

Protonation of Ferrocene in the Gas Phase

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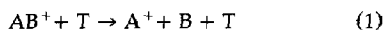
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Hydrogen-deuterium exchange, proton and deuterium transfer, and collision-induced dissociation experiments involving protonated ferrocene, $[\text{Fe}(\text{C}_5\text{H}_5)_2]\text{H}^+$, and isotopically labeled analogues have been carried out using a Fourier transform ion cyclotron resonance (FTICR) spectrometer and a double-focusing mass spectrometer of reversed geometry. These experiments reveal that the structure in which the added proton is bound to one of the cyclopentadienyl rings, possibly via agostic interaction with the iron atom, plays an important role in the gas-phase behavior of protonated ferrocene. It is demonstrated that extensive hydrogen atom scrambling occurs in the cyclopentadiene ring and that the extra hydrogen can also switch from one ring to the other, probably via the iron atom. An interpretation is presented which implicates slow thermal unimolecular rearrangement on the FTICR time scale from a metal-protonated form to a ring-protonated form which is higher in energy. This interpretation successfully rationalizes the current data as well as previous gas-phase measurements and is found to be in good agreement with solution and matrix isolation studies. (*J Am Soc Mass Spectrom* 1994, 5, 274–281)

Bonding in gas-phase transition metal species has been examined extensively, and with the advent of new experimental methods considerable progress has been made during the last fifteen years in understanding both the qualitative and quantitative aspects of metal-ligand binding [1]. Mass spectrometry has been a particularly valuable tool in this regard and frequently collision-induced dissociation (CID) [2] and ion-molecule reactions have been used to deduce gross structural features of metal-containing ions. In CID experiments accelerated ions, AB^+ , undergo collision with an inert target gas, T, and the resulting fragment ions are detected (eq 1). Fragmentation frequently occurs via simple bond cleavages and the resulting spectrum therefore provides strong clues to the nature of the bonding in the parent ion. Ion-molecule reactions also provide valuable information about the behavior and structure of organometallic ions in the gas phase [3].



Proton transfer studies in high pressure ion sources have supplied accurate proton affinities of numerous organic and inorganic molecules [4]. However, the data available for transition metal species are somewhat limited. One compound that has received con-

siderable attention is ferrocene [5–9]. In a detailed study of the kinetics of proton transfer to ferrocene [7], it was deduced that ferrocene has a significantly higher degree of symmetry than protonated ferrocene, $[\text{FeCp}_2]\text{H}^+$. Based on solution-phase data (see below), it had been assumed initially that the site of protonation in ferrocene is at the iron atom [5]. However, the change from a negative to a positive temperature dependence of the rate constant for proton transfer from protonated acetophenone to ferrocene [7] led to the suggestion that a secondary protonation site (the cyclopentadienyl ring) might be accessible, and which is $\sim 42 \text{ kJ mol}^{-1}$ less energetically favorable. However, the authors cautioned that their interpretation “remains speculative.” Meot-Ner [8] has also carried out high pressure mass spectrometric experiments involving deuteration of ferrocene. Based on the observation that following deuterium transfer to FeCp_2 subsequently exclusive D^+ transfer to bases of higher proton affinity occurred, he concluded that there is no scrambling of the added proton with the cyclopentadienyl ring hydrogen atoms in protonated ferrocene. Thus it was suggested that the added proton is different from all other hydrogen atoms and must therefore occupy a unique position. This observation was taken to support the contention that the protonation site is either directly on iron, on the ring in an exo position, or in an agostically bonded position bridging the metal and the ring. Meot-Ner also determined the binding

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energy of $[\text{FeCp}_2]\text{H}^+$ to acetonitrile to be ~ 33 kJ mol $^{-1}$. In apparent contrast to this, Hunt and Sethi [6] had shown earlier that $[\text{FeCp}_2]\text{D}^+$, generated via chemical ionization of ferrocene with ND_3 as reagent gas at total pressures from 0.7 to 1.3 mbar, exchanges cyclopentadienyl hydrogens for deuterium. Incorporation of as many as five deuterium atoms was observed. This near thermoneutral exchange of the ring hydrogens for deuterium suggests that for $[\text{FeCp}_2]\text{D}^+$ the incorporated deuterium exchanges with the ring hydrogens before another hydrogen/deuterium (H/D) exchange with ND_3 takes place. Another possibility is that this represents a case of multiple proton transfers within the complex formed between deuterated ferrocene and ND_3 . In such a complex, deuteron transfer from the iron atom, in a metal deuterated $[\text{FeCp}_2]\text{D}^+$, to ND_3 within the complex followed by deuteron transfer to the ring, scrambling within the ring, proton transfer back to ND_3 and finally D^+ transfer back to the metal followed by dissociation of the complex could then lead to the observed increase in deuterium content of the ferrocenium ion. Whatever the mechanism, this observation of relatively facile H/D exchange is seemingly in disagreement with the failure to observe exchange in Meot-Ner's experiment.

