Sequential Iron(I)-Mediated Homologization of Olefins by Methanol and Methyl Halides in the Gas Phase

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The gas-phase chemistry of simple $Fe(olefin)^+$ complexes with CH_3X (X = OH, F, Cl, Br, I) has been studied by Fourier-transform ion cyclotron resonance mass spectrometry. C−C bond formation between the alkene and CH_3X occurs via initial insertion of Fe^+ into the C−X bond, followed by a migratory insertion of the olefin into the iron−carbon bond of $(X)Fe(CH_3)^+$. This step constitutes a gas-phase analog of the initial stage in the Ziegler−Natta type C−C bond formation; a combination of subsequent β-H shift and reductive elimination of HX completes the reaction. In the case of $Fe(propene)^+$ a remarkable regioselectivity is observed in that the addition results in the exclusive formation of an unbranched $Fe(butene)^+$ complex. Starting from $Fe(ethene)^+$, up to two consecutive methylations occur using CH_3OH as a reactant; with methyl halides the number of methylations varies from 2 (for X = I) to 4 (for X = F). For alkyl halides RX bearing a β-hydrogen, Fe^+-mediated dehydrohalogenation of RX competes efficiently with the C−C coupling of RX and $Fe(olefin)^+$.

Introduction

Gas-phase studies using Fourier-transform ion cyclotron mass spectrometry (FTICR) as a highly sophisticated "reaction vessel"[1] have provided profound insight into the chemistry of "bare" ions in general and transition-metal cations in particular.[2] Further, the potential of sequentially attaching ligands L to a metal ion provides a unique means to specifically tune the metal ion's reactivity, a topic of both scientific and practical importance.[3] The ligands may act as mere "spectator ligands" or as "modifiers" by enhancing or decreasing the reactivity of the metal ion, or the ligands themselves may be activated in the course of reaction.[3c]

Despite earlier reports,[4] thermalized Fe^+ does not react with methanol in the gas phase, and even the formation of $Fe(OH)^+$ is endothermic by at least 5 kcal/mol.[5,6] However, activation of methanol can be achieved by $Fe(CH_3)^+$,[7a] $Fe(CH_2O)^+$,[7b] $Fe(OH)^+$,[7c] and FeO^+.[7d] Here, we report the reactions of $Fe(olefin)^+$ complexes with methanol and methyl halides, CH_3X, which lead to the corresponding homologous $Fe(olefin)^+$ complexes via a formal CH_2 transfer (eq 1).

$$Fe(RCH{=}CH_2)^+ + CH_3X \rightarrow Fe(RCH{=}CHCH_3)^+ + HX \quad (1)$$

While transition-metal-mediated coupling of olefins and halogen-substituted hydrocarbons is a common reaction in organic synthesis,[8] the reaction is only rarely encountered in gas-phase organometallic chemistry.[9] Further, for X = OH the realization of eq 1 in the condensed phase is hampered by the acidity of the hydroxy group, and organometallic compounds which effect C−C bond formation processes using alcohols are relatively scarce and usually involve radical mechanisms.[10]

Experimental Section

All experiments were performed with a Spectrospin CMS 47X FT-ICR mass spectrometer equipped with an external ion source and a superconducting magnet (Oxford Instruments, 7.05 T). The instrument and its operation have been described in detail previously.[11] In brief, Fe^+ ions were generated *via* laser desorption/laser ionization by focusing the beam of a Nd:YAG laser (1064 nm) onto an iron rod.[12] The cations were extracted from the ion source and transferred to the analyzer cell by a system of electrostatic potentials and lenses. Isolation of $^{56}Fe^+$ and all subsequent isolation steps were performed by

