

# NMR Spectroscopic Characterization of the Two Isomers of $[\text{HFe}_4(\text{CO})_{13}]^-$

Colin P. Horwitz and Duward F. Shriver\*

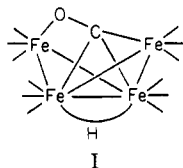
Department of Chemistry, Northwestern University, Evanston, Illinois 60201

Received November 22, 1983

Low-temperature  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra of  $[\text{HFe}_4(\text{CO})_{13}]^-$  demonstrate the presence of two distinct hydride species which are in equilibrium at room temperature. One of these displays a  $^1\text{H}$  NMR resonance at  $-24.9$  ppm and is assigned to a butterfly geometry for the  $\text{Fe}_4$  framework while the other has a  $^1\text{H}$  resonance at  $-16.9$  ppm and appears to be due to a closed  $\text{Fe}_4$  tetrahedron. Both species begin to equilibrate at approximately  $-30^\circ\text{C}$ . The low-temperature,  $-80^\circ\text{C}$ ,  $^{13}\text{C}$  NMR spectrum of the species which is assigned the butterfly geometry is in full accord with the previously determined X-ray structure. The proposed tetrahedral isomer of  $[\text{HFe}_4(\text{CO})_{13}]^-$  displays a single  $^{13}\text{C}$  resonance at  $216.7$  ppm, indicating rapid fluxional behavior down to the lowest temperatures studied ( $-80^\circ\text{C}$ ).  $^{17}\text{O}$  NMR spectra were obtained, but they do not provide further insight into the nature of the two isomers.

## Introduction

The compound  $[\text{HFe}_4(\text{CO})_{13}]^-$  was first synthesized in Hieber's laboratory<sup>1</sup> and was later shown to have an unusual butterfly structure with a dihapto CO ligand bridging the wingtips.<sup>2</sup> The disposition of CO ligands was used to infer the bridging position for the hydrogen ligand which is shown in I. It has been pointed out that the dihapto



CO group in this compound may serve as a molecular analogue of an intermediate or transition state in the cleavage of CO on metal surfaces,<sup>3</sup> which is a reaction of importance in Fischer-Tropsch catalysis.<sup>4</sup> Compound I also is implicated as an intermediate in the recently discovered proton-induced reduction of carbon monoxide.<sup>5,6</sup>

The  $^1\text{H}$  NMR of I displays two temperature- and solvent-independent resonances, in the metal hydride region, a peculiarity which has been commented upon but never resolved.<sup>2</sup> We describe here an NMR study of this phenomenon.

## Experimental Section

**Materials.** Standard Schlenk techniques under prepurified nitrogen were used throughout.  $\text{CH}_2\text{Cl}_2$  and  $\text{CD}_2\text{Cl}_2$  were dried over  $\text{P}_2\text{O}_5$ , and pentane was dried over sodium/benzophenone. All were freshly distilled under  $\text{N}_2$  prior to use. Diethyl ether was degassed with  $\text{N}_2$  and  $(\text{CD}_3)_2\text{CO}$  was vacuum distilled. All manipulations of the cluster compounds were performed under an inert atmosphere.

$\text{Fe}(\text{CO})_5$  (Alfa),  $[\text{PPh}_4]\text{Br}$  (Alfa), and  $[\text{PPN}]\text{Cl}$  (PPN = bis-(triphenylphosphine)nitrogen(1+)) were used without further purification.  $\text{HSO}_3\text{CF}_3$  (Aldrich) was purified by distillation under

reduced pressure as was  $\text{HSO}_3\text{F}$  (Aldrich).  $[\text{PPN}]_2[\text{Fe}_4(\text{CO})_{13}]$  (II), the  $[\text{PPh}_4]^+$  salt of this anion, and the corresponding salts of  $[\text{HFe}_4(\text{CO})_{13}]^-$  were prepared by a published procedure.<sup>7,8</sup> Solutions of  $[\text{Fe}_4(\text{CO})_{13}]^{2-}$  salts in  $\text{CH}_2\text{Cl}_2$  were enriched to approximately 25%  $^{13}\text{C}$  by exposure to  $^{13}\text{CO}$  gas (Mound Labs, 99%  $^{13}\text{CO}$ ) for a period of 6-7 days. The degree of enrichment was monitored by IR of the gas phase. A similar procedure was followed for  $\text{C}^{17}\text{O}$  enrichment by using 30%  $\text{C}^{17}\text{O}$  gas (Prochem). The final enrichment of the cluster was typically between 1% and 5%.

