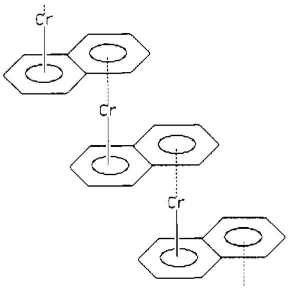
naphthalene)chromium when this compound is dissolved in ND_3 (3.42 ppm) as opposed to 6.96 ppm when dissolved in C_6D_6. Earlier we attributed this large upfield shift to anisotropy caused by the naphthalene moieties of bis(η^6-naphthalene)chromium being constrained to the eclipsed configuration; it is therefore reasonable to speculate that poly[(μ-η^6,η^6-naphthalene)chromium] exists in the eclipsed topology (III) while dissolved in ND_3. The argument gains strength from the recognition that the metal sites in the poly[(μ-η^6,η^6-naphthalene)chromium] structure are electron-deficient from the point of view of formal electron count. This electronic arrangement would encourage the coordination of solvent ammonia molecules to the metal sites; the eclipsed configuration (III) provides for easier access to the metal sites by solvent ammonia molecules than does the staggered configuration (VII).



VII

It is well-known that bis(η^6-naphthalene)chromium exists as the eclipsed configuration in the crystalline solid.[7] Poly[(μ-η^6,η^6-naphthalene)chromium is not soluble in C_6D_6, while freely rotating bis(η^6-naphthalene)chromium is; eclipsed bis(η^6-naphthalene)chromium exists in ND_3 as it does in the crystalline state. Thus, it is reasonable to speculate that poly[(μ-η^6,η^6-naphthalene)chromium] is eclipsed in the solid state; however, only an X-ray crystal structure will elucidate this point. It appears that the solubility of poly[(μ-η^6,η^6-naphthalene)chromium] in liquid ammonia resides in the ability of the basic solvent to stabilize the eclipsed configuration.

Acknowledgment. We thank Mr. Z. Sui, Dr. H. Stefink, and Mr. J. Wallin for their technical assistance and especially Dr. B. Shoulders for helpful discussions. We are grateful for generous support of the Texas Advanced Technology Research Program and the Robert A. Welch Foundation.

Reactions of Sc$^+$ with Alkenes in the Gas Phase

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Fourier transform mass spectrometry (FTMS) was used to study the exothermic reactions of laser desorbed Sc$^+$ with various linear, branched, and cyclic olefins. Single and double dehydrogenations were observed to be the predominant processes in marked contrast to Fe$^+$ and Co$^+$ which yield predominantly C–C bond cleavage products. Structures of some of the commonly occurring product ions were probed by collision-induced dissociation and ion–molecule reactions, including H/D exchange. Evidence is presented for two stable isomers of $ScC_4H_6^+$, $ScC_4H_4^+$, and $ScC_5H_6^+$. A modification to the experimental pulse sequence was implemented which made possible the formation and isolation of various endothermic reaction products. In particular Sc$^+$–H was generated by an endothermic reaction of Sc$^+$ with ethane and was used to bracket the Sc$^+$–benzene bond strength at $D°(Sc^+\text{–benzene}) = 53 \pm 5$ kcal/mol.

Introduction

Over the past several years, the study of transition-metal ions in the gas phase has become the focus of a great deal of attention. These studies provide fundamental information on the kinetics, mechanisms and thermochemistry of these chemically important species in the absence of complicating effects due to solvent or ligand interferences. In addition, studies of the transition-metal ions are also important because of the promise these ions hold as selective chemical ionization reagents for mass spectral analysis.[1]

Most of the work to date has centered on the first-row groups 8–10 metals Fe$^+$, Co$^+$, and Ni$^+$. The reactions of these metals with alkanes, alkenes, and other organic compounds have been studied by a number of laboratories.[2] Studies involving the early first-row transition-metal ions, however, are fewer in number. A variety of V$^+$–ligand bond strengths have been reported,[3] in addition to studies of the reactions of this first-row group 5 metal ion with various alkanes.[4] Allison and Ridge have studied the reactions of olefins with Ti$^+$,[5] and Tolbert and Beauchamp have studied both alkane activation by Ti$^+$ [4b] and the reactions of saturated hydrocarbons with Sc$^+$.[6] In these cases some interesting differences in reactivity, as com-

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[4] (a) Jackson, T. C.; Carlin, T. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 1120. (b) Tolbert, M. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 7509.

