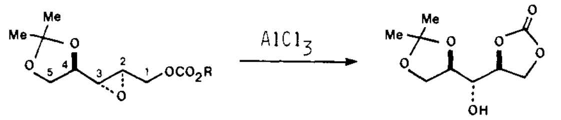

17a : R = $CH_2C_6H_5$
17b : R = CH_3
17c : R = $CH_2C_6H_4OMe$-p

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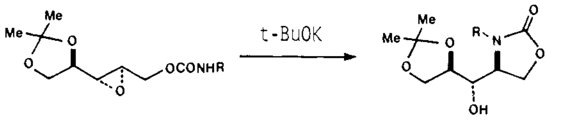
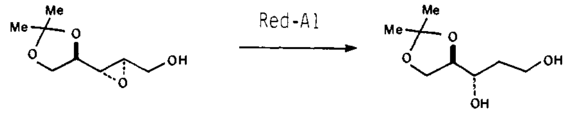


19a : R = $CH_2C_6H_5$
19b : R = H

9 : R = $CH_2C_6H_5$



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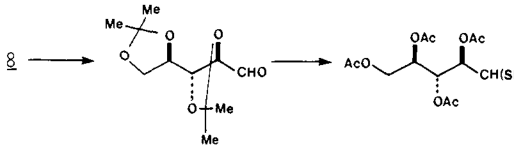
product originating from the ring opening by the oxygen atom of the urethane moiety was detected in this reaction. It is interesting to add the observation that the urethane **19b**[3,21] was recovered unchanged under the same conditions. The gross structure of **9** was concluded on the basis of spectroscopic data, while its stereochemistry was assigned on the basis of analogy to the corresponding carbonate case and also on the fact that the cyclic urethanes **11**[3] (78% overall yield; mp 102–103 °C; $[\alpha]_D$ −12.9° ($CHCl_3$, *c* 0.31)), **13**[3] (65% overall yield; mp 106–108 °C; $[\alpha]_D$ +31.7° ($CHCl_3$), *c* 0.31)), and **15**[3] (78% overall yield; mp 112–113 °C; $[\alpha]_D$ −72.0° ($CHCl_3$, *c* 0.32)) were obtained from the epoxides **5**–**7**, respectively. Cyclic urethanes **9**, **11**, **13**, and **15** were transformed into the corresponding 2-amino-2-deoxy-D-pentitol 4,5-acetonide 1,2,3-triacetates[3] in three steps [(1) Li/liquid NH_3/−78 °C, (2) $LiOH/H_2O/EtOH$/reflux, and (3) Ac_2O/Py/room temperature] in excellent yield.

Third, reductive ring opening of the epoxide **4** was regiospecifically realized by using Red-Al [$NaAlH_2(OCH_2CH_2OCH_3)_2$/ThF/room temperature];[22] the product, 2-deoxy-D-arabitol 4,5-acetonide (**20**), was isolated and characterized as its diacetate[3] ($[\alpha]_D$ −23.2° ($CHCl_3$, *c* 0.63)) in 89% overall yield. The NMR and TLC analyses of the crude product showed practically no 3-deoxy-D-adonitol 4,5-acetonide 1,2-diacetate formed in this reduction. The same sequence of reactions on the epoxide **6** yielded 2-deoxy-D-arabitol 4,5-acetonide 1,2-diacetate, while these on the epoxides **5** and **7** gave 2-deoxy-D-xylitol 4,5-acetonide 1,2-acetate[3] ($[\alpha]_D$ +36.7° ($CHCl_3$, *c* 0.29)) in about 90% overall yield.

