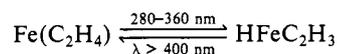


to form the dinuclear iron ethylene adduct.

(b) $\text{Fe}_2(\text{C}_2\text{H}_4)_2$. Table VI lists the infrared frequencies measured for the diethylene-diiron complex. The spectrum exhibited by this complex is again characteristic of a π -complex. Two isomeric forms of $\text{Fe}_2(\text{C}_2\text{H}_4)_2$, denoted as isomer A and isomer B, have been matrix isolated. Isomer A was formed spontaneously upon the cocondensation of iron with ethylene in excess argon. Upon photolysis in the UV the absorptions due to A diminished with the concomitant growth of peaks at lower frequency, suggesting photoisomerization taking place from A to B. It is interesting that the spectra exhibited by $\text{Fe}_2(\text{C}_2\text{H}_4)$, B, and $\text{Fe}_2(\text{C}_2\text{H}_4)_2$, A, are very similar. Furthermore, their carbon-13 and deuterium shifts are extremely close, suggesting very similar structures.

Summary of Results

1. A new type of interaction between a metal atom and an olefin has been demonstrated in this study. Monatomic iron is found to hydrogen bond to ethylene in two distinct forms. One of these forms was shown to be a necessary precursor for the formation of the insertion product, vinyliron hydride. An oxidative-addition/reductive-elimination reaction, which is photoreversible, has been observed:



i.e., interconversion of ethylene iron to vinyliron hydride and vice versa.

2. The complexes $\text{Fe}(\text{C}_2\text{H}_4)_2$, $\text{Fe}_2(\text{C}_2\text{H}_4)$, and $\text{Fe}_2(\text{C}_2\text{H}_4)_2$ have been isolated in argon and krypton matrices. Only $\text{Fe}(\text{C}_2\text{H}_4)_2$ was observed in neat ethylene matrices. The interaction between the metal and the olefin in this system follows the Dewar-Chatt-Duncanson model where the ethylene acts as a σ -donor through the (C=C) π -orbital and a π -acceptor through the (C=C) π^* orbital. Photoexcitation of these π -complexes did not lead to the C-H activation of ethylene.

3. A d-d "forbidden" transition of Fe_2 has been observed for the first time in the infrared region. The activation of this electronic transition is the result of the complexation of the metal dimer to ethylene. A very small deuterium shift, 1 cm^{-1} , has been measured, which is a further proof of its assignment to a $\text{Fe}_2(\text{C}_2\text{H}_4)$ complex.

Acknowledgment. This work has been supported by the National Science Foundation under Grant no. CHE-8315959. We thank Dr. Leif Fredin for the many useful discussions that were carried out during the course of this study.

Registry No. 4, 98800-34-1; 4 (^{13}C -labeled), 98800-35-2; 4- d_4 , 98800-36-3; 9, 98778-48-4; $\text{Fe}_2(\text{C}_2\text{H}_4)_2$ (isomer A), 98778-47-3; $\text{Fe}_2(\text{C}_2\text{H}_4)_2$ (isomer B), 98778-49-5; $\text{Fe}(\text{C}_2\text{H}_4)_2$, 98778-46-2; $^{13}\text{C}_2\text{H}_4$, 51915-19-6; C_2D_4 , 683-73-8; Fe, 7439-89-6; ethylene, 74-85-1.

Matrix-Isolation Studies of the Reactions of Iron Atoms and Iron Dimers with Acetylene in an Argon Matrix. The FTIR Spectrum of Ethynyliron Hydride

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Abstract: The reactions of acetylene with iron vapors in argon matrices at 15 K have been investigated with Fourier-transform infrared spectroscopy. These studies indicated that at very low concentrations of acetylene and iron the monoiron-acetylene adduct, $\text{Fe}(\text{C}_2\text{H}_2)$, was formed. The metal is found to be bonded through one of the hydrogen atoms of acetylene. This hydrogen-bonded complex rearranges upon near-ultraviolet photolysis to give ethynyliron hydride, HFeC_2H . At higher iron concentrations a diiron adduct, $\text{Fe}_2(\text{C}_2\text{H}_2)$, is formed where the iron molecule is π -coordinated to acetylene. Studies with carbon-13 acetylene and deuterated acetylene support these findings.

