oxygen–oxygen distances is thereby limited, while succinate has rotamers with carboxyl groups gauche and trans to each other. As described before, the interactions of gauche and trans rotamers of succinate with $[Co(en)_3]^{3+}$ could be replaced by those of maleate and fumarate, respectively. Thus the oxygen–oxygen distances between two carboxyl groups, which are the best distances matching the H–H distance of the axial amine protons in $[Co(en)_3]^{3+}$, are 3.2, 3.0, and 2.3 Å for oxalate, malonate, and the gauche form of succinate, respectively. The distance between two carboxyl groups matches better with the H–H distance of amine protons as the skeleton carbon increases. Thus, the dicarboxylates associate with the complex ion in the order oxalate < malonate < succinate (gauche form).

By contrast, glutarate and adipate can exist as several rotamers. The possible rotamers of glutarate are trans–trans (T–T), trans–gauche (T–G), and two gauche–gauche (G–G) forms. Though the CD changes for these dicarboxylates cannot be separated into the contributions from each rotamer, it is possible to tackle this problem with the aid of molecular models. According to a consideration of such molecular models, G–T and T–T rotamers contribute to the CD change only as singly charged anions would. The oxygen–oxygen distances between two carboxyl groups for these two rotamers are ~6 Å. These distances do not fit the H–H distance of amine protons in $[Co(en)_3]^{3+}$. Only a G–G rotamer can fit the complex ion and lead to a great CD change. However, the population of this rotamer seems to be small since it is electrostatically at a disadvantage due to the repulsion between two carboxyl groups.[8] Thus the sum of the contributions from these rotamers will give a small CD change, and its pattern comes to be similar to that for a singly charged anion.

Factors other than steric ones which affect the interactions between the complex ion and dicarboxylate anions will now be examined. The dipolar effect may be one of these factors. However, it is not so important because *m*-phthalate, which has a certain dipole moment, behaves as a singly charged anion. In contrast, oxalate, which has no dipole, associates with the complex ion to a great extent (Table II). This result cannot be interpreted in terms of the dipolar effect. Thus the interaction between the complex ion and the dicarboxylate anion seems to be controlled predominantly by the steric effect, though the dipolar effect cannot be ruled out.

It is concluded that the degree of the interaction between $[Co(en)_3]^{3+}$ and a dicarboxylate anion depends predominantly on the relative position of two carboxyl groups in the dicarboxylate anion. The better match of the H–H distance of axial amine protons in the complex with the oxygen–oxygen distance of the anion results in a smooth association (group A). On the other hand, the dicarboxylate anion with the greater oxygen–oxygen distance between two carboxyl groups cannot interact with $[Co(en)_3]^{3+}$ through the two carboxyl groups simultaneously and thus associates poorly with the complex ion. These anions only slightly alter the CD spectrum of $[Co(en)_3]^{3+}$ and the CD change pattern is similar to that usually observed for a singly charged anion (group B). One more noteworthy conclusion is as follows. Succinate, glutarate, and adipate have more than two rotamers. Of these, only one rotamer can interact substantially with the complex ion and give a large CD change. This rotamer, however, only gives a small CD change contribution because of its low concentration compared with the other components. Thus, the overall CD changes are relatively small for these dicarboxylate anions.

Registry No. Λ-$[Co(en)_3]^{3+}$, 27228-84-8; Δ-$[Co(en)_3]^{3+}$, 16569-46-3; *o*-phthalate, 3198-29-6; *m*-phthalate, 42966-02-9; *p*-phthalate, 3198-30-9; sulfate, 14808-79-8; oxalate, 338-70-5; malonate, 156-80-9; maleate, 142-44-9; glutarate, 56-16-6; adipate, 764-65-8; benzoate, 766-76-7; propionate, 72-03-7; fumarate, 142-42-7; succinate, 56-14-4.

References and Notes

(1) F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Am. Chem. Soc.*, **81**, 290 (1959).
(2) T. Taura and H. Yoneda, *Chem. Lett.*, 71 (1977).
(3) S. F. Mason and J. Norman, *J. Chem. Soc. A*, 307 (1966).
(4) H. L. Smith and B. E. Douglas, *Inorg. Chem.*, **5**, 784 (1966).
(5) Katayama and Tamamushi have reported on the basis of conductance measurements that the association constant of maleate with $[Co(en)_3]^{3+}$ is about 3 times as large as that of fumarate: S. Katayama and R. Tamamushi, *Bull. Chem. Soc. Jpn.*, **44**, 1812 (1971).
(6) R. E. Cramer and R. L. Harris, *Inorg. Chem.*, **13**, 2208 (1974).
(7) K. R. Butler and M. R. Snow, *Inorg. Chem.*, **10**, 1838 (1971).
(8) K. G. R. Pachler, *Z. Anal. Chem.*, **224**, 211 (1967).