**Spectroscopy.**  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra were obtained on a JEOL FX90Q spectrometer operating at 22.49 and 89.55 MHz, respectively. The  $^{17}\text{O}$  spectral data were obtained on a JEOL FX270 spectrometer operating at 36.52 MHz. Both instruments were equipped with variable temperature controllers.  $^{13}\text{C}$  and  $^1\text{H}$  shifts are referenced to external  $\text{Me}_4\text{Si}$  while  $^{17}\text{O}$  spectra are relative to  $\text{H}_2\text{O}$ , with positive values being downfield.

**Low-Temperature  $[\text{Fe}_4(\text{CO})_{13}]^{2-} + \text{H}^+$  Reaction and NMR.** The appropriately enriched  $[\text{Fe}_4(\text{CO})_{13}]^{2-}$  salt was weighed in the glove box and loaded into a 10-mm NMR tube which was fitted with a rubber septum. The NMR tube was kept at 77 K while both solvent, precooled to  $-78^\circ\text{C}$ , and approximately 1 equiv of  $\text{HSO}_3\text{CF}_3$  were added. Approximately 5 min before the NMR tube was placed in the precooled probe,  $-80^\circ\text{C}$ , the tube was warmed to  $-78^\circ\text{C}$  to dissolve the  $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ . The tube was then rapidly transferred into the probe.

**Low-Temperature Dissolution of  $[\text{HFe}_4(\text{CO})_{13}]^-$  Salts and NMR.** The enriched monohydride was placed in a 10-mm NMR tube fitted with a rubber septum. The tube was maintained at  $-196^\circ\text{C}$  while  $\text{CD}_2\text{Cl}_2$  was added. The tube was warmed to  $-78^\circ\text{C}$  just prior to placing it in the precooled probe.

Replacement of  $\text{PPN}^+$  with  $\text{PPh}_4^+$  has no effect on the  $^1\text{H}$  or  $^{13}\text{C}$  NMR spectra, nor does the use of  $(\text{CD}_3)_2\text{CO}$  instead of  $\text{CD}_2\text{Cl}_2$ .

## Results and Discussion

As shown in Figure 1 the  $^1\text{H}$  NMR spectrum of  $[\text{PPN}][\text{HFe}_4(\text{CO})_{13}]$  obtained at ambient probe temperature,  $30^\circ\text{C}$ , contains two resonances in the high-field region, at  $-17.0$  and  $-24.8$  ppm, in a roughly 1:2 intensity ratio. In contrast to the expectation for the presence of two isomers in equilibrium, the ratio of intensities is not significantly temperature dependent. In an attempt to observe the spectrum of a pure isomer,  $[\text{PPN}][\text{HFe}_4(\text{CO})_{13}]$  was dissolved at low temperature and the  $^1\text{H}$  NMR spectrum was obtained at low temperature without allowing the sample to warm up in the interim. The resulting spectrum dis-

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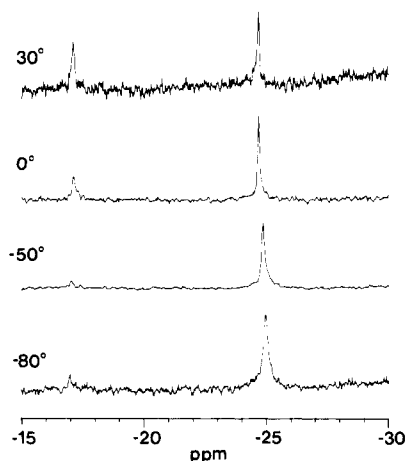
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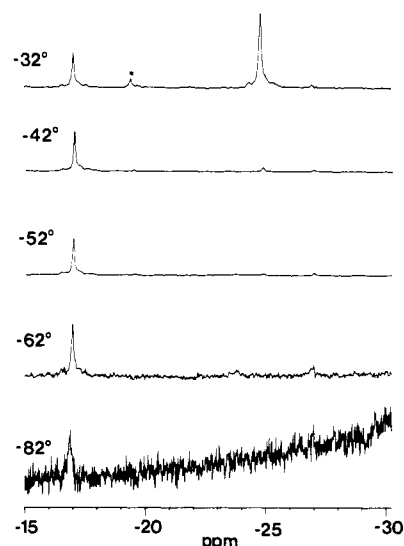
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**Figure 1.**  $^1\text{H}$  NMR spectra for  $[\text{PPN}][\text{HFe}_4(\text{CO})_{13}]$  dissolved in  $\text{CD}_2\text{Cl}_2$  at  $-80^\circ\text{C}$ . Spectra were obtained at  $-80^\circ\text{C}$  and the successively higher temperatures indicated in the figure.