The role of transition metals, particularly iron, in heterogeneous catalytic processes is of great interest. The structure and bonding of small molecules to transition metals have been extensively investigated with use of metal surfaces and metal cluster chemistry.¹⁻¹⁶ In particular, the interactions of acetylene with iron

surfaces have been studied with new surface science techniques.¹⁷⁻¹⁹ It has been postulated that the bonding patterns for unsaturated hydrocarbons in metal cluster chemistry are relatively similar to those found on transition-metal surfaces;¹⁹⁻²⁰ thus, mono- and

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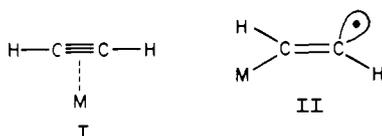
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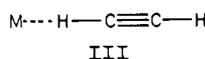
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diiron organometallic clusters with acetylene as a ligand have been investigated.²¹⁻²³

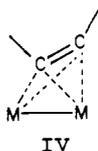
Matrix-isolation studies afford an additional technique whereby metal atom-hydrocarbon interactions can be studied. Much work has been reported on transition-metal vapor-acetylene cryochemistry, notably with nickel, copper, gold, and silver.²⁴⁻²⁶ Matrix isolation electron spin resonance studies of copper report a copper(0)-monoacetylene complex as shown in I, a π -coordinated structure consistent with the Dewar-Chart-Duncanson scheme. Kasai and co-workers have determined that silver atoms do not interact with acetylene in rare-gas matrices to make a bona fide complex; yet, when silver and acetylene reacted in the gas phase, a silver-acetylene radical of the vinyl form II was generated.²⁴ Ab initio calculations support these findings.²⁷ Matrix isolation electron spin resonance studies of gold gave spectral patterns characteristic of complexes I and II, indicating that both types of complexes were produced.²⁵ Ozin and co-workers have generated acetylene complexes of nickel and copper atoms in rare-gas matrices.²⁶ Infrared and UV-vis spectroscopies supported a Dewar-Chart-Duncanson bonding picture for both complexes, with the copper-acetylene adduct having less delocalization of charge from the metal to the ligand. Ab initio calculations on manganese-acetylene adducts also predicted a weak π -bonded complex.²⁸



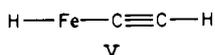
The literature thus contains several studies of transition metal-acetylene interactions, yet no matrix isolation studies involving iron, one of the most reactive metals, are reported. Therefore, experiments were initiated in our laboratory to study the chemistry of iron atoms with acetylene in an argon matrix. Our results indicate the formation of a new type of adduct III, in which the iron atom interacts, or adducts, with acetylene through the hydrogen atom. This is the first evidence for a transition metal hydrogen bonding to an alkyne. Diiron was found to interact



with the π -orbitals of the $C\equiv C$ bond of acetylene. The diiron-acetylene adduct is proposed to be as pictured in IV.



The photochemistry of the adducts was studied via broad-band irradiation of the matrices with a Hg-discharge lamp. It was found that atomic iron photoinjects into the C-H bond of acetylene to give ethynyliron hydride, V. It was also demonstrated that the hydrogen-bonded acetylene-iron adduct is the necessary precursor for this photoinjection product.



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Table I. FTIR Frequencies (cm^{-1}) Measured for C_2H_2 , $^{13}\text{C}_2\text{H}_2$, and C_2D_2 in Solid Argon

vibrational mode	C_2H_2^a	$^{13}\text{C}_2\text{H}_2$	C_2D_2^a
ν_1 , CH or CD s-stretch	3373.7 (R)		2700.5 (R)
ν_2 , $C\equiv C$ stretch	1973.8 (R)		1762.4 (R)
ν_3 , CH or CD a-stretch	3288.5	3284.9	2441.9
ν_4 , CH or CD s-bend	611.8 (R)		505 (R)
ν_5 , CH or CD a-bend	736.7	735.0	542.6
$\nu_4 + \nu_5$, CH or CD s-bend + a-bend	1334.5	1324.1	1043.3

^aFrequencies for Raman active modes of $\text{C}_2\text{H}_2(\text{g})$ and $\text{C}_2\text{D}_2(\text{g})$ were obtained from ref 36.

