Reactivity Tuning by Ligand Effects: Gas-Phase Reactions of $Fe(C_6H_6)O^+$ versus "Bare" FeO^+

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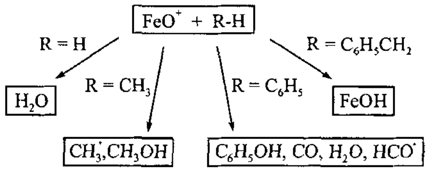
The presence of a benzene ligand in $Fe(C_6H_6)O^+$ (**1**) has a profound effect on the gas-phase reactivity of FeO^+. While the latter oxide is known to act as an efficient C–H/C–C bond-activation reagent, the ligated species **1** is entirely unreactive in that respect. However, **1** serves as an excellent reagent for transferring oxygen to various olefins. In addition, it is demonstrated that the ligand substitution $Fe(C_6H_6)O^+ + X \rightarrow Fe(X)O^+ + C_6H_6$ follows two principally different pathways. For $X = C_6D_6$ and C_5H_5N the traditional direct substitution process with attack at the metal centre is operative. However, for X = olefins it is argued that the olefin will not initially attack the metal center; rather, the reaction commences by coordinating the olefin X to the oxygen atom of $Fe(C_6H_6)O^+$. The resulting intermediate $(C_6H_6)Fe(OX)^+$ will then fall apart either to separated $Fe(OX)^+/C_6H_6$ or to $Fe(C_6H_6)^+/OX$, thus bringing about an epoxidation of the olefin rather than ketone formation.

Understanding the mechanistic details that underly transition-metal oxide mediated activation of C–H and C–C bonds is a necessary condition for improving numerous important processes in biochemistry, organic and organometallic chemistry[1]. Recently, we reported on the gas-phase oxidation of molecular hydrogen[2], methane[3], benzene[4], and toluene[5] by "bare" FeO^+. By using a combined experimental/theoretical approach it was demonstrated[6] that detailed insight into crucial mechanistic features is available not the least due to the fact that the gas-phase system is not perturbed by effects which are usually operative in the condensed phase and which obscure the intrinsic properties of the reactive species. The richness of the gas-phase chemistry of "bare" FeO^+ with simple molecules RH (R = H, CH_3, C_6H_5, $C_6H_5CH_2$) is indicated in Scheme 1; here, the main reactions are depicted when thermalized FeO^+ under single-collision conditions "hits" RH: (i) For molecular hydrogen, in a kinetically extremely inefficient process[6c,7] the only product formed corresponds to H_2O; (ii) CH_4 reacts preferentially with FeO^+ either via H-atom transfer (to generate $CH_3^\bullet$) or oxygenation of CH_4 to CH_3OH; (iii) the reaction of benzene commences with an electrophilic attack by FeO^+, and the major products correspond to C_6H_5OH, CO, H_2O and $HCO^\bullet$; (iv) for toluene yet another reaction is observed involving a formal H^- transfer from the methyl group to yield neutral FeOH and the benzylium ion. Not surprisingly, the outcome of the gas-phase process depends strongly on the neutral substrate chosen and, as repeatedly demonstrated, on the nature of the transition metal of the oxide MO^+[8].

Ligands L are also known to change the intrinsic properties of transition-metal cations[9], and here we will demonstrate that the presence of a single benzene ligand will profoundly affect the oxidation behavior of "bare" FeO^+[10]. In addition, a comparison of the reactivity of "bare" FeO^+ with $Fe(C_6H_6)O^+$ is expected to bridge the behavior of gas-phase transition-metal chemistry and organometallic chemistry in the condensed phase.

Scheme 1



We will first describe the generation and structural characterization of $Fe(C_6H_6)O^+$ and then discuss its reactions with a wide range of neutral molecules X employing the method of Fourier-transform ion cyclotron resonance (FTICR) mass spectrometry.

Results and Discussion

$Fe(C_6H_6)O^+$ is conveniently formed by reaction of $Fe(C_6H_6)^+H$ with N_2O (Eq. 1a). The pseudo first-order rate constant for Eq. (1) has been determined to be $k_f = 8.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}; thus, the reaction proceeds at collision rate[11] ($k_{coll} = 7.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}). As byproducts, the cationic species $Fe(C_5H_6)^+$ and $Fe(C_6H_4)O^+$ are generated. Both thermochemical considerations[12] and secondary reactions with benzene[13] suggest that the C_5H_6 ligand most likely corresponds to cyclopentadiene while $Fe(C_6H_4)O^+$ presumably consists of a benzyne ligand attached to FeO^+.

