Transition-Metal Mediated Heteroatom Removal by Reactions of FeL^+ [L = O, C_4H_6, *c*-C_5H_6, *c*-C_5H_5, C_6H_6, $C_5H_4(=CH_2)$] with Furan, Thiophene, and Pyrrole in the Gas Phase

R. Bakhtiar and D. B. Jacobson
Department of Chemistry, North Dakota State University, Fargo, North Dakota

Reactions of Fe^+ and FeL^+ [L = O, C_4H_6, *c*-C_5H_6, C_5H_5, C_6H_6, $C_5H_4(=CH_2)$] with thiophene, furan, and pyrrole in the gas phase by using Fourier transform mass spectrometry are described. Fe^+, $Fe(C_5H_5)^+$, and $FeC_6H_6^+$ yield exclusive rapid adduct formation with thiophene, furan, and pyrrole. In addition, the iron–diene complexes [$FeC_4H_6^+$ and $Fe(c\text{-}C_5H_6)^+$], as well as $FeC_5H_4(=CH_2)^+$ and FeO^+, are quite reactive. The most intriguing reaction is the predominant direct extrusion of CO from furan by $FeC_4H_6^+$, $Fe(c\text{-}C_5H_6)^+$, and $FeC_5H_4(=CH_2)^+$. In addition, $FeC_4H_6^+$ and $Fe(c\text{-}C_5H_6)^+$ cause minor amounts of HCN extrusion from pyrrole. Mechanisms are presented for these CO and HCN extrusion reactions. The absence of CS elimination from thiophene may be due to the higher energy requirements than those for CO extrusion from furan or HCN extrusion from pyrrole. The dominant reaction channel for reaction of $Fe(c\text{-}C_5H_6)^+$ with pyrrole and thiophene is hydrogen-atom displacement, which implies $D^O(Fe(C_5H_5)^+\text{-}C_4H_4X) > D^O(Fe(C_5H_5)^+\text{-}H) = 46 \pm 5$ kcal mol^{-1}. $D^O(Fe^+\text{-}C_4H_4S)$ and $D^O(Fe^+\text{-}C_4H_5N) \approx D^O(Fe^+\text{-}C_4H_6) = 48 \pm 5$ kcal mol^{-1}. Finally, 55 ± 5 kcal mol^{-1} = $D^O(Fe^+\text{-}C_6H_6) > D^O(Fe^+\text{-}C_4H_4O) > D^O(Fe^+\text{-}C_2H_4) = 39.9 \pm 1.4$ kcal mol^{-1}. FeO^+ reacts rapidly with thiophene, furan, and pyrrole to yield initial loss of CO followed by additional neutral losses. $D^O(Fe^+\text{-}CS) > D^O(Fe^+\text{-}C_4H_4S) \approx 48 \pm 5$ kcal mol^{-1} and $D^O(Fe^+\text{-}C_4H_5N) \approx 48 \pm 5$ kcal mol^{-1} > $D^O(Fe^+\text{-}HCN) > D^O(Fe^+\text{-}C_2H_4) = 39.9 \pm 1.4$ kcal mol^{-1}. *(J Am Soc Mass Spectrom 1996, 7, 938–952)*

Catalytic hydrodesulfurization (HDS) [1], hydrodeoxygenation (HDO) [2], and hydrodenitrogenation (HDN) [3] are important processes for removal of sulfur, oxygen, and nitrogen from petroleum feedstocks. Industrial HDS, HDN, and HDO catalysis, in general, involves the use of heterogeneous catalysts that consist of either cobalt–molybdenum sulfides (CoMo) or nickel–molybdenum sulfides (NiMo) supported on alumina under conditions of high temperatures and elevated hydrogen pressures [4]. Although Ru-, Os-, Rh-, and Ir-based catalysts are more active than Mo-based catalysts, Mo-based catalysts most commonly are used in industry owing to their availability and economic feasibility [5]. A number of iron complexes, due to their low cost and environmental acceptability, also have been examined as potential catalysts in heteroatom removal [6]. These catalysts convert organosulfur, -nitrogen, and -oxygen to H_2S, NH_3, and H_2O, which are removed from the feedstock.

There are several reasons for removal of organosulfur, -nitrogen, and -oxygen from petroleum feedstocks. Emissions of SO_x and NO_x from combustion contribute to acid rain. Large quantities of oxygen-containing species are rather unstable; for example, they quickly form deposits when exposed to air. The basic nature of the nitrogen-containing species effectively poisons the acidic hydrocracking and reforming catalysts used in the refining process. The sulfur-containing compounds poison sulfur-sensitive precious metal catalysts used in catalytic converters of automobiles. Often, petroleum feedstocks are hydrogenated during the refining process, and many *reactive* organo-oxygen, -nitrogen, and -sulfur compounds are converted to H_2O, NH_3, and H_2S. Most heterogeneous catalysts are poisoned by these species [7]. In contrast, CoMo and NiMo catalysis of HDS, HDN, and HDO are *not* poisoned by these species. In fact, these catalysts often experience rate enhancement in the presence of H_2S [8].

Despite the large scale use of HDS, HDN, and HDO catalysts, the mechanisms likely to be involved in these processes (eq 1) are poorly understood.

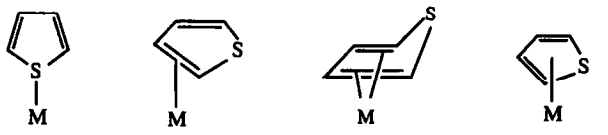
$$C_xH_yX + nH_2 \xrightarrow{\text{metal catalyst}} \text{hydrocarbons} + H_2X \qquad X = S, NH, O \qquad (1)$$

Address reprint requests to Ray Bakhtiar, Mail Stop RY80L-109, Merck Research Laboratories, Rahway, NJ 07065-0900.

© 1996 American Society for Mass Spectrometry
1044–0305/96/$15.00
PII S1044-0305(96)00024-4

Received March 13, 1996
Accepted April 11, 1996

The mechanisms for HDS have been studied most intensely, and these studies have employed thiophenic compounds as models. Although petroleum feedstocks contain a variety of organosulfur compounds which include thiols, cyclic sulfides, and thiophenes; thiophenes were selected for model studies because they contain the most refractory form of sulfur. Because the $CoMo-Al_2O_3$ catalyst surface is complex, the mode(s) of thiophene absorption and reaction is (are) still not well established. Consequently, the interaction (reaction) of thiophenes with both highly characterized transition-metal surfaces and homogeneous transition-metal complexes has been the focus of recent studies that are aimed at gaining an understanding of HDS catalysis. Studies of thiophenes on surfaces [5, 9–12] and of homogeneous transition-metal–thiophenic complexes [13] have been focused on binding geometry and subsequent reactivity. Several different binding geometries have been characterized for homogeneous transition-metal–thiophene complexes including η^1-S bound [14, 15], η^2-bound [16], η^4-bound [17–19], and η^5-bound [17, 20–22], **1–4**.

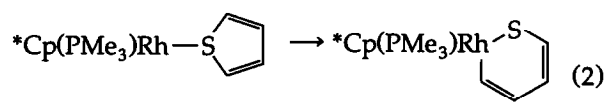


S-bound η^2-bound η^4-bound η^5-bound

1 **2** **3** **4**

The binding geometry of thiophene is affected by steric and electronic properties of other ligands on the metal center.

In spite of intense efforts to study the reactions of thiophenes in organometallic complexes, desulfurization of thiophene to yield gas-phase products has not been observed. Although most of the early η^1-S-bound thiophene complexes were weakly bound and consequently, easily displaced, more recent results have demonstrated that η^1-S- and η^4-bound thiophenes can undergo oxidative cleavage of the C—S bond. For example, Jones and co-workers [23] have reported C—S oxidative addition, which occurs by initial coordination of the thiophene sulfur (η^1-S-bound), followed by migration of the α-carbon to the metal center to yield a six-membered metallathiohexadiene ring (eq 2).



(2)

*Cp = c-C_5Me_5

Angelici and co-workers [24] also observed C—S oxidative addition in a related iridium complex, although the immediate precursor was an η^4-thiophene ligand.

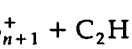
By analogy to thiophene, furan and pyrrole organometallic complexes may serve as models for HDO and HDN catalysts, respectively. In contrast to thiophene, there is much less known about the coordination geometry and reactivity of furan and pyrrole in organometallic complexes [25]. η^5-Bound pyrrolyl [26] and η^5-bound pyrrole [27] complexes are known. However, furan is not as likely to form π-complexes as thiophene because the electronegativity of oxygen is increased, which limits electron delocalization and thereby reduces π-interaction with the metal [25]. An η^5-bound furan complex *CpRu(η^5-furan)$^+$, however, was recently prepared [28].

In an investigation of Fe-based catalysts Rauchfuss and co-workers [6k], studied the reactions of $Fe(CO)_5$ and $Fe_3(CO)_{12}$ with thiophene and benzo[*b*]thiophene, respectively. In the reaction of $Fe(CO)_5$ with thiophene, a thiaferrole complex, $Fe_2(C_4H_4S)(CO)_6$, which goes onto a ferrole product, was proposed as the intermediate. In a study by Chivers and Timms [6j], a similar ferrole product was obtained upon the reaction of gaseous atomic iron with thiophene in a CO atmosphere. In related work, Angelici and co-workers [13a] reported the iron promoted removal of sulfur from 2,3-dihydrothiophene (2,3-DHT) in the decomposition of $Fe(CO)_4$(2,3-DHT). The black solid residue obtained from the reaction was characterized as FeS. The FeS elimination was facile at 120 °C, but became slower at room temperature. The mechanism for the elimination of the butadiene, however, was not well understood. The formation of an iron–sulfur–carbonyl cluster followed by a single concerted step for butadiene loss was proposed as a possible mechanism. Iron also has been used in Chevrel phase catalysts, where it has comparable HDS activity to Mo-based catalysts [29].

Apart from the interest in stereoelectronic effects of ligands, an increasing amount of effort has been directed to explore the utility of metal oxides in the desulfurization process [30]. Lew et al. [30a] reported high temperature H_2S removal from fuel gases by bulk Zn-Ti-O and ZnO. They demonstrated enhanced efficiency of zinc oxide–titanium dioxide mixtures over neat zinc oxide for the desulfurization of coal-derived fuel gases. Grindley and Steinfeld [30b] studied the H_2S removal efficiency of mixed oxide compound zinc ferrite ($ZnFe_2O_4$). They observed comparable efficiencies for both ZnO and $ZnFe_2O_4$. Sasaoka et al. [30c] examined the reactivity of iron oxide high temperature desulfurization sorbents. An increase in conversion of FeO to FeS was observed at elevated temperatures and with increased addition of the binder SiO_2. It was proposed that the reactivity of iron oxide was controled by SiO_2 addition and temperature.

Here we describe the reactivity of Fe^+ and FeL^+ [L = O, C_4H_6, c-C_5H_6 (1,3-butadiene), c-C_5H_5, C_6H_6 (benzene), $C_5H_4(=CH_2)$ (fulvene)] with furan, thiophene, and pyrrole in the gas phase [31]. Freiser and co-workers [32] reported a novel, direct desulfuriza-

tion reaction of ethylene sulfide by Fe^+ in the gas phase (eq 3).

$$FeS_n^+ + \text{  } \rightarrow FeS_{n+1}^+ + C_2H_4 \quad (3)$$

$n = 0–5$

The iron-sulfide ion formed in eq 3 was studied subsequently [33]. The reaction of Fe^+ with isothiocyanates also was studied in the gas phase and desulfurization reactions were observed [34]. We observe novel CO and HCN extrusions, respectively, from furan and pyrrole by the Fe(diene)$^+$ complexes ($FeC_4H_6^+$ and Fe-*c*-$C_5H_6^+$) as well as CO abstraction from furan by $FeC_5H_4(=CH_2)^+$. In addition, FeO^+ reacts with C_4H_4X (X = S, O, NH) by ring cleavage to yield initial CO elimination.

