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OCT 77 R WEISS, R N GRIMES N00014-75-C-0305
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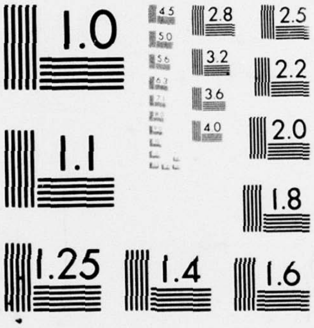

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OFFICE OF NAVAL RESEARCH

(15) Contract No. N00014-75-C-0305

Task No. ~~NR 053-569~~

(9) TECHNICAL REP[redacted]T NO. 24 (14) TR-24

(6) New Ferraboranes. Structural Analogues of Hexaborane (10) and Ferrocene. A Complex of Cyclic $B_5H_{10}^{(-)}$, a Counterpart of $C_5H_5^{(-)}$

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Prepared for Publication

in the

Journal of the American Chemical Society

401 147

(11) Oct[redacted]77

401 147

New Ferraboranes. Structural Analogues of Hexaborane(10) and Ferrocene. A Complex of Cyclic $B_5H_{10}^-$, a Counterpart of $C_5H_5^-$

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Abstract. A new metalloborane, 2-(η^5-C_5H_5)FeB_5H_{10} (I), was prepared in the reaction of $FeCl_2$, $Na^+C_5H_5^-$, and $Na^+B_5H_8^-$ in tetrahydrofuran at 25° and isolated as violet crystals via silica gel chromatography. At 175-180° I slowly rearranged to a new isomer, 1-(η^5-C_5H_5)FeB_5H_{10} (II). From electron-impact and chemical ionization mass spectra, ^{11}B NMR, and ^1H NMR, I and II were structurally characterized as nido-ferraboranes analogous to B_6H_{10}, having a pentagonal pyramidal framework with the (C_5H_5)Fe group occupying a basal position in I and the apex in II. Both species are isoelectronic with ferrocene, but II is also isostructural with that complex and contains a cyclic $B_5H_{10}^-$ ligand; accordingly, II can be described as "pentaboraferrocene". Complexes I and II are also analogues of B_6H_{10}. Compound II is the first known example of a complex containing a cyclic pentaboranyl ligand.

We report the preparation and characterization of two isomers of a new metalloborane, $(\eta^5\text{-}C_5H_5)FeB_5H_{10}$, which are isoelectronic, and in one case also isostructural, with $(\eta^5\text{-}C_5H_5)_2Fe$ (ferrocene). The reaction of anhydrous $FeCl_2$ with $Na^+C_5H_5^-$ and $Na^+B_5H_8^-$ in tetrahydrofuran at 25°C afforded violet crystals of $2\text{-}(\eta^5\text{-}C_5H_5)FeB_5H_{10}$ (I), whose proposed structure is shown in Figure 1. This compound was isolated in low yield as a moderately air-sensitive solid by extraction with methylene chloride followed by chromatography on a silica gel column. Large quantities of ferrocene and small amounts of other ferraboranes, currently under investigation, were also obtained. The fact that I is the major ferraborane product is in sharp contrast with the reaction of $CoCl_2$, $Na^+C_5H_5^-$, and $Na^+B_5H_8^-$ which generated a host of three- and four-boron metalloboranes but gave no detectable five-boron products.[1]

The characterization of I was accomplished from its electron-impact mass spectrum, which exhibited a parent ion with the major cutoff at m/e 186; the chemical ionization mass spectrum (calc. for $^{56}Fe^{11}B_5{}^{12}C_5{}^{1}H_{16}{}^+$ (M + 1 peak), 187.1067, found, 187.1062); the undecoupled and proton-decoupled ^{11}B Fourier transform NMR spectra (Table I); and the undecoupled and ^{11}B-decoupled proton NMR spectra (Table II), which confirm the presence of five

B-$H_{terminal}$ units and five bridging hydrogen atoms. The high-field proton NMR signal of two of the bridging hydrogen atoms is consistent with the presence of two Fe-H-B bridge groups. The assigned nido geometry is in agreement with these data as well as with the presence of 16 skeletal valence electrons (1 from $(C_5H_5)Fe$, 1 from each H bridge, and 2 from each BH unit) in a 6-vertex framework, corresponding to a (2n + 4)-electron system.[2]