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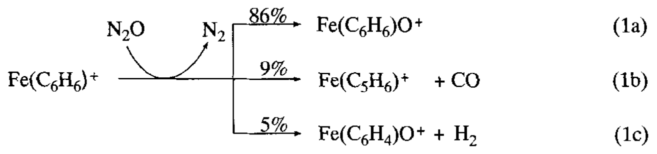


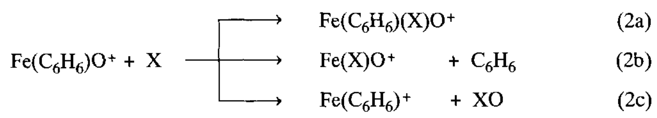
$$Fe(C_6H_6)^+ \xrightarrow{N_2O \; \frown \; N_2} \begin{cases} \xrightarrow{86\%} Fe(C_6H_6)O^+ & (1a) \\ \xrightarrow{9\%} Fe(C_5H_6)^+ + CO & (1b) \\ \xrightarrow{5\%} Fe(C_6H_4)O^+ + H_2 & (1c) \end{cases}$$

The structure of the major product of Eq. (1), $Fe(C_6H_6)O^+$ (**1**), corresponds to a benzene ligand attached to FeO^+. This assignment is based on several criteria: (i) In the ion/molecule reactions of $Fe(C_6H_6)O^+$ with neutral molecules X (to be discussed in detail further below), the intact C_6H_6 unit can be replaced by, for example, C_6D_6 or pyridine without any H/D exchange. In addition, other ion/molecule reactions demand the presence of *two distinct* C_6H_6 and O ligands rather than one C_6H_6O group or other combinations, e.g. C_6H_4/H_2O etc.

(ii) H/D exchange[14] is not observed in the reactions of $Fe(C_6H_6)O^+$ with D_2O, D_2 or C_2D_4, thus excluding the presence of functional groups like O–H or Fe–H. Furthermore, the absence of H/D exchange processes in the reactions of $Fe(C_6H_6)O^+$ with D_2O rules out a phenol or a 2,4-cyclohexadienone unit[6b], in line with the findings to be discussed further below.

(iii) A structural characterization of $Fe(C_6H_6)O^+$ was also attempted by a collision-induced dissociation (CID) experiment. To this end, mass-selected $Fe(C_6H_6)O^+$ was translationally excited ($E_{lab} \leq 0-90$ eV) under FTICR conditions and allowed to collide with argon. The CID spectrum of $Fe(C_6H_6)O^+$ is shown in Figure 1b, and a comparison with the CID spectrum of an independently generated[15] isomer $Fe(C_5H_6)CO^+$ (Figure 1a) exhibits pronounced differences. For $Fe(C_5H_6)CO^+$ the dominant process corresponds to loss of the weakly bound CO ligand [to generate $Fe(C_5H_6)^+$]; at higher energy ($E_{lab} > 35$ eV) combined CO/H$^•$ loss opens up a new channel, and at collision energies $E_{lab} > 60$ eV both ligands are evaporated. In the spectrum of $Fe(C_6H_6)O^+$ (Figure 1b) we note the losses of C_6H_6O as well as of CO at relatively low energy ($E_{lab} \approx$ 20 eV), followed by the expulsion of C_6H_6 and CO/H$^•$ at much higher energies ($E_{lab} \geq 60$ eV). The absence of C_6H_6 elimination at low collision energies strongly suggests that – upon collisional activation – the $Fe(C_6H_6)O^+$ ion prior to dissociation undergoes isomerization to presumably $Fe(C_5H_6)CO^+$ and $Fe(C_6H_6O)^+$.