Experimental Section

The theory, instrumentation, and methodology of ion cyclotron resonance (ICR; for reviews on ICR, see [35]) spectrometry and Fourier transform mass spectrometry (FTMS; for reviews on FTMS, see [36]) were discussed at length elsewhere. All experiments were performed by using a modified Nicolet (Madison, WI) FTMS-1000 Fourier transform mass spectrometer equipped with a 5.08-cm cubic trapping cell and 3.0-T superconducting magnet [37]. A Bayard–Alpert type ionization gauge was used to monitor pressure [36]. Pressures of reagent neutrals subsequently were corrected by using ionization cross sections [38]. Absolute pressure uncertainties are believed to be $< 50\%$ with relative uncertainties $< 10\%$ for furan, thiophene, and pyrrole. The uncertainty in pressure is the largest contributor to the uncertainty of the measured rate constants. As a consequence, rate constants are assigned an absolute error of $\pm 50\%$. Chemicals were obtained commercially in high purity and were used as supplied except they were subjected to multiple freeze–pump–thaw cycles to remove noncondensable gases.

Fe^+ was generated by laser desorption-ionization from a high purity iron foil attached to the rear trapping plate of the cell [39]. $FeC_4H_6^+$, Fe-*c*-$C_5H_6^+$, and $FeC_6H_6^+$ were generated by dehydrogenation of, respectively, 1-butene, cyclopentene, and cyclohexadiene by Fe^+ [40]. Fe-*c*-$C_5H_5^+$ was formed by collision-activated dissociation (CAD) [41, 42] of Fe-*c*-$C_5H_6^+$ (eq 4) [43]. $FeC_5H_4(=CH_2)^+$ (fulvene) was generated by dehydrogenation of methylenecyclopentane (eq 5).

$$\text{Fe-}c\text{-}C_5H_6^+ \xrightarrow{CAD} \text{Fe-}c\text{-}C_5H_5^+ + H \quad (4)$$

$$Fe^+ + C_5H_8(=CH_2) \rightarrow FeC_5H_4(=CH_2)^+ + 2H_2 \quad (5)$$

The product of eq 5 was structurally characterized by reaction with propene-d_6 and benzene-d_6 where only two H/D exchanges were observed [44]. In contrast, authentic Fe(benzene)$^+$ does *not* yield H/D exchange with either propene-d_6 or benzene-d_6. Therefore, a Fe(fulvene)$^+$ structure was *assumed* for the product obtained from eq 5. FeO^+ was generated by reaction of Fe^+ with N_2O (eq 6) [45].

$$Fe^+ + N_2O \rightarrow FeO^+ + N_2 \quad (6)$$

Details for CAD in conjunction with FTMS were described elsewhere [46, 47]. CAD breakdown curves were obtained by variation of the kinetic energy of the ions (typically between 1 and 50 eV) by adjustment of the duration of the electric field pulse (typically between 100 and 600 μs). The maximum kinetic energy acquired by an irradiated ion (in excess of thermal energy) was calculated by using eq 7,

$$E_{tr(max)} = (E_{rf})^2 q^2 t^2 / 8m \quad (7)$$

where E_{rf} is the electric field amplitude, q is the electric charge, t is the duration of the electric field pulse, and m is the mass of the ion [35a]. (It has been suggested [48] that the kinetic energy obtained by an irradiated ion is much less than that calculated from eq 7.) CAD fragment ion abundances were plotted as a fraction of the initial parent ion abundance (no excitation) versus kinetic energy. This allows both the energy dependency for fragmentation and the fragmentation efficiency to be compared directly for related systems. CAD breakdown curves are reproducible with $< 3\%$ absolute variation in ion abundances for replicate curves. The spread in ion kinetic energy is dependent on the total average kinetic energy and is 65% at 1 eV, 19% at 10 eV, 11% at 30 eV, and 6% at 100 eV [49]. In addition to conventional on-resonance FTMS-CAD, CAD by using sustained "off-resonance" irradiation (SORI) [50] was used also. SORI-CAD is analogous to infrared multiphoton dissociation (IRMPD) [51] to probe the lowest energy pathway for ion dissociation.

All precursor hydrocarbons were admitted into the vacuum chamber by using a pulsed solenoid inlet valve to minimize complicating side equations with background neutrals. (A detailed description of pulsed valve introduction of reagent gases in conjunction with FTMS can be found elsewhere [52].) The pulsed valve was triggered off the quench pulse, and the valve duration was varied (typically between 2 and 3 ms) to control the amount of pulsed reagents. The ballast pressure in the pulsed valve assembly was < 1 torr. A variable delay following ionization (~ 1 s) was employed to allow the pulsed neutral precursor to be removed from the vacuum chamber; following this, desired ions were isolated by swept-ejection pulses [53]. The isolated ions subsequently were allowed to

react with a static pressure of specific reagents or were induced to fragment by CAD. A static pressure of 1×10^{-5} torr of Ar was maintained throughout these experiments and served as a bath gas to facilitate ion thermalization prior to reaction and as the target for CAD. Pressure of reactive neutral reagents were typically on the order of $2–5 \times 10^{-8}$ torr.

Results and Discussion

Fe^+ and FeL^+ [L = C_4H_6, c-C_5H_6, c-C_5H_5, C_6H_6, $C_5H_4(=CH_2)$]

Fe^+ yields exclusive adduct formation (no neutrals eliminated) with thiophene, furan, and pyrrole; the rate constants (k) are $(1.8 \pm 0.9) \times 10^{-11}$, $(1.7 \pm 0.8) \times 10^{-10}$, and $(6.5 \pm 3.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, respectively. These adducts are presumably stabilized by infrared radiative emission [54]. CAD of these adducts yields exclusive formation of Fe^+.

The product distributions and rate constants for reaction of FeL^+ [L = C_4H_6, c-C_5H_6, c-C_5H_5, C_6H_6, $C_5H_4(=CH_2)$] with thiophene, furan, and pyrrole are summarized in Table 1. In many cases, either exclusive or significant adduct formation is observed. For example, Fe-c-$C_5H_5^+$ and $FeC_6H_6^+$ yield exclusive *rapid* adduct formation with thiophene, furan, and pyrrole (Table 1). CAD of these adducts yields exclusive initial elimination of the heterocycle. The heterocycles in the $Fe(c\text{-}C_5H_5)(C_4H_4X)^+$ and $Fe(C_6H_6)(C_4H_4X)^+$ (X = S, O, NH) adducts are probably molecularly bound and are similar to structures **1–4** for thiophene; however, C—H and C—X insertion species cannot be ruled out. The mixed sandwich compound, $Fe(c\text{-}C_5H_5)(\eta^5\text{-}C_4R_4S)^+$ was generated and characterized in solution [55, 56]. The π-coordinated thiophene derivatives of Cr [57], Mn [58], and Ru [59] are also known. In addition, an η^5-pyrrole–iron complex [$Fe(c\text{-}C_5H_5)(C_4H_4NMe)^+$] has been synthesized [27e] along with $[Cr(C_4H_4NMe)(CO)_3]$ [27] and $[Co(C_5H_5)(C_4Me_4NMe)]$ [27], although the pyrrole ligands are only weakly coordinated in these species. The η^1-S-bound thiophene adducts are unlikely due to the weakly coordinating nature of sulfur atoms in thiophene [13a]. Theoretical calculations have revealed that metal–sulfur π-back bonding of a filled metal d orbital with the empty $3b_1(\pi^*)$ orbital (lowest unoccupied molecular orbital) of thiophene is weak, which results in a weak η^1-S interaction [60]. Therefore, η^1-S bonding of thiophene to $3d$ metals is relatively weak. Based on analogies to studies of solution-phase phenomena, it is highly likely that the foregoing thiophene and pyrrole adducts contain thiophene and pyrrole π-bound to $Fe(c\text{-}C_5H_5)^+$ and $FeC_6H_6^+$. Furan, on the other hand, may form either π-coordinated [28] or η^1-O-coordinated metal complexes [25].

The chemistry of the iron–diene complexes [$FeC_4H_6^+$ and $Fe(c\text{-}C_5H_6)^+$] and the fulvene complex [$FeC_5H_4(=CH_2)^+$] is considerably more complicated, especially in reactions with furan and pyrrole (Table 1). The most intriguing reactions are the predominant direct extrusion of CO from furan (eqs 8, 9, and 10)

Table 1. Summary of kinetic data and percentages of neutrals lost in the primary reactions of FeL^+ with C_4H_4X (X = O, S, and NH)

Reaction	Neutral losses													Adduct	k_{exp}[a]	Eff.[b]
	H	H_2	NH	CH_2N	(CH_2O)	C_2H_2	C_2H_2O	C_2H_4O	C_3H_4	C_4H_6	C_2H_4	HCN	CO			
$FeC_4H_6^+ + C_4H_4S$										27				73	$9.8(4.9) \times 10^{-10}$	1.2
$FeC_4H_6^+ + C_4H_5N$						2			7	17		2		72	$1.6(0.8) \times 10^{-9}$	1.2
$FeC_4H_6^+ + C_4H_4O$		14			25		2	7					40	12	$7.5(3.7) \times 10^{-10}$	0.92
Fe-c-$C_5H_6^+ + C_4H_4S$	98										2				$1.2(0.6) \times 10^{-9}$	1.5
Fe-c-$C_5H_6^+ + C_4H_5N$	70	3	3									17		7	$1.1(0.5) \times 10^{-9}$	0.87
Fe-c-$C_5H_6^+ + C_4H_4O$													100		$1.1(0.5) \times 10^{-9}$	1.3
Fe-c-$C_5H_5^+ + C_4H_4S$														100	$1.1(0.5) \times 10^{-9}$	1.3
Fe-c-$C_5H_5^+ + C_4H_5N$														100	$1.6(0.8) \times 10^{-9}$	1.2
Fe-c-$C_5H_5^+ + C_4H_4O$														100	$8.2(4.1) \times 10^{-10}$	1.0
$FeC_6H_6^+ + C_4H_4S$														100	$7.2(3.6) \times 10^{-10}$	0.92
$FeC_6H_6^+ + C_4H_5N$														100	$1.1(0.5) \times 10^{-9}$	0.91
$FeC_6H_6^+ + C_4H_4O$														100	$3.7(1.8) \times 10^{-10}$	0.47
$FeC_5H_4(=CH_2)^+ + C_4H_4S$		39												61	$9.2(4.6) \times 10^{-10}$	1.2
$FeC_5H_4(=CH_2)^+ + C_4H_5N$														100	$1.7(0.8) \times 10^{-9}$	1.3
$FeC_5H_4(=CH_2)^+ + C_4H_4O$					9								86	5	$8.5(4.2) \times 10^{-10}$	1.1

[a] Observed bimolecular rate coefficient for disappearance of reactant ion in the units of cubic centimeters per molecule per second with uncertainties (±50%) in parentheses.

[b] Overall reaction efficiency is equal to k_{obs}/k_{coll}. Collision rates calculated by using the average dipole orientation approximation.

and the minor amount of HCN extrusion from pyrrole (eqs 11 and 12).

$$FeC_4H_6^+ + C_4H_4O \rightarrow FeC_7H_{10}^+ + CO \quad (8a)$$

$$\rightarrow FeC_7H_8^+ + (H_2CO) \quad (8b)$$

$$Fe(c\text{-}C_5H_6)^+ + C_4H_4O \rightarrow FeC_8H_{10}^+ + CO \quad (9)$$

$$FeC_5H_4(=CH_2)^+ + C_4H_4O \rightarrow FeC_9H_{10}^+ + CO \quad (10a)$$

$$\rightarrow FeC_9H_8^+ + (H_2CO) \quad (10b)$$

$$FeC_4H_6^+ + C_4H_5N \rightarrow FeC_7H_{10}^+ + HCN \quad (11)$$

$$Fe(c\text{-}C_5H_6)^+ + C_4H_5N \rightarrow FeC_8H_{10}^+ + HCN \quad (12)$$

We will summarize some aspects of the binding energies of these heterocycles to Fe^+ and FeL^+ before we consider the mechanisms of CO and HCN extrusion from furan and pyrrole.

