

Catalytic Dehydrogenation of Liquid Organic Hydrogen Carrier Model Compounds by CpM^+ ($\text{M}=\text{Fe}, \text{Co}, \text{Ni}$) in the Gas Phase

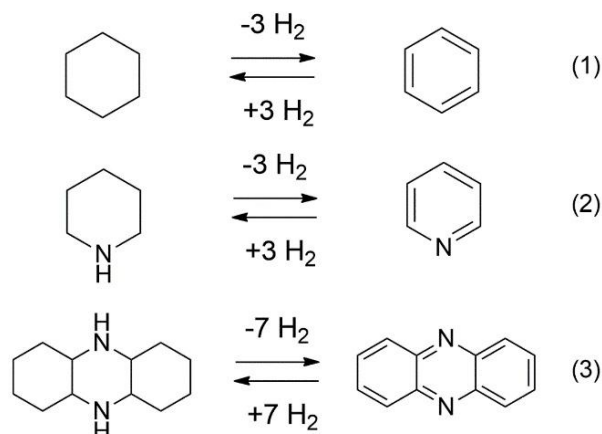
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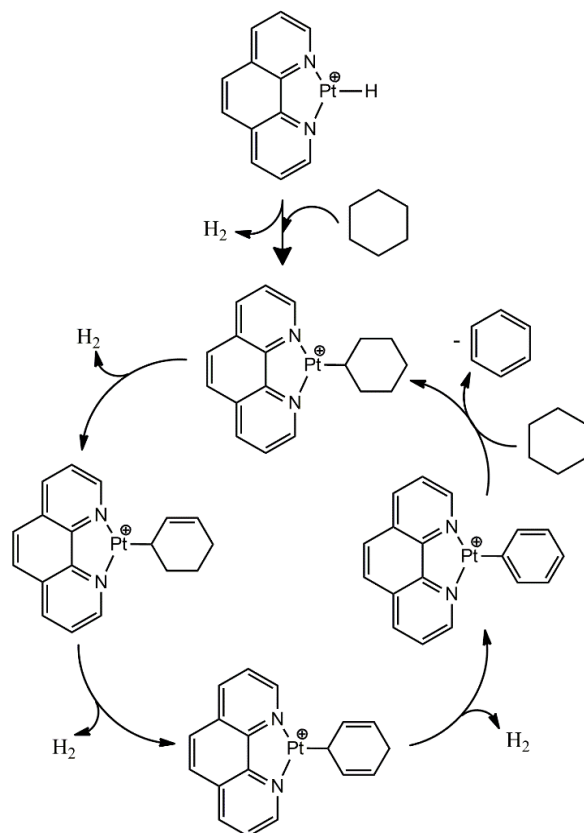
ABSTRACT: Although there is much interest in developing liquid organic hydrogen carriers (LOHCs) and new metal catalysts to release hydrogen on demand for application in energy generation, few studies have provided mechanistic insights into the crucial metal-catalyzed dehydrogenation reactions. Here we use multistage mass spectrometry experiments and DFT calculations to examine the dehydrogenation of the LOHC model compounds cyclohexane, pyrrolidine, N-methylpyrrolidine and piperidine by the half-sandwich cyclopentadienyl cations, $[\text{CpM}]^+$ ($\text{M} = \text{Fe}, \text{Co}, \text{and Ni}$). The $[\text{CpM}]^+$ ions were generated via collision-induced dissociation (CID) of precursor ions generated via electrospray ionization (ESI) of solutions of the compounds $\text{CpFe}(\text{CO})_2\text{I}$, Cp_2Ni , and Cp_2Co . The $[\text{CpFe}]^+$ ion was found to catalyze triple dehydrogenation of cyclohexane to benzene via a combination of ion-molecule reactions (IMR) and CID experiments. Reactions of $[\text{CpM}]^+$ ($\text{M}=\text{Co}, \text{Ni}$) were found to be more complex as dehydrogenation was accompanied by significant cyclohexane ring cleavage. Reactions of $[\text{CpFe}]^+$ with the N-heterocyclic model compounds showed catalytic double dehydrogenation of pyrrolidine/N-methylpyrrolidine and triple dehydrogenation of piperidine. However, multiple side reactions were found, especially in the case of N-methylpyrrolidine and piperidine. They included proton transfer/hydride abstraction to/from the LOHC model methyl loss from the N-methylpyrrolidine complex, and NH_2/NH_3 extrusion from the piperidine complex. DFT calculations shed light on the structure of the key intermediates in all these systems.

INTRODUCTION

The use of hydrogen gas as an environmentally clean energy source presents a unique set of challenges in transportation and storage. Thus, there has been considerable interest in developing liquid organic hydrogen carriers (LOHCs) as safe hydrogen storage alternatives. Multiple reviews¹⁻⁵ outline stable liquid and solid substrates (shown in eqs. 1-3) that have favorable H_2 capacity per system (measured in wt%) for the transport of hydrogen, in accord with the Department of Energy guidelines on hydrogen driven transport methods.⁶ Cyclic alkanes and N-heterocyclic species are of special interest due to their stability and high energy density. Cycloalkane LOHC's such as cyclohexane and benzene are good models for mechanistic studies.^{7,8} Others that are viable on the industrial scale include perhydro-dibenzyl toluene/dibenzyl toluene^{9,10} and methylcyclohexane/toluene^{11,12}. Although the cyclohexane/benzene system (eq. 1) is not very useful in the context of scaling up owing to the carcinogenic properties of benzene, it is often used as a model due to its relatively easy access to mechanistic studies and has been investigated in the context of reactant/product separation.^{13,14} N-Heterocycle¹⁵ couples such as piperidine/pyridine (eq. 2, and derivatives)¹⁶ octahydroindole/indole,¹⁷ and perhydrophenazine/phenazine¹⁸ (eq. 3) are all viable substrates for stable hydrogen storage. N-heterocycles have the added benefits of relatively better biodegradability, low volatility, and more efficient hydrogen liberation.¹⁵

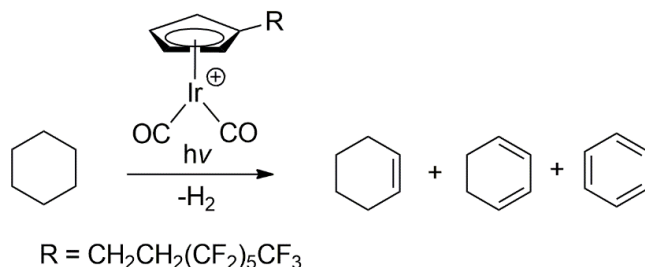


A key requirement of these LOHC systems is the need for dehydrogenation catalysts to liberate hydrogen on demand and much work has been carried out to develop both homogeneous and heterogeneous catalysts.^{10,19–22} While heterogeneous catalysts seem to hold most promise for large-scale dehydrogenation, the use of homogeneous catalysts offer advantages in studying reaction mechanisms and characterizing reactive intermediate. Multiple groups have investigated molecular catalysts involving the dehydrogenation of not only homocyclic compounds, but N-heterocycles as well. For example, our recent work showed that the [(phen)Pt(H)]⁺ cationic complex (where phen = 1,10-phenanthroline) can activate and catalytically dehydrogenate cyclohexane via eq. 1 in the gas phase, as shown in Scheme 1.²³ Søgaard *et al.* have also shown the dehydrogenation of indole derivatives in biphasic (molten salt/organic) conditions with Crabtree's iridium-based catalyst.²¹ Other literature reports often include sacrificial additives similar to work done by Khaskin *et al.* on the dehydrogenation of cyclohexane by a dimethylplatinum(II) complex supported with an anionic dimethyl-di(4-*tert*-butyl-2-pyridyl)borate ligand in the presence of *tert*-butylethene.²⁴



Scheme 1. Catalytic cycle for C-H activation/dehydrogenation of cyclohexane by [(phen)Pt(H)]⁺.

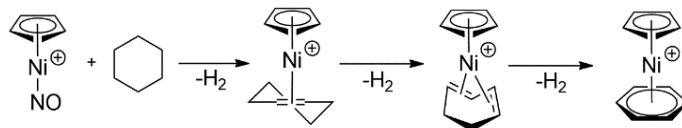
Among a vast array of available metal complexes, cyclopentadienyl (Cp)-ligated species have shown particular promise as dehydrogenation catalysts. For instance, $\text{CpRh}(\text{L}^1\text{L}^2)$ ($\text{L}^1 = \text{PMe}_3$, $\text{L}^2 = [\text{Me}_2\text{pz}]^-$ ($[\text{Me}_2\text{pz}]^- = 3,5$ -dimethylpyrazolide), or $\text{L}^1\sim\text{L}^2 = [\text{Me}_2\text{pz}\cdot\text{H}\cdot\text{pzMe}_2]^+$) were shown to be efficient catalysts to facilitate hydrogen production from aminoboranes.²⁵ The complex $\text{Cp}^*\text{Ir}(\text{CO})_2$ showed catalytic activity under UV light to dehydrogenate cyclohexane into a mixture of cyclohexene, cyclohexadiene, and benzene (Scheme 2).²⁶



Scheme 2. Dehydrogenation of cyclohexane by the $\text{Cp}^*\text{Ir}(\text{CO})_2$ catalyst.