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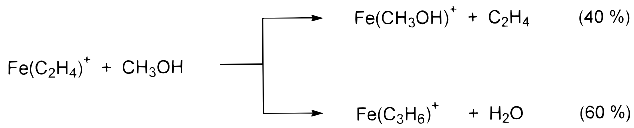
Scheme 1



using FERETS,[13] a computer-controlled ion-ejection protocol which combines single-frequency ion-ejection pulses with frequency sweeps to optimize ion isolation. Fe(olefin)$^+$ complexes were prepared from Fe^+ *via* well-known ion−molecule reactions, by pulsing-in appropriate amounts of reactant gases; e.g., $Fe(C_2H_4)^+$ and $Fe(C_3H_6)^+$ were generated from propane and Fe(i-C_4H_8)$^+$ was generated from neopentane.[14] Subsequently, the ions were thermalized by pulsing-in argon for about 2 s at a pressure of 5×10^{-5} mbar (>1000 collisions), and the ions of interest were carefully isolated to avoid off-resonance excitation.[15] CH_3X (X = OH, F, Cl, Br, I) was admitted to the FT-ICR cell *via* a leak valve at pressures of ca. 10^{-8} mbar. Branching ratios were derived from the pseudo-first-order kinetics of 2−7 independent measurements and are reported within ±10% error. For collision-induced dissociation (CID)[16] argon was present at a pressure of $(2-5) \times 10^{-7}$ mbar.

The bond-dissociation energy of $Fe(CH_3OH)^+$ has been estimated by monitoring the metastable ion fragmentation of $(CH_3OH)Fe(CO)^+$ in a modified VG ZAB/HF/AMD four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sectors); details of the instrument and its operation have been described previously.[17] For the generation of the complex, a (1:10:1) mixture of CH_3OH, CO, and $Fe(CO)_5$ was ionized in a chemical ionization source (repeller voltage ca. 0 V) by 100-eV electron bombardment. The ions were accelerated to 8 keV kinetic energy and mass-selected by means of B(1)/E(1) at a resolution of $m/\Delta m = 3000$. The unimolecular fragmentation of metastable ions occurring in the field-free region preceding B(2) were recorded by scanning this sector, and the relative intensities for losses of CO versus CH_3OH were converted in relative bond-dissociation energies using Cooks' kinetic method.[18]

Reactions of $Fe(C_2H_4)^+$ with Methanol

In the reaction of $Fe(C_2H_4)^+$ with methanol two competing reactions occur: (i) Ligand exchange to yield $Fe(CH_3OH)^+$; (ii) formation of $Fe(C_3H_6)^+$ concomitant with loss of water (see Scheme 1). The branching ratio of both processes is very sensitive to the experimental conditions and ranges from 70:30 to 40:60 dependent on the thermalization and isolation procedures which affect the internal and the kinetic energy content of the $Fe(C_2H_4)^+$ complex. The more carefully the mass selection and thermalization steps were performed, the less ligand displacement occurred. Our reported ratio (Table 2) refers to the "final" value which did not change upon further cooling with argon in the thermalization procedure or the use of even more refined ejection pulses during the mass selection. The observed energy dependence suggests that the kinetic requirements for the exit channels of the ethene loss and the competing coupling process are comparable. BDE(Fe^+−methanol) has not yet been reported, and the observed ligand displacement indicates that it is similar to BDE(Fe^+−ethene) = 34.5 ± 1.4 kcal/mol.[5] For a verification of this argument, we applied Cooks' kinetic method[18] which represents a very sensitive tool to determine relative BDEs. To this end, mixtures of $Fe(CO)_5$ and CO with methanol and [D_4]-ethene, respectively, were subjected to chemical ionization in the ion source of the four-sector mass spectrometer to afford the bisligated complexes $(CH_3OH)Fe(CO)^+$ and $(C_2D_4)Fe(CO)^+$. In the unimolecular dissociation of these metastable ions the intensities of the $Fe(CO)^+$ signals relative to those of $(CH_3OH)Fe^+$ and $(C_2D_4)Fe^+$ were very similar (1:33 versus 1:35, respectively), suggesting ΔBDE = 0.1 kcal/mol for Fe^+−methanol and Fe^+−[D_4]ethene. This finding is not only in perfect agreement with the observed exchange reaction but also accounts for the strong energy dependence of the branching ratio for the reaction of $Fe(C_2H_4)^+$ with methanol, because thermoneutral ligand exchange (having hardly any barrier) and CC-coupling (which may be subject to a significant barrier) compete with each other. Finally, using BDE(Fe^+−CO) = 31.2 ± 1.8 as an absolute reference,[5] we can further convert[18b] the relative bond energies to an absolute value of BDE(Fe^+−CH_3OH) = 34.4 ± 2.2 kcal/mol.