The unique pattern in the arrangement of the protecting groups of carbonates **8**–**15** allows achievement of further useful manipulations. For example, the carbonate **8** was transformed to the diacetonide aldehyde **21**[3] ($[\alpha]_D$ −11.8° ($CHCl_3$, *c* 0.97)) in five steps [(1) 1 N NaOH/MeOH/0 °C, (2) $(C_6H_5)_2(t\text{-Bu})SiCl$/Py/40 °C, (3) CSA/$MeC(OMe)_2Me$/acetone/room temperature, (4) $(n\text{-Bu})_4NF$/THF/room temperature, and (5) PCC/NaOAc/CH_2Cl_2/room temperature] in 67% overall yield. The aldehyde **21** was converted to D-ribose via the thioacetal **22**.[23] Alternatively, the aldehyde group of **21** could be utilized for the next chain extension.



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Acknowledgment. The support of the National Institutes of Health (NS-12108) and the National Science Foundation (CHE 78-06296) is gratefully acknowledged.

Registry No. 1, 22323-80-4; **2**, 79060-23-4; **3**, 80532-35-0; **4**, 80532-36-1; **5**, 80581-19-7; **6**, 80581-20-0; **7**, 80581-21-1; **8**, 80532-37-2; **9**, 80532-38-3; **10**, 80581-22-2; **11**, 80581-23-3; **12**, 80581-24-4; **13**, 80581-25-5; **14**, 80581-26-6; **15**, 80581-27-7; **16**, 80532-39-4; **16** epoxide isomer 1, 80532-40-7; **16** epoxide isomer 2, 80581-28-8; **6** (R^1, R^2 = $(C_6H_5)_2(t\text{-Bu})Si$) isomer 1, 80532-41-8; **16** (R^1, R^2 = $(C_6H_5)_2(t\text{-Bu})Si$) isomer 2, 80581-29-9; **16** (R^1 = $C_6H_5CH_2$, R^2 = $(Me)_3CCO$) isomer 1, 80532-42-9; **16** (R^1 = $C_6H_5CH_2$, R^2 = $(Me)_3CCO$) isomer 2, 80581-30-2; **17a**, 80532-43-0; **18**, 80532-44-1; **19a**, 80532-45-2; **19b**, 80532-46-3; **20** diacetate, 80532-47-4; **21**, 50866-82-5; adonitol pentaacetate, 7208-42-6; 2-amino-2-deoxy-D-penitol-4,5-acetonide 1,2,3-triacetate isomerl, 80532-48-5; 2-amino-2-deoxy-D-penitol-4,5-acetonide 1,2,3-triacetate isomer 2, 80581-31-3; 2-amino-2-deoxy-D-penitol-4,5-acetonide 1,2,3-triacetate isomer 3, 80581-32-4; 2-amino-2-deoxy-D-penitol-4,5-acetonide 1,2,3-triacetate isomer 4, 80581-33-5; 2-deoxy-D-xylitol-4,5-acetonide 1,3-acetate, 80581-34-6; 2-deoxy-D-arabitol-4,5-acetonide 1,3-diacetate, 80532-47-4.

Supplementary Material Available: Spectroscopic data for new compounds described in this paper (63 pages). Ordering information is given on any current masthead page.

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(21) This substance was prepared from **2** in two steps, i.e., (1) $CCl_3CON{=}C{=}O/CH_2Cl_2$/0 °C and (2) $K_2CO_3/H_2O/MeOH$/0 °C → room temperature.

(22) The remarkable regiospecificity observed has been shown to be primarily due to the alcoholic group: Finan, J. M.; Kishi, Y.; manuscript in preparation.

(23) Jordaan, J. H.; Serfontein, W. J. *J. Org. Chem.* **1963**, *28*, 1395.