Since I is isoelectronic with ferrocene, it was of interest to attempt the thermal rearrangement of I to the $1-(\eta^5-C_5H_5)FeB_5H_{10}$ isomer (II) in which iron occupies the apex position in the FeB_5 pyramid, corresponding to ferrocene with one $C_5H_5^-$ ligand replaced by $B_5H_{10}^-$. Precedent for a metalloborane rearrangement of this kind was given by the thermal conversion[1a,1] of the square pyramidal species $2-(\eta^5-C_5H_5)CoB_4H_8$ to the 1-isomer, in which cobalt moves from a basal to an apical location. In the present system, the isomerization of I to II was conducted by heating a 20-mg sample without solvent in a sealed tube at 175°, which in 20.5 h resulted in the isomerization of approximately a third of the sample as measured by NMR. The mixture was placed in toluene-d_8 and heated for 70 h at 175° and 5 h at 180° with periodic monitoring by ^1H NMR, producing essentially complete conversion to isomer II together with small amounts of insoluble decomposition products.

The proposed structure of II (Figure 1) is supported by its NMR spectra as given in Tables I and II. The observation of only one boron environment, and of single B-$H_{terminal}$ and B-H-B resonances, virtually establishes the structure shown. Compound II represents the first known complex containing a cyclic B_5 ligand, although the planar $C_2B_3H_7^{2-}$ and $C_2B_3H_5^{4-}$ ligands are found in such species as $(\eta^5\text{-}C_5H_5)CoC_2B_3H_7$[3], $(CO)_3FeC_2B_3H_7$[4], and 1,7,2,3- and 1,7,2,4-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$[3,5]; the last three structures mentioned have been confirmed by X-ray studies.[5a,6,7] Examples are also known of transition metals pentacoordinated to a B_5 ring which is part of a larger borane ligand, as in the $(\eta^5\text{-}C_5H_5)NiB_{11}H_{11}^-$ ion.[8] Both I and II may be viewed as analogues of B_6H_{10} with a $(\eta^5\text{-}C_5H_5)$FeH group replacing a basal or apical BH unit, and are similarly related to the known species $(CO)_3FeB_5H_9$.[9] At the same time, the metallocene-like sandwich structure of II suggests the trivial name "pentaboraferrocene". These complexes further illustrate the structural and electronic relationship which is currently emerging between the borane and metallocene classes[2a,5c,10] in much the same manner that the recently reported Co_3B_3, Co_3B_4, and Co_4B_4 metalloboron clusters[1] tend to bridge the gap between the metal clusters and the polyhedral boranes. Systematic studies of their chemistry should help to define more clearly the nature and extent of these analogies.

Acknowledgment. This work was supported by the Office of Naval Research.

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Table I. 32.1-MHz ^{11}B NMR Data (toluene-d_8)

Compound	Rel. Area	δ^a	$J_{B-H_t}(Hz)^b$
I	2	44.4	145
	2	8.2	146
	1	-53.0	140
II		5.1	145

[a] Ppm relative to $BF_3 \cdot O(C_2H_5)_2$, with positive sign indicating shift to lower field. [b] All signals were observed as doublets in the undecoupled spectra, and as singlets in the ^1H-decoupled spectra.

Table II. 100-MHz ^1H NMR Data (toluene-d_8)

Compound	δ^a	Multiplicity(J,Hz)	Rel. Area	Assignment
I	4.04	singlet	5	C_5H_5
	6.96	quartet (147)	2	H_t-B
	3.86	quartet (153)	2	H_t-B
	-0.55	quartet (141)	1	H_t-B
	-1.70	broad singlet	2	B-H-B
	-2.33	broad singlet	1	B-H-B
	-15.99	quartet (70)	2	Fe-H-B
II	4.23	singlet	1	C_5H_5
	3.50	singlet[b]	1	H_t-B
	-4.52	broad singlet	1	B-H-B

