1984**, *106*, 29. (c) Schraml, J.; Bellama, J. M. *Two-Dimensional NMR Spectroscopy*; Wiley: New York, 1982 and references therein.

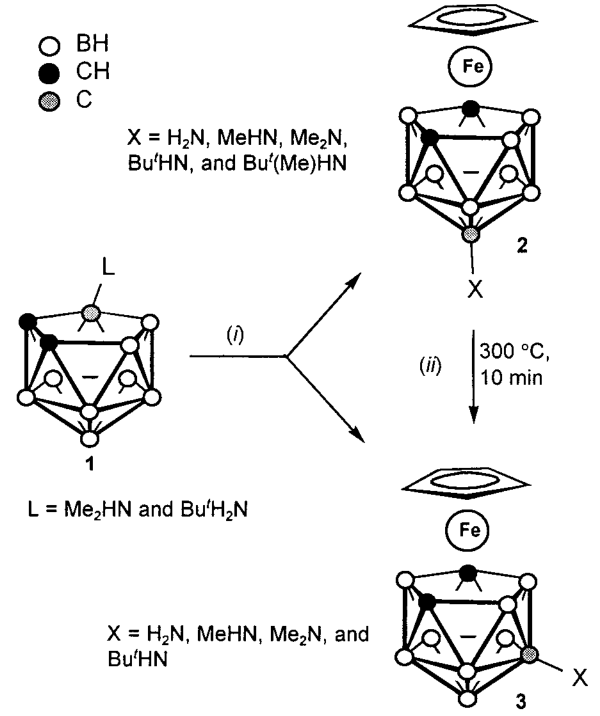
(7) Fontaine, X. L. R.; Kennedy, J. D. *J. Chem. Soc., Dalton Trans.* **1987**, 1573.

(8) Plešek, J.; Štíbr, B.; Fontaine, X. L. R.; Kennedy, J. D.; Heřmánek; S.; Jelínek, T. *Collect. Czech. Chem. Commun.* **1991**, *56*, 1618−1635.

(9) McFarlane, W. *Proc. R. Soc. London, Ser. A* **1968**, *306*, 185.

(10) Sheldrick, G. M. *SHELX97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany 1997.

Scheme 1



isomeric compounds of type **3** (see path i in Scheme 1) was achieved by raising slightly (ca. 20 °C) the reaction temperature in comparison with those of previous experiments in xylene.[4]

This observation prompted us to synthesize complexes of type **3** (where X = H$_2$N (**3a**), MeHN (**3b**), Me$_2$N (**3c**), and Bu^{t}HN (**3d**)) more efficiently, which was achieved by heating complexes of type **2** (where X = H$_2$N (**2a**), MeHN (**2b**), Me$_2$N (**2c**), Bu^{t}HN (**2d**), and Bu^t(Me)N (**2e**)) at ca. 300 °C for 10 min (path ii in Scheme 1). The resulting complexes of type **3** were isolated by TLC separation from the unreacted part of the starting complex of structure **2**. The pyrolysis of **2e** was associated with a complete loss of isobutene under the formation of **2b** and **3b**. It should also be noted that compounds of type **3** have generally have lower melting points than their counterparts of structure **2**.

All the complexes of type **3** contain amine functions in meta positions with respect to the metal center. Inspection of path i in Scheme 1 may suggest that the formation of complexes of type **2** by dsd-type movement of the substituted cluster carbon into the bottom of the cluster during the complexation should proceed via structure **3**. Nevertheless, the formation of complexes of this constitution has never been detected under milder reaction conditions (up to 140 °C).[4] As present experiments suggest, at higher temperatures the opposite is true and the substituted cage C-vertex starts moving into the area of higher crowding, however, with retention of the original maximum separation of the cage carbons. This unexpected 9 → 10 rearrangement can be then reasonably explained by the higher thermodynamic stability of the 10-substituted isomers under the experimental conditions employed.

