8318205) and by the National Institutes of Health (Grant GM 22566) for purchase of the diffractometer. Acknowledgement is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support.

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Supplementary Material Available: Tables of anisotropic thermal parameters and calculated hydrogen atom positions (14 pages); tables of observed and calculated structure factors (54 pages). Ordering information is given on any current masthead page.

The Making and Breaking of C–H Bonds on a Metal Cluster Framework. Analysis of the Tautomerization and Deprotonation of $Fe_3(CO)_9CH_4$ Leading to the Interconversion of FeHFe and CHFe Interactions

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The hydrocarbyl cluster having the composition $Fe_3(CO)_9CH_4$ (I) is shown to exist in solution as a mixture of three tautomers: $(\mu\text{-H})_3Fe_3(CO)_9(\mu_3\text{-CH})$, A; $(\mu\text{-H})_2Fe_3(CO)_9(\mu_3\text{-HCH})$, B; $(\mu\text{-H})Fe_3(CO)_9(\mu_3\text{-H}_2CH)$, C. Deprotonation of I yields the anion $[(\mu\text{-H})Fe_3(CO)_9(\mu_3\text{-HCH})]^-$. Protonation of this anion is kinetically controlled, leading exclusively to C at low temperature. Rearrangement to the equilibrium distribution of tautomers occurs at higher temperatures. Aspects of the nature of the hydrocarbon–triiron interaction in the three tautomers are revealed by analyses of deuterium isotope effects and comparison of ^{13}C–H coupling constants. The latter suggests decreasing s character of the capping carbon atom in going from A to C. All these data show that the three different distributions of endo hydrogens on the capped trimetal framework are of nearly equal energy and that the interconversion of FeHC and FeHFe interactions is a facile process for this cluster system.

Besides intrinsic curiosity concerning a new class of compounds, one of the major driving forces behind the rapid development of transition-metal cluster chemistry has been the metal cluster–metal surface analogy with its relevance to chemical catalysis.[1] If the latter is to be fully meaningful, the intra- and intermolecular reactivity of the pertinent cluster models must be understood. The myriad of known cluster structures has now been rationalized in several elegant ways[2] with this topological understanding being supplemented by studies on the electronic properties of clusters.[3] However, predictions of reactivity based on generalizations derived from stable structures suffer from the fact that a reaction path observed may reflect the high reactivity of a minor isomer rather than that of the most stable (and structurally characterized) reactant.[4] Further, relative reactivity depends on small energy differences; i.e., small perturbations can induce large changes in rates. Indeed, the sequence of reactions occurring on a catalyst is driven by small perturbations between states of nearly equal energy. Hence, if one wants to model catalytic reactivity with cluster chemistry, small barrier processes must be understood.

In the following, we present an investigation of the most stable positions, mobilities, and Brønsted acidities of the three endo cluster hydrogens of the geometrically simple cluster $Fe_3(CO)_9CH_4$ (I).[5] This cluster system demonstrates tautomerism involving reversible formation of CHFe interactions from FeHFe interactions, sensitivity of hydrogen arrangement to cluster charge (number of endo protons), and kinetic control of the protonation of the anionic cluster $[Fe_3(CO)_9CH_3]^-$. Formally, the results constitute a demonstration of facile intramolecular formation and destruction of CH interactions in a metal cluster. Although a substantial number of mononuclear and polynuclear metal complexes containing CHM interactions have been identified,[6] equilibria in which a CHM interaction is reversibly formed from a MHM interaction are not as common.[7-9] Hence, our analysis is pertinent

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(1) See for example: Muetterties, E. L. *Chem Soc. Rev.* **1982**, *11*, 283.

(2) See: Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. Mingos, D. M. P. *Chem. Soc. Rev.* **1986**, *15*, 31 and references therein.

(3) See for example: Hall, M. B. In *Organometallic Chemistry*; Shapiro, B. L., Ed.; Texas A&M Press: College Station, TX, 1983; p 334. Root, D. R.; Blevins, C. H.; Lichtenberger, D. L.; Sattelberger, A. P.; Walton, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 953. Barreto, R. D.; Fehlner, T. P.; Hsu, L.-Y.; Jan, D.-Y.; Shore, S. G. *Inorg. Chem.* **1986**, *25*, 3572.

(4) Kochi goes so far to suggest that if a compound obeys the 18-electron rule, it will not be an intermediate in a system. Kochi, J. K. *J. Organomet. Chem.* **1986**, *300*, 139.

(5) A preliminary report has appeared: Vites, J. C.; Jacobsen, G.; Dutta, T. K.; Fehlner, T. P. *J. Am. Chem. Soc.* **1985**, *107*, 5563.

(6) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

(7) Shapley and co-workers demonstrated that the equilibrium, $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-HCH}_2) = (\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$, involves the interconversion of a CHOs interaction and a OsHOs interaction. Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225. Calvert, R. B.; Shapley, J. R.; Schultz, A. J.; Williams, J. M.; Suib, S. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1978**, *100*, 6240. Calvert, R. B.; Shapley, J. R. *Ibid.* **1978**, *100*, 7726. Recently Lewis and co-workers have reported the equilbrium $(\mu\text{-H})Ru_4(CO)_{12}CH = (\mu\text{-H})_2Ru_4(CO)_{12}C$. Cowie, A. G.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Organomet. Chem.* **1986**, *306*, C63.