Next, we will describe and discuss the ion/molecule reactions of $Fe(C_6H_6)O^+$ with the substrates X (Eq. 2 and Table 1). Depending on the nature of the neutral molecule X, three different reaction channels are observed: (i) Association of X takes place to form $Fe(C_6H_6)(X)O^+$ (Eq. 2a); (ii) the intact C_6H_6 ligand is replaced by X (Eq. 2b); (iii) oxygen atom transfer from $Fe(C_6H_6)O^+$ to X occurs (Eq. 2c).



$$Fe(C_6H_6)O^+ + X \begin{cases} \longrightarrow Fe(C_6H_6)(X)O^+ & (2a) \\ \longrightarrow Fe(X)O^+ + C_6H_6 & (2b) \\ \longrightarrow Fe(C_6H_6)^+ + XO & (2c) \end{cases}$$

Before discussing these processes, we note that all other substrates X studied (X = H_2, CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, i-C_4H_{10}, N_2O and CO_2) are entirely unreactive toward $Fe(C_6H_6)O^+$, i.e. if the reactions occur at all, their rate constants must be smaller than 10^{-14} cm^3 molecule^{-1} s^{-1}. This observation already demonstrates the huge effect of the benzene ligand in $Fe(C_6H_6)O^+$ when compared with "bare" FeO^+ (see above and Scheme 1). In particular, C–H and C–C bond activations, which are hallmarks of the chemistry of "bare" FeO^+[6c], are no longer possible. Rather, the only chemical process taking place corresponds to the transfer of an oxygen atom to olefins (Eq. 2c).

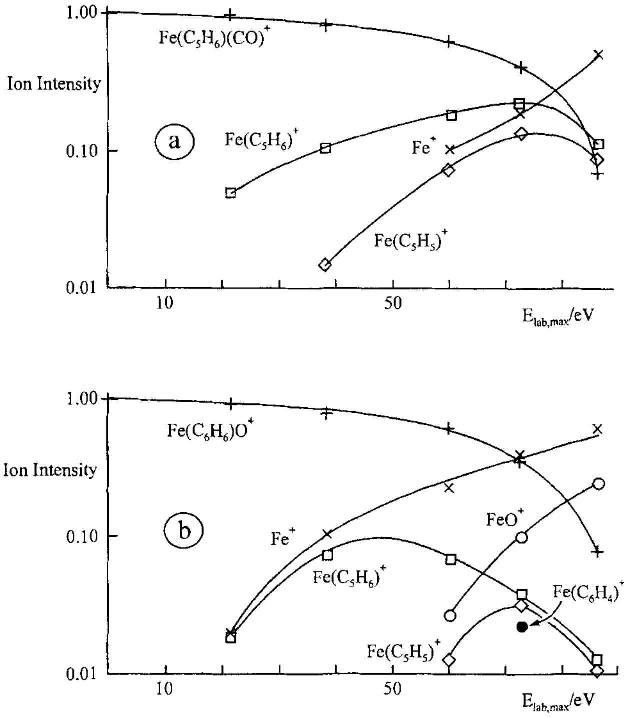


Figure 1. CID experiments with the isomers $Fe(C_5H_6)CO^+$ ⓐ and $Fe(C_6H_6)O^+$ ⓑ

As shown in Table 1, $Fe(C_6H_6)O^+$ is not capable – in contrast to $Fe(CH_3)^+$ or $Fe(OH)^+$[16] – to activate the O–H bond of water. As the heat of formation of $Fe(C_6H_6)O^+$ is unknown, it is not possible to decide whether hydrogen atom transfer is inhibited on thermochemical or on kinetic grounds. The absence of oxygen atom transfer (Eq. 2c) to generate H_2O_2 is due to the endothermicity[12] of this process. The non-occurrence of reaction 2b suggests that the benzene ligand in $Fe(C_6H_6)O^+$ is more strongly bound than H_2O in $Fe(H_2O)O^+$. What remains is the formation of the adduct $Fe(C_6H_6)(H_2O)O^+$, which is formed with collision rate (k_r/k_{coll} = 1.1) and which is presumably stabilized by collisional or radiative cooling[17]. Formation of a genuine adduct $Fe(C_6H_6)(H_2O)O^+$ is indicated by subjecting the species to a CID experiment ($E_{lab} \leq 22$ eV), in which the following products are formed: H_2O (46%), C_6H_6 (20%), Fe^+ (4%). Formation

Table 1. Branching ratios, rate constants k_f [10^{-10} cm^3 molecule^{-1} s^{-1}], and reaction efficiencies k_f/k_{coll} for the reactions of $Fe(C_6H_6)O^+$ with neutral molecules X (Eq. 2a–c)

