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A Series of the Twelve-Vertex Ferratricarbollides [2-(η^5-C_5H_5)-9-X-*closo*-2,1,7,9-$FeC_3B_8H_{10}$] (Where X = H_2N, MeHN, Me_2N, Bu^tHN, Bu^t(Me)N). A Highly Stable Metallatricarbaborane System with Amine Functions in the Para Position to the Metal Center

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Treatment of the zwitterionic amine tricarbollides of general formula 7-XH-*nido*-7,8,9-$C_3B_8H_{10}$ (**1**) [X = H_2N (**1a**), Me_2N (**1b**), Bu^tHN (**1c**), Bu^t(Me)N (**1d**)] with [(η^5-C_5H_5)Fe(CO)$_2$]$_2$ in refluxing xylene for 24 h resulted in the formation of a series of new mixed-sandwich metallatricarbollides [2-(η^5-C_5H_5)-9-X-*closo*-2,1,7,9-$FeC_3B_8H_{10}$] (**2**) [X = H_2N (**2a**), Me_2N (**2b**), Bu^tHN (**2c**), Bu^t(Me)N (**2d**)] in yields 16−54%. The reaction of **1d** is associated with partial loss of isobutylene and formation of the 9-MeHN-derivative **2e**. Derivatives **2a** and **2c** were also isolated from reactions between the thallium salts Tl^+[7-X-*nido*-7,8,9-$C_3B_8H_{10}$]$^-$ (Tl^+**1**$^-$) [X = H_2N (Tl^+**1a**$^-$), BuH^tN (Tl^+**1c**$^-$)] and [(η^5-C_5H_5)Fe(CO) $_2$I] in refluxing toluene (yields 38 and 55%, respectively). All complexes of type **2** contain amine functionalities in para-positions with respect to the metal center, the complexation being in all cases associated with an extensive rearrangement of the cluster carbons into positions of maximum separation. The structures of all compounds were established by high-field NMR spectroscopy and mass spectrometry, and that of **2c** was determined by an X-ray diffraction study.

Introduction

We have recently reported the synthesis of the ligand derivatives of general formula 7-L-*nido*-7,8,9-$C_3B_8H_{10}$ (where L = amines),[1] which are zwitterionic derivatives of the parent[2] tricarbollide anion [*nido*-7,8,9-$C_3B_8H_{11}$]$^-$. Metallacarborane chemistry of these eleven-vertex tricarbaboranes (tricarbollides) has so far been restricted to the complexation of the Tl^+ salt of the latter anion with [(η^5-C_5H_5)Fe(CO) $_2$I] in refluxing toluene under the formation of the unsubstituted complex [2-(η^5-C_5H_5)-*closo*-2,1,7,10-$FeC_3B_8H_{11}$], while a similar reaction of the isomeric [7,8,10-$C_3B_8H_{11}$]$^-$ anion resulted in boron removal to give the eleven-vertex species [1-(η^5-C_5H_5)-*closo*-1,2,3,4-$FeC_3B_7H_{10}$].[3] As there is a good precedent for metal complexation of the zwitterionic amine monocarbaboranes containing at least one acidic hydrogen on the ligand nitrogen,[4] it was surmised that the analogous tricarbaborane counterparts would display similar behavior. This presumption became correct and we report here two simple procedures leading to smooth rearrangement complexation of compounds of type **1** to produce a series of new metallatricarbollide isomers that contain chemically flexible amine functionalities in *p*-positions with respect to the metal center and are isomeric with the unsubstituted complex [2-(η^5-C_5H_5)-*closo*-2,1,7,10-$FeC_3B_8H_{11}$] previously reported.[3]

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 TLC, were carried out in air. The starting compounds of type **1** were prepared according to the literature.[1] 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 × 200 × 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, EI ionization). Proton (^1H) and boron (^{11}B) NMR spectroscopies were performed at 7.05 and 11.75 T on Bruker ARX 300 and Varian UNITY 500 instruments, respectively. The [^{11}B−^{11}B] COSY[6] and $^1H\{^{11}B(\text{selective})\}$[7] NMR experiments were essentially as described in other related papers

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Table 1. Products from Reactions between Zwitterions 7-XH-*nido*-7,8,9-$C_3B_8H_{10}$(**1**) and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (Method A)

					calcd (found)		
substrate	product(s)	yield (%)	mp (°C)	R_f	%C,	%H	*m*/*e* (%, interpretation)
1a	**2a**	16	95	0.30[a]	35.63 (34.51),	6.36 (6.50)	271 (55, $[M]^+$) 270 (100, $[M]^+$-H)
1b	**2b**	48	106	0.55[a]	40.35 (39.82),	7.11 (7.01)	299 (50, $[M]^+$) 298 (85, $[M]^+$-H)
1c	**2c**	54	164	0.50[b]	44.24 (44.53),	7.74 (7.82)	327 (18, $[M]^+$) 326 (30, $[M]^+$-H)
1d	**2d**	5	93	0.87[c]	45.95 (44.83),	8.01 (7.89)	285 (45, $[M]^+$-C_4H_8) 284 (100, $[M]^+$- C_4H_9)
	2e	45	106	0.24[c]	38.11 (38.58),	6.75 (6.55)	285 (55, $[M]^+$) 284 (100, $[M]^+$-H)

[a] 100% $CHCl_3$. [b] 100% benzene. [c] 20% hexane in toluene.