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pared to the groups 8–10 transition metals, were reported.

In this paper we expand the previous study of Sc^+ with the saturated hydrocarbons by monitoring the reactions of Sc^+ with various linear, branched, and cyclic olefins. Comparisons are made between the reactions of Sc^+ with the olefins versus the saturated hydrocarbons as well as with the analogous reactions of the first-row groups 8–10 transition metals. A brief comparison is also made to the reactions of Ti^+ with olefins. Structural information on some of the predominant and recurring product ions was obtained through a combination of collision-induced dissociation (CID) experiments and specific ion–molecule reactions including deuterium exchange.[7]

Experimental Section

All experiments were performed on a prototype Nicolet FTMS-1000 mass spectrometer which has been previously described in detail[8] and is equipped with a 5.2-cm cubic trapping cell situated between the poles of a Varian 15-in. electromagnet maintained at 0.85 T. Mounted on the front transmitter plate are a variety of metal targets. Several of these consist of metal rods with a 1-mm diameter hole drilled through them lengthwise and countersunk to form a bevelled edge. These tunnel targets vary in length from 2 to 6 mm (the Sc target used in this work was 4 mm) with an outer diameter of approximately 4 mm. Sc^+ was generated by focussing a Quanta Ray Nd:YAG laser (frequency doubled to 532 nm) onto the bevelled edge of the scandium tunnel target. The diameter of the laser beam was approximately 0.3 mm, and the power density was estimated to be about 10^8 W cm^{-2}. The laser pulse generates a plume consisting mainly of positively charged metal ions, electrons, and neutrals. A fraction of the metal ions produced enter the cell. Positively biased trapping plates annihilate any negatively charged species and trap the positively charged metal ions. Neutral atoms immediately condense on the cell walls and, therefore, do not participate in the experiment. Since the plume is generated outside of the cell, the frequency in which the cell has to be removed for cleaning is greatly reduced. Tantalum, which is a common impurity in Sc samples, was not found to be an interference in this study.[9]

The product ion distributions are reproducible to within ±10% absolute. Product distributions from secondary reactions were determined by using swept double resonance ejection techniques to isolate the ions of interest.[10] These ions were then allowed to react and the products subsequently detected.

In the CID experiment, the collision energy of the ions can be varied, typically between 0 and 100 eV, from which plots of CID product ion intensities vs collision energy (i.e. CID breakdown curves) can be made. 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.[11] CID can yield unambiguous structural assignments for simple metal ion complexes.[12] Since the ions are formed via different reaction paths, they initially should have different internal energies as well as possibly different structures. Two ions of the same structure, but having different internal energies should be evident as having qualitatively similar CID breakdown curves, only shifted in kinetic energy. For complexes containing ligands possessing five or more carbon atoms, however, facile rearrangement of these complexes may yield CID spectra that are not very diagnostic. Therefore, while CID spectra of the major ions were obtained, many of the structures are necessarily assigned as "reasonable" as opposed to proven. The methodology and interpretation of the CID experiment is described elsewhere.[8,12,13] Photodissociation experiments[14] were performed, when possible, to give added support for the results obtained by the other methods used.

