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Theoretical study of hydrogen exchange in the reaction of $FeC_5H_6^+$ with H_2

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Abstract

Density functional theory (B3LYP/6-31G*) has been used to study the mechanism of deuterium/hydrogen exchange which is known to occur from mass spectrometric studies of D_2 plus $FeC_5H_6^+$. The computational results are in accord with the currently accepted mechanism. There is a fast equilibrium between $FeC_5H_6^+$ and a hydrido-cyclopentadienyl iron complex ($HFeC_5H_5^+$) which is 3.2 kcal/mol less stable. The $FeC_5H_6^+$ complex or the $HFeC_5H_5^+$ complex can coordinate H_2 (14.2 or 10.4 kcal/mol exothermic, respectively). The dihydrogen–hydrogen exchange at the iron center has an activation enthalpy of only 7.1 kcal/mol. Slower exchange of the remaining five hydrogen is enabled by an exo-1,2-hydrogen migration in the cyclopentadiene ring of $FeC_5H_6^+$ (24.9 kcal/mol) or H_2–$FeC_5H_6^+$ (23.6 kcal/mol). (Int J Mass Spectrom 201 (2000) 143–149) © 2000 Elsevier Science B.V.

Keywords: Ab initio; H_2 exchange; Iron complex; Cyclopentadienyl ring; $FeC_5H_6^+$

1. Introduction

The interaction of dihydrogen with transition metal complexes has been of interest for many years [1–4]. Dihydrogen can add oxidatively to form a hydride complex or can retain a H–H bond and form a dihydrogen complex. Examples of each are well known as well as examples where dihydrogen and hydride ligands are both present on the same transition metal center [5–9]. The addition of dihydrogen to a transition metal can be the first step in catalytic hydrogenation. The elimination of molecular hydrogen from a transition metal center is an important step in many catalytic cycles.

Significant progress has been made in the study of H_2 binding to metal cations by Freiser and co-workers [10–16]. As an example of reversible H_2 coordination, D/H exchange exchange was probed in the $FeC_5H_6^+$ plus D_2 system with Fourier transform mass spectrometry and collision-induced dissociation [10,11,15–17]. The first exchange

$$FeC_5H_6^+ + D_2 \rightarrow FeC_5H_5D^+ + HD \qquad (1)$$

was found to be 30 times faster than for the second exchange

$$FeC_5H_5D^+ + D_2 \rightarrow FeC_5H_4D_2^+ + HD \qquad (2)$$

A mechanism was proposed which implied that a hydrido-cyclopentadienyl complex ($HFeC_5H_5^+$) was the active species. This species adds D_2 which, in

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turn, exchanges the substitutients on iron (D$_2$/H → DH/D). Elimination of HD gives the first exchange. A 1,2-hydrogen migration in the iron-cyclopentadiene cation allows the label to move from the unique methylene position to an adjacent position on the ring and enables another D/H exchange with a second molecule of D$_2$. The slow secondary exchange suggests that 1,2-migration is slower than the D$_2$/H → DH/D reaction on iron.

The current study was undertaken to investigate the $FeC_5H_6^+ + H_2$ potential energy surface (PES) with the aim to determine stationary points on the PES and to determine barrier heights between different species. The $FeC_5H_6^+$ cation is a well-known species in mass spectrometry and reactions are known with other coordinating molecules. An understanding of the reaction with H$_2$ is the first step in unraveling more complicated mechanisms.

2. Computational methods

All geometries were fully optimized [18] in the given symmetry by using density functional theory with the B3LYP choice of exchange and correlation functionals [19,20]. A 6-31G(d) basis set was used for carbon and hydrogen and a $(22s/16p/4d/1f)$ primitive basis set contracted to $(5s/4p/2d/1f)$ was used for iron [21]. This basis set contains two sets of Cartesian d functions (6 functions/iron) and one set of spherical f functions (7 functions/iron) with an 0.8 exponent. Vibrational frequencies were calculated at the B3LYP/6-31G(d) level to determine the nature of the stationary points and to make zero point, heat capacity, and entropy corrections.

Molecular plots of the relevant structures are given in Fig. 1. Tables of total energies (Hartrees) and zero-point energies (kcal/mol) are given in Table 1.