Table II. FTIR Frequencies (cm^{-1}) Measured for $(\text{C}_2\text{H}_2)_2$, $(^{13}\text{C}_2\text{H}_2)_2$, and $(\text{C}_2\text{D}_2)_2$ in Solid Argon

approx type of vibrational mode	$(\text{C}_2\text{H}_2)_2$	$(^{13}\text{C}_2\text{H}_2)_2$	$(\text{C}_2\text{D}_2)_2$
CH or CD stretch	3265.6	3259.8	2424.3
$C\equiv C$ stretch	1968.5		1760.2
	1716.8		
CH or CD bend	757.6	749.0	549.6
s-bend + a-bend	1356.4	1347.2	1067.2

Table III. FTIR Measured Frequencies (cm^{-1}) for Iron/Acetylene Products in Solid Argon

$\text{Fe}/\text{C}_2\text{H}_2$	$\text{Fe}/^{13}\text{C}_2\text{H}_2$	$\text{Fe}/\text{C}_2\text{D}_2$	assignment ^a
(a) Before Photolysis			
3270.2	3263.7	2428.2	$\text{Fe}(\text{C}_2\text{H}_2)$
1613.4			$\text{Fe}_n(\text{C}_2\text{H}_2)$
1600.6	1553.1	1521.3	$\text{Fe}_2(\text{C}_2\text{H}_2)$
927.1	911.7	775.7	$\text{Fe}_n(\text{C}_2\text{H}_2)$
863.0	871.3	646.3	$\text{Fe}_2(\text{C}_2\text{H}_2)$
760.1	756.9	565.3	$\text{Fe}_2(\text{C}_2\text{H}_2)$
652.8	649.7		$\text{Fe}_2(\text{C}_2\text{H}_2)$
538.8	540.0		$\text{Fe}_n(\text{C}_2\text{H}_2)$
(b) After Photolysis			
3276.2	3276.0	2432.8	HFeC_2H (I)
1976.4	1905.6	1862.7	HFeC_2H (I)
1974.8	1904.1	1861.0	HFeC_2H (I)
1971.9	1901.2	1857.8	HFeC_2H (II)
1969.0	1898.3	1855.4	HFeC_2H (III)
1966.8	1896.4	1853.7	HFeC_2H (II)
1765.0	1765.0	1269.4	HFeC_2H (I)
1762.6	1762.6	1267.7	HFeC_2H (I)
1755.9	1755.9	1262.4	HFeC_2H (II)
1752.5	1752.3	1259.3	HFeC_2H (II)
1740.2	1740.2	1255.4	HFeC_2H (III)
1738.3	1738.3	1250.4	HFeC_2H (III)
1732.7	1732.7	1246.3	HFeC_2H (III)
1729.8	1729.8	1244.6	HFeC_2H (III)

^aPeaks assigned to HFeC_2H were grouped in I, II, and III, denoting different configurations. Note that within each group, there is more than one set of frequencies, possibly due to different matrix sites.

Experimental Section

A complete description of the matrix-isolation apparatus is to be published.²⁹ The metal was placed inside an alumina crucible enclosed in a tantalum furnace. Iron vapors were obtained by resistively heating the tantalum furnace over the range 1150-1450 $^\circ\text{C}$, as determined by a microoptical pyrometer (Pyrometer Instrument Co.). The concentration of iron (Aesar, 99.98%) was varied from 0 to 20 parts per thousand argon (Matheson, 99.9998%) while the concentration of acetylene (Big Three Industries, A.A., 99.6% min.) was varied from 0 to 10 parts per thousand argon. A quartz crystal microbalance was used to determine the rates of deposition of iron, acetylene, and argon. Acetylene and iron atoms were codeposited in excess argon onto a polished rhodium-plated copper surface. The surface was maintained at 15 K by use of a closed-cycle helium refrigerator. After a 30-min deposition, the matrix block was rotated 180 $^\circ$ and an infrared spectrum was measured over the range 4000-500 cm^{-1} with a vacuum IBM IR-98 Fourier-transform infrared spectrometer.