Preparation and Characterization of $HFe_4(BH_2)(CO)_{12}$. A Hydrogenated Iron Boride Cluster

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Received November 5, 1981

In a continuing effort to synthesize five-atom ferraboranes in order to experimentally define the relationship between boranes and small metal clusters,[1] we have prepared a tetrairon system, namely, $HFe_4(BH_2)(CO)_{12}$ (I). This compound, which is a $HFe_4(CO)_{12}$ "butterfly" with a BH_2 fragment bridging the wing tips, is a product of the reaction of $B_2H_6Fe_2(CO)_6$[2] with $Fe_2(CO)_9$. It is isoelectronic with $HFe_4(CH)(CO)_{12}$,[3] an iron cluster exhibiting a Fe–H–C interaction, and as such it is a member of a growing class of tetrairon butterfly complexes.[4-9] In addition, I is a structural analogue for $HFe_4(CH_2)(CO)_{12}^+$, a presumed intermediate in the conversion of $Fe_4(CO)_{13}^{2-}$ to methane by protonic acids.[5] In this paper, we describe the structural properties of this compound and present evidence indicating that I is properly

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(1) See, for example: Haller, K. J.; Andersen, E. L.; Fehlner, T. P. *Inorg. Chem.* **1981**, *20*, 309. Andersen, E. L.; DeKock, R. L.; Fehlner, T. P. *Ibid.* **1981**, *20*, 3291.

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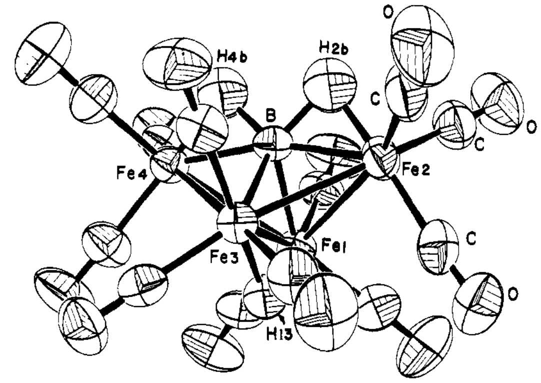

Figure 1. Structure of $HFe_4(BH_2)(CO)_{12}$.

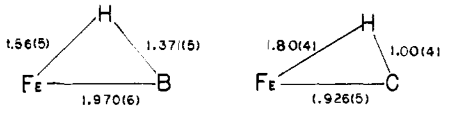

Figure 2. Comparison of the Fe–H–B interaction in $HFe_4(BH_2)(CO)_{12}$ (X-ray, 20 °C) with the Fe–H–C interaction in $HFe_4(CH)(CO)_{12}$ (X-ray, −100 °C, one independent molecule only. The equivalent neutron diffraction values are as follows: Fe–H, 1.753 (4); C-H, 1.191 (4); Fe–C, 1.927 (2); ref 3).

described as the first example of a structurally characterized iron boride cluster.[10]

Previously we have demonstrated that $B_2H_6Fe_2(CO)_6$ can be considered as a hexahydrodiborate or "activated" diborane coordinated to $Fe_2(CO)_6$.[1] As such, it contains an electron-rich boron–boron bond of a type known to be reactive with respect to electrophiles.[11] The reaction of this compound with excess $Fe_2(CO)_9$, a formal source of the $Fe(CO)_4$ fragment, in pentane at 25 °C for 7 h yields two products. These products are separated by sublimation, the major and least volatile product being a very dark brown solid, soluble in hydrocarbons, and somewhat air sensitive. Crystals suitable for an X-ray diffraction study were grown from a polycrystalline sample at 45–50 °C in an evacuated capillary. A single crystal, $0.3 \times 0.2 \times 0.15$ mm^3, was chosen for analysis.

The cluster crystallizes ($Z = 4$) in the monoclinic space group $P2_1/c$ with $a = 16.429$ (5) Å, $b = 8.740$ (3) Å, $c = 13.237$ (3) Å, $\beta = 94.32$ (1)°, $V = 1896$ Å^3. the current final conventional residual was $R_1 = 0.044$ and the weighted residual, $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.045$. All hydrogen atoms were refined isotropically, and all other atoms were refined anisotropically. The final difference Fourier synthesis displayed a background density of 0.2–0.3 e Å^{-3} throughout the unit cell.[12]