Contribution No. 3829 from the Department of Chemistry,
University of California, Los Angeles, California 90024

Synthesis of Electron-Deficient Biferracarboranes

C. G. SALENTINE and M. F. HAWTHORNE*

Received October 25, 1977

The polyhedral expansion of $3,1,2\text{-}C_5H_5FeC_2B_9H_{11}$ produced three new electron-deficient biferracarboranes $(C_5H_5Fe)_2C_2B_9H_{11}$, $(C_5H_5Fe)_2C_2B_8H_9(OH)$, and $[C_5H_5FeC_2B_9H_{11}FeC_2B_9H_{11}]^-$. All three complexes contained formal Fe(III) atoms and were diamagnetic. The proposed structures, based on spectroscopic and crystallographic data, contain nonbonded iron atoms. These complexes constitute the first examples of long-range electron-spin coupling through a carborane polyhedron.

Ferracarboranes have been synthesized containing formal Fe(II) and Fe(III) oxidation states.[1] Those of formula $[Fe(C_2B_nH_{n+2})_2]^{2-}$ and $[C_5H_5FeC_2B_nH_{n+2}]^-$ contain formal Fe(II) and are readily air oxidized to the stable Fe(III) complexes $[Fe(C_2B_nH_{n+2})_2]^-$ and $C_5H_5FeC_2B_nH_{n+2}$. These latter iron(III) metallocarboranes can be viewed as two-carbon carboranes in which a $\{C_5H_5Fe\}$ vertex has replaced a $\{BH\}$ vertex. Because $\{C_5H_5Fe^{II}\}$ is formally "isoelectronic" with $\{BH\}$, the Fe(III) complexes represent polyhedra containing one electron less than the required $2n + 2$ framework electrons.[2] A result of this electron deficiency is that polyhedral rearrangements have not yet been observed in this class of metallocarboranes. Crystallographic studies[1d] have shown that these iron(III) metallocarboranes possess regular closo-polyhedral geometries, indicating that one-electron deficiency has little or no effect upon polyhedral structure.

Prior to this work, only one electron-deficient biferracarborane had been reported,[3] the two-electron deficient species $(C_5H_5Fe^{III})_2C_2B_6H_8$ prepared by polyhedral expansion of $4,5\text{-}C_2B_7H_9$. This curious compound was initially obtained in a paramagnetic ($\mu_{eff} = 3.05\ \mu_B$) form presumably containing two unpaired electrons. It underwent a slow transformation to a diamagnetic species and a crystal structure[3] of the diamagnetic complex showed a unique 10-vertex closo-

0020-1669/78/1317-1498$01.00/0

polyhedral geometry incorporating an iron–iron bond (2.571 (1) Å), much different from the bicapped square antiprismatic geometry usually observed in 10-vertex carboranes and metallocarboranes. The structure was described as a derivation of a tricapped trigonal prism, the next lower polyhedron for which the biferracarborane did satisfy the electronic requirements. Recently, structurally novel 14-vertex *nido*-biferracarboranes which do satisfy the polyhedral electronic requirements were reported.[4]

As a continuation of our studies[5] of electronic effects upon geometry in metallocarborane polyhedra, we report here the synthesis of several new electron-deficient biferracarboranes incorporating two formal iron(III) metal atoms into 12- and 13-vertex metallocarborane polyhedra.

Results and Discussion

Polyhedral Expansion of 3-(η^5-C_5H_5)-3-Fe-1,2-$C_2B_9H_{11}$. The reduction of 3-(η^5-C_5H_5)-3-Fe-1,2-$C_2B_9H_{11}$ with 3 equiv of sodium followed by treatment with NaC_5H_5 and $FeCl_2$ afforded a mixture of products. Two neutral biferracarboranes were isolated by column chromatography on silica gel, and a third anionic bimetallic species was precipitated from water as the tetramethylammonium salt.

$$C_5H_5FeC_2B_9H_{11} \xrightarrow[C_{10}H_8]{3Na} \xrightarrow[FeCl_2]{C_5H_5^-} \underset{\text{I}}{(C_5H_5Fe)_2C_2B_9H_{11}} +$$

$$\underset{\text{II}}{[C_5H_5FeC_2B_9H_{11}FeC_2B_9H_{11}]^-} + \underset{\text{III}}{(C_5H_5Fe)_2C_2B_8H_9(OH)}$$