The absence of benzene displacement for reaction of the heterocycles with $FeC_6H_6^+$ combined with specific heterocycle loss for CAD of the $Fe(C_6H_6)C_4H_4X^+$ adducts (vide supra) indicates that $D°(Fe^+\text{-}C_4H_4X)$ are all less than $D°(Fe^+\text{-}C_6H_6)$, which is 55 ± 5 kcal mol^{-1} [61]. The dominant channel for reaction of $Fe(c\text{-}C_5H_6)^+$ with thiophene and pyrrole is hydrogen displacement (eq 13), which implies that $D°(Fe(c\text{-}C_5H_5)^+\text{-}C_4H_4X) > D°(Fe(c\text{-}C_5H_5)^+\text{-}H) = 46 \pm 5$ kcal mol^{-1} [44]. Collisional activation of the products of the reaction in eq 13 yields exclusive initial loss of the heterocycle.

$$Fe(c\text{-}C_5H_6)^+ + C_4H_4X \rightarrow Fe(C_5H_5)C_4H_4X^+ + H \quad X = S, NH \quad (13)$$

Thiophene and pyrrole yield both adduct formation and C_4H_6 (1,3-butadiene) displacement with $FeC_4H_6^+$ (eq 14).

$$FeC_4H_6^+ + C_4H_4X \rightarrow Fe(C_4H_6)C_4H_4X^+ \quad (14a)$$

$$\rightarrow FeC_4H_4X^+ + C_4H_6 \quad X = S, NH \quad (14b)$$

The adducts of eq 14a undergo rapid subsequent C_4H_6 displacement with the heterocycle (eq 15).

$$Fe(C_4H_6)(C_4H_4X)^+ + C_4H_4X \rightarrow Fe(C_4H_4X)_2^+ + C_4H_6 \quad X = S, NH \quad (15)$$

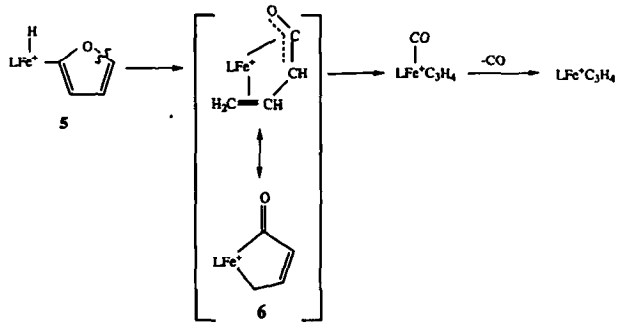
The outcome of this latter reaction indicates that $D°(FeC_4H_4X^+\text{-}C_4H_4X) > D°(FeC_4H_4X^+\text{-}C_4H_6)$. 1,3-Butadiene ($C_4H_6$) reacts with $FeC_4H_4S^+$ to yield adduct formation (~0.85) and C_4H_4S displacement (~0.15). SORI-CAD of the $Fe(C_4H_6)C_4H_4S^+$ adduct yields competitive C_4H_6 (0.66) and C_4H_4S (0.34) losses. These results suggest that $D°(Fe^+\text{-}C_4H_4S) \approx D°(Fe^+\text{-}C_4H_6) = 48 \pm 5$ kcal mol^{-1} [61]. 1,3-Butadiene (C_4H_6) reacts with $FeC_4H_5N^+$ to yield both adduct formation (~0.90) and C_4H_5N displacement (~0.10) along with a small amount of C_3H_4 elimination. SORI-CAD of the $Fe(C_4H_6)C_4H_5N^+$ adduct yields competitive C_4H_6 (~0.63) and C_4H_5N (~0.37) losses. These results also suggest that $D°(Fe^+\text{-}C_4H_5N) \approx D°(Fe^+\text{-}C_4H_6) = 48 \pm 5$ kcal mol^{-1} [61]. Finally, furan displaces ethene from $FeC_2H_4^+$, which indicates that $D°(Fe^+\text{-}C_4H_4O) > D°(Fe^+\text{-}C_2H_4) = 39.9 \pm 1.4$ kcal mol^{-1} [62], but less than $D°(Fe^+\text{-}C_6H_6) = 55 \pm 5$ kcal mol^{-1} [61].

We now consider mechanisms for CO extrusion from furan (eqs 8a, 9, and 10a). A proposed mechanism that involves initial insertion into the C—H bond α to the heteroatom is presented in Scheme I. The C—H insertion forms the furanyl complex (**5**). Hydrogen migration leads to C—O bond cleavage, which produces **6**, which subsequently extrudes CO. Electron-rich low-valence organometallic complexes preferentially insert into C—H bonds of furan [63, 64], pyridine [64], and thiophene [65] α to the heteroatom. The heteroatom in these heterocycles makes the proton on the carbon α to the heteroatom more acidic. Because the acidity of the C—H proton seems to play an important role in C—H oxidative addition reactions [66], it is not surprising that it is the more acidic proton that adds to the metal [63–65]. Direct CO abstraction from furan on Mo surfaces (100 and 110) was recently reported, where insertion into the α C—H bond was the proposed initial step [67].

Support for initial C—H bond insertion involves the reaction of $FeC_5H_4(=CH_2)^+$ with benzene-d_6, where exclusive rapid adduct formation is observed (eq 16):

$$FeC_5H_4(=CH_2)^+ + C_6D_6 \rightarrow Fe(C_5H_4(=CH_2))C_6D_6^+ \quad (16)$$

Upon collisional activation, this adduct yields exclusive benzene loss as C_6D_6 (0.25), C_6D_5H (0.39), and $C_6D_4H_2$ (0.36), which indicates that H/D scrambling



Scheme I

has occurred. The isotopolog distribution for benzene losses upon SORI-CAD of this adduct is shown in eq 17:

$$(C_6D_6)FeC_5H_4(=CH_2)^+$$

$$\xrightarrow{\text{SORI-CAD}} \begin{cases} \xrightarrow{0.52(0.54)} FeC_6H_4D_2^+ + C_6H_2D_4 & (17a) \\ \xrightarrow{0.44(0.43)} FeC_6H_5D^+ + C_6HD_5 & (17b) \\ \xrightarrow{0.04(0.03)} FeC_6H_6^+ + C_6D_6 & (17c) \end{cases}$$

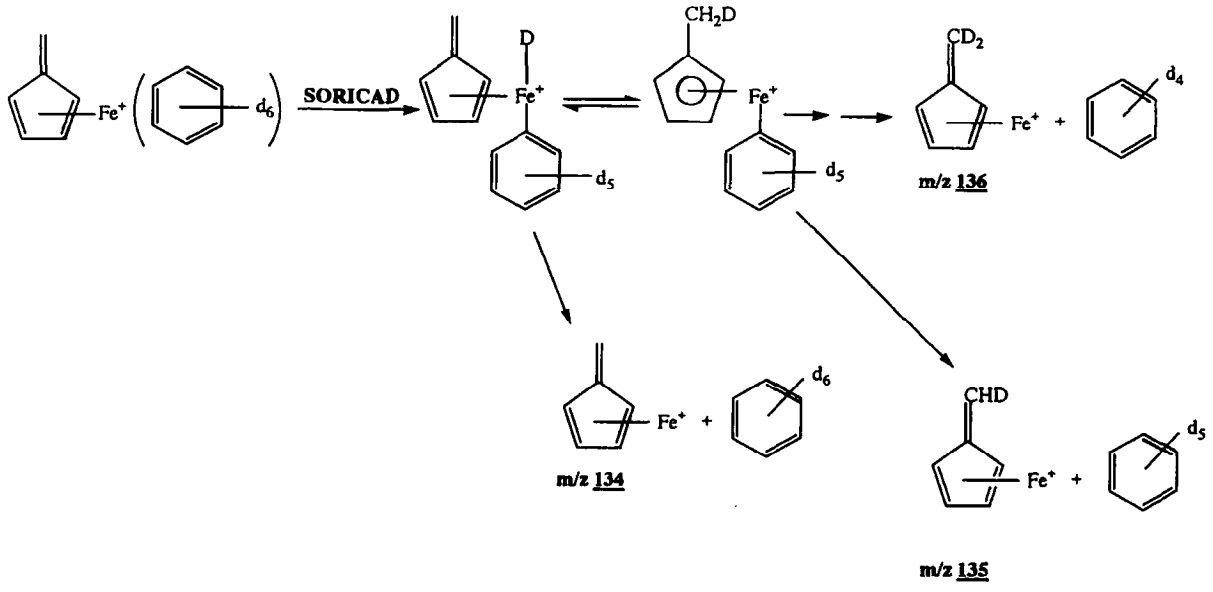
It is significant that only two hydrogen atoms on the fulvene ligand are exchangeable. A mechanism for this H/D exchange is presented in Scheme II and involves metal ion insertion into the aromatic C—D bond and migration of D to the methylene group of fulvene. Scheme II predicts that only the methylene hydrogens of fulvene are exchangeable. The isotopolog distribution for random scrambling where only the two methylene hydrogens are exchangeable is shown in parentheses in eq 17. The experimental distribution agrees quite well with the calculated random distribution predicted by Scheme II. The exclusive loss of benzene upon SORI-CAD of the fulvene–benzene complex indicates that $D°(Fe^+\text{-fulvene}) > D°(Fe^+\text{-benzene}) = 55 \pm 5$ kcal mol^{-1} [61]. The observation that $FeC_5H_4(=CH_2)^+$ inserts into aromatic C—H bonds supports initial C—H insertion of furan (Scheme I). The Fe(c-C_5H_6)$^+$ undergoes facile hydrogen-atom displacement with benzene and $FeC_4H_6^+$ yields facile C_4H_6 displacement with benzene. Consequently, it was not possible to probe aromatic C—H bond insertion for these two species. Both Fe(c-C_5H_5)$^+$ and $FeC_6H_6^+$ do not undergo H/D exchange with benzene-d_6.

CO extrusion also may involve direct C—O insertion. Direct C—S insertion of thiophene was observed for discrete organometallic species [23, 24, 63]. Here, initial, direct C—O insertion would yield furanometallacycle **7** (Scheme III) with subsequent hydrogen migration to yield **8**, which may rearrange to either **6** or **9** followed by CO extrusion. To our knowledge, there are no reports of the direct insertion of a discrete organometallic complex into the C—O bond of furan.

