Organometallics **1999,** *18,* 40−44

Dehydrogenation of Ethane by CpM$^+$ (M = Fe, Co, Ni) in the Gas Phase. An FT-ICR-MS Study

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Received May 13, 1998

CpCo$^+$ and CpNi$^+$ (Cp = η_5-C$_5$H$_5$, cyclopentadienyl) dehydrogenate ethane in ion molecule reactions in an FT-ICR-MS cell. CpFe$^+$ does not. The differences in reactivity are rationalized using MO theory. The theoretical calculations show that the electronic structures of the metals in the organometallic complexes are perturbed by the Cp ligand to different degrees. The strong metal 4s character of the LUMOs for CpCo$^+$ and CpNi$^+$ favors the C−H bond activation step, leading to dehydrogenation. Available unoccupied metal 4s orbitals have previously been shown to facilitate C−H and H−H bond activation in reactions with naked metal ions.

Introduction

Hydrogenation and dehydrogenation reactions are important in chemistry.[1] Because hydrogenation reactions have very high activation barriers,[2] they always require the presence of a catalyst. The catalysts most often used are transition metals of groups 8, 9, and 10 in the periodic table. The catalyst may be either a pure metal, an alloy, a metal oxide, or a metal deposited on a support, e.g., graphite. Hydrogenation reactions have also been shown to occur homogeneously catalyzed by metal complexes (e.g., Wilkinson's catalyst) in organic solvents.[3]

It is of great general interest to know the mechanisms of metal-catalyzed hydrogenation reactions. Of course, from the principle of microscopic reversibility, equivalent insight can be gained by observation of the reverse process: alkane dehydrogenation. The molecular factors that govern the interaction between an alkane and a catalyst can be obtained by studying suitable model systems in the gas phase. A number of studies have been performed in which positive atomic metal ions of almost all the transition metals have been found to react with different saturated hydrocarbons, of which ethane is the simplest.[4] All first-row transition metal (Sc−Zn) ions, except Cr$^+$, Mn$^+$, Zn$^+$, and Cu$^+$, dehydrogenate ethane in ion beam experiments.[4]

$$M^+ + C_2H_6 \rightarrow MC_2H_4{}^+ + H_2 \qquad (1)$$

The ion beam experiments suggest, however, that except for Sc$^+$ and Ti$^+$ the dehydrogenation reactions of ethane with ground-state first-row transition metal ions (eq 1) are endothermic or have an activation barrier. The reactions with Fe$^+$, Co$^+$, and Ni$^+$ have been reported to be exothermic,[4,5] but the ion beam experiments suggest a threshold indicating a barrier to reaction. These fundamental studies have emphasized the importance of the effect of the electronic state and the spin state upon the metal ion reactivity.

The reactivity of transition metal ions with alkanes is influenced by ligands bonded to the metal.[4b,6−8] The atomic metal ion Fe$^+$, for example, does not react with ethane, but FeL$^+$ (L = CH$_2$, C$_5$H$_6$, O) does react with ethane to give a series of products.[7] The complex CpCo$^+$ (Cp = η-C$_5$H$_5$, cyclopentadienyl) has been found to dehydrogenate ethane.[8] So far no reactions of CpFe$^+$ or CpNi$^+$ with ethane have been reported. In this paper we will present results for reactions between ethane and CpM$^+$ (M = Fe, Co, and Ni).

In the same way that a ligand modifies the reactivity of a metal, the support (e.g., graphite) modifies the reactivity of hydrogenation catalysts used in the synthetic laboratory. The interaction between the metal and the support influences the electronic state of the metal and thereby its reactivity. From this viewpoint the systems studied here may be regarded as gas-phase

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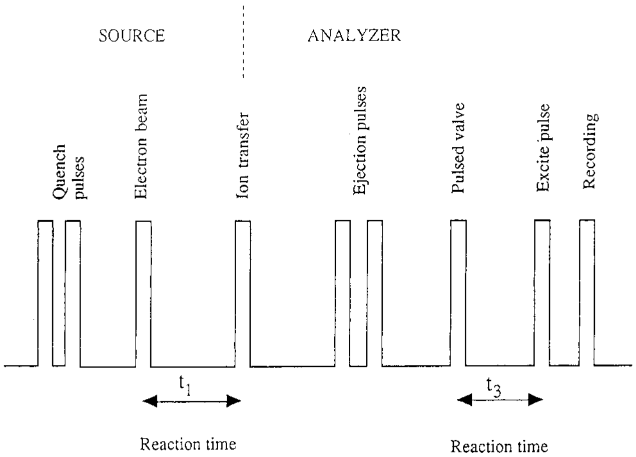

Figure 1. Pulse sequence used in the FTMS experiments.

models of real catalysts. To understand how the Cp ligand modifies the electronic structure of the metal, we have analyzed the experimental results in terms of frontier orbital theory.