A key research front in the search for new LOHC dehydrogenation catalysts involves the search for metal complexes containing less expensive, earth abundant metals such as iron, cobalt, and nickel. Thus, we were interested in investigating the ability of $\text{CpM}(\text{L})$ -type complexes to dehydrogenate LOHCs. Indeed, scattered literature reports suggest that such complexes may hold promise. For example, the reactivity of $[\text{CpM}]^+$ ($\text{M} = \text{Ni}, \text{Co}, \text{Fe}$) has been studied in the gas phase. Goll and Müller²⁷ showed that $[\text{CpNi}(\text{NO})]^+$ facilitated dehydrogenation and other C-H activation pathways of both cyclic and linear alkanes. In a reaction with cyclohexane, it formed cyclohexene, cyclohexadiene, and benzene complexes (Scheme 3). Innorta and Torroni²⁸ also examined reactions of $[\text{CpNi}]^+$ and $[\text{CpCo}]^+$ with propane which resulted in dehydrogenation without the production of methane as a cracking product. Ridge and co-workers studied reactions of $[\text{CpCo}]^+$ and $[\text{CpNi}]^+$ with multiple alkanes and found that they promote their dehydrogenation and cracking.^{29,30} All three $[\text{CpM}]^+$ ($\text{M} = \text{Ni}, \text{Co}, \text{Fe}$) were shown to dehydrogenate silicon-substituted cyclohexanes resulting in elimination of one, two, and three hydrogen molecules in various proportions.³¹ Jacobson and Freiser showed that $[\text{CpCo}]^+$ promoted elimination of one and two hydrogen molecules from cyclohexane, while reaction with cyclohexene resulted in predominant loss of two hydrogen molecules, thus forming $[\text{CpCo}(\text{benzene})]^+$.³¹ Interestingly, not only can the final product, $[\text{CpM}(\text{benzene})]^+$, be directly obtained by the direct gas-phase reaction of $[\text{CpM}]^+$ with benzene,³² in the case of $\text{M} = \text{Fe}$ it has also been isolated³³ and its crystal structure elucidated.³⁴

Gas-phase studies offer advantages for the evaluation of possible homogeneous dehydrogenation catalysts of LOHCs due to the relatively high throughput capabilities and high sensitivity (low sample requirements) of mass



Scheme 3. Sequential dehydrogenation of cyclohexane in $[\text{CpNi}]^+$ complexes.

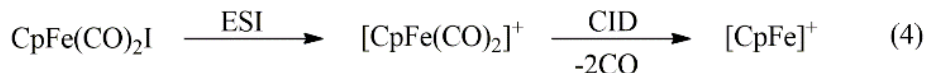
spectrometry (MS)-based techniques. Gas-phase reactivity allows for fast and facile mechanistic interpretations as well as insight to common molecular catalysis hurdles such as side reactions. Ion-molecule reactions have been an integral part of such studies since they probe the fundamental reactivity of any cationic or anionic catalyst precursor or intermediate, giving direct information on both the desired dehydrogenation reactivity as well as side reactions that result in catalyst poisoning and/or undesirable degradation of the LOHC. In combination with high-level computational calculations, this approach provides valuable mechanistic information that may allow the design of catalysts from the ground up.³⁵

Most of the prior gas-phase studies on $[\text{CpM}]^+$ systems were carried out decades ago prior to the advent of electrospray ionization and the development of sophisticated ion trap mass spectrometers with multistage tandem mass spectrometry capabilities. Moreover, they lack the complementary information provided by high-level theoretical calculations. Thus, in this work we probe the mechanism and structure of key intermediates in the gas-phase dehydrogenation of cyclohexane and several other LOHC models by $[\text{CpM}]^+$ ($\text{M} = \text{Ni}, \text{Co}, \text{Fe}$), with the goal of answering the following questions: i) whether they can perform complete dehydrogenation, and ii) whether this process can be made catalytic. In addition to being potential homogeneous catalysts for LOHC dehydrogenation, these $[\text{CpM}]^+$ systems also serve as suitable models for heterogeneous catalysis by the way of the accessible metal ion above the plane of the cyclopentadienyl ligand mimicking a metal atom supported on carbon (graphene) surface (i.e., single atom catalysis).³⁶

RESULTS AND DISCUSSION

(A) Generation of $[\text{CpM}]^+$ (M= Fe, Co, Ni) species

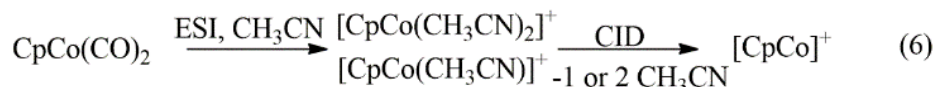
Electrospray ionization of $\text{CpFe}(\text{CO})_2\text{I}$ dissolved in MeOH led to production of $[\text{CpFe}(\text{CO})_2]^+$ which underwent fragmentation under collisional activation to produce $[\text{CpFe}]^+$ (eq. 4; Fig S1). Although this method was straightforward, the intensities of starting ions were unfavorably low.



Similarly, in respect to the ionization parameters, the electrospray of $\text{CpFe}(\text{CO})_2\text{I}$ dissolved in CH_3CN led to the production of $[\text{CpFe}(\text{CH}_3\text{CN})]^+$ and $[\text{CpFe}(\text{CH}_3\text{CN})_2]^+$ which are fragmented under collision-induced dissociation (CID) to produce $[\text{CpFe}]^+$ (eq. 5; Fig S2):



In the same way as the iron complex, $[\text{CpCo}]^+$ could be isolated from collisionally activated acetonitrile adducts $[\text{CpCo}(\text{CH}_3\text{CN})]^+$ and $[\text{CpCo}(\text{CH}_3\text{CN})_2]^+$ (eq 6; Fig S3):



Nickelocene dissolved in MeOH can be oxidized under ESI conditions leading to the respective cationic species that can be fragmented by CID to yield $[\text{CpNi}]^+$, albeit in low abundance due to the energetically unfavorable loss of a radical cyclopentadienyl ligand (eq. 7; Fig S4).



In all the gas-phase studies described below, the cationic complex with the most abundant metal isotope was mass selected (i.e. ^{56}Fe , ^{59}Co and ^{58}Ni).

In the presentation of computational results (Sections D, E, F), the formal electron count in the valence shell of the metal is presented (as MVE = metal valence electrons), typically 12, 14, 16, 18, and occasionally 19 or 20, and the equations above illustrate this procedure, e.g. $\text{CpFe}(\text{CO})_2\text{I}$: Fe^{2+} (d^6) + Cp^- (6e), $2'\text{CO}'$ (4e) + I^- (2e) = 18.

(B) Reaction of $[\text{CpM}]^+$ (M= Fe, Co, Ni) species with cyclohexane

The cyclopentadienyliron cation, $[\text{CpFe}]^+$ (**1-Fe**, m/z 121), reacted rapidly with cyclohexane forming the adduct, $[\text{CpFe}(\text{C}_6\text{H}_{12})]^+$ (**2-Fe**, m/z 205), along with a small quantity of the doubly dehydrogenated adduct, $[\text{CpFe}(\text{C}_6\text{H}_8)]^+$ (**4-Fe**, m/z 201), as shown in Fig. 1a. In addition, **1-Fe** reacts with adventitious water present in the ion trap forming an adduct at m/z 139. The cyclohexane adduct **2-Fe** upon collisional activation produces the adducts with cyclohexadiene (corresponding to the loss of two H_2 molecules), **4-Fe**, and the benzene adduct, $[\text{CpFe}(\text{C}_6\text{H}_6)]^+$ (**5-Fe**, m/z 199), the result of three H_2 losses, as can be seen in Fig. 1b. The loss of the whole molecule of cyclohexane leading back to $[\text{CpFe}]^+$ (m/z 121) is also seen. Interestingly, the single dehydrogenation adduct at m/z 203 (**3-Fe**) is present only in a very small abundance. Fragmentation of the resulting **4-Fe** species leads to the benzene adduct **5-Fe** as the only product (Fig. 1c). Its further fragmentation (MS^6) produces the original $[\text{CpFe}]^+$ species (**1-Fe**, m/z 121) as shown in Fig. 1d, but this stage requires very high collision energy and the resulting **1-Fe** reacts rapidly with cyclohexane or water. However, by re-forming the $[\text{CpFe}]^+$ species we show that the catalytic cycle for the dehydrogenation of cyclohexane to benzene (eq. 1) is closed. The summary of these reactions is shown in Scheme 4.