As shown in Scheme 1, $Fe(C_3H_6)^+$ represents the major product from the reaction of $Fe(C_2H_4)^+$ with methanol. CID of this product yields Fe^+ as ionic fragment, exclusively. In addition, when the $Fe(C_3H_6)^+$ formed is reacted with [D_6]acetone which was pulsed-in to 50% conversion of $Fe(C_3H_6)^+$, nothing else but ligand displacement to $Fe(C_3D_6O)^+$ takes place. Both observations are in line with an intact C_3H_6 moiety, complexed to Fe^+, and we conclude that the Fe(propene)$^+$ complex has been formed. This structural assignment is further substantiated by secondary reactions of $Fe(C_3H_6)^+$ with methanol, which yield $Fe(C_4H_8)^+$ as product (see below). A reasonable mechanism for the coupling reactions of $Fe(C_2H_4)^+$ with CH_3X is depicted in Scheme 2. After formation of the encounter complex **1**, the reaction is initiated by oxidative insertion of Fe^+

Scheme 2

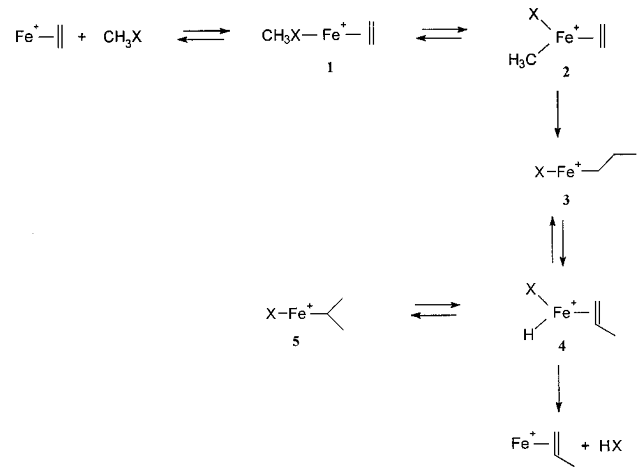


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Table 1. Ratios of HX/DX Losses in the Reactions of Isotopologous $Fe(C_2H_4)^+$ Complexes with [D$_0$]- and [D$_4$]Methanol

reactants		HX/DX ratios	
		exptl data	calcd data[a]
$Fe(C_2D_4)^+$	CH_3OH	0.5 ± 0.1^b	0.75^b
$Fe(C_2H_4)^+$	CD_3OD	4.7 ± 0.4^c	1.3^c
$Fe(CH_2CD_2)^+$	CH_3OH	3.0 ± 0.2^b	2.5^b
$Fe(CH_2CD_2)^+$	CD_3OD	1.2 ± 0.1^c	0.4^c

[a] Calculated assuming a statistical equivalency of all H/D atoms attached to carbon atoms. [b] X = OH. [c] X = OD.

into the CH_3-X bond to yield **2**.[19] The next step (**2** → **3**) can be regarded as carbometalation by migratory insertion of the ethene ligand into the Fe^+−methyl bond,[20] which constitutes a gas-phase analogue of C−C bond formation in the Ziegler−Natta process.[19b] The resulting intermediate **3**, which has also been postulated for the reaction of Fe^+ and *n*-propanol,[21] undergoes a β-hydrogen transfer to the Fe^+ center to yield **4** which can either rearrange further to **5** or eliminate water (X = OH) to form $Fe(C_3H_6)^+$. The overall process $Fe(C_2H_4)^+ + CH_3OH \rightarrow Fe(C_3H_6)^+ + H_2O$ is exothermic by 19 kcal/mol.[22] The sequence described in Scheme 2 formally corresponds to the methylation of ethene by methanol (X = OH).