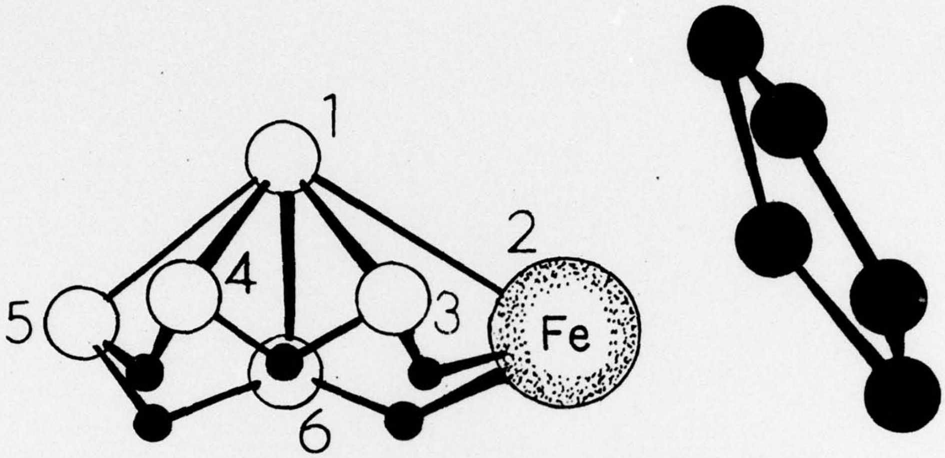
[a] Ppm relative to $(CH_3)_4Si$, with positive sign indicating shift to lower field.

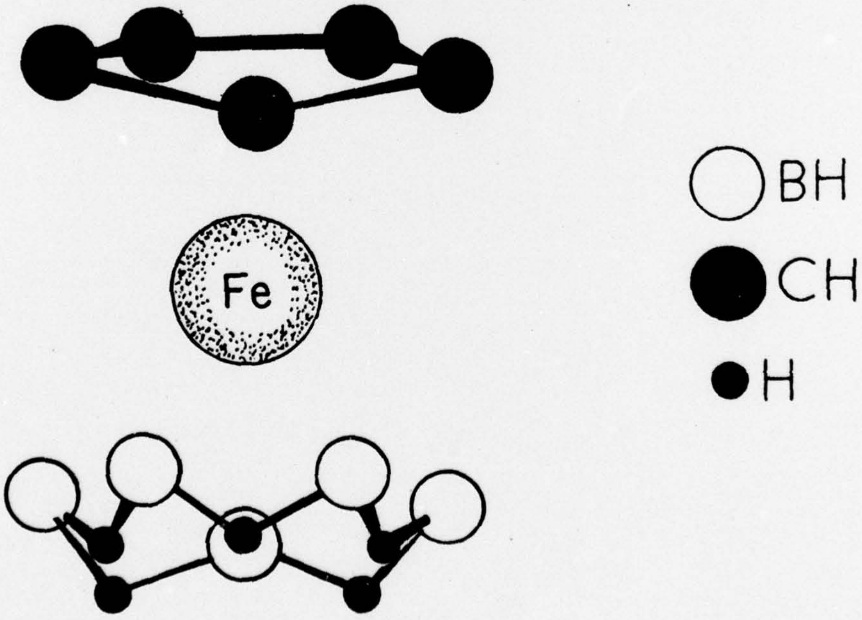
[b] Measured from ^{11}B-decoupled spectrum.

Figure Caption

Figure 1. Proposed structures of 2-(η^5-C_5H_5)FeB_5H_{10} (I) and 1-(η^5-C_5H_5)FeB_5H_{10} (II). Connecting lines between iron and boron are omitted in II in order to emphasize the sandwich-like arrangement of ligands.

$(C_5H_5)FeB_5H_{10}$ ISOMERS





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4. TITLE (and Subtitle) New Ferraboranes. Structural Analogues of Hexaborane(10) and Ferrocene. A Complex of Cyclic $B_5H_{10}^-$, a Counterpart of $C_5H_5^-$		5. TYPE OF REPORT & PERIOD COVERED Interim 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Richard Weiss and Russell N. Grimes		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-0305
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Virginia Department of Chemistry Charlottesville, Virginia 22901		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 053-569
11. CONTROLLING OFFICE NAME AND ADDRESS Chemistry Branch, Office of Naval Research Arlington, Virginia 22217		12. REPORT DATE October, 1977 13. NUMBER OF PAGES 8
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Metalloboranes	Cycloborane complex
Ferraboranes	Iron
Hexaborane(10)	
Ferrocene	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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