as the most abundant ion. Charge exchange reactions were used to bracket the electron affinities of these clusters, producing values which were in good agreement with photodetachment results. Collision-induced dissociation was used to investigate the fragmentation pathways. In general, the collisional activation of these cluster ions resulted in aluminum atom elimination for all clusters, except Al_7^-, Al_6^-, and Al_3^-, which fragmented primarily by electron detachment. Similar results have recently been reported for the photofragmentation of aluminum cluster negative ions.[22]

These clusters ions are quite unreactive with small molecules, such as CH_4 and N_2O. Some of these clusters will react with O_2 to generate AlO_2^- and AlO^-, along with the appropriate neutral aluminum cluster or aluminum cluster oxide. For Al_n^- where $n > 8$, the even-numbered clusters were observed to react more rapidly than the odd-numbered clusters with oxygen, yielding AlO^- and AlO_2^- as the ionic products.

We are currently studying the extension of laser ionization FTMS for the examination of other metal cluster anions. This instrumental technique, with its high resolution measurement and ion trapping capabilities, offers great promise for examining the reactivities and structures of metal cluster ions.

Acknowledgment. This research was sponsored jointly by the National Cancer Institute (Interagency Agreement No. 0485-0485-A1) and by the Office of Health and Environmental Research, U.S. Department of Energy (Contract DE-AC05-84OR21400), with Martin Marietta Energy Systems, Inc. The author thanks Michelle Buchanan, Bob Compton, and Marc Wise for helpful technical discussions.

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Heteronuclear Diatomic Transition-Metal Cluster Ions in the Gas Phase: Reactions of $ScFe^+$ with Hydrocarbons

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Received December 19, 1988

Abstract: Fourier transform mass spectrometry was used to study the chemistry of the heteronuclear diatomic metal cluster $ScFe^+$. As has been observed for a variety of other metal dimer ions involving first-row transition metals, this cluster was found to be reactive with various alkenes but unreactive with alkanes. In the reactions with alkenes, C–H bond-activation processes predominate over C–C bond activations. In a number of the observed reactions, cleavage of the cluster occurs, implying a weak Sc^+–Fe bond. Also, collision-induced dissociation was performed on a variety of $ScFe^+$–ligand species, resulting almost exclusively in cleavage of the cluster yielding neutral losses of either Fe, FeH, or FeH_2. These observations provide further support for a weak Sc^+–Fe bond relative to the corresponding Sc^+–ligand bond strengths as well as to other M^+–Fe dimer bonds.

The interest in both ionic and neutral metal clusters has increased dramatically in the past decade. The ability to generate and study clusters of varying sizes and compositions has shed new light on the physical and chemical properties of these species. Understanding the chemistry of these metal clusters is important because it can provide insights into processes occurring in a wide variety of areas such as astronomy, surface science, and catalysis.

As the subject has developed, a growing variety of techniques have become available for these studies. In some of the earlier work on neutral clusters, matrix isolation techniques have been used in conjunction with optical,[1] ESR,[2] and Mossbauer[3] spectroscopy. Knudsen cell mass spectrometry has also proven to be a useful technique for obtaining bond energies for various neutral metal dimers.[4] Smalley and co-workers have developed a supersonic expansion source with a fast-flow reaction tube and have studied hydrogen chemisorption on niobium and cobalt clusters.[5] Kaldor and co-workers have also used a fast-flow chemical reactor with photoionization/time-of-flight detection to determine ionization potentials of various transition-metal clusters.[6] More recently, Smalley and co-workers have interfaced a supersonic expansion source to a Fourier transform mass spectrometer to study ionic metal clusters,[7] while Anderson and co-workers have studied ionic metal clusters generated in a sputter source.[8] Multiphoton dissociation/ionization of metal cluster carbonyl complexes has also been used successfully for generating ionic clusters.[9]

In our laboratory, we have developed a method for synthesizing, in situ, small mixed-metal cluster ions. This method, which involves the reaction of laser-generated metal ions with volatile metal carbonyl complexes such as $Fe(CO)_5$, has been used to generate and study a variety of MFe^+ species including M = V,[10] Fe,[11] Co,[12] Cu,[13] Rh,[14] La,[15] and Nb.[16] In this paper, we extend