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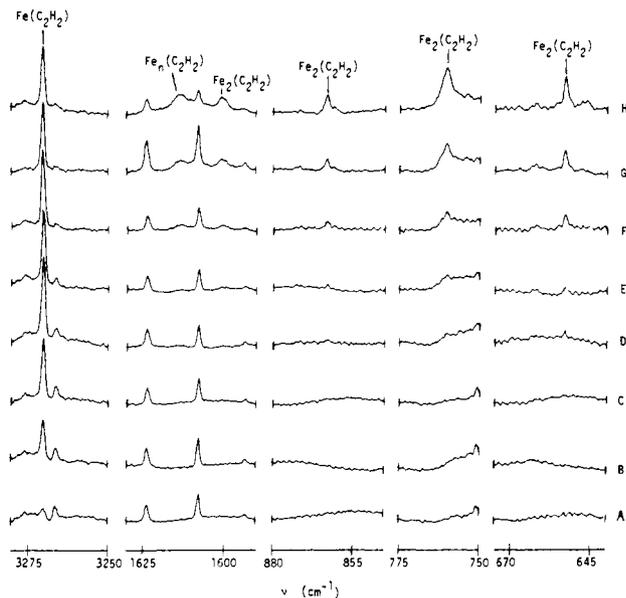


Figure 1. An iron concentration study. Molar ratio of $C_2H_2:Ar \sim 1.1:1000$. Molar ratio of $Fe:1000Ar$: $A = 0.00$, $B = 0.26$, $C = 0.45$, $D = 1.00$, $E = 2.10$, $F = 4.50$, $G = 9.80$, $H = 19.10$. The peaks located at 1607.9 and 1623.8 cm^{-1} are due to residual water in the vacuum system.

Visible or ultraviolet photolysis was applied after deposition by exposing the matrices to a medium-pressure 100-W Hg lamp. Cut-off filters (500- and 400-nm) as well as a band-pass filter in the range 360 to 280 nm were used in the photolysis experiments.

Carbon-13 enriched acetylene (Prochem Isotopes, 75% isotopic purity) and deuterated acetylene (MSD Isotopes, 99.0% isotopic purity) were also deposited with iron in excess argon in similar experiments.

Results and Discussion

FTIR spectra of C_2H_2 , $^{13}C_2H_2$, and C_2D_2 in solid argon at 15 K were obtained for reference purposes, and their measured frequencies are listed in Table I. Acetylene has a tendency to "dimerize", or, more specifically, two molecules of acetylene tend to align and interact with each other in the argon matrix.³⁰ The FTIR frequencies for these dimers were measured and are recorded in Table II. The acetylene concentration was kept very low (1 part per thousand) in order to eliminate or minimize the formation of $(C_2H_2)_2$. When iron was cocondensed with acetylene in an argon matrix, new product peaks appeared and are listed in Table III. The iron concentration was varied between 0 and 20 parts per thousand in order to determine the nuclearity of the iron-acetylene adducts formed upon the cocondensation of iron with acetylene in argon matrices. This study is depicted in Figure 1. Close inspection of Figure 1 reveals a peak at 3270.2 cm^{-1} observed at low iron dispersion. This peak varied linearly with increasing iron concentration until it stopped growing when the molar ratio of iron to argon reached ~ 1 part per thousand. The peak at 3270.2 cm^{-1} is located at a lower frequency than that of the asymmetric C-H stretching frequency of free acetylene, 3288.5 cm^{-1} , indicative of a perturbed, weakened H-C bond. This frequency has been assigned to the iron-acetylene adduct pictured in III. No peaks were detected in the $1900\text{--}1700\text{ cm}^{-1}$ region, characteristic of an activated and perturbed $C\equiv C$ stretch for a π -complexed metal-acetylene as pictured in II. Indeed, Ozin reports values of 1729 and 1870 cm^{-1} for the activated mode of the π -complexes $M(C_2H_2)$ where $M = \text{nickel}$ and copper , respectively.²⁶ The absence of any perturbed absorption bands between the $\nu_{C\equiv C}$ and the $\nu_{C=C}$ regions and the observed shift in the C-H stretching frequency suggest that a different type of interaction is taking place between monoatomic iron and acetylene in solid argon. We thus propose that the acetylene-iron complex is a hydrogen-bonded one rather than a π -complex. This is further