The molecular structure of $HFe_4(BH_2)(CO)_{12}$ is shown in Figure 1. The atoms, including hydrogens, are represented at 50% thermal ellipsoids. The molecule has C_{2v} symmetry, each iron atom being approximately octahedral and the boron atom having a coordination number of six. The bond distances and angles in the $HFe_4(CO)_{12}$ fragment are similar to those found in other "saturated" iron butterfly complexes,[3-9] the average Fe–Fe edge distance in I being 2.667 (1) Å and the H-bridged Fe–Fe distance 2.637 (1) Å. The average Fe–C distance is 1.788 (6) Å, the C–O distance 1.137 (6) Å, and the Fe–H (Fe–H–Fe) distance 1.67 (4) Å. The dihedral angle of the butterfly is 114°. The Fe_4–B–Fe_2 angle is 162°, and the boron lies only 0.3 Å from the line connecting the wing-tip iron atoms. The geometry of the averaged Fe–H–B interaction is shown in Figure 2. The Fe–H and B–H distances are similar to those found in another ferraborane, $B_3H_7Fe_2(CO)_6$,[1] containing Fe–H–B interactions (1.56 (5) and 1.371 (5) Å for I vs. 1.61 (4) and 1.32 (4) Å); however, the Fe–B distances (and Fe–H–B angles) are very different (1.970 (6) Å for I vs. 2.263 (4) Å). On the basis of the observed molecular geometry, we have previously suggested that $B_3H_7Fe_2(CO)_6$ contains open[13] three-center Fe–H–B interactions. The comparison of the structural parameters characterizing the Fe–H–B interactions demonstrates unambiguously that I contains closed three-center Fe–H–B interactions, i.e., there is a direct iron–boron interaction.

The spectroscopic data on I suggest that the structure in solution is the same as that in the solid state. The infrared spectrum shows no evidence for bridging carbonyls. The 100-MHz ^1H FT NMR spectrum in C_6D_6 exhibits a broad resonance at δ −11.9 (200 Hz, fwhm) and a sharp singlet at δ −25.4. On ^{11}B decoupling the broad resonance sharpens considerably and, hence, is assigned to the two Fe–H–B protons, the chemical shift being similar to the Fe–H–B protons in $B_2H_6Fe_2(CO)_6$ (δ −10.3).[2] The high field resonance is assigned to the Fe–H–Fe proton, the chemical shift falling in a range typical of metal hydrides.[14] The 32.1-MHz ^{11}B proton-decoupled FT NMR consists of a singlet at 106 ppm downfield of $BF_3 \cdot O(C_2H_5)_2$. This chemical shift, which is even at lower field than resonances of typical trigonal boron compounds,[15] is consistent with considering I as a boride. Williams et al. have proposed an empirical relationship between the ^{11}B chemical shift and the ^{13}C chemical shift for analogous boranes and carbocations.[16] From the observed chemical shifts of carbide clusters (260–470 ppm downfield of Me_4Si),[6,17] one can estimate that the analogous borides should exhibit ^{11}B shifts from about 60 to 130 ppm downfield relative to $BF_3 \cdot O(C_2H_5)_2$. The low field position of the resonances of encapsulated carbon atoms have been attributed to cationic character[17] and, presumably, the same character may be attributed to the boron of I.

Compound I obeys Wade's electron counting rules[18] if one assumes that the boron is effectively interstitial and not occupying a vertex of the deltahedron used to define the cluster structure. Thus, I is considered to be a four-atom cluster with 14 skeletal electrons (2 from each $Fe(CO)_3$, 3 from B, and 1 from each bridging hydrogen) and is arachno. The dihedral angle of the iron butterfly (114°) is similar to that of the arachno borane, B_4H_{10} (118°).[13] On the other hand, the compound is a "saturated" 62-electron cluster in the manner of Lauher;[19] however, this approach does not suggest any special character for the boron. As an arachno cluster, I can be ideally considered as derived from an octahedral metal boride by cleaving off two metal atoms and diprotonating the open face and hence its designation as a hydrogenated iron boride cluster.