The golden orange-brown crystalline I exhibited a mass spectrum with a cutoff at *m/e* 376 corresponding to the ${}^{12}C_{12}{}^{1}H_{21}{}^{11}B_9{}^{56}Fe_2{}^+$ ion. Elemental analysis also confirmed this empirical formula. The diamagnetism of I was indicated from its NMR spectra. The 60-MHz ${}^1H$ NMR spectrum (in CD_2Cl_2) showed a sharp resonance at τ 5.14 and a broad resonance at τ 10.81 of relative areas 5:1. These were assigned to equivalent cyclopentadienyl groups and equivalent carborane C–H groups, respectively. The 80.5-MHz ${}^{11}B$ NMR spectrum contained resonances of area 1:2:4:2 at −113.1, −42.4, −22.4, and −5.7 ppm, relative to $Et_2O{\cdot}BF_3$. This high degree of symmetry within a 13-vertex polyhedron considerably limits the structural possibilities. Although fluxionality within a less symmetric polyhedron[1c] is one possible explanation of the NMR data, the ${}^{11}B$ NMR spectrum of I was unchanged to −75 °C. The resonance at −113 ppm almost certainly arises from a low-coordinate boron atom adjacent to two metal vertices (see ref 3 and 5a). The proposed fluxional process[1c] would "average" the low-coordinate boron position in the intermediate structure and a very low field resonance would not be expected in the ${}^{11}B$ NMR spectrum. Based on the above, we therefore postulate that I is not fluxional in solution, in contrast to other 13-vertex metallocarboranes such as 4-(η^5-C_5H_5)-4-Co-1,6-$C_2B_{10}H_{12}$[1c] and 4,5-(η^5-C_5H_5)$_2$-4,5-Co_2-1,6-$C_2B_9H_{11}$.[6]

The observed diamagnetism of I would tend to imply the existence of a metal–metal bond;[3] however, preliminary x-ray crystallographic results[7] indicate an Fe–Fe distance of ~3.20 Å. The preceding considerations lead to a proposed structure for I, 4,5-(η^5-C_5H_5)$_2$-4,5-Fe_2-2,3-$C_2B_9H_{11}$, as shown in Figure 1. The metal atoms reside at their favored high-coordinate positions in the 13-vertex polyhedron. The structure with carbon atoms at the 10,11 positions is not possible because replacement of one $C_5H_5^-$ ligand with a $C_2B_9H_{11}{}^{2-}$ ligand (complex II, vide infra) would render the carborane C–H groups nonequivalent in II, and they remain equivalent. The 12,13 positions for the carbon atoms are less likely because the starting material contained both carbon atoms adjacent to iron.

The low-coordinate 1 position in the structure proposed for I is occupied by boron—this is the first 13-vertex *closo*-metallocarborane synthesized that does not have carbon at its favored low-coordinate position.[8] Isolation of such a thermodynamically unstable species is possible with the *electron-deficient* ferracarboranes because they have been found not to undergo polyhedral rearrangement.

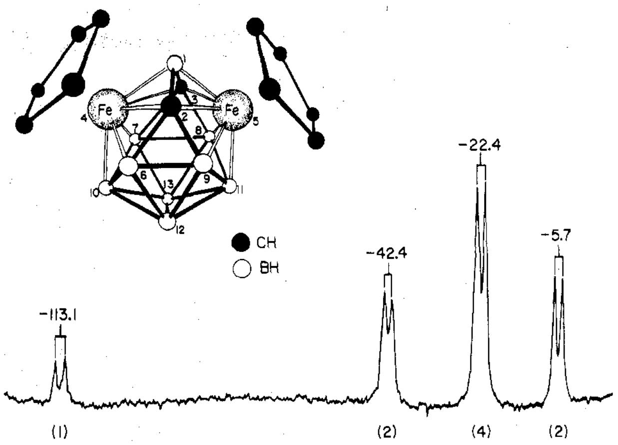

Figure 1. Proposed structure and 80.5-MHz ${}^{11}B$ NMR spectrum of I, 4,5-(η^5-C_5H_5)$_2$-4,5-Fe_2-2,3-$C_2B_9H_{11}$.

Table I. Electronic Spectra and Electrochemical Data

Complex	λ_{max}, nm (log ϵ)[a]	$E_{p/2}$ (V) vs. SCE[b]
I	725 (1.60), 545 (3.30), 418 (3.36), 349 (3.64), 275 (sh, 4.20), 237 (4.46), 206 (4.35)	−0.59 red +1.36 ox[c]
II	790 (1.60), 594 (3.445), 447 (3.425), 371 (3.72), 280 (sh, 4.32), 248 (4.415), 211 (4.41)	−0.70 red +1.07 ox[c] +1.76 ox[c]
III	756 (1.70), 575 (sh, 2.34), 419 (3.16), 350 (sh, 3.60), 248 (4.505), 223 (490)	*d*

[a] Measured in spectroquality CH_3CN. [b] Cyclic voltammetry in CH_3CN with 0.1 M $(C_2H_5)_4N^+PF_6^-$ supporting electrolyte, platinum button electrode; reversible waves except where noted; red = reduction, ox = oxidation. [c] Irreversible wave. [d] All waves irreversible, none well-defined.