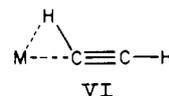
Table IV. FTIR Measured Frequencies (cm^{-1}) for the Isotomers of Acetylene-Iron in Solid Argon

approx type of vibrational mode	$Fe(C_2H_2)$	$Fe(^{13}C_2H_2)$	$Fe(C_2D_2)$
CH or CD stretch	3270.2	3263.7	2428.2

Table V. FTIR Measured Frequencies (cm^{-1}) for the Isotomers of the Acetylene-Diiron Complex in Solid Argon

approx type of vibrational mode	$Fe_2(C_2H_2)$	$Fe_2(^{13}C_2H_2)$	$Fe_2(C_2D_2)$
$C\equiv C$ stretch	1600.9	1553.1	1521.3
CH or CD deformations	863.0	871.3	646.3
	760.1	756.9	565.3
	652.8	649.7	

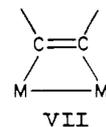
supported by a recent study carried out by Kafafi et al.,³¹ who have demonstrated that monoatomic iron interacts with ethylene through one or more of its hydrogens. However, one cannot totally rule out the possibility that Fe may be interacting simultaneously with carbon and hydrogen as depicted in VI.



Iron was also codeposited with carbon-13 enriched acetylene and deuterated acetylene to measure isotopic shifts and to determine frequency mode assignments. The measured frequencies for $Fe(C_2H_2)$, $Fe(^{13}C_2H_2)$, and $Fe(C_2D_2)$ are listed in Table IV. The absence of absorptions due to the IR active $\nu_{C\equiv C}$ for $Fe(C_2H_2)$ may possibly be attributed to its being too weak to be observed.

As the iron concentration was increased from 1 to 20 parts per thousand, peaks appeared and steadily increased at 1600.9 , 863.0 , 760.1 , and 652.8 cm^{-1} , as indicated in Figure 1. This new set of peaks was assigned to acetylene-diiron. FTIR frequencies measured for $Fe_2(C_2H_2)$, $Fe_2(^{13}C_2H_2)$, and $Fe_2(C_2D_2)$ are reported in Table V. Another peak also appeared at 1613.4 cm^{-1} and grew with higher iron concentrations. However, this peak did not maintain the same intensity relative to the peak at 1600.9 cm^{-1} and is probably associated with an iron cluster interacting with the acetylene.

The proposed structure for the diiron-acetylene adduct is IV, although one cannot totally eliminate structure VII where the acetylene ligand binds parallel to the M-M bond. This di-



metallacyclobutene structure is known for few transition-metal complexes such as $[Pt_2(\text{PhC}_2\text{Ph})(\text{cod})_2]$ ³² ($\text{cod} = \text{cyclooctadiene}$) and $[\text{Rh}_2\{\mu_2(\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)\}(\text{CO})_2(\eta^2\text{-C}_5\text{H}_5)_2]$.³³ In almost all dinuclear metal-acetylene complexes, however, the acetylenes are found in a $\mu_2\text{-}\eta^2$ fashion to give an M_2C_2 quasitetrahedral structure with substantial lengthening of the $C\equiv C$ bond.^{9,10} The interaction of the carbon orbitals with the metal orbitals can be viewed by orbital symmetry. In the orbital interaction diagram for bonding an acetylene to an $M_2(\text{CO})_6$ fragment, the acetylene provides two donor orbitals, its π -orbitals of a_1 and b_2 symmetry and two acceptor orbitals, π^* , of a_2 and b_1 symmetry. The dimetal acceptor orbitals are b_2 and $2a_1$, and the donor orbitals are $1a_1$ and b_1 . This is discussed at length in ref 10. There are several acetylene-dimetal clusters with neutral ligands in which the acetylene binds perpendicular to the metal-metal bond.^{9,15} The $Fe_2(t\text{-Bu}_2\text{C}_2)$ -