3. Results and discussion

Density functional calculations appear to be very well suited for computing transitional metal complexes where the charge and multiplicity of the transition metal changes. Russoi et al. [22] computed the ionization energies and electronic state separations in transition metal atoms and cations and found that the results were comparable to calculations which included electron correlation at the quadratic configuration interaction single double (triple) [QCISD(T)] level. Hybrid functionals such as B3LYP, which includes a certain fraction of Hartree-Fock exchange, are able to reproduce bond dissocations of metal hydrides with remarkable accuracy. Barone et al. [23] have used the B3LYP method to calculate a bond energy of 56.5 kcal/mol for the $^5\Delta$ state of FeH$^+$ compared to an experimental value of 48.8 kcal/mol. Wang and Schwarz [24] have recently found that density functional theory produces reasonable results for metal dihalides, including FeF$_2$ and FeCl$_2$. Glukhovtsev et al. [25] carried out a survey of iron-containing compounds using B3LYP with a effective core potential for the core electrons of iron. The

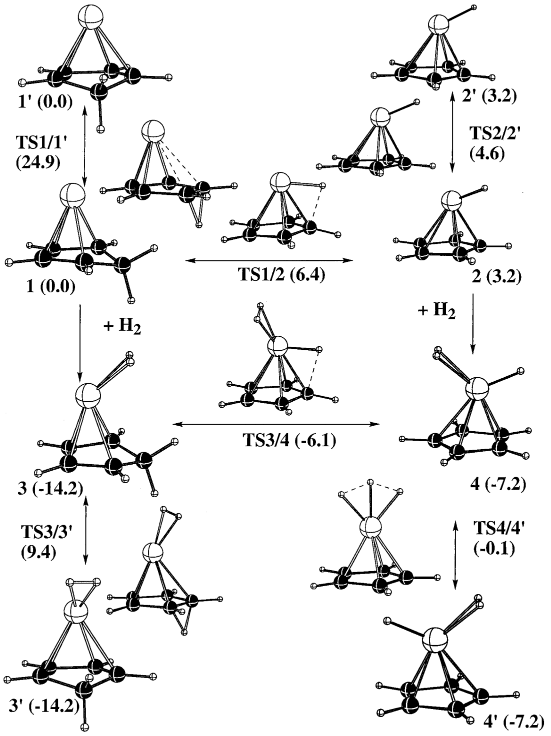

Fig. 1. Molecular plots of species optimized at the B3LYP/6-31G* level. Numbers in parentheses are enthalpies at 298 K relative to $FeC_5H_6^+$ ($^4A''$) + H$_2$.

Table 1
Total energies (Hartrees), zero-point energies (kcal/mol), heat capacity corrections to 298 K (kcal/mol) and entropies (cal mol/K)

	PG	State	B3LYP/6-31G (d)[a]	ZPE (NIF)[b]	Cp corr	Entropy
H	K_h	^2S	−0.500 27 (0.75)	0.00	1.48	27.42[c]
H_2	$D_{\infty h}$	$^1\Sigma^+$	−1.17548	6.37 (0)	2.07	31.13
C_5H_5	C_{2v}	$^2A_2$	−193.462 32 (0.77)	49.04 (1)	3.07	65.82
C_5H_6	C_{2v}	$^1A_1$	−194.101 06	58.29 (0)	3.19	65.31
C_5H_6–TS	C_s	$^1A'$	−194.054 97	56.24 (1)	2.98	65.50
Fe^+	K_h	^6D	−1263.237 44 (8.75)	0.00	1.48	43.14[c]
Fe^+ (quartet)[d]	K_h		−1263.213 74 (4.63)	0.00	1.48	43.14[c]
FeH^+	$C_{\infty v}$	$^5\Delta$	−1263.827 70 (6.02)	2.73 (0)	2.07	49.99
$FeC_5H_5^+$	C_s	$^5A''$	−1456.840 87 (6.01)	52.17 (0)	3.91	78.41
$FeC_5H_5^+$	C_s	$^5A'$	−1456.840 89 (6.01)	52.03 (1)	3.44	74.88
$FeC_5H_5^+$	C_1	^5A	−1456.840 92 (6.01)	52.30 (0)	3.72	77.26
$FeC_5H_6^+$ (**1**)	C_s	$^4A''$	−1457.424 28 (3.90)	59.06 (0)	4.02	78.04
$FeC_5H_6^+$	C_s	$^6A''$	−1457.405 28 (8.75)	58.90 (0)	4.34	81.94
$HFeC_5H_5^+$ (**2**)	C_s	$^4A''$	−1457.415 17 (3.90)	56.21 (0)	4.30	79.48
$HFeC_5H_5^+$	C_{5v}	$^6A_1$	−1457.414 56 (8.76)	56.25 (0)	4.23	79.72
TS1/2	C_1	^4A	−1457.409 56 (3.86)	56.22 (1)	3.97	78.26
TS1/1′	C_s	$^4A'$	−1457.381 10 (3.86)	56.83 (1)	3.99	78.57
TS2/2′	C_s	$^4A'$	−1457.413 79 (3.90)	55.44 (1)	4.18	79.08
H_2–$FeC_5H_6^+$ (**3**)	C_s	$^4A''$	−1458.627 04 (3.82)	69.10 (0)	4.98	89.28
H_2–$FeC_5H_6^+$ (**3x**)	C_s	$^4A'$	−1458.616 22 (3.84)	68.14 (0)	5.16	86.00
H_2–$HFeC_5H_5^+$ (**4**)	C_s	$^4A''$	−1458.611 00 (3.85)	66.20 (0)	5.13	84.68
H_2–$HFeC_5H_5^+$ (**4x**)	C_s	$^4A'$	−1458.610 79 (3.85)	66.86 (0)	4.89	82.93
TS3/4	C_1	^4A	−1458.608 67 (3.84)	66.45 (1)	4.56	80.72
TS3/3′	C_1	^4A	−1458.584 99 (3.78)	66.99 (1)	4.65	82.18
TS4/4′	C_s	$^4A''$	−1458.597 09 (3.82)	65.12 (1)	4.73	82.87