0276-7333/87/2306-0842$01.50/0

Table I. ^1H and ^{13}C NMR Data (δ) for $Fe_3(CO)_9CH_4$ and $[Fe_3(CO)_9CH_3]PPN$

compd	tautomer (% abund)[a]	^1H NMR[b]	^{13}C NMR[c]
$Fe_3(CO)_9CH_4$	A (84)	11.4 (1 H, J_{CH} = 168 Hz); –24.3 (3 H)	232 (μ_3-CH, J_{CH} = 166 Hz); 205 (9 CO)
	B (12)	–1.78 (2 H, J_{CH} = 116 Hz); –24.2 (2 H)	210 (9 CO); 115 (HCH)
	C (4)	–8.5 (3 H, J_{CH} = 105 Hz); –21.2 (1 H)	not obsd
$[Fe_3(CO)_9CH_3]PPN$		7.7–7.5 (m, 30 H); 6.6 (d, 1 H, J_{HH} = 18, J_{CH} = 150 Hz); –10.1 (d, 1 H, J_{HH} = 18, J_{CH} = 60 Hz); –20.3 (s, 1 H)	216.5 (2 CO); 215.4 (4 cO); 215.2 (1 CO); 214.4 (2 CO); 133.3, 131.3, 128.8, 126.2 (PPN^+); 118.5 (μ-CH_2, $J_{CH(t)}$ = 155, $J_{CH(\mu)}$ = 65 Hz)

[a] Based on ^1H NMR integrals in C_6D_6. [b] Neutral compound in C_6D_6 at 20 °C; anion in $C_6D_5CD_3$ at –60 °C. [c] Neutral compound in C_6D_6 at 20 °C; anion in CD_2Cl_2 at –80 °C.

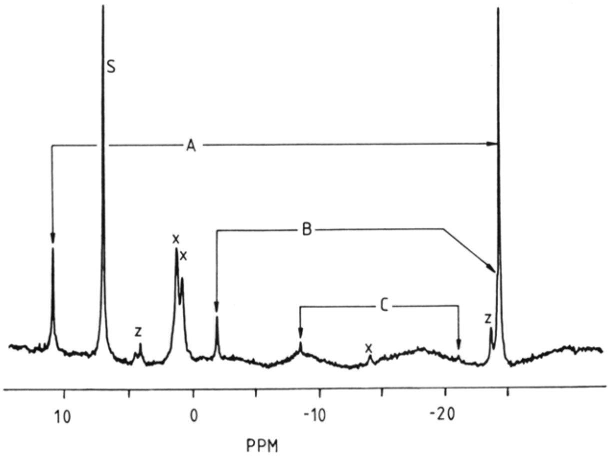
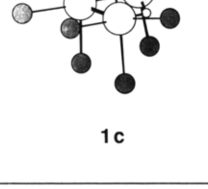


Figure 1. The ^1H NMR spectrum (100 MHz, C_6D_6, 30 °C) of $Fe_3(CO)_9CH_4$ showing tautomers A, B, and C. Peaks marked S, X, and Z are due to solvent, hexane residue, and $H_3Fe_3(CO)_9CR$ (R ≠ H), respectively.

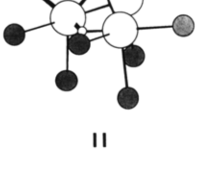
to the behavior of hydrocarbon fragments undergoing hydrogenation/dehydrogenation on a trimetal atom site as well as to a discussion of the general problem of CH bond activation.[7]

Results and Discussion

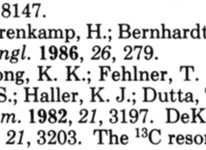
$Fe_3(CO)_9CH_4$. The (μ-H)$_3$Fe$_3$(CO)$_9$(μ_3-CCH$_3$) molecule has been characterized spectroscopically in solution as well as crystallographically in the solid state[10] and has structure **1a** with a methyl group replacing the terminal CH shown.



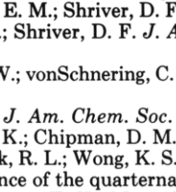
1a



1b



1c



II

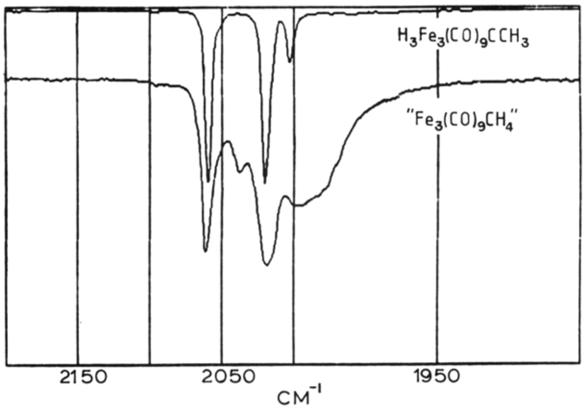


Figure 2. Infrared spectra of $H_3Fe_3(CO)_9CCH_3$ (top) and $Fe_3(CO)_9CH_4$ (bottom) in hexane.

The ^1H and ^{13}C chemical shifts of the FeHFe protons and quarternary carbon, respectively, serve as diagnostic indicators of endo-hydrogen location at the iron base and a μ_3-carbon capping the triiron base. Attempts to isolate a derivative in which the exo-methyl substitutent is replaced with hydrogen yielded ^1H NMR spectra illustrated in Figure 1. The most intense signals (marked A in Figure 1 and Table I) are consistent with structure **1a**, which is analogous to (μ-H)$_3$Fe$_3$(CO)$_9$(μ_3-CCH$_3$). However, despite repetitive chromatography, the persistent presence of other signals (B and C) at constant relative intensities suggests isomerization. The relative intensities of the signals A, B, and C in the ^1H spectrum were approximately independent of temperature (0–60 °C). The ^{13}C NMR data (Table I) tell a similar story. Resonances at chemical shifts consistent with structure **1a** are evident, but other low-intensity signals persist.