Table 2. IR Spectra (KBr)

compound	frequency (cm^{-1})
Ti^+**1b**$^-$	3576 (m), 3400 (m), 3176 (m), 2964 (s), 2872 (sh), 2520 (s), 1610 (m), 1470 (m), 1452 (m), 1378 (s), 1364 (s), 1222 (m), 1202 (m), 966 (m), 736 (w)
2a	3436 (s), 3364 (s), 3244 (m), 3140 (m), 2928 (vs), 2856 (m), 2588 (vs), 2532 (vs), 1610 (m), 1452 (w), 1378 (w), 1258 (m), 1110 (vs), 1032 (m), 1004 (m), 968 (m), 894 (w), 860 (vs), 732 (m), 450 (s), 418 (s)
2b	3444 (m), 2948 (m), 2872 (w), 2836 (m), 2800 (m), 2612 (vs), 2548 (sh), 2520 (vs), 1738 (w), 1660 (w), 1466 (m), 1452 (m), 1286 (m), 1226 (w), 1138 (m), 1258 (m), 1106 (vs), 1050 (m), 1004 (vs), 828 (s), 728 (m), 652 (m), 454 (s), 436 (m)
2c	3428 (br), 3364 (m), 3240 (sh), 3088 (w), 2956 (m), 2920 (s), 2864 (m), 2612 (s), 2520 (s), 1628 (w), 1458 (m), 1388 (m), 1360 (s), 1216 (s), 1110 (s), 1032 (m), 1004 (s), 972 (m), 828 (s), 726 (m), 556 (w), 436 (s)
2d	3416 (br), 3028 (sh), 2956 (m), 2920 (m), 2872 (m), 2808 (sh), 2612 (s), 2512 (s), 1462 (m), 1410 (w),1392 (m), 1364 (m), 1258 (m), 1216 (s), 1152 (m), 1124 (s), 1106 (sh), 1068 (m), 990 (s), 828 (s), 754 (w), 726 (m), 658 (w), 556 (w), 444 (s)
2e	3436 (m), 3328 (s), 3284 (sh), 2956 (w), 2912 (w), 2852 (w), 2796 (w), 2604 (vs), 2524 (vs), 1734 (w), 1664 (w), 1636 (w), 1472 (m), 1442 (w), 1410 (m), 1238 (w), 1162 (w), 1110 (s),1034 (m), 1004 (m), 964 (m), 830 (s), 734 (m), 666 (w), 508 (w), 450 (s), 428 (m), 326 (m)

from our laboratories.[8] Chemical shifts are given in ppm to high-frequency (low field) of $\Xi = 32.083971$ MHz (nominally $F_3B{\cdot}OEt_2$ in $CDCl_3$) for ^{11}B (quoted ±0.5 ppm) and $\Xi = 100$ MHz ($SiMe_4$) for ^1H (quoted $\pm$ 0.05 ppm), Ξ being defined as in ref 9. Solvent resonances were used as internal secondary standards. Coupling constants $^1J(^{11}B-^1H)$ are taken from resolution-enhanced ^{11}B spectra with digital resolution ±8 Hz and are given in Hz. IR spectra were obtained on a EU 9512 Pye-Unicam Fourier transform spectrometer. Elemental analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry of the Academy of Sciences of the Czech Republic. For IR spectra and NMR data see Tables 2 and 3, respectively.

Tl^+[7-X-*nido*-7,8,9-$C_3B_8H_{10}$]$^-$ (Tl^+1^-) [X = H_2N (Tl^+1a^-), Bu^{t}HN (Tl^+1b^-)]. Compounds **1a** (0.75 g, 5 mmol) or **1c** (1.00 g, 5.0 mmol) were dissolved in 20 mL of 1 M NaOH, and the solutions were precipitated by adding 1.33 g (5 mmol) of solid $TlNO_3$ under stirring for 0.5 h. The white precipitates were isolated by filtration and vacuum-dried at room temperature for 6 h to isolate 1.66 g (94%) and 1.94 g (95%) of white solids, which were identified by NMR spectroscopy as Tl^+**1a**$^-$ and Tl^+**1c**$^-$, respectively. Anal. Found for Tl^+**1a**$^-$: C, 9.83; H, 3.56. Calcd: C, 10.20; H, 3.71. Anal. Found for Tl^+**1c**$^-$: C, 20.11; H, 4.79. Calcd: C, 20.54; H, 4.93.

Preparation of the [2-(η^5-C_5H_5)-9-X-*closo*-2,1,7,9-$FeC_3B_8H_{10}$] (2) Complexes [X = H_2N (2a), Me_2N (2b), Bu^{t}HN (2c), Bu^t(Me)N (2d), MeHN (2d)]. Method A, from 7-XH-*nido*-7,8,9- $C_3B_8H_{10}$ (1) Compounds [X = H_2N (1a), Me_2N (1b), Bu^{t}HN (1c), Bu^t(Me)N (1d)]. Compounds of type **1** (1.5 mmol) were heated with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (266 mg, 0.75 mmol) in 20 mL of xylene at reflux for 24 h. The xylene was evaporated at reduced pressure, and the resulting mixtures were separated by preparative TLC to isolate the main orange fraction(s). All compounds of type **2** are air-stable and can be recrystallized by slow evaporation of hexane solutions. For products, separation conditions, yields, and other characteristics, see Table 1 (for IR spectra, see Table 2).