The proposed geometry for the two-electron-deficient I has the same gross structure as found for $C_5H_5CoC_2B_{10}H_{12}$ which obeys the $2n + 2$ electron rule. Considering the structural result of $(C_5H_5Fe)_2C_2B_6H_8$,[3] it is possible that I could adopt a different polyhedral geometry. While this proposed structure is necessarily tentative, it agrees well with the available data. A single-crystal x-ray diffraction study of complex II has been initiated and may provide further structural information.

Complex I represents the first diamagnetic metallocarborane containing two paramagnetic centers not within bonding distance. The diamagnetism appears to be a result of spin pairing by interactions of the two iron atoms through the carborane ligand. Studies by Taube[9] and Day[10] have suggested that two metals can interact strongly through conjugated π-electron systems. The first example of complete electron delocalization through a bridging ligand in an organometallic complex was shown[11] recently for the bis(fulvalene)diiron dication, $[(C_{10}H_8)_2Fe_2]^{2+}$, which contains two Fe(III) centers separated by about 3.9 Å and yet is diamagnetic. The cyclic voltammogram of I showed a reversible reduction at $E_{p/2} = -0.59$ V and an irreversible oxidation at $E_{p/2} = +1.36$ V. The reduction is presumably to a mixed-valence Fe(II)–Fe(III) system. Further investigation of the reduced species is under way.

The second product isolated from the polyhedral expansion reaction was the diamagnetic green complex, II. Elemental analysis was consistent with the formulation $[(CH_3)_4N][C_5H_5FeC_2B_9H_{11}FeC_2B_9H_{11}]$. The 60-MHz ${}^1H$ NMR spectrum, measured in acetone-d_6, exhibited resonances of area 12:5:2:2 at τ 6.57, 5.06, 7.50, and 10.27, assigned to tetramethylammonium, cyclopentadienyl, carborane C–H, and carborane C–H protons, respectively. The carborane C–H resonance at τ 7.50 was within about 1 ppm to that observed[1a] for $[3\text{-}(\eta^5\text{-}C_5H_5)\text{-}3\text{-}Fe\text{-}1,2\text{-}C_2B_9H_{11}]^-$, and the resonance at τ 10.27 was within 0.5 ppm to that observed for I. The 80.5-MHz ^{11}B NMR spectrum of II also closely corresponded to a superposition of the ^{11}B spectra of I and $[3\text{-}(\eta^5\text{-}C_5H_5)\text{-}3\text{-}Fe\text{-}1,2\text{-}C_2B_9H_{11}]^-$. Doublets corresponding to the $\eta^5\text{-}1,2\text{-}C_2B_9H_{11}{}^{2-}$ ligand were observed in areas 1:1:4:2:1 at −7.7, +0.5, +4.8, +17.5, and +20.6 ppm. Resonances corresponding to the $C_2B_9H_{11}{}^{4-}$ bimetallic cage were observed in areas 1:1:1:2:2:2 at −110.1, −46.1, −39.8, −23.9, −22.6, and −5.8 ppm, assigned by comparison with the ^{11}B NMR spectrum of I. The area 4 resonance in the ^{11}B NMR spectrum of I, at −22.4 ppm, was split into two area 2 peaks in II at −23.9 and −22.6 ppm. Likewise, the area 2 resonance of I at −42.4 ppm was split into two area 1 peaks in II at −46.1 and −39.8 ppm. These data are consistent with a structure for II entirely analogous to I, with a $C_5H_5{}^-$ ligand replaced by a $1,2\text{-}C_2B_9H_{11}{}^{2-}$ ligand (see Figure 1). This substitution allows an assignment of the ^{11}B NMR spectrum of complex I: the area 1 resonance at −113.1 ppm is due to B1; the area 2 resonance at −42.4 ppm is due to B10, B11; the area 4 resonance at −22.4 ppm is due to B6, B7, B8, B9; and the area 2 resonance at −5.7 ppm is due to B12, B13. Thus II is formulated as $[(CH_3)_4N][4\text{-}(\eta^5\text{-}C_5H_5)\text{-}5\text{-}(\eta^5\text{-}1,2\text{-}C_2B_9H_{11})\text{-}4,5\text{-}Fe_2\text{-}2,3\text{-}C_2B_9H_{11}]$.