Finally, in Figure 2 the infrared spectra in the carbonyl regions for (μ-H)$_3$Fe$_3$(CO)$_9$(μ_3-CCH$_3$) and $Fe_3(CO)_9CH_4$ are compared. Clearly a species containing the $Fe_3(CO)_9$ fragment of structure **1a** is present, but the complex spectrum shows the presence of other species containing terminal CO's. There is no evidence for bridging carbonyls. All these observations are consistent with some type of isomerism, and we suspected a tautomerism of the type already reported in osmium and ruthenium systems.[8] Convincing proof resulted from deprotonation of $Fe_3(CO)_9CH_4$ followed by low-temperature protonation, as shown below.

Deprotonation. Deprotonation of $Fe_3(CO)_9CH_4$ by weak bases is facile, and the PPN^+ [bis(triphenylphosphine)nitrogen(1+)] and $N(n\text{-}C_4H_9)_4^+$ salts have been characterized.[6] The infrared spectrum of the PPN salt (Figure 3) suggests that the anion exists in a single predominant form. As expected, the frequencies are shifted to lower energy relative to the neutral, and the symmetry of the $Fe_3(CO)_9$ fragment is lower than C_{3v}. The infrared signature is typical of that of a cluster containing the (μ-H)Fe$_3$(CO)$_9$ fragment. With the exception of the cation resonances, the ^1H NMR is nearly silent at 20 °C. On

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(8) Examples of cluster isomerization are becoming more common. See, for example: Kolis, J. W.; Holt, E. M.; Shriver, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 7307. Horwitz, C. P.; Shriver, D. F. *J. Am. Chem. Soc.* **1985**, *107*, 8147.

(9) Vahrenkamp, H.; Bernhardt, W.; vonSchnering, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *26*, 279.

(10) Wong, K. K.; Fehlner, T. P. *J. Am. Chem. Soc.* **1981**, *103*, 966. Wong, K. S.; Haller, K. J.; Dutta, T. K.; Chipman, D. M.; Fehlner, T. P. *Inorg. Chem.* **1982**, *21*, 3197. DeKock, R. L.; Wong, K. S.; Fehlner, T. P. *Ibid.* **1982**, *21*, 3203. The ^{13}C resonance of the quarternary carbon of **1a** has now been observed at δ 271: Dutta, T. K.; Meng, X.; Vites, J. C.; Fehlner, T. P., unpublished data.

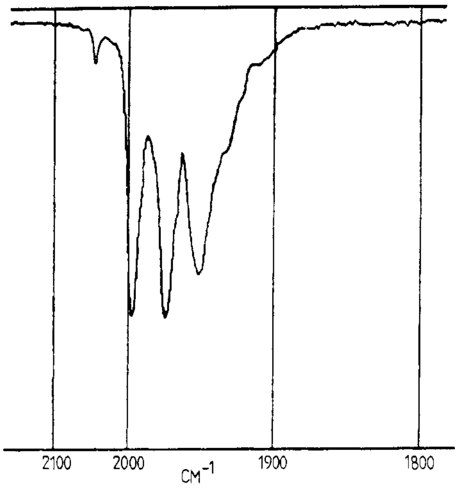

Figure 3. Infrared spectrum of $[Fe_3(CO)_9CH_3]PPN$ in acetone.

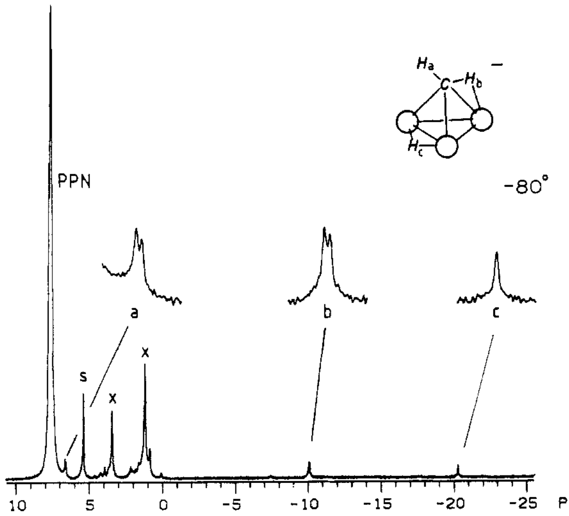

Figure 4. The ^1H NMR spectrum (300 MHz, CD_2Cl_2, -80 °C) of $[Fe_3(CO)_9CH_3]PPN$. Peaks marked S and X are due to solvent and $(C_2H_5)_2O$, respectively.

cooling, a resonance at δ −20.3 appears followed by the simultaneous growth of doublets at δ 6.6 and −10.1 (Figure 4). On the basis of chemical shifts for related compounds, the resonance at δ −20.3 is easily assigned to a FeHFe proton while that at δ 6.6 is assigned to a CH terminal proton. The chemical shift of the resonance at δ −10.1 does not unambiguously define the environment of this proton. The value observed is consistent with either a FeH terminal proton or a CHFe bridging (agostic)[6] proton. However, selective decoupling of the signals at δ 6.6 and −10.1 at −80 °C demonstrates that the 18-Hz coupling is due to geminal coupling of the CH terminal proton to the proton at δ −10.1. In addition, at temperatures above −60 °C, irradiation of either δ 6.6 or −10.1 causes complete collapse of both without affecting δ −20.3, thereby demonstrating a more facile exchange involving the first two protons. Finally, for a ^{13}C-enriched sample, ^{13}C satellites are observed in the ^1H spectrum for δ 6.6 (J = 150 Hz) and −10.1 (J = 60 Hz). In summary, (a) the high-field chemical shift of the δ −10.1 proton places it in the vicinity of iron, (b) the HH geminal coupling between the δ 6.6 and the δ −10.1 protons and the ^{13}C coupling observed for the δ −10.1 proton demonstrate bonding to the capping carbon, and (c) the reduced value of the ^{13}C coupling constant for the δ −10.1 proton relative to the δ 6.6 proton is consistent with a bridging interaction. Hence, the δ −10.1 resonance is assigned to a CHFe "agostic" hydrogen,[6] and we postulate structure II for the anion. The predominant form of the anion produced on deprotonation contains CH, CHFe, and FeHFe interactions.[11]