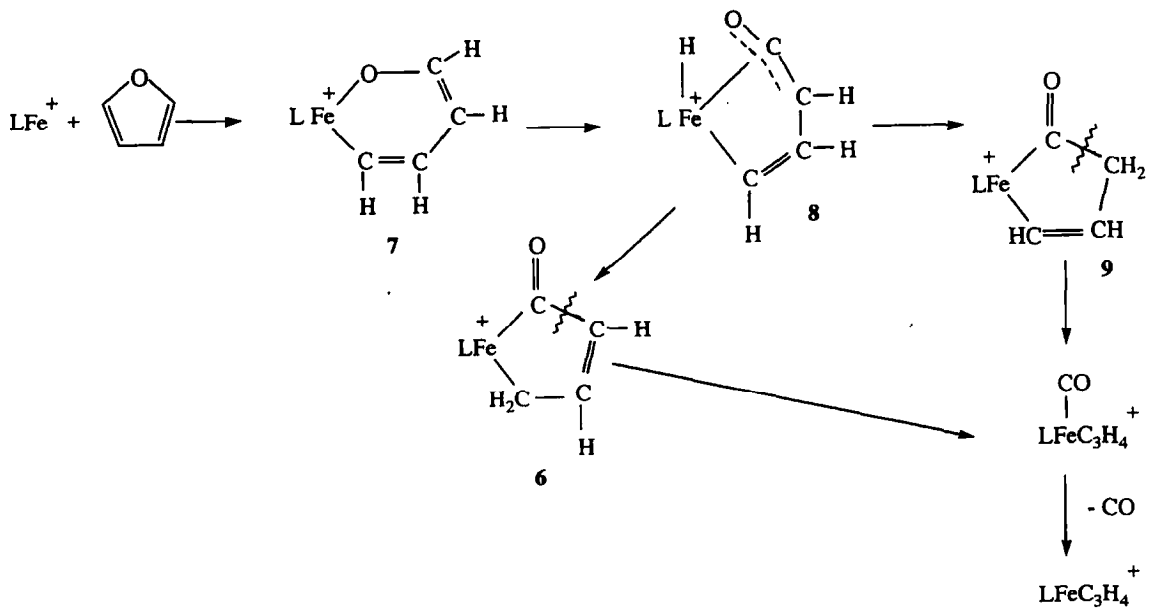
A third mechanism, which may be applicable only to Fe(c-C_5H_6)$^+$, is presented in Scheme IV and involves hydrogen migration from the cyclopentadiene ligand to an α-carbon atom of furan, which results in C—O cleavage to yield the 1-oxapentadienyl complex **10**. Hydrogen migrations subsequently result in CO extrusion. It was demonstrated that Fe(c-C_5H_6)$^+$ readily undergoes hydrogen-atom migration to yield (H)Fe(C_5H_5)$^+$ upon reaction with ethene [68]. A $Re(PPh_3)_2H_7$ complex was reported to undergo ring cleavage of furan to yield propene and CO, presumably by hydrogen migration to furan that resulted in C—O bond cleavage [69]. In addition, C—S bond cleavage of a thiophene by hydride addition to Ru(Cp)(η^5-thiophene)$^+$ was reported (eq 18) [70].

$$(Cp)Ru(\eta^5\text{-thiophene})^+ + XH^- \longrightarrow \text{(Cp)Ru(S, CH, CH, CH}_2\text{=CH)} + X \qquad (18)$$

Other nucleophiles [SMe^-, SEt^-, S(i-Pr), and $CH(CO_2Me_2^-)$] also react with Ru(Cp)(η^5-thiophene)$^+$



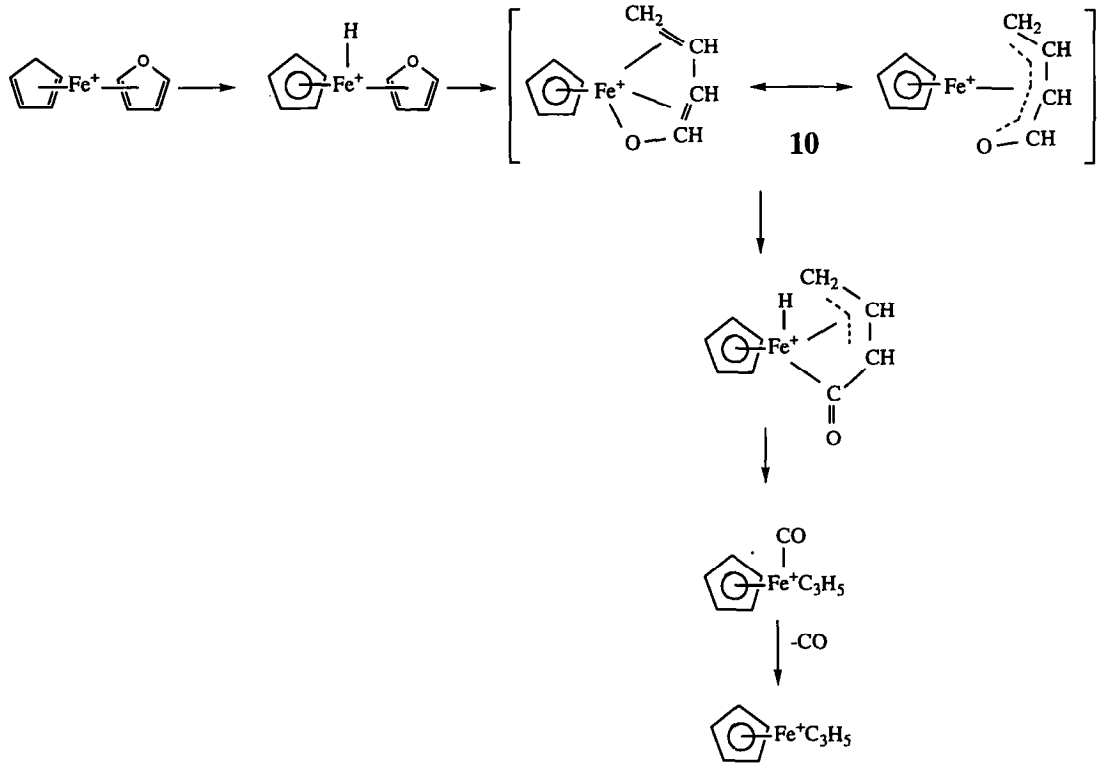
Scheme II



Scheme III

to give ring-opened products analogous to those in eq 18. In contrast, Mn(η^5-thiophene)$(CO)_3$ undergoes hydride addition to yield an allyl sulfide closed-ring species [70].

CO extrusion from the decomposition of a tetrahydrofuran-like Mo complex also was observed [68]. The small amount of HCN eliminations (eqs 11 and 12) may proceed by processes similar to that for CO extrusion of furan (Schemes I, III, and IV). The difference in the reactivity of thiophene, pyrrole, and furan with the FeL^+ complexes, on first glance, appears puzzling. One possible explanation is that it is more difficult to insert into C—X and C—H bonds of thiophene and pyrrole than of furan. This seems unlikely based on the examples of C—H and C—S bond insertion of thiophenes by organometallic species [23, 24, 63, 64]. Con-



Scheme IV

sideration of the overall thermochemistry, however, indicates that CO extrusion from furan is 25 kcal mol^{-1} more favorable than the corresponding abstraction of HCN from pyrrole and 55 kcal mol^{-1} more favorable than CS elimination from thiophene. (Auxiliary thermochemical information taken from Ref. 72.) These calculations assume formation of identical C_3H_4 species upon heteroatom extrusion. Hence, CS extrusion simply may be energetically inaccessible. Dehydrogenation of thiophene by $FeC_5H_4(=CH_2)^+$ (Table 1) supports initial C—H insertion (Scheme I). In this case, dehydrogenation may result in formation of a fused-ring system. Surprisingly, pyrrole yields exclusive adduct formation with $FeC_5H_4(=CH_2)^+$ (Table 1).

The selectivity for CO extrusion by FeC_4H_6, Fe(*c*-$C_5H_6)^+$, and $FeC_5H_4(=CH_2)^+$ is intriguing. To gain further insight into ligand effects for this process, the reactivity of Fe(toluene)$^+$, Fe(norbornadiene)$^+$, Fe(cycloheptatriene)$^+$, and Fe(ethenylcyclopentadiene)$^+$ with furan was examined. Fe(toluene)$^+$ and Fe(cycloheptatriene)$^+$ both yield exclusive rapid adduct formation with furan. Fe(norbornadiene)$^+$ reacts with furan to give primarily adduct formation (0.65) along with CO (0.08) and (H_2CO) (0.27) eliminations with furan. Fe(ethenylcyclopentadiene)$^+$ formed by dehydrogenation of ethenylcyclopentadiene (eq 19) yields predominant facile [$k = (8.6 \pm 4.3) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}; Eff. = 1.1; overall reaction efficiency (Eff.) is taken as k_{obs}/k_{coll}; k_{coll} was calculated by using the average dipole orientation approximation [73]] CO extrusion (eq 20):

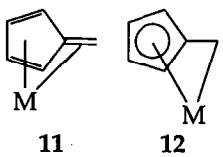
$$Fe^+ + \text{ethenylcyclopentane} \rightarrow Fe(\text{ethenylcyclopentadiene})^+ + 2H_2 \quad (19)$$

$$Fe(\text{ethenylcyclopentadiene})^+ + C_4H_4O \xrightarrow{0.08} Fe(C_7H_8)C_4H_4O^+ \quad (20a)$$

$$\xrightarrow{0.70} FeC_{10}H_{12}^+ + CO \quad (20b)$$

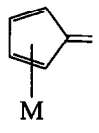
$$\xrightarrow{0.22} FeC_{10}H_{10}^+ + (H_2CO) \quad (20c)$$

Both $FeC_4H_6^+$ and Fe(*c*-$C_5H_6)^+$ contain η^4-bound conjugated diene ligands [40]. A number of transition-metal fulvene complexes were synthesized and structurally characterized, and a number of different binding modes were observed [74]. In many cases, the exocyclic carbon atom is bent toward the metal atom. For example, the exocyclic carbon atom in $Cr(CO)_3$(fulvene) is bent down by 30° [75]. The tetramethylfulvene ligand is generally bound in an η^6 fashion to early transition metals and it has been described as intermediate between two extremes (**11** and **12**) [76].



11 **12**

A different bonding of the fulvene group is observed in late transition-metal fulvene complexes, where in some cases the ligand appears to be bonded as η^4-diene [77] (**13**) or η^2-olefin [78], and extrusion of the fulvene ligand is observed [79].



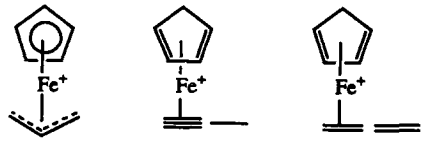
13

It is quite appealing to invoke η^4-bound Fe(fulvene)$^+$ (**13**) for the reaction in eq 10a. The Fe(ethenylcyclopentadiene)$^+$ species also may be η^4 bound through the ring-diene system. This interpretation then suggests that it is η^4-bound diene ligands that are required for CO extrusion from furan. The nonconjugated diene-bound ligand norbornadiene yields predominant adduct formation with furan (vide supra). If fulvene is bound to Fe^+ in an η^4-fashion, then it should be displaced by traditional η^6-ligands such as benzene. However, benzene is more weakly bound to Fe^+ than fulvene, and this suggests that fulvene acts as an η^6-ligand (vide supra). In addition, the ethenyl group of the ethenylcyclopentadiene ligand also may interact with the metal center. Consequently, it appears too simplistic to attribute η^4-bound conjugated diene–Fe^+ complexes to CO abstraction from furan. There are no other simple factors such as ionization potential that also can account for the observed reactivity.

The structures of the products for CO extrusion from furan (eqs 8a and 9) were probed by CAD. CAD of $FeC_8H_{10}^+$, formed in eq 9, yields H_2, C_2H_4, C_3H_5, and C_8H_{10} eliminations (Figure 1). These losses are identical to those reported for CAD of $FeC_8H_{10}^+$ formed in eq 21, where structure **14** was proposed [44].

$$Fe(c\text{-}C_5H_6)^+ + C_3H_8 \rightarrow FeC_8H_{10}^+ + 2H_2 \quad (21)$$

However, structures **15** and **16** are also possible, and it is quite likely that all three of these structures can readily interconvert upon activation.



14 **15** **16**

Therefore, the $FeC_8H_{10}^+$ ions formed in eqs 9 and 21 probably have similar structures. Finally, $FeC_8H_{10}^+$ produced in eq 9 is inert with fulvene.

The mechanism for CO abstraction from furan by $FeC_4H_6^+$ is probably complicated by butadiene–furan coupling. Such coupling easily can account for the

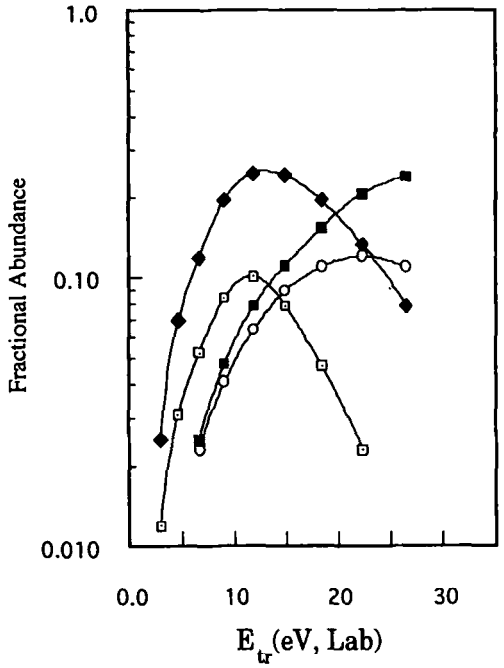


Figure 1. Variation of fractional fragment ion abundances as a function of kinetic energy (laboratory frame) for CAD of $FeC_8H_{10}^+$ formed in eq 9: $FeC_8H_8^+$ (⊡); $FeC_6H_6^+$ (♦); $FeC_5H_5^+$ (○); Fe^+ (■).