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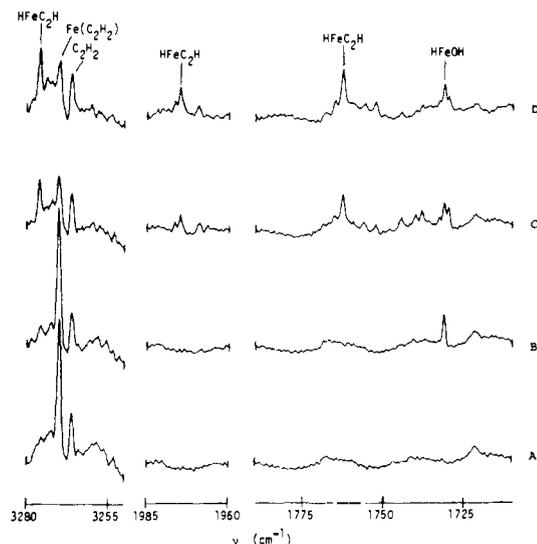


Figure 2. A photolysis study. Molar ratios of $\text{Fe}:\text{C}_2\text{H}_2:\text{Ar} \sim 0.26:1.1:1000$: A, no photolysis; B, $\lambda \geq 400$ nm, 0.5 h; C, $360 \text{ nm} \geq \lambda \geq 280$ nm, 1 h; D $360 \text{ nm} \geq \lambda \geq 280$ nm, 2 h.

Table VI. FTIR Measured Frequencies (cm^{-1}) for the Isotopomers of Ethynyliron Hydride in Solid Argon

approx type of vibrational mode	HFeC_2H	$\text{HFe}^{13}\text{C}_2\text{H}$	DFeC_2D
CH or CD stretch	3276.2	3276.0	2432.8
$\text{C}\equiv\text{C}$ stretch	1976.4	1905.6	1862.7
	1974.8	1904.1	1861.0
FeH or FeD stretch	1765.0	1765.0	1269.4
	1762.6	1762.6	1267.2

$(\text{CO})_6$ complex has the acetylene ligand roughly perpendicular to the metal-metal bond, with a slight twisting of $4\text{--}5^\circ$.¹⁰ A double bond exists between the two iron atoms.²² These results all support the structure of a bridging acetylene perpendicular to the metal-metal axis.

Most dinuclear metal-acetylene complexes have carbon-carbon bond lengths between 1.31 and 1.38 Å, characteristic of a double bond. Further support for acetylenic ligands with double-bond character in these dinuclear metal complexes is found in their infrared spectra. For example, $[\text{Ni}_2\{\mu_2(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)\}(\text{cod})_2]$ has a frequency of 1526 cm^{-1} , and $[\text{Ni}_2\{\mu_2(\eta^2\text{-CF}_3\text{C}_2\text{CF}_3)\}(t\text{-BuNC})_4]$ has a frequency of 1562 cm^{-1} , characteristic of a carbon-carbon double bond.³² The 1600.9-cm^{-1} peak showed a carbon-13 shift of 46.9 cm^{-1} and was assigned to the $\text{C}=\text{C}$ stretch of the matrix-isolated $\text{Fe}_2(\text{C}_2\text{H}_2)$ adduct. The lower peaks are associated with C-H deformation modes. The C-H stretch of the dinuclear adduct was not observed.