In the studies reported here, typically the laser-generated metal ions were trapped in the presence of a static pressure of the alkene of interest. After a predetermined reaction time, the product ions were detected. Since it is possible to generate ions with excess electronic or kinetic energy,[15] two variations of the experiment were used to minimize any excess energy of the metal ions and to ensure that only exothermic processes were observed.[16] One variation involved admitting a relatively high-pressure argon pulse immediately after laser generation of Sc^+. This pulse has a peak pressure of $\sim 10^{-5}$ Torr at 150 ms, and a total pump out time of 400 ms during which time collisional damping of Sc^+ occurs. After this cooling step, Sc^+ was isolated and allowed to react with the alkene of interest which was present at a static background pressure of $\sim 2 \times 10^{-7}$ Torr. In the second variation argon was kept at a static background pressure of about 2×10^{-7} Torr throughout the entire experiment. After formation, Sc^+ was trapped in the presence of the argon for 250 ms. Following this period, the alkene being studied was pulsed into the cell and allowed to react with the Sc^+. These variations provided approximately 10–80 collisions of Sc^+ with argon which should be sufficient to have an effect on the observed chemistry, if a large population of nonthermal ions were present. The results obtained by using these two sets of conditions, however, were the same within experimental error. In addition, no noticeable differences in product distributions were observed in the absence of these collisional cooling procedures, indicating that the majority of the Sc^+ ions monitored were generated with little or no excess energy. These results, however, are not totally conclusive proof that no excited ions are present.

Deuterium exchange was performed by adding the deuteriating agent (either C_2D_4 or C_3D_6) at pressures of $(1–9) \times 10^{-6}$ Torr. The lowest pressure of deuteriating agent possible was used in order to suppress any secondary reactions with the deuterated compound which would complicate the interpretation. Pulsed-valve introduction of the alkene eliminated any complications due to the secondary reaction of the hydrocarbon itself. Pulsed-valve addition of reagent gases as applied to FTMS has been described in detail elsewhere.[17]

Chemicals were obtained commercially in high purity and used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensable gases. C_2D_4 (>99 atom % D), C_3D_6 (>98 atom % D), and 2-(methyl-d_3)propene-*3,3,3*-d_3 (>98 atom % D) were obtained from MSD isotopes, Merck Chemical Division. CD_3CN (99.7 atom % D) was obtained from Stohler/KOR Stable Isotopes. Hydrogen cyanide was generated by mixing KCN and H_2SO_4 under vacuum and collecting the evolved gas. Sample pressures were monitored with a Bayard-Alpert ionization gauge, and argon was used as a collision gas.

Results and Discussion

Reactions with Linear Alkenes. Table I lists the reactions of Sc^+, Fe^+, and Co^+ with 11 linear alkenes. Sc^+ is observed to react with every compound used in this study in contrast to Fe^+ and Co^+. Dehydrogenation is the only reaction observed for Sc^+ with ethene (reaction 1),

$$Sc^+ + C_2H_4 \rightarrow ScC_2H_2^+ + H_2 \qquad (1)$$

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[8] Cody, R. B.; Burnier, R. C.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 96.

[9] The scandium sample supplied by Alfa was previously found to contain about 5% tantalum by weight (Galbraith Laboratories, Inc., Knoxville, TN).

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Table I. Neutral Products Lost in the Primary Reactions of Sc^+, Fe^+, and Co^+ with Linear Alkenes

		neutral fragments lost, in %												
alkene	M^+	H_2	$2H_2$	$3H_2$	CH_4	CH_4,H_2	$CH_4,2H_2$	C_2H_4	(C_2H_6)	$(C_2H_6)H_2$	C_3H_6	(C_3H_8)	C_4H_8	(C_4H_{10})
ethene	Sc	100												
	Fe[a]		no reaction											
	Co[b]		no reaction											
propene	Sc	100												
	Fe[a]		no reaction											
	Co[b]		no reaction											
linear butenes	Sc	93	7											
(1, *cis*, *trans*)	Fe[a]	100												
	Co[b]	97						3						
1-pentene	Sc	7	53		9			3	28					
	Fe[a]	13			19			49			19			
	Co[b]	11			13			58			18			
trans-2-pentene	Sc	7	69		8				16					
	Fe[a]	19			29			30			22			
	Co[b]	28			33			29			10			
1-hexene	Sc	3	34	16		23			17			7		
	Fe[a]	10			6			14	16		42		12	
	Co[b]	5						16			69		10	
trans-2-hexene	Sc	3	43	10		25			13			6		
	Fe[a]	10			9			25	22		13	5	12	4
	Co[c]	6			4			34	41		6		9	
trans-3-hexene	Sc	3	41	14		33			4			5		
	Fe[a]	12	4		14			24	18		10	4	9	5
	Co[c]	4			8			33	31		10		14	
1-heptene	Sc	2	7	3	1	4	8		35	6		32		
	Fe[c]	19									34	19	28	
	Co[c]	21									19	37	23	