[a] Values in parentheses are unprojected spin-squared values.
[b] Zero-point energy with number of imaginary frequencies (NIF) in parentheses.
[c] Entropies for H and Fe^+ are taken from experiment [37].
[d] Not a pure state.

B3LYP method has also been applied to the study [26] of gas-phase thermochemistry of iron oxides.

The B3LYP/6-31G* computational method used in the present study was tested against experiment for iron-containing compounds in Table 2 to see whether binding enthalpies can be reproduced. It has previ-

Table 2
Comparison of calculated and experimental binding enthalpies (kcal/mol) at 0 K

	Calculated binding enthalpy		
Fragments → Product	B3LYP/6-31G (d)	+ZPE	Expt.[a]
$Fe^+ + C_5H_6 \rightarrow$ **1**	53.8	53.0	55 ± 5[b]
$Fe^+ + C_5H_5 \rightarrow FeC_5H_5^+$	88.6	85.3	88 ± 7
$FeH^+ + C_5H_5 \rightarrow$ **2**	78.5	74.1	
$H + Fe^+ \rightarrow FeH^+$	56.5	53.8	48.8 ± 1.4
$H + C_5H_5 \rightarrow C_5H_6$	86.9	77.7	78.0 ± 1.4
$H + FeC_5H_5^+ \rightarrow$ **1**	52.1	45.3	46 ± 5
Fe^+ (^6D) $\rightarrow$ Fe^+ (quartet)	14.9	14.9	5.8[c]

[a] Taken from [31] except where noted.
[b] See [15].
[c] The Fe^+ ($^6D \rightarrow {}^4F$) j-averaged values taken from [38].

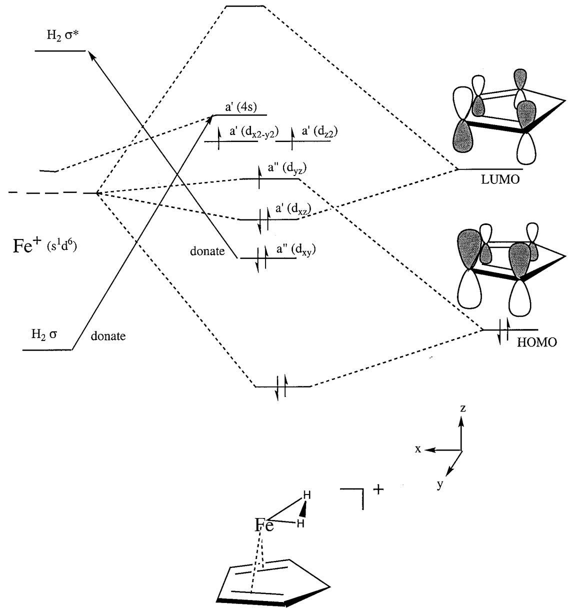

Fig. 2. Molecular orbital interaction diagram for the interaction of Fe^+ and H_2–Fe^+ with C_5H_6.