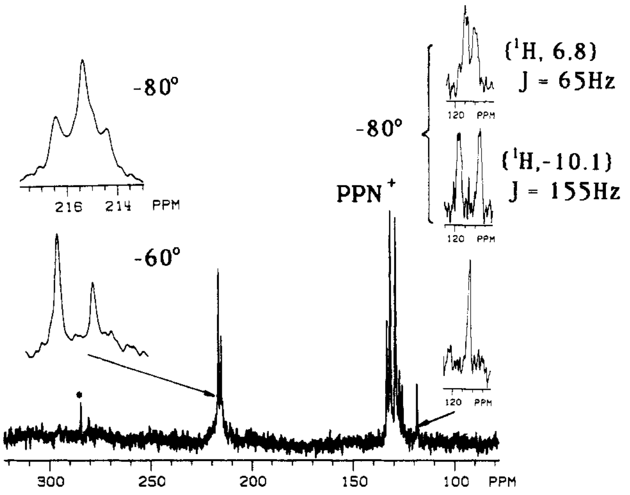

Figure 5. The ^{13}C {^1H} NMR spectrum (75 MHz, CD_2Cl_2, −80 °C) of $[Fe_3(CO)_9CH_3]PPN$. The peak with an asterisk is an artifact. The inset (upper left) shows the CO region at −80 °C while the inset (upper right) shows the results of selective ^1H decoupling at −80 °C on the resonance at δ 118.5.

The above conclusion is fully supported by the variable-temperature ^{13}C NMR spectrum of $[Fe_3(CO)_9CH_3]^-$, which is shown in Figure 5. The skeletal carbon resonance is found at δ 118.5, considerably further upfield than that observed for the CH carbon in structure **1a** of $Fe_3(CO)_9CH_4$ but consistent with the chemical shift expected for a bridging methylene in a multinuclear cluster.[12] Coupling to the two "methylene" protons at δ 6.6 and −10.1 is demonstrated by selective proton decoupling. Hence, both the chemical shift and the CH coupling are consistent with the asymmetrically bound CH_2 group postulated in structure II. Information on the symmetry of the anion comes from an analysis of the terminal CO region in the ^{13}C spectrum. At −60 °C two types of CO in a ratio of 2:1 freeze out on top of a broad resonance. At −80 °C the integral of the CO resonances relative to that of the PPN signals is about 3 times higher than that of the two sharp resonances observed at −60 °C. This shows that six more CO's freeze out at the lower temperature. Assuming localized site exchange, these observations are consistent with the freezing out of one $Fe(CO)_3$ group followed by the other two and imply a plane of symmetry in the anion. The limiting-low-temperature chemical shifts listed in Table I average to δ 215.4 vs. 215.2 observed at 20 °C. These results serve to support structure II.

Protonation. Protonation of $[HFe_3(CO)_9(HCH)]^-$ with excess CF_3COOH at −80 °C produces a single species (by ^1H NMR, Figure 6) with the spectroscopic signature of species C observed in the characterization of $Fe_3(CO)_9CH_4$ (Table I, see above). This species is stable for hours at −70 °C, but at higher temperatures the proton signals of B and then A grow in. At about 0 °C the proton spectrum is about the same as that of $Fe_3(CO)_9CH_4$ shown in Figure 1. Assuming each species has four hydrogens, the system composition as a function of temperature can be derived

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[11] The spectroscopic measurements do not eliminate the possibility of a HCFe interaction rather than the CHFe interaction proposed for the δ −10.1 proton (See: Edwin, J.; Boehm, M. C.; Chester, N.; Hoffman, D. M.; Hoffmann, R.; Pritzkow, H.; Siebert, W. *Organometallics* **1983**, *2*, 1666). However, the geometrical constraints of placing two hydrogens within bonding distances of the μ_3-carbon with a reasonable HCH angle require one hydrogen to be within bonding distance of an iron atom.

[12] Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 209.

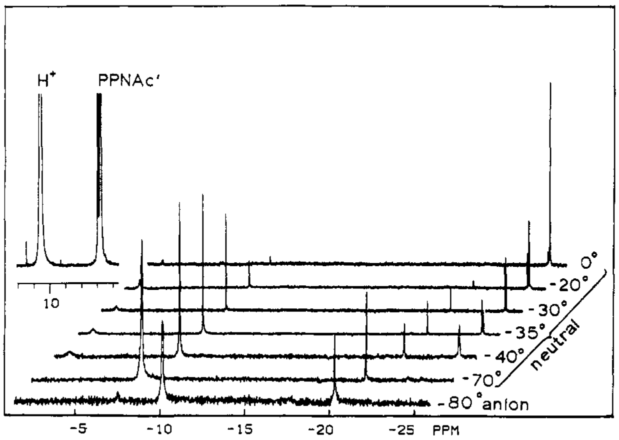

Figure 6. The changes in the high-field ^1H NMR spectra upon low-temperature acidification of $[HFe_3(CO)_9(HCH)]^-$ at −80 °C with excess CF_3COOH. The approximate average heating rate was 0.3 °C/min. The spectra above −35 °C have been line narrowed to show the two FeHFe resonances at δ −24.2 and −24.3.