[a] See ref 21. [b] See ref 20. [c] Hettich, R. L.; Freiser, B. S., unpublished results. The parentheses indicate empirical formula only, e.g. C_3H_8 could be H_2, C_3H_6.

implying $D°(Sc^+–C_2H_2) > 41.7$ kcal/mol.[18] Exclusive loss of HD from CH_2CD_2 is observed in accordance with Armentrout and coworkers.[19] indicating a 1,2-dehydrogenation to form a Sc^+–acetylene complex. CID of $ScC_2H_2^+$ yields only loss of the entire ligand providing supporting evidence for the acetylene structure. $ScC_2H_2^+$, produced in reaction 1, also reacts with ethene by dehydrogenation producing what would be expected to be the Sc^+–bis(ethyne) species $Sc(C_2H_2)_2^+$. This, however, may not be the isomer formed. CID of this ion yields three products (reactions 2–4). Reaction 2, which predominates at low kinetic energies, may involve some type of coupling of the two acetylene ligands on the metal center, while reaction 4 predominates at higher kinetic energies. In order to determine which hydrogens are lost in reaction 2, a mixed-ligand species was generated by first reacting Sc^+ with C_2D_4 and then allowing the resulting $ScC_2D_2^+$ to react with C_2H_4, thus producing $Sc(C_4H_2D_2)^+$. During this reaction neither $Sc(C_2HD)^+$ nor $Sc(C_2H_2)^+$ was observed, which has mechanistic implications as discussed below. For reaction 2, HD loss was predominant (>80%), while approximately equal amounts of D_2 and H_2 loss were observed. Also, monitoring the loss of acetylene (reaction 3) revealed three peaks corresponding to losses of C_2D_2, C_2HD, and C_2H_2, indicating that some scrambling occurs. Unfortunately, these products were too low in intensity to derive meaningful isotopic distributions. A comparison of results obtained for several isomeric $ScC_4H_4^+$ ions will be discussed in greater depth below.

$$ScC_4H_4^+ \xrightarrow{CID} \begin{cases} ScC_4H_2^+ + H_2 & (2) \\ ScC_2H_2^+ + C_2H_2 & (3) \\ Sc^+ + C_4H_4 & (4) \end{cases}$$

Dehydrogenation was also the only reaction observed for Sc^+ with propene (reaction 5), implying $D°(Sc^+–allene) > 41.0$ kcal/mol.[18] CID on $Sc^+–C_3H_4$, generated in reaction

$$Sc^+ + C_3H_6 \rightarrow ScC_3H_4^+ + H_2 \qquad (5)$$

5, yields predominantly loss of H_2 at low energies and loss of C_3H_4 at high energies. Deuterium exchange using C_3D_6 on $Sc^+–C_3H_4$ yields 4 rapid H/D exchanges indicating an allene structure as opposed to a propyne structure.

The secondary reaction of $ScC_3H_4^+$ with propene is more complex than that observed for the ethene case. $ScC_3H_4^+$ not only singly and doubly dehydrogenates propene, but losses of CH_4 and C_2H_4 are also observed (reactions 6–9). The product ions in reactions 7–9 are commonly observed in this study, and their structures are discussed in a later section.

$$ScC_3H_4^+ + C_3H_6 \rightarrow \begin{cases} \xrightarrow{27\%} ScC_6H_8^+ + H_2 & (6) \\ \xrightarrow{29\%} ScC_6H_6^+ + 2H_2 & (7) \\ \xrightarrow{23\%} ScC_5H_6^+ + CH_4 & (8) \\ \xrightarrow{21\%} ScC_4H_6^+ + C_2H_4 & (9) \end{cases}$$