Table 3
Natural population charges at the B3LYP/6-31G* level for $FeC_5H_6^+$ and H_2–$FeC_5H_6^+$

Fe orbital population[a]	$FeC_5H_6^+$	H_2–$FeC_5H_6^+$
$4s$	0.21	0.32
$3d_{x2-y2}$	1.03	0.99
$3d_{z2}$	1.00	1.02
$3d_{yz}$	1.11	1.21
$3d_{xz}$	1.51	1.64
$3d_{xy}$	1.85	1.58
Total	6.71	6.76

[a] For coordinate system see Fig. 2.

ously been pointed out [27] that the B3LYP method with an all-electron basis set fails to reproduce the ^6D–^4F splitting in Fe^+. Since the H_2/D_2 exchange reaction occurs on the quartet potential energy surface, errors in multiplicity separations are not expected to affect the results. Indeed, except for the FeH^+ binding enthalpy, the average difference between experiment and theory for bond energies is less than 2 kcal/mol (Table 2).

It is noteworthy to mention two theoretical studies of gas phase iron-containing cations. Musaev and Morokuma [28] carried out a multireference-complete active space self-consistent field (MR-CASSCF) study of the addition of H_2 to $FeCH_2^+$, whereas Koch and co-workers [29] studied the addition of Fe^+ to the C–C and C–H bonds of ethane.

The CH_2 group interacts with the Fe^+ cation to form a $^4B_2$ state. If the CH_2 group is considered as a carbene, there is some similarity to the interaction diagram of Fe^+ with C_5H_6 (Fig. 2). The out-of-plane acceptor orbital on CH_2 interacts with (and stabilizes) the d_{xz} orbital, in a similar fashion as the highest occupied molecular orbital (HOMO) of C_5H_6. On the other hand, the lone pair of CH_2 points directly toward the Fe atom, unlike the HOMO of C_5H_6.

The $FeCH_2^+$ ($^4B_2$) and $FeC_5H_6^+$ ($^4A''$) complexes both have two doubly occupied d orbitals (d_{xy} and d_{xz}) which help coordinate dihydrogen by donating electrons into the H_2 σ^* orbital. In the case of H_2–$FeCH_2^+$, the $d_{xz} \rightarrow \sigma^*$ is more important as judged by the T-shaped coordination. In H_2–$FeC_5H_6^+$, the $d_{xy} \rightarrow \sigma^*$ interaction is more important as judged by the geometry (H_2 is attached to the side) and Natural Bond Population (NBO) analysis [30]. The $4s$ orbital of Fe is a very strong acceptor orbital. The NBO population analysis of the B3LYP/6-31G* wave function is presented in Table 3 for the d orbitals of $FeC_5H_6^+$ ($^4A''$) and H_2–$FeC_5H_6^+$ ($^4A''$). Upon H_2 coordination, the $4s$ orbital acquires 0.11 e^- whereas the d_{xy} orbital loses 0.17 e^-. The binding energy of H_2 to $FeCH_2^+$ ($^4B_2$), calculated at the MR-SDCI//CASSCF (9/10) level, is 5.8 kcal/mol [28], which is substantially less than the 14.2 kcal/mol binding enthalpy of H_2 to $FeC_5H_6^+$ ($^4A''$).

In a density functional theory (DFT) study of Fe^+-mediated C–C and C–H bond activations, Holthausen et al. [29] calculated the $FeC_2H_4^+$ complex ($^4B_2$) as well as the H_2–$FeC_2H_4^+$ complex. At the B3LYP level, dihydrogen is bound by 13 kcal/mol.