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Table I. Primary and Secondary Reactions of ScFe$^+$ with Linear Alkenes

linear alkene	primary product ion	neutral loss	secondary product ion	neutral loss
ethene	NR			
propene	NR			
linear butenes (1-, *cis*-, *trans*-)	$Sc(C_4H_6)^+$ (~90%)	FeH_2	$Sc(C_4H_6)_2^+$ (100%)	H_2
	$Fe(C_4H_6)^+$ (~10%)	ScH_2		
1-pentene	$ScFe(C_5H_6)^+$ (100%)	$2H_2$	$Sc(C_5H_5)_2^+$ (100%)	$FeH_2 + H_2$
1-hexene	$ScFe(C_6H_6)^+$ (100%)	$3H_2$	$ScFe(C_6H_6)_2^+$ (100%)	$3H_2$
1-heptene	$ScFe(C_7H_8)^+$ (100%)	$3H_2$	$ScFe(C_7H_8)_2^+$ (58%)	$3H_2$
			$ScFe(C_{14}H_{14})^+$ (42%)	$4H_2$

this study by examining the chemistry of ScFe$^+$. This dimer is a combination of an early transition metal and a late transition metal and has a relatively low metal–metal bond strength compared to other similar metal dimers. The main focus of this study was to compare the behavior of ScFe$^+$ to the other early–late dimers and in particular to LaFe$^+$, which also involves a group III early transition metal. In general, MFe$^+$ clusters show a preference for C–H bond activations in reactions with alkenes and are inert toward alkanes. LaFe$^+$, however, is one of the few dimers that reacts with alkanes. If the trend for increased reactivity while descending a group exists, ScFe$^+$ may not react with alkanes. But, if valence electrons play an important role in determining reactivity, ScFe$^+$ may activate alkanes and show similar chemistry to LaFe$^+$. Thus, a comparison of these two clusters is of interest.

Experimental Section

All experiments were performed on a prototype Nicolet FTMS-1000 Fourier transform mass spectrometer which has previously been described in detail[17] and is equipped with a 5.2-cm cubic trapping cell situated between the poles of a Varian 15 in. electromagnet maintained at 0.9 T. Sc$^+$ was generated by focusing a Quanta Ray Nd:YAG laser (using either the 1064-nm fundamental line or the frequency doubled 532-nm line) onto a scandium target mounted on the front plate of the ICR cell. Details of the laser ionization technique have been described elsewhere.[18]

Collision-induced dissociation (CID) experiments were performed to obtain relative bond strengths of various ligated metal cluster cations. In the CID experiment, the laboratory collision energy of the ions can be varied, typically between 0 and 100 eV. The spread in ion kinetic energies is dependent on the total average kinetic energy and is approximately 35% at 1 eV, 10% at 10 eV, and 5% at 30 eV.[19]

Chemicals were obtained commercially in high purity and used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensable gases. $Fe(CO)_5$ was introduced into the vacuum chamber via a pulsed valve as described previously.[20] The hydrocarbon reagents were kept at a static pressure of $\sim 2 \times 10^{-7}$ Torr. Argon was used as the collision gas in the CID experiments at a total pressure of $\sim 5 \times 10^{-6}$ Torr. An uncalibrated Bayard-Alpert ionization gauge was used to monitor the pressure. Absence of a reaction implies a bimolecular rate constant of $<1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

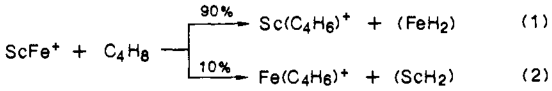
ScFe$^+$ was synthesized in the FTMS using a multistep sequence that began with laser desorption of scandium metal. The resulting Sc$^+$ species was allowed to react with $Fe(CO)_5$, producing predominantly $ScFe(CO)_3^+$. Collisional activation of this ion results in the sequential elimination of the carbonyls generating the bare cluster ScFe$^+$. After isolation of ScFe$^+$, it was trapped for 500 ms in the presence of the background argon for collisional cooling purposes. ScFe$^+$ was then reisolated and reacted with a variety of organic reagents. A small population of nonthermal ions is evident in one reaction, but it is believed that all of the major products arise from thermalized ions.

Reactions with Alkanes

ScFe$^+$ is unreactive with C_3–C_6 cyclic alkanes and C_1–C_6 acyclic alkanes. This is consistent with other first-row metal dimers such as VFe$^+$,[10] CoFe$^+$,[12] Co_2^+,[21] and CuFe$^+$.[13] In contrast to this inertness, RhFe$^+$, RhCo$^+$, and LaFe$^+$ have recently been found to react with alkanes.[14] The lack of reactivity of ScFe$^+$ also strongly contrasts the reactivity of the atomic metal ions Sc^{+22} and Fe^{+},[23] which both show abundant C–C and C–H bond activation processes toward alkanes. Interestingly, $ScFe(CO)_x^+$ (x = 1–3) were observed in preliminary experiments to undergo a few exothermic reactions with the various alkanes. This reactivity may be a result of the carbonyls polarizing the electron density around the cluster, as has been previously suggested for the enhanced reactivity of Co_2CO^+ relative to Co_2^+.[24] These reactions, however, were not pursued in this study.