In the reactions of Sc^+ with the linear butenes, the predominant reaction is dehydrogenation resulting in the formation of $ScC_4H_6^+$ (reaction 10), implying $D°(Sc^+–butadiene) \geq 29.0$ kcal/mol.[18] Double dehydrogenation to

$$Sc^+ + C_4H_8 \rightarrow \begin{cases} \xrightarrow{93\%} ScC_4H_6^+ + H_2 & (10) \\ \xrightarrow{7\%} ScC_4H_4^+ + 2H_2 & (11) \end{cases}$$

form $ScC_4H_4^+$ (reaction 11) is also observed as a minor product. For Fe^+ and Ti^+, single dehydrogenation is the only reaction observed. In the case of Co^+, along with single dehydrogenation, there is also a small amount of C–C bond cleavage. CID of the $ScC_4H_6^+$ ion from reaction 10 shows predominant loss of the entire ligand over the

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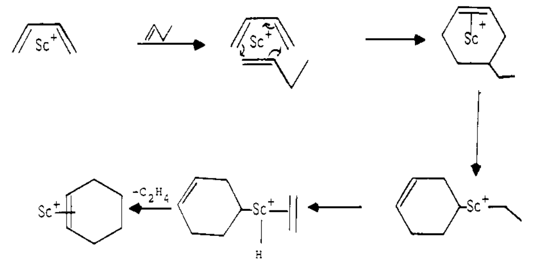
(18) Calculated by using values in: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, Suppl. 1.

(19) Sunderlin, L.; Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.* **1987**, *109*, 78.

Scheme I



energy range studied (0–100 eV), with losses of C_2H_4 and H_2 also observed (reactions 12–14). The proposed

$$ScC_4H_6^+ \xrightarrow[44\ eV]{CID\quad 69\%} Sc^+ + C_4H_6 \qquad (12)$$

$$\xrightarrow{15\%} ScC_2H_2^+ + C_2H_4 \qquad (13)$$

$$\xrightarrow{16\%} ScC_4H_4^+ + H_2 \qquad (14)$$

mechanism for the dehydrogenation process of the linear butenes involves the formation of a methallylmetal hydride followed by a β-hydrogen abstraction and reductive elimination of H_2.[20] The intensity of the $ScC_4H_4^+$ ion from reaction 11 was too low for its CID spectra to be studied. As with propene, the secondary reactions of $ScC_4H_6^+$ generated from the linear butenes (reactions 15 and 16),

$$ScC_4H_6^+ + C_4H_8 \xrightarrow{70\%} ScC_8H_{12}^+ + H_2 \qquad (15)$$

$$\xrightarrow{30\%} ScC_6H_{10}^+ + C_2H_4 \qquad (16)$$

yield an intense C–C bond cleavage product. CID of $ScC_8H_{12}^+$ generated in reaction 15 yields loss of C_4H_6 at low energy and loss of C_8H_{12} at higher energy, which supports the stable bis(butadiene) structure.

A possible mechanism for reaction 16 is given in Scheme I, which invokes a Diels–Alder reaction generating an ethyl cyclohexene intermediate. This process is competitive with a β-hydrogen abstraction and reductive elimination of H_2 which generates the Sc^+–bis(butadiene) species in reaction 15. After formation of the ethyl cyclohexene intermediate, C–C bond cleavage occurs in the branch of the ring followed by a β-hydrogen abstraction and reductive elimination of ethene. Starting with butadiene and butene, the formation of ethylcyclohexene is about 40 kcal/mol exothermic while the formation of cyclohexene and ethylene is about 16 kcal/mol exothermic.[18] Thus, the mechanism in Scheme I requires that $D°(Sc^+\text{–butadiene}) - D°(Sc^+\text{–ethylcyclohexene}) \lesssim 40$ kcal/mol and $D°(Sc^+\text{–butadiene}) - D°(Sc^+\text{–cyclohexene}) \lesssim 16$ kcal/mol to be energetically feasible. Although the specific bond energies are not as yet known, neither of these requirements seems unreasonable.

