in CH_2Cl_2 gives **7b** (R = H) and, quite rapidly at room temperature, **8b** (R = H) (60%).[26,27] Acid cleavage (CF_3CO_2H/C_6H_6) readily gives α-methylene-γ-butyrolactone (**9b**, R = H).

Complexes **7** and **8** represent stabilized, independently synthesized analogues of the proposed catalytic intermediates **3** and **4**. The fact that they react as suggested in reactions 4 and 5 strongly supports the mechanism proposed, reactions 3–6 above. Preliminary kinetic results[28] indicate that the rate, expressed in turnovers per unit time, is first order in CO pressure and independent of substrate concentration above 1 M. Under normal catalytic conditions the rate-determining step is therefore reaction 6, uptake of carbon monoxide by palladium(II).

The observation that both the insertion and the cleavage steps are much slower for the internal-acetylene-derived **7a** and **8a** than for the terminal-acetylene-derived **7b** and **8b** suggests that the catalyst system will be much more effective for the synthesis of α-methylenelactones than for α-alkylidenelactones. Work in progress generally bears out this prediction. However, conversion of appropriate actylenic alcohols to chloroformates, addition to Pd^0, insertion, and acid cleavage offer a potential two-flask stoichiometric synthesis of α-alkylidenelactones.

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(6) The deuterium label in the alcohol is 69% (by integration of the NMR spectrum) incorporated into the downfield methylene proton at δ 6.2 in $CDCl_3$. The presumption that the downfield proton is cis to the lactone carbonyl is supported by our observation that it shifts 2.62 times as much as the upfield methylene proton upon addition of $Eu(fod)_3$.

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(19) ^{1}H NMR (C_6D_6): δ 1.46 (t, 3 H), 1.78 (m, 2 H), 3.20 (t, 2 H). IR: 1660, 1096 cm^{-1}.

(20) ^{1}H NMR (C_6D_6): δ 1.48 (m, 2 H), 1.82 (m, 3 H), 3.39 (t, 2 H). IR: 1725, 1610 cm^{-1}.

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(26) The use of anhydrous KF gives **8b** directly in good yield: apparently the acetylide ion resulting from the cleavage inserts rapidly and protonation by adventitious water then gives **8b**. The use of $KF{\cdot}2H_2O$ results in protonation before insertion: a 3300-cm^{-1} IR band assigned to the intermediate **7b** can be observed for a few hours, but then disappears as the bands characteristic of **8b** continue to grow.

(27) ^{1}H NMR of **8b** (C_6D_6): δ 1.45 (m, 2 H), 3.20 (t, 2 H), 7.32 (tt, 1 H). IR of **8b**: 1734, 1599 cm^{-1}.

(28) Kinetic data are obtained from initial rates measured by GLC sampling during the initial homogeneous phase of the reaction. Eventually turnovers per unit time decrease and palladium metal is deposited.

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

Sir:

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

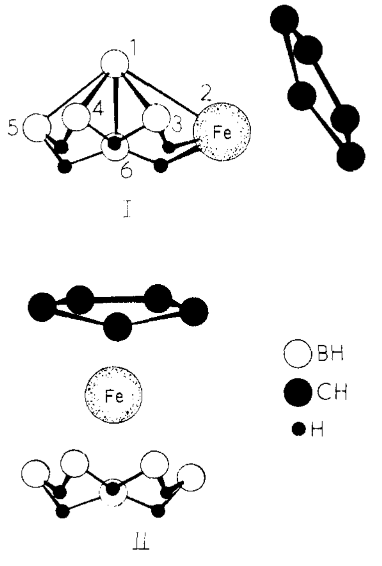

Figure 1. Proposed structures of $2\text{-}(\eta^5\text{-}C_5H_5)FeB_5H_{10}$ (I) and $1\text{-}(\eta^5\text{-}C_5H_5)FeB_5H_{10}$ (II). Connecting lines between iron and boron are omitted in II to emphasize the sandwichlike arrangement of ligands.

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

Compd	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] Parts per million 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)

Compd	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] Parts per million relative to $(CH_3)_4Si$, with positive sign indicating shift to lower field. [b] Measured from ^{11}B-decoupled spectrum.

spectrum (calcd for $^{56}Fe^{11}B_5{}^{12}C_5{}^1H_{16}{}^+$ (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$_{\text{terminal}}$ units and five bridging hydrogen atoms. The high-field ^1H 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-(η^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,b] of the square pyramidal species 2-(η^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 °C, 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 °C and 5 h at 180 °C 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$_{\text{terminal}}$ 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 (η^5-C_5H_5)-$CoC_2B_3H_7$,[3] $(CO)_3FeC_2B_3H_7$,[4] and 1,7,2,3- and 1,7,2,4-$(\eta^5$-$C_5H_5)_2Co_2C_2B_3H_5$;[3,5] the last three stuctures 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 (η^5-C_5H_5)$NiB_{11}H_{11}{}^-$ ion.[8] Both I and II may be viewed as analogues of B_6H_{10} with a (η^5-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 define more clearly the nature and extent of these analogies.

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Green Plant Photosynthesis. Upconversion or Not?

Sir:

Franck[1] suggested an uphill conversion model for photosynthesis to explain the enhancement[2] of O_2 evolution in far red (system I wavelength region) light by red light (system II region) (also see ref 3–5). In this model, one light quantum raised the chlorophyll a molecule to a singlet which, by intersystem crossing, formed a triplet state. The second quantum, then, raised it to a higher triplet level, from where photochemistry took place. This hypothesis was soon abandoned because the interaction of two pigment systems required 6,7 chemical intermediates (quinones, cytochrome *f* and plastocyanin) and, therefore, such a physical cooperation of two light quanta is untenable. Recently, Fong[8–10] has proposed that such an uphill conversion (e.g., "upconversion") to a higher state (which he calls charge transfer, CT, state) operates in both pigment systems I and II. His scheme[11] is as follows.

$$2S_0 + 2h\nu \rightarrow 2S_1 \tag{1}$$

where S_0 = ground state, S_1 = first singlet excited state, and $h\nu$ = light quantum.

$$S_1 \rightarrow T_0 \tag{2}$$

where T_0 (first triplet state) is produced by intersystem crossing followed by upconversion to a charge transfer state.