THE FIRST EXAMPLES OF METALLATRICARBOLLIDES. ISOMERIC TWELVE-VERTEX CYCLOPENTADIENYL FERRATRICARBADODECABORANES [(η^5-C_5H_5)-*closo*-$FeC_3B_8H_{11}$]

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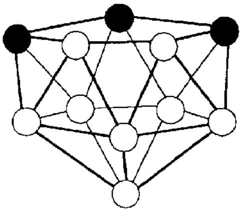
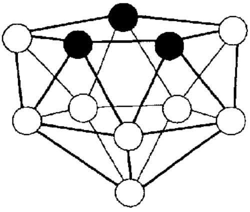
The first metallatricarbollides, six isomeric twelve-vertex metallatricarbaboranes of general structure [(η^5-C_5H_5)-*closo*-$FeC_3B_8H_{11}$], are formed in the reaction between TI[*nido*-7,8,9-$C_3B_8H_{11}$] and [(η^5-C_5H_5)-$Fe(CO)_2I$] in toluene at reflux. Two of them have so far been satisfactorily identified as [3-(η^5-C_5H_5)-*closo*-3,1,2,4-$FeC_3B_8H_{11}$] and [2-(η^5-C_5H_5)-*closo*-2,1,8,11-$FeC_3B_8H_{11}$] by NMR spectroscopy.

There is a current interest in the area of tricarbollide (eleven-vertex *nido* tricarbaborane) chemistry due to the potential use of these compounds as structurally flexible complexation agents. We have recently reported on the synthesis of ligand derivatives 7-L-*nido*-7,8,9-$C_3B_8H_{11}$ (where L = amines)[1,2], from which the parent tricarbollide anion [*nido*-7,8,9-$C_3B_8H_{11}$]$^-$ (*I*) can be obtained via deamination with sodium metal[1,3]. The trimethylamine derivative and also the anion *I* can be easily converted into their isomeric analogues 10-(Me_3N)-*nido*-$C_3B_8H_{10}$ and [*nido*-7,8,10-$C_3B_8H_{11}$]$^-$ (*II*) at elevated temperatures[4]. Sneddon's group has also recently reported[5] the synthesis of *C*-substituted derivatives of anion *II*, [10-R-*nido*-$C_3B_8H_{10}$]$^-$ (where R = Me and $PhCH_2$), by boron insertion into the anion [9-R-*nido*-5,6,9-$C_3B_7H_{10}$]$^-$. Due to the presence of a three-carbon pentagonal open face, all of these tricarbollide compounds were expected to be structurally designed for metal incorporation reactions. This has now proved to be

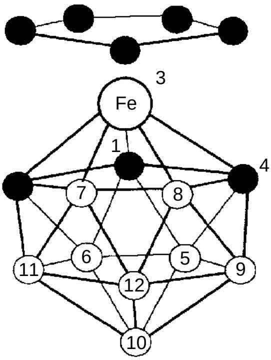

I


II

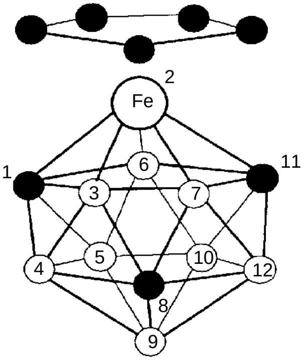
true and we wish to report herein our first siting experiments that directly lead to the formation of the first representatives of the long-anticipated twelve-vertex *closo* metallatricarbaborane family.

The reaction between TI[*nido*-7,8,9-$C_3B_8H_{11}$] (*I*) and [(η^5-C_5H_5)Fe$(CO)_2$I] in toluene under reflux for 3 h resulted in the formation of six isomeric complexes of the general composition [(η^5-C_5H_5)-*closo*-$FeC_3B_8H_{11}$]. The overall yield of these complexes has been 31% (unoptimized). The isomeric mixture was partially separated by sequential preparative TLC in hexane–CH_2Cl_2 mixtures. Till now we have been able to satisfactorily separate and identify two of these complexes: an orange [3-(η^5-C_5H_5)-*closo*-3,1,2,4-$FeC_3B_8H_{11}$] (*III*) and yellow [2-(η^5-C_5H_5)-*closo*-2,1,8,11-$FeC_3B_8H_{11}$] (*IV*) in equal 5% yields. The structure of compounds *III* and *IV* was proposed on the basis of NMR spectroscopy and mass spectrometry. The ^{11}B NMR spectrum of *III* consists of five doublets of relative areas 2 : 1 : 2 : 1 : 2 and that of *IV* shows also five doublets, but of different order of intensities 1 : 2 : 1 : 2 : 2. The ^{1}H NMR spectra of both isomers well indicate the presence of the cyclopentadienide ligand together with two cage {CH} resonances of relative intensities 2 : 1. The crosspeaks found in the [^{11}B-^{11}B]-COSY NMR spectra[6], although weak in some cases due to the presence of four cluster heteroatoms, agree well with the proposed cluster configurations as in *III* and *IV*. The constitution of the remaining four isomers will be assigned after a more detailed separation by preparative HPLC, followed by structure assignments.