Reactions with Small (C_2–C_4) Olefins

The reactions of ScFe$^+$ with linear olefins are listed in Table I. ScFe$^+$ is unreactive with ethene and propene, which is consistent with other heteronuclear diatomic cluster ions. There has been no reported observation of a cluster reacting with ethene, and only NbFe^{+16} has been observed to react with propene (by dehydrogenation). As for the atomic metal ions, Fe$^+$ is also inert toward these olefins. However, this contrasts the reactivity of Sc$^+$, which is observed to dehydrogenate both ethene and propene.[25] When ScFe$^+$ is allowed to react with the linear butenes or isobutene, unique processes reflective of the weak Sc$^+$–Fe bond are observed. In a previous study,[26] $D°(Sc^+–Fe)$ was determined to be 48 ± 5 kcal/mol, which is weak compared to, for example, $D°(V^+–Fe)$ = 75 ± 5 kcal/mol and $D°(Co^+–Fe)$ = 62 ± 5 kcal/mol. ScFe$^+$ reacts with 1-butene, *cis*-2-butene, and *trans*-2-butene by cleaving the Sc$^+$–Fe bond, generating $Sc(C_4H_6)^+$ and eliminating either FeH_2 or Fe and H_2 as neutrals, reaction 1. Loss of FeH_2 as the neutral is at least 22 kcal/mol more exothermic than loss of Fe and H_2.[27]



$$ScFe^+ + C_4H_8 \xrightarrow{90\%} Sc(C_4H_6)^+ + (FeH_2) \quad (1)$$

$$ScFe^+ + C_4H_8 \xrightarrow{10\%} Fe(C_4H_6)^+ + (ScH_2) \quad (2)$$

The uncertainty of $D°(Fe–H_2)$ prohibits obtaining any useful information on $D°(Sc^+–C_4H_6)$. In analogy to reaction 1, a small amount of $Fe(C_4H_6)^+$ is also generated, reaction 2. This reaction indicates $D°(Sc–H_2) > D°(Sc^+–Fe) + \Delta H_{rxn3} - D°(Fe^+–C_4H_6)$ = 26 ± 10 kcal/mol, by using the value

$$C_4H_8 \rightarrow C_4H_6 + H_2 \qquad \Delta H_{rxn} = 26 \text{ kcal/mol} \qquad (3)$$

$D°(Fe^+–C_4H_6)$ = 48 ± 5 kcal/mol[28] and ΔH_{rxn3} = 26 kcal/mol.[29] Interestingly, neutral ScH_2 has been observed to be a stable molecule in matrix isolation studies.[30] For $Fe(C_4H_6)^+$, any further reaction with the butenes is rarely seen and, when it is observed, it is in very low yield. $Sc(C_4H_6)^+$, on the other hand, as observed

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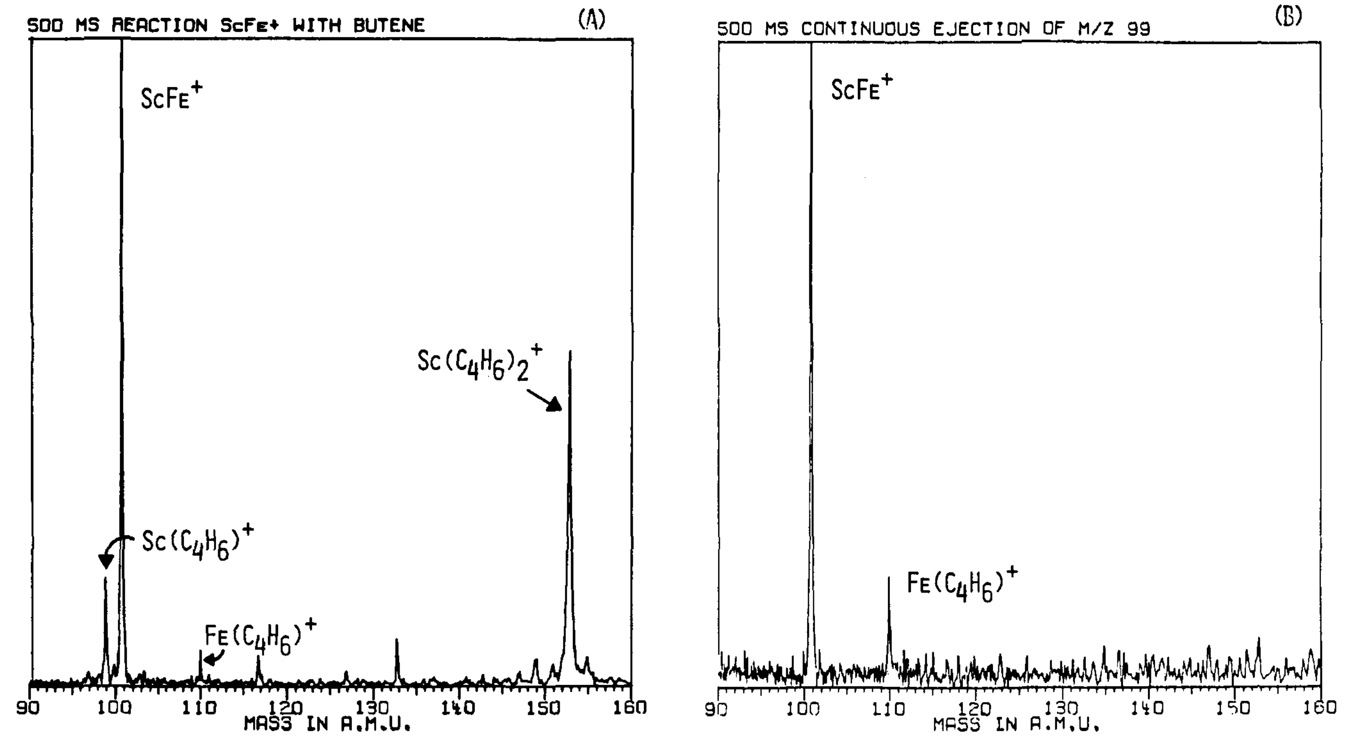