In a recent study from this laboratory [9] pulsed ionization high pressure mass spectrometry (HPMS) was used to examine the energetics of clustering of protonated iron pentacarbonyl, $[\text{Fe}(\text{CO})_5]\text{H}^+$, with CH_3CN . The binding energy was found to be moderately high, 71 kJ mol $^{-1}$, which was considered to be indicative of a hydrogen-bonded complex involving the transition metal center. In view of the large difference between the $[\text{FeCp}_2]\text{H}^+$ and $[\text{Fe}(\text{CO})_5]\text{H}^+$ bond strengths to CH_3CN , it was proposed that iron pentacarbonyl protonates on the metal center, whereas the hydrogen bond in $[\text{FeCp}_2\text{H}^+/\text{CH}_3\text{CN}$ might involve a ring hydrogen atom or an agostically bound hydrogen atom bridging the ring and the metal center, which would then weaken the hydrogen-bond interaction with acetonitrile. This appeared to be supported by the results of preliminary CID experiments in which $[\text{Fe}(\text{CO})_5]\text{H}^+$ exclusively lost CO units, whereas the most abundant dissociation processes of $[\text{FeCp}_2]\text{H}^+$ were loss of cyclopentadiene, C_5H_6 , and loss of H^+ .

In the present work, detailed CID data for $[\text{FeCp}_2]\text{H}^+$ and isotopically labeled analogues from experiments performed at low and at high ion translational energy using a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer and a double-focusing mass spectrometer of reversed geometry, respectively, are presented. For direct comparison with the data presented by Hunt and Sethi [6] and Meot-Ner [8], H^+/D^+ transfer and H/D exchange ion-molecule reactions were also examined. The results obtained provide evidence for the direct involvement of a structure for protonated ferrocene in which interchange of ring and metal bound hydrogens may occur.

Experimental

Most experiments were performed with a Bruker Spectrospin CMS 47 FTICR spectrometer (Bruker, Billerica, MA) equipped with a high pressure external ion source [10]. FeCp_2 present as the minor component ($< 0.1\%$) in CH_4 bath gas was used to generate $[\text{FeCp}_2]\text{H}^+$ ions via proton transfer chemical ionization. Ion source pressures up to 4 mbar were used and 2 keV electrons accomplished the ionization. The temperature of the high pressure source was ~ 30 °C. The chemical ionization product ions (almost exclusively $[\text{FeCp}_2]\text{H}^+$) were transferred from the high pressure ion source to the ICR cell and trapped. An initial 2 second delay was used to allow translational thermalization of the ions by collision with argon present in the ICR cell at 5.0×10^{-8} mbar as indicated by the ionization gauge. (The ions entered the argon-containing ICR cell with a center-of-mass energy of less than 0.15 eV.) As discussed previously, the very low kinetic energy of the ions associated with the transfer process from the high pressure source to the ICR cell results in the facile thermalization of the ion population [11]. In experiments where reactions which are very sensitive to the effects of ion kinetic energy were examined, thermalization delays beyond 2 seconds at 5×10^{-8} mbar Ar provided no observable effect [11] despite the relatively small number of collisions that the average ion will have undergone under these conditions. By ejecting all other ions from the ICR cell, the ion of interest was isolated, whereupon a radiofrequency (RF) pulse at the exact cyclotron frequency of this ion was used to increase its translational energy to an accurately known value determined by the duration and amplitude of the RF pulse [11]. In the subsequent delay (usually 100 ms), CID took place with argon as target gas. The fragment ions were detected in both broad-band mode (full mass spectrum) and narrow-band mode (high resolution). Each time the transients from 16 experiments were accumulated to obtain a good signal-to-noise ratio. To examine ion-molecule reactions, ion activation was omitted from the procedure described above and the reactivity of the isolated ion with certain substrates, such as $(\text{CH}_3\text{CH}_2)_3\text{N}$ or pyridine (both at 3.5×10^{-8} mbar) or NH_3 (at 9.0×10^{-8} mbar), was examined by varying the delay between isolation of the ion of interest and detection. To prevent extensive reactions prior to isolation of the ion, these experiments were performed with an initial delay after introduction of the ions to the ICR cell of only 5 ms.