To gain more detailed mechanistic insight, we have investigated the reactions of $Fe(C_2H_4)^+$ with CD_3OD and that of $Fe(C_2D_4)^+$ with CH_3OH. In addition, [D$_0$]- and [D$_4$]methanol were reacted with $Fe(CD_2CH_2)^+$ which itself was prepared by reacting Fe^+ with [2,2-D$_2$]-propane.[23] From the results of the labeling experiments (Table 1), several conclusions can be drawn: (i) The absence of D_2O loss from the $Fe(C_2D_4)^+/CH_3OH$ couple and of H_2O from the $Fe(C_2H_4)^+/CD_3OD$ couple indicates that the original O−H or O−D bonds of methanol are not activated in the course of reaction. (ii) However, all other H/D atoms, including those of the methyl group of methanol, take part in exchange processes, thus indicating that the β-H shifts **3** ⇄ **4** ⇄ **5** are reversible and, quite likely, involve **5** as an intermediate en route of the H/D exchange.[21b] Yet, the deviation of the experimental and the calculated statistical HX/DX ratios for all reacted isotopologues proves that the H/D exchange is not complete and direct dissociation of **4** to Fe(propene)$^+$ competes efficiently with the rearrangement to **5**. (iii) Only a relatively small intramolecular kinetic isotope effect (KIE) is operative in the reactions of $Fe(C_2H_2D_2)^+$ with methanol, although an exact number cannot be derived due to the contribution of H/D-exchange processes. This suggests that neither β-H migration nor reductive elimination of water is rate-determining for the overall reaction; rather, the insertion into the C−O bond (**1** → **2**) or the subsequent insertion (**2** → **3**) of ethene in the Fe^+−carbon bond serve as rate-limiting step(s). While the insertion of Fe^+ in the CH_3-X bond is likely to be reversible,[24] the latter reaction step is connected with a large reverse barrier, as concluded from the absence of C−C bond activation in the fragmentation of metastable Fe(*n*-propanol)$^+$.[21b] Note however, that $(HO)Fe(CH_3)^+$ can be generated from Fe(*n*-propanol)$^+$ upon collisional activation.[19a] In conclusion, migratory insertion in the double bond is suggested to constitute the rate-determining step in the reaction of $Fe(C_2H_4)^+$ with methanol.[25]

Table 2. Product Distribution for the Reactions of Fe(olefin)$^+$ Complexes with Methanol

	product	branching ratio (%)
$Fe(C_2H_4)^+$	$Fe(C_3H_6)^+ + H_2O$	60[a]
	$Fe(CH_3OH)^+ + C_2H_4$	40[a]
$Fe(C_3H_6)^+$	$Fe(C_4H_8)^+ + H_2O$	100
$Fe(n\text{-}C_4H_8)^+$	$Fe(C_4H_6)(CH_3OH)^+ + H_2$	100
$Fe(i\text{-}C_4H_8)^+$	$Fe(C_5H_{10})^+ + H_2O$	80
	$Fe(C_4H_6)(CH_3OH)^+ + H_2$	15
	$Fe(C_4H_8)(CH_3OH)^+$	5
$Fe(C_4H_6)^+$	$Fe(C_4H_6)(CH_3OH)^+$	100
$Fe(C_6H_6)^+$	$Fe(C_6H_6)(CH_3OH)^+$	100

[a] Branching ratio depends on the isolation and thermalization procedure (see text).

Interestingly, we found that the olefin complexes of Co^+ and Ni^+ only undergo ligand displacement or adduct formation when reacted with methanol, whereas C−C bond formation does not take place. At first, the different reactivity may be due to the fact that oxidative addition to a formal metal(III) intermediate is more facile for iron than for cobalt and nickel, because Co(III) and Ni(III) are less stable than Fe(III). Further, thermochemical properties differ among these three metals, and Fe^+ exhibits the largest BDE(M^+−OH), i.e. 87, 72, and 56 kcal/mol for M = Fe, Co, and Ni.[5] Therefore, the inserted species **2** possesses more internal energy to overcome the barrier for addition to the double bond than the less excited analogous intermediates for Co^+ and Ni^+. This reasoning lends further support to our suggestion that the step **2** → **3** is rate-determining in the reaction sequence depicted in Scheme 2. However, a more detailed understanding of the different reactivities of these metals requires the knowledge of the potential-energy surface, in particular with respect to the role of different electronic states.[26]