Figure 1. The 500-ms reaction of $ScFe^+$ with butene: (A) without continuous ejection of $Sc(C_4H_6)^+$ (m/z 99); (B) with continuous ejection of $Sc(C_4H_6)^+$ (m/z 99) during reaction time.

previously,[25] reacts rapidly with the butenes through a dehydrogenation process, reaction 4. The $Sc(C_4H_6)_2^+$ produced in this

$$Sc(C_4H_6)^+ + C_4H_8 \rightarrow Sc(C_4H_6)_2^+ + H_2 \qquad (4)$$

$$ScFe^+ + C_4H_8 \rightarrow ScFe(C_4H_4)^+ + 2H_2 \qquad (5)$$

reaction has the same nominal mass as a possible double dehydrogenation of the butenes by $ScFe^+$, reaction 5. Two experiments were performed that prove conclusively that the ion observed was actually $Sc(C_4H_6)_2^+$ and not $ScFe(C_4H_4)^+$. CID of the product ion showed a predominant loss of 54 amu, which must be C_4H_6, producing $Sc(C_4H_6)^+$ as the daughter ion. In a previous study,[25] collisional activation of $Sc(C_4H_6)_2^+$ generated from sequential reactions of the linear butenes with Sc^+ also yielded loss of C_4H_6 producing the $Sc(C_4H_6)^+$ daughter ion. In addition to the CID experiment, the $Sc(C_4H_6)_2^+$ ion generated in the reactions of $ScFe^+$ with the linear butenes was also confirmed by using double-resonance ejection experiments. Figure 1A shows a 500-ms reaction time for $ScFe^+$ with 1-butene. $Sc(C_4H_6)^+$ is clearly being generated and is reacting further to form $Sc(C_4H_6)_2^+$. When $Sc(C_4H_6)^+$ is continuously ejected, Figure 1B, the peak corresponding to $Sc(C_4H_6)_2^+$ is absent. Thus, these two experiments conclusively show that the linear butenes cleave the Sc^+–Fe bond and eventually generate $Sc(C_4H_6)_2^+$.

The reactivity of $ScFe^+$ with isobutene is very similar but not identical to that with the linear butenes. Cleavage of the cluster and generation of $Sc(C_4H_6)^+$ occur as they did for the linear butenes. However, for isobutene, $Sc(C_4H_6)^+$ does not go on to dehydrogenate a second isobutene but instead condenses, forming $Sc(C_4H_6)(C_4H_8)^+$. This peak has the same nominal mass as a single dehydrogenation of isobutene by $ScFe^+$, reaction 6. CID

$$ScFe^+ + iso\text{-}C_4H_8 \rightarrow ScFe(C_4H_6)^+ + H_2 \qquad (6)$$

of the product ion shows loss of 56 amu, which can either be Fe or C_4H_8. Conclusive evidence for the $Sc(C_4H_6)(C_4H_8)^+$ structure is obtained, however, by double resonance which shows no product ion when $Sc(C_4H_6)^+$ is continuously ejected during the reaction time. High-resolution measurements would also provide a method of discriminating between isobars. However, due to the multistep sequence needed to generate the product ions, as well as the high background pressure of argon for CID, high-resolution studies were not successfully accomplished.