CID of $ScC_6H_{10}^+$ yields a variety of products (reactions 17–22). Although the products in reactions 17–19 are

$$ScC_6H_{10}^+ \xrightarrow[32\ eV]{CID} $$

$$\xrightarrow{11\%} ScC_6H_8^+ + H_2 \qquad (17)$$

$$\xrightarrow{16\%} ScC_6H_6^+ + 2H_2 \qquad (18)$$

$$\xrightarrow{4\%} ScC_6H_4^+ + 3H_2 \qquad (19)$$

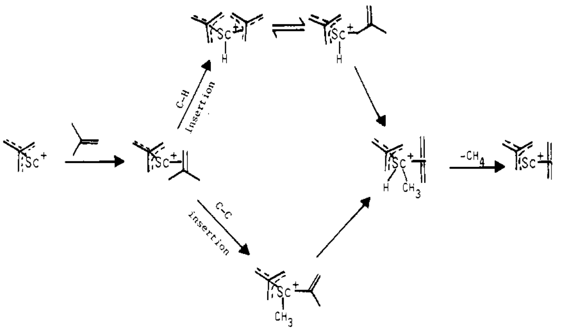
$$\xrightarrow{11\%} ScC_5H_6^+ + CH_4 \qquad (20)$$

$$\xrightarrow{12\%} ScC_5H_5^+ + CH_4 + H\cdot \qquad (21)$$

$$\xrightarrow{46\%} Sc^+ + C_6H_{10} \qquad (22)$$

consistent with the Sc^+–cyclohexene structure predicted by the mechanism in Scheme I, reactions 20 and 21 clearly indicate the presence of other structures and, therefore, other reaction pathways.

Scheme II



It is with the linear pentenes that C–C bond cleavage is first seen in the primary reactions for Sc^+. Single and double dehydrogenations, however, are still the predominant reactions and account for approximately 60% of the products observed in reactions with 1-pentene and 76% of the products observed in reactions with *trans*-2-pentene. Double dehydrogenation itself is responsible for about 53% and 69% of the reaction products, respectively. It is interesting to note that neither Fe^+ nor Co^+ dehydrogenates any linear alkene more than once, except in the case of Fe^+ with *trans*-3-hexene where double dehydrogenation accounts for only 4% of the total product ion distribution.[21] For Ti^+, however, double dehydrogenations exclusively are observed for alkenes with a five-carbon chain or longer.[5] This behavior supports the trend for the preference of C–H bond insertion by the early transition metals, whereas C–C bond insertion predominates for the later transition metals.

As the chain length increases, the ratio of dehydrogenation to C–C bond cleavage is expected to decrease due in part to lower C–C bond energies, and this is what is observed for the three linear hexenes and 1-heptene studied. The dehydrogenation products from the hexenes still represent the majority of the products, but the C–C bond cleavage processes become much more competitive.

The trend for dehydrogenation at first glance seems to come to an abrupt end in the reactions of Sc^+ with 1-heptene. Only 12% of the total products results from dehydrogenation processes alone. However, as the chain length increases, multiple losses (i.e., loss of a small alkane together with loss of H_2) begin to dominate the product ion distributions which again demonstrates the extent to which dehydrogenation is a favorable process for Sc^+.

Reactions with Branched Alkenes. The reactions of Sc^+ with branched alkenes also reveal a preference for dehydrogenation as opposed to C–C bond cleavage (Table II). Sc^+ reacts with isobutene producing $ScC_4H_6^+$ with a loss of H_2. CID of this ion gives the same three products observed for $ScC_4H_6^+$ generated from linear butenes (reactions 12–14). However, loss of H_2 is not as favored from $ScC_4H_6^+$ generated from isobutene, which may suggest that the dehydrogenation product of isobutene is a Sc^+–trimethylenemethane species. This would be consistent with the 1,3-dehydrogenation processes observed for Sc^+ with alkanes.[6] More striking differences of the $ScC_4H_6^+$ isomers will be discussed later. In an attempt to elucidate the mechanism of the dehydrogenation reaction with isobutene, 2-(methyl-d_3)propene-*3,3,3*-d_3 was studied. Statistical scrambling with an apparent isotope effect of $K_H/K_D \approx 1.7$ was observed, suggesting rapid equilibration between a hydridomethallyl intermediate and isobutene

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[20] Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6624.