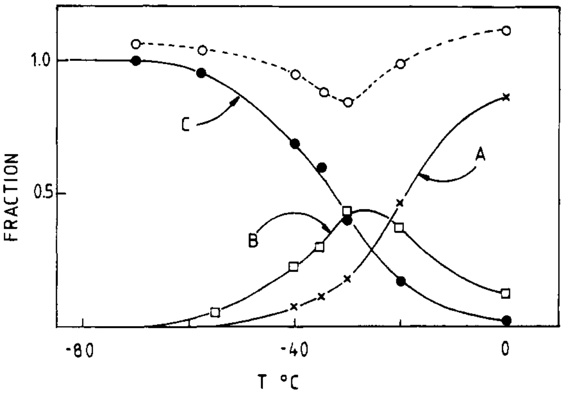

Figure 7. Isomer distribution (by ^1H NMR) as a function of temperature. (These are not equilibium distributions.) The open circles are a relative measure of the total ^1H signal intensity and constitute a mass balance, assuming equal sensitivities for all three species. The "dip" at −30 °C is probably due to low integration for B as the low-field signal in this temperature range was broad (see Figure 6).

from the signal intensities illustrated in Figure 6 and the result is shown in Figure 7. A "mass balance" confirms that B and C are tautomeric forms of A and that protonation is quantitative. Hence, these experiments establish that the relationship (eq 1) between tautomers of the

$$(\mu\text{-H})_3Fe_3(CO)_9(\mu_3\text{-CH})\ [A] \Leftrightarrow (\mu\text{-H})_2Fe_3(CO)_9(\mu_3\text{-HCH})\ [B] \Leftrightarrow (\mu\text{-H})Fe_3(CO)_9(\mu_3\text{-H}_2CH)\ [C] \quad (1)$$

triiron-capped cluster $Fe_3(CO)_9CH_4$ is one in which FeHFe and FeC interactions are progressively converted into FeFe and FeHC interactions in going from A to C.

These experiments clearly demonstrate that protonation of $[HFe_3(CO)_9(HCH)]PPN$ with CF_3COOH is a kinetically controlled process; i.e., lowering the temperature does not regenerate species B and then C. Examples of kinetically controlled protonation of clusters exist, and steric factors have been suggested to be important.[13] In the case of this capped trimetal cluster, the terminal CO's shield the FeFe edges, leaving the CFe edges of the tetrahedral core much more accessible to an incoming associated acid. Rearrangement to yield the more stable FeFe-edge-bridged species takes place more slowly. We also emphasize that the energetic preference of FeFe over CFe edge bridging is small; i.e., a mixture of tautomers is observed. This implies the relationship between the interaction energies given in eq 2. As $E(\text{FeFe}) < E(\text{FeHFe})$,[14] this suggests

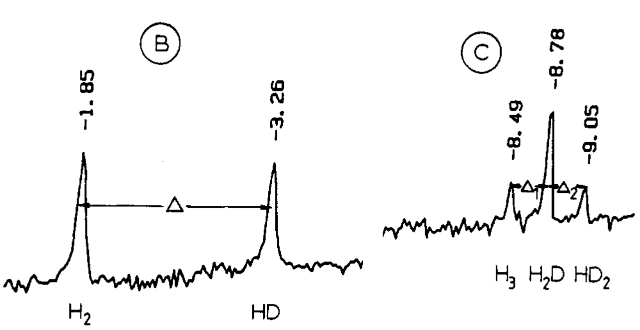

Figure 8. The ^1H NMR (300 MHz, C_6D_6, 20 °C) of partially deuteriated $Fe_3(CO)_9CH_4$ showing the changes in the δ −1.85 and −8.49 signals of tautomers B and C, respectively, on deuteriation.

$$E(\text{CFe}) + E(\text{FeHFe}) \approx E(\text{FeFe}) + E(\text{CHFe}) \quad (2)$$

that the entire interaction energy of the CHFe three-atom unit is likewise larger than that for a CFe interaction.

Tautomer Characterization. Although the tautomers of $Fe_3(CO)_9CH_4$ have not been isolated, considerable information on their structures can be derived from spectroscopic information. As already pointed out, tautomer A has NMR properties (Table I) consistent with those of structure **1a**, and we assume that the basic tetrahedral Fe_3C skeleton established for $H_3Fe_3(CO)_9CCH_3$ is retained in all three tautomers. The relative intensities observed for C (Figure 6) show that the proton added to the anion goes to a CFe edge. Hence, structure **1c** is one possibility for tautomer C. To accommodate the ^1H NMR data, the CH and CHFe protons of C must be rapidly scrambling at −70 °C. Thus, different arrangements of two CHFe and one FeHFe hydrogens on the CFe_3 framework must be of similar energy. For tautomer B, relative signal intensities are consistent with structure **1b**, one of three ways of distributing two CHFe and two FeHFe hydrogens on the CFe_3 framework. One of the two CHFe interactions in C has become a FeHFe interaction in B. Again the ^1H NMR data require that the CH and CHFe protons of B are rapidly scrambling at 0 °C and the breadth of the resonance at δ −1.8 at −40 °C (Figure 6) is consistent with a fluxional process. The ^{13}C NMR shift (Table I) supports the presence of a CH_2 fragment similar to that in II.