Method B, from Tl^+ Salts. A mixture of Tl^+**1a**$^-$ (500 mg, 1.4 mmol) or Tl^+**1c**$^-$ (574 mg, 1.4 mmol) and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ (469 mg, 1.5 mmol) in 20 mL of toluene was heated at reflux for 12 h. The mixture was then cooled to room temperature, and the yellow precipitate of TlI was removed by filtration. The filtrate was evaporated, and the orange oily residue was dissolved in benzene (5 mL) and separated by preparative TLC using $CHCl_3$ and benzene, respectively, as mobile phases to isolate individual orange bands. The reaction of Tl^+**1a**$^-$ yielded the complex **2a** (144 mg, 38%), while that of Tl^+**1c**$^-$ gave **2c** (219 mg, 55%) and **2a** (21 mg, 6%) as orange crystals which were recrystallized by evaporation from concentrated hexane solutions and characterized as in the preceding experiment.

X-ray Crystallography. The crystal of compound **2c** of dimensions 0.76 × 0.26 × 0.15 mm was mounted on glass fibers with epoxy cement and measured on a four-circle diffractometer CAD4-MACHIII at 293(2) K with Mo Kα radiation. The crystallographic details are summarized in Table 4. The structure was solved by the direct method (SHELXS86[10]) and refined by a full matrix least squares procedure based on F^2 (SHELXL93[11]). Numerical absorption correction was applied during data reduction (JANA96[12]). Hydrogen atoms were localized on a difference Fourier map and refined isotropically. The

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Table 3. NMR Data

compound	nucleus	δ (assignment, J_{BH} (Hz))
$Tl^+[7-(H_2N)-$*nido*$-7,8,9-C_3B_8H_{10}]^-$ (Tl^+**1a**$^-$)	$^{11}B^a$	−15.3 (B10, ∼ 135^b), −16.0 (B6,11, ∼128^b), −16.6 (B5, -^{b}), −19.3 (B4, 162), −24.2 (B3, ∼147^b), −25.0 (B2, ∼131^b), −46.7 (B1, 141)
	$^{11}B-^{11}B^c$	crosspeaks:[d]B10−B6,11; B10−B5; B6,11-B5; B6,11-B2; B6,11-B1; B5−B4; B5−B1; B4−B1; B3−B2; B3−B1; B2−B1
	$^1H^e$	2.37 (H9), 1.50 (H8), 1.49 (H4), 1.44 (H3), 1.43 (H5), 1.31 (H10), 1.04 (H11), 0.97 (H6), 0.83 (H2), 0.05 (H1)
$Tl^+[7-(Bu^tNH)-$*nido*$-7,8,9-C_3B_8H_{10}]^-$ (Tl^+**1c**$^-$)	$^{11}B^a$	−14.4 (B6, 134), −15.9 (B10,11, ∼125^b), −18.1 (B5, ∼132^b), −18.9 (B4, ∼152^b), −23.1 (B3, ∼152^b), −23.9 (B2, ∼135^b), −47.1 (B1, 141)
	$^{11}B-^{11}B^c$	crosspeaks:[d] B6−B10,11; B6−B5; B6−B2; B6−B1; B10,11-B5; B10,11-B2; B5−B4; B5−B1; B4−B3; B3−B2; B3−B1; B2−B1
	$^1H^e$	2.58 (H9), 2.04 (H5,10), 1.64 (H4), 1.63 (H4,8), 1.53 (H3), 1.30 (H6), 1.22 (*Bu*^{t}HN), 1.21 (H11), 1.07 (H2), 0.18 (H1)
$[2-(\eta^5-C_5H_5)-9-(H_2N)-$*closo*$-2,1,7,9-FeC_3B_8H_{10}]$ (**2a**)	$^{11}B^a$	−10.6 (B6,11, 150), −14.3 (B3, 164), −16.5 (B5,12, 170), −19.0 (B10, 156), −23.8 (B4,8, 174)
	$^{11}B-^{11}B^c$	crosspeaks: B6,11-B5,12; B6,11-B10; B3−B4,8; B5,12-B10; B5,12-B4,8
	$^1H^e$	4.56 (C_5H_5), 3.83 (H3), 2.71 (H_2N), 2.69 (H6,11), 2.29 (CH1,7), 2.03 (H5,12), 1.90 (H4,8), 1.48 (H10)
$[2-(\eta^5-C_5H_5)-9-(Me_2N)-$*closo*$-2,1,7,9-FeC_3B_8H_{10}]$ (**2b**)	$^{11}B^{a,}$	−10.9 (B6,11, 150), −14.6 (B3, 165), −17.9 (B5,12, 171), −21.7 (B10, 156), −24.8 (B4,8, 171)
	$^{11}B-^{11}B$	crosspeaks: B6,11-B5,12; B6,11-B10; B3-B4,8; B5,12-B10; B5,12-B4,8
	^1H	4.59 ($C_5\mathit{H}_5$), 3.84 (H3), 2.70 (H6,11), 2.44 (Me_2N), 2.15 (CH1,7), 2.08 (H5,12), 1.94 (H4,8), 1.53 (H10)
$[2-(\eta^5-C_5H_5)-9-(Bu^tHN)-$*closo*$-2,1,7,9-FeC_3B_8H_{10}]$ (**2c**)	$^{11}B^a$	−11.1 (B6,11, 150), −14.8 (B3, 165), −16.6 (B5,12, 171), −18.9 (B10, 156), −23.5 (B4,8, 171)
	$^{11}B-^{11}B^c$	crosspeaks: B6,11-B5,12; B6,11-B10; B3−B4,8; B5,12-B10; B5,12-B4,8
	$^1H^e$	4.56 (C_5H_5), 3.82 (H3), 2.69 (H6,11), 2.56 ($Bu^t\mathit{H}N$), 2.18 (CH1,7), 2.14 (H5,12), 2.02 (H4,8), 1.65 (H10), 1.14 (*Bu*^{t}HN)
$[2-(\eta^5-C_5H_5)-9-(Bu^tMeN)-$*closo*$-2,1,7,9-FeC_3B_8H_{10}]$ (**2d**)	$^{11}B^a$	−11.2 (B6,11, 150), −15.1 (B3, ∼165), −16.2 (B5,12, ∼175), −19.2 (B10, 156), −23.5 (B4,8, 170)
	$^{11}B-^{11}B^c$	crosspeaks: B6,11-B5,12; B6,11-B10; B3−B4,8; B5,12-B10; B5,12-B4,8
	$^1H^e$	4.58 ($C_5\mathit{H}_5$), 3.78 (H3), 2.66 (H6,11), 2.63 ($Bu^t\mathit{Me}N$), 2.14, 2.12 (CH1,7), 2.24 (H5,12), 2.06 (H4,8), 1.70 (H10), 1.27 (*Bu*^{t}MeN)
$[2-(\eta^5-C_5H_5)-9-(MeHN)-$*closo*$-2,1,7,9-FeC_3B_8H_{10}]$ (**2e**)	$^{11}B^{a,}$	−10.8 (B6,11, 150), −14.5 (B3, 162), −16.6 (B5,12, 171), −20.5 (B10, 155), −24.6 (B4,8, 171)
	$^{11}B-^{11}B$	crosspeaks: B6,11-B5,12; B6,11-B10; B3−B4,8; B5,12-B10; B5,12-B4,8
	^1H	4.58 ($C_5\mathit{H}_5$), 3.85 (H3), 2.71 (H6,11), 2.35 (*Me*HN), 2.21 (CH1,7), 2.03 (H5,12), 1.91 (H4,8), 1.51 (H10)