Linear Olefins

As the size of the alkene increases to five carbons or greater, the cluster cleavage process is no longer observed in the primary reactions. However, cluster cleavage still predominates in the CID of all of the major product ions generated in the reactions with the linear alkenes and is also observed in some of the secondary reactions with these alkenes. $ScFe^+$ doubly dehydrogenates 1-pentene to generate $ScFeC_5H_6^+$, exclusively. The second dehydrogenation is probably a dehydrocyclization process that generates $ScFe^+$–cyclopentadiene and implies $D°(ScFe^+\text{–cyclopentadiene}) > 37$ kcal/mol.[29] CID of this ion yields a neutral loss of Fe over the energy range studied with a loss of FeH at higher energies which, as discussed below, supports a cyclic structure for the C_5H_6 ligand. Interaction of $ScFeC_5H_6^+$ with a second pentene results in the cleavage of the cluster, reaction 7, generating presumably

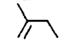
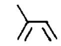
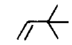
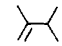
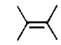
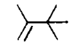
$$ScFeC_5H_6^+ + 1\text{-pentene} \rightarrow Sc(C_5H_5)_2^+ + FeH_2 + 2H_2 \qquad (7)$$

a Sc^+–bis(cyclopentadienyl) ion or scandocenium. Loss of C_5H_5 is observed in the CID of this ion, just as it is in the CID of $Sc(C_5H_5)_2^+$ generated from cyclopentene, supporting the bis(cyclopentadienyl) structure.

The only product observed in the reaction of $ScFe^+$ with 1-hexene is $ScFeC_6H_6^+$. CID of this ion results in loss of either Fe or C_6H_6 in about a 2:1 ratio at low collision energy and a 1:1 ratio at higher energies. This result is identical within experimental error with the CID of $ScFeC_6H_6^+$ generated from cyclohexene, which suggests a dehydrocyclization of hexene to benzene and implies $D°(ScFe^+\text{–benzene}) > 30$ kcal/mol.[29] The relative peak intensities from the CID experiment indicate that $D°(Sc^+\text{–}C_6H_6) > D°(Sc^+\text{–Fe})$, which is in accord with the previously reported bond strengths of $D°(Sc^+\text{–benzene}) = 53 \pm 5$ kcal/mol[25] and $D°(Sc^+\text{–Fe}) = 48 \pm 5$ kcal/mol.[26] The $ScFe(C_6H_6)^+$ produced from 1-hexene reacts slowly with a second hexene, producing $ScFe(C_{12}H_{12})^+$, which is probably $ScFe^+$–bis(benzene). CID on this ion yields a neutral loss of Fe, generating $ScC_{12}H_{12}^+$ at low CID energy, and shows small amounts of $ScC_6H_6^+$ appearing at higher CID energies. This is identical with the CID of $ScFe(C_{12}H_{12})^+$ generated from cyclohexene and, thus, is good evidence for the $ScFe^+$–bis(benzene) structure.

Triple dehydrogenation is the only process observed in the reaction of $ScFe^+$ with 1-heptene. CID of the $ScFeC_7H_8^+$ product

Table II. Primary Reactions of $ScFe^+$ with Branched Alkenes (C_5–C_7) and CID of the Resulting Product Ions

branched alkene	product ion	neutral loss	CID results of product ion
	$ScFeC_5H_6^+$	$2H_2$	$ScC_5H_6^+ + Fe$
	$ScFeC_5H_6^+$	H_2	$ScC_5H_6^+ + Fe$
	$ScFeC_5H_6^+$	$H_2 + CH_4$	$ScC_5H_6^+ + Fe$
	$ScFeC_6H_8^+$	$2H_2$	$ScC_6H_6^+ + (FeH_2)$
	$ScFeC_6H_8^+$	$2H_2$	$ScC_6H_6^+ + (FeH_2)$
	$ScFeC_6H_8^+$	$H_2 + CH_4$	$ScC_6H_6^+ + (FeH_2)$

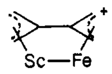
ion results in cleavage of the cluster as expected. At low energy, Fe is the only neutral loss observed, while at higher CID energies, FeH_2 is eliminated. This result is similar to the CID results of $ScFeC_7H_8^+$ generated from 1-methyl-1-cyclohexene, which may indicate that a $ScFe^+$–toluene structure is generated in the reactions with 1-heptene. A suitable $ScFe^+$–cycloheptatriene ion could not be generated for further comparison. Thus, this likely candidate cannot be ruled out.

Reactions with Branched Olefins

The primary reactions of $ScFe^+$ with a variety of branched olefins involve either single or double dehydrogenations or single dehydrogenation in conjunction with loss of methane. There is no evidence for cluster cleavage in these reactions with the exception of isobutene, which was discussed earlier. The reactions with the branched olefins studied typically give rise to one of two stable products, $ScFeC_5H_6^+$ or $ScFeC_6H_8^+$. It is the CID of these product ions that once again reveals a relatively weak cluster bond. The primary reaction products and CID results for the reaction of $ScFe^+$ with branched alkenes (C_5–C_7) are given in Table II.