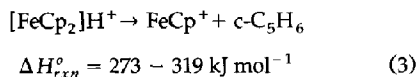
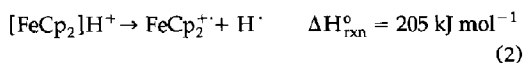
Additional experiments were performed with the VG Analytical ZAB-2E mass spectrometer (VG Analytical, Manchester, UK) at McMaster University [12]. This instrument is equipped with a standard chemical ionization source and contains a collision cell in the second field-free region between the B and E sectors permitting CID. The CID mass spectra of 8 keV ions were obtained by using O_2 as the target gas. The gas

pressure was adjusted to give a main ion beam transmission of 80%.

All compounds were of commercial origin and showed no detectable impurities. D₂O (99.9 atom% D) and Fe(c-C₅D₅)₂ (96.8 atom% D) were supplied by MSD Isotopes (Montreal, Canada).

Results

Chemical ionization of FeCp₂ with CH₄ in the external high pressure ion source of the FTICR spectrometer produced a strong [FeCp₂]H⁺ signal. The most prominent processes upon collisional activation of [FeCp₂]H⁺ ions having a center-of-mass energy of 12 eV and a CID delay time of 100 ms were loss of H⁺ and loss of c-C₅H₆, although a minor loss of c-C₅H₅ was also observed (see Figure 1a). A signal at *m/z* 56, Fe⁺, was present as well, presumably due to a consecutive fragmentation process, but *m/z* 57, FeH⁺, was absent. Reduction of the CID delay time to 10 ms (i.e., single collision conditions [11]) did not change the spectrum significantly (apart from a significant reduction of the signal at *m/z* 56), thus establishing that *m/z* 121 and 122 did not result from consecutive fragmentation of *m/z* 186. By adjusting the length of the RF excitation pulse, an assessment of the center-of-mass energy dependence of the fragmentation of the [FeCp₂]H⁺ ions could be obtained. At low center-of-mass energies (< 5 eV) H⁺ loss became more intense than c-C₅H₆ loss. Thus, H⁺ loss is less energy demanding than c-C₅H₆ loss, in keeping with existing thermochemical data [13] (eqs 2 and 3). (All thermochemical data are from ref 13 unless otherwise stated. Δ_fH([FeCp₂]H⁺) was calculated from the proton affinity of FeCp₂, 866 kJ mol⁻¹ [8]. The most accurate values of the heat of formation of FeCp⁺ can be derived from recent determinations of the Fe⁺-Cp bond strength; experimentally this bond strength has been determined to be 368 kJ mol⁻¹ [14a] and theoretically a value of 322 kJ mol⁻¹ was obtained [14b]. These new values result in Δ_fH^o(FeCp⁺) of 1048 and 1094 kJ mol⁻¹, respectively.)



The dominance of cyclopentadiene loss at higher center-of-mass energies, above 5 eV, is therefore indicative of a more energy demanding but mechanistically simpler process. Jacobsen and Freiser [15] reported the CID mass spectrum of protonated ferrocene obtained via reaction 4 at unspecified collision energy in an FTICR spectrometer and found the spectrum to be dominated by H⁺ loss with a minor signal corresponding to c-C₅H₆ loss.