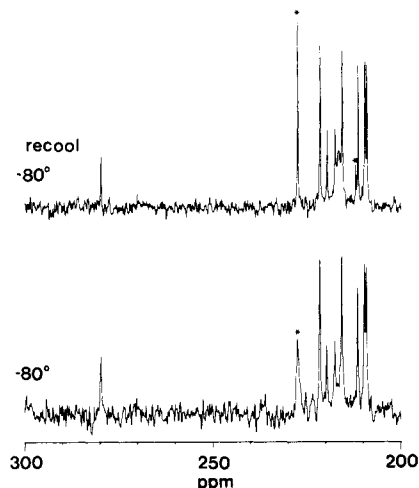


**Figure 2.**  $^1\text{H}$  NMR spectra for the product of the reaction of  $\text{HSO}_3\text{CF}_3$  with  $[\text{PPN}]_2[\text{Fe}_4(\text{CO})_{13}]$  in  $\text{CD}_2\text{Cl}_2$  at  $-82^\circ\text{C}$ . Spectra were obtained at  $-82^\circ\text{C}$  and the successively higher temperatures indicated in the figure. An asterisk denotes possible formation of  $\text{HFe}_3(\text{CO})_{13}\text{CH}$  (see text).

plays a single feature at  $-24.9$  ppm. Upon warming above  $-30^\circ\text{C}$ , a new signal is observed at  $-16.9$  ppm having roughly half the intensity of the  $-24.9$  ppm resonance. Thus it appears that the resonance at  $-24.9$  ppm originates from the butterfly, I.

The low-temperature,  $-78^\circ\text{C}$ , reaction of  $[\text{Fe}_4(\text{CO})_{13}]^{2-}$  with  $\text{HSO}_3\text{CF}_3$  results in the appearance of an upfield signal at  $-16.9$  ppm in the  $^1\text{H}$  NMR spectrum. This signal is seen to increase in intensity with increasing temperature (Figure 2) until approximately  $-30^\circ\text{C}$  where a second upfield resonance at  $-24.9$  ppm appears. The intensity ratio of the two signals is again approximately 1:2, with the more upfield resonance predominating. The weak resonance at  $-20.5$  ppm is likely due to  $\text{HFe}_3(\text{CO})_{10}\text{CH}$ ,<sup>9</sup> a species similar to  $[\text{Fe}_3(\text{CO})_{10}\text{CH}]^-$  which was recovered from the reaction of  $[\text{Fe}_4(\text{CO})_{13}]^{2-}$  in neat  $\text{HSO}_3\text{CF}_3$ .<sup>10</sup>

The apparent slow reaction of  $[\text{Fe}_4(\text{CO})_{13}]^{2-}$  with  $\text{HSO}_3\text{CF}_3$  is likely due to the low miscibility of the acid in  $\text{CD}_2\text{Cl}_2$ , approximately  $100\ \mu\text{L}$  of  $\text{HSO}_3\text{CF}_3$  in  $3\ \text{mL}$  of



**Figure 3.**  $^{13}\text{C}$  NMR spectra for  $[\text{PPN}][\text{HFe}_4(\text{CO})_{13}]$  in  $\text{CD}_2\text{Cl}_2$ . Top: the solid dissolved at  $-80^\circ\text{C}$ , allowed to warm to room temperature, and then re-cooled to  $-80^\circ\text{C}$ . Bottom: the solid dissolved at  $-80^\circ\text{C}$ . An asterisk denotes  $[\text{Fe}_4(\text{CO})_{13}]^{2-}$  and  $\text{Fe}_3(\text{CO})_{12}$  impurities.

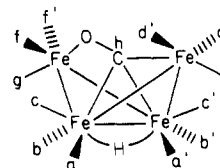
**Table I.** NMR Spectral Data for Low-Temperature Species<sup>a, b</sup>

	$^{13}\text{C}$	$^1\text{H}$
$[\text{HFe}_4(\text{CO})_{13}]^-$	279.7 (1), 221.5 (2), 219.7 (1) 217.5 (1), 215.6 (2), 211.4 (2) 209.5 (2), 209.1 (2)	$-24.9$
$\text{H}^+ + [\text{Fe}_4(\text{CO})_{13}]^{2-}$	216.7	$-16.9$

<sup>a</sup> Values are in ppm relative to external  $\text{Me}_4\text{Si}$ . <sup>b</sup> Values in parentheses are relative intensities.

