listed in Table I; all of these distances are over 3 Å.

Every attempt to fit the data with a low-dimensional model was unsuccessful. In order to look for other possible superexchange interactions, we considered the possibility of pathways through the two neighbors at 4.812 Å, with strengths comparable to that in the linear chain. Even in this case, treating the problem as a diamond lattice, with four nearest neighbors and three-dimensional ordering, a satisfactory fit could not be obtained.

Only in the case of a three-dimensional (simple cubic) $S = {}^1/_2$ Heisenberg model, with six magnetic neighbors, was a fit obtained. Using the Pade approximants to the high temperature series expansion for which 10 terms are known,[7] we obtained a remarkable fit to the experimental values with $\langle g \rangle = 2.21$ and $J/k_B = 0.465$ K. Demagnetization effects have been corrected in the calculated values with the expression

$$\chi_{cor} = \chi/(1 + D\chi)$$

estimating D from the maximum experimental value of the susceptibility at the peak. Moreover, the value obtained for J coincides with that predicted from the experimental value of the transition temperature and the known critical value for this model of $J/k_BT_c = 0.597$.

One factor that may contribute to the three-dimensional magnetic interactions is that the crisscrossing of the chains in the lattice may cause an enhancement of the dipolar interactions between the chains. This would then lead to a three-dimensional coupling model. The ordering occurs at low enough temperatures for dipole–dipole interaction to be a contributing factor.[8]

Specific heat measurements below 1 K would be particularly valuable in order to further elucidate the nature of the magnetic properties of this material.

We are therefore faced with the paradoxical result that the data require a three-dimensional magnetic interaction while only a one-dimensional superexchange path is apparent in the crystal structure. Nevertheless, our result is a real one and illustrates the primitive nature of our understanding of magnetic interactions and superexchange paths.

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Matrix-Isolation Studies of the Iron/Cyclopentadiene System: Infrared Detection of Cyclopentadienyliron Hydride

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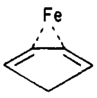
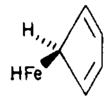
There has been much work done in the area of matrix-isolated metal atom chemistry, not only in the study of the metal atoms themselves[1-3] but also in studying reactions of metal atoms with other matrix-isolated species.[4-6] One specific area of recent investigation has been the study of metal atom insertion into the bonds of small molecules. For example, earlier work from this laboratory has shown that iron atoms will, upon photolysis, insert into the carbon–hydrogen bonds of methane[5] and the oxygen–hydrogen bonds of water.[7,8] Many other metals are found to react similarly.[9] Klabunde has found[10] that Al atoms will spontaneously insert into the C–H bonds of methane. Even more recently, it was found that iron atoms will photoinsert into the carbon–carbon bonds of cyclopropane, forming a four-membered metallacyclic ring.[11]

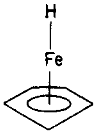
With these results in mind, it was decided to investigate the reactions of iron atoms with cyclopentadiene (C_5H_6) in an argon matrix at 14 K. It is possible that a reaction might lead simply to the very stable and well-known compound, ferrocene ($FeCp_2$); this compound was found by Timms in 60% yield via direct condensation of Fe vapors and cyclopentadiene at liquid nitrogen temperatures.[12] However, in the case of a 1:1 reaction, one might envision several possible products, such as **1**–**4**.



1



2



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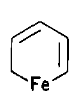
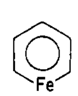


4a



4b

1 is a simple π-bonded adduct. Product **2** is the result of iron atom insertion into a carbon–hydrogen bond to form a σ-bonded product. Product **3** is also a product of C–H bond insertion, but in this case a η^5 complex is formed. Products **4a** and **4b** are the result of an iron atom inserting into a carbon–carbon bond of cyclopentadiene. **4a** is a simple insertion product with the conjugated double bond system intact. **4b**, on the other hand, represents an interesting possibility: Would the iron atom insert into one of the C–C bonds of cyclopentadiene and donate an electron to the π-electron system and by hence satisfying Hückel's rule make an aromatic ring? If found, this would be the first metal-substituted benzene ring detected.

Experimental Section

A complete description of the matrix-isolation device is forthcoming.[13] Typical matrix concentrations for iron were 0–10 parts per thousand and for cyclopentadiene were <1–20 parts per thousand. Concentrations were measured by utilizing a quartz crystal microbalance with a frequency of approximately 6 MHz. The iron was deposited from an alumina crucible wrapped with tantalum foil, which was resistively heated to the temperature range 1150–1350 °C. Temperatures were measured by viewing the tantalum furnace with a microoptical pyrometer from the Pyrometer Instrument Co. The iron was obtained from Aesar, and had a purity of 99.98%. The cyclopentadiene was freshly cracked from dicyclopentadiene obtained from the Enjay Chemical Co. When not in use, the cyclopentadiene was stored over molecular sieves and in a freezer. During deposition the cyclopentadiene vapor flow was regulated by a high-precision needle valve. In order to decrease the formation of dicyclopentadiene in the vapor, heating tape was wrapped around the stainless-steel delivery tube, which was kept at a temperature of approximately 70 °C. Comparison of spectra obtained with and without heating the delivery tube showed heating to be an efficient method for reducing peaks attributed to the cyclopentadiene dimer. Argon (Matheson, 99.9998%) was used without further purification.