The third product of the reaction was a brown crystalline material, isolated in low yield by column chromatography, $(C_5H_5Fe)_2C_2B_8H_9(OH)$, III. The mass spectrum showed a cutoff at m/e 380 corresponding to the $^{12}C_{12}{}^1H_{20}{}^{11}B_8{}^{56}Fe_2{}^{16}O^+$ ion. A high-resolution mass spectrum confirmed the formula; calcd for $^{12}C_{11}{}^{13}C^1H_{20}{}^{11}B_8{}^{57}Fe_2{}^{16}O^+$ 383.1000, found 383.1003. This biferracarborane was also diamagnetic, showing one cyclopentadienyl resonance in the ^1H NMR spectrum (acetone-d_6) at τ 4.99. The 80.5-MHz ^{11}B NMR spectrum contained doublets of area 2:2:2:1:1 at −26.4, −19.3, −17.3, −3.6, and −0.8 ppm and indicated that OH substitution had occurred at a carborane carbon atom. The infrared spectrum contained a peak at ~3500 cm^{-1} assigned to ν_{O-H}. Assuming a gross icosahedral geometry for III, there are only four possibilities for the structure: $1\text{-}OH\text{-}2,3\text{-}(\eta^5\text{-}C_5H_5)_2\text{-}9,10\text{-}Fe_2\text{-}1,7\text{-}C_2B_8H_9$, $1\text{-}OH\text{-}9,10\text{-}(\eta^5\text{-}C_5H_5)_2\text{-}9,10\text{-}Fe_2\text{-}1,7\text{-}C_2B_8H_9$, $1\text{-}OH\text{-}3,6\text{-}(\eta^5\text{-}C_5H_5)_2\text{-}3,6\text{-}Fe_2\text{-}1,2\text{-}C_2B_8H_9$, $1\text{-}OH\text{-}8,10\text{-}(\eta^5\text{-}C_5H_5)_2\text{-}8,10\text{-}Fe_2\text{-}1,2\text{-}C_2B_8H_9$. The first two possibilities contain adjacent iron atoms, while the last two contain adjacent carbon atoms. Because the starting material contained adjacent carbon atoms, and it has been shown (vide supra) that a direct iron–iron bond is not necessary for diamagnetism, we favor the last two possibilities over the first two. Also, because the carbon atoms were adjacent to iron in the starting material, $1\text{-}OH\text{-}3,6\text{-}(\eta^5\text{-}C_5H_5)_2\text{-}3,6\text{-}Fe_2\text{-}1,2\text{-}C_2B_8H_9$ is the most probable structure of III. Traces of water or hydroxide in the polyhedral expansion reaction mixture could have resulted in the production of III, analogous to the synthesis of $3,6\text{-}(\eta^5\text{-}C_5H_5)_2\text{-}3,6\text{-}Co_2\text{-}1,2\text{-}C_2B_8H_{10}$ by treatment of $3\text{-}(\eta^5\text{-}C_5H_5)\text{-}3\text{-}Co\text{-}1,2\text{-}C_2B_9H_{11}$ with KOH, $C_5H_5{}^-$, and $CoCl_2$.[12] The geometry found for III could also be easily generated from I by removal of the low-coordinate boron position with the formation of the C2–C3 bond (Figure 1). As with I, it is possible that the geometry of III may deviate significantly from icosahedral, as III is also two-electron deficient.

Isolation of a stable derivative of $(C_5H_5Fe)_2C_2B_8H_{10}$ led to attempts to prepare the parent compound. The polyhedral expansion of $1\text{-}(\eta^5\text{-}C_5H_5)\text{-}1\text{-}Fe\text{-}2,3\text{-}C_2B_8H_{10}$ with $C_5H_5{}^-$ and $FeCl_2$ produced unstable ferracarboranes which rapidly decomposed to ferrocene in solution; use of $[C_5H_5FeC_6H_6]^+$ as a FeC_5H_5 source produced a red compound which eluted from silica gel in dichloromethane. The mass spectrum showed a cutoff at m/e 364 corresponding to $(C_5H_5Fe)_2C_2B_8H_{10}$. The 60-MHz ^1H NMR spectrum contained two broad peaks of equal area in the cyclopentadienyl region and indicated that the compound was paramagnetic. Cyclic voltammetry showed a reversible reduction at $E_{p/2} = -0.56$ V and a quasi-reversible reduction at $E_{p/2} = -1.40$ V. This complex was also unstable, even in the solid state, and decomposed in a few days to $1\text{-}(\eta^5\text{-}C_5H_5)\text{-}1\text{-}Fe\text{-}2,3\text{-}C_2B_8H_{10}$. Apparently, the bimetallocarborane resulting from polyhedral expansion of $1\text{-}(\eta^5\text{-}C_5H_5)\text{-}1\text{-}Fe\text{-}2,3\text{-}C_2B_8H_{10}$, which contains nonadjacent carbon atoms, did not have a stable isomeric arrangement of heteroatoms within the polyhedron. It is interesting that the only other paramagnetic biferracarborane, $(C_5H_5Fe)_2C_2B_6H_8$, was also unstable with respect to transformation to a diamagnetic form.