The method of partial deuteriation, developed by Shapley et al., has been used to confirm structures **1b** and **1c** postulated for B and C as well as to provide additional information on the nature of the CHFe interactions.[7] Deuterium was introduced into $Fe_3(CO)_9CH_4$ by reacting $[HFe_3(CO)_9(HCH)]^-$ with excess D_3PO_4/D_2O. The ^1H NMR of partially deuteriated I was similar to that shown in Figure 1 except that two resonances now appear in the δ −2 region and three in the δ −8 region. These are illustrated in Figure 8, where δ −1.85 is assigned to tautomer B (CH_2), δ −3.26 to tautomer B (CHD), δ −8.49 to tautomer C (CH_3), δ −8.78 to tautomer C (CH_2D), and δ −9.05 to tautomer C (CHD_2). The large change in chemical shift on deuteriation relative to normal isotope effects on chemical shifts proves, as postulated above, that these resonances are averages of CH and CHFe protons. The zero point energy difference between CH and CHFe hydrogens in B, for example, causes the DC(μ-H)Fe species to predominate over the HC(μ-D)Fe species and results

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[13] Stevens, R. E.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1982**, *104*, 6454.

[14] Vites, J.; Fehlner, T. P. *Organometallics* **1984**, *3*, 491.

in a substantial upfield shift for the observed ^1H signal of the partially deuteriated species. The number of signals observed, i.e., two for B and three for C, constitutes the minimum number of hydrogens associated with the corresponding resonance in the unlabeled compound; i.e., if two hydrogens are involved, CH_2, CHD, and CD_2 will give rise to two signals in the proton spectrum.

Comparison of ^1H and ^2H NMR intensities as well as the three signals observed for B showed that a significant amount of $Fe_3(CO)_9CH_2D_2$ was present. This suggests that $Fe_3(CO)_9CH_4$ exchanges protons in the presence of D^+, and, indeed, the deuterium content of $Fe_3(CO)_9CH_4$ depended on the acidification time. For this reason the isotope effect on the equilibria represented by eq 1 could not be determined. However, by assuming only $Fe_3(CO)_9CH_3D$ and $Fe_3(CO)_9CH_2D_2$ are present and by ignoring the tautomers B and C, the fractions of the deuteriated species present in equilibria 3 and 4[15] as well as the distribution of D

$$H_3Fe_3(CO)_9CD \leftrightarrow DH_2Fe_3(CO)_9CH \quad 3K \qquad (3)$$

$$DH_2Fe_3(CO)_9CD \leftrightarrow D_2HFe_3(CO)_9CH \quad K \qquad (4)$$

between CH and FeHFe sites can be calculated from the ^1H and ^2H intensities. For a typical sample, the fractions of the D and D_2 species calculated are 0.7 and 0.3, respectively, with a calculated $K = 0.7$. With this information and the artificial restriction of no isotopic preference for CH vs. CHFe vs. FeHFe sites, i.e., site statistics alone determines distribution, the relative intensities of the signals due to isomers B and C can be estimated. For B the estimated CH_2:CHD = 0.40:0.53 vs. observed relative intensities (Figure 8; δ −1.85, −3.26) = 0.46:0.54. For C the estimated CH_3:CH_2D:CHD_2 = 0.17:0.65:0.15 vs. observed relative intensities (δ −8.49, −8.78, −9.05) = 0.24:0.57:0.19.

The chemical shift difference (Δ in Figure 8) reflects the isotopic fractionation factor (defined as f and equal to the ratio of the CHFe and CDFe populations) resulting from the zero point energy difference between CH (terminal) and CHFe (agostic) hydrogens. These factors are not 1 as was assumed in the simplified calculations above. To evaluate the fractionation factors, the actual chemical shifts of the protons involved in the exchange must be known. On the basis of the observed shifts of the protons in $[HFe_3(CO)_9(HCH)]^-$, a reasonable, but not unique, fit is for B, δ(CH) 6.8 and δ(CHFe) −10.5, and C, δ(CH) −4.5 and δ(CHFe) −10.5, with fractionation factors of 1.39 and 1.50, respectively.[16] Taking the CH and CHFe frequencies as 3100 and 2600 cm^{-1}, respectively,[6] one estimates a fractionation factor of 1.43. For C Δ_1 is slightly (but reproducibly) larger than Δ_2 proving that there are two CHFe and one CH rather than one CHFe and two CH hydrogens.[17] On the other hand, the unexpectedly high-field position of the calculated chemical shift of the CH (terminal) proton suggests that it is in the vicinity of the metal atoms. In agreement with this observation, reasonable geometric models[18] for the capping μ_3-H_2CH moiety suggest that the "terminal" hydrogen is probably displaced by the CHFe hydrogens toward the metal base. However, the average coupling constant (see below) still suggests the presence of a terminal and two CHFe hydrogens as opposed to three CHFe hydrogens. Hence, the chemical shift of this hydrogen reflects environment but not bonding. We conclude that A contains a μ_3-methylidyne (**1a**), B a μ_3-methylene "chelating" through one CH bond (**1b**), and C a μ_3-methyl "chelating" through two CH bonds (**1c**).[19]

Scheme I

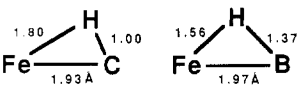

Table II. Measured and Estimated ^{13}C–H Coupling Constants for the Tautomeric Forms of $Fe_3(CO)_9CH_4$

tautomer	J_{CH} (obsd), Hz	J_{CH} (term), Hz	J_{CH} (bridge), Hz
A	168	168	
B	116	(145)[a]	89
C	105	(118)[a]	98

[a] Calculated by using $J_{BH} = 0.8J_{CH}$ and the correlation in ref 20.