Experimental Section

The experiments were carried out with a dual-cell Fourier transform mass spectrometer (FTMS-2000, Finnigan, Madison, WI).[9] A suitable neutral precursor was introduced to the source cell of the mass spectrometer and ionized using a short electron beam pulse. This gives rise to fragment ions of the type CpM^+. After a time delay, the CpM^+ ions were transferred to the differentially pumped analyzer cell by opening the gate potential of the aperture plate between the two cells for a predetermined time. By a careful choice of excitation pulse frequency widths and amplitudes, all ions, except the CpM^+ ions, were ejected from the analyzer cell.[10] Thereafter, a computer-controlled pulsed valve was opened for a short time, allowing ethane to enter the analyzer cell.[11] CpM^+ and ethane were then allowed to react. The mass spectrum was recorded after a variable reaction time, t_3. The pulse sequence used is shown in Figure 1. The neutral precursors used were $Fe(\eta_5\text{-}C_5H_5)(CO)_2I$, $Co(\eta_5\text{-}C_5H_5)(CO)_2$, and $Ni(\eta_5\text{-}C_5H_5)(CO)_2$. All chemicals were of commercial grade and were checked for purity using electron impact ionization (EI). The instrument was operated at sufficiently high resolution to identify all reactants and products by precise mass measurement. This was important because isobaric ions containing either CO or C_2H_4 had to be differentiated. For the kinetic measurements the pressure was determined using an ionization gauge corrected for relative ionization cross sections by the method of Bartmess and Georgiadis.[12]

Theory

Extended Huckel (EH) calculations provided a qualitative molecular orbital picture of interactions of Cp with Fe^+, Co^+, and Ni^+. The 4s and 3d valence orbital ionization energies used for the calculations were 7.10 and 8.68 eV for Fe, 7.33 and 9.37 eV for Co, and 7.54 and 10.03 eV for Ni, respectively. These values are statistically weighted averages of the ionization energies for a 4s or 3d electron from all the states derived from the $3d^64s^2$, $3d^74s^2$, and $3d^84s^2$ ground configurations of Fe, Co, and Ni atoms.[13] The 2p valence orbital ionization energy for C atom was taken as 10.77 eV. Overlap integrals were calculated numerically using orbital exponents recommended by Clementi and Raimonde.[14] The Wolfsberg Helmholtz constant was taken as 1.75.

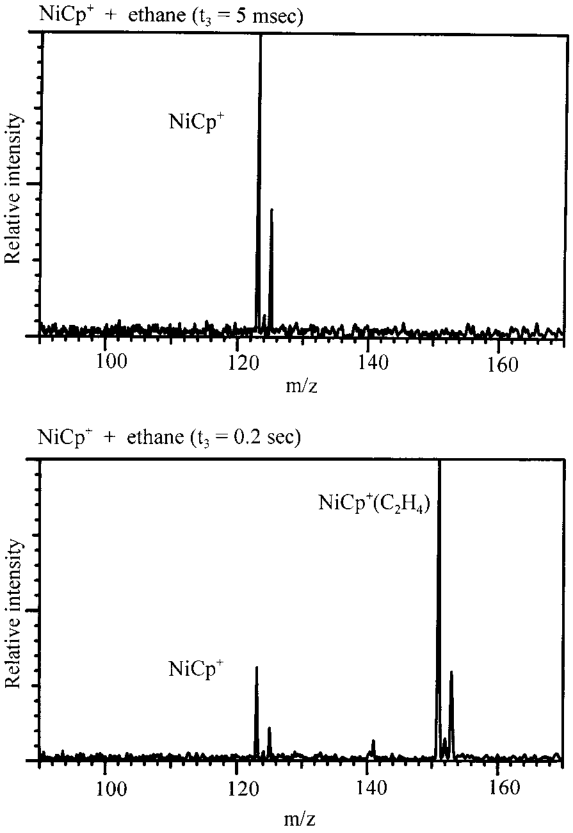

Figure 2. Mass spectrum obtained after (a) $t_3 = 5$ ms and (b) $t_3 = 200$ ms in the reaction between $CpNi^+$ and ethane. Peaks due to the two isotopes of Ni (^{58}Ni and ^{60}Ni) are present. The small peak at m/z 141 is a water adduct ($CpNiH_2O^+$).