X	H_2O	CH_3CN	C_5H_5N	C_6D_6[a]	CO	C_2H_4	C_3H_6	(*Z*)-2-Butene	(*E*)-2-Butene	Isobutene	1,3-Butadiene	*c*-C_6H_{10}[b]	1,3-*c*-C_6H_8[b]
Eq. 2a	1.00	1.00	0.55	0.00	0.00	0.05	0.13	0.00	0.00	0.00	0.00	0.00	0.02
Eq. 2b	0.00	0.00	0.45	1.00	0.00	0.00	0.00	0.02	0.03	0.03	0.91	0.82	0.80
Eq. 2c	0.00	0.00	0.00	0.00	1.00	0.95	0.87	0.98	0.97	0.97	0.09	0.18	0.18
k_f	23	38	19	10	7.5	10.5	12	12	11	12	13	12	12
k_f/k_{coll}[c]	1.1	1.1	1.0	0.5	1.1	1.1	1.1	1.1	1.0	1.0	1.2	1.1	1.1

[a] Similar results are obtained by using toluene, i.e. only Eq. 2b is valid with $k_f/k_{coll} = 0.95$. – [b] In the reaction of $Fe(C_6D_6)O^+$ with cyclohexene (*c*-C_6H_{10}) and 1,3-cyclohexadiene (1,3-*c*-C_6H_8) the branching ratios are identical with those observed for $Fe(C_6H_6)O^+$. – [c] k_{coll} is calculated as described in ref.[11].

of $C_6H_6^{+\bullet}$ (30%) implies that *IE*(C_6H_6) = 9.246 eV[12] < *IE*-[$Fe(H_2O)O$].

CH_3CN reacts similarly to H_2O with $Fe(C_6H_6)O^+$ (Table 1), in that only association takes place (Eq. 2a). Upon CID in addition to benzene loss, at higher energies ($E_{lab} \geq 12$ eV) the intact CH_3CN ligand is eliminated, and when subjected to thermal ion/molecule reactions with CD_3CN we observe the exchange of CD_3CN for CH_3CN without any H/D scrambling.

Pyridine (C_5H_5N) also forms an association complex with $Fe(C_6H_6)O^+$, and CID of the product $Fe(C_6H_6)(C_5H_5N)O^+$ follows the same pattern in that benzene loss needs less energy ($E_{lab} \approx 10$ eV). As acetonitrile in $Fe(C_6H_6)(CH_3CN)O^+$ can be replaced by C_5H_5N, the following ligand bond strength of X in $Fe(C_6H_6)(X)O^+$ emerges: $H_2O < CH_3CN < C_5H_5N$. The much larger bond dissociation energy (*BDE*) of pyridine as compared to benzene and acetonitrile is also reflected in the observation that pyridine is capable to bring about the substitution reaction 2b. As already mentioned, the clean replacement of L (L = C_6H_6, C_6D_6) in $Fe(L)O^+$ by L′ (C_6D_6, C_6H_6, C_5H_5N) without any H/D exchange requires the presence of an *intact* benzene ligand in the $Fe(L)O^+$ complex formed in the oxidation of FeL^+ by N_2O (Eq. 1a).

Surprisingly, the substitution process (Eq. 2b) dominates also the reactions of $Fe(C_6H_6)O^+$ with X = 1,3-butadiene, 1,3-cyclohexadiene and cyclohexene. Control experiments employing $Fe(C_6D_6)O^+$ demonstrate that in the course of the substitution no transfer-hydrogenation[9b] has taken place. Thus, one may argue that these ligands X are more strongly bound to the iron center in FeO^+ than the benzene ligand, which would be difficult to explain. For Fe^+ itself, the *BDE*s follow the sequence *BDE*(Fe^+–isobutene) = 40 kcal/mol < *BDE*(Fe^+–1,3-butadiene) = 48 kcal/mol < *BDE*(Fe^+–benzene) = 55 kcal/mol[16b,18]. However, CID experiments of the resulting $Fe(X)O^+$ products clearly suggest that a connectivity with two separate ligands X and O, i.e. $XFeO^+$, is no longer present. For example, in the whole energy regime applied *no* signal corresponding to FeO^+ is observed; rather, ions due to Fe^+ or $Fe(C_xH_y)^+$ are detected. In addition, if in secondary reactions the product $Fe(X)O^+$ is allowed to react with olefins no oxygen atom transfer is observed. Therefore, we conclude that replacement of benzene by X = 1,3-butadiene, cyclohexene and 1,3-cyclohexadiene is not a simple ligand-exchange process as implied by Eq. 2b. Rather, the "incoming" ligand X is interacting with the oxygen atom of the iron oxide. We will return to this point later in the context of the oxygen atom transfer to X (Eq. 2c).