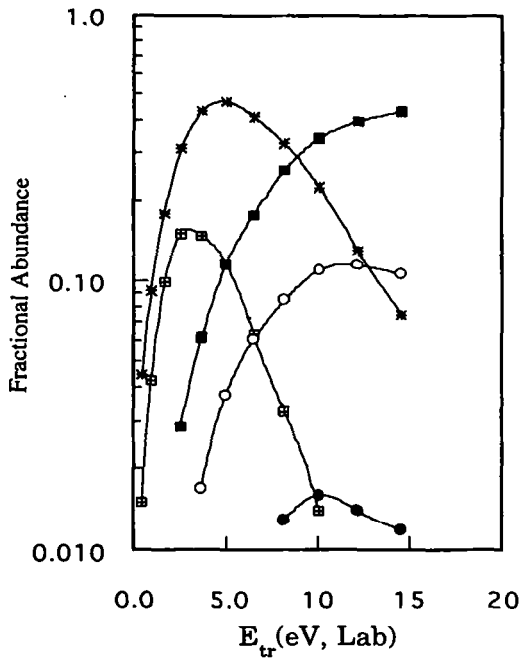


Figure 2. Variation of fractional fragment ion abundances as a function of kinetic energy (laboratory frame) for CAD of $FeC_7H_{10}^+$ formed in eq 8a: $FeC_7H_8^+$ (⊞); $FeC_7H_7^+$ (●); $FeC_5H_6^+$ (*); $FeC_5H_5^+$ (○); Fe^+ (■).

additional products observed for this system (Table 1). The structures of $FeC_7H_{10}^+$, and $FeC_7H_8^+$ formed by the reaction in eq 8 were probed by both CAD and reaction with furan. CAD of $FeC_7H_{10}^+$ (Figure 2) and $FeC_7H_8^+$ (Figure 3) shows that C_2H_4 elimination is the dominant decomposition channel for $FeC_7H_{10}^+$ with significant H_2 elimination also observed (Figure 2). Significant H_2 elimination (Figure 2) suggests that the reaction in eq 8b may proceed by sequential CO and H_2 losses. Although there are some qualitative differences, the CAD breakdown curve (Figure 3) for $FeC_7H_8^+$ is not clearly distinguishable from that for CAD of authentic Fe(cycloheptatriene)$^+$ (Figure 4), Fe(norbornadiene)$^+$ (Figure 5), or Fe(ethenylcyclopentadiene)$^+$ (Figure 6; same fragmentations and similar distributions); however, it is clearly distinguished from that for Fe(toluene)$^+$, which yields exclusive loss of C_7H_8. If ligand coupling does not occur during CO extrusion, then an Fe(butadiene)$C_3H_4^+$ complex would be formed, where the C_3H_4 ligand would most likely be propyne or allene. We recently showed that Fe(butadiene)$^+$ reacts rapidly with propyne to yield Fe(toluene)$^+$ ([80] and Bakhtiar, R.; Jacobson, D. B., unpublished results). Allene reacts in an analogous fashion to yield Fe(toluene)$^+$ ([80] and Bakhtiar, R.; Jacobson, D. B., unpublished results). Consequently, ligand coupling must occur prior to CO extrusion in the reaction of $FeC_4H_6^+$ with furan because Fe(toluene)$^+$ is not the product of eq 8b.

Further insight into the structure of $FeC_7H_8^+$ formed in eq 8b is obtained by studying reactions of $FeC_7H_8^+$ with furan. $FeC_7H_8^+$ formed in eq 8b reacts with furan [$k = (2.2 \pm 1.1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}; Eff. = 0.28 [73]] to yield significant CO extrusion (eq 22).

$$FeC_7H_8^+ + C_4H_4O \xrightarrow{0.10} Fe(C_7H_8)C_4H_4O^+ \quad (22a)$$

$$FeC_7H_8^+ + C_4H_4O \xrightarrow{0.28} FeC_{10}H_{12}^+ + CO \quad (22b)$$

$$FeC_7H_8^+ + C_4H_4O \xrightarrow{0.62} FeC_{10}H_{10}^+ + (H_2CO) \quad (22c)$$

This is in contrast to authentic $FeC_7H_8^+$ isomers (cycloheptatriene and norbornadiene) that react to yield either exclusive or predominant adduct formation with furan (vide supra). Although Fe(ethenylcyclopentadiene)$^+$ yields the same products when it reacts with furan (eq 20), the product distributions and reaction rate constants are dramatically different. Consequently, we were unable to determine the structure of $FeC_7H_8^+$ produced in eq 8b. It seems quite likely, however, that a single ion structure is produced in eq 8b because the subsequent reaction with furan occurs by pseudo-first-order kinetics.

FeO$^+$

The product distributions and rate constants for reaction of FeO^+ with furan, thiophene, and pyrrole are summarized in Table 2. FeO^+ reacts with furan to yield Fe^+ and $FeC_2H_4^+$ (eq 23). The product was con-

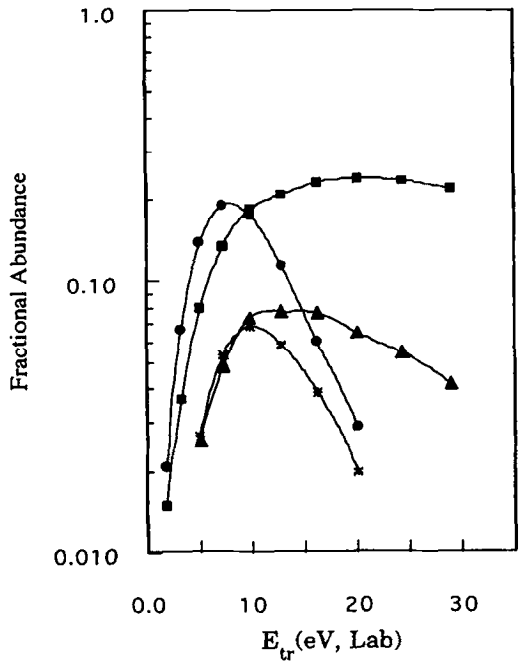


Figure 3. Variation of fractional fragment ion abundances as a function of kinetic energy (laboratory frame) for CAD of $FeC_7H_8^+$, formed in eq 8b: $FeC_7H_7^+$ (●); $FeC_5H_6^+$ (∗); $FeCH_2^+$ (▲); Fe^+ (■).

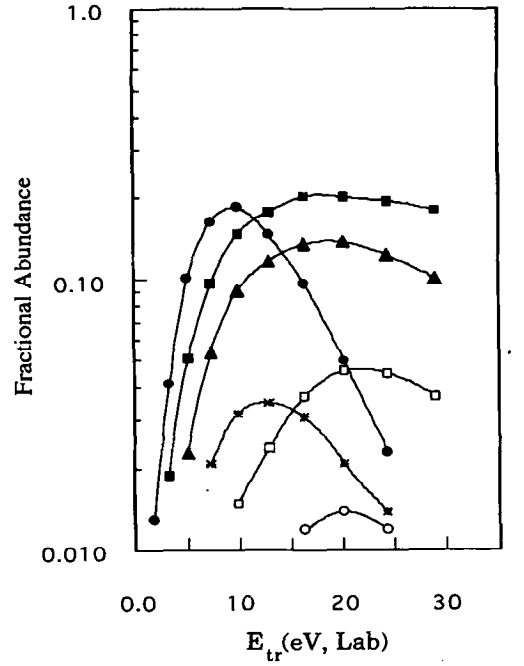


Figure 5. Variation of fractional ion abundances as a function of kinetic energy (laboratory frame) for CAD of authentic Fe(norbornadiene)$^+$: $FeC_7H_7^+$ (●); $FeC_5H_6^+$ (∗); $FeC_5H_5^+$ (○); $FeCH_2^+$ (▲); Fe^+ (■); $C_7H_7^+$ (□).

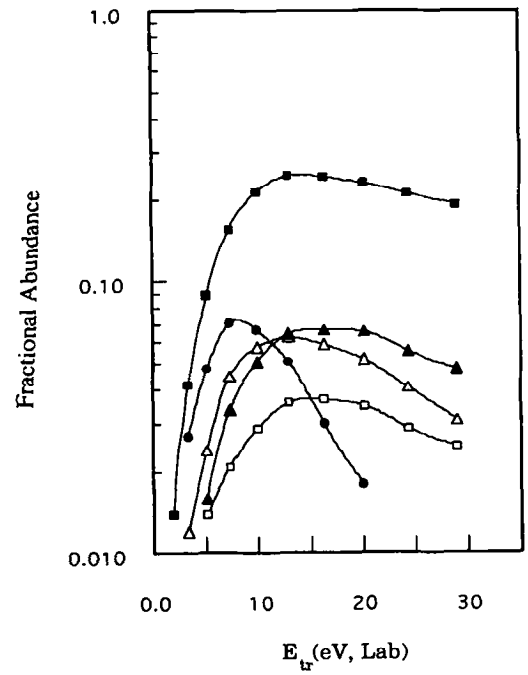


Figure 4. Variation of fractional fragment ion abundances as a function of kinetic energy (laboratory frame) for CAD of authentic Fe(cycloheptatriene)$^+$: $FeC_7H_7^+$ (●); $C_7H_8^+$ (△); $C_7H_7^+$ (□); $FeCH_2^+$ (▲); Fe^+ (■).

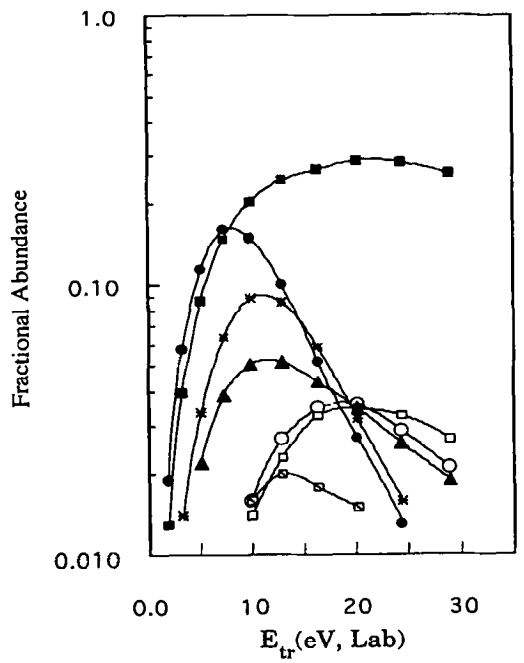


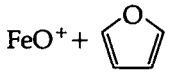
Figure 6. Variation of fractional fragment ion abundances as a function of kinetic energy (laboratory frame) for CAD of authentic Fe(ethenylcyclopentadiene)$^+$: $FeC_7H_7^+$ (●); $FeC_5H_6^+$ (∗); $FeC_5H_5^+$ (○); $FeC_2H_2^+$ (⧅); $FeCH_2^+$ (▲); Fe^+ (■); $C_7H_7^+$ (□).

Table 2. Summary of kinetic data and percentages of ion product distribution in the primary reaction of FeO^+ with C_4H_4X (X = O, S, and NH)

Neutral reactant	Percent ion product distribution									k_{exp}[b]	Eff.[c]
	Fe^+	FeS^+	$FeCH_3N^+$	$FeC_2H_4^+$[a]	$FeCS^+$	$FeC_3H_4S^+$	$FeCH_2S^+$	$Fe(HCN)^+$	$FeC_3H_5N^+$		
C_4H_4S		6			58	31	5			1.07(0.5) × 10^{-9}	1.2
C_4H_5N	30		15					35	20	1.9(0.9) × 10^{-9}	1.3
C_4H_4O	76			24						9.4(4.7) × 10^{-10}	1.1

[a]Confirmed by exact mass measurement.
[b]Observed bimolecular rate coefficient for disappearance of reactant ion in the units of cubic centimeters per molecule per second with uncertainties (±50%) in parentheses.
[c]Overall reaction efficiency is equal to k_{obs}/k_{coll}. Collision rates calculated by using the average dipole orientation approximation.

