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Migratory Insertion of Ethylene into the Iron–Carbon Bond of $Fe(NH_2)CH_3^+$ and Further Characterization of a Reaction Intermediate Central to the Fe^+-Mediated Dissociation of *n*-Propylamine in the Gas Phase

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Summary: The reaction of ethylene with $Fe(NH_2)CH_3^+$ is best explained in terms of a migratory insertion of ethylene into the iron–carbon bond of $Fe(NH_2)CH_3^+$ which is followed by β-hydrogen transfer and subsequent propene loss. $Fe(NH_2)CH_3^+$ is generated by the ion–molecule reaction of atomic Fe^+ with 2-amino-2-methylbutane in an ICR mass spectrometer. The structure assignment of $Fe(CH_5N)^+$, either $H_3C–Fe–NH_2^+$ or $Fe(CH_3NH_2)^+$, is based on CID experiments and the application of the NRMS technique. The ion–molecule reactions of $Fe(NH_2)CH_3^+$ with ethylene give further insight into the previously proposed mechanism of the n-$C_3H_7NH_2/Fe^+$ system; they serve also as a further example to probe the initial stage of the Ziegler–Natta type C–C bond formation in the gas phase.

Recently, we presented data for the metastable ion (MI) decompositions of *n*-C_3H_7X/M^+ complexes (X = OH, NH_2; M = Fe, Co, Ni) in the gas phase.[1] Extensive labeling studies suggested a mechanism for the reaction of *n*-propylamine with the metal ions M^+ (M = Fe, Co, Ni) that constituted a modification of the reaction sequence previously suggested[2] to account for reactions of atomic transition-metal ions with a variety of alkanes and of monosubstituted alkanes.[3] Highlights of these studies[1] were, inter alia, the observation that (i) Fe^+-mediated ethylene loss from *n*-$C_3H_7NH_2$ involves the α- and β-methylene units and (ii) "scrambling" of these two intact methylene groups precedes the β-hydrogen transfer, which eventually leads to NH_3 and C_3H_6 from *n*-$C_3H_7NH_2/Fe^+$. Several mechanistic scenarios were considered, and the reaction sequence depicted in Scheme I was found to be in keeping with the experimental observations.

We proposed the olefin complex **3** as the central species common to the production of C_2H_4, C_3H_6, and NH_3.[4] This complex, which can be formed by oxidative addition of the C(β)–C(γ) bond to the "anchored" Fe^+ followed by cycloreversion (**1**-Fe^+ → **2** → **3**), serves two functions: (i) **3** can be viewed as the immediate precursor for the detachment of C_2H_4 containing exclusively the α- and β-methylene groups; (ii) complex **3** also accounts for the "equilibration" of the α- and β-CH_2 groups by rotation of the olefin around the Fe–C_2H_4 bond, followed by migratory insertion of the ethylene unit into the Fe^+–CH_3 bond, thus rendering the original α- and β-methylene groups indistinguishable. Rapid irreversible hydrogen transfer (**4** → **5**) leads to the propene–$Fe(H)NH_2^+$ complex **5**, which decomposes to C_3H_6 and NH_3. Of particular mechanistic interest in the present context is the insertion step **3** → **4**, which constitutes a gas-phase analogue of the initial stage in the Ziegler–Natta type C–C bond formation.[5] In view of the fact that neither $Fe(CH_3)^+$ nor $Fe(NH_2)^+$ reacts with C_2H_4,[6] independent experimental evidence is needed in order to substantiate the mechanistic proposal put forward in Scheme I. To this end, $Fe(NH_2)CH_3^+$ was generated, structurally characterized, and then reacted with C_2X_4 (X = H, D) by using Fourier transform ion cyclotron resonance (FTICR) mass spectrometry. The results not only fully support our previous proposal[1] but also provide further insight into several fundamental aspects of gas-phase organometallic chemistry.[3]

Experimental Section

The apparatus (a Spectrospin CMS-47 X equipped with an external ion source) and its operation have been described in detail previously.[7] Atomic Fe^+ is formed via laser desorption/ionization[8] in the external ion source[9] by focusing the beam of a Nd:YAG laser (Spectron Systems, fundamental frequency 1064 nm) onto a stainless steel target which was affixed in the external ion source. The ions are extracted from the source and transferred into the analyzer cell by a system of electrostatic potentials and lenses. After deceleration, the Fe^+ ions are trapped in the field

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[3] For a recent, comprehensive review on the mechanistic aspects of organometallic chemistry in the gas phase, see: Eller, K.; Schwarz, H. *Chem. Rev.* **1991,** *91,* 1121.