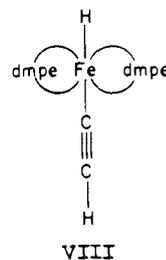
The spectra in Figure 2 summarize the results of the photolysis study carried out on the $\text{Fe}/\text{C}_2\text{H}_2$ system in solid argon. Photolysis with a 500-nm cut-off filter had no observable effect. Photolysis with a 400-nm cut-off filter produced the monoiron-water insertion product, HFeOH , characterized by the peak at 1731.7 cm^{-1} due to the Fe-H stretch.³⁴ This is the result of the photochemistry taking place between iron and residual water present in the vacuum system. However, upon photolysis with near-ultraviolet light the monoiron-acetylene adduct peak at 3270.2 cm^{-1} decreased as the photoproduct peaks appeared in different regions of the FTIR spectrum. These new peaks were concentrated in mainly two regions: the iron-hydrogen and the $\text{C}\equiv\text{C}$ stretching regions. Deuterium and carbon-13 enriched studies of acetylene with iron confirmed the above. A list of the photoproduct frequencies is given in Table IIIb, and its FTIR spectrum is depicted in Figure

2c. Further UV photolysis caused the bleaching of most peaks with the further growth of the set of peaks at 3276.2 , 1974.8 , and 1762.6 cm^{-1} , respectively. The product peak at 1762.6 cm^{-1} is in the region characteristic of the Fe-H stretch, as determined by comparison with known values for matrix-isolated HFeOH ,³⁴ HFeCH_3 ,³⁵ and HFeC_2H_3 .³¹ A large deuterium shift was measured for this frequency in support of its assignment to ν_{FeH} . The product peak at 3276.2 cm^{-1} is in the C-H stretching region with a deuterium isotopic shift of 843.4 cm^{-1} . The product peak at 1974.8 cm^{-1} is in the $\nu_{\text{C}\equiv\text{C}}$ region with a carbon-13 isotopic shift of 70.7 cm^{-1} . These FTIR frequencies are summarized in Table VI. The above results indicate that this photoproduct contains an Fe-H, a $\text{C}\equiv\text{C}$, and a C-H bond. We propose that photolysis has caused the insertion of atomic iron into the C-H bond of acetylene forming ethynyliron hydride of structure V. This result is analogous to the photolytic study carried out on the monoiron-ethylene adduct $\text{Fe}(\text{C}_2\text{H}_4)$, in which instance iron photoinserted into one of the C-H bonds to give ethynyliron hydride, HFeC_2H .³¹ The Fe-C stretch of HFeC_2H was not observed in the present study. It is plausible that ν_{FeC} for V is beyond the range of the mid-IR region, $4000\text{--}500 \text{ cm}^{-1}$, investigated in this study. Kafafi et al.³¹ report a value of 507.2 cm^{-1} for ν_{FeC} in HFeC_2H_3 .

No photoproduct peaks were observed for the $\text{Fe}_2(\text{C}_2\text{H}_2)$ adduct in spite of its depletion upon photolysis, which suggests that acetylene-diiron may have just photodissociated.

The additional bands in the $\text{C}\equiv\text{C}$ and Fe-H stretching regions observed in the initial near-UV photolysis must be due to the same photoinsertion product, since further photolysis caused their disappearance with the further growth of the HFeC_2H peaks. A possible explanation for this spectrum is that there is more than one geometrical isomer of HFeC_2H . Thus, HFeC_2H may be trapped or isolated in different configurations in different matrix sites where prolonged UV photolysis causes its rearrangement to the most favored geometry, which is expected to be the linear structure.

Structure V has direct analogues in organometallic clusters, most notably, that of the iron [bis(dimethylphosphino)ethane]-hydridoacetylide complex,²¹ VIII. VIII has an infrared spectrum (hexene) with ν_{FeH} of 1725 cm^{-1} and $\nu_{\text{C}\equiv\text{C}}$ of 1894 cm^{-1} . In this



configuration the HFeC_2H portion of the complex is colinear where both the hydrogen and the ethynyl group occupy two of the vertices of the octahedral structure. By analogy with this transition-metal complex we propose that the most stable form of ethynyliron hydride will have a linear structure with a very low HFeC bending-force constant.

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