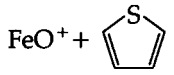
firmed as $FeC_2H_4^+$ (eq 23b) by exact mass measurement.



$$FeO^+ + \text{(furan)} \longrightarrow Fe^+ + (C_2H_4 + 2CO) \quad (23a)$$

$$\longrightarrow FeC_2H_4^+ + (2CO) \quad (23b)$$

Thiophene yields several products in reaction with FeO^+; they include primarily $FeCS^+$ and $FeC_3H_4S^+$ (Table 2; eq 24).



$$FeO^+ + \text{(thiophene)} \longrightarrow FeCS^+ + (C_2H_4 + CO) \quad (24a)$$

$$\longrightarrow FeC_3H_4S^+ + CO \quad (24b)$$

CAD of $FeCS^+$ results in loss of CS, exclusively. CAD of $FeC_3H_4S^+$ results in losses of C_2H_4, C_2H_2, C_3H_4, and C_3H_4S (Figure 7). SORI-CAD [50] of $FeC_3H_4S^+$

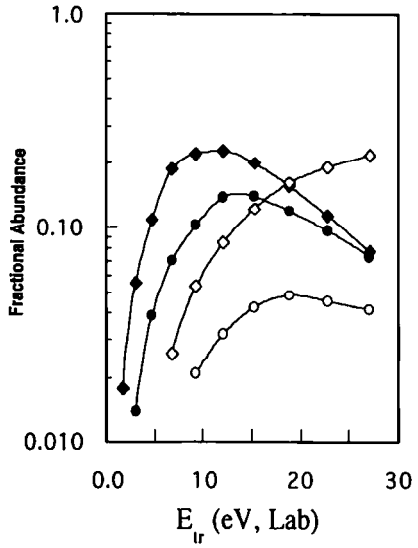
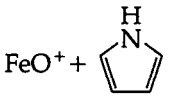


Figure 7. Variation of fractional fragment ion abundances as a function of kinetic energy (laboratory frame) for CAD of $FeC_3H_4S^+$ formed in eq 24b; $FeCSH_2^+$ (●); $FeCS^+$ (◆); FeS^+ (○); Fe^+ (◇).

affords predominant elimination of C_2H_4 (0.93); some C_2H_2 (0.07) elimination also is observed at low energies. $FeCS^+$ is inert with ethene and yields exclusive adduct formation with thiophene. The structure of $FeC_3H_4S^+$ produced according to eq 24b was probed by reaction with ethene-$^{13}C_2$, ethene-d_4, and thiophene. No reaction was observed for $FeC_3H_4S^+$ with ethene-$^{13}C_2$ and ethene-d_4; however, thiophene yields exclusive adduct formation. These results suggest that $FeC_3H_4S^+$ formed according to eq 24b does not have an $Fe(C_2H_4)(CS)^+$ structure, but rather contains a single intact C_3H_4S ligand. The structure $Fe(C_2H_4)(CS)^+$ should yield ethene displacement with isotopically labeled ethene. Failure with either ethene or thiophene to displace CS from $FeCS^+$ implies $D°(Fe^+\text{-}CS) > D°(Fe^+\text{-}C_2H_4) = 39.9 \pm 1.4$ kcal mol^{-1} [62] and $D°(Fe^+\text{-}CS) > D°(Fe^+\text{-thiophene}) \approx 48 \pm 5$ kcal mol^{-1} (vide infra). The $D°(Fe^+\text{-}CO) = 31.3 \pm 1.8$ kcal mol^{-1} [81] indicates that CS is much more strongly bound to Fe^+ than is CO. Both CO and CS are bound to transition metals through the carbon atom and each acts as a $2e^-$ ligand [82].

The reaction of pyrrole with FeO^+ also is more complicated than that for furan (see eq 25). CAD of $FeC_3H_5N^+$ yields losses of C_2H_4, C_2H_2, and C_3H_5N (Figure 8).



$$FeO^+ + \text{(pyrrole)} \longrightarrow Fe^+ + C_3H_5N + CO \quad (25a)$$

$$\longrightarrow Fe(HCN)^+ + (C_2H_4 + CO) \quad (25b)$$

$$\longrightarrow FeC_3H_5N^+ + CO \quad (25c)$$

$$\longrightarrow FeCH_3N^+ + (C_2H_2 + CO) \quad (25d)$$

SORI-CAD of $FeC_3H_5N^+$ yields both C_2H_4 (~0.64) and C_2H_2 (~0.36) eliminations. $FeC_3H_5N^+$ is inert with C_2D_4, but gives exclusive adduct formation with pyrrole. The absence of C_2H_4 displacement in $FeC_3H_5N^+$ by C_2D_4 rules out a $Fe(C_2H_4)(HCN)^+$ structure and is consistent with an intact C_3H_5N ligand in the complex. In addition, C_2H_4 does not undergo dehydrogenation with $Fe(HCN)^+$ as is ob-

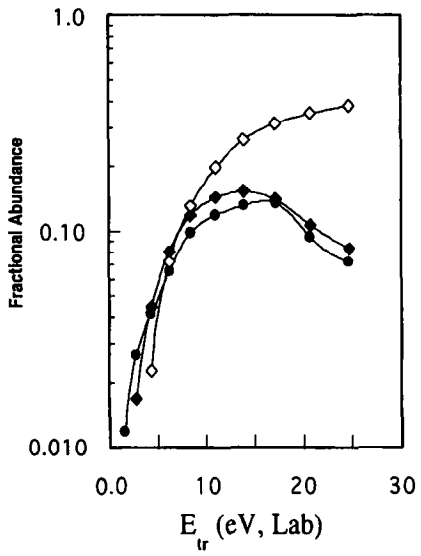


Figure 8. Variation of fractional fragment ion abundances as a function of kinetic energy (laboratory frame) for CAD for $FeC_3H_5N^+$ formed in eq 27c: $FeCH_3N^+$ (♦); $FeHCN^+$ (●); Fe^+ (◇).

served for CAD of $FeC_3H_5N^+$ (C_2H_2 loss). Finally, HCN in $Fe(HCN)^+$ is readily displaced by pyrrole [$k = (1.7 \pm 0.85) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}; Eff. = 1.2 [73]]; however, ethene does not displace HCN from $Fe(HCN)^+$. This implies that the binding energy of HCN to Fe^+ is between that of pyrrole [$D°(Fe^+$-pyrrole) $\approx 48 \pm 5$ kcal mol^{-1}; vide infra] and ethene [$D°(Fe^+$-$C_2H_4) = 39.9 \pm 1.4$ *kcal mol*$^{-1}$] [62].

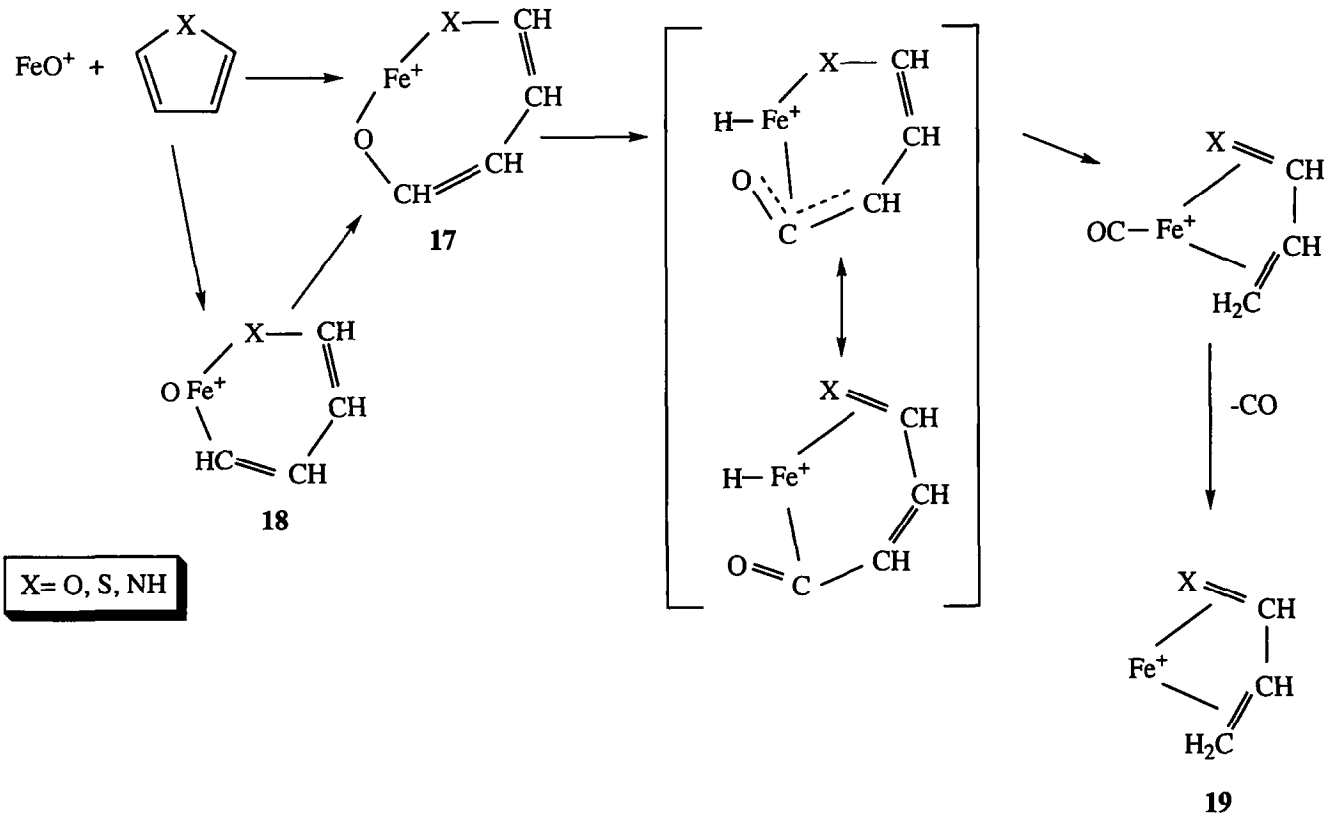
A proposed mechanism for reaction of FeO^+ with these heterocycles is presented in Scheme V. The initial process is proposed to be insertion of FeO^+ into the C—X bond to form either the seven-membered ring, **17**, directly or a six-membered ring species, **18**, followed by ring expansion to **17**. Hydrogen migrations then result in initial elimination of CO to yield **19**. Product ion **19** subsequently may decompose further to yield the products listed in Table 2. Scheme V predicts formation of an Fe(propenal)$^+$ complex upon CO extrusion of furan. Fe^+ reacts rapidly with propenal (CH_2=CH—CHO) to cause *exclusive* CO loss (confirmed by exact mass measurement; eq 26).

$$Fe^+ + CH_2{=}CH{-}CHO \rightarrow FeC_2H_4^+ + CO \quad (26)$$

This is precisely what is observed for reaction of furan with FeO^+ (eq 23b; sequential CO losses). Unfortunately, stable sulfur and nitrogen analogs to propenal are not available to test further the mechanism presented in Scheme V.