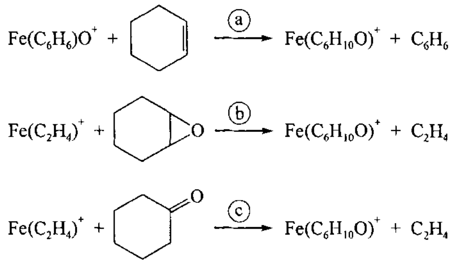
From the data in Table 1 it is obvious that oxygen transfer takes place only to CO, alkenes and alkadienes. Interestingly, in the reaction of $Fe(C_6H_6)O^+$ with the unsaturated hydrocarbons we do not observe any product that points to the activation of C–H or C–C bonds, processes which are typical of the reactions of "bare" FeO^+ with these substrates. Further, the absence of a kinetic isotope effect in the reaction of $Fe(C_6H_6)O^+$ with C_2D_4 also underlines our supposition that the presence of the benzene ligand in the metal oxide suppresses C–H bond activation of the "incoming" olefin X. Although in an FTICR experiment the nature of the neutral products formed in ion/molecule reactions cannot be probed directly, in the following we will present circumstantial evidence that for X = cyclohexene (and presumably also for other olefins) the oxygen transfer product $C_6H_{10}O$ most likely corresponds to a genuine epoxide. In addition, arguments will be presented that both the epoxide formation (Eq. 2c) as well as the formal ligand exchange (Eq. 2b) with olefins are proceeding via the same intermediate. To this end, we have subjected the $Fe(C_6H_{10}O)^+$ ion, formed in the reaction of $Fe(C_6H_6)O^+$ with cyclohexene to a series of experiments. As already mentioned above, several independent results demonstrate that the "$C_6H_{10}O$" unit does not correspond to two separate ligands, e.g. an oxo and a cyclohexene group. In fact, the question centers around the problem as to whether "$C_6H_{10}O$" is an epoxide ligand or its isomeric keto form. A clear-cut distinction is provided by the data reported in Table 2. In the thermal ion/molecule reaction of 1,3-butadiene with $Fe(C_6H_{10})O^+$ isomers, identical branching ratios are obtained for the ions formed via pathways ⓐ and ⓑ in Scheme 2, thus pointing to identical product ions. In contrast, the $Fe(C_6H_{10})O^+$ ion formed by reaction of $Fe(C_2H_4)^+$ with cyclohexanone (process ⓒ) behaves distinctly different.

Taken all experimental findings together, the reaction sequence depicted in Scheme 3 for X = cyclohexene seems very plausible and accounts for the unusual behavior of

Table 2. Branching ratios for the reactions of 1,3-butadiene with $Fe(C_6H_{10}O)^+$ isomers formed according to Scheme 2

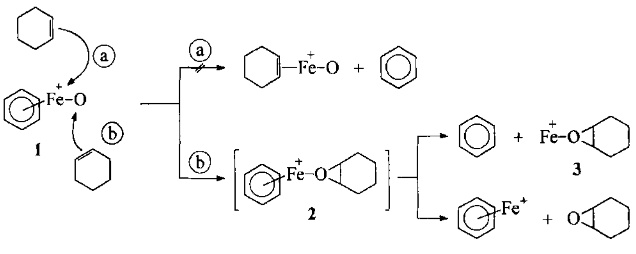
$Fe(C_6H_{10}O)^+$ from reaction	Fe^+	$Fe(C_6H_8O)^+$	Product intensities for $Fe(C_6H_6)^+$	$Fe(C_{10}H_{14}O)^+$	$Fe(C_{10}H_{12}O)^+$
ⓐ	0.10	0.61	0.29	0.00	0.00
ⓑ	0.11	0.58	0.31	0.00	0.00
ⓒ	0.00	0.00	0.00	0.48	0.52

Scheme 2



$Fe(C_6H_6)O^+$ toward alkenes. Rather than attacking the metal ion directly, followed by expulsion of C_6H_6 (Path ⓐ), the reaction is suggested to commence with approache of the oxygen atom resulting in the formation of the intermediate **2** (path ⓑ). Depending on thermochemical aspects, this species has two options: (i) formation of **2** proceeds by elimination of C_6H_6 to generate $Fe(OC_6H_{10})^+$ (**3**) and C_6H_6. (ii) The "$C_6H_{10}O$" unit evaporates from the complex as an epoxide leaving behind $Fe(C_6H_6)^+$.