Reactions of Higher Fe(olefin)$^+$ Complexes with Methanol

Fe(propene)$^+$ reacts with methanol yielding $Fe(C_4H_8)^+$ exclusively (Table 2). In this process, the newly formed C_4H_8 ligand can correspond to either *n*- or isobutene (Scheme 3). CID experiments and further ion−molecule reactions clearly demonstrate that an Fe^+ complex of a linear butene (either 1- or 2-butene) is generated with high selectivity (see below). The observation of H/D exchange[27] in the $Fe(C_3H_6)^+/CD_3OD$ couple indicates

(19) For X = OH and NH$_2$ the inserted structures CH_3-Fe^+-X have been characterized as stable intermediates: (a) Schröder, D.; Fiedler, A.; Hrušák, J.; Schwarz, H. *J. Am. Chem. Soc.* **1992**, *114*, 1215. (b) Karrass, S.; Stöckigt, D.; Schröder, D.; Schwarz, H. *Organometallics* **1993**, *12*, 1449.

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(22) BDE(Fe^+−propene) taken from: Martinho Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629. See also ref 3c.

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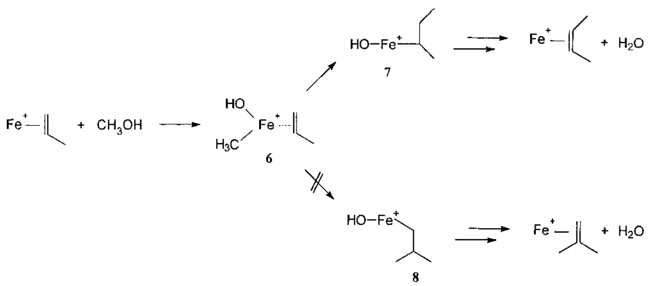
(25) A reversible β-methyl migration has been reported recently: McNeill, K.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 3625.

(26) See for example: Shaik, S.; Danovich, D.; Fiedler, A.; Schröder, D.; Schwarz, H. *Helv. Chim. Acta* **1995**, *78*, 1393.

(27) $Fe(C_4H_5D_3)^+$ and $Fe(C_4H_6D_2)^+$ are formed in a ca. 10:1 ratio.

Scheme 3



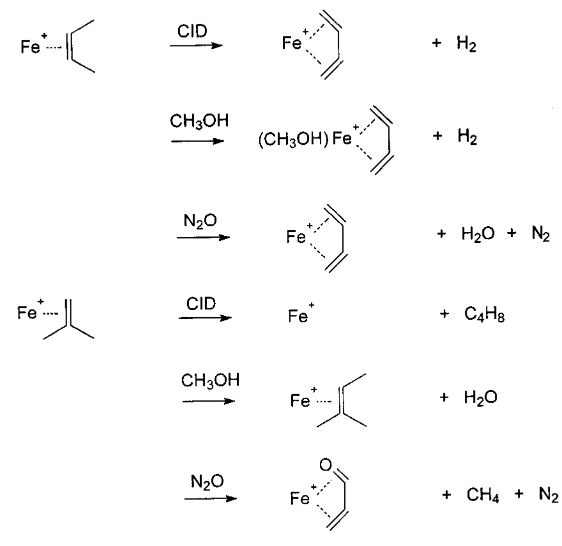
that the β-H transfer preceding water loss is partially reversible, in analogy to the reaction of $Fe^+(C_2H_4)$ with methanol. Finally, the absence of ligand exchange supports the BDE(Fe^+-CH_3OH) derived above because BDE(Fe^+–propene) = 37.0 kcal/mol.[22]