The results presented above clearly demonstrate that the complexation of *I* with iron(II) is associated with an extensive dissipation of the three carbon vertices over the icosahedral surface of the resulting {$FeC_3B_8H_{11}$} moiety. This progressive cluster isomerization is achieved under relatively mild reaction conditions (compare, for example, a more enforced isomerization of the isolelectronic and isostructural metalladicarollides of type {$CoC_2B_9H_{11}$}, ref.[7]), in agreement with the presence of the three



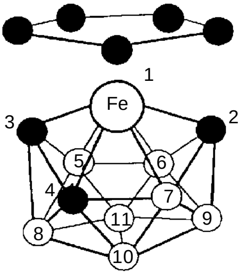
III



IV

positively charged cluster {CH} units of enhanced tendency for space separation due to sheer electrostatic repulsion.

In contrast to anion *I*, the Cs^+ salt of the isomeric anion *II* reacted with $[(\eta^5\text{-}C_5H_5)\text{-}Fe(CO)_2I]$ in refluxing THF for 3 h to give a single violet complex which was identified as eleven-vertex $[1\text{-}(\eta^5\text{-}C_5H_5)$-*closo*-$1,2,3,4\text{-}FeC_3B_7H_{10}]$ (*V*) by comparison of its NMR data with those of its *C*-methyl derivative[8]. Although there is no direct evidence for the reaction mechanisms, the formation of *V* seems to be associated with the elimination of one open-face boron vertex in structure *II*. Nevertheless, compound *V* is the first unsubstituted eleven-vertex metallatricarbaborane since all compounds of this family thus far prepared[8] have been substituted at the C-2 carbon.



V

In conclusion, it should be noted that the reaction discussed above has generated the first examples of the long-anticipated twelve-vertex family of *closo* metallatricarbollides and apparently opened an extensive area of cluster boron chemistry, well comparable to that of metalladicarbollides[9]. Metallatricarbadodecaborane complexes are expected to exhibit enormous structural diversity derived from different metal centers and isomeric configurations and are also anticipated to exhibit variable reactions, such as polyhedral contraction and expansion, as already encountered in comparable dicarbollide chemistry[9a]. Therefore, experiments leading to the incorporation of other-than-iron metals into the cages of anions *I* and *II* are ongoing, as are syntheses leading to cluster degradation and substitution.

EXPERIMENTAL

All reactions were carried out with use of standard vacuum or inert-atmosphere techniques as described by Shriver[10], although some operations, such as preparative TLC chromatography, were carried out in air. The starting $TI[7,8,9\text{-}C_3B_8H_{11}]$ was obtained by the precipitation of aqueous $Cs^+[7,8,9\text{-}C_3B_8H_{11}]^-$ (ref.[1]) with an equivalent amount of $TINO_3$, $Cs^+[7,8,10\text{-}C_3B_8H_{11}]^-$ was prepared according to the literature[4], and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ purchased from Aldrich. The Aldrich tetrahydrofuran (THF) and toluene were dried over Na/benzophenone, hexane and CH_2Cl_2 over CaH_2, and freshly distilled before use. Preparative TLC was carried out using silica gel (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. Analytical TLC was carried out on Silufol (Kavalier, silica gel on aluminum foil; detection by UV 254 or diiodine vapor, followed by 2% aqueous $AgNO_3$ spray). 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 (^{1}H) and boron (^{11}B) NMR spectroscopy was performed at 7.05 and 11.75 tesla on a Bruker ARX 300 and Varian XL 500 instruments in $CDCl_3$ solutions at 293 K. The [^{11}B-^{11}B]-COSY and ^{1}H-{^{11}B(selective)} NMR experiments were essentially as described in other recent papers from our laboratories[11]. Chemical shifts are given in ppm to high-frequency (low field) of Ξ = 32.083971 MHz (nominally F_3B . OEt_2 in $CDCl_3$) for ^{11}B (quoted ± 0.5 ppm) and Ξ = 100 MHz ($SiMe_4$) for ^{1}H (quoted ± 0.05 ppm), Ξ being defined as in ref.[12]. Solvent resonances were used as internal secondary standards. Coupling constants $^1J(^{11}B\text{-}^1H)$ are taken from resolution-enhanced ^{11}B spectra with digital resolution ±8 Hz and are given in Hz; in some cases these were determined from [^{1}H-^{11}B]-correlation spectra[13] with enhanced resolution of ca ±1 Hz.