Bauschlicher and Sodupe [31,32] have computed the $FeC_5H_5^+$ and $FeC_5H_6^+$ cations at the modified coupled-pair functional (MCPF) level. They found the $^5E_2$ state to be lowest in energy for $FeC_5H_5^+$ with a binding energy of 77 ± 10 kcal/mol [31]. Because the Jahn-Teller distortion in the symmetrical C_{5v} structure was expected to be small, lower symmetry

Table 4
Comparison of quartet–sextet relative energies (kcal/mol) for $FeC_5H_6^+$ and $HFeC_5H_5^+$

	MCPF[a]	DFT[a]	B3LYP/6-31G*	+ZPC
$FeC_5H_6^+$ (quartet)	0.0	0.0	0.0	0.0
$FeC_5H_6^+$ (sextet)	1.9	17.5	11.9	11.7
$HFeC_5H_5^+$ (quartet)	8.3	13.8	5.7	2.9
$HFeC_5H_5^+$ (sextet)	6.6	17.1	6.1	3.3

[a] See [32].

species were not optimized. In the present study, the global minimum is a C_1 structure with a 0.13 Å difference between the longest and shortest Fe–C distance and 0.02 Å between the longest and shortest C–C distance. However, $^4A'$ and $^4A''$ stationary structures are less than 0.1 kcal/mol higher in energy (Table 1).

For $FeC_5H_6^+$ and $HFeC_5H_5^+$, the results obtained here are generally in good agreement with Bauschlicher and Sodupe [32]. The geometry of quartet and sextet states of $FeC_5H_6^+$ are very similar. In the $FeC_5H_6^+$ sextet, the Fe–C distances are an average of 0.338 Å longer than in the $FeC_5H_6^+$ quartet due to the reduced bonding between Fe^+ and C_5H_6. The Fe-hydride is aligned along the C_5 axis in the $HFeC_5H_5^+$ sextet and bends over and bisects the C–Fe–C angle in the $HFeC_5H_5^+$ quartet. In the Bauschlicher and Sodupe study [32], different Fe^+ reference states were used (^6D or ^4F) depending on whether the iron d-orbital population was closer to six or seven electrons. In the present study, multiplicity differences were computed directly (i.e. not corrected for errors in the computed ^6D–^4F separation of Fe^+). However, if corrections were made, the sextet states would be raised (relative to the quartet state) by almost 10 kcal/mol which would reduce the likelihood that the sextet potential energy surface is involved the H_2/D_2 exchange reaction. A comparison of the quartet and sextet states of $FeC_5H_6^+$ and $HFeC_5H_5^+$ is made in Table 4.

The first step in the mechanism is to consider the interconversion of $FeC_5H_6^+$ (**1**) and $HFeC_5H_5^+$ (**2**). The activation enthalpy is 6.4 kcal/mol in the forward direction and 3.2 kcal/mol in the reverse direction (Table 5 and Fig. 3). The transferring hydrogen is 1.577 Å from iron and 1.671 Å from carbon. The transition structure is close to C_s symmetry which means that the movement of the metal-hydride to assume a bisected orientation occurs after the transition structure.

It is interesting to point out that the $FeC_5H_6^+$ to $HFeC_5H_5^+$ stability difference is relevant to the site of metal/ring protonation in ferrocene (i.e. Cp–$FeC_5H_6^+$ or Cp–$HFeC_5H_5^+$). The latest results at the DFT level indicate that the two forms have equal stability [33] or that Cp–$FeC_5H_6^+$ is 3 kcal/mol more stable [34] than

Table 5
Energies, enthalpies (298 K), and free energies (298 K) (kcal/mol) for species on the $FeC_5H_6^+$ ($^4A''$) + H_2 surface

	B3LYP/6-31G (d)	+ZPE	ΔH (298 K)	ΔG (298 K)
$FeC_5H_6^+$ (**1**) + H_2	0.0	0.0	0.0	0.0
$HFeC_5H_5^+$ (**2**) + H_2	5.7	2.9	3.2	2.8
H_2–$FeC_5H_6^+$ (**3**)	−17.1	−13.1	−14.2	−8.3
H_2–$HFeC_5H_5^+$ (**4**)	−7.0	−6.2	−7.2	0.1
TS1/1′ + H_2	27.1	24.9	24.9	24.7
TS1/2 + H_2	9.2	6.4	6.4	6.3
TS2/2′ + H_2	6.6	4.4	4.6	4.3
TS3/4	−5.6	−4.6	−6.1	2.4
TS3/3′	9.2	10.8	9.4	18.6
TS4/4′	1.6	1.3	−0.1	7.7

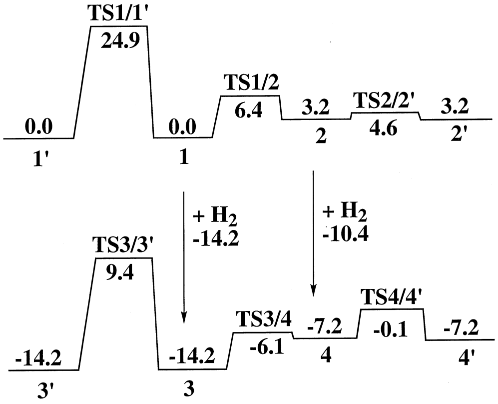

Fig. 3. Relative enthalpies for the $FeC_5H_6^+$ + H_2 surface at the B3LYP/6-31G*//B3LYP/6-31G* + ZPC level with heat capacity corrections to 298 K.