We now consider thermochemical implications for reaction of FeO^+ with these heterocycles. Equation 27 is 9.3 kcal mol^{-1} exothermic for furan, but it is 15.2 and 45.3 kcal mol^{-1} endothermic, respectively, for pyrrole and thiophene (for pyrrole, CX is assumed to be hydrogen cyanide) [72, 83].

$$FeO^+ + C_4H_4X \rightarrow Fe^+ + CX + C_2H_4 + CO \quad (27)$$
$$X = O, S, NH$$



Scheme V

Observation of significant Fe^+ formation (eq 25a) suggests that C_3H_5N is eliminated as either $CH_2{=}CH{-}CH{=}NH$ (2.6 kcal mol^{-1} exothermic) or CH_3CH_2CN (17.3 kcal mol^{-1} exothermic) [72, 83]. In addition, eq 25a may include some elimination of an intact C_3H_4O species, presumably $CH_2{=}CH{-}CHO$ (13.4 kcal mol^{-1} exothermic). The absence of Fe^+ formation for reaction of FeO^+ with thiophene is due to the fact that elimination of intact C_3H_4S species is endothermic [72, 83] [$D^\circ_{298}(Fe^+\text{-}O) = 3.57 \pm 0.06$ eV (82.3 ± 1.4 kcal mol^{-1})]. Equation 28 requires $D^\circ(Fe^+\text{-}HCN)$ to exceed 15.2 kcal mol^{-1} and $D^\circ(Fe^+\text{-}CS)$ to exceed 45.3 kcal mol^{-1} for it to be energetically accessible [both $D^\circ(Fe^+\text{-}HCN)$ and $D^\circ(Fe^+\text{-}CS)$ binding energies exceed these values; vide supra].

$$FeO^+ + C_4H_4X \rightarrow FeCX^+ + C_2H_4 + CO \quad (28)$$
$$X = S, NH$$

Conclusions

$FeC_4H_6^+$, $Fe(c\text{-}C_5H_6)^+$, $FeC_5H_4(=CH_2)^+$, and Fe(ethenylcyclopentadiene)$^+$ all cause predominant direct CO extrusion from furan (Table 1). Mechanisms that involve initial C—H insertion (Scheme I) and C—X insertion (Scheme III) are proposed for this process. Insertion into aromatic C—H bonds by $FeC_5H_4(=CH_2)^+$ combined with dehydrogenation of thiophene by $FeC_5H_4(=CH_2)^+$ provides support for mechanisms that involve initial C—H insertion (Scheme I). Another mechanism is presented for CO extrusion from furan by $Fe(c\text{-}C_5H_6)^+$, and the process involves hydrogen-atom migration from the C_5H_6 ring to an α-carbon (Scheme IV) [68]. There is support for such a process in organometallic complexes in solution [69, 70]. In contrast to CO elimination from furan, only a small amount of HCN extrusion from pyrrole is observed (eqs 11 and 12), and no CS extrusion is found for thiophene. HCN extrusion from pyrrole may involve mechanisms similar to that for CO extrusion from furan. The decreased reactivity of pyrrole and thiophene compared to that of furan may be due to the increased energy required for CS and HCN extrusions or to a poorly favorable insertion into C—H and C—X bonds. Dehydrogenation of thiophene by $FeC_5H_4(=CH_2)^+$ suggests that C—H bond insertion can occur; however, CS extrusion simply may be endothermic.

$FeC_5H_5^+$, $FeC_6H_6^+$, Fe(toluene)$^+$, and Fe(cycloheptatriene)$^+$ all react to give exclusive adduct formation with furan. Fe(norbornadiene)$^+$ yields predominant adduct formation with a small amount of CO extrusion with furan. We do not understand why there is this dramatic difference in reactivity of these unsaturated π-complexed-Fe^+ species. One possibility is that η^4-coordinated 1,3-diene ligands are required for CO extrusion of furan. However, this simplistic explanation is unlikely on the basis of the range of reactive FeL^+ species [L = C_4H_6, $c\text{-}C_5H_6$, $C_5H_4(=CH_2)^+$, ethenylcyclopentadiene].

FeO^+ is very reactive with thiophene, furan, and pyrrole, and CO extrusion is the initial process (Scheme V). $FeC_3H_4X^+$ (X = S, O, NH) formed from CO extrusion decomposes further. The extent of decomposition of the $FeC_3H_4X^+$ is governed by the overall energetics: $FeC_3H_4O^+$ (from furan) dissociates completely to $FeC_2H_4^+$ and Fe^+, but to a lesser degree for $FeC_3H_4S^+$ (from thiophene).

These results reveal that $Fe(L)(C_4H_4X)^+$ (X = S, O, NH) have a rich chemistry in the gas phase. We are expanding this study and will probe stereoelectronic effects of ligands on the reactivity of FeL^+. In addition, reaction with substituted furans, pyrroles, and thiophenes as well as with isotopically labeled heterocycles will reveal insight into the reaction mechanism. Finally, the reactivity of dihydro- and tetrahydroheterocycles will be explored. These results should complement the growing body of organometallic chemistry of heterocyclic species in solution.

Acknowledgments

We acknowledge the National Science Foundation NSF-EPSCoR program (Grant RII-861075), the Society for Analytical Chemists of Pittsburgh, and the VG Corporation for partial support for this research. We are grateful to Professor M. L. Gross for helpful comments.

References

1. (a) Schuman, S. C.; Shalit, H. *Catal. Rev.* **1970**, *4*, 245; (b) Mitchell, P. C. H. *Catalysis* **1981**, *4*, 175; (c) Prins, R.; deBeer, V. H. J.; Somorjai, G. A. *Catal. Rev. Sci. Eng.* **1989**, *31*, 1; (d) Garcia, J. J.; Maitlis, P. M. *J. Am. Chem. Soc.* **1993**, *115*, 12200; (e) Selegue, J. P.; Swarat, K. A. *J. Am. Chem. Soc.* **1993**, *115*, 6448; (f) Chianelli, R. R. *Catal. Rev. Sci. Eng.* **1984**, *26*, 361; (g) Lang, J. F.; Masel, R. I. *Surf. Sci.* **1987**, *183*, 44; (h) Nagai, M.; Miyao, T.; Tuboi, T. *Catal. Lett.* **1993**, *18*, 9; (i) Kuhn, W. K.; He, J. W.; Goodman, D. W. *J. Phys. Chem.* **1994**, *98*, 264; (j) Bianchini, C.; Meli, A. *J. Chem. Soc., Dalton Trans.* **1996**, 801.
2. (a) Furmisky, E. *Catal. Rev. Sci. Eng.* **1983**, *25*, 421; (b) Furmisky, E. *Appl. Catal.* **1983**, *6*, 159; (c) Abe, H.; Bell, A. T. *Catal. Lett.* **1993**, *18*, 1 and references cited therein; (d) Huuska, M. K. *Polyhedron* **1986**, *5*, 233; (e) Satterfield, C. N.; Yang, S. H. *J. Catal.* **1983**, *81*, 335; (f) Caldwell, T. E.; Abdelrehim, I. M.; Land, D. P. *J. Am. Chem. Soc.* **1996**, *118*, 907.
3. (a) Laine, R. M. *Catal. Rev. Sci. Eng.* **1983**, *25*, 459; (b) Sonnemans, J.; Van Den Berg, G. H.; Mars, P. *J. Catal.* **1973**, *31*, 220; (c) Abe, H.; Cheung, T-K.; Bell, A. T. *Catal. Lett.* **1993**, *21*, 11; (d) Schlatter, J. C.; Oyama, S. T.; Metcalf, J. E.; Lambert, J. M. *Ind. Eng. Chem. Res.* **1988**, *27*, 1648.
4. Topsoe, H.; Clausen, B. S. *Catal. Rev. Sci. Eng.* **1984**, *26*, 395.
5. Wiegand, B. C.; Friend, C. M. *Chem. Rev.* **1992**, *92*, 491.
6. (a) Luh, T-Y.; Wong, C. S. *J. Org. Chem.* **1985**, *50*, 5413; (b) Kaesz, H. D.; King, R. B.; Mannuel, T. A.; Nichols, L. D.; Stone, F. G. A. *J. Am. Chem. Soc.* **1960**, *82*, 4750; (c) Huberer, P.; Weiss, F. *J. Organomet. Chem.* **1977**, *129*, 105; (d) Broadhurst, P. V.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Am. Chem. Soc.* **1981**, *103*, 3198; (e) Alper, H.; Sibtain, F.; Heveling, J. *Tetrahedron Lett.* **1983**, *24*, 5329; (f) Choi, M-G.; Angelici, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 8753; (g) Huckett, S. C.; Sauer, N. N.; Angelici, R. J. *Organometallics* **1987**, *6*, 591; (h) Karroua, M.; Ladriere, J.; Matralis, H.; Grange, P.; Delmon, B. *J. Catal.*

1992, *138*, 640; (i) Catheline, D.; Astruc, D. *J. Organomet. Chem.* **1984**, *272*, 417; (j) Chivers, T.; Timms, P. L. *Can. J. Chem.* **1977**, *55*, 3509; (k) Ogily, A. E.; Draganjac, M.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1988**, *7*, 1171; (l) Bachmann, P.; Singer, H. Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* **1976**, *31*, 525; (m) Trost, B. M.; Zimon, S. D. *J. Org. Chem.* **1973**, *38*, 932; (n) Daub, J.; Endress, G.; Erhardt, U.; Jogun, K. H.; Joachim, K.; Laumer, A.; Pfiz, R.; Stezwoski, J. J. *Chem. Ber.* **1982**, *115*, 1787.