As $HFe_4(CH)(CO)_{12}$ has been proposed as a model for CH interaction with a metal surface,[20] it is of interest to compare the Fe–H–C interaction with the Fe–H–B interaction in isoelectronic I. This is done in Figure 2 where it is seen that in both cases the interaction is clearly a closed three-center interaction but that the latter is much more symmetrical than the former.[21] The B–H–M

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(10) The mass, IR, and ^1H NMR spectra of the ruthenium analogue of I have been reported. Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1977**, 477. The compound reported as $(CO)_{18}Co_6B$ may be a boride. Schmid, G.; Batzel, V.; Etzrodt, G.; Pfeil, R. *J. Organomet. Chem.* **1975**, *86*, 257.

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(12) Data (4820) were collected on a Syntex P$\bar{1}$ diffractometer equipped with a graphite-monochromated Mo Kα radiation source using θ–2θ scans. Of the independent data, 2817 were regarded as observed [$F_o > 3\sigma(F_o)$]. No absorption correction has been applied [μ(Mo Kα) = 30.6 cm^{-1}] as yet, and $\rho_{calcd} = 2.01$ g cm^{-3}. Periodically monitored check reflections revealed no significant variation in intensity throughout the experiment.

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(21) As the X-ray diffraction study of $HFe_4(CH)(CO)_{12}$ was done at −100 °C while that of I was done at 20 °C, the distances in Figure 2 may not be strictly comparable. The neutron diffraction stucture analysis of $HFe_4(CH)(CO)_{12}$ has been completed; see ref 3.

interaction has been considered a limiting model for the C–H–M interaction,[22] and this point is clearly illustrated by these two isoelectronic compounds. Futhermore, if the Fe–H–C interaction observed in $HFe_4(CH)(CO)_{12}$ is taken to represent the initial stage of the cleavage of a C–H bond on a metal surface, the Fe–H–B interaction in I models the cleavage further along the reaction coordinate. Thus, not only are metalloboranes useful synthetic intermediates,[23] but compounds such as I and $B_2H_6Fe_2(CO)_6$ can be used as reasonable models for hydrocarbons in metal-bonding configurations that may be intrinsically unstable and, hence, unable to be isolated. Further details of this and related studies will be published in due course.

Acknowledgment. The aid of D. Schifferl with the NMR spectra is gratefully acknowledged as is the support of the National Science Foundation (CHE 81-09503). We thank the University of Notre Dame Computer Center for providing some of the computing time.

Registry No. I, 80572-82-3.

Supplementary Material Available: List of atomic coordinates and thermal parameters for $HFe_4(BH_2)(CO)_{12}$ (4 pages). Ordering information is given on any current masthead page.

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Total Syntheses of (±)-Pseudomonic Acids A and C

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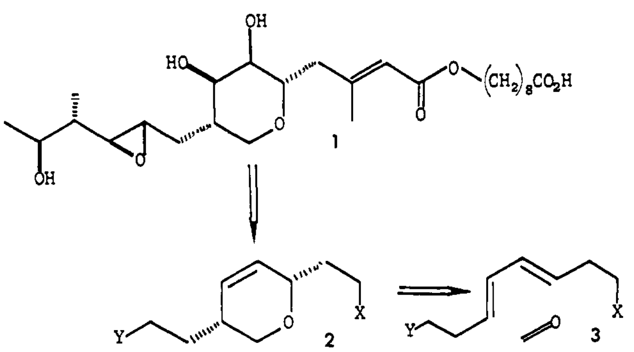
Received July 9, 1981