Results and Discussion

Figure 2 shows the mass spectra of the $CpNi^+ + C_2H_6$ system recorded immediately after introduction of ethane at $t_3 = 0.005$ s (Figure 2a) and at $t_3 = 0.200$ s (Figure 2b). The dominant peak at short time is at m/z 123, which corresponds to the reactant $CpNi^+$ ion. After 0.2 s reaction 2 reveals itself by the appearance of a peak at m/z 151, which corresponds to $CpNiC_2H_4^+$. A parallel reaction is observed for $CpCo^+$ producing $CpCoC_2H_4^+$.

$$CpM^+ + C_2H_6 \xrightarrow{M = Co, Ni} CpMC_2H_4^+ + H_2 \qquad (2)$$

For $CpFe^+$ the reaction pattern is quite different. Figure 3a,b shows the mass spectra recorded at $t_3 = 0.005$ s and $t_3 = 0.200$ s, respectively. Immediately after

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ethane is introduced the $CpFe^+$ peak at m/z 121 is the only peak observed. After 0.200 s the $m/z = 121$ peak is still dominant, but a small peak at m/z 97 has emerged and precise mass measurement gives the elemental composition $Fe(C_3H_5)^+$. This suggests reaction 3:

$$CpFe^+ + C_2H_6 \rightarrow FeC_3H_5^+ + C_4H_6 \qquad (3)$$

An even smaller peak at m/z 99 suggests the formation of a small amount of $FeC_3H_7^+$ in competition with formation of $FeC_3H_5^+$. It is important to notice that no peak due to $CpFeC_2H_4^+$ at m/z 149 resulting from ethane dehydrogenation can be observed. At a somewhat higher ethane pressure we observe termolecular association between ethane and $CpFe^+$ to give $Cp\ Fe_{11}C_2H_6^+$ (m/z 151):

$$CpFe^+ + C_2H_6 \xrightarrow{[C_2H_6]} CpFeC_2H_6^+ \qquad (4)$$

In addition a subsequent reaction of $FeC_3H_5^+$ is seen:

$$FeC_3H_5^+ + C_2H_6 \rightarrow FeC_5H_9^+ + H_2 \qquad (5)$$

The product ion $FeC_5H_9^+$ has m/z 125. This suggests that FeL^+ dehydrogenates ethane when L = allyl, but not when L = Cp. To test whether the $FeC_3H_5^+$ product orginates from a small impurity of ethene in the ethane sample, $FeCp^+$ was exposed to an ethene sample. No $FeC_3H_5^+$ was observed.

Relative rate constants for reactions 2 and 3 can be determined from spectra such as those shown in Figures 2 and 3. For a reactant ion R^+ reacting with neutral N to give products P_i^+, the relative intensities in spectra such as those shown in Figures 2 and 3 are related to the total rate constant for reaction k by eq 6:

$$\ln\left(\frac{[R^+]}{[R^+] + [P_i^+]}\right) = -k \int_0^{t_3} [N(t)]\, dt \qquad (6)$$

where ion concentrations $[R^+]$ and $[P_i^+]$ are proportional to the relative intensities of the signals of the R^+ and P_i^+ ions in the spectrum obtained at delay time t after the pulsed valve opens, and $[N(t)]$ represents the time-dependent concentration of N. The right-hand-side integral in eq 6 is constant at constant t and constant reservoir pressure. Spectra in Figures 2 and 3 were obtained at constant reservoir pressure, and hence with eq 6 they readily provide relative rate constants for reactions 2 and 3. The absolute rate constant for reaction of $CpCo^+ + C_2H_6$ was measured by conventional single-cell FTICR techniques, and hence values for all the absolute rate constants can be established. A more extensive description of methods for measuring both relative and absolute rate constants using pulsed valve techniques is the subject of a recent paper.[15]