[a] $\delta(^{11}B)$ values in CD_3CN determined from $^{11}B\{^1H(broadband)\}$ measurements with assignments by $[^{11}B-^{11}B]$ COSY NMR spectroscopy and by graphical intercomparison of the ^{11}B NMR patterns of compounds of type **2**. [b] Values uncertain due to peak overlap. [c] Measured under the conditions of $\{^1H(broadband)\}$ decoupling. [d] Crosspeaks of some closely separated signals uncertain. [e] Assignments by $^1H\{^{11}B(broadband)\}$ and $^1H\{^{11}B(selective)\}$ NMR spectroscopy; unless stated otherwise, all signals are singlets of relative intensity 1 in the $^1H\{^{11}B(broadband)\}$ NMR spectrum.

final difference map had no peaks of chemical significance. Scattering factors were those implemented in the SHELX programs.

Results and Discussion

Complexes of type $[2-(\eta^5-C_5H_5)-9-X-$*closo*$-2,1,7,9-FeC_3B_8H_{10}]$ (**2**) [X = H_2N (**2a**), Me_2N (**2b**), Bu^tHN (**2c**), $Bu^t(Me)N$ (**2d**)] can be prepared easily in yields 16−55% (for yields, R_f values, elemental analyses, and mass spectra, see Table 1) from the ligand derivatives $7-XH-$*nido*$-7,8,9-C_3B_8H_{10}$ (**1**) [X = H_2N (**1a**), Me_2N (**1b**), Bu^tHN (**1c**), $Bu^t(Me)N$ (**1d**)] by heating with $[(\eta^5-C_5H_5)Fe(CO)_2]_2$ in xylene at reflux for 24 h (Scheme 1).

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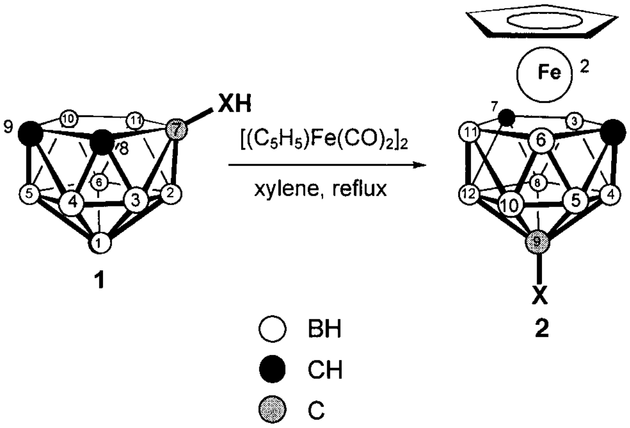
Table 4. Crystal Data and Structure Refinement for **2c**