Fe^+(*n*-butene) itself, prepared from the displacement reactions of 2-butene with $Fe(C_2H_4)^+$, reacts with methanol *via* liberation of H_2 to form $(C_4H_6)Fe(CH_3OH)^+$ (Table 2). Reaction with [D$_4$]methanol demonstrates that dihydrogen is lost from the butene ligand, exclusively. This reaction can be regarded as a ligand-induced dehydrogenation[28] of butene to yield the corresponding butadiene complex. The incoming methanol ligand provides the complexation energy in the collision complex, and instead of C–C coupling, dehydrogenation of the butene ligand takes place. In contrast, Fe(isobutene)$^+$ and CH_3OH give rise to the loss of water accompanied with C–C bond formation (i.e. $Fe(C_5H_{10})^+$) as the dominant process (80%); side reactions amount to adduct formation (5%) and ligand-induced dehydrogenation of the isobutene ligand (15%). While it is obvious that the C–C coupling reaction of $Fe(i\text{-}C_4H_8)^+$ will initially lead to an $Fe(i\text{-}C_5H_{10})^+$ isomer, the structural characterization of this product will prove difficult as it has been demonstrated earlier that an unambiguous structural characterization of branched $Fe(C_5H_{10})^+$ isomers by means of CID experiments is not possible; this is due to facile rearrangements, e.g. to bisligated complexes $(C_2H_4)Fe(C_3H_6)^+$.[29] Although the reaction $C_5H_{10} \rightarrow C_3H_6 + C_2H_4$ is ca. 25 kcal/mol endothermic, complexation of the two olefins to Fe^+ can render this process thermoneutral. Consequently, the observed losses of CH_4, C_2H_4, and, C_3H_6 as neutral fragments upon CID of the $Fe(C_5H_{10})^+$ product from the coupling of Fe(isobutene)$^+$ and methanol are not conclusive with respect to the isopentene isomer formed initially. Similarly, ligand exchange of the so-formed $Fe(C_5H_{10})^+$ with benzene yields the products $(C_2H_4)Fe(C_6H_6)^+$, $(C_3H_6)Fe(C_6H_6)^+$, and $Fe(C_6H_6)^+$. While the latter product is in keeping with partial formation of intact Fe(pentene)$^+$, the former products point to the presence of $(C_2H_4)Fe(C_3H_6)^+$.

More unsaturated complexes, like Fe(butadiene)$^+$ and Fe(benzene)$^+$, prepared from the reactions of Fe^+ with *n*-butene[29] and benzene, respectively, only form adducts with methanol (Table 2) and do not show evidence for C–C bond formation.

According to Scheme 3, the reaction of Fe(propene)$^+$ with methanol may result in a linear or a branched Fe(butene)$^+$ complex, depending on the carbon atom to which the methyl group is attached during the addition step. Thus, the information on the regiochemistry of the C–C bond formation step can be derived from the structure of the resulting $Fe(C_4H_8)^+$ product. To this end, we used a combination of CID and ion–molecule reactions to distinguish authentic Fe(*n*-butene)$^+$ and Fe(isobutene)$^+$, and the structurally indicative products are shown in Scheme 4: (i) CID of Fe(*n*-butene)$^+$ yields $Fe(C_4H_6)^+$ and Fe^+ as ionic fragments, while for Fe(*i*-butene)$^+$ only Fe^+ is observed. (ii) A further distinction of *n*- and isobutene complexes is provided in their reactions with methanol (see above), and dehydration is characteristic for Fe(*i*-butene)$^+$, only. (iii) In addition, both isomeric $Fe(C_4H_8)^+$ complexes are readily identified by their reactions with N_2O. Here Fe(*n*-butene)$^+$ yields $Fe(C_4H_6)^+$ as the major product (70%), which is not observed for Fe(*i*-butene)$^+$, and vice versa Fe(*i*-butene)$^+$ leads to $Fe(C_3H_6O)^+$ (60%), while Fe(*n*-butene)$^+$ does not.[30] Especially these latter reactions provide a suitable monitor for the presence of the two isomers.

Scheme 4



These clear-cut differentiating processes have been applied to $Fe(C_4H_8)^+$, which was generated in the reaction of $Fe(C_3H_6)^+$ with methanol, thermalized by pulsed-in argon, and mass-selected. We observe only products characteristic for Fe(*n*-butene)$^+$. In particular, the complete absence of the oxidation product $Fe(C_3H_6O)^+$ in the reaction with N_2O demonstrates that the homologization of Fe(propene)$^+$ by methanol leads to a linear butene, exclusively. Thus, we conclude that carbometalation of propene involves selectively **7** (Scheme 3) in that iron adds to the higher substituted carbon atom of propene while the methyl group is attached to the sterically better accessible terminal methylene group. A similar result has been obtained by Freiser and co-workers for the reaction of Fe(propene)$^+$ with chlorobenzene.[9c] These authors proposed steric effects to be responsible for the remarkable regioselectivity but could not exclude the operation of electronic factors, too. In the present case, a 100% selectivity for **7** can hardly be explained via steric effects. As an alternative, we propose that the regioselectivity of gas-phase carbometalation is effected by charge-transfer stabilization