7. (a) Satterfield, C. N.; Modell, M.; Wilking, J. A. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *20*, 62; (b) Inui, T.; Tanabe, Y. *J. Catal.* **1978**, *52*, 375; (c) Satterfield, C. N.; Carter, D. L. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *20*, 538.
8. Satterfield, C. N.; Gultikin, S. *Ind. Eng. Chem. Process Des. Dev.* **1981** *20*, 62.
9. (a) Roberts, J. T.; Friend, C. M. *J. Am. Chem. Soc.* **1986**, *108*, 7204; (b) Roberts, J. T.; Friend, C. M. *J. Am. Chem. Soc.* **1987**, *109*, 4423; (c) Roberts, J. T.; Friend, C. M. *J. Am. Chem. Soc.* **1987**, *109*, 3872; (d) Roberts, J. T.; Friend, C. M. *Surf. Sci.* **1987**, *186*, 201; (e) Friend, C. M.; Roberts, J. T. *Acc. Chem. Res.* **1988**, *21*, 394; (f) Calhorda, M. J.; Hoffman, R.; Friend, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 50.
10. Lang, J. F.; Masel, R. I. *Surf. Sci.* **1987**, *183*, 44.
11. (a) Schoofs, G. R.; Preston, R. E.; Benziger, J. B. *Langmuir* **1985**, *1*, 313; (b) Preston, R. E.; Benziger, J. B. *J. Phys. Chem.* **1985**, *89*, 5010.
12. Kelly, D. G.; Odriozola, J. A.; Somorjai, G. A. *J. Phys. Chem.* **1987**, *91*, 5695.
13. (a) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387 and references cited therein; (b) Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991**, *39*, 259; (c) Angelici, R. J. *Coord. Chem. Rev.* **1990**, *105*, 61.
14. Draganjac, M.; Ruffing, C. J.; Rauchfuss, T. B. *Organometallics* **1985**, *4*, 1909.
15. (a) Choi, M. G.; Angelici, R. J. *Organometallics* **1991**, *10*, 2436; (b) Choi, M. G.; Robertson, M. J.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 4005.
16. Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 5969.
17. Ogilvy, A. E.; Skaugset, A. E.; Rauchfuss, T. B. *Organometallics* **1989**, *8*, 2739.
18. Skaugset, A. E.; Rauchfuss, T. B.; Stern, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 2432.
19. (a) Chen, J.; Angelici, R. J. *Organometallics* **1989**, *8*, 2277; (b) Chen, J.; Angelici, R. J. *Organometallics* **1990**, *9*, 849.
20. Sanchez-Delgado, R. A.; Marquez-Silva, R. L.; Puga, J.; Tiripicchio, A.; Camellini, M. *J. Organomet. Chem.* **1986**, *316*, C35.
21. (a) Lackemeyer, J. R.; Rauchfuss, T. B.; Rheingold, A. L.; Wilson, S. R. *J. Am. Chem. Soc.* **1989**, *111*, 8828; (b) Ganja, E. A.; Rauchfuss, T. B.; Stern, C. L. *Organometallics* **1991**, *10*, 270.
22. (a) Huckett, S. C.; Miller, L. L.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1988**, *7*, 686; (b) Spies, G. H.; Angelici, R. J. *Organometallics* **1987**, *6*, 1897; (c) Hachgenei, J. W.; Angelici, R. J. *Organometallics* **1989**, *8*, 14; (d) Hachgenei, J. W.; Angelici, R. J. *J. Organomet. Chem.* **1988**, *335*, 359; (e) Huckett, S. C.; Sauer, N. N.; Angelici, R. J. *Organometallics* **1987**, *6*, 591.
23. (a) Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1991**, *113*, 559; (b) Dong, L.; Duckett, S. B.; Ohman, K. F.; Jones, W. P. *J. Am. Chem. Soc.* **1992**, *114*, 151.
24. Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 199.
25. Kershner, D. L.; Basolo, F. *Coord. Chem. Rev.* **1987**, *79*, 279.
26. Zakrzewski, J.; Giannotti, C. *J. Organomet. Chem.* **1990**, *388*, 175.
27. (a) Joshi, K. K.; Pauson, P. L.; Quazi, A. R.; Stubbs, W. H. *J. Organomet. Chem.* **1964**, *1*, 471; (b) Seel, F.; Sperver, V. *J. Organomet. Chem.* **1968**, *14*, 405; (c) Ofele, K.; Dotzauer, E. *J. Organomet. Chem.* **1971**, *30*, 211; (d) Huttner, G.; Mills, O. S. *Chem. Ber.* **1972**, *105*, 301; (e) Kuhn, N.; Horn, E.-M.; Zauder, E.; Blaser, D.; Boese, R. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 579; (f) Kuhn, N.; Bruggemann, H.; Winter, M.; de Bellis, V. M. *J. Organomet. Chem.* **1987**, *320*, 391.
28. Chaudret, B.; Jalon, F. A. *J. Chem. Soc., Chem. Commun.* **1988**, 711.
29. (a) McCarty, K. F.; Anderegg, J. W.; Schrader, G. L. *J. Catal.* **1985**, *93*, 375; (b) McCarty, K. F.; Schrader, G. L. *Ind. Eng. Chem. Prod. Res. Dev.* **1984**, *23*, 519.
30. (a) Lew, S.; Jothimurugesan, K.; Flytzani-Stephanopoulos, M. *Ind. Eng. Chem. Res.* **1989**, *28*, 535; (b) Grindley, T.; Steinfeld, G. Final Report DOE/MC/16545-1125; METC, Morgantown, WV, 1981; (c) Sasaoka, E.; Sakamoto, M.; Ichio, T.; Kasaoka, S.; Sakata, Y. *Energy Fuels* **1993**, *7*, 632; (d) Uchida, H. *Nenryo Kyokaishi* **1983**, *62*, 792; (e) Woods, M. C.; Gangwal, S. K.; Jothimurugesan, K.; Harrison, D. P. *Ind. Eng. Chem. Res.* **1990**, *29*, 1160; (f) Silaban, A.; Harrison, D. P.; Berggren, M. H.; Jha, M. C. *Chem. Eng. Commun.* **1991**, *107*, 55.
31. Russell, D. H., Ed. *Gas Phase Inorganic Chemistry*; Plenum Press: New York, 1989.
32. Carlin, T. J.; Wise, M. B.; Freiser, B. S. *Inorg. Chem.* **1981**, *20*, 2743.
33. McMahon, T. J.; Jackson, T. C.; Freiser, B. S. *J. Am. Chem. Soc.* **1989**, *111*, 421.
34. Eller, K.; Akkok, S.; Schwarz, H. *Helv. Chim. Acta* **1990**, *73*, 229.
35. (a) Beauchamp, J. L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 257; (b) Lehman, T. A.; Bursey, M. M. *Ion Cyclotron Resonance Spectrometry*; Wiley-Interscience: New York, 1976.
36. (a) Marshall, A. G.; Schweikhard, L. *Int. J. Mass Spectrom. Ion Processes* **1992**, *118/119*, 37; (b) Marshall, A. G.; Grosshans, P. B. *Anal. Chem.* **1991**, *63*, 215A and references cited therein; (c) Buchanan, M. B., Ed. *Fourier Transform Mass Spectrometry*; American Chemical Society: Washington, DC, 1987; (d) Buchanan, M. V.; Comisarow, M. B. In *FTMS: Evolution, Innovation, and Applications*; Buchanan, M. V., Ed.; ACS Symposium Series 359; American Chemical Society: Washington, DC, 1989; p 1; (e) Dunbar, R. C. *Analytical Applications of FTICRMS*; VCH: New York, 1991; Chap. 1; (f) Gross, M. L.; Rempel, D. L. *Science (Washington, D.C.)* **1984**, *226*, 261; (g) Marshall, A. G. *Acc. Chem. Res.* **1985**, *18*, 316.
37. Jacobson, D. B. *J. Am. Chem. Soc.* **1989**, *111*, 1626.
38. Bartmess, J. E.; Geordiadis, R. M. *Vacuum* **1983**, *33*, 149.
39. (a) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360; (b) Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 5944.
40. Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7484, 7492.
41. (a) Busch, K. L.; Glish, G. L.; McLuckey, S. A. *Mass Spectrometry/Mass Spectrometry*; VCH: New York, 1988; (b) McLuckey, S. A. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 599.
42. McLafferty, F. W., Ed. *Tandem Mass Spectrometry*; Wiley: New York, 1983.
43. Huang, Y.; Freiser, B. S. *J. Am. Chem. Soc.* **1993**, *115*, 737.
44. Huang, Y.; Freiser, B. S. *J. Am. Chem. Soc.* **1990**, *112*, 5085.
45. Kappes, M. M.; Staley, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 1286.
46. (a) Cody, R. B.; Freiser, B. S. *Int. J. Mass Spectrom. Ion Processes* **1982**, *41*, 199; (b) Cody, R. B.; Burnier, R. C.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 96; (c) Burnier, R. C.; Cody, R. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 7436.
47. Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 736, 7484.
48. Grosshans, P. B.; Shields, P.; Marshall, A. G. *J. Am. Chem. Soc.* **1990**, *112*, 1275.
49. Comisarow, M. B. *J. Chem. Phys.* **1971**, *55*, 187.

50. Gauthier, J. W.; Trautman, T. R.; Jacobson, D. B. *Anal. Chim. Acta* **1991**, *246*, 211.
51. Thorne, L. R.; Beauchamp, J. L. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1984; Vol. 3, p 41.
52. Carlin, T. J.; Freiser, B. S. *Anal. Chem.* **1983**, *55*, 571.
53. Marshall, A. G.; Verdun, F. R. *Fourier Transforms in Optical, NMR, and Mass Spectrometry: A User's Handbook*; Elsevier: Amsterdam, 1990, Chap. 7.
54. (a) Woodin, R. L.; Beauchamp, J. L. *Chem. Phys.* **1979**, *41*, 1; (b) Dunbar, R. C. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *54*, 109.
55. (a) Bachman, P.; Singer, H. *Z. Naturforsch B: Anorg. Chem., Org. Chem.* **1976**, *31*, 525; (b) Guerchais, V.; Astruc, D. *J. Organomet. Chem.* **1986**, *316*, 335; (c) Lee, C. C.; Igbal, M.; Gill, U. S.; Sutherland, R. G. *J. Organomet. Chem.* **1985**, *288*, 89.
56. (a) Spies, G. H.; Angelici, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 5569; (b) Draganjac, M.; Ruffing, C. J.; Rauchfuss, T. B. *Organometallics* **1985**, *4*, 1909.
57. Baily, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1306.
58. Lesch, D. A.; Richardson, J. W., Jr.; Jacobson, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 2901.
59. Sauer, N. N.; Angelici, R. J. *Organometallics* **1987**, *6*, 1146.
60. Harris, S.; Chaienelli, T. T. *J. Catal.* **1984**, *86*, 400.
61. Hettich, R. L.; Jackson, T. C.; Stanko, E. M.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 5086.
62. Armentrout, P. B.; Clemmer, D. E. In *Energetics of Organometallic Species*; Simoes, J. A. M., Ed.; Kluwer: Amsterdam, 1992; p 321.
63. (a) Arce, A. J.; Deeming, A. J.; DeSanctic, Y. H.; Machado, R.; Manzur, J.; Rivas, C. *J. Chem. Soc., Chem. Commun.* **1990**, 1568; (b) Himmelreich, D.; Muller, G. *J. Organomet. Chem.* **1985**, *297*, 341.
64. Selnau, H. W.; Merola, J. S. *Organometallics* **1993**, *12*, 1583.
65. (a) Benson, J. W.; Angelici, R. J. *Inorg. Chem.* **1993**, *32*, 1871; (b) Huckett, S. C.; Angelici, R. J.; Ekman, M. E.; Schrader, G. L. *Catalysis* **1988**, *113*, 36; (c) Dong, L.; Duckett, S. B.; Ohman, K. F.; Jones, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 151.
66. (a) Crabtree, R. H.; Hamilton, D. H. *Adv. Organomet. Chem.* **1988**, *28*, 299; (b) Wasserman, E. P.; Morre, C. B.; Bergman, R. G. *Science* **1992**, *253*, 315; (c) Stoutland, P. O.; Bergman, R. G.; Nolan, S. P.; Hoff, C. D. *Polyhedron* **1988**, *7*, 1429; (d) McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 4246.
67. Tinesth, G. R.; Watson, P. R. *J. Am. Chem. Soc.* **1991**, *113*, 8549.
68. (a) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7492; (b) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 72.
69. Baudry, D.; Daran, J.-C.; Dromzie, Y.; Ephritekhine, M.; Felkin, H.; Jeannin, Y.; Zakrzewsaki, J. *J. Chem. Soc., Chem. Commun.* **1983**, 813.
70. Hachgenei, J. W.; Angelici, R. J. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 909.
71. Drage, J. S.; Vollhardt, P. C. *Organometallics* **1985**, *4*, 191.
72. Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.
73. Su, R.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 1, Chap. 3.
74. Fandos, R.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1991**, *10*, 1637.
75. (a) Downtown, P. A.; Sayer, B. G.; McGlinckey, M. J. *Organometallics* **1992**, *11*, 3281; (b) Andrianov, V. G.; Struchkov, Y. T. *J. Organomet. Chem.* **1977**, *18*, 251; (c) Rausch, M. D.; Kowalski, D. J.; Mintz, E. A. *J. Organomet. Chem.* **1988**, *342*, 201.
76. (a) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629; (b) Pattiasina, J. W.; Van Bohhuis, F.; Teuben, J. H. *Angew. Chem. Int. Ed. Engl.* **1987**, *99*, 342; (c) Bottomly, F.; Egharevba, G. O.; Lin, I. J. B.; White, P. S. *Organometallics* **1985**, *4*, 550.
77. (a) Weiss, F.; Hubel, W. *Chem. Ber.* **1962**, *95*, 1186; (b) Edelmann, F.; Lubke, B.; Behrens, U. *Chem. Ber.* **1982**, *115*, 1325.
78. Christofides, A.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Organomet. Chem.* **1982**, *232*, 279.
79. Werner, H.; Crisp, G. T.; Jolly, P. W.; Krause, H.-J.; Kruger, C. *Organometallics* **1983**, *2*, 1369.
80. Bakhtiar, R.; Drader, J. J.; Jacobson, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 8304.
81. Schultz, R. H.; Crellin, K. C.; Armentrout, P. B. *J. Am. Chem. Soc.* **1991**, *113*, 8590.
82. (a) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Coord. Chem. Rev.* **1975**, *21*, 219; (b) Yaneff, P. V. *Coord. Chem. Rev.* **1977**, *23*, 183; (c) Werner, H.; Leonhard, K. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 627; (d) Broadhurst, P. B.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1980**, 812.
83. (a) Loh, S. K.; Fisher, E. R.; Lian, L.; Schultz, R. H.; Armentrout, P. B. *J. Phys. Chem.* **1989**, *93*, 3157. (b) Schröder, D.; Schwarz, H. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1973 and references cited therein.