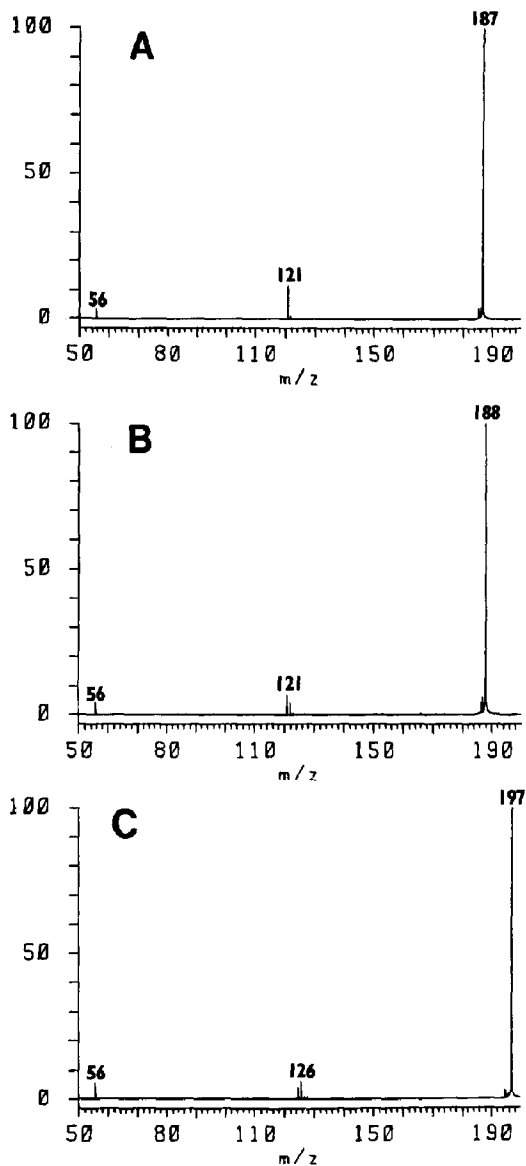
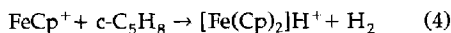


Figure 1. FTICR CID mass spectra of [FeCp₂]H⁺ (a), [FeCp₂]D⁺ (b), and [FeCp₂]²⁺H⁺ (c). The center-of-mass energy of the ions was 12.0 eV and the CID delay time was 100 ms. Argon was the target gas.



The 8 keV CID mass spectrum obtained with the ZAB-2E contained more fragment ions than the low energy CID mass spectrum (compare Figures 2a and 1a). Although the higher translational energy allowed more endothermic reactions to occur (e.g., generation of FeC₂H⁺ and FeC₃H₃⁺), H⁺ loss was still the single most abundant process. The FeCp⁺ signal was slightly

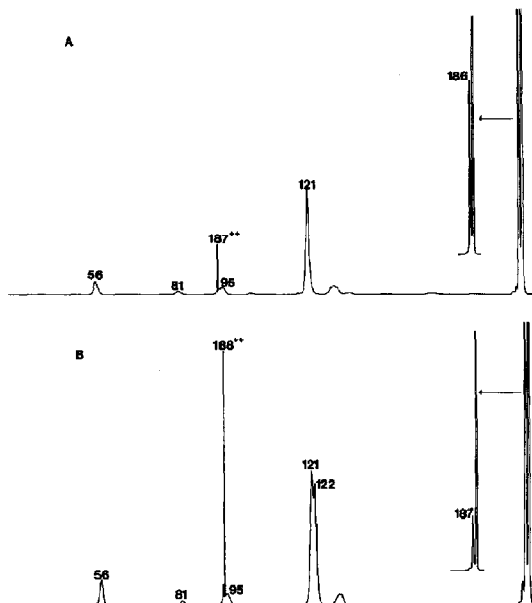


Figure 2. CID mass spectra of $[\text{FeCp}_2]\text{H}^+$ (a) and $[\text{FeCp}_2]\text{D}^+$ (b) ions having a translational energy of 8 keV recorded with a ZAB-2E mass spectrometer of reversed geometry (B-E). The target gas was oxygen.

asymmetric, suggesting that a small peak which corresponds to $c\text{-C}_5\text{H}_5$ loss could be present, as observed in the low energy CID mass spectrum. Fairly intense doubly charged ions were observed as well.

Addition of a small amount of either D_2O or *tert*-butylchloride-*d*9 to the mixture admitted to the external ion source of the FTICR spectrometer resulted in generation of a mixture of $[\text{FeCp}_2]\text{D}^+$ and $[\text{FeCp}_2]\text{H}^+$ ions with ratios of the intensities of m/z 188 and m/z 187 in favor of the deuterated form. The CID mass spectrum of $[\text{FeCp}_2]\text{D}^+$ is presented in Figure 1b. Loss of both $c\text{-C}_5\text{H}_5\text{D}$ and $c\text{-C}_5\text{H}_6$ (100:56) occurred upon collisional activation and, somewhat surprisingly, loss of H^+ was much more intense than loss of D^+ (16:1). The 8 keV CID mass spectrum was in excellent agreement with this spectrum (compare Figures 2b and 1b). In the high energy spectrum H^+ loss was 17 times more abundant than D^+ loss and m/z 121 and 122, $c\text{-C}_5\text{H}_5\text{D}$ and $c\text{-C}_5\text{H}_6$ loss, respectively, were present in the ratio 100:90.