$\text{CD}_2\text{Cl}_2$  at room temperature. In addition to the low miscibility, the acid may be frozen at temperatures below  $-50^\circ\text{C}$ . Reaction of the cluster with  $\text{HSO}_3\text{F}$  results in immediate and complete protonation with appearance of a single resonance at  $-16.9$  ppm. This is attributed to the greater miscibility of the acid in  $\text{CD}_2\text{Cl}_2$  as well as the lower freezing point,  $-87.3^\circ\text{C}$ . Appearance of the resonance at  $-24.9$  ppm again occurs at approximately  $-30^\circ\text{C}$ .

The low-temperature,  $-80^\circ\text{C}$ ,  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[\text{HFe}_4(\text{CO})_{13}]^-$  is shown in Figure 3. This spectrum displays a series of seven resonances in the region typical for terminally bound metal carbonyls and a single downfield resonance at  $279.7$  ppm. The single downfield resonance is assigned to the unique dihapto carbonyl while the signals in the terminal region conform to the symmetry of the molecule III. The integrated intensity pattern is



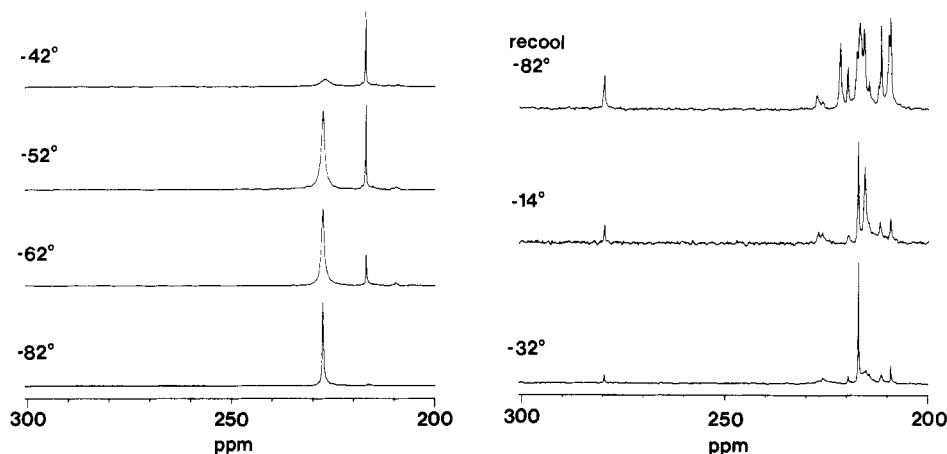
III

1:2:1:1:2:2:2:2<sup>11</sup> starting with the  $\eta^2\text{-CO}$  and moving in an upfield direction (Table I). By the use of selective proton decoupling, the resonances at  $221.6$  and  $215.7$  ppm are assigned to carbonyls  $aa'$  and  $bb'$  on the "hinge" of the butterfly. The other hinge carbonyls  $c$  and  $c'$  point up and away from the hydride and are not affected by decoupling.

After the NMR tube and contents are warmed to room temperature (at which point both isomers exist) and then re-cooled to  $-80^\circ\text{C}$ , the upper spectrum in Figure 3 is generated. This spectrum is similar to that for the starting

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**Figure 4.**  $^{13}\text{C}$  NMR spectra for the product of the reaction of  $\text{HSO}_3\text{CF}_3$  with  $[\text{PPN}]_2[\text{Fe}_4(\text{CO})_{13}]$  in  $\text{CD}_2\text{Cl}_2$  at  $-82^\circ\text{C}$ . Spectra were obtained at  $-82^\circ\text{C}$  and the successively higher temperatures indicated in the figure. The top right of the figure denoted recool  $-82^\circ$  refers to solid protonated at  $-82^\circ\text{C}$ , allowed to warm to room temperature, and then recooled to  $-82^\circ\text{C}$ .

cluster except for the resonance at 216.7 ppm. As will be discussed below, this new resonance corresponds to the second isomer.

Reaction of  $\text{HSO}_3\text{CF}_3$  with  $[\text{Fe}_4(\text{CO})_{13}]^{2-}$  was also monitored by  $^{13}\text{C}$  NMR spectroscopy. At  $-82^\circ\text{C}$ , in addition to the resonance due to unreacted  $[\text{Fe}_4(\text{CO})_{13}]^{2-}$  (227.7 ppm)<sup>11</sup> a very weak absorption at approximately 216.7 ppm is observed (Figure 4). Increasing the temperature to  $-42^\circ\text{C}$  causes an increase in intensity of this resonance and a concurrent decrease in the resonance due to  $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ . If  $\text{HSO}_3\text{F}$  replaces  $\text{HSO}_3\text{CF}_3$  the 216.7 ppm resonance is observed at  $-80^\circ\text{C}$  and shows no intensity changes upon warming to  $-60^\circ\text{C}$ . The spectrum obtained at  $-32^\circ\text{C}$  shows the growth of a variety of peaks in the terminal region as well as a single downfield resonance, 280.1 ppm. Appearance of the downfield resonance at this temperature is consistent with the observation of the second hydride resonance at  $-24.8$  ppm in the  $^1\text{H}$  NMR spectrum.