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Table 3. Branching Ratios for C−C Coupling and Amounts of H/D Exchange for the Primary Reactions of $Fe(C_2D_4)^+$ with Methanol and Methyl Halides, CH_3X

X	C−C coupling (%)	ratio of HX/DX losses	Δ_rH (kcal/mol)	largest alkene complex[a]
OH	60	0.50	−20	$Fe(C_4H_8)^+$
F	100	0.30	−17	$Fe(C_6H_{12})^+$
Cl	100	0.31	−13	$Fe(C_6H_{12})^+$
Br	100	0.77	−11	$Fe(C_5H_{10})^+$
I	75	1.03	−8	$Fe(C_4H_8)^+$

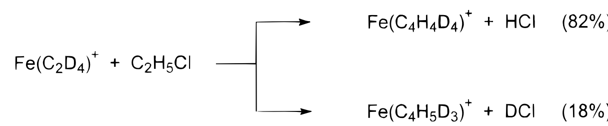
[a] Obtained in the consecutive methylation of $Fe(C_2H_4)^+$ after 30 s of reaction time at a CH_3X pressure of ca. 10^{-8} mbar. For clarity, the number of deuterium atoms is omitted.

via a resonance structure in which an electron is transferred from carbon to iron. This results in a structure where a carbocation center interacts with neutral FeOH (IE = 7.9 eV). According to that, **7** involves cationic character at a secondary position of the *n*-butyl group (IE = 7.3 eV), while a primary cation in the isobutyl fragment of **8** is less favorable (IE = 7.9 eV). Following this argument, **7** experiences a larger stabilization than **8**, which would account for the observed 100% regioselectivity.

Reactions of $Fe(C_2H_4)^+$ with Methyl Halides and Ethyl Chloride

In analogy to the methylation of olefins with methanol (Schemes 1−3), it has been shown earlier[9a,c] that Fe(cyclopentadienyl)$^+$ and Fe(benzyne)$^+$ complexes react with methyl halides by methylation of the ligand and concomitant dehydrohalogenation. Here, we describe the results obtained for the reactions of $Fe(C_2D_4)^+$ with methyl halides CH_3X (X = F, Cl, Br, I) with an emphasis on the question whether the hydroxy group in methanol behaves as a "pseudohalide" in the above process (eq 1 and Schemes 1 and 2). Indeed, there are striking similarities: Methyl fluoride, chloride, and bromide yield Fe(propene)$^+$, exclusively, *via* losses of HX and DX (Table 3). For methyl iodide, formation of a formal allyl iodide complex $[FeC_3H_5I^+]$ is observed in a competing reaction, while elimination of HI (DI) remains the dominant process. Interestingly, the deuterium content of the resulting Fe(propene)$^+$ complexes greatly varies for the different methyl halides. The degree of H/D equilibration is lowest for X = F and X = Cl; this points to a favored, direct dissociation of **4** without substantial rearrangement to **5** (Scheme 2). For methyl bromide the ratio of HBr vs DBr losses is already close to the statistical limit, and in the case of methyl iodide, loss of HI is even slightly more pronounced than elimination of DI, indicating that a kinetic isotope effect is operative after complete H/D equilibration. The increasing tendency for H/D exchange correlates inversely with the exothermicities of the reactions. It is a reasonable assumption that the lifetimes of the intermediates **3** and **5** are responsible for the extent of H/D equilibration (Scheme 2). These lifetimes are directly related to the barrier height for reductive elimination of HX (DX) from **4**. Due to similar reaction mechanisms for all X, we can use the Hammond postulate to establish a trend for the heights of the barriers from the reaction enthalpies which decrease from X = F to I. Thus, reductive elimination of HF involves a lower energetic barrier than elimination of HI. As a consequence, activation