Finally, CID of protonated $\text{Fe}(\text{C}_5\text{D}_5)_2$, $[\text{FeCp}_2^d]\text{H}^+$, was examined. Signals corresponding to loss of $c\text{-C}_5\text{D}_5\text{H}$ and $c\text{-C}_5\text{D}_6$ were present and loss of the added proton was considerably weaker than D^+ loss (see Figure 1c). The results for $[\text{FeCp}_2]\text{D}^+$ and $[\text{FeCp}_2^d]\text{H}^+$ indicate that the CID fragmentations are independent of the exothermicity of the reaction used to protonate or deuterate the ferrocene (D_3O^+ , D_5O_2^+ , or *t*- C_4D_9^+ for $[\text{FeCp}_2]$; CH_3^+ or C_2H_5^+ for $[\text{FeCp}_2^d]$), which argues against a mixture of noninterconverting metal-

ring-protonated forms of ferrocene being present prior to activation.

Thus, all of the CID data obtained show evidence for mobility of the added hydrogen in protonated ferrocene. However, this mobility may be due either to the energy supplied by collisional activation or it may already be present at thermal energies in the unactivated ion. The elucidation of which of these phenomena is operative may be found by probing the hydrogen mobility in unactivated $[\text{FeCp}_2]\text{H}^+$ ions via ion-molecule reaction.

The HPMS deuteration experiments carried out by Meot-Ner [8] argue against a protonated ferrocene structure which permits H/D scrambling at thermal energies on the time scale of the HPMS experiment. To obtain a direct comparison with Meot-Ner's [8] proton transfer experiments, $[\text{FeCp}_2]\text{D}^+$ ions, generated in the external high pressure source, were trapped in the ICR cell and allowed to react with $(\text{C}_2\text{H}_5)_3\text{N}$ and pyridine. Both $(\text{C}_2\text{H}_5)_3\text{N}$ and pyridine have a higher proton affinity (PA) than ferrocene ($\text{PA}(\text{C}_2\text{H}_5)_3\text{N} = 972 \text{ kJ mol}^{-1}$ [13], $\text{PA}(\text{pyridine}) = 924 \text{ kJ mol}^{-1}$ [13], and $\text{PA}(\text{FeCp}_2) = 866 \text{ kJ mol}^{-1}$ [8]). With $(\text{C}_2\text{H}_5)_3\text{N}$ in the ICR cell, both $[(\text{C}_2\text{H}_5)_3\text{N}]\text{H}^+$ and $[(\text{C}_2\text{H}_5)_3\text{N}]\text{D}^+$ were formed and the ratio of the intensities of the latter two ions increased with trapping time with ratios of 100:81 after 4 seconds, 100:34 after 15 seconds, and 100:25 after 30 seconds. With pyridine present, again, both the protonated and deuterated form were observed. The ratio of protonated versus deuterated base increased with trapping time, being 100:75 after 4 seconds and 100:55 after 15 seconds. Significantly, the extent of hydrogen transfer increases with increasing trapping time.

To make a direct comparison with Hunt and Sethi's [6] isotope exchange data, isolated $[\text{FeCp}_2^d]\text{H}^+$ ions (m/z 197) were trapped for longer periods of time in the ICR cell in the presence of NH_3 , which has a proton affinity 8 kJ mol^{-1} weaker than that of FeCp_2 [7]. Figure 3 shows the spectrum obtained with a 30 second trapping time. The presence of signals at m/z 196, 195, 194, and 193 shows that extensive D/H exchange with NH_3 takes place, in excellent agreement with the data of Hunt and Sethi [6]. With a reaction delay of 100 seconds, exchange of up to seven deuterium atoms was observed. However, as the number of exchanges increases, the rate for D/H exchange is statistically reduced and at the same time proton transfer to low levels of amine impurities in NH_3 led to a serious loss of signal intensity in protonated ferrocene type ions.