[4] In the MI spectra of *n*-$C_3H_7NH_2/Fe^+$ the neutrals C_2H_4, C_3H_6, and NH_3 are formed in the relative ratio 14:5:1. In addition, loss of molecular hydrogen from the β- and γ-positions takes place via "remote functionalization".[1] For this concept, see: Schwarz, H. *Acc. Chem. Res.* **1989,** *22,* 282.

[5] For examples of these kinds of gas-phase reactions as well as theoretical and more recent studies in the condensed phase, see: (a) Uppsal, J. S.; Johnson, D. E.; Staley, R. H. *J. Am. Chem. Soc.* **1981,** *103,* 508. (b) Jolly, C. A.; Marguick, D. S. *J. Am. Chem. Soc.* **1989,** *111,* 7968. (c) Christ, C. S., Jr.; Eyler, J. R.; Richardson, D. E. *J. Am. Chem. Soc.* **1990,** *112,* 596. (d) Brookhart, M.; Volpe, A.-F., Jr.; Lincoln, D. M.; Horvárth, I. I.; Millar, J. M. *J. Am. Chem. Soc.* **1990,** *112,* 5634. (e) Sishta, C.; Hathorn, R. M.; Marks, T. J. *J. Am. Chem. Soc.* **1992,** *114,* 1112. (f) Wang, L.; Flood, T. C. *J. Am. Chem. Soc.* **1992,** *114,* 3169. (g) Guo, B. C.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1992,** *114,* 6152. (h) For other examples of the migratory insertion of C_2H_4 into a M^+–CH_3 bond (M = Y, Sc), see: Huang, Y.; Hill, Y. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1991,** *113,* 840. Huang, Y.; Hill, D.; Sodupe, M.; Bauschlicher, C. W., Jr.; Freiser, B. S. *J. Am. Chem. Soc.* **1992,** *114,* 9106.