Among the results of these studies is the important observation that paramagnetic metal centers not within bonding distance may participate in long-range coupling through a carborane cage. The greater stability and ease of purification of complex I as compared to the bis(fulvalene)diiron dication[11] make it an attractive candidate for further physical studies.

Experimental Section

Physical Measurements. Ultraviolet–visible spectra were measured with a Cary 14 spectrophotometer. Infrared spectra were determined using a Perkin-Elmer Model 137 sodium chloride spectrophotometer. Proton NMR spectra were obtained on a Varian A-60D spectrometer. The 80.5-MHz ^{11}B NMR spectra were obtained with an instrument designed by Professor F. A. L. Anet of this department. Electrochemical data were obtained on an instrument described previously.[13] Mass spectra were measured using an Associated Electrical Industries MS-9 spectrometer.

Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

Materials. Literature methods were used to prepare $3\text{-}(\eta^5\text{-}C_5H_5)\text{-}3\text{-}Fe\text{-}1,2\text{-}C_2B_9H_{11}$,[1a] $1\text{-}(\eta^5\text{-}C_5H_5)\text{-}1\text{-}Fe\text{-}2,3\text{-}C_2B_8H_{10}$,[1b] and $[C_5H_5FeC_6H_6][PF_6]$.[14] Anhydrous sublimed ferric chloride and hydrogen reduced iron powder were obtained from Matheson Coleman and Bell. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride and stored under nitrogen prior to use. All other solvents were reagent grade and used without further purification. Naphthalene, Spectroquality acetonitrile, and tetramethylammonium chloride were obtained from Matheson Coleman and Bell. Sodium hydride, as a 50% dispersion in mineral oil, was obtained from ROC/RIC Chemical Corp. Dicyclopentadiene was obtained from Aldrich Chemical Co. and converted to cyclopentadiene immediately prior to use. THF solutions of sodium cyclopentadienide were prepared as previously described[1c] and immediately used. Sodium metal was purchased from Allied Chemical Co. Silica gel powder, 60–200 mesh, was obtained from J. T. Baker Chemical Co. for use in column chromatography. Preparative thick-layer chromatography was performed with Chrom AR Sheet 1000 purchased from Mallinckrodt Chemical Co.

Polyhedral Expansion of $3\text{-}(\eta^5\text{-}C_5H_5)\text{-}3\text{-}Fe\text{-}1,2\text{-}C_2B_9H_{11}$. Into a nitrogen-flushed three-necked 500-mL round-bottomed flask equipped with a mechanical stirrer and nitrogen inlet was placed 2.53 g (10.0 mmol) of $3,1,2\text{-}C_5H_5FeC_2B_9H_{11}$ followed by 100 mL of THF. To this was added freshly cut sodium metal (0.70 g, 30 mmol) and 1.0 g of naphthalene. The solution was stirred 6 days under nitrogen, yielding an orange-green color with all the sodium consumed. To this solution was added a THF solution of 35 mmol of NaC_5H_5 followed by a THF slurry of 30 mmol of $FeCl_2$ (prepared by refluxing 0.70 g of Fe powder with 3.24 g of $FeCl_3$ for 18 h under nitrogen). The mixture was stirred 16 h under nitrogen, then oxygen was bubbled through the solution for 20 min. The solution was filtered through Celite and added to 40 g of silica gel. Solvent was removed and the solids were placed atop a 4 × 30 cm silica gel chromatography column prepared in hexane. Elution with hexane produced a yellow band containing 1.6 g of ferrocene. Elution with 20% CH_2Cl_2/hexane developed a large red-purple band which yielded 0.98 g of a mixture of starting material and $(C_5H_5Fe)_2C_2B_9H_{11}$, I. These were separated by thick-layer chromatography to yield 290 mg of the less polar starting material and 647 mg (17%) of I as shiny metallic copper-colored plates, decomposition above ~180 °C without melting. Anal. Calcd for $C_{12}H_{21}B_9Fe_2$: C, 38.51; H, 5.66; B, 26.00; Fe, 29.84. Found: C, 38.15; H, 5.50; B, 25.00; Fe, 28.61. High-resolution mass measurement calcd for $^{12}C_{12}{}^{1}H_{21}{}^{11}B_9{}^{56}Fe_2{}^+$ 376.1168, found 376.1202. Infrared spectrum (Nujol mull): 3070 (w), 2600 (w), 2510 (vs), 2470 (vs), 1420 (s), 1120 (w), 1130 (w), 1070 (m), 1060 (w) 1025 (s), 1010 (m), 965 (m), 935 (w), 925 (w), 910 (w), 905 (w), 885 (m), 875 (w), 860 (w), 850 (s), 835 (s), 755 (w), 738 (m), 728 (m), 720 (m) cm^{-1}.