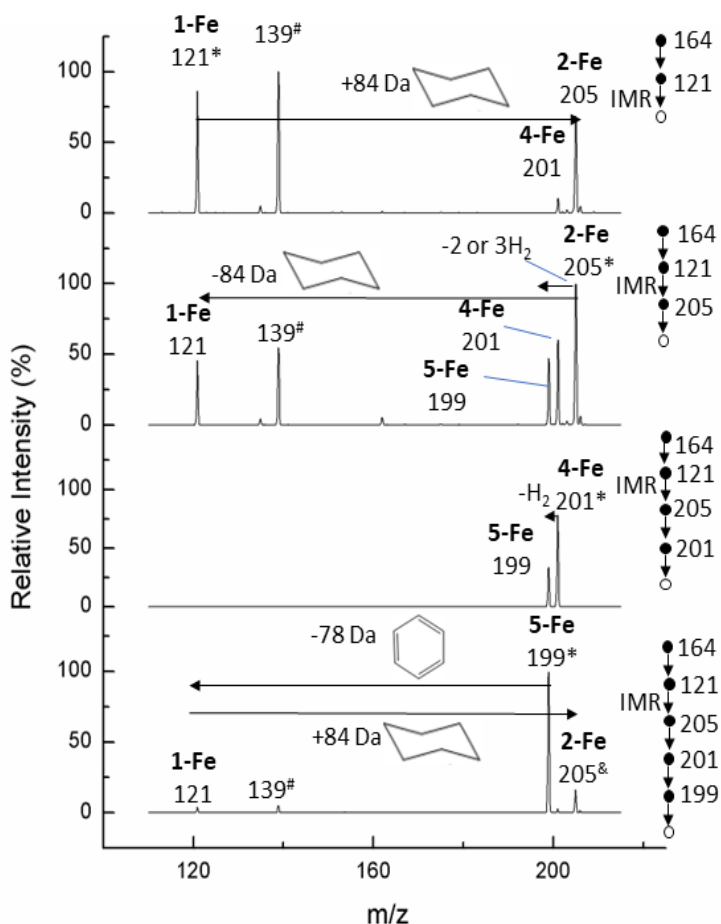
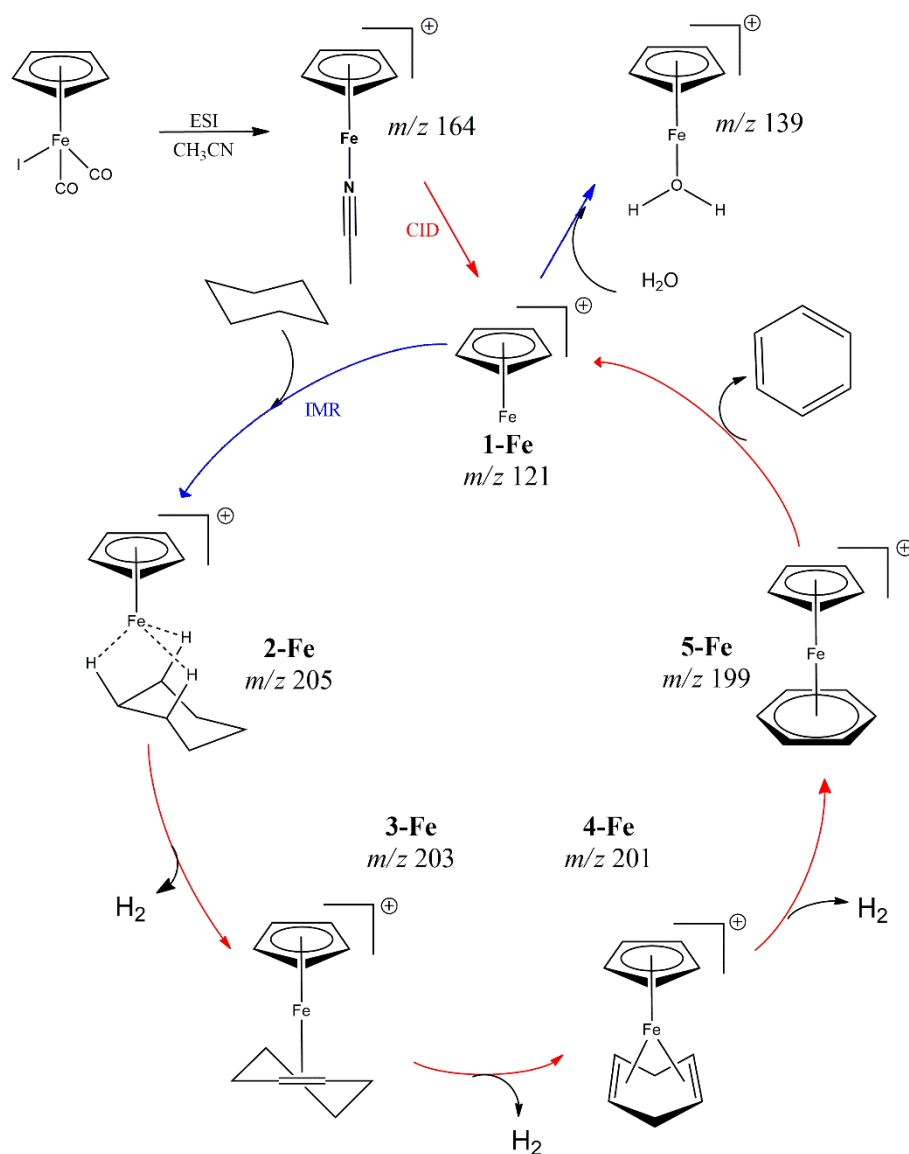


Figure 1. a) IMR of **1-Fe** with cyclohexane (isolation width 2 m/z ; reaction time 30 ms); b) CID of **2-Fe** (isolation width 2 m/z ; fragmentation NCE 12); c) CID of **4-Fe** (isolation width 2 m/z ; fragmentation NCE 15); d) CID of **5-Fe** (isolation width 2 m/z ; fragmentation NCE 20); # indicates water adduct; & denotes **2-Fe** peak formed by IMR of **1-Fe** with cyclohexane present in the ion trap during CID.

The cyclopentadienylnickel cation, $[\text{CpNi}]^+$ (**1-Ni**, m/z 123) reacted with cyclohexane readily to produce $[\text{CpNi}(\text{C}_6\text{H}_{12})]^+$ (**2-Ni**, m/z 207) and $[\text{CpNi}(\text{C}_6\text{H}_{10})]^+$ (**3-Ni**, m/z 205) with the first dehydrogenation product being the most abundant product (Fig. S5). Similar to the iron complex, **1-Ni** reacted with ambient water in the ion trap to form an adduct at m/z 141. **3-Ni** isolated from the IMR, when collisionally activated not only produced the doubly and triply dehydrogenated species $[\text{CpNi}(\text{C}_6\text{H}_8)]^+$ (**4-Ni**, m/z 203) and $[\text{5-Ni}, \text{CpNi}(\text{C}_6\text{H}_6)]^+$ (m/z 201) in small amounts, but also produced fragment ions consistent with cyclohexene ring breaking products (Fig. S5). Those include $[\text{CpNi}(\text{C}_3\text{H}_6)]^+$ (m/z 165) and $[\text{CpNi}(\text{C}_4\text{H}_6)]^+$ (m/z 177) corresponding to the neutral losses of undetermined fragment(s).³⁷ This observation is consistent with the work of Goll and Müller²⁷ as well as our recent work²³ showing that Ni(II) complexes can extrude smaller hydrocarbons from a cyclohexyl ring. Additional peaks at m/z 127 possibly representing $[\text{C}_5\text{H}_9\text{Ni}]^+$ and its cyclohexane adduct $[\text{C}_5\text{H}_9\text{Ni}(\text{C}_6\text{H}_{12})]^+$ (m/z 209) (due to IMR with the neutral present in the ion trap) would have to come from more complex transformations. Thus, the reaction of $[\text{CpNi}]^+$ with cyclohexane does not seem to be catalytic.