[21] Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7484.

Table II. Neutral Products Lost in the Primary Reactions of Sc^+, Fe^+, and Co^+ with Branched Alkenes

		neutral fragments lost, in %										
alkene	M^+	H_2	$2H_2$	$3H_2$	CH_4	CH_4,H_2	C_2H_4	(C_2H_6)	C_3H_6	(C_3H_8)	C_4H_8	(C_4H_{10})
2-methylpropene	Sc	100										
	Fe[a]		no reaction									
	Co[b]	88					12					
2-methyl-1-butene	Sc	65	23		5			7				
	Fe[a]	26			41		28		5			
	Co[b]	46			26		20		8			
3-methyl-1-butene	Sc	53	29		7			11				
	Fe[a]	21			42		29		8			
	Co[b]	35			35		22		8			
2-methyl-2-butene	Sc	64	30					6				
	Fe[a]	35			34		24		7			
	Co[b]	34			30		26		10			
2-methyl-1-pentene	Sc	5	33	8	8	11		25		10		
	Fe[a]	9			18		54		2	4	11	2
	Co[c]	2			8		83		1		6	
3-methyl-1-pentene	Sc	6	56	4	2	6		23		3		
	Fe[c]	20			20		7	26	5	3	19	
	Co[c]	13			8		9	47	7	5	11	
4-methyl-1-pentene	Sc	3	26	9	4	25		19		14		
	Fe[a]	4			22		6		56	8	2	2
	Co[c]	4			8		2		86			
2-methyl-2-pentene	Sc	6	17	6	8	14		39		10		
	Fe[a]	12			30		37		6	5	6	4
	Co[c]	22			45		17	2	9		5	
3-methyl-2-pentene	Sc	6	78	3	2	3		7		1		
	Fe[a]	14			24		23	19	3	4	9	4
	Co[c]	7			56		14	14	4		5	
4-methyl-2-pentene	Sc	3	33	9	2	31		14		8		
	Fe[c]	11			44		3	1	22	6	8	5
	Co[c]	10			58		13		12	4	3	
2,3-dimethyl-1-butene	Sc	27	38	5	5	8		9		8		
	Fe[a]	16			62		6	4	2	6	1	3
	Co[c]	19			49		12	11	4		5	
3,3-dimethyl-1-butene	Sc	2	<1	1	57	28		4		8		
	Fe[a]	10			67		10		2	6	2	3
	Co[c]	15			63		12		7		3	
2,3-dimethyl-2-butene	Sc	27	20	5	7	9		21		11		
	Fe[a]	20			57		8	4		5	4	2
	Co[b]	29			46		20				5	

[a] See ref 21. [b] See ref 20. [c] Hettich, R. L.; Freiser, B. S., unpublished results. The parentheses indicate empirical formula only, e.g. C_3H_8 could be H_2, C_3H_6.

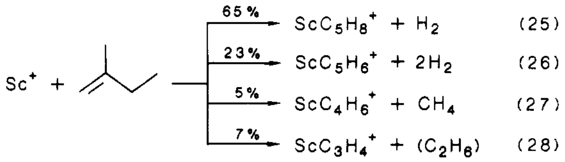
occurs prior to loss of H_2. As in the case of the linear butenes, the secondary reactions of isobutene include C–C bond cleavage in addition to C–H bond cleavage (reactions 23 and 24). A proposed mechanism for reaction 24 is given

$$ScC_4H_6^+ + \text{isobutene} \xrightarrow{75\%} ScC_8H_{12}^+ + H_2 \qquad (23)$$