Apart from the differences observed with respect to the products formed, there is also a substantial difference in reaction rates. In the case of M = Co and Ni there is only one reaction product, $CpMC_2H_4^+$. The second-order rate constants for reaction 2 were measured to be $k_{Co} = 1.2 \times 10^{-10}$ cm^3 s^{-1} and $k_{Ni} = 4.8 \times 10^{-11}$ cm^3 s^{-1}, respectively. In the case of $CpFe^+$, analysis of the data gives a total rate constant for reaction 3 of $k_{Fe} = 1.2 \times 10^{-12}$ cm^3 s^{-1}.

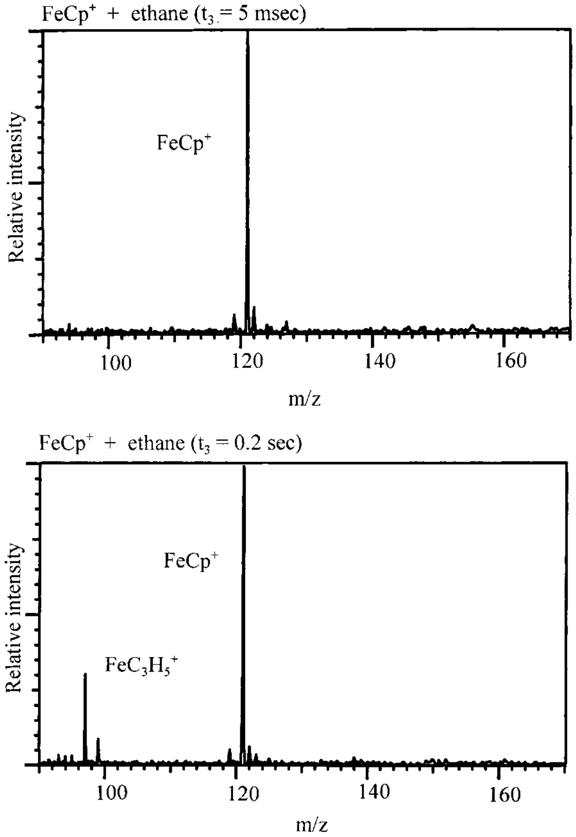

Figure 3. Mass spectrum obtained after (a) $t_3 = 5$ ms and (b) $t_3 = 200$ ms in the reaction between $CpFe^+$ and ethane. Peaks due to the two minor isotopes of iron (^{54}Fe and ^{57}Fe) and the major ^{56}Fe isotope are present. A small peak at m/z 99 represents a minor product discussed in the text.

At higher reservoir pressures and longer reaction times the $CpCo^+$ and $CpNi^+$ species react completely, suggesting that the observed chemistry is characteristic of ground-state species and not just of excited states formed by electron impact. The $CpFe^+$ species, however, does not react completely. The extent of conversion to product evident in Figure 3 is not exceeded at higher pressures or longer times. This suggests reaction 3 is characteristic of one or more excited states of $CpFe^+$ and that ground-state $CpFe^+$ is unreactive with ethane.

EH molecular orbital calculations have been shown to be very useful in analyzing the reactivity of organometallic compounds. To understand the differences in reactivity (k_{Fe}:k_{Co}:k_{Ni} = (<0.01):1.00:0.40) and the nature of the products, we consider the electronic structures for the series MCp^+ (M = Fe, Co, and Ni). The MO diagram for $CpFe^+$ is depicted in Figure 4a. The 12 valence electrons of the complex fill all the bonding MOs, forming a stable closed electron shell. This gives a strong bond between the metal and the ligand. On this basis $CpFe^+$ should be relatively inert, and the failure to react with ethane is not surprising. The coefficients of one of the degenerate e_1 LUMOs shown in Figure 4b indicate metal d and carbon 2p character. Such an orbital could play a role in reaction 3, which clearly involves the ring carbons, but is not particularly conducive to oxidation addition of C−H bonds.