The cyclopentadienylcobalt cation, $[\text{CpCo}]^+$ (**1-Co**, m/z 124) reacted to form the singly dehydrogenated adduct $[\text{CpCo}(\text{C}_6\text{H}_{10})]^+$ (**3-Co**, m/z 206) in addition to the low-abundance water adduct at m/z 142 (Fig S7). Isolation and collisional activation of **3-Co** displayed the dehydrogenation to the benzene complex $[\text{CpCo}(\text{C}_6\text{H}_6)]^+$ (**5-Co**, m/z 202) along with multiple other peaks among which $[\text{CpCo}(\text{C}_4\text{H}_6)]^+$ (m/z 178) and $[\text{CpCo}(\text{C}_3\text{H}_4)]^+$ (m/z 164) were attributed to the cyclohexene ring cracking (Fig. S7), similar to the Ni chemistry described above. Ring cracking has been described before by Byrd *et al.* in the reactions of $[\text{CpCo}]^+$ with hydrocarbons.²⁹



Scheme 4. Catalytic cycle of cyclohexane dehydrogenation by $[\text{CpFe}]^+$. Blue arrows represent pathways corresponding to products formed spontaneously in the ion trap during the reaction of 1-Fe with cyclohexane; red arrows indicate the pathways requiring extra energy.

(C) Reaction of $[\text{CpFe}]^+$ with N-Heterocycles

Ion-molecule reactions of 1-Fe with piperidine (Fig. 2a) shows formation of the adduct at m/z 206 (6-Fe) and the single and double dehydrogenation adducts (7-Fe and 8-Fe at m/z 204 and 202, respectively). In addition, there are two small peaks at m/z 84 and 86 corresponding to the proton transfer to and hydride abstraction from piperidine by 1-Fe . Piperidine can undergo three dehydrogenations in total, the last of which can be accomplished by CID fragmentation of the double dehydrogenation adduct, 8-Fe , m/z 202, (Fig. 2b) leading to the pyridine adduct $[\text{CpFe}(\text{pyridine})]^+$, 9-Fe , m/z 200. Interestingly, in addition to the small peak corresponding to the triple dehydrogenation product, 9-Fe , and the initial 1-Fe ion, the main products of these CID reaction correspond to the losses of 17 and 16 Da (m/z 185 and 186). These ions most likely originate from the metal insertion into C-N bonds leading to the extrusion of NH_3 and $\text{NH}_2\bullet$. This type of heteroatom extrusion via Fe insertion into C-heteroatom bonds was reported by Bakhtiar and Jacobson for reactions of various FeL^+ ions (where $\text{L} = \text{Cp}$, benzene, and other hydrocarbon ligands) with furan and thiophene, although they did not study piperidine.³⁸

The ion-molecule reaction data for the reaction of 1-Fe with pyrrolidine are shown in Fig. 2c. There is again significant similarity to the reaction with cyclohexane (Fig. 1a) – the adduct 10-Fe at m/z 192 is formed along with the ions

corresponding to the loss of one (**11-Fe** at m/z 190) and two (**12-Fe** at m/z 188) hydrogen molecules from the adduct. There are two peaks at m/z 70 and 72 corresponding to the proton transfer to and hydride abstraction from pyrrole by **1-Fe**, but they are much smaller than in the case of piperidine described above. Fragmentation of **12-Fe** (Fig. 2d), the pyrrole adduct to $[\text{CpFe}]^+$, leads back to **1-Fe**, m/z 121, thus completing the catalytic cycle for double dehydrogenation of pyrrolidine (Scheme S8). Bakhtiar and Jacobson have previously observed the formation of **12-Fe** in the reaction of **1-Fe** and pyrrole and found the adduct to be a stable species in the gas phase.³⁸

The ion-molecule reaction of **1-Fe** with N-methylpyrrolidine (isomeric to piperidine) is shown in Fig. 2e. It is similar to the case of pyrrole discussed above and shows formation of the adduct at m/z 206 (**13-Fe**) and the single and double dehydrogenation adducts (**14-Fe** and **15-Fe** at m/z 204 and 202, respectively). CID of the N-methylpyrrolidine adduct at m/z 202 (**15-Fe**) gives small quantity of **1-Fe**, but the loss of 15 Da (presumably, methyl group) is the dominant channel (Fig. 2e). One major difference from pyrrolidine is that the intensity of the proton transfer/hydride abstraction peaks at m/z 84 and 86 is significantly higher. This correlates well with the ionization energy of N-methylpyrrolidine being substantially lower than that of pyrrolidine (8.41 vs 8.77 eV, respectively)³⁹, which allows for a much more facile initial charge transfer from the $[\text{CpFe}]^+$ ion followed by the formation of more stable even-electron ions at m/z 84/86 (the ionization energy of piperidine is even lower at 8.20 eV⁴⁰ and m/z 84/86 peaks are very prominent as seen in Fig. 2a).

Thus, only pyrrole shows truly catalytic dehydrogenation by **1-Fe**, while the other two N-heterocycles display side reactions that are more prominent than dehydrogenation.

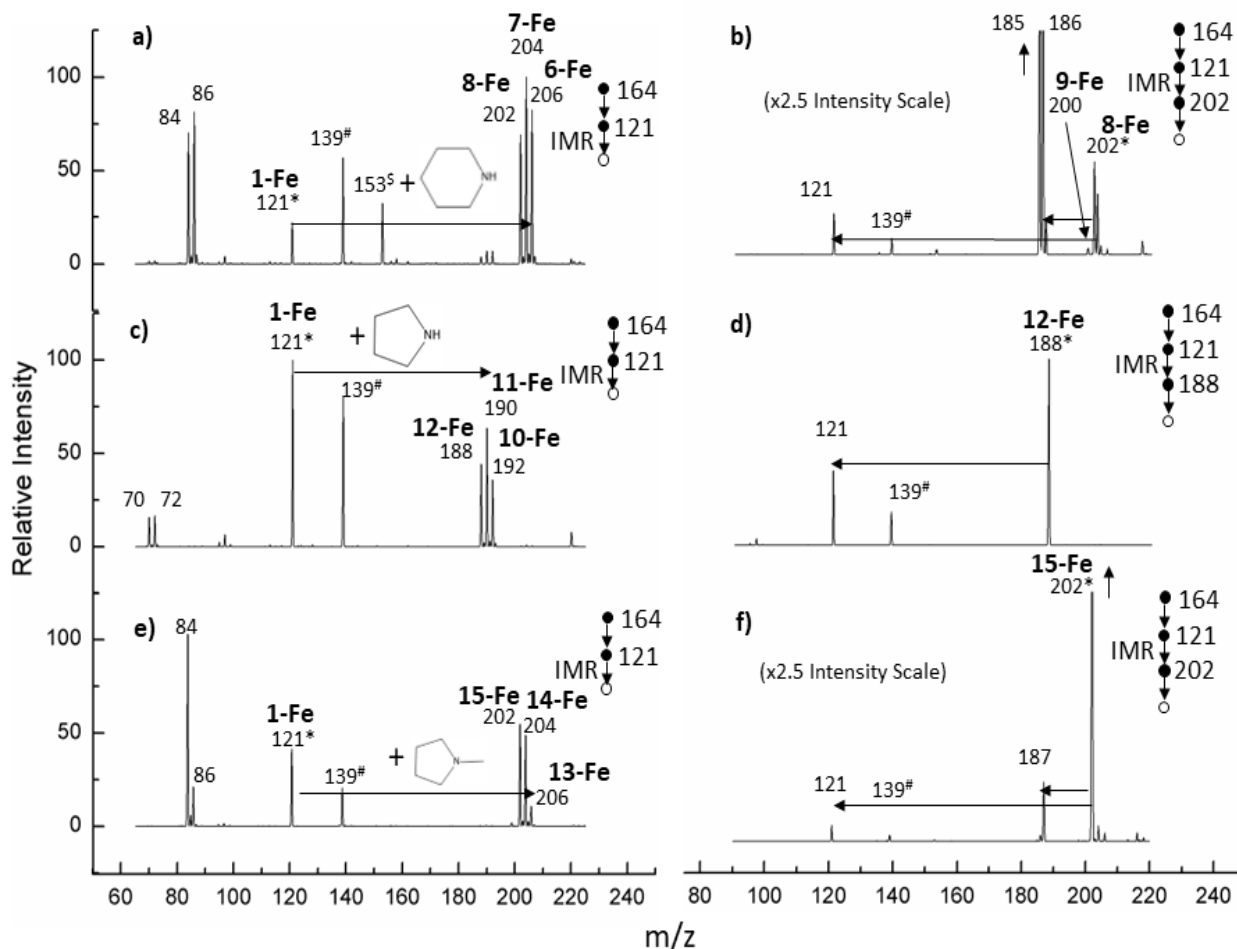


Figure 2. a) IMR of **1-Fe** with piperidine (isolation width 2 m/z ; reaction time 80 ms); b) CID of **8-Fe** (isolation width 2 m/z ; fragmentation NCE 25); c) IMR of **1-Fe** with pyrrolidine (isolation width 2 m/z ; reaction time 30 ms); d) CID of **12-Fe** (isolation width 2 m/z ; fragmentation NCE 25); e) IMR of **1-Fe** with N-methylpyrrolidine (isolation width 2 m/z ; reaction time 30 ms); f) CID of **15-Fe** (isolation width 2 m/z ; fragmentation NCE 29); # indicates water adduct; \$ indicates oxygen adduct.