Scheme 5



of the β-position in **3** and a facile dissociation of **4** result in the preferred elimination of DF in the reaction of $Fe(C_2D_4)^+$ and CH_3F. In contrast, the higher barrier for elimination of HI (DI) renders a complete equilibration of H and D atoms possible in the case of methyl iodide. Noteworthy, the HX/DX ratio for methanol (X = OH) in its reaction with $Fe(C_2D_4)^+$ does not fit into this simple model. Although the reaction of $Fe(C_2H_4)^+$ with methanol is the most exothermic one, the corresponding HX/DX ratio is located between the values obtained for methyl chloride and methyl bromide. Since it was shown above that the hydroxy group is not activated, another, presently unknown effect must be responsible for the increased tendencies for H/D exchange in this system. In spite of this minor discrepancy, the OH group by and large can be regarded as a pseudohalide, since homologization of alkene complexes occurs upon reaction with both methanol and the methyl halides.

Table 3 also includes the maximal number of methylation steps, which are observed in the reactions of $Fe(C_2H_4)^+$ and CH_3X. A crude correlation of methyl halide reactivity to the thermochemistry is found again. C_6 alkenes are only generated from the most exothermically reacting halides, i.e. methyl fluoride and methyl chloride, whereas the bromide and the iodide only yield C_5 or C_4 units, respectively. As shown above, only two consecutive methylations of $Fe(C_2H_4)^+$ are achieved using methanol, due to the dehydrogenation of the generated *n*-butene complex. In part, this competing reaction can be ascribed to the higher complexation energy of methanol compared to the methyl halides.

It is a widely accepted fact that transition-metal-mediated coupling of organic halides to olefins is often restricted to halides which lack an aliphatic β-hydrogen atom. Otherwise, dehydrohalogenation of the halide becomes the dominant if not exclusive reaction. For gas-phase processes, the same restriction was identified for the first time by Corderman and Beauchamp,[9a] who compared the reactions of M(cyclopentadienyl)$^+$ with methyl and ethyl bromide. In the present context of metal-mediated methylations of olefins, we studied as a simple system the reaction of $Fe(C_2D_4)^+$ with ethyl chloride (Scheme 5) and found indeed a competition between C−C bond formation and direct dehydrochlorination of ethyl chloride. The main product (80%) has the composition $Fe(C_4H_4D_4)^+$ for which the structure of a butene or bis(ethene) complex is reasonable. In order to probe its structure, which in turn might shed light on the mechanisms, this ion was subjected to ion−molecule reactions. In the reaction with background water we observe the displacement of one ethene ligand to form $(C_2D_4)Fe(H_2O)^+$ and $(C_2H_4)Fe(H_2O)^+$ (approximate ratio of 5:4). This result clearly demonstrates that loss of HCl is accompanied with the formation of $(C_2H_4)Fe(C_2D_4)^+$ in the reaction of $Fe(C_2D_4)^+$ with C_2H_5Cl and indicates that dehydrochlorination rather than C−C bond formation takes place. However, the minor product, $[Fe,C_4,H_5,D_3]^+$, generated by loss of DCl (20%), does not exchange an ethene ligand. In addition, reaction of a mixture of both products with C_2D_4 yields complexes $[Fe,C_4,H_{4-n},D_{4+n}]^+$ (n = 1−4) with various contents of deuterium atoms due to an H/D exchange process involving allylic positions.[31] Both observations point to the formation of a butene complex by a CC-coupling reaction. Thus, although direct dehydrochlorination of C_2H_5Cl is more efficient, C−C bond formation can still compete, to some extent.

Conclusions

In contrast to the complexes of Co^+ and Ni^+, $Fe(L)^+$ complexes (L = C_2H_4, C_3H_6, *i*-C_4H_{10}) react with methanol via loss of water and C−C bond formation. The mechanism of C−C bond formation consists of a sequence of insertion, addition, and elimination steps. In the addition of $(X)Fe^+{-}CH_3$ across the C−C double bond of propene, a remarkable regioselectivity is observed favoring the formation of *n*-butene complexes. The methyl halides are even more powerful coupling agents to achieve higher olefin homologs and insert up to four methylene units to ethene. Interestingly, C−C coupling can also be achieved in the reaction of Fe^+−ethene with ethyl chloride, although HCl loss from the alkyl part dominates.

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