I can be profitably compared with the isoelectronic and isoprotonic boron analogue $[(\mu\text{-}H)Fe_3(CO)_9(\mu_3\text{-}H_2BH)]^-$, which has an endo-hydrogen arrangement equivalent to structure **1c**.[20] That is, the structure of the least stable form of I corresponds to the most stable structure of the borane analogue. In B and C the CH and CHFe protons exchange more readily with each other than with the FeHFe proton, whereas in the borane analogue it is the BHFe and FeHFe protons that exchange more readily. This contrasting behavior reflects an intrinsic difference in the BHFe and CHFe bonds. We have directly compared the structural parameters of a CHFe and BHFe three-center interaction in analogous environments where the CFe and BFe distances are nearly equal.[21] As shown in Scheme I, in going from the CHFe to the BHFe situation the hydrogen is displaced parallel to the Fe–C(B) bond toward the Fe atom. Viewed as a proton, the bridging hydrogen appears to follow the charge as the electronegativity difference between the main-group atom and the iron atom is decreased. This suggests that the BH interaction in the three-center BHFe bond is weaker than the CH in the three-center CHFe bond and the HFe interaction in the BHFe bond is stronger than the HFe of the CHFe bond.[21] Hence, the structural parameters and dynamic behavior of I and its boron analogue are internally consistent.

Further information on the nature of the CH interactions in the three tautomers of I is contained in the ^{13}CH

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(15) Calvert, R. B.; Shapley, J. R.; Schultz, A. J.; Williams, J. M.; Suib, S. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1978**, *100*, 6240.

(16) If one assumes the CHFe resonance of B is at δ −10.5, the observed average at −1.85 fixes the CH resonance at δ 6.8. For the CHD species the average resonance is observed at δ −3.26; hence the fractionation factor, f, is given by $(6.8 - 10.5f)/(f + 1) = -3.26$. Again assuming the CHFe resonances of C lie at δ −10.5, the observed average at δ −8.49 fixes CH at δ −4.47. The average resonance of the CH_2D allows one to calculate a $f = 1.50$; i.e., $[-4.47 - (1 + f)(10.5)]/(2 + f) = -8.78$. With use of this fractionation factor, an average resonance of δ −8.99 is calculated for the CHD_2 species vs. an observed value of δ −9.05; i.e., $[(-4.47) - 2f(10.5)]/(1 + 2f) = -8.99$.

(17) Consider the consequences of one CH and two CHFe interactions. For one D only $DC(HFe)_2$ and HC(HFe)(DFe) are possible and one CHFe (high field) always has full weight. For two D only DC(HFe)(DFe) and $HC(DFe)_2$ are possible and one CHFe has zero weight. As H's are being observed, $\Delta_1 > \Delta_2$. Now consider two CH and one CHFe interactions. For one D only HDCHFe and H_2CDFe are possible and one CH (low field) always has full weight. For two D only D_2CHFe and DHCDFe are possible and one CH has zero weight. Hence, $\Delta_1 < \Delta_2$. See: Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726.

(18) Placing two hydrogens on FeC edges of a carbon-capped triiron fragment in the known geometry of the FeHC interaction in $HFe_4(CO)_{12}CH$ (Beno, M. A.; Williams, J. M.; Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 1485) and using a H(term)CH(bridge) angle of 99° result in a H(terminal)–Fe distance of 2.1 Å. Increasing the HCH angle to 109° results in three equivalent hydrogens, each 1.75 Å from an iron atom.

(19) C constitutes an example of an alkyl radical chelating via two CH bonds and approaches Crabtree's suggested alkane coordination compound with multiple CH chelation.[6]

(20) Vites, J. C.; Housecroft, C. E.; Eigenbrot, C.; Buhl, M. L.; Long, G. J.; Fehlner, T. P. *J. Am. Chem. Soc.* **1986**, *108*, 3304.

(21) Fehlner, T. P.; Housecroft, C. E.; Scheidt, W. R.; Wong, K. S. *Organometallics* **1983**, *2*, 825. The proton fluxional behavior of isoelectronic and isoprotonic tetrairon B and C clusters also supports this conclusion. Housecroft, C. E.; Fehlner, T. P. *Organometallics* **1986**, *5*, 1279.

coupling constants (Table II). That observed for A is a true coupling constant and has a reasonable value for a μ_3-capping CH fragment. For tautomers B and C reduced coupling constants are observed; however, these are average coupling constants and resolution into values for terminal and bridging protons can only be done indirectly. Again, comparison with isoelectronic ferraboranes is useful. We have previously suggested a correlation between the coupling constant of the terminal proton to the capping main-group atom and the number of main-group–hydrogen bridge interactions.[20] Note that the estimated values for B are in reasonable agreement with those measured for II. Application to the three tautomers being discussed here gives the results in Table II. As the terminal coupling decreases, the bridge coupling increases; i.e., the values approach those in methane. Note that the trend in coupling constants suggests a reduction in the difference between the strengths of the terminal and bridging CH interactions. Thus, the total s character of the capping carbon of I decreases as the number of CHFe interactions increases.

Interestingly, like the analogous ruthenium and osmium systems,[7,22,23] the addition of excess phosphine to I results in the formation of methane. This reaction is similar to the reaction of $[HFe_3(CO)_9(H_2BH)]^-$ with Lewis bases whereby base adducts of BH_3 are observed as one type of product.[24] The ready displacement of main-group fragments from a multinuclear site may be enhanced by the presence of MHX interactions. Interestingly, Paine has reported an instance of the reverse process. The loss of CO by $CpFe(CO)_2PR_2{\cdot}BH_3$ results in the formation of a FeHB interaction.[25]

Conclusions

The beauty of the $Fe_3(CO)_9CH_4$ system lies in the delicate balance between the various ways the endo hydrogens can interact with the Fe_3C framework—a balance that is achieved for iron but not for ruthenium[22] nor osmium,[26] for I but not for the methyl derivative,[10] and for the hydrocarbyl cluster but not for the isoelectronic ferraborane anion.[20] Clearly, this balance results from a fortuitous combination of factors, but, even so, the cluster serves to model a catalytic site at which CH bond formation and cleavage occurs. In I, CH interactions can be formed and broken with little expenditure of energy and only a small stress on the system can result in a large change in composition. Although methylidyne, methylene, and methyl intermediates have been directly observed on a nickel catalyst,[27] it remains to be seen whether CHM interactions are also important for CH_x adsorbed on metal surfaces.