(D) Ligand effects on reactivity

Previous work done by Schwarz and co-workers⁴¹ on the reactivity of first row bare metal cations with cyclohexane allows us to make a direct comparison between M^+ and $[CpM]^+$ and thus ascertain the effect of the Cp ligand on the ion reactivity. All three M^+ ($M = Fe, Co, Ni$) reacted with cyclohexane at the collision rate resulting in no adduct formation but mostly leading to the adducts with cyclohexene and cyclohexadiene (arising from single or double dehydrogenation). In addition, Fe^+ and Co^+ showed a small amount of triple dehydrogenation, while Co^+ and Ni^+ displayed C-C bond activation via loss of propene. The latter is consistent with our data on $[CpNi]^+$ and $[CpCo]^+$ which mediated C-C cleavage alongside C-H activation in the gas phase. Additionally, $[CpFe]^+$ reactivity towards cyclohexane mirrors that of bare Fe^+ cations - both ions have been found to only mediate C-H activation without C-C cleavage of cyclohexane.

Where $[CpM]^+$ ion reactivity deviates from the bare-metal analogues is the abundance of the single dehydrogenation product on a millisecond timescale. Metal cations Fe^+ , Ni^+ , and Co^+ predominately yield single dehydrogenation products. $[CpNi]^+$, and $[CpCo]^+$ have also been found to produce a single dehydrogenation product of cyclohexane (Figs. S5 and S7), while $[CpFe]^+$ gave predominately the cyclohexane adduct (Fig. 1). To achieve double and triple dehydrogenation as well as C-C insertion observed in bare metal ion reactivity, extra energy is required in CpM^+ systems that can be imparted by CID. This discrepancy can be rationalized in terms of strong coordinative unsaturation of bare metal cations. This leads to very favorable energetics in the interaction of M^+ with cyclohexane with the energy released sufficient to drive dehydrogenation and, in the case of Co^+ and Ni^+ , C-C insertion and the associated chemistry.

The study of the ligand effects on the iron reactivity towards cyclohexane and N-heterocycles were extended to the complex $[CpFe(NCCH_3)]^+$, shown in Figure S14a. IMR between $[CpFe(NCCH_3)]^+$ and cyclohexane shows no reactivity even at longer reaction times (1000 ms). In contrast, the reaction of the $[CpFe(NCCH_3)]^+$ ion with piperidine gives a peak at m/z 206 that indicates a ligand replacement (from acetonitrile to piperidine) at 30 ms. In addition, a peak at m/z 291 is seen corresponding to addition of another piperidine molecule. (Fig S14b) Similarly, pyrrolidine reacted with $[CpFe(NCCH_3)]^+$ by replacing the acetonitrile ligand forming the peak at m/z 192, which in turn added another molecule of pyrrolidine, m/z 263. (Fig S14c) Collisional activation of the piperidine and pyrrolidine adducts, **6-Fe** and **13-Fe**, respectively, gave the same chemistry as described above and presented in Fig. 2. These ligand replacement reactions can be easily explained by the higher $[CpFe]^+$ binding energy (BE) of piperidine and pyrrolidine compared to acetonitrile. While those BE values have not been measured,⁴² they are known to be proportional to proton affinities of the ligands.⁴³ The proton affinity values of piperidine and pyrrolidine (954 and 948 kJ.mol, respectively) are much higher than that of acetonitrile (779 kJ/mol), making the ligand replacement energetically favorable. This also explains why cyclohexane (proton affinity of 687 kJ/mol³⁹) fails to displace acetonitrile from the $[CpFe(NCCH_3)]^+$ complex.

Computational Analysis of Key Species Detected in Mass Spectrometric Studies of Dehydrogenation

Computation for the $[CpM]^+$ ($M = Fe, Co, Ni$)/cyclohexane systems was undertaken, with cyclohexane chosen as a “benchmark” reagent for the study of hydrocarbon LOHCs. It was anticipated that results would provide guidance for subsequent studies of the cyclic amines piperidine, pyrrolidine and N-methylpyrrolidine. Previous studies of the electronic structure for the reagent cations $[CpM]^+$ ($M = Fe, Co, Ni$)^{28,29,44} illustrate the occurrence of open-shell configurations, e.g. doublet for Co and triplet for Ni. Application of our computational procedure to this system confirmed these assignments, and for singlet $[CpFe(benzene)]^{+45,46}$ and doublet $[CpCo(benzene)]^{+46,47}$. Thus, all organometallic species studied herein were examined as singlets, triplets and quintets for $d^6 Fe^{II}$, doublets and quartets for $d^7 Co^{II}$, and singlets and triplets for $d^8 Ni^{II}$.

(E) Reaction of $[CpM]^+$ ($M = Fe, Co, Ni$) with Cyclohexane

In gas-phase ion-molecule reactions, unlike the reactions in the condensed phase, the energy of the reactants stays in the system and is the only driving force of the reaction.⁴⁸ CID experiments, on the other hand, impart significant energy into the ions and can be used to drive forward endothermic processes. Computation for the reaction of $[CpM]^+$ (**1-M**; $M = Fe, Co, Ni$) with cyclohexane (Figure 3) illustrates the very favorable initial interaction to form adducts **2-M**, followed by the endothermic loss of three molecules of hydrogen (**2** $\rightarrow$ **3** $\rightarrow$ **4** $\rightarrow$ **5**). Higher energy species are shown in blue. Alternative structures for complexes of dienes are illustrated (**4-M**, **4-M'**), and structures with essentially identical energy were obtained for the two electronic states of $[CpCo(cyclohexene)]^+$ (quartet **3-Co** and doublet **3-Co'**). The formal number of metal valence electrons at the metal atom (MVE) is shown for all structures, together with m/z values to provide a link to mass spectrometric Figures.

Computation of the energy required for the release of benzene from cations **5-M** is summarized in eq. 8 for the three metals.



M = Fe (250.4 kJ/mol), M = Co (215.1 kJ/mol), M = Ni (201.6 kJ/mol)

The adducts **2-M** exhibit similar structures that involve three weak M...H interactions (ca. 2 Å) with the cyclohexane group retaining the chair configuration on forming these interactions. The cyclohexene (**3-M**), cyclohexadiene (**4-M**) and benzene (**5-M**) complexes have these ligands present as 2e⁻, 4e⁻ and 6e⁻ donors, respectively.

We now consider the changes in energy of species in Figure 3, and their relationship to the mass spectrometric results.