A yellow-brown band was eluted from the column in 60% CH_2Cl_2/hexane which upon rotary evaporation of solvent produced 60 mg (1.6%) of green-brown crystals of III, $(C_5H_5Fe)_2C_2B_8H_9OH$, mp >300 °C. Mass measurement calcd for $^{12}C_{12}{}^{1}H_{20}{}^{11}B_8{}^{56}Fe_2{}^{16}O^+$ 380.0957, found 380.0973; calcd for $^{12}C_{11}{}^{13}C^{1}H_{20}{}^{11}B_8{}^{57}Fe_2{}^{16}O^+$ 383.1000, found 383.1003. Infrared spectrum (Nujol mull): 3450 (w), 3090 (w), 2490 (vs), 1425 (m), 1415 (m), 1275 (m), 1150 (m), 1110 (s), 1070 (s), 1045 (w), 1020 (m), 1015 (m), 988 (m), 938 (w), 882 (m), 844 (s), 720 (w), 688 (m) cm^{-1}.

The silica gel was then extracted with CH_3CN, yielding a deep green solution. Removal of CH_3CN followed by addition of H_2O, filtration, and addition of excess $(CH_3)_4NCl$ produced a green precipitate. The precipitate (150 mg) was dissolved in acetone and stripped onto silica gel and chromatographed on a 2 × 15 cm silica gel column. Elution with CH_2Cl_2 removed impurities while elution with 10% acetone/CH_2Cl_2 eluted the green band. Addition of 1-propanol to the filtrate followed by slow rotary evaporation produced 84 mg (1.6%) of dark green crystals of II, $[(CH_3)_4N][C_5H_5FeC_2B_9H_{11}FeC_2B_9H_{11}]$, mp >300 °C. Anal. Calcd for $C_{13}H_{39}B_{18}Fe_2N$: C, 30.28; H, 7.62; B, 37.73; Fe, 21.66; N, 2.72. Found: C, 30.17; H, 7.76; B, 36.51; Fe, 21.74; N, 2.69. Infrared spectrum (Nujol mull): 3100 (w), 2500 (vs), 1490 (s), 1425 (m), 1290 (w), 1155 (w), 1125 (w), 1070 (m), 1060 (w), 1035 (m), 1025 (m), 995 (m), 977 (m), 950 (m), 883 (m), 860 (w), 840 (s), 760 (m), 740 (m), 724 (m) cm^{-1}.

Polyhedral Expansion of 1-(η^5-C_5H_5)-1-Fe-2,3-$C_2B_8H_{10}$. This reaction was performed as above with 0.98 g (4.06 mmol) of 1,-2,3-$C_5H_5FeC_2B_8H_{10}$. To the reduced solution was added, as a solid, 6.5 g (19 mmol) of $[C_5H_5FeC_6H_6][PF_6]$. The mixture was stirred 120 h under nitrogen and worked up as above. Elution of the chromatography column with hexane produced ferrocene, and elution with 20% CH_2Cl_2–hexane yielded 60 mg of starting material. A red band eluted in CH_2Cl_2. Addition of a small amount of hexane followed by rotary evaporation of the solvent produced 90 mg of red-purple crystals, mp >310 °C, whose mass and ^1H NMR spectra were consistent with the formulation $(C_5H_5Fe)_2C_2B_8H_{10}$. No 80.5-MHz ^{11}B NMR spectrum was observable for the paramagnetic species. The elemental analysis and magnetic susceptibility were close to that expected for $C_5H_5FeC_2B_8H_{10}$, due presumably to solid-state decomposition.

Acknowledgment. We are grateful to the Office of Naval Research for financial support.

Registry No. I, 65915-58-4; II, 65915-60-8; III, 65915-57-3; 3,1,2-$C_5H_5FeC_2B_9H_{11}$, 37185-23-2; 1,2,3-$C_5H_5FeC_2B_8H_{10}$, 42769-15-3; $(C_5H_5Fe)_2C_2B_8H_{10}$, 65982-53-8.

References and Notes

(1) See, for example, the following: (a) M. F. Hawthorne, et al., *J. Am. Chem. Soc.*, **90**, 879 (1968); (b) W. J. Evans, G. B. Dunks, and M. F. Hawthorne, *ibid.*, **95**, 4565 (1973); (c) D. F. Dustin, G. B. Dunks, and M. F. Hawthorne, *ibid.*, **95**, 1109 (1973); (d) A. Zalkin, D. H. Templeton, and T. E. Hopkins, *ibid.*, **87**, 3988 (1965).