Scheme 3



In conclusion, the benzene ligand in $Fe(C_6H_6)O^+$ does not behave like a simple spectator ligand in the gas-phase reactions of this organometallic complex with various substrates X. Rather, it brings about a fundamental change in reactivity as compared with "bare" FeO^+. While the latter metal oxide mediates C–H/C–C bond activation (Scheme 1), these processes are entirely absent in $Fe(C_6H_6)O^+$. Instead, oxygen transfer to alkenes and replacement of C_6H_6 by X are the dominant processes. Most interestingly, while the ligand exchange $Fe(C_6H_6)O^+ + X \rightarrow Fe(X)O^+ + C_6H_6$ corresponds to a well-known substitution process for X = C_6D_6 and C_5H_5N, for X = 1,3-butadiene, cyclohexane and 1,3-cyclohexadiene evidence is presented that the "incoming" ligand X rather than attacking the metal center will first coordinate to the oxygen atom (Scheme 3, path ⓑ), and the intermediate **2** thus formed will, depending on thermochemical grounds, fall apart either to $Fe(OC_6H_{10})^+$ (**3**)/C_6H_6 or $Fe(C_6H_6)^+$/epoxide.

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Experimental

Gas-phase experiments were performed by using a Spectrospin CMS 47X Fourier-transform ion cyclotron resonance mass spectrometer[19], which was equipped with an external ion source[20]. Metal ions were generated by laser desorption/ionization by focusing the beam of a Nd:YAG laser (Spectron Systems; λ = 1064 nm) on a metal target which was mounted in the external ion source. The ions were transferred from the source to the analyzer cell by a system of electrostatic potentials and ion lenses. The ion source, the ion transfer system, and the main vacuum chamber of the spectrometer were differentially pumped by three turbo molecular pumps. After deceleration, the ions were trapped in the field of a 7-T superconducting magnet (Oxford Instruments). The ions were isolated by using FERETS[21], a computer-controlled ion-ejection protocol which combines single-frequency ion ejection pulses with frequency sweeps to optimize ion isolation. Great care was applied to avoid any off-resonance excitation of the ion to be isolated while ejecting the ^{13}C-isotope signals[22]. All functions of the instrument including all pulse-sequence steps were controlled by a Bruker Aspekt-3000 minicomputer. For collisional cooling of any excited states possibly formed, argon was present as a buffer gas at a constant "background" pressure of a ca. 5×10^{-7} mbar. For the generation of $Fe(C_6H_6)^+$, cyclohexene was introduced through a pulsed valve[23] according to literature procedures[24]. A second pulsed valve contained N_2O for the production of $Fe(C_6H_6)O^+$. Further substrates were submitted to the cell by using a leak valve. Pseudo first-order rate constants reported in this study were determined from the logarithmic decay of a reactant intensity over time and are reported with ±30% error unless stated otherwise. Branching ratios were determined from the temporal ion distributions acquired during kinetic analysis and are reported with ±10% uncertainty. CID[19,25] experiments were performed as described previously.

Cyclohexene, 1,2-epoxycyclohexane, cyclohexanone, pyridine, benzene, D_2O and [D_6]benzene (98% pure; Aldrich) were used as supplied except for several freeze-pump-thaw cycles. In addition, 1,3-cyclohexadiene was also distilled before use in order to exclude dimerization products. Other reagent gases were obtained from commercial sources and were used without further purification.

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[15] $Fe(C_5H_6)CO^+$ is generated first by reaction of Fe^+ with cyclopentene to generate $Fe(C_5H_6)^+ + H_2$ (D. B. Jacobson, B. S. Freiser, *J. Am. Chem. Soc.* **1983**, *105*, 7492); in the presence of Ar ($p_{Ar} = 5 \times 10^{-7}$ mbar) this ion undergoes ligand association with pulsed-in CO to generate $Fe(C_5H_6)CO^+$. When this complex is allowed to react with X ($X = H_2O, C_2H_4, CH_3CN$) under thermal conditions, in keeping with the presence of a CO ligand the substitution process $Fe(C_5H_6)CO^+ + X \rightarrow Fe(C_5H_6)X^+ + CO$ takes place.

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