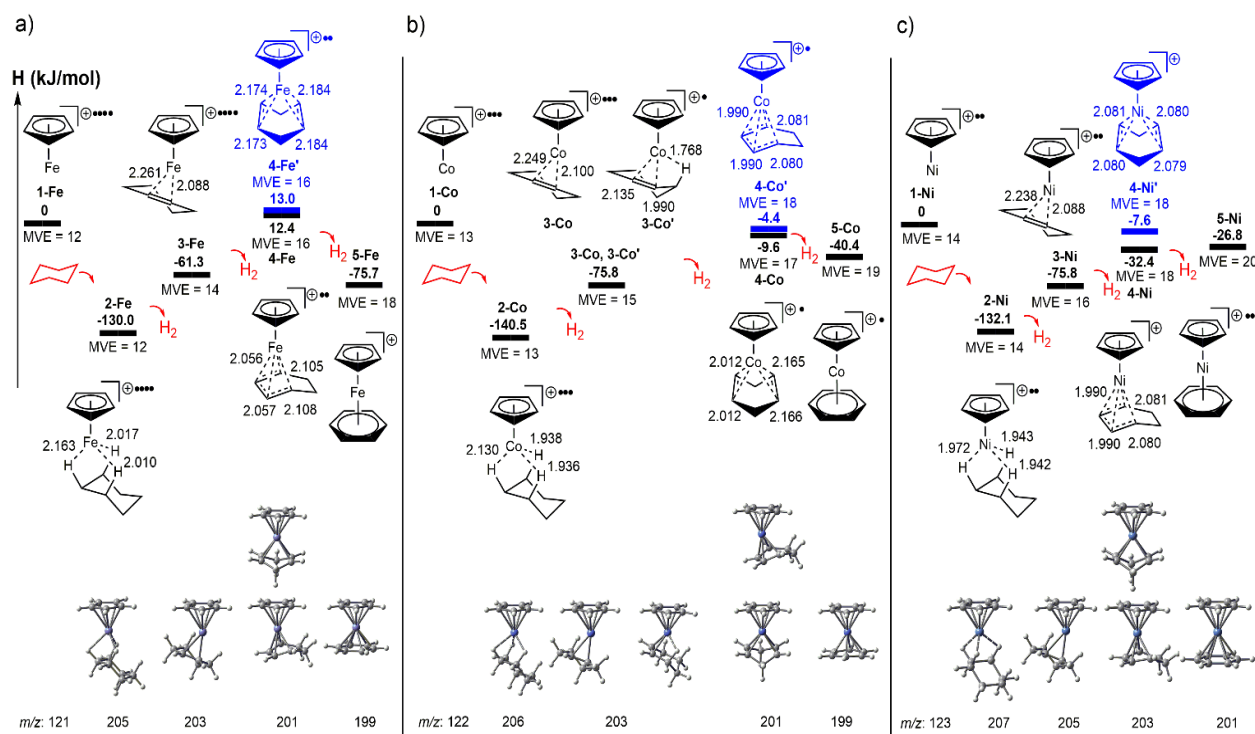


Figure 3. Energy diagram for the ion molecule reaction and collision-induced dissociation processes in the reaction of $[\text{CpM}]^+$ (**1-M**) with cyclohexane, forming adduct (**2-M**) which liberate H_2 in successive steps. Higher energy species are shown in blue, noting that isomers **3-Co** and **3-Co'** compute as having identical energy a) M = Fe, b) M = Co, c) M = Ni. Gaussview pictures are shown, and relative energies are given in kJ/mol and calculated at the B3LYP-D3BJ/BS2//M06/BS1 level of theory. For a), singlet and triplet states, respectively, compute as higher than quintets, in kJ/mol: **1-Fe** (109.4, 49.7), **2-Fe** (48.8, 29.2), **3-Fe** (77.2, 14.5); singlet and quintet states for triplets: **4-Fe** (88.6, 25.7), **4-Fe'** (57.7, 4.2); and triplet and quintet states for **5-Fe** (92.4, 65.0). For b), doublet states compute as higher than the quartet states for **1-Co** (31.7) and **2-Co** (20.9); and quartets higher than doublets for **4-Co** (17.6), **4-Co'** (17.8), and **5-Co** (80.8). For c), singlet states compute as higher than triplet states for **1-Ni** (80.1), **2-Ni** (45.1), **3-Ni** (56.3) and **5-Ni** (66.2); and triplet states higher than singlets for **4-Fe** (53.4) and **4-Fe'** (17.4).

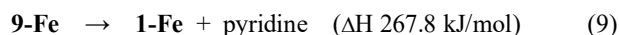
The substantial lowering in energy on formation of the adducts **2** from $[\text{CpM}]^+$ (**1**) is similar for the three metals, in the range ΔH -130.0 to -140.5 kJ/mol. In a similar manner, noting the unknown requirement to achieve transition states, loss of the first molecule of H_2 from **2** to form **3** exhibit similar energy requirements, ΔH 56.3 - 68.7 kJ/mol. The overall energy of **3-M** species is consistent with experimental reactivity data. As **3-Co** and **3-Ni** (-75.8 kJ/mol) are more favored thermodynamically than **3-Fe** (-61.3 kJ/mol), it is consistent with the IMR data where **1-Co** and **1-Ni** proceed to the first dehydrogenation complex **3-M** (Figs. S5 and S7), while Fe stops at the cyclohexane adduct **2-M** (Fig. 1).

Loss of the second molecule of H_2 from **3-Fe,Co** to form **4-Fe,Co**, ΔH 66.2, 73.7 kJ/mol, but is lower for Ni (**3-Ni** $\rightarrow$ **4-Ni**), 43.4 kJ/mol. Interestingly, **4-Fe** is 12 kJ/mol above the energy of the reactants (**1-Fe** + cyclohexane). The fact that a small quantity of these ions is formed in the IMR between **1-Fe** + cyclohexane (Fig. 1) can possibly be explained by a fraction of "hot" **1-Fe** ions that are formed under CID conditions or during ion isolation in the ion trap (the tail end of the Boltzmann distribution).⁴⁸ In addition, loss of two molecules of hydrogen is entropically favored. Loss of the third molecule of H_2 is exothermic for Fe and Co, -88.1 and -30.8 kJ/mol from **4-Fe,Co** to form **5-Fe,Co**, but this process computes as slightly endothermic for Ni (5.6 kJ/mol).

These trends in the energy profiles for the model LOHCs, $2 \rightarrow 3 \rightarrow 4 \rightarrow 5$, suggest that iron is a more suitable model as the energy requirement for the loss of the first two molecules of H_2 is similar for the three metals, but the loss of the third H_2 molecule is substantially more exothermic for iron (Figure 3a). Moreover, experimental dehydrogenation of cyclohexane by $[CpM]^+$ ($M=Ni, Co$) was accompanied by C-C insertion side reactions and was not catalytic. Thus, in developing this project further to include nitrogen heterocycles we have confined the study to iron.⁴⁹

(F) Reaction of $[CpFe]^+$ with Piperidine

Computation undertaken in a similar manner to the cyclohexane system, including exploration of structures exhibiting $Fe \cdots \pi$ -interactions and/or $Fe \cdots N$ -interactions, led to the construction of Figure 4. Higher energy species are shown in blue. Presence of the nitrogen donor center in piperidine results in formation of a complex with both an Fe-N bond and two weak $Fe \cdots H$ interactions (**6-Fe**), in a manner analogous to interaction with cyclohexane (Figure 3). Reflecting this much stronger interaction with the Fe center, the formation of quintet **6-Fe** is considerably more exothermic than for the cyclohexane interaction, ΔH -271.6 kJ/mol compared with -130.0 kJ/mol for cyclohexane (**2-Fe** in Figure 3). Eq. 9 documents computation of the energy required for the release of pyridine from **9-Fe**.



The successive loss of H_2 molecules generates structures in which the lowest energy species are quintets, and an Fe-N bond formed after loss of the hydrogen atom from nitrogen is a significant feature in all of the lowest energy structures (**7-Fe**, **8-Fe**, **8-Fe'**, **9-Fe**), although noting the small energy difference between quintet **8-Fe** and singlet **8-Fe'** (ΔH 2.7 kJ/mol). The structure of the 14e⁻ pyridine complex, quintet **9**, is of particular interest, computing as lower energy than the 18e⁻ π -bonded pyridine complex, singlet **9-Fe'**. A related 15e⁻ quartet structure for $[CpCo(2-X-C_5H_4N)]^+$ and a 16e⁻ triplet structure for $[CpNi(2-X-C_5H_4N)]^+$ ($X = F, Br$) have been reported, and in these cases there is an additional weak $M \cdots X$ interaction.⁴⁴

Successive loss of H_2 molecules provides an overall similar profile to that obtained with benzene, in that the first two losses are endothermic and the third loss exothermic. As found for benzene, loss of the third molecule of H_2 required the higher energy conditions associated with collision-induced dissociation (CID).