Pseudomonic acid A (**1**), an antibiotic produced by a strain of *Pseudomonas fluorescens*, functions as a competitive inhibitor of isoleucyl-tRNA synthetase[2] and is an effective antimicrobial agent against gram-positive bacteria, *Haemophilus influenzae*, *Neisseria gonorrhoeae*, and mycoplasmal pathogens.[3] The absolute and relative stereochemistry have been determined by spectroscopic studies[4] and X-ray analysis.[5] More recently, pseudomonic acid C, with a double bond instead of an epoxy group in the side chain, has been isolated.[6] The novel structure and complex stereochemistry and functionality of pseudomonic acid have made it a popular synthetic target.[7,8]

Our approach was based on the retrosynthetic analysis shown in Scheme I. The vicinal diol of pseudomonic acid can easily be constructed from the double bond of **2** and the two side chains can be elaborated from differently functionalized two-carbon fragments. The dihydropyran **2** can be made by a Diels–Alder reaction of **3** and formaldehyde. Since we have recently shown that Me_2AlCl is an efficient catalyst for the Diels–Alder reaction of aldehydes and dienes,[9] this is an attractive approach if the regiochemistry of the Diels–Alder reaction can be controlled.

Scheme I

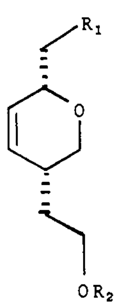


We have developed a novel and potentially general approach to control this regiochemistry which we term a quasi-intramolecular Lewis acid catalyzed Diels–Alder reaction. Complexation of both the diene and dienophile to the Lewis acid (e.g., **9**) leads to the regiochemical, and possibly sterochemical, control typical of intramolecular Diels–Alder reactions. The success of this approach depends on the reaction of an alkylaluminum halide with a functional group in the diene, such as an alcohol, to give a complex which loses an alkane to generate a new Lewis acid containing the diene moiety which can complex to the dienophile.

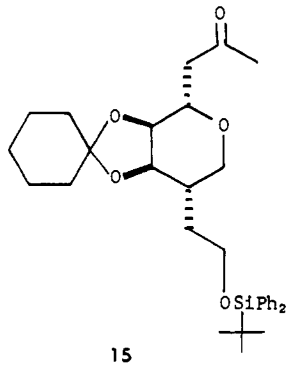
This method can be applied to the synthesis of pseudomonic acid by treating **3**, X = OH, with $RAlCl_2$. The resulting complex will irreversibly lose an alkane (RH) generating an alkoxyaluminum dihalide which can complex to formaldehyde. The resulting complex will undergo a quasi-intramolecular Lewis acid catalyzed Diels–Alder reaction. In turn, the required homoallylic alcohol **3**, X = OH, should be available by an alkylaluminum halide catalyzed ene reaction of formaldehyde with the terminal double bond of **6**.[9]

The desired acetate **6** is easily constructed from 1,5-hexadiene (**4**) by a Me_2AlCl catalyzed ene reaction with formaldehyde (0.9 equiv of CH_2O, 1.4 equiv of Me_2AlCl, 30 min, 0 °C) which gives **5** as an 8:1 mixture of trans and cis isomers in 80% yield. This mixture is used without purification since ene adducts derived from the cis isomer of **6** will not undergo the Diels–Alder reaction. Acetylation gives **6** in quantitative yield. Only traces of 2:1 adducts can be obtained in the ene reaction, even when excess paraformaldehyde and Me_2AlCl are used. Presumably electron withdrawal by the aluminum alkoxide deactivates the double bond of **5** so that the methyl group of Me_2AlCl simply adds to formaldehyde.

Treatment of **6** (25 mmol) with 3 equiv of CH_2O and 4.5 equiv of $EtAlCl_2$ in 1:1 nitromethane–methylene chloride for 12 h at 25 °C gives a 35–40% yield of **11** and ≈2% of the undesired



11, R_1–CH_2OH, R_2–Ac
12, R_1–CHO, R_2–Ac
13, R_1–$CHCH_3OH$, R_2–H
14, R_1–$COCH_3$, R_2–$SiPh_2$



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