$ScFe^+$ doubly dehydrogenates 2-methyl-1-butene, generating the stable $ScFeC_5H_6^+$. CID of this ion breaks apart the cluster, producing $ScC_5H_6^+$ with a neutral loss of Fe, implying $D°(Sc^+–C_5H_6) > D°(Sc^+–Fe)$. Similarly, $ScFe^+$ only singly dehydrogenates 2-methyl-1,3-butadiene to generate $ScFeC_5H_6^+$. CID of this $ScFeC_5H_6^+$ also produces $ScC_5H_6^+$ by a neutral loss of Fe. When the β-hydrogen is absent, as in the case of 3,3-dimethyl-1-butene, double dehydrogenation is not observed. Instead, $ScFeC_5H_6^+$ is formed through loss of H_2 and CH_4. CID of $ScFeC_5H_6^+$ generated from 3,3-dimethyl-1-butene again results in cleavage of the cluster generating $ScC_5H_6^+$. The absence of a neutral loss of FeH to generate $ScC_5H_5^+$ in the CID of the three $ScFeC_5H_6^+$ species is support for an acyclic ligand on the cluster.

$ScFeC_6H_8^+$ product ions are observed for branched butenes that are substituted on both the second and third carbons. This is exemplified by 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene, which both undergo a double dehydrogenation process generating $ScFeC_6H_8^+$. The first dehydrogenation step probably occurs by an initial coordination of the metal cluster to the double bond of the alkene. This can be followed by an insertion into an allylic C–H bond, which is on carbon 3 for 2,3-dimethyl-1-butene and carbon 1 or 4 in 2,3-dimethyl-2-butene. Next, a β-hydrogen shift followed by reductive elimination of H_2 results in the formation of 2,3-dimethyl-1,3-butadiene. The second dehydrogenation process can occur by hydrogen abstraction from each of the two methyl groups which results in the formation of a tetramethyleneethane-bridged species,[12] structure I. This is also the probable structure in the case of 2,3,3-trimethyl-1-butene, which generates $ScFeC_6H_8^+$ through single dehydrogenation and loss of methane. In this particular case, a β-methyl shift can be followed by a hydrogen abstraction resulting in a reductive elimination of methane, once again generating the 2,3-dimethyl-1,3-butadiene intermediate, which can then eliminate H_2 producing the tetramethyleneethane-bridged structure. Although an initial β-hydrogen shift is possible with 2,3,3-trimethyl-1-butene, this would result in a species with no energetically favorable pathways leading to the tetramethyleneethane structure. Surprisingly, CID of $ScFeC_6H_8^+$ generated in all three cases results in a loss of FeH_2 leaving $ScC_6H_6^+$.



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Reactions with Cyclic Olefins

The reactions of $ScFe^+$ with cyclic olefins are listed in Table III. In the reactions of $ScFe^+$ with cyclic olefins containing one degree of unsaturation, double dehydrogenations are the predominant processes observed. This is seen, surprisingly, in the reaction with cyclopentene producing $ScFeC_5H_4^+$. CID of this ion yields $ScC_5H_4^+$ by eliminating neutral Fe. $ScFeC_5H_4^+$ reacts with a second cyclopentene, this time by cleaving the cluster and eliminating neutral FeH_2. The $ScC_{10}H_{10}^+$ product is Sc^+–bis(cyclopentadienyl), or scandocenium, as implied by CID, which shows loss of 65 amu (C_5H_5) producing $ScC_5H_5^+$.

Two products are observed in the reactions of $ScFe^+$ with cyclohexene. The major reaction corresponds to formation of the cluster benzene, reaction 8, while the other process cleaves the

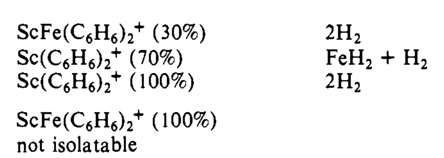

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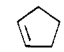
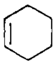
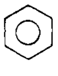
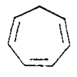
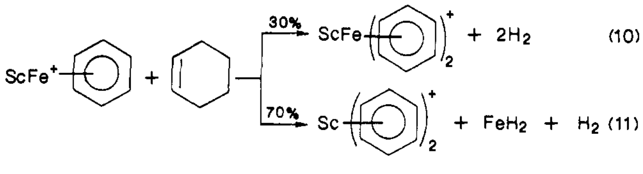
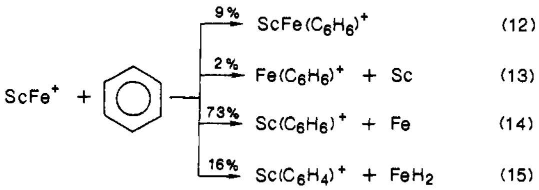
Table III. Primary and Secondary Reactions of $ScFe^+$ with Cyclic Alkenes