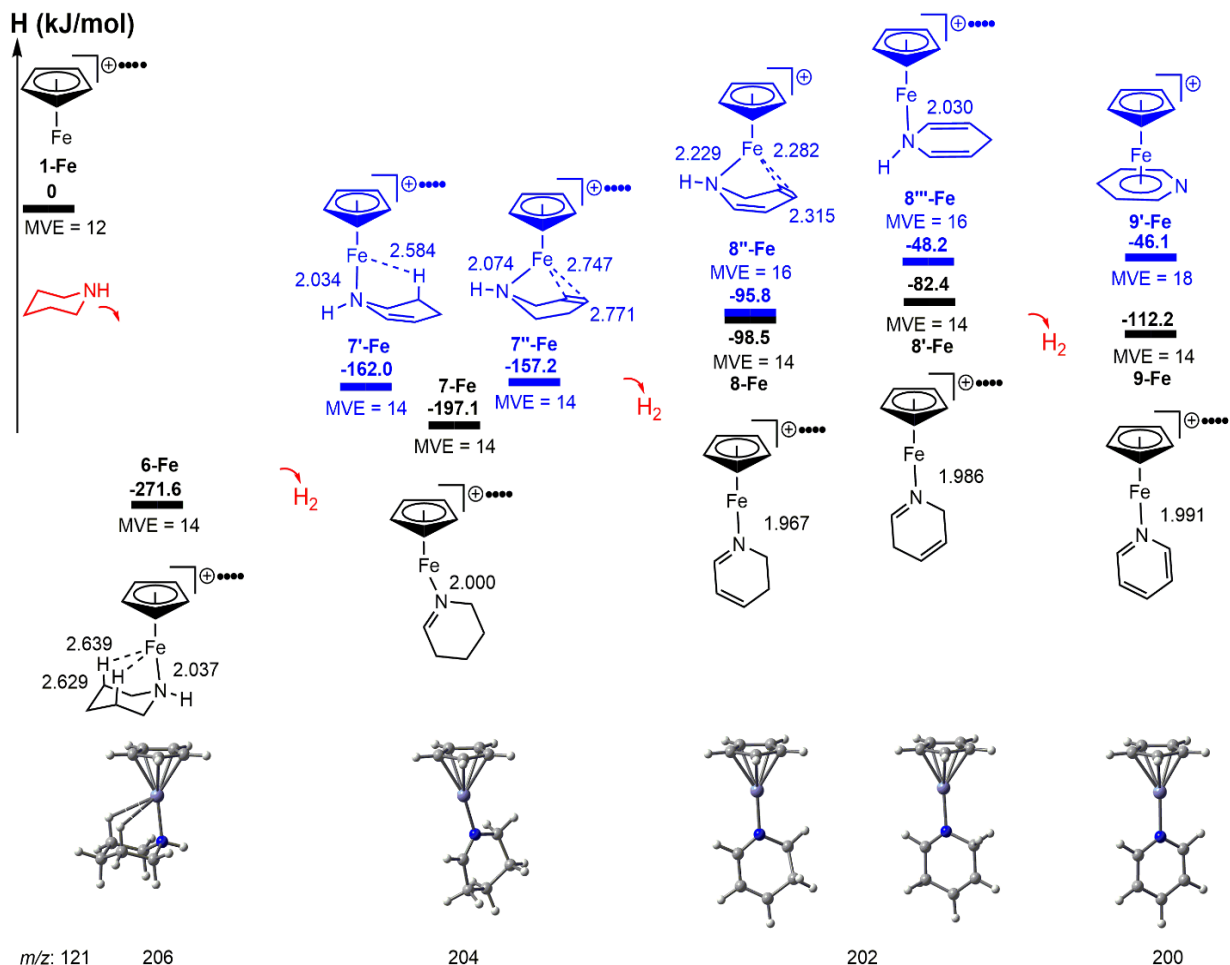
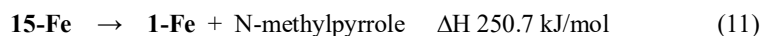


Figure 4. Energy diagram for the ion molecule reaction and collision induced dissociation processes in the reaction of $[\text{CpFe}]^+$ (**1-Fe**) with piperidine, forming adduct (**6**) which liberates H_2 in successive steps. Higher energy species are shown in blue. Gaussview pictures are shown, and relative energies are given in kJ/mol and calculated at the B3LYP-D3BJ/BS2//M06/BS1 level of theory. Singlet and triplet states, respectively, compute as higher than quintets, in kJ/mol: **1-Fe** (109.4, 49.7), **6-Fe** (118.7, 56.3), **7-Fe** (126.5, 63.2), **7-Fe'** (52.0, 25.9), **7-Fe''** (52.9, 17.1), **8-Fe** (134.7, 66.5), **8-Fe'** (169.8, 77.3), **8-Fe''** (9.9, 25.5), **9-Fe** (144.1, 65.5); triplet and quintet states for **8-Fe''** (63.8, 48.0), **9-Fe'** (86.6, 58.5).

(G) Reaction of $[\text{CpFe}]^+$ with pyrrolidine and N-Methylpyrrolidine

Computed profiles (Figure 5) exhibit an initial exothermic interaction with formation of adducts (**10-Fe**, **13-Fe**) similar to that found for piperidine (**6-Fe**, Figure 4, higher energy species are shown in blue), noting similar ΔH values and presence of an Fe-N interaction together with two weak $\text{Fe} \cdots \text{H}$ interactions in the adducts. Eq. 10 and 11 document computation of the energy required for the release of pyrrole and N-methylpyrrole from **12-Fe** and **15-Fe**.



For pyrrolidine, the first loss of H_2 provides quintet **11-Fe** as the lowest energy structure, with Fe-N bonded after loss of a hydrogen atom from nitrogen, analogous to the structure formed by piperidine (**7-Fe**, Figure 4). The loss of a second H_2 molecule provides an 18 π singlet (**12-Fe**) with pyrrole as a 6 π donor, rather than N-bound alternatives (**12-Fe'**, **12-Fe''**), in direct contrast with a 14 π N-bound quintet found for the potential 6 π donor pyridine (**9-Fe**) in the piperidine system.

For N-methylpyrrolidine, lacking a reactive N-H bond, options for variation in structure are more limited, so that loss of the first H_2 molecule provides quintet **14-Fe**, analogous to the unfavorable higher energy analog for pyrrolidine (**11-**

Fe'). Loss of the second molecule of H₂ provides π -bonded N-methylpyrrole in an 18e⁻ singlet (**15-Fe**) analogous to the pyrrolidine system (**12-Fe**).