Discussion

Three possible protonation sites for ferrocene can be considered: (1) the metal center, (2) the cyclopentadienyl ring, and (3) an agostic position bridging the metal center and the cyclopentadienyl ring. The first

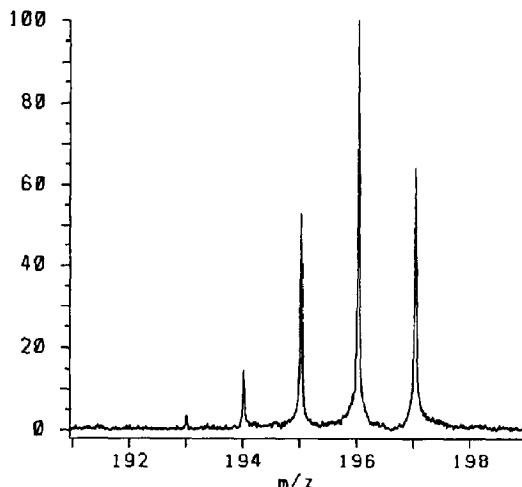


Figure 3. FTICR mass spectrum obtained by trapping isolated $[\text{FeCp}_2]_2\text{H}^+$ ions for 30 seconds in the ICR cell in the presence of NH_3 . The ion at m/z 197 represents $[\text{FeCp}_2]_2\text{H}^+$ and those at m/z 196, 195, 194, and 193 show the exchange of 1, 2, 3, and 4 ring deuterium atoms for hydrogen, respectively.

proton NMR studies of ferrocene in strongly acidic solutions [16] showed that ferrocene was evidently metal-protonated and that all of the ring hydrogens remained equivalent. It was on this basis that Kebarle and co-workers [7] and Beauchamp and co-workers [5] presumed in their HPMS and ICR studies, respectively, that iron-protonation also occurred in the gas phase. Meot-Ner [8] concluded, based on the failure to observe hydrogen scrambling in deuteration experiments, that either iron-protonation or some other unique site protonation was occurring. However, more recent solution-phase investigations of ferrocene protonation in a variety of media [17] demonstrated that both metal- and ring-protonation can occur with the site of protonation dependent on the nature of the medium. In particular, in weakly acidic, aprotic media it appears that the cyclopentadienyl ring is preferentially protonated. In addition, the observation of the exchange of ring hydrogen atoms for deuterium [16, 18, 19] supports involvement of a ring-protonated structure in weakly acidic media. Interaction of the cyclopentadienyl rings of ferrocene with a mildly protic medium was also suggested by an earlier UV spectroscopic study [19].

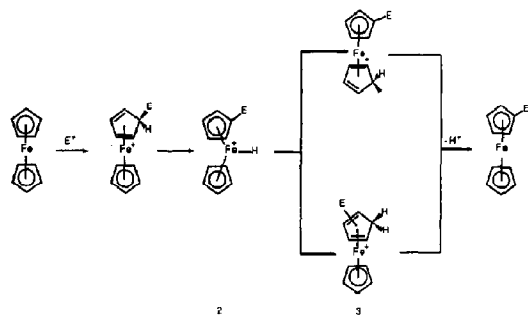
Recently, a detailed solution-phase study has appeared which describes the Friedel-Crafts acetylation of bis(trimethylsilyl) and bis(trimethylstannyl)ferrocene [20]. From the results obtained a general mechanism for electrophilic substitution of ferrocenes was formulated (see Scheme I) in which exclusive involvement of electrophilic attack at the iron atom was excluded. Exo electrophilic attack generates a σ -complex, **1**, which undergoes a ring-to-metal proton transfer. Subsequent proton transfer back to one of the rings

produces a new σ -complex as intermediate, **3**, which upon exo loss of a proton gives the substituted product. (Note that the complexes **1** and **3** could also be agostic structures.) Based on these results Cunningham [20] suggested that protonation of ferrocene may also arise from exo attack on the ring by H^+ . With $\text{E}^+ = \text{H}^+$, the $1 \rightarrow 3 \rightarrow 1 \rightarrow \text{etc.}$ process described in Scheme I explains exchange of ring hydrogens for deuterium in solution [16, 18, 19] and the evidence suggests that this mechanism might then also be operative in the gas phase [6].

On the basis of the weak binding energy of $[\text{FeCp}_2]_2\text{H}^+$ to CH_3CN we had predicted that ring-protonation, possibly in an agostic position, might occur in the gas phase [9]. The latter possibility was also acknowledged by Corderman and Beauchamp [5b] in an extension of earlier work from the same laboratory. Intramolecular two-electron, three-center agostic carbon-hydrogen-metal interactions are known to be quite common among transition metal complexes [21]. Frequently, gas-phase data are observed to parallel the behavior observed in low temperature matrix isolation studies [22]. Several infrared studies of the interaction between ferrocene and phenol, HCl or $(\text{CF}_3)_3\text{COH}$, in a liquid xenon matrix [23] indicate that the resulting hydrogen bonding involves the cyclopentadienyl ring as well as or instead of the metal atom.