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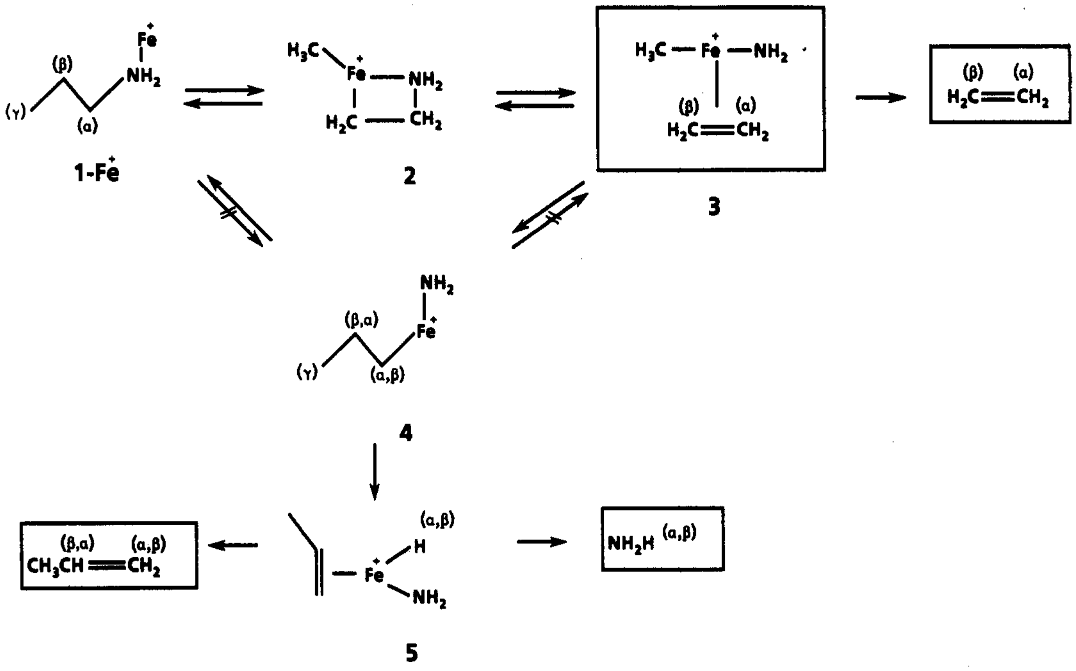
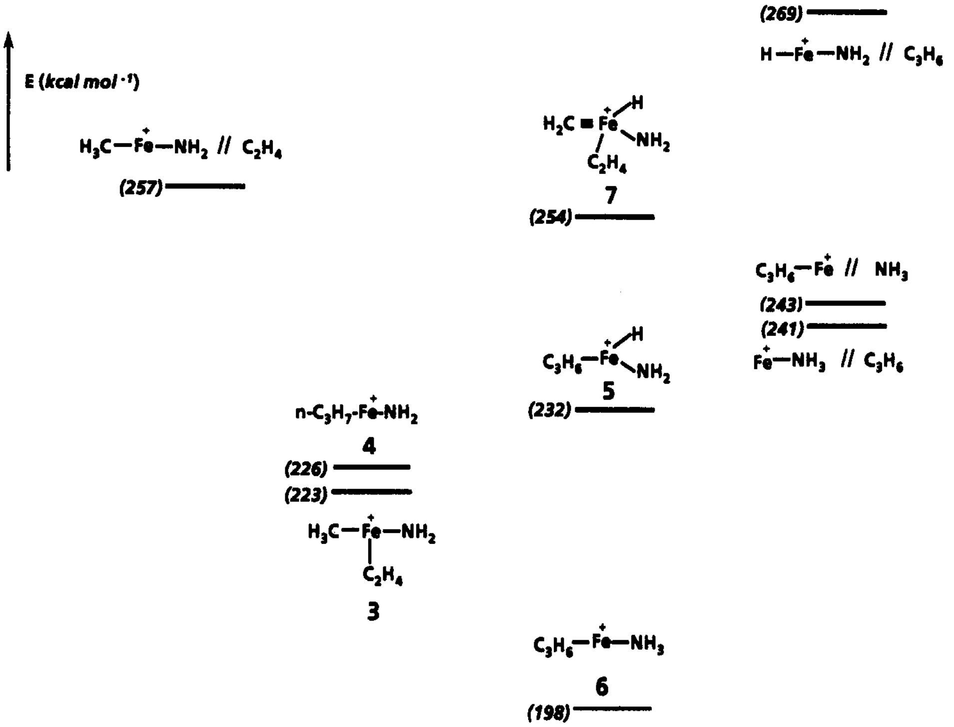
Scheme I. Gas-Phase Dissociation Products of the *n*-$C_3H_7/NH_2/Fe^+$ System[1]



Scheme II. Estimated[19,23] Thermochemical Data for Conceivable $[Fe,C_3,H_9,N]^+$ Isomers and Products Thereof[a]



[a] Energies are given in kcal mol^{-1}. The symbol // indicates a complete separation of the fragments.

of the superconducting magnet (Oxford Instruments), which has a maximum field strength of 7.05 T. For the generation of $Fe(NH_2)CH_3^+$ the metal's most abundant isotope, $^{56}Fe^+$, was isolated by using FERETS[10] and allowed to react with 2-amino-2-methylbutane that was present with a constant pressure of (1–2) × 10^{-9} mbar; reaction times are typically 1–10 s. For collisional cooling of excited states possibly formed, removal of kinetic energy remaining from the transfer, and collision-induced decomposition (CID) experiments,[11] argon was present as a buffer gas with a constant pressure of 5 × 10^{-8} mbar. For the reaction of C_2X_4 (X = H, D) with $Fe(NH_2)CH_3^+$, ethylene was present at a constant pressure of 5 × 10^{-8} mbar. For the CID experiment described in eq 3 (see below), ethylene was introduced in the ICR cell through a pulsed valve.[6a,12] The pressure of the various gases were measured with an ionization gauge (Balzers IMG 070). For

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[10] Forbes, R. A.; Laukien, F. M.; Wronka, J. *Int. J. Mass Spetrom. Ion Processes* **1988**, *83*, 23.