Cp–$HFeC_5H_5^+$. The latter difference is very close to the enthalpic difference between $FeC_5H_6^+$ and $HFeC_5H_5^+$ (3.2 kcal/mol) calculated in this study.

The H_2–$FeC_5H_6^+$ complex, which is 14.2 kcal/mol exothermic with respect to H_2 and $FeC_5H_6^+$, has an 8.1 kcal/mol activation barrier to form the H_2–$HFeC_5H_5^+$ complex. The complex, in turn, has a 7.1 kcal/mol activation barrier to form a transition structure where two of the H–H distances become equivalent, thereby exchanging a hydrogen between the coordinated H_2 and the metal hydride. A very similar transition structure was found by Bayse et al. [35] in the exchange of H_2 and H at tungsten in the complex H_2–$HW(H)_3(PH_3)C_5H_5^+$. Even though their system is different from H_2–$HFeC_5H_5^+$, they calculate a similar activation energy of 7.0 kcal/mol at the CCSD//MP2 (second order Møller-Plesset) level.

Elimination of H_2 and conversion of $HFeC_5H_5^+$ to $FeC_5H_6^+$ completes the transformation where one hydrogen is exchanged between H_2 and the endo hydrogen of the coordinated cyclopentadiene group. This mechanism explains the first exchange between D_2 and $FeC_5H_6^+$ in the mass spectrometer.

The mechanism of additional D/H exchanges is thought to take place by exo 1,2-hydrogen migration in the complex. We computed two alternative pathways for this process. The 1,2-migration can take place before H_2 is coordinated (i.e. in $FeC_5H_6^+$) or after H_2 coordination (i.e. in H_2–$FeC_5H_6^+$). As it turns out, the computed activation barrier for 1,2-hydrogen migration is not sensitive to the presence of Fe^+ or H_2–Fe^+. In the free ligand, the activation barrier is 27.0 kcal/mol (compared to an experimental [36] value of 23.6 kcal/mol). For $FeC_5H_6^+$, the barrier is 24.9 kcal/mol, whereas in the H_2–$FeC_5H_6^+$ complex the barrier is 23.6 kcal/mol. Of course, the actual route taken will depend on the relative concentrations of C_5H_6 (probably very low), $FeC_5H_6^+$ and H_2–$FeC_5H_6^+$. The 1,2-hydrogen migration has a much higher activation barrier than the H_2/H exchange which explains why the first D/H exchange in $FeC_5H_6^+$ is faster than the remaining five D/H exchanges. The PES is summerized in Fig. 3.

4. Conclusions

A computational study at the B3LYP/6-31G* level on the addition of H_2 to $FeC_5H_6^+$ supports the previously proposed mechanism and rationalizes the two rates of D/H exchange in the mass spectrometric studies. The ring- and metal-protonated forms of FeC_5H_5 ($FeC_5H_6^+$ and $HFeC_5H_5^+$) are predicted to have very similar enthalpies and to interconvert readily. Dihydrogen is predicted to bind to $FeC_5H_6^+$ with a binding enthalpy of 14.2 kcal/mol and to $HFeC_5H_5^+$ with a binding enthalpy of 10.4 kcal/mol. The interchange of a H_2 and H in H_2–$HFeC_5H_5^+$ through a C_s-symmetry transition structure with two equal H–H distances occurs with an activation enthalpy of 8.1 kcal/mol. The rate-determining step in the exchange of hydrogens in $FeC_5H_6^+$ is the 1,2-hydrogen migration. The predicted enthalpic barrier for the exo 1,2-migration in the cyclopentadiene ring is 24.9 kcal/mol in $FeC_5H_6^+$ and 23.6 kcal/mol in H_2–$HFeC_5H_5^+$.

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