Iron and cyclopentadiene were codeposited with excess argon onto a polished rhodium-plated copper surface cooled to 14 K with a closed-cycle helium refrigerator. Each deposition listed 30 min. After deposition, the surface was rotated 180° and the infrared spectrum was mea-

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Table I. Infrared-Active Fundamental Modes of Cyclopentadiene and Cyclopentadiene-d_6 in Argon Matrices (in cm^{-1})

vib mode	C_5H_6	C_5D_6
ν_1 (C—H str)	3087.5	2335.4
	3082.7	
ν_2 (C—H str)	3058.8	2283.1
	3049.9	
ν_3 (CH_2 str)	2894.2	2124.0
ν_4 (C=C str)		1485.2
		1459.4
ν_5 (C—H bend)	1382.5	1247.2
ν_6 (CH_2 sciss)	1370.2	1050.8
ν_7 (C—H bend)		934.8
ν_8 (ring)	992.4	816.7
ν_9 (ring)	914.3	733.3
ν_{10} (ring)		707.7
ν_{15} (C—H str)	3112.4	2330.1
ν_{16} (C—H str)		2294.4
ν_{17} (C=C str)	1572.9	
ν_{18} (C—H bend + ring)	1294.5	1234.2
	1223.1	
ν_{19} (C—H bend + ring)	1240.0	1003.8
ν_{20} (CH_2 wag)	1091.0	835.3
ν_{21} (C—H bend + ring)	958.2	764.9
ν_{22} (ring bend)	806.1	
ν_{23} (CH_2 str)	2906.0	2179.9
ν_{24} (C—H bend)		808.0
ν_{25} (CH_2 rock)	894.3	714.3
ν_{26} (C—H bend)	665.6	
	662.9	

Table II. Infrared-Active Fundamental Modes of Ferrocene at Various Temperatures (in cm^{-1})

vib mode	298 K[18]	88 K[19]	15 K[a]
ν_8 (C-H str)	3058		3095.0
ν_9 (C-H bend)	811	812	817.7
ν_{10} (ring breathe)	1108	1097	1110.3
ν_{11} (ring-metal str)	478	474	
ν_{17} (C-H str)	3075		3107.2
ν_{18} (C-H bend)	1002	1006	1006.2
ν_{19} (C-H bend)	834	849	838.9
ν_{20} (C-C str)	1411	1409	1415.3
ν_{21} (ring tilt)	492	483	
ν_{22} (ring-metal-ring bend)	170	178	

[a] This work.

sured with an IBM IR 98 Fourier transform infrared spectrophotometer.

The spectrum of ferrocene was measured in a similar manner. Ferrocene was synthesized in the laboratory by following the procedure of Wilkinson.[14] The molar ratio of ferrocene to argon was on the order of 20–30 parts per thousand.

Perdeuteriocyclopentadiene (C_5D_6) was also synthesized in the laboratory by following the procedure of Gallinella and Mirone.[15] NMR and mass spectra confirmed the purity of the hexadeuterated product.

Results and Discussion

Spectra of Cyclopentadiene, Cyclopentadiene-d_6, and Ferrocene. The infrared spectra of matrix-isolated cyclopentadiene, cyclopentadiene-d_6, and ferrocene are shown in Figure 1-S of the supplementary material. The assignments of the infrared-active fundamental vibrations of cyclopentadiene and ferrocene made by comparison to room-temperature spectra[15–19] are given in Tables I and II, respectively.

It was noted early in the study that certain peaks in the cyclopentadiene spectrum grew at a rate inconsistent with that of the other peaks, especially at high cyclopentadiene concentrations. Knowing that cyclopentadiene undergoes an intermolecular Diels–Alder reaction, it was thought that these peaks could be attributed to the cyclopentadiene dimer formed in the vapor phase before deposition. Heating the stainless-steel delivery tube during the experiment as described earlier resulted in the disappearance of these particular peaks, which appeared at 728.5, 757.4, 2970.6, and 2972.3 cm^{-1}. These peaks were therefore assigned to dicyclopentadiene.