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[13] For leading reviews, see: (a) Schwarz, H. *Pure Appl. Chem.* **1989**, *61*, 685. (b) Holmes, J. L. *Mass Spectrom. Rev.* **1989**, *8*, 513. (c) Terlouw, J. K. *Adv. Mass Spectrom.* **1989**, *11*, 984. (d) McLafferty, F. W. *Science* **1990**, *247*, 925.

[14] Schröder, D.; Sülzle, D.; Hrušák, J.; Böhme, D. K.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1991**, *110*, 145.

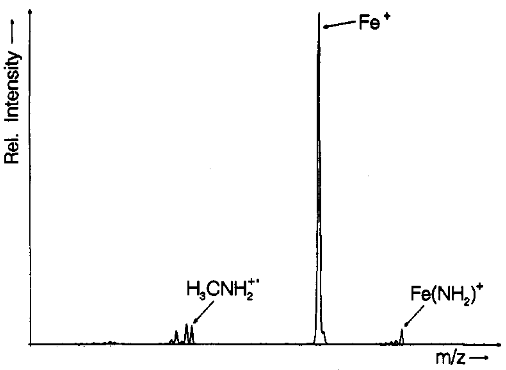

Figure 1. NR mass spectrum of CH_3–Fe–NH_2^+ (Xe, 80%, T//O_2 80% T). See the text for details.

the structural characterization of $Fe(NH_2)CH_3^+$, we not only used FTICR but also performed a neutralization–reionization (NR) experiment,[13] as it has been shown recently[14] that NRMS is a powerful technique to structurally identify organometallic isomers in the gas phase. To this end, mixtures of $Fe(CO)_5$ and 2-amino-2-methylbutane to generate $Fe(NH_2)CH_3^+$ or methylamine to generate the adduct $Fe(CH_3NH_2)^+$ were bombarded with 100 eV of electrons in the chemical ionization source of a BEBE mass spectrometer[15] and the ions formed accelerated to 8-keV translational energy. Species of the elemental composition $Fe(CH_5N)^+$ were mass-selected by means of B(1)E(2), neutralized in the first collision cell (located between E(2) and B(1)) by collision with xenon (80% transmission, T), and the resulting beam of neutrals reionized by colliding it with oxygen (80% T) in the second collision cell. The resulting ions were recorded by scanning B(2).

Results and Discussion

Previous studies have shown that the $Fe(CH_3)^+$ ion has the metal methyl structure Fe–CH_3^+ and not the hydrido methylidene structure H–Fe–CH_2^+;[16] similarly, it was demonstrated[6b] that $Fe(NH_2)^+$ corresponds to an iron amide and not the metal hydride nitrene isomer H–Fe–NH^+. For the $Fe(CH_5N)^+$ ions, the NMRS experiments point to the existence of two different isomers. The CH_3–Fe–NH_2^+ ion pertinent to the present study is formed from 2-amino-2-methylbutane and Fe^+ via loss of C_4H_8;[17] its NR mass spectrum (Figure 1) contains a structure-indicative signal due to cleavage of the H_3C–$Fe(NH_2)^+$ bond. On the basis of thermochemical data, for the basic systems Fe–CH_3^+ and Fe–NH_2^+ cleavage of the Fe–C bond is favored by 10 kcal mol^{-1}.[6b,18,19] The signals for Fe^+ and $CH_3NH_2^{\bullet+}$ in Figure 1 are due to reductive-elimination processes. For the $Fe(CH_5N)^+$ system, formed by the ligand substitution reaction of $Fe(CO)_5^+$ with CH_3NH_2, the NR mass spectrum (not shown) is dominated by signals for Fe^+ (100%) and $CH_3NH_2^{\bullet+}$ (15%). The signal which corresponds to $Fe(NH_2)^+$ is a factor of ca. 20 smaller than that shown in Figure 1. These findings are in line with the formation of $Fe(NH_2)CH_3^+$ upon dissociative ion–molecule reactions of Fe^+ with 2-amino-2-methylbutane; in contrast, chemical ionization of a mixture of $Fe(CO)_5$ and CH_3NH_2 results in the generation of the adduct complex $Fe(CH_3NH_2)^+$.[20]

