

mation on clays was rationalized *only* in terms of eq 1 and a terminating step which involved the formation of an inactive adenylate ester bond (A-P).²⁰⁻²⁴ Equation 1 is likely to describe the polymerization of adenylates on clays since the adenylate binds to them while amino acids do not. In reversed micelles, however, eq 2 cannot be ignored since amino acids formed from the hydrolysis of the amino acyl adenylates remain in the aqueous core of the reversed micelle in close contact with other adenylates. The chain termination step of the clay mediated polymerization (ester formation, A-P) rested upon the observed high percentages of peptides which contained terminal adenylate acid.²⁰ Our inability to detect terminal adenylate acid in the peptides in the present work (either by absorption or ²⁵²Cf plasma desorption mass spectroscopy) may imply different mechanisms in the clay and micellar systems. Alternatively, inactive amino acid esters of AMP (A~P) could have been present as impurities in the amino acyl adenylates (A~P) used in the clay experiments.^{21,24} A~P could react, of course, with A~P to give A₂-P and P. It has been shown that the dicyclohexylcarbodiimide, DCC, mediated synthesis of amino acyl adenylates, the method used to prepare A~P in the clay experiments,^{21,24} contained up to 20% A~P impurity.¹⁷ The reaction of this ester impurity with the amino acyl adenylates (or peptide acyl adenylates) would result in peptides with a terminal AMP ester. Conversely, the method of preparation used in this work for A~P does not lead to A~P contamination.¹⁴

The micelle performs at least three functions which result in the formation of high molecular weight peptides: (1) they concentrate A~P, (2) they maintain the reaction at a pH >7, and (3) they minimize competing hydrolysis. The kinetics and mechanism of the condensation of amino acyl adenylates to high molecular weight peptides is the subject of our current and intensive investigation. The use of more complex functional micelles and colloidal aggregates is expected to result in even more efficient polycondensations.

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- [¹⁴C] Alanyl and alanyl adenylate were synthesized using the *tert*-butoxycarbonyl protected amino acids in anhydrous solvents: D. W. Armstrong, R. Seguin and J. H. Fendler, submitted for publication.
- In water at pH <7, amino acyl adenylates hydrolyze. However, condensation to oligopeptides, as well as hydrolysis, occurs in buffered solutions at higher pH.¹⁷ The role of functional surface active hexadecyltrimethylammonium bicarbonate surfactant is to buffer itself. This surfactant was obtained by dialysis of 0.30 M cetyltrimethylammonium bromide in a supersaturated solution of NaHCO₃. One dialysis replaces ~82% of Br⁻ with HCO₃⁻. Two dialyses replace ~96% of Br⁻ with HCO₃⁻. The dialyzed solution must be lyophilized, as the surfactant decomposed easily and is very hygroscopic. The dried surfactant, above its critical micelle concentration, gives a pH of 8.8 in aqueous solution and buffers itself.
- In all three systems, 30 mg of [¹⁴C]-L-alanyl adenylate was stirred in 5.0 mL of the appropriate solution for 30 min at room temperature. All reactions were completely homogeneous, although the adenylate dissolved more slowly in the reversed micelle reaction. Aliquots from each finished reaction were spotted on Whatman No. 1 chromatographic paper. Descending chromatography (with 12:2:1, 2-propanol-acetic acid-water, v/v, as solvent) was run. The co-chromatographed standards (consisting of the alanine monomer, dimer, trimer, tetramer, pentamer, and polyaniline with a molecular weight distribution of 1000-5000, purchased from the Sigma Chemical Co.) and the monomer alanine from the reactions could be located on the dried chromatogram by spraying with ninhydrin. Radioactive products were located and quantified both by a Hewlett-Packard Model 7201 radiochromatographic scanner or alternatively by scintillation counting the ¹⁴C eluted (4 M HCl) from each 2-cm portion of the chromatogram. Completion of the reaction was demonstrated by the lack of formation of hydroxamic acid derivatives upon the addition of hydroxylamine.
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- The products of five reversed micellar reactions (containing a total of 250 mg of alanyl adenylate) were rotary evaporated to a viscous liquid. The remaining liquid was redissolved in 25 mL of methanol-water solution (67:33, v/v). This solution was placed on a 2.5 m X 3.0 cm Sephadex LH-50 column previously equilibrated with the MeOH-H₂O 67:33, v/v, solution; 10.0-mL fractions were collected on a Gilson automatic fraction collector. The absorbance of each fraction was detected manually (240 nm) on a Cary 118C UV-visible spectrophotometer.
- The degree of polymerization for polyaniline (DP_{Ala}) was determined from the following equation:

$$DP_{Ala} = 1 + (\text{mol wt} - 89.1)/71.08$$
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A Diborane(6) Bridged Diiron Hexacarbonyl: Preparation of B₂H₆Fe₂(CO)₆

Sir:

The ferraboraneS, B₄H₈Fe(CO)₃¹ and B₅H₉Fe(CO)₃,² have been produced in good yield from the co-pyrolysis of B₅H₉ and Fe(CO)₅.³ Both the geometrical^{1,2} and electronic structures⁴ of these compounds demonstrate, in agreement with Wade's predictions,⁵ that the equivalent boranes, B₅H₉ and B₆H₁₀, are useful models for these compounds. We are interested in exploring this analogy as the number of iron atoms in the cage increases. In addition we have demonstrated that the Fe(CO)₃ fragment provides a means of photochemical modification of the cage⁶ and we are interested in the behavior of species with two such fragments. Herein we report the preparation and characterization of the diiron ferraborane, B₂H₆Fe₂(CO)₆.⁷

In a typical preparation, the addition of 2.2 mmol of Fe(CO)₅ and 3.0 mmol of B₅H₉ to a clear solution of 2.0 mmol of LiAlH₄ in 19.7 mL of diethyl ether resulted in the rapid formation of a deep red solution and a dark precipitate.⁸ After standing at room temperature overnight, the nonvolatiles were removed at -196 °C. On treatment with 7.0 mmol of HCl, ~6.8 mmol of noncondensibles was evolved and the solid dissolved. Fractionation yielded unreacted starting materials, B₄H₈Fe(CO)₃, and a less volatile compound identified as indicated below as B₂H₆Fe₂(CO)₆. The reaction has been carried out several times on 2- and 8-mmol scales and the yield varies from 1 to 10% depending on the length of time and method of workup. The new compound is a yellow-brown liquid at room temperature and is very air sensitive.