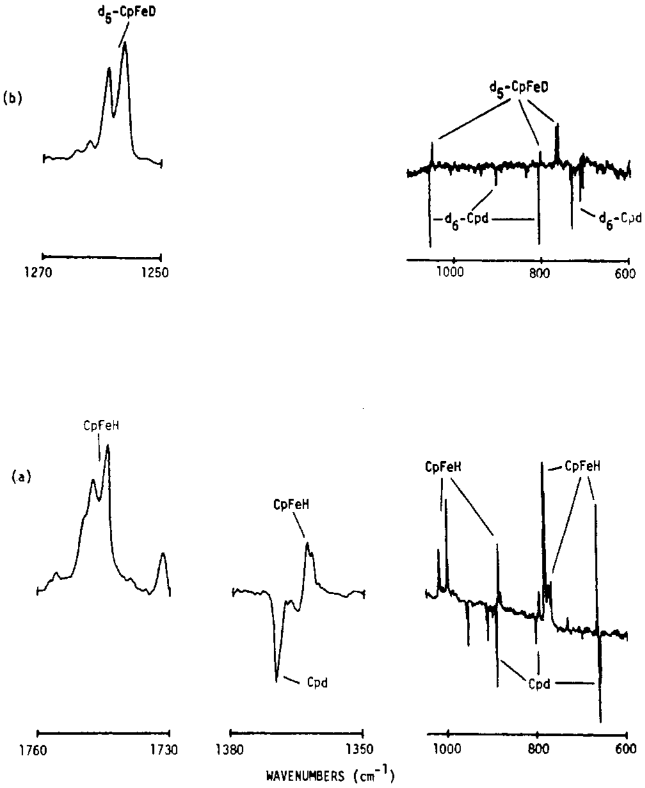

Figure 1. Difference spectra showing infrared absorptions of cyclopentadienyliron hydride: (a) Fe:cyclopentadiene:Ar = 5.6:7.2:1000 (molar ratio); (b) Fe:cyclopentadiene-d_6:Ar = 8.0:4.6:1000. Positive peaks show absorptions of the matrix product, while negative peaks indicate loss of cyclopentadiene due to reaction with iron atoms (Cpd = cyclopentadiene; Cp = cyclopentadienyl).

Table III. Infrared Absorptions of Cyclopentadienyliron Hydride in an Argon Matrix (in cm^{-1})

$(\eta^5\text{-}C_5H_5)FeH$	$(\eta^5\text{-}C_5D_5)FeD$	tentative assgnt
3106.5		C-H str
1748.6, 1745.4, 1731.0	1264.4, 1262.4, 1257.1	Fe-H str
1363.2, 1362.2		C-C str
	1044.3	ring
1021.4, 1002.8	768.5, 763.9	C-H bond
889.5	803.7	ring
798.4		C-H bend
785.1, 777.4, 774.3, 771.6		C-H bend
667.7		C-H bend

Ferrocene has a very simple spectrum that is very easy to assign (see Table II and Figure 1-S). It is interesting to note that matrix-isolated ferrocene has an olive green color instead of its characteristic orange color. Two phase transitions are known for ferrocene, occurring at 242 and 164 K.[20,21] Observation of the matrix during warm-up showed a color change from olive green to orange in the temperature range 150–170 K. It is concluded that the color change corresponds to the phase transition at 164 K and that the structure of ferrocene in the matrix corresponds to the metastable low-temperature solid phase of ferrocene.[20]

Spectra of Cyclopentadiene/Iron. Iron was codeposited with cyclopentadiene and cyclopentadiene-d_6 in excess argon in con-

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centration that were varied as described earlier. Because the emphasis in this study was on the change in the spectrum due to the presence of Fe atoms (indicating a chemical reaction between cyclopentadiene and iron), a spectrum showing the difference between the iron/cyclopentadiene spectrum and the cyclopentadiene "blank" spectrum was calculated; the relevant portions of the difference spectra are shown in Figure 1. It is noted that all of the cyclopentadiene absorptions showed a decrease in intensity, as indicated by the negative peaks in the difference spectrum, while simultaneously a new set of peaks appeared, as indicated by the positive peaks in the difference spectrum. The frequencies of the "product" peaks are given in Table III. The formation of the product was spontaneous and did not require photolysis; subsequent photolysis of the matrices showed no change in the spectrum. No annealing studies were done. Full absorption and difference spectra (Figures 2-S and 3-S) are available as supplementary material.

It is noteworthy that, at constant cyclopentadiene concentration, all of the cyclopentadiene peaks showed a decrease in intensity as the iron concentration was increased. This indicates that cyclopentadiene was consumed by reaction with Fe atoms. Since no new bands appeared in the conjugated C=C region, **2** can be discounted as a product.