Recently, several computational studies of the protonation of ferrocene have been carried out [24] which should be directly relevant to the gas-phase data. All of these calculations indicate that the metal-protonated form is more stable and, according to the latest study [24c], at the highest level the difference in energy between metal- and ring-protonated forms is 176 kJ mol^{-1} . However, optimization of a structure involving a hydrogen interacting agostically with the ring and the metal was not successful. Such an agostic structure might be expected to be more favorable than a straightforward iron-protonated form. In addition, the proton affinity of ferrocene for metal protonation was calculated to be 1050 kJ mol^{-1} , whereas the experimental value is only 866 kJ mol^{-1} [8].

The current FTICR proton/deuteron transfer experiments show that $[\text{FeCp}_2]_2\text{D}^+$ transfers both H^+ and D^+



Scheme I.

to bases of higher proton affinity. This indicates that, on the FTICR time scale, either the added deuteron does not occupy a unique site or that intramolecular exchange occurs between the unique protonation site and the ring hydrogens. At the shorter reaction times examined (4 seconds), a slight excess of H^+ versus D^+ transfer is seen but this excess is considerably less than the 10:1 excess expected if complete H/D scrambling had occurred. With increasing reaction time the extent of H^+ versus D^+ transfer increases, consistent with a move toward a more statistical product distribution. This behavior is decidedly inconsistent with H/D scrambling induced by any slight (< 0.5 eV) kinetic energy associated with the transfer of $[FeCp_2]D^+$ from the external source to the FTICR cell. If this were the cause of the scrambling, then as the trapping time increased, unreactive collisions would reduce the ion kinetic energy, and correspondingly the extent of any collisionally activated scrambling would be expected to diminish rapidly, exactly the opposite of what is observed. Similarly, for the H/D exchange experiments involving $[FeCp_2^d]^+$ and NH_3 , the extensive exchange observed for well-thermalized protonated ferrocene type ions during the ≥ 30 seconds trapping times implicates the involvement of structure(s) other than a fixed metal-protonated ferrocene. In contrast to these data, Meot-Ner [8] has observed that thermal deuterated ferrocene ions at 100 °C in the high pressure ion source environment transfer uniquely the added deuteron.

All of the FTICR, HPMS, and CID results can potentially be rationalized with the following view of ferrocene protonation.

The most energetically favorable site of protonation of ferrocene is indeed at the iron atom either without, or more probably with, an agostic ring interaction. However, a second protonated structure, 40–80 $kJ\ mol^{-1}$ higher in energy, exists in which protonation occurs on the ring and which permits loss of identity of the extra ring hydrogen, likely via sigmatropic rearrangement. The trapping time in all of the FTICR experiments exceeds 2 seconds, whereas the ion source residence time in HPMS experiments is on the order of 2 ms. In Meot-Ner's [8] HPMS kinetic experiments, this second structure is not accessed to any significant extent and only the added deuteron is subsequently transferred to a base of higher proton affinity. However, in the FTICR it is possible for thermal energy ions to access the ring-protonated structure within the very long observational time scale of this experiment and to thereby undergo complete, or nearly complete, randomization of H and D atoms in $[FeCp_2]D^+$ and $[FeCp_2^d]H^+$. For example, consider a simple Arrhenius kinetic model for the conversion of metal-protonated to ring-protonated forms involving an activation energy of 42 $kJ\ mol^{-1}$, as suggested by the data of Ikonomou et al. [7], and a preexponential factor of $10^{10}\ s^{-1}$. The rate constant at 298 K calculated from these Arrhenius parameters, $\sim 500\ s^{-1}$, is greater than the

collision frequency of $\sim 2\ s^{-1}$ and therefore suggests that the ring-protonated structure might be reached at least at the thermalization rate. If the scrambling within the ring via sigmatropic shift is much faster than this (a reasonable assumption), then scrambling can easily occur on the FTICR time scale while remaining unobservable on the HPMS time scale at sufficiently low temperature. In this regard it is noteworthy that Jacobsen and Freiser [25] have previously rationalized six H/D exchanges by $Fe(c-C_5H_6)^{2+}$ in the presence of excess D_2 by invoking a mechanism in which $Fe(c-C_5H_6)^{2+}$ is in rapid equilibrium with $HFeCp^+$, the species reactive towards D_2 . This is followed by the rate-limiting 1,5 sigmatropic H atom transfer in the former species. While theoretical calculations have shown that as much as 75 $kJ\ mol^{-1}$ may be required for the hydrogen scrambling via 1,5 sigmatropic H atom transfer in ionized cyclopentadiene [26], this value may be considerably reduced in coordinated cyclopentadiene. To accommodate the scrambling with ND_3 observed by Hunt and Sethi [6], a fairly high ion energy must be invoked due possibly to either the ion source temperature or electric fields within the chemical ionization source. In support of the slow unimolecular isomerization mechanism proposed here, it should be noted that significantly endothermic unimolecular dissociations and isomerizations on even longer time scales have recently been demonstrated in this laboratory [27].