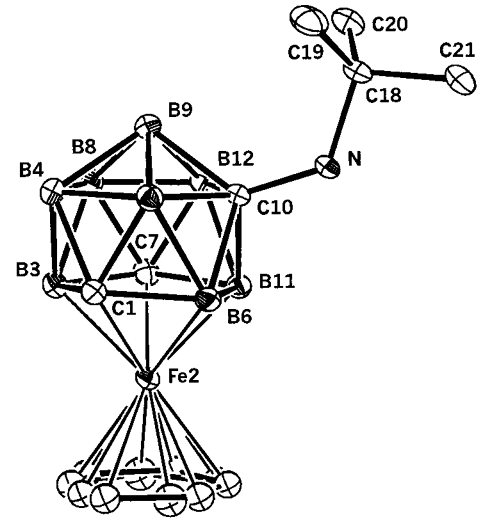


Figure 1. Molecular structure of **3d** with selected bond distances (Å): mean Fe−C(Cp ring) 2.068(7), Fe−C(1) 2.0429(17), Fe−C(7) 2.037(2), Fe−B(3) 2.034(2), Fe−B(6) 2.031(2), Fe−B(11) 2.0252(19), C(10)−N 1.4411(19). Other C−B and B−B distances fall within usual limits. The Cp ring is disordered, adopting two orientations. Hydrogen positions are omitted for clarity.

The structure of the 10-Bu^{t}HN-substituted complex **3d** was determined by an X-ray diffraction study (see Figure 1). The figure clearly shows that in contrast to complexes of type **2**[4] the substituted carbon is now meta-positioned with respect to the iron center, as is in the parent compound [2-(η^5-C$_5$H$_5$)-*closo*-2,1,7,10-FeC$_3$B$_8$H$_{11}$] reported previously.[4] In the solid state the Cp ligand (Cp = η^5-C$_5$H$_5^-$) adopts two equally populated orientations, indicating a low rotation barrier of the Cp group. Mean planes of the two partially occupied Cp groups and the C$_2$B$_3$ pentagon are essentially parallel, as shown by the mutual dihedral angles of ca. 2°. The B(9)−Fe vector approximately intersects the centers of the Cp groups, as suggested by the B(9)−Fe−Cp(ring centroid) angles of 177.0 and 176.5°. The molecule thus adopts an approximate C_s symmetry structure with a pseudo-mirror-plane bisecting the atoms N, Fe(2), B(3), B(9), C(10), C(18), and C(21). The Fe−C (C$_2$B$_3$ pentagon) and Fe−B distances fall within usual limits, as do other intracluster C−B and B−B separations. These data point to a 12-vertex 26-cage-electron closo geometry with a maximum separation of the cluster {CH} vertexes. The iron center caps the C(1)−B(3)−C(7)−B(11)−B(6) pentagonal face of a [2-(Bu^{t}NH)-2,8,10-C$_3$B$_8$H$_{10}$]$^-$ tricarbollide ligand, contributing one electron to the cluster bonding scheme.[11]

The observed NMR data for all the amino derivatives of type **3**, together with the results of mass spectrometry, are in excellent agreement with the observed crystallographic structure of **3d**. All the cluster ^{11}B and ^{1}H resonances were interrelated by [^{11}B−^{11}B] COSY[6] and ^{1}H−{^{11}B(selective)}[7] experiments, which permitted complete assignments and thence comparisons with the unsubstituted [2-(η^5-C$_5$H$_5$)-*closo*-2,1,7,10-FeC$_3$B$_8$H$_{11}$].[3]

As seen in Figure 2, the most significant feature of complexes of type **3** are the 2:1:1:2:2 patterns of ^{11}B resonances, in contrast to the isomeric compounds of type **2**, which exhibit different, 2:1:2:1:2, patterns.[4] The comparison also reveals straightforward similarity of the corresponding ^{11}B and ^{1}H resonances for all complexes of type **3**. The figure (left-hand part) shows that positions adjacent to the substituted carbon are generally deshielded, while those β-positioned {BH(4,8)} are slightly shielded. The middle diagram in Figure 2 demonstrates a good linear relationship between ^{11}B and ^{1}H resonances for all cluster positions except for the antipodal[12] {BH(3)} vertex (para-positioned to the substituted cage carbon). The right-hand part of Figure 2 details remarkable shielding of this antipodal vertex by individual amino substituents, showing also a reasonable linear correlation between ^{11}B and ^{1}H shieldings of the antipodal

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[11] Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1−66.
[12] Heřmánek, S. *Chem. Rev.* **1992**, *92*, 325 and references therein.