The new compound has the molecular formula Fe₂B₂C₆O₆H₆ (⁵⁶Fe₂¹¹B₂¹²C₆¹⁶O₆¹H₆⁺, calcd 307.9048 amu, obsd 307.9066 amu; ⁵⁶Fe₂¹¹B₂¹²C₅¹⁶O₅¹H₆⁺, calcd 279.9099 amu,

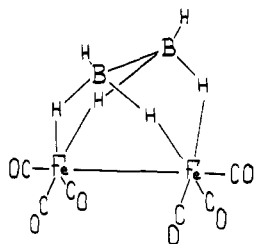
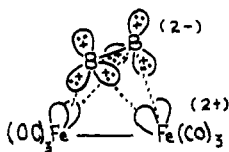


Figure 1. The proposed structure of $B_2H_6Fe_2(CO)_6$.

obsd 279.9094 amu). The parent ion in the mass spectrum fragments by the sequential loss of six CO molecules and the envelopes of the parent ion and first two fragment ions are inconsistent with a molecule containing more than two boron atoms. The Fe_2^+ ion is also present in the fragmentation pattern. The gas phase infrared spectrum exhibits bands in the CO region at 2070 (s), 2058 (sh), and 2003 (s) cm^{-1} . The IR spectrum of a film of the compound also contains a band at 2530 (w) cm^{-1} which is attributed to ν_{BH} . No bands were observed in the BHB bridging region. The 100-MHz 1H FT NMR spectrum in CD_2Cl_2 exhibits a broad resonance (300 Hz, fwhm, relative area 1) at δ 0.2 and a broad resonance (250 Hz, fwhm, relative area 2) at -10.3 . On ^{11}B decoupling both resonances sharpen considerably (40 Hz, fwhm) and retain the same relative areas. The 25.2-MHz ^{11}B FT NMR spectrum consists of a broad resonance at -24 ppm (200 Hz, fwhm).⁹ The resonance is a doublet ($J \approx 90$ Hz) each component of which appears to be an incompletely resolved multiplet.

The compound is formulated as $B_2H_6Fe_2(CO)_6$ and the NMR and IR spectra are consistent with the structure shown in Figure 1. The broad 1H resonance at $\delta -10.3$ is assigned to the four BHFe protons while the resonance at 0.2 is assigned to the two terminal protons.¹⁰ For this structure the ^{11}B NMR spectrum is expected to consist of a doublet of triplets. The observed spectrum is consistent with this prediction; however, the B-H-Fe coupling is not resolved. The IR spectrum in the carbonyl region is not unlike that reported for $S_2Fe_2(CO)_6$ ¹¹ and, thus, is also consistent with the proposed structure.

In terms of the electron counting rules,⁵ the framework is nido having 12 skeletal electrons (2 from each $Fe(CO)_3$, 2 from each BH, and 1 from each BHFe) in a four-atom cage. As such it is the analogue of B_4H_8 , an unstable borane that has been detected¹² but not isolated. Alternatively, the compound can be viewed as the eight-electron donor $B_2H_6^{2-}$ bound to the $Fe_2(CO)_6^{2+}$ dimer as a structure in which the 18-electron rule is satisfied. The high negative charge on the borane implied



by this formulation is consistent with the small BH terminal coupling constant suggested by the ^{11}B spectrum.¹³

The new compound is isoelectronic with $C_2H_2Co_2(CO)_6$, the parent of the known $C_2R_2Co_2(CO)_6$.¹⁴ As such it is a new member of the growing class of bridged X_2 dimetal carbonyl compounds.^{15,16} It is also the third example of a B_nM_n cage¹⁷ and another bridge between metal clusters and boranes, e.g., $H_4Ru_4(CO)_{12}$ and B_4H_8 . As the compound is volatile, the UV photoelectron spectrum is presently being obtained. This study, as well as the results of other ongoing chemical investigations, should reveal more of the nature of this compound.

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A Simple Synthesis of Sulfur Substituted Cyclopropanes. Effect of Solvent and Gegenion upon Mechanism and Product Composition

Sir:

In connection with another project, we had occasion to prepare sulfides of general structure **I**. We reasoned that, based upon the well known propensity for methyl 4-bromocrotonate to undergo S_N2 displacement reactions,^{1,2} mercaptide induced displacement of bromide from the bromocrotonate would suffice.³ We were therefore somewhat surprised to find that the product isolated in good yield (65–85%) from the reaction of methyl 4-bromocrotonate with lithium *sec*-butyl- or *tert*-butylmercaptide did not show any vinyl hydrogens in the 1H NMR. Combustion and complete spectral analysis⁴ showed that the *trans*-cyclopropane **2** was the product.⁵

We were intrigued by the potential mechanistic and synthetic implications of this observation. Why did we not observe the formation of the expected product **1**? Could we vary the