empirical formula	$C_{12}H_{25}B_8FeN$
M	325.66
crystal system	monoclinic
space group	$P2_1/c$
a, Å	8.8353(4)
b, Å	16.7280(10)
c, Å	12.2105(9)
β, deg	112.543(4)
Z	4
V, Å^3	1666.8(2)
μ, mm^{-1}	0.892
D_{calcd}, Mg/m^3	1.298
wavelength, Å	0.71069
F(000)	680
θ range, deg	2.18−24.96
scan mode	$\theta - 2\theta$
h, *k*, *l* collected	$h\,\langle -10, 9\rangle$, $k\,\langle 0, 19\rangle$, $l\,\langle -11, 14\rangle$
no. of reflcns measd	4486
no. of unique reflcns	2935 [R(int) = 0.0176]
no. of parameters	299
Goodness-of-fit on F^2	1.021
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0300, wR2 = 0.0828
R indices (all data)	R1 = 0.0369, wR2 = 0.0879
max, min transmission	0.769, 0.717
$\Delta\rho$, max, min, e Å^{-3}	0.392, −0.231

Scheme 1



1 **2**

Chromatographic separation of the characteristic orange bands from individual reaction mixtures by preparative TLC resulted in the isolation of a series of orange, air-stable complexes of structure **2**. The reaction is in agreement with the stoichiometry of eq 1:

$$\underset{\mathbf{1}}{7\text{-XH-}nido\text{-}7,8,9\text{-}C_3B_8H_{10}} + {}^1/_2[\eta^5\text{-}(C_5H_5)Fe(CO)_2]_2 \rightarrow \underset{\mathbf{2}}{[2\text{-}\eta^5\text{-}(C_5H_5)\text{-}9\text{-X-}closo\text{-}2,1,7,9\text{-}FeC_3B_8H_{10}]} + 2CO + {}^1/_2H_2 \quad (1)$$

In the case of **1d** the prevailing reaction mode is, however, isobutylene elimination (for a similar $CH_2{=}CMe_2$ elimination see also ref 1) under the formation of the MeHN-derivative **2e** (yield 45%), which is then isolated as the main reaction product besides the expected Bu^t(Me)-derivative **2d** (yield 5%). In this manner, it is possible to prepare **2e** in the absence of the still unreported 7-(MeNH$_2$)-*nido*-7,8,9-$C_3B_8H_{10}$.

As demonstrated by the synthesis of compounds **2a** and **2c**, an alternative method for the synthesis of complexes of type **2** consists of the reaction between the thallium salts $Tl^+[7\text{-X-}nido\text{-}7,8,9\text{-}C_3B_8H_{10}]^-$ ($Tl^+\mathbf{1}^-$) [X = H$_2$N ($Tl^+\mathbf{1a}^-$), Bu^{t}HN ($Tl^+\mathbf{1c}^-$)] and [(η^5-C_5H_5)Fe(CO)$_2$I] (reaction scale ca. 1.5 mmol) in toluene at reflux for 12 h:

$$\underset{(Tl^+\mathbf{1}^-)}{Tl^+[7\text{-X-}nido\text{-}C_3B_8H_{10}]^-} + [(\eta^5\text{-}C_5H_5)Fe(CO)_2I] \rightarrow \underset{\mathbf{2}}{[2\text{-}(\eta^5\text{-}C_5H_5)\text{-}9\text{-X-}closo\text{-}2,1,7,9\text{-}FeC_3B_8H_{10}]} + TlI \quad (2)$$

Complexes **2a** and **2c** were isolated in yields 38 and 55%, respectively, the complexation of $Tl^+\mathbf{1c}^-$ being again accompanied by the loss of isobutylene and a side (6%) formation of **2a**. The starting thallium salts were isolated in high yields (>90%) as white semicrystalline materials by precipitating aqueous alkaline solutions of the corresponding Na$^+$ salts of the [7-X-*nido*-7,8,9-$C_3B_8H_{10}$]$^-$ anions $\mathbf{1}^-$ with $TlNO_3$. Comparison of the NMR data in Table 3 with those of the protonated compounds of type **1** previously reported[1] shows straightforward similarities and thus confirms undoubtedly their structures.

As shown in Scheme 1, the reactions of eqs 1 and 2 are in agreement with the insertion of the iron atom into the open, pentagonal face of the *nido* compounds **1** or $\mathbf{1}^-$. In contrast to the comparable dicarbollide complexation,[13] this process is, however, associated with an extensive rearrangement of the cluster {CX} and{CH} units into positions of maximum space separation over the cluster area. We have observed the same effect in the formation of the isomeric, unsubstituted metallatricarbollide [2-(η^5-C_5H_5)-*closo*-2,1,7,10-$FeC_3B_8H_{11}$].[3] The complexes of tyoe **2** are, however, likely to be formed by involvement of a different dsd-type mechanism resulting in the movement of the substituted {XC} cluster unit from the open-face site into the bottom position to achieve a different cluster configuration with the amino group positioned para to the metal center. This rearrangement is extremely clean, and no other isomer was found in the reaction mixture under reaction conditions employed.

The structure of the ferratricarbollides of structure **2** was determined by an X-ray diffraction study of the Bu^{t}HN-derivative **2c**. The crystal data and structure refinement parameters are in Table 4, and selected bond distances and angles are in Table 5. As shown in Figure 1, the molecule adopts a twelve-vertex 26-cage-electron *closo* geometry with the iron center capping the C(1)−B(3)−C(7)−B(11)−B(6) pentagonal face of a [1-(Bu^{t}NH)-1,7,9-$C_3B_8H_{10}$]$^-$ tricarbollide ligand and contributing one electron to the cluster bonding scheme.[14] As expected, the shape of the tricarbaborane cage is very regular. The deviations of atoms from the C(1)−B(3)−C(7)−B(11)−B(6) least-squares plane are not significant and the associated fold angles[15] θ and ψ of the tricarbollide ligand are also small at 0.69(0.15) and 1.86(20)°, respectively. The dihedral angle between the C(1)−B(6)−B(11)−C(7) and C(1)−B(3)−C(7) planes is 2.50(0.21)°.

The observed NMR data for the aminoderivatives of type **2** (Table 3), together with the results of mass spectrometry, are in excellent agreement with their formal descriptions as 9-amino-substituted derivatives of the yet unknown metallatricarbollide isomer [2-(η^5-C_5H_5)-*closo*-2,1,7,9-$FeC_3B_8H_{11}$]. All the cluster ^{11}B and ^{1}H resonances were interrelated by [^{11}B−^{11}B] COSY[6] and/or ^{1}H{^{11}B(selective)}[7] experiments, which permitted complete assignments and thence comparisons with the isomeric complex [2-(η^5-C_5H_5)-*closo*-2,1,7,10-$FeC_3B_8H_{11}$].[3]

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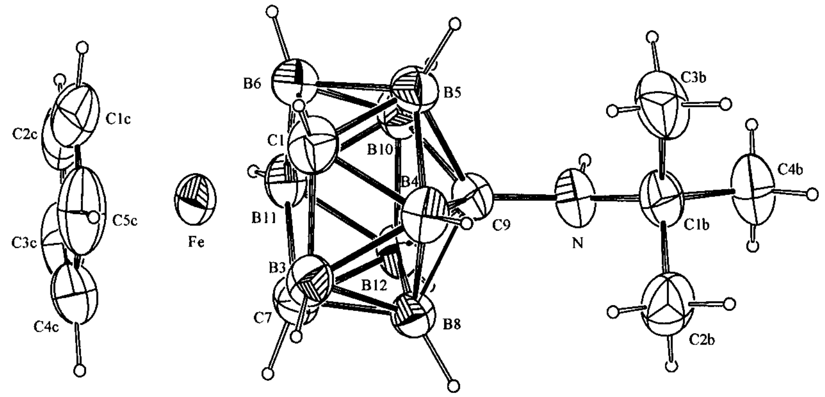


Figure 1. ORTEP representation of the crystal and molecular structure of [2-(η^5-C_5H_5)-9-(Bu^tNH)-*closo*-2,1,7,9-$FeC_3B_8H_{10}$] (**2c**).

Table 5. Selected Bond Lengths [Å] and Angles [deg] for **2c**

Bond Lengths

Fe−C(7)	2.030(2)	Fe−B(6)	2.036(2)	B(6)−B(11)	1.737(3)	B(6)−B(10)	1.762(3)
Fe−B(3)	2.039(2)	Fe−C(1)	2.040(2)	C(7)−B(11)	1.709(3)	C(7)−B(12)	1.725(3)
Fe−B(11)	2.041(2)	C(1)−B(6)	1.709(3)	C(7)−B(8)	1.729(3)	B(8)−C(9)	1.728(3)
C(1)−B(3)	1.724(3)	C(1)−B(5)	1.727(3)	B(8)−B(12)	1.754(3)	C(9)−N	1.430(2)
C(1)−B(4)	1.743(3)	B(3)−C(7)	1.708(3)	C(9)−B(10)	1.718(3)	C(9)−B(12)	1.719(3)
B(3)−B(8)	1.758(3)	B(3)−B(4)	1.775(3)	B(10)−B(11)	1.750(3)	B(10)−B(12)	1.760(3)
B(4)−C(9)	1.707(3)	B(4)−B(8)	1.763(3)	B(11)−B(12)	1.742(3)	N−C(1B)	1.476(2)
B(4)−B(5)	1.766(3)	B(5)−C(9)	1.733(3)	mean Fe−Cp ring	2.050(3)	mean C−C (Cp ring)	1.392(5)
B(5)−B(10)	1.750(3)	B(5)−B(6)	1.755(3)	N−H	0.76(3)	mean C−C (Bu^t)	1.525(3)

Bond Angles

C(7)−Fe−B(6)	86.08(9)	C(7)−Fe−B(3)	49.64(9)	B(11)−C(7)−B(8)	110.4(2)	B(12)−C(7)−B(8)	61.05(12)
B(6)−Fe−B(3)	87.04(9)	C(7)−Fe−C(1)	84.77(8)	B(3)−C(7)−Fe	65.44(10)	B(11)−C(7)−Fe	65.49(10)
B(6)−Fe−C(1)	49.57(9)	B(3)−Fe−C(1)	50.01(9)	B(12)−C(7)−Fe	120.32(13)	B(8)−C(7)−Fe	120.75(13)
C(7)−Fe−B(11)	49.63(9)	B(6)−Fe−B(11)	50.44(9)	C(9)−B(8)−C(7)	104.56(14)	C(9)−B(8)−B(12)	59.15(11)
B(3)−Fe−B(11)	86.54(9)	C(1)−Fe−B(11)	85.47(9)	C(7)−B(8)−B(12)	59.36(12)	C(9)−B(8)−B(3)	105.5(2)
B(6)−C(1)−B(3)	109.6(2)	B(6)−C(1)−B(5)	61.41(13)	C(7)−B(8)−B(3)	58.66(12)	B(12)−B(8)−B(3)	106.9(2)
B(3)−C(1)−B(5)	111.0(2)	B(6)−C(1)−B(4)	110.6(2)	C(9)−B(8)−B(4)	58.52(11)	C(7)−B(8)−B(4)	106.6(2)
B(3)−C(1)−B(4)	61.60(13)	B(5)−C(1)−B(4)	61.19(13)	B(12)−B(8)−B(4)	107.3(2)	B(3)−B(8)−B(4)	60.56(13)
B(6)−C(1)−Fe	65.08(11)	B(3)−C(1)−Fe	64.96(11)	N−C(9)−B(4)	126.6(2)	N−C(9)−B(10)	115.0(2)
B(5)−C(1)−Fe	120.26(14)	B(4)−C(1)−Fe	120.18(14)	B(4)−C(9)−B(10)	111.57(14)	N−C(9)−B(12)	112.58(14)
C(7)−B(3)−C(1)	106.2(2)	C(7)−B(3)−B(8)	59.82(12)	B(4)−C(9)−B(12)	111.59(14)	B(10)−C(9)−B(12)	61.61(12)
C(1)−B(3)−B(8)	107.3(2)	C(7)−B(3)−B(4)	106.9(2)	N−C(9)−B(8)	119.4(2)	B(4)−C(9)−B(8)	61.77(12)
C(1)−B(3)−B(4)	59.73(13)	B(8)−B(3)−B(4)	59.86(12)	B(10)−C(9)−B(8)	111.53(14)	B(12)−C(9)−B(8)	61.19(12)
C(7)−B(3)−Fe	64.93(10)	C(1)−B(3)−Fe	65.03(11)	N−C(9)−B(5)	123.8(2)	B(4)−C(9)−B(5)	61.79(12)
B(8)−B(3)−Fe	118.81(14)	B(4)−B(3)−Fe	118.62(14)	B(10)−C(9)−B(5)	60.92(12)	B(12)−C(9)−B(5)	111.18(14)
C(9)−B(4)−C(1)	104.8(2)	C(9)−B(4)−B(8)	59.71(11)	B(8)−C(9)−B(5)	111.79(14)	C(9)−B(10)−B(5)	59.96(11)
C(1)−B(4)−B(8)	106.2(2)	C(9)−B(4)−B(5)	59.84(12)	C(9)−B(10)−B(11)	105.6(2)	B(5)−B(10)−B(11)	107.5(2)
C(1)−B(4)−B(5)	58.96(13)	B(8)−B(4)−B(5)	108.6(2)	C(9)−B(10)−B(12)	59.21(11)	B(5)−B(10)−B(12)	108.5(2)
C(9)−B(4)−B(3)	105.7(2)	C(1)−B(4)−B(3)	58.67(12)	B(11)−B(10)−B(12)	59.51(12)	C(9)−B(10)−B(6)	106.1(2)
B(8)−B(4)−B(3)	59.58(12)	B(5)−B(4)−B(3)	106.8(2)	B(5)−B(10)−B(6)	59.95(13)	B(11)−B(10)−B(6)	59.28(12)
C(1)−B(5)−C(9)	104.4(2)	C(1)−B(5)−B(10)	106.5(2)	B(12)−B(10)−B(6)	107.2(2)	C(7)−B(11)−B(6)	107.3(2)
C(9)−B(5)−B(10)	59.12(12)	C(1)−B(5)−B(6)	58.77(13)	C(7)−B(11)−B(12)	59.97(12)	B(6)−B(11)−B(12)	109.1(2)
C(9)−B(5)−B(6)	105.8(2)	B(10)−B(5)−B(6)	60.37(13)	C(7)−B(11)−B(10)	107.8(2)	B(6)−B(11)−B(10)	60.70(13)
C(1)−B(5)−B(4)	59.86(13)	C(9)−B(5)−B(4)	58.37(11)	B(12)−B(11)−B(10)	60.53(12)	C(7)−B(11)−Fe	64.88(10)
B(10)−B(5)−B(4)	107.3(2)	B(6)−B(5)−B(4)	107.4(2)	B(6)−B(11)−Fe	64.63(10)	B(12)−B(11)−Fe	118.89(14)
C(1)−B(6)−B(11)	107.0(2)	C(1)−B(6)−B(5)	59.81(13)	B(10)−B(11)−Fe	118.80(14)	C(9)−B(12)−C(7)	105.14(14)
B(11)−B(6)−B(5)	107.9(2)	C(1)−B(6)−B(10)	106.8(2)	C(9)−B(12)−B(11)	105.9(2)	C(7)−B(12)−B(11)	59.05(12)
B(11)−B(6)−B(10)	60.02(12)	B(5)−B(6)−B(10)	59.68(13)	C(9)−B(12)−B(8)	59.67(11)	C(7)−B(12)−B(8)	59.59(12)
C(1)−B(6)−Fe	65.35(11)	B(11)−B(6)−Fe	64.93(10)	B(11)−B(12)−B(8)	107.7(2)	C(9)−B(12)−B(10)	59.19(11)
B(5)−B(6)−Fe	119.10(14)	B(10)−B(6)−Fe	118.47(14)	C(7)−B(12)−B(10)	106.7(2)	B(11)−B(12)−B(10)	59.96(12)
B(3)−C(7)−B(11)	109.8(2)	B(3)−C(7)−B(12)	110.6(2)	B(8)−B(12)−B(10)	108.3(2)	C(9)−N−C(1B)	126.6(2)
B(11)−C(7)−B(12)	60.98(13)	B(3)−C(7)−B(8)	61.52(12)	C(9)−N−H	111(2)	C(1B)−N−H	111(2)

As seen in Figure 2, the most significant feature of complexes of type **2** are the 2:1:2:1:2 patterns of ^{11}B resonances, in contrast to the 1:2:1:2:2 patterns exhibited by the isomeric [2-(η^5-C_5H_5)-*closo*-2,1,7,10-$FeC_3B_8H_{10}$] compound.[3] The comparison (see also Table 3) reveals straightforward similarity of the corresponding ^{11}B and ^1H resonances for all complexes of type **2**. The most marked are only the changes in chemical shifts for the resonances of the BH(4,8) and BH(10) cluster units α-positioned with respect to the substituted C(9) carbon at the bottom of the molecule. Inspection of the ^1H NMR spectra also reveals negligible changes in the chemical shifts of the cyclopentadiene ligands despite these are positioned para to the substituted C(9) atom. As also demonstrated graphically in Figure 2, there is an approximately linear correlation between the ^{11}B and ^1H chemical shifts for all the C-substituted derivatives of type **2** thus far isolated. Due to the extreme

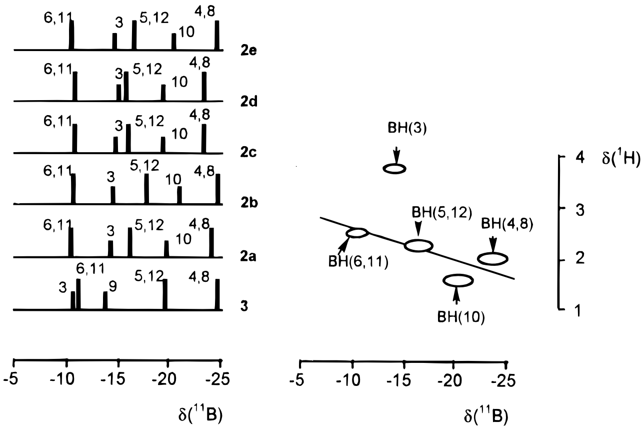
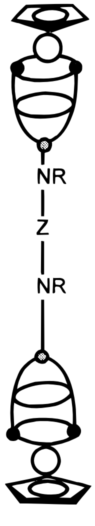


Figure 2. The left diagram is a stick representation and comparison of the ^{11}B NMR chemical shifts and relative intensities for the aminosubstituted twelve-vertex metallatricarbollides of general formulation [2-(η^5-C_5H_5)-9-X-*closo*-2,1,7,9-$FeC_3B_8H_{10}$] (**2**). The data are related to those of the isomeric complex [2-(η^5-C_5H_5)-*closo*-2,1,7,-10-$FeC_3B_8H_{11}$] **3** (data from ref 3). The right diagram is a plot of δ-(^{1}H) versus δ(^{11}B) for the complexes of type **2**. Data points for individual {BH} cluster units for complexes of type **2** fall within the areas marked by ellipsoids.

downfield ^{1}H shift, exempted from this correlation is the BH-(3) vertex which is connected to the two cage carbons and to the Fe center.

Conclusions

Since the discovery of the first representative of the metallatricarbaborane family, the seven-vertex [2-Me-7-$(CO)_3$-*closo*-7,2,3,4-$MnC_3B_3H_5$], by Grimes' group in 1969,[16] there has been current and developing interest in the chemistry of metallatricarbaboranes.[17] In this respect, the simple synthesis of the extremely stable ferratricarbollides of structure **2** significantly extends the scope of the twelve-vertex metallatricarbollide chemistry. An important feature of this chemistry is the facile generation of the amino functionality in view of difficulties encountered in other areas of carborane chemistry.[18] Moreover, the amino group is formed in the para position with respect to the metal center and the complexes of type **2** can be thus employed as ending groups for linearly shaped molecular assemblies as outlined, for example, in simplified structures **I** (Z = spacer group, e.g., $(-CH_2-)_n$, $-CO(CH_2)_nCO-$, etc.) and **II** (rigid rod). Reminiscent of these structures are the recently reported bis(cobaltacarborane)-based linear chains.[19] Moreover, various reactions on the amino group are expected to lead to extended derivatization of the cage of **2**. All these synthetic approaches will now be studied in more detail along with those of cluster chemistry of this particular metallatricarbollide system.



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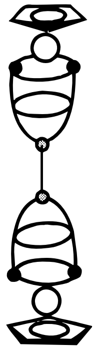

II

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, full bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters for **2c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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