Experimental Section

General Data. All reactions and manipulations were carried out under inert atmospheres or in a vacuum line with standard techniques.[28] Solvents were dried (THF over KOH pellets and hexane over molecular sieve), degassed, and distilled before use; methanol and dichloromethane were dried over molecular sieve and degassed before use. $Fe(CO)_5$ was fractionated in a vacuum line, $BH_3{\cdot}THF$ (1 M, Aldrich) was titrated, $NaHB(OCH_3)_3$ (Aldrich) was dissolved in THF, centrifuged, and titrated, and H_3PO_4 (85%) was degassed before use. The following were used as received: CF_3COOH (Aldrich), $(C_4H_9)_4NBr$ (Aldrich), and [PPN]Cl [bis(triphenylphosphine)nitrogen(1+) chloride] (Aldrich). Column chromatography was performed on 60–200 mesh silica gel (Baker).

Most ^{13}C and ^1H FT NMR spectra were obtained on a Nicolet 300-MHz spectrometer although some ^1H spectra were obtained on a Varian XL-100 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer, and mass spectra were run on an AEI-MS 9 spectrometer. ^{13}C shifts are reported with respect to Me_4Si (δ 0) and ^1H shifts with respect to Me_4Si (δ 0). A Carle Model 311 gas chromatograph with molecular sieve and porapak columns in series and argon carrier gas was used to qualitatively identify CH_4. Authentic gas samples were used for calibration.

Preparation of I. To a flask containing glass beads and 5 mmol of $NaHB(OCH_3)_3$ in 10 mL of THF at −20 °C was added 5 mmol of $Fe(CO)_5$ with stirring. The flask was placed in a water bath (22 °C), and 10 mmol of additional $Fe(CO)_5$ was rapidly added. This was followed by the slow (5 min period) addition of 10 mmol of $BH_3{\cdot}THF$. (*Caution*! This reaction is exothermic.) After the mixture was stirred 1 h, all solvents and volatiles were removed under vacuum. The remaining red oil was treated with 10 mL of H_3PO_4 and extracted with two 10-mL portions of hexane. Vigorous agitation was required for efficient acidification. The concentrated hexane extracts were applied to a short silica gel column that was then washed with hexane until the eluant was free of $Fe_3(CO)_{12}$. The material remaining on the column was removed with CH_3OH and reacidified as indicated above. Centrifugal chromatography on a 1-mm silica gel plate previously treated with a solution of $\sim$0.06 M H_3PO_4 in CH_3OH yielded four bands, the first of which was yellow $Fe_3(CO)_9CH_4$. The yield varied but was always 10% or less based on iron. Mass spectrum: p^+ 436 (9 CO), $^{56}Fe_3{}^{12}C_{10}{}^1H_4{}^{16}O_9$ (435.784 measd, 435.790 calcd). Treatment of a hexane solution of I with a CH_3OH solution of [PPN]Cl results in clean deprotonation. Removal of CH_3OH under vacuum followed by extraction with $(C_2H_5)_2O$ yields II. Protonation of II with CF_3COOH quantitatively (by NMR) regenerates I. I is less stable than II, and the latter has a half-life of ca. 1 week when stored at −10 °C in the solid state under nitrogen.

Reaction of a 0.3-mmol sample of $Fe_3(CO)_9CH_4$ in hexane with 1.0 mmol of $Ph(CH_3)_2P$ at 25 °C for 20 min resulted in the formation of methane plus some H_2 and CO as determined by gas chromatography. The reaction of $H_3Fe_3(CO)_9CCH_3$ under the same conditions produced only H_2 and CO.

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(22) A related equilbrium is observed in a Ru_4 system,[7] and the reversible formation of an intermediate with a RuHC interaction preceding elimination of CH_3R from $(\mu\text{-}H)_3Ru_3(CO)_9CR$ has been proposed. Duggan, T. P.; Barnett, D. J.; Muscatella, M. J.; Keister, J. B. *J. Am. Chem. Soc.* **1986**, *108*, 6076. The protonation of the same compound leads to the formation of a RuHC interaction. Bower, D. K.; Keister, J. B. *J. Organomet. Chem.* 1986, *312*, C33.

(23) Calvert, R. B. Ph.D. Thesis, University of Illinois, Urbana, IL, 1978. As referenced by: Muetterties, E. L. *Chem. Soc. Rev.* **1982**, *11*, 283.

(24) Housecroft, C. E.; Fehlner, T. P. *Inorg. Chem.* **1986**, *25*, 404.

(25) Paine, R. T.; McNamara, W. F.; Duesler, E. N. *Abstr. Pap.—Am. Chem. Soc.* **1986**, *192nd*, INORG 97.

(26) No evidence of similar equilibria for $Os_3(CO)_9CH_4$ has been reported[7] although exchange of the μ-H and CH protons has been demonstrated. VanderVelde, D. G.; Shapley, J. R. *Abstr. Pap.—Am. Chem. Soc.* **1984**, *187th* INORG 129. Note that a tautomeric equilibrium for the $Os_3(CO)_{10}CH_4$ system has been observed.[7]

(27) Kaminsky, M. P.; Winograd, N.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1986**, *108*, 1315.

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