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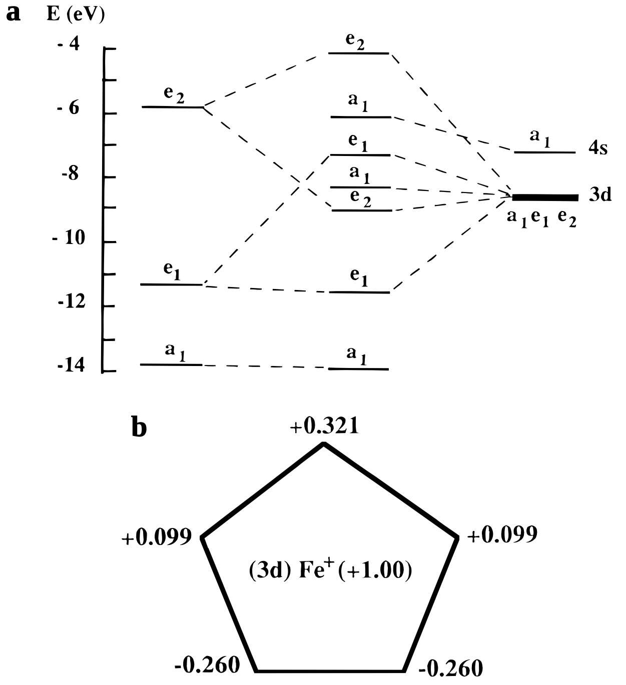

Figure 4. (a) Molecular orbital diagram and (b) LUMO MO coefficients for CpFe$^+$. The coefficients for the carbon $2p_z$ and the iron $3d_{xy}$ ($3d_{yz}$) atomic orbitals are indicated.

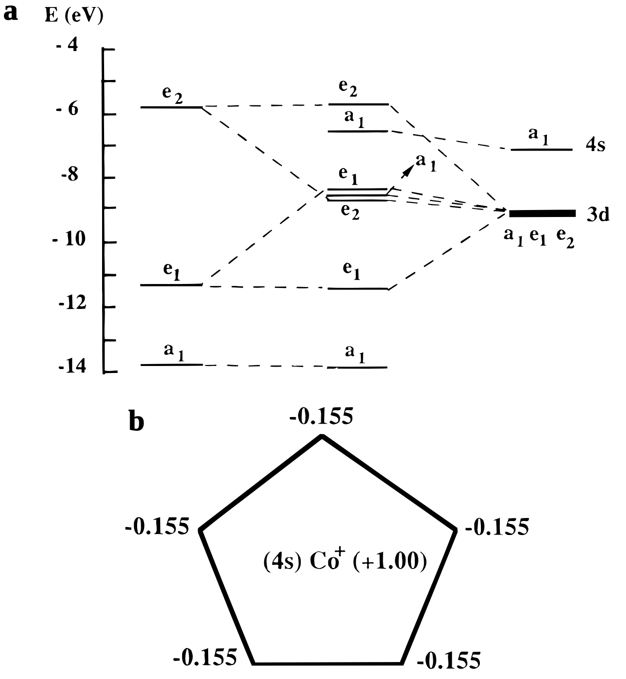

Figure 5. (a) Molecular orbital diagram and (b) LUMO MO coefficients for CpCo$^+$. The coefficients for the carbon $2p_z$ and the cobalt 4s atomic orbitals are indicated.

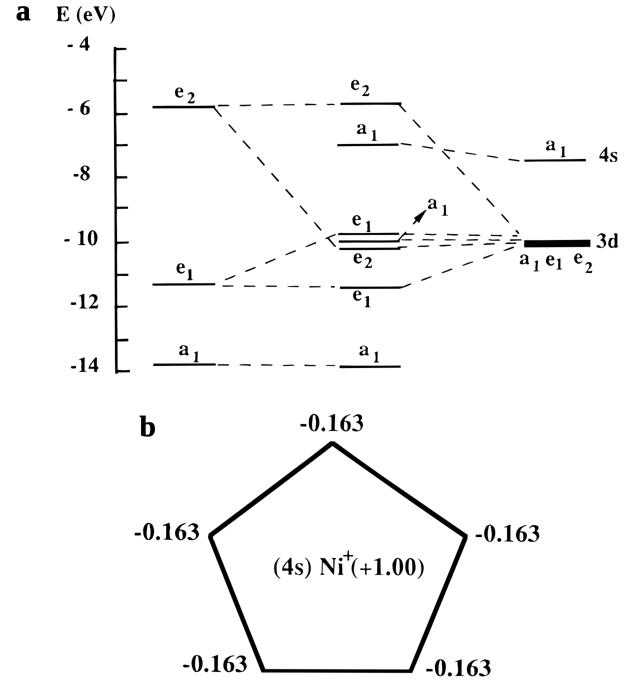

Figure 6. (a) Molecular orbital diagram and (b) LUMO MO coefficients for CpNi$^+$. The coefficients for the carbon $2p_z$ and the nickel 4s atomic orbitals are indicated.