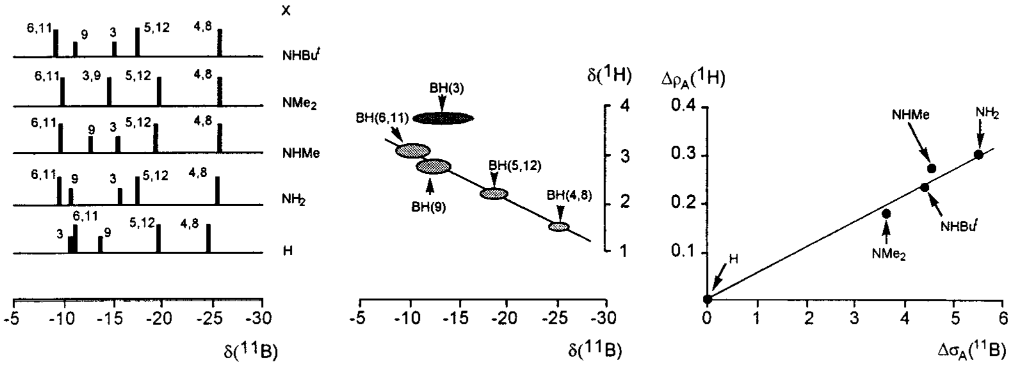

Figure 2. Left-hand diagram is a stick representation and comparison of the ^{11}B NMR chemical shifts and relative intensities for the amino-substituted metallatricarbollides of general formulation $[2\text{-}(\eta^5\text{-}C_5H_5)\text{-}10\text{-}X\text{-}\textit{closo}\text{-}2,1,7,10\text{-}FeC_3B_8H_{10}]$ (**3**) (for X = H see ref 3). The middle diagram is a plot of $\delta(^1H)$ vs $\delta(^{11}B)$ for complexes of type **3**. Data points for individual {BH} cluster units for complexes of type **3** fall within the areas marked by ellipsoids. The right-hand diagram is a plot of $\Delta\rho_A(^1H)$ vs $\Delta\rho_A(^{11}B)$ for the antipodal (A) BH(3) site (where $\Delta\rho_A = \delta_H - \delta_X$ and subscripts H and X relate to hydrogen and individual substituents X).

cluster site increasing in the order $Me_2N < Bu^tNH < MeHN < H_2N$.

The simple synthesis of stable ferratricarbollides of structure **3** significantly extends the scope of the 12-vertex metallatricarbollide chemistry. An important feature of these compounds is the presence of a reactive amino functionality in the meta position with respect to the metal center. Therefore, complexes of type **3** can be employed as ending groups for constructing L-shaped molecular assemblies by spanning nitrogen centers of two molecules with suitable spacer groups (e.g., $(-CH_2-)_n$, $-CO(CH_2)_nCO-$). Moreover, other reactions on the amino group are expected to lead to extended derivatization of the cage of **3**. All these synthetic approaches will now be studied in more detail along with other aspects of cluster chemistry of this particular metallatricarbollide system.

Acknowledgment. We thank DGICYT (Project PB94-0226), CIRIT (Project QNF 4-4614), and Grant No. 1996 SGR 00038 to B. G.), Academy of Finland (Project No. 42932 to A.L. and grant to R.K.), the Grant Agency of the Czech Republic (Grant No. 203/001042), the Grant Agency of the Czech Academy of Sciences (Grant No. S4032007), and Ministry of Education of the Czech Republic (Project LB98233) for support. We also thank Drs. J. Fusek and Z. Plzák for partial NMR measurements and mass spectra, and we thank Mrs. E. Večerníková for IR measurements.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of **3d**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC991375S