cyclic alkene	primary product ion	neutral loss	secondary product ion	neutral loss
	$ScFeC_5H_4^+$ (100%)	$2H_2$	$Sc(C_5H_5)_2^+$ (100%)	FeH_2
	$ScFe(C_6H_6)^+$ (84%)	$2H_2$	$ScFe(C_6H_6)_2^+$ (30%)	$2H_2$
			$Sc(C_6H_6)_2^+$ (70%)	$FeH_2 + H_2$
	$Sc(C_6H_6)^+$ (16%)	$FeH_2 + H_2$	$Sc(C_6H_6)_2^+$ (100%)	$2H_2$
	$ScFe(C_6H_6)^+$ (9%)		$ScFe(C_6H_6)_2^+$ (100%)	
	$Fe(C_6H_6)^+$ (2%)	Sc	not isolatable	
	$Sc(C_6H_6)^+$ (73%)	Fe	$Sc(C_6H_6)_2^+$ (100%)	
	$Sc(C_6H_4)^+$ (16%)	FeH_2	$Sc(C_{12}H_{10})^+$ (100%)	
	$ScC_7H_8^+$ (67%)	Fe	$Sc(C_7H_8)_2^+$ (21%)	
			$Sc(C_{14}H_{12})^+$ (29%)	$2H_2$
			$Sc(C_{13}H_{14})^+$ (17%)	CH_2
			$Sc(C_{12}H_{12})^+$ (33%)	C_2H_4
	$ScC_7H_6^+$ (22%)	FeH_2	$Sc(C_7H_6)_2^+$ (64%)	H_2
			$Sc(C_{12}H_{12})^+$ (17%)	C_2H_2
			$Sc(C_{12}H_{10})^+$ (19%)	C_2H_4
	$ScC_6H_6^+$ (11%)	$FeCH_2$	$Sc(C_7H_8)^+$ (100%)	C_6H_6

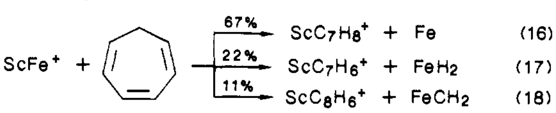
cluster, generating Sc^+–benzene, reaction 9. Generation of Sc^+–benzene is ~30 kcal/mol more exothermic than generation of Fe^+–benzene, which explains the absence of Fe^+–benzene.[31] Also, for reaction 9 to be exothermic, the neutrals lost must be FeH_2 and H_2. CID of $ScFe^+$–benzene yields approximately equal amounts of $ScFe^+$ and Sc^+–benzene, with Sc^+–benzene being slightly favored at low CID energy. In addition, no production of Fe^+–benzene was observed. The secondary reactions of $ScFe^+$–benzene with cyclohexene are similar to the primary reactions of $ScFe^+$ as can be seen in reactions 10 and 11. However, there is a greater occurrence of cleavage of the cluster, which indicates that the benzene ligand on the cluster weakens the metal–metal bond. Assuming that the neutrals lost in reaction 11 are, once again, FeH_2 and H_2, for this process to be exothermic, $D°(ScFe^+–benzene)$ must be ≤51 kcal/mol, which agrees with the preliminary photodissociation results of $D°(ScFe^+–benzene) = 47 \pm 4$ kcal/mol.[32] CID of $ScFe(benzene)_2^+$ shows exclusive loss of Fe neutral generating $Sc(benzene)_2^+$, which is the identical process found in the CID of $VFe(benzene)_2^+$. In general, the preference for elimination of neutral Fe in the CID of $MFe(benzene)_2^+$ increases as M becomes an early transition metal, which may imply a strong interaction between the empty d orbitals of the early transition metal and the π electrons of the benzene rings. The reactions of $ScFe^+$ with benzene are listed in eq 12–15.





Reaction 14 is in accord with $D°(Sc^+–Fe) = 48 \pm 5$ kcal/mol $< D°(Sc^+–C_6H_6) = 53 \pm 5$ kcal/mol.[25] Since $D°(Fe^+–Sc) = 79 \pm 5$ kcal/mol[26] and $D°(Fe^+–C_6H_6) = 55 \pm 5$ kcal/mol,[28] the observation of reaction 13 suggests the presence of a small population of "hot" $ScFe^+$. Observation of reaction 15 together with $D°(Sc^+–Fe) = 48 \pm 5$ kcal/mol[26] and a recently determined value of $D°(Sc^+–C_6H_4) = 85 \pm 5$ kcal/mol[34] suggest a limit of $D°(Fe–H_2) > 43 \pm 10$ kcal/mol which can be compared to the earlier limit of 22 kcal/mol.[27]

The reactions of $ScFe^+$ with cycloheptatriene show exclusive cluster cleavage processes, reactions 16–18. Losses of neutral Fe and FeH_2 have been common observations in this study. However, the loss of neutral $FeCH_2$ in reaction 18 is unique and implies $D°(Fe–CH_2) > 65 \pm 10$ kcal/mol, which compares favorably to $D°(Fe–CH_2) = 87 \pm 7$ kcal/mol determined recently.[35] The absence of any $ScFeC_7H_8^+$ prevented the earlier comparison discussed above with $ScFe^+$–toluene.