In the reaction of *bare* Fe^+ with 2-amino-2-methylbutane under FTICR conditions, besides other products (eq 1), the $Fe(CH_5N)^+$ ion is formed in greatest abundance.

$$\begin{aligned} Fe^+ + CH_3CH_2C(CH_3)_2NH_2 &\xrightarrow{7\%} C_5H_{11}^+ + FeNH_2 \\ &\xrightarrow{15\%} Fe(NH_3)^+ + C_5H_{10} \\ &\xrightarrow{50\%} Fe(CH_5N)^+ + C_4H_8 \\ &\xrightarrow{10\%} Fe(C_5H_8)^+ + NH_3 + H_2 \\ &\xrightarrow{16\%} Fe(C_4H_{10}N)^+ + CH_3^\bullet \\ &\xrightarrow{2\%} Fe(C_5H_{11}N)^+ + H_2 \qquad (1) \end{aligned}$$

If $Fe(CH_5N)^+$ is isolated and reacted with C_2D_4, three reaction channels are observed (eq 2) with an overall rate constant $k = 2.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (±50%). This rate constant is small as compared with the collision limit ($k_L = 1.0 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}).

$$\begin{aligned} Fe(CH_5N)^+ + C_2D_4 &\xrightarrow{15\%} Fe(NH_2D)^+ + C_3H_3D_3 \\ &\xrightarrow{40\%} Fe(CH_4DN)^+ + C_2HD_3 \\ &\xrightarrow{45\%} Fe(C_3H_5D_4N)^+ \qquad (2) \end{aligned}$$

These three processes deserve to be discussed separately. (i) For the association product $Fe(C_3H_5D_4N)^+$, which is stabilized either by radioactive means[21] or by collisional cooling with the argon buffer gas, CID experiments of the isolated species clearly point to the formation of the adduct **3**. At low collision energies the loss of intact C_2D_4 dominates; at higher energies loss of CH_3NH_2 as well as the generation of Fe^+ is observed. No evidence for the operation of H/D exchange processes is found. A typical high-energy CID product distribution is given in eq 3.

(ii) In passing we note that H_3C–Fe–NH_2^+, in distinct contrast[6] to either Fe–CH_3^+ or Fe–NH_2^+, undergoes one hydrogen/deuterium exchange with C_2D_4. The elucidation

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(15) For a detailed description of the instrument and its operation, see: (a) Srinivas, R.; Sülzle, D.; Weiske, T.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1991**, *107*, 369. (b) Srinivas, R.; Sülzle, D.; Koch, W.; DePuy, C. H.; Schwarz, H. *J. Am. Chem. Soc.* **1991**, *113*, 5970.

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(17) For a possible mechanism of the metal-ion-induced C_4H_8 loss from this and other amines; see: Karrass, S.; Eller, K.; Schwarz, H. *Chem. Ber.* **1990**, *123*, 939.

(18) Fisher, E. R.; Schultz, R. H.; Armentrout, P. B. *J. Phys. Chem.* **1989**, *93*, 7382.

(19) We are, of course, aware that the bonding properties of the diligated system $M(X)Y^+$ cannot necessarily be described in terms of a superposition of the properties of the individual monoligated species MX^+ and MY^+, respectively. Consequently, the data used in this article to describe the thermochemistry of the $Fe(C_3H_5N)^+$ system, by assuming additivity of bond strengths, are at best qualitative in nature. For detailed discussions, see: (a) Armentrout, P. B.; Beauchamp, J. L. *Acc. Chem. Res.* **1989**, *22*, 315. (b) Freiser, B. S. In *Bonding Energetics in Organometallic Compounds*; Marks, T. J., Ed.; ACS Symposium Series 428; American Chemical Society: Washington, DC, 1990; p 55. (c) Martinho Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629. (d) Reference 3.