One of the stronger product peaks occurs at 1748.4 cm^{-1} (see Figures 1 and 2-S and Table III). A similar absorption is shifted down to 1259.5 cm^{-1} for the deuterated product (see Figures 1 and 3-S and Table III). On the basis of its large deuterium shift as well as studies of Fe atom reactions with H_2O, CH_4, and other molecules,[5,7,8] this absorption is assigned to an iron–hydrogen stretch, indicating that the product has an Fe–H bond. This discounts structures **1**, **4a**, and **4b**.

It is seen that several of the product absorptions in Figure 2-S—especially those at 785.1, 1002.1, and 3106.5 cm^{-1}—correspond very well to certain absorptions of ferrocene, in particular the carbon-hydrogen modes; these peaks are assigned accordingly. This would indicate that the matrix product contains a hydrocarbon moiety similar to that in ferrocene, *i.e.*, a cyclopentadienyl ring. This argument, coupled with the fact that the product has an iron-hydrogen bond, indicates that the product is **3**, or cyclopentadienyliron hydride.

This identification is supported by an infrared spectrum of $Ni(\eta^5\text{-}C_5H_5)NO$. A vibrational assignment of this compound by Feltham and Fateley[22] lists vibrations of the C_5H_5 moiety that include absorptions at 3106, 1004, 895, and 807 cm^{-1} that correspond very well with vibrations of the matrix product; absorptions that appear at 1425 and 1050 cm^{-1} also seem to correspond with those of the matrix product.

There was no indication of ferrocene itself in any of the spectra, presumably because the matrices were too dilute in cyclopentadiene for ferrocene formation. Also, there was no indication of diiron products, again because the concentration of iron atoms in the matrices was too low for significant diiron formation. It was initially intended to keep the matrix concentrations too low for any dimer formation to occur.

Two other cyclopentadienyl metal hydrides are known: cyclopentadienylberyllium hydride[23–27] and cyclopentadienylmagnesium hydride.[28,29] Cyclopentadienylberyllium hydride has been reported by Dewar and Rzepa to be one of the most stable cyclopentadienylberyllium compounds.[24] Cyclopentadienylmagnesium hydride was reported by Goel and Ashby[28] and was synthesized by reacting cyclopentadiene with MgH_2 in THF. A comparison of the infrared spectra of CpBeH and CpMgH would be useful, but the infrared spectrum of CpBeH has not yet been reported, while spectra of CpMgH show[30] that the molecule exists as a solvated dimer in THF solution, thereby negating the value of a direct comparison of IR spectra.

A molecule of this type has C_{5v} symmetry. It has 30 normal vibrational modes that can be classified as follows:

$$\Gamma_{vib} = 5\ A_1 + A_2 + 6\ E_1 + 6\ E_2 \qquad (1)$$

The A_1 and E_1 vibrations are infrared-active, giving 11 IR-active modes, 9 of which have been detected.

A thermodynamic cycle can be constructed, and literature values[31–34] can be used to give the overall ΔH_{reacn}:

$$\begin{gathered} C_5H_6(g) + Fe(atom) \rightarrow (\eta^5\text{-}C_5H_5)FeH \\ \Delta H_{reacn} \sim -40 \text{ to } -60 \text{ kcal/mol} \end{gathered} \qquad (2)$$

The reaction, hence, has a substantial driving force, assuming $\Delta H \simeq \Delta G$ at very low temperatures. In the absence of any restrictive kinetic barriers, it would therefore be expected that this reaction be a spontaneous one.

Cyclopentadienyliron hydride is the first cyclopentadienyl transition-metal hydride detected. As is the case with metallocenes, it can be expected that other transition metals will form similar compounds under similar conditions; such syntheses are planned.

Acknowledgment. The authors thank the Robert A. Welch Foundation and the National Science Foundation for financial support. The assistance of Ellen Kline and Dr. Terry Marriott with NMR and mass spectrometric studies of cyclopentadiene-d_6 is also greatly appreciated.

Registry No. **3**, 97877-77-5; **3**-d_6, 97877-78-6; Fe, 7439-89-6; C_5H_6, 542-92-7; C_5D_6, 2102-16-1; $(\eta^5\text{-}C_5H_5)_2Fe$, 102-54-5.

Supplementary Material Available: Spectra of matrix-isolated ferrocene, cyclopentadiene, and cyclopentadiene-d_6 (Figure 1-S) and typical cyclopentadiene/iron codeposition spectra (Figures 2-S and 3-S) (3 pages). Ordering information is given on any current masthead page.

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EXAFS Studies of Zintl-Phase Solutions. Evidence for As_4^{2-} and As_6^{4-} Polyanions

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Solutions of Zintl phases, formed by fusion of an alkali metal with a main-group element, in basic solvents (ethylenediamine (en), ammonia) yield homo- or heteroatomic polyanions. In the 1930s Zintl established the stoichiometry of some of these ions in solution by potentiometric titration and analysis of solvent-extracted alloy phases.[2] Generally, solvent evaporation from the

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