In the CID experiments complete statistical loss of positional identity of the H and D atoms in $[FeCp_2]D^+$ would yield a 10:1 ratio for H^+ versus D^+ loss. For $[FeCp_2^d]H^+$ this ratio would be 1:10. Because deuterium isotope effects [28] also affect the ratios obtained experimentally, the CID data for $[FeCp_2]D^+$ and $[FeCp_2^d]H^+$ could be compatible with these numbers. The relative intensity of H^+ versus D^+ loss observed for $[FeCp_2]D^+$ and $[FeCp_2^d]H^+$ in the CID experiments (see Table 1) suggests that there is an isotope effect favoring H^+ loss. The data for cyclopentadiene loss from $[FeCp_2]D^+$ and $[FeCp_2^d]H^+$ (see Table 1) could be compatible with the picture pre-

Table 1. Relative fragment ion intensities in the CID mass spectra of $[FeCp_2]D^+$ and $[FeCp_2^d]H^+$ ions having a center-of-mass energy of 12.0 eV^a

	$[FeCp_2]D^+$	$[FeCp_2^d]H^+$
– H^+ ; – D^+	16:1 <i>10:1</i>	1:3.7 <i>1:10</i>
– $c-C_5H_6$; – $c-C_5H_5D$	1:1.8 ^b <i>1:1.2</i>	
– $c-C_5HD_5$; – $c-C_5D_6$		1.6:1 <i>1.2:1</i>

^aThe CID delay time was 100 ms and argon was the target gas. The relative intensities were determined under high resolution conditions (narrow-band mode). The expected ratios if complete isotope scrambling were to occur are presented in italics.

^bCorrected for the contributions from loss of $c-C_5H_4D^+$ radicals from $[FeCp_2]D^+$.

sented above as well, although they could also simply suggest that complete equivalence of the hydrogen atoms of both rings is not reached. However, if the latter is the case the isotope effects favoring H⁺ loss over D⁺ loss must be relatively large.

Thus, within this model, both CID and FTICR proton-transfer data require involvement of noniron-protonated ferrocene, even though it is a structure of higher energy than the metal-protonated form and has a transient existence.

Alternatively, the current FTICR deuteron/proton transfer and scrambling results as well as the data of Hunt and Sethi [6] might be explained on the basis of multiple proton transfers within the proton transfer intermediate. However, this model would be incompatible with the failure by Meot-Ner [8] to observe proton transfer from deuterated ferrocene to amine bases.

Conclusions

Low and high translational energy CID mass spectra have been recorded for $[\text{Fe}(\text{C}_5\text{H}_5)_2]\text{H}^+$, $[\text{Fe}(\text{C}_5\text{H}_5)_2]\text{D}^+$, and $[\text{Fe}(\text{C}_5\text{D}_5)_2]\text{H}^+$ using an FTICR mass spectrometer and a double-focusing mass spectrometer of reversed geometry. H⁺/D⁺ transfer and H/D exchange experiments were performed with these species as well. The results show that the hydrogen atoms in protonated ferrocene are rather mobile. We propose that the extensive hydrogen atom scrambling in the rings, and the hydrogen atom switching from one ring to the other, occur via a mechanism analogous to that suggested by Cunningham [20] for electrophilic substitution of ferrocenes (Scheme I). Therefore, the structure in which the added proton is bound to the ring, possibly via agostic interaction with the iron atom, must play a prominent role, which is supported by our earlier deductions based on the binding energy of $[\text{FeCp}_2]\text{H}^+$ to CH_3CN [7]. However, this cannot be taken as evidence that the ring-protonated form is the thermodynamically more stable isomer. Indeed, recent calculations of the interaction between ferrocene and H⁺ [24] show that the iron-protonated form is more stable than the ring-protonated form. This energetic difference very nicely accounts for the difference in behavior observed for FTICR and HPMS kinetic experiments and validates the data of Hunt and Sethi [6].

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