(2) R. W. Rudolph, *Acc. Chem. Res.*, **9**, 446 (1976).

(3) K. P. Callahan, W. J. Evans, F. Y. Lo, C. E. Strouse, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **97**, 296 (1975).

(4) (a) W. M. Maxwell, R. F. Bryan, and R. N. Grimes, *J. Am. Chem. Soc.*, **99**, 4008 (1977); (b) W. M. Maxwell, R. Weiss, E. Sinn, and R. N. Grimes, *ibid.*, **99**, 4016 (1977).

(5) (a) C. G. Salentine, C. E. Strouse, and M. F. Hawthorne, *Inorg. Chem.*, **15**, 1832 (1976); (b) C. G. Salentine and M. F. Hawthorne, *ibid.*, **15**, 2872 (1976).

(6) W. J. Evans and M. F. Hawthorne, *Inorg. Chem.*, **13**, 869 (1974).

(7) K. P. Callahan, preliminary crystallographic study of complex II.

(8) M. F. Hawthorne, K. P. Callahan, and R. J. Wiersema, *Tetrahedron*, **30**, 1795 (1974).

(9) C. Creutz and H. Taube, *J. Am. Chem. Soc.*, **95**, 1086 (1973), and references therein.

(10) B. Mayoh and P. Day, *J. Am. Chem. Soc.*, **94**, 2885 (1972).

(11) C. LeVanda, K. Bechgaard, D. O. Cowan, U. T. Mueller-Westerhoff, P. Eilbracht, G. A. Candela, and R. L. Collins, *J. Am. Chem. Soc.*, **98**, 3181 (1976).

(12) J. Plešek, B. Štibr, and S. Heřmánek, *Synth. Inorg. Met.-Org. Chem.*, **3**, 291 (1973).

(13) T. E. Paxson, M. K. Kaloustian, G. M. Tom, R. J. Wiersema, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **94**, 4882 (1972).

(14) R. B. King, "Organometallic Syntheses", Vol. 1, Academic Press, New York, N.Y., 1965, p 138.

Contribution from the Department of Chemistry,
Michigan State University, East Lansing, Michigan 48823

Porphyrin Intercalation in Mica-Type Silicates

SHARMAINE S. CADY and T. J. PINNAVAIA*

Received November 11, 1977

This paper reports the reactions of *meso*-tetraphenylporphyrin ($TPPH_2$) with selected cations on the interlamellar surfaces of montmorillonite, a swelling layer lattice silicate related to mica. Strongly acidic hydrated Fe^{3+} and VO^{2+} ions react quantitatively with the free base porphyrin to afford the protonated porphyrin dication ($TPPH_4{}^{2+}$) in the form of intercalated monolayers. Monolayers of $TPPH_4{}^{2+}$ are also formed by reaction of the free base porphyrin with hydronium ions on the silicate surfaces. Weakly acidic hydrated Na^+ and Mg^{2+} on the surface-exchange sites afford only trace amounts of $TPPH_4{}^{2+}$. No porphyrin dication is formed with $(n\text{-}C_3H_7)N^+$. Co^{2+}, Cu^{2+}, and Zn^{2+} react to give mainly metalloporphyrin in solution and a hydronium-exchange form of the silicate. Only a small fraction of the neutral metalated porphyrin remains physically adsorbed to the silicate layers. The Bronsted acidity of hydrated cations is further demonstrated by the surface-catalyzed reactions of benzaldehyde and pyrrole. All of the above cations with the exception of $(n\text{-}C_3H_7)_4N^+$ form an intercalated porphyrin intermediate from the aldehyde and pyrrole in aqueous solution. The intermediate, which forms $TPPH_2$ and $TPPH_4{}^{2+}$ when desorbed from the silicate surface, is believed to be a porphomethene or -dimethene. The importance of this latter reaction as a possible mechanism for the prebiotic formation of porphyrins is briefly discussed.

Introduction

Montmorillonite and related swelling mica-type compounds are capable of intercalating a variety of guest molecules between their negatively charged silicate sheets. The formation of coordination complexes with metal-exchange ions on the interlamellar surfaces is among the more common mechanisms available for substrate binding. Although much remains to be learned concerning the coordination chemistry of metal ions on the interlayer surfaces, recent studies[1] suggest that certain complexes retain their solution-like mobility and constitution in the intercalated state, even to the extent of being able to catalyze solution-like reactions in the solid state.[2]

In the present study we have examined the reactions of *meso*-tetraphenylporphyrin with hydrated metal ions in the

0020-1669/78/1317-1501$01.00/0 © 1978 American Chemical Society