$$\xrightarrow{25\%} ScC_7H_{10}^+ + CH_4 \qquad (24)$$

in Scheme II which involves either C–H or C–C insertion. The intermediate in the C–H insertion pathway has no β-hydrogens, thus leaving only the possibility for a β-methyl shift and reductive elimination of methane. Conversely, the intermediate in the C–C insertion pathway has β-hydrogens which can undergo β-hydrogen shifts to generate a complex that will also reductively eliminate methane. Support for the final product proposed in Scheme II is found in the CID results which show loss of the allene ligand to be the predominant process. In comparing the reactivity of other transition-metal ions with isobutene, we note that Fe^+ is unreactive while Co^+ both dehydrogenates and also cleaves a C–C bond resulting in a loss of C_2H_4. Interestingly, CID on $CoC_4H_6^+$ from isobutene yields exclusive loss of C_4H_6 suggesting a rearranged Co^+–butadiene structure.[22]

Approximately 94% of the products in the reactions of Sc^+ with 2-methyl-2-butene and 88% of the products in the reaction with 2-methyl-1-butene result from dehydrogenations. The product distribution for the reaction with 2-methyl-1-butene is given in reactions 25–28. It is somewhat surprising that the dehydrogenation to C–C bond cleavage ratio is larger for the isomeric branched butenes than the linear pentenes. It is also interesting to note that neither Fe^+ nor Co^+ dehydrogenates any of these branched alkenes more than once. CID on $ScC_5H_6^+$ from reaction 26 shows fragmentation and loss of the entire ligand (reactions 29–34). As discussed in greater detail below, these results indicate that this ion does not rearrange to a cyclopentadiene ring structure.



$$ScC_5H_6^+ \xrightarrow[60\ eV]{CID} \xrightarrow{14\%} ScC_5H_5^+ + H\cdot \qquad (29)$$

$$\xrightarrow{1\%} ScC_5H_4^+ + H_2 \qquad (30)$$

$$\xrightarrow{9\%} ScC_3H_4^+ + C_2H_2 \qquad (31)$$

$$\xrightarrow{9\%} ScC_3H_3^+ + C_2H_3 \qquad (32)$$

$$\xrightarrow{27\%} ScC_3H_2^+ + C_2H_4 \qquad (33)$$

$$\xrightarrow{40\%} Sc^+ + C_5H_6 \qquad (34)$$

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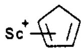
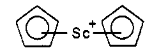
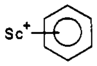
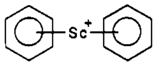
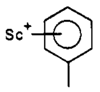
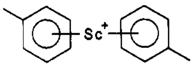
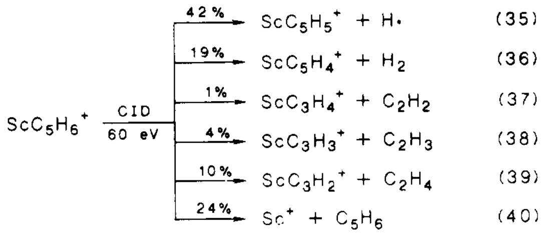
(22) Hettich, R. L. Ph.D. Thesis, Purdue University, 1986.

Table III. Neutral Products Lost in the Primary and Secondary Reactions of Sc^+ with Cyclic Alkenes

alkene	primary neutral lost	rel %	primary product ion	secondary neutral lost	rel %	secondary product ion
cyclopentene	H_2	>98		$2H_2$	100	
cyclohexene	$2H_2$	100		$2H_2$	100	
1-methylcyclohexene	$2H_2$	100		$2H_2$	100	

The reactions of Sc^+ with 2,3-dimethyl-2-butene (I), 2,3-dimethyl-1-butene (II), and 3,3-dimethyl-1-butene (III) offer additional insight. For both I and II, dehydrogenation reactions are the major processes observed (>50%). However, dehydrogenations account for <5% of the total products observed for III. This supports the idea that Sc^+ initially coordinates to alkenes at the double bond. Following coordination, I and II both have β-hydrogens which can be transferred onto the metal to initiate the dehydrogenation process. Since there are no β-hydrogens in