Conclusions

This study has characterized the gas-phase chemistry of $ScFe^+$, which is influenced in part by the relatively weak Sc^+–Fe bond. In some of the reactions of $ScFe^+$ (i.e., with the butenes, cyclopentene, cyclohexene, and benzene), the cluster is cleaved due to a stronger Sc^+–ligand versus Sc^+–Fe bond. Also, CID of a variety of $ScFe^+$–ligand species always results in cleavage of the cluster, yielding neutral losses of Fe, FeH, or FeH_2. This is a further consequence of the weak cluster bond. Corresponding thermochemical information has been determined from these results.

When compared to the reactivity of the atomic metal ions Sc^+ and Fe^+, the cluster appears to behave more like the early transition metal, Sc^+. Dehydrogenations account for almost all of the processes observed in the reactions of $ScFe^+$ with the alkenes studied. Dehydrogenations are also the predominant processes in the reactions of Sc^+ with alkenes, whereas Fe^+ shows a chemistry also rich in C–C bond activation.[36] However, this behavior may not be dictated by the presence of an early transition metal in a dimer, because the preference for C–H bond activation over C–C bond activation has been observed for the other dimers studied in our laboratory. Overall, the reactivities of Sc^+ and Fe^+ are far greater than that of the $ScFe^+$ cluster.

From the results of previous studies of various metal dimers, certain similarities and differences can be pointed out. In general, the clusters show a significantly decreased reactivity compared with the corresponding atomic metal ions, and the reactivity that is observed for reactions of these clusters with alkenes is almost exclusively dehydrogenations. This is also true for $ScFe^+$. The main difference between $ScFe^+$ and $CoFe^+$, a late-transition-metal dimer, for example, is that $ScFe^+$ typically undergoes multiple dehydrogenations while $CoFe^+$ typically undergoes single dehydrogenations with only isolated cases of multiple dehydrogenations observed. $NbFe^+$ has also been observed to yield slightly more multiple dehydrogenations than $CoFe^+$ but still not as many as $ScFe^+$. Additionally, $ScFe^+$ has a greater tendency of eliminating Fe in ion–molecule reactions. In accordance with this, while CID of various MFe^+–ligand species tend to yield the bare cluster, CID of $ScFe^+$–ligand species cleaves the cluster. This, once again, is reflective of the weak $ScFe^+$ bond relative to the other dimers.

A final point of interest is to compare the reactivity of dimers containing group III metals, i.e., $ScFe^+$, YFe^+, and $LaFe^+$. In preliminary studies conducted in our laboratory, YFe^+ has been observed to undergo numerous multiple dehydrogenation processes with alkenes similar to those studied in this work. All in all, the chemistries of $ScFe^+$ and YFe^+ seem to be similar to each other but significantly different from that of $LaFe^+$, which is one of the three dimers observed to activate alkanes.

Acknowledgment is made to the Division of Chemical Sciences in the Office of Basic Energy Sciences in the United States Department of Energy (DE-FG02-87ER13766) for supporting this research and to the National Science Foundation (CHE-8612234) for continued support of the FTMS. J.R.G. gratefully acknowledges the National Science Foundation for fellowship support.

Registry No. $ScFe^+$, 107474-37-3; Sc, 7440-20-2; $Fe(CO)_5$, 13463-40-6; ethene, 74-85-1; propene, 115-07-1; 1-butene, 106-98-9; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; 1-pentene, 109-67-1; 1-hexene, 592-41-6; 1-heptene, 592-76-7; 2-methyl-1-butene, 563-46-2; 2-methyl-1,3-butadiene, 78-79-5; 3,3-dimethyl-1-butene, 558-37-2; 2,3-dimethyl-1-butene, 563-78-0; 2,3-dimethyl-2-butene, 563-79-1; 2,3,3-trimethyl-1-butene, 594-56-9; cyclopentene, 142-29-0; cyclohexene, 110-83-8; benzene, 71-43-2; cycloheptatriene, 544-25-2.

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(31) Using $D°(Fe^+–benzene) = 55 \pm 5$ kcal/mol from ref 28, $D°(Sc^+–benzene) = 53 \pm 5$ kcal/mol from ref 25, and other heats of formation from ref 29.

(32) Lech, L. M.; Freiser, B. S., unpublished results.

(33) Using $\Delta H_f(C_6H_4) = 420 \pm 20$ kJ/mol (100.4 ± 4.8 kcal/mol) from Moini, M.; Leroi, G. E. *J. Phys. Chem.* **1986**, *90*, 4002 and values from ref 29.

(34) Huang, Y.; Sun, D.; Freiser, B. S., *J. Am. Chem. Soc.*, submitted.

(35) Jacobson, D. B.; Gord, J. R.; Freiser, B. S. *Organometallics*, in press.

(36) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7484.