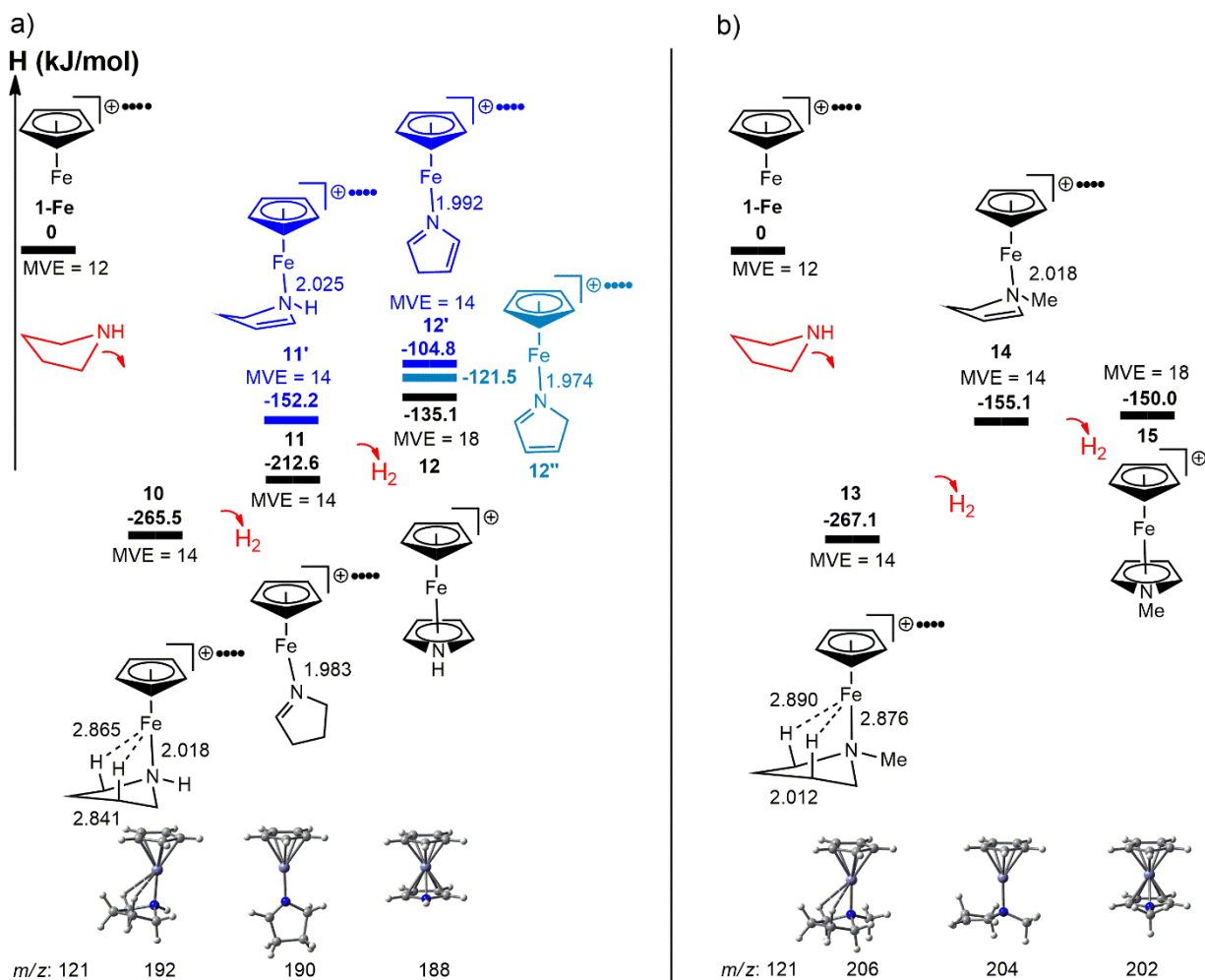


Figure 5. Energy diagram for the ion-molecule reaction and collision-induced dissociation processes in the reaction of [CpFe]⁺ (**1-Fe**) with a) pyrrolidine, forming adduct **10-Fe**, and b) N-methylpyrrolidine to form adduct **13-Fe**, where **10-Fe** and **13-Fe** liberate H₂ in successive steps. Higher energy species are shown in blue. Gaussview pictures are shown, and relative energies are given in kJ/mol and calculated at the B3LYP-D3BJ/BS2//M06/BS1 level of theory. Singlet and triplet states, respectively, compute as higher than quintets, in kJ/mol: **1-Fe** (109.4, 49.7), **10-Fe** (113.2, 61.1), **11-Fe** (34.3, 77.7), **11-Fe'** (32.0, 22.8), **12-Fe'** (126.8, 75.6), **12-Fe''** (129.8, 66.0), **13-Fe** (109.3, 63.1), **14-Fe** (25.1, 15.9); and triplet and quintet states for **12-Fe** (48.3, 23.2) and **15-Fe** (50.7, 28.6).

CONCLUSIONS

In this work, we have investigated the gas-phase reactions of [CpM]⁺ cations (M=Fe, Co, Ni) with cyclohexane and [CpFe]⁺ with nitrogen-containing heterocycles – piperidine, pyrrolidine, and N-methylpyrrolidine. While it has been shown previously that [CpM]⁺ cations can dehydrogenate alkanes in the gas phase, this is, to our knowledge, the first report showing that [CpFe]⁺ catalyzes triple dehydrogenation of cyclohexane to benzene via a combination of ion-molecule reactions and collision-induced dissociation experiments. Reactions of [CpM]⁺ (M=Co, Ni) were found to be more complex, and dehydrogenation was accompanied by dominant cyclohexane ring cleavage.

Similarly, IMR of [CpFe]⁺ with pyrrolidine and N-methylpyrrolidine resulted in double (full) dehydrogenation, and successive CID experiments lead to the release of pyrrole and N-methylpyrrole products, respectively, thus closing the catalytic cycle. However, [CpFe(N-methylpyrrole)]⁺ displayed minor side reactions (loss of 15 Da) upon CID. Contrary to this, IMR of [CpFe]⁺ with piperidine stopped at double dehydrogenation (out of three possible) leading to the [CpFe(dihydropyridine)]⁺ species. Its fragmentation under CID conditions produced only a minor fraction of the pyridine

(full, triple dehydrogenation) complex while the main channel corresponded to expulsion of NH_3 and $\text{NH}_2^\bullet$, likely via iron insertion into C-N bonds. It is interesting to note that $[\text{CpFe}(\text{piperidine})]^+$ (**6-Fe**) and $[\text{CpFe}(\text{pyrrolidine})]^+$ (**13-Fe**) species can be formed in the gas phase by reaction of the acetonitrile adduct $[\text{CpFe}(\text{NCCH}_3)]^+$ with piperidine and pyrrolidine (but not with cyclohexane) via ligand exchange. Since the acetonitrile complex is more likely to exist in solution than the coordinatively unsaturated $[\text{CpFe}]^+$ species, this provides a plausible pathway to forming **6-Fe** and **13-Fe** in the condensed phase. This opens the opportunity to study less volatile N-containing LOHC compounds to replace coordinated acetonitrile ligands in solution leading to $[\text{CpFe}(\text{LOHC})]^+$ complexes for subsequent hydrogen production.

DFT calculations shed light on the structure of the key intermediates and required examination of multiple spin states to locate lowest energy species, elucidating preferences for spin states in each system. Computation is consistent with experiment, although transition states were not examined. In reactions with cyclohexane, the $[\text{CpFe}(\text{cyclohexane})]^+$ (**2-Fe**) complex is stabilized by three $\text{Fe} \cdots \text{H}$ interactions. Upon dehydrogenation, these interactions are replaced by $\text{Fe}-\pi$ bonds in cyclohexene (**3-Fe**) or cyclohexadiene (**4-Fe**) complexes, eventually leading to a symmetric benzene complex (**5-Fe**). Reactions of $[\text{CpFe}]^+$ with N-heterocycles initially lead to more stable complexes since they act as strong σ donors. Following dehydrogenation, pyridine remains σ -bound while pyrrole and N-methylpyrrole are predicted by DFT to switch to π bonding.

MATERIALS AND METHODS

Materials

Cyclopentadienyl(dicarbonyl)iodoiron, $[\text{CpFe}(\text{CO})_2\text{I}]$, nickelocene, $[\text{Cp}_2\text{Ni}]$, cyclopentadienyl(dicarbonyl)cobalt, $[\text{CpCo}(\text{CO})_2]$, cyclohexane, piperidine, pyrrolidine, and N-methylpyrrolidine were all purchased from Sigma-Aldrich (St. Louis, MO and Madison, WI). All neutral reagents were introduced into the ion trap by constant injection into the helium line as described in other works.⁵⁰ $[\text{CpFe}(\text{CO})_2\text{I}]$ or $[\text{CpCo}(\text{CO})_2]$ were dissolved in CH_3CN (or CH_3OH for the iron species) to a concentration of 0.2 mg/mL and introduced into the system via electrospray ionization (ESI). Similarly, $[\text{Cp}_2\text{Ni}]$ was dissolved in CH_3OH and introduced in the same way as other species.

Mass Spectrometry

Experiments were performed with a Thermo Fisher LTQ (Thermo Fisher Scientific; San Jose, CA) which has been modified for ion-molecule reactions (IMR) allowing direct injection of neutral molecules into the helium line. A flow rate of 4 $\mu\text{L}/\text{min}$ was used to introduce metal complexes to the ESI spray chamber for ionization. A spray voltage of 4 kV, an inlet temperature of 275 $^\circ\text{C}$, and 20 a.u. nitrogen flow rate was used as ionization parameters. With MS^n capabilities of the LTQ, $[\text{CpM}]^+$ ($\text{M}=\text{Fe}, \text{Co}, \text{Ni}$) fragments were isolated in the linear trap from captured ions of $[\text{CpFe}(\text{CH}_3\text{CN})]^+$, $[\text{Cp}_2\text{Ni}]^+$, and $[\text{CpCo}(\text{CH}_3\text{CN})_2]^+$ which were isolated within a 2 m/z isolation window and fragmented in the ion trap by CID (collision-induced dissociation) to the respective $[\text{CpM}]^+$ species. In each case the cationic complex with the most abundant metal isotope was mass selected (i.e. ^{56}Fe , ^{59}Co and ^{58}Ni). After isolation of the $[\text{CpM}]^+$ ions in a 2 m/z isolation window, neutral reagent vapors were injected at a constant rate of 0.05 $\mu\text{L}/\text{hr}$ into the trap by use of the modified helium line to allow for ion-molecule reactions. Reaction times varied from 10 to 100 ms. Adduct products of the IMR, as well as their fragmentation products, were isolated in a 1.5 m/z isolation window and analyzed based on their fragmentation patterns. The proposed complexes and intermediates elucidated from the experimental spectra were then confirmed by high precision DFT calculations.

DFT Calculations

Gaussian 16 was used⁵¹ to perform all calculations at the M06 level of density functional theory (DFT)⁵² All geometries were optimized without symmetry constraints and vibrational frequency calculations were calculated at the same level of theory as the optimization. The SDD basis set was chosen to describe Fe, Co, and Ni⁵³ and the 6-311G(d) basis set was used for other atoms.⁵⁴ This basis set combination is referred to as BS1. To more fully account for dispersion, the energies obtained from the M06/BS1 calculations were further refined to include single-point energy calculations carried out with the def2-TZVPP basis set (BS2)⁵⁵ for all atoms at the B3LYP-D3BJ level of theory.^{56–59} The enthalpy change for reactions (ΔH) is given for all DFT calculated reaction energies rather than the enthalpies or Gibbs free energies at a specific temperature for the following reasons: (1) the low energy CID “heating” method used involves multi-collision conditions with the helium bath gas. As a consequence, the effective temperature is unknown and varies with each different system studied; (2) the ion-molecule reactions are in the low-pressure region, and thus the Gibbs free energy is not the relevant thermodynamic parameter to use.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. SI contains mass spectra for CID and IMR reactions and energies for all structures calculated.

Notes

The authors declare not competing financial interest.

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