Recooling the solution to  $-82^\circ\text{C}$ , after warming to room temperature, yields the upper spectrum in Figure 4. This spectrum is similar to the recooled spectrum in Figure 3. Thus the cause of the additional resonance at 216.7 ppm in Figure 3 is due to the presence of the "second" isomer.

The  $^{17}\text{O}$  NMR spectra of  $[\text{Fe}_4(\text{CO})_{13}]^{2-}$  and  $[\text{HFe}_4(\text{CO})_{13}]^-$  were obtained over the temperature range of  $-90$  to  $+30^\circ\text{C}$ .  $[\text{Fe}_4(\text{CO})_{13}]^{2-}$  displays a single resonance at 388.4 ppm over the entire temperature range. No evidence for either the semibridging or the triply bridging carbonyls was found. The resonances for  $[\text{HFe}_4(\text{CO})_{13}]^-$  also appear in the range typical for terminally bonded carbonyls,<sup>12</sup> and no unique resonance could be found for the  $\eta^2\text{-CO}$ , possibly due to excessive quadrupolar broadening. A similar explanation has been advanced for  $\text{Cp}_2\text{Fe}_2(\text{CO})_4\cdot 2\text{Al}(i\text{-Pr})_3$  in which the oxygen-coordinated carbonyls are not observed.<sup>13</sup>

The lack of a resonance assigned to an  $\eta^2\text{-CO}$  in the  $^{13}\text{C}$  NMR of the product of the low-temperature protonation and the highly fluxional character of this species indicate that a tetrahedral metal framework is probably maintained. The position of the proton resonance at  $-16.9$  ppm clearly indicates attachment to the metal framework, but the exact disposition cannot be determined from the available data. Conversely, the hydride resonance at  $-24.9$  ppm clearly originates from the butterfly species, III. Above  $-30^\circ\text{C}$  both forms exist in solution starting from either the isolated  $[\text{HFe}_4(\text{CO})_{13}]^-$  or the protonation of  $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ . Between  $-30$  and  $+30^\circ\text{C}$  no change is observed in the ratio of the concentrations of the two species, indicating a low enthalpy for interconversion. Equilibrium measurements below  $-30^\circ\text{C}$  are precluded by the slow rate of interconversion in this temperature range.

Scission of one Fe-Fe bond and formation of the  $\eta^2\text{-CO}$  bridge in  $[\text{HFe}_4(\text{CO})_{13}]^-$  have been attributed to the relief of steric strain induced in the parent cluster by addition of the proton.<sup>2</sup> These arguments were based upon the observation that the carbonyls in  $[\text{Fe}_4(\text{CO})_{13}]^{2-}$  are tightly packed.<sup>14</sup> However, this steric argument is no longer compelling in view of the recent synthesis and structural characterization of a tetrahedral cluster with 14 carbonyl ligands,  $[\text{Fe}_3\text{Cr}(\text{CO})_{14}]^{2-}$ .<sup>15</sup> In this compound the average M-M distances are roughly  $0.1 \text{ \AA}$  longer than the average M-M distance in  $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ . Thus the compound  $[\text{Fe}_3\text{Cr}(\text{CO})_{14}]^{2-}$  relieves strain arising from CO-CO repulsion by the expansion of the metal framework. In any case, the present evidence for the coexistence in solution of butterfly and tetrahedral forms of  $[\text{HFe}_4(\text{CO})_{13}]^-$  indicates that the added steric repulsion arising from the hydride cannot be large.

**Acknowledgment.** This research was funded by NSF Grant CHE-8204401. C.P.H. was the recipient of an E. I. du Pont de Nemours fellowship. C.P.H. thanks J. Hriljac for helpful discussions and R. Wieboldt for assistance with the NMR spectrometers.

**Registry No.**  $[\text{HFe}_4(\text{CO})_{13}]^-$  (isomer 1), 62361-87-9;  $[\text{HFe}_4(\text{CO})_{13}]^-$  (isomer 2), 79795-90-7; Fe, 7439-89-6.

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