The MO diagram of CpCo$^+$ is shown in Figure 5a. In this case there are 13 valence electrons, and the system necessarily has an open shell electron structure. Occupation of antibonding orbitals will weaken the metal ligand interaction, and the molecule will be more open for reaction. The metal d orbitals are more weakly perturbed by the presence of the ligand in CpCo$^+$ than in CpFe$^+$, and occupation in a high-spin sense is expected. The resulting LUMO becomes an a_1 orbital which is strongly 4s in character. The coefficients for the LUMO are given in Figure 5b. This situation may explain the higher reactivity. An empty 4s character orbital is known to be conducive to H−H and C−H bond activation on a metal center.[16] The C−H σ bond can donate electron density to the empty 4s metal orbital, helping to initiate oxidative addition.

For CpNi$^+$ the situation is quite similar to CpCo$^+$. The MO diagram is shown in Figure 6a. Also in this case (14 valence electrons) high spin is expected due to the relatively weak perturbation caused by the ligand. The LUMO (Figure 6b) is also in this case strongly 4s in its character and available for ethane dehydrogenation.

Alkane dehydrogenation by atomic metal ions has been suggested to proceed via a three-step mechanism.[4] The first step of the mechanism is the oxidative addition of a C−H bond to the metal. In the second step the β-hydrogen of the alkyl group is transferred to the metal. In the last step H_2 is reductively eliminated. While it has been suggested that in at least some instances the last two steps occur in a concerted way through a four-center transition state,[17] it is still generally thought that the initial oxidative addition is facilitated by a metal LUMO with 4s character. We suggest that CpCo$^+$ and CpNi$^+$ with their a_1 predominantly metal 4s LUMOs react by the same oxidative addition mechanism used by the atomic metal ions. Such a mechanism is depicted in Scheme 1. Similarly the failure of CpFe$^+$ to dehydrogenate ethane is consistent with a LUMO that is not predominantly metal 4s in nature.

Permitting ourselves to speculate on the apparent excited-state reaction of CpFe$^+$, we consider first of all the possible nature of the excited state. A triplet $[a_1]^1$-$[e_1]^1$ state might be expected to be long-lived enough to

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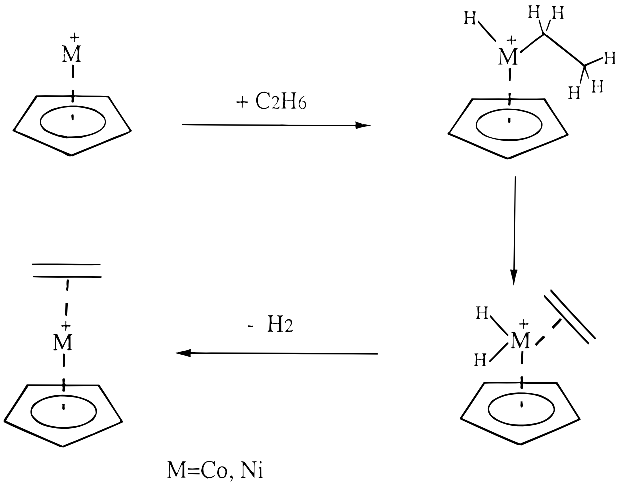
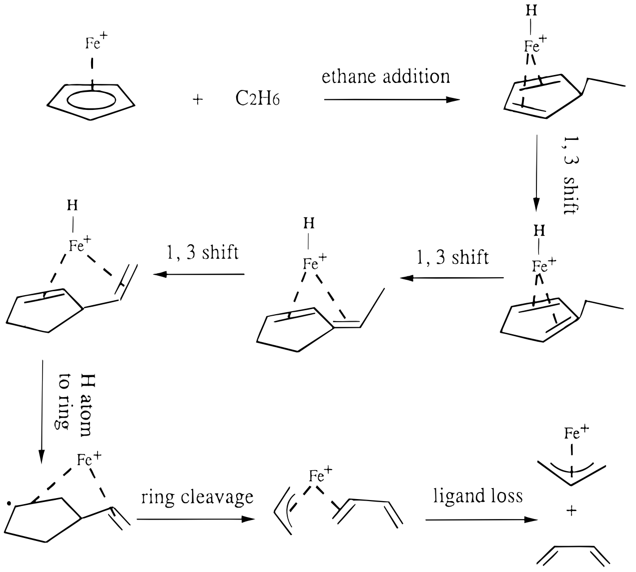
Scheme 1