(20) A reviewer has argued that in the reaction of $Fe(CO)_x^{\bullet+}$ (x = 1–5) with CH_3NH_2 isomers such as H–Fe–$CH_2NH_2^+$ and H–Fe–$NHCH_3^+$ might be generated rather than the substitution product $Fe(NH_2CH_3)^+$. We discard this possibility on the grounds that (i) this conjecture is not supported by the genesis of the species and (ii) analogous experiments on the related $Fe(HOCH_3)^+$ system demonstrate that ions such as H–Fe–CH_2OH^+ and H–Fe–OCH_3^+ do not correspond to minima on the respective potential energy surface (Schröder, D.; Fiedler, A.; Hrušák, J.; Schwarz, H. *J. Am. Chem. Soc.* **1992**, *114*, 1215).

(21) (a) Dunbar, R. C. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 423. (b) Dunbar, R. C. *Mass Spectrom. Rev.* **1992**, *11*, 309.

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\begin{aligned}
\mathrm{Fe(C_3H_5D_4N)^+} \xrightarrow{\mathrm{CID}} \overset{55\%}{\rightarrow}\ & \mathrm{Fe(CH_5N)^+ + C_2D_4} \\
\overset{15\%}{\rightarrow}\ & \mathrm{Fe(C_2D_4)^+ + CH_3NH_2} \\
\overset{30\%}{\rightarrow}\ & \mathrm{Fe^+ + C_2D_4 + CH_3NH_2} \qquad (3)
\end{aligned}
$$

of the mechanism of this reaction, which clearly points to a synergistic effect of the two ligands, is presently under study.[22]

(iii) Of particular importance with regard to Scheme I are the formations of $Fe(NH_2D)^+$ and $C_3H_3D_3$ in the reaction of $H_3C\text{–}Fe\text{–}NH_2^+$ with C_2D_4. This result provides further support for the central role of **3** in the Fe^+-mediated dissociation of *n*-$C_3H_7NH_2$; also, it lends strong support to our supposition of a migratory insertion of ethylene into a carbon–iron bond. Although reliable thermochemical data are not yet available for the $Fe(C_3H_9N)^+$ system,[19] the estimated heats of formation of conceivable intermediates (Scheme II), using literature-known data[23] in a simple additivity scheme, rule out several candidates. For example, a metathesis-like reaction proceeding from **3** via **7** (rather than **3** → **4**) is unlikely due to the high heat of formation of **7**. Similarly, the product ion $Fe(NH_2X)^+$ (X = H, D) most likely corresponds to an intact iron ammonia complex ($Fe\text{–}NH_2X^+$) rather than the insertion product $X\text{–}Fe\text{–}NH_2^+$. The absence of NH_2D loss in the reaction of $H_3C\text{–}Fe\text{–}NH_2^+$ with C_2D_4 may reflect the different bond strengths of the $Fe\text{–}NH_2D^+$ bond as compared to the binding energy of propene to Fe^+ (38.5 kcal mol^{-1} versus 37 kcal mol^{-1} 23). It also seems appropriate to recall that, in the MI mass spectrum of *n*-$C_3H_7NH_2/Fe^+$, loss of C_2H_4 forms the major reaction channel in spite of the fact that the formations of $H_3C\text{–}Fe\text{–}NH_2^+$ and C_2H_4 are energetically less favored than loss of C_3H_6 (Scheme II). We presume that this is a consequence of a "bottleneck" in the multistep transformation of **3** to the products $Fe(NH_3)^+$ and C_3H_6. Support for this supposition is provided by the small rate constant for the reaction of $H_3C\text{–}Fe\text{–}NH_2^+$ with ethylene (see above).

In conclusion, the present study provides the missing link for a more detailed understanding of the unusual gas-phase behavior[1] of the seemingly simple *n*-$C_3H_7NH_2/Fe^+$ system and also points to the operation of synergetic effects of ligands in the course of CH/CC bond activation processes.[3]

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[22] While the mechanistic details of the hydrogen/deuterium exchange in the $H_3C\text{–}Fe\text{–}NH_2^+/C_2D_4$ system deserve attention, as stated by the reviewers, the details of this reaction are not likely to be relevant to the topic of migratory insertion of ethylene into the Fe–C bond.

[23] Thermochemical data were taken from: (a) references 6b and 17. (b) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7492. (c) Elkind, J. L.; Armentrout, P. B. *J. Phys. Chem.* **1986**, *90*, 5736. (d) Marinelli, P. J.; Squires, B. R. *J. Am. Chem. Soc.* **1989**, *111*, 4101.