[3-(η^5-C_5H_5)-*closo*-3,1,2,4-$FeC_3B_8H_{11}$] (*III*) and [2-(C_5H_5)-*closo*-2,1,8,11-$FeC_3B_8H_{11}$ (*IV*)

To a suspension of Tl[7,8,9-$C_3B_8H_{11}$] (*I*) (150 mg; 0.5 mmol) in 15 cm^3 of toluene was added [(η^5-C_5H_5)-$Fe(CO)_2I$] (151 mg; 0.5 mmol) and the mixture was heated under reflux for 3 h. After cooling to room temperature, the mixture was filtered through a layer of silica gel (ca 5 g) and the silica gel washed with CH_2Cl_2 (3 × 5 cm^3). The filtrate was then evaporated to dryness and the dark-orange oily residue subjected to multiple preparative TLC in mixtures containing variable hexane–CH_2Cl_2 ratios to isolate the most intense bands, from which individual compounds were removed by washing with CH_2Cl_2 and evaporation: R_F (prep., 30% CH_2Cl_2–hexane) 0.35 (orange fraction A); R_F (prep., 10% CH_2Cl_2–hexane) 0.22 (mixed red fraction B); R_F (prep., 10% CH_2Cl_2–hexane) 0.31 (mixed yellow fraction C); and R_F (prep., 10% CH_2Cl_2–hexane) 0.47 (yellow fraction D). Fractions B (20 mg; 16%) and C (6 mg; 5%) were identified as mixtures of two pairs of isomeric [(η^5-C_5H_5)-*closo*-$FeC_3B_8H_{11}$] complexes that need a more detailed HPLC separation. Fraction A (6 mg, 5%), MS, *m/z*: 256. ^{11}B NMR: –10.5 d, *J* = 154 (B-5, B-6); –14.3 d, *J* = 161 (B-12); –17.3 d, *J* = 171 (B-7, B-8); –21.0 d, *J* = 158 (B-10); –24.3 d, *J* = 176 (B-9, B-11). ^{1}H NMR: 4.58 s, (C_5H_5); 2.03 brs (H-2, H-4); 1.58 brs (H-1) was identified as complex *III*. Fraction D, MS, *m/z*: 256. ^{11}B NMR: –9.3 d, *J* = 161 (B-6); –10.2 d, *J* = 167 (B-3, B-7); –12.3 d, *J* ≈ 150 (B-9); –18.4 d, *J* = 172 (B-4, B-12); –23.7 d, *J* = 160 (B-5, B-10). ^{1}H NMR: 4.73 s (C_5H_5); 2.16 brs (H-1, H-11); 1.91 brs (H-8) was identified as compound *IV*. Both products were obtained as crystalline materials upon cooling their hexane solutions to ca –5 °C.

[1-(η^5-C_5H_5)-*closo*-1,2,3,4-$FeC_3B_7H_{10}$] (*V*)

A mixture of Cs^+[*nido*-7,8,9-$C_3B_8H_{11}$]$^-$ (*IV*) (133 mg; 0.5 mmol) and [(η^5-C_5H_5)$Fe(CO)_2I$] (151 mg; 0.5 mmol) was heated in THF (30 cm^3) at reflux for 3 h. The THF was evaporated and the dark residue digested with CH_2Cl_2 (15 cm^3). The mixture was then filtered through silica gel (ca 5 g) and washed out from the silica with additional CH_2Cl_2 until the eluate was colourless. The filtrate was reduced in volume and subjected to preparative TLC in hexane to isolate a single violet band of R_F (prep. ca 0.30). This was extracted with CH_2Cl_2, the extract was evaporated and the violet compound crystallized from a concentrated hexane solution by refrigeration at ca –5 °C to obtain 42 mg (35%) of complex V. MS, *m/z*: 244. ^{11}B NMR: –3.5 d, *J* = 156 (B-9); –4.9 d, *J* = 173 (B-8); –10.6 d, *J* = 125 (B-5); –11.2 d, *J* = 122 (B-6); –26.1 d, *J* = 145 (B-11); –28.9 d, *J* = 156 (B-10); –33.0 d, *J* = 159 (B-7). ^{1}H NMR: 6.89 brs (H-3); 6.20 brs (H-4); 4.73 s (C_5H_5); 2.88 q (H-9); 2.72 q (H-8); 2.56 q (H-5); 1.60 q (H-6); 0.50 q (H-11); 0.31 q (H-7); 0.22 q (H-10).

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