Scheme 2



participate in reactions. Even with Jahn–Teller distortion, a LUMO involving ligand orbitals similar to that shown in Figure 4 would still be expected.

We then speculate further on the detailed mechanism of the necessarily complex ring rearrangement in the reaction between $CpFe^+$ and ethane to form $CpFeC_3H_5$. Reactions of deuterated $CpFe^+$ with ethane or $CpFe^+$ with deuterated ethane (C_2D_6) give no observable products. This result indicates a strong isotope effect ($k_H/k_D > 10$), suggesting that the reaction potential surface involves at least two "bottlenecks": one associated with shift of an ethane H atom and the other associated with the shift of a cyclopentadienyl H atom. A mechanism consistent with our observations is depicted in Scheme 2. The first step, as suggested by the LUMO depicted in Figure 4b, involves both the metal and a ring carbon. The addition of the ethyl group to the ring is reminiscent of the reaction of $FeCp^+$ with CH_3Br reported by Corderman and Beauchamp[18] in which the methyl group adds to the ring and Br to the metal. Note that this first step involves cleavage of an ethane C–H bond and could be the source of an isotope effect. The mechanism in Scheme 2 proceeds by a series of three 1,3 allylic H atom shifts, perhaps facilitated by the metal. The first H atom shift involves cleavage of a cyclopentadienyl C–H bond and could give rise to an isotope effect. Corderman and Beauchamp also found it necessary to postulate a similar shift of a Cp H atom following the methyl addition. Only in this way could the sequential methylation of $FeCp^+$ by CH_3Br be explained.[18]

Other mechanisms might be envisioned, but that depicted in Scheme 2 is recommended by three considerations: (1) It is consistent with a plausible LUMO of excited $FeCp^+$. (2) It accounts for the observed double iotope effect. (3) It is very similar to the mechanism suggested by Corderman and Beauchamp for the only other reported reaction of $FeCp^+$ in which new C–C bonds are formed involving Cp carbons.

Formation of the $FeC_3H_7^+$ product in very low abundance must involve a very energetic ring cleavage producing highly unsaturated neutral products. Extraction of a methyne from the Cp group, combination of the methyne with ethane to give a C_2H_7 ligand, and elimination of the residue of the Cp group of two acetylenes would account for the product. The weakness of the product signal makes further characterization of the process and its product intractable at present.

Summary

$CpCo^+$ and $CpNi^+$ dehydrogenate ethane, while $CpFe^+$ does not. The ratio of the rate constants for the overall reaction of the three ions is k_{Fe}:k_{Co}:k_{Ni} = (<0.01):1.00:0.40. This is consistent with the probable electronic structure of the three ions. $CpFe^+$ has 12 valence electrons, just enough to fill metal ligand bonding orbitals. The LUMO has metal d and carbon 2p character, which is not particularly conducive to oxidative addition of C–H bonds to the metal. $CpCo^+$ and $CpNi^+$ have occupied metal ligand antibonding orbitals. The weaker metal ligand interaction probably leads to high-spin states with LUMOs having strong metal 4s character. This is conducive to oxidative addition of a C–H bond and consistent with the observed reactivity of $CpCo^+$ and $CpNi^+$.

The reaction of $CpFe^+$ with ethane to give $FeC_3H_5^+$ appears to involve an excited state of the reactant ion. This process can be rationalized in terms of MO arguments, similar to those used to rationalize the ground-state reactivities.

Acknowledgment. E.U. wishes to thank VISTA (Statoil and the Norwegian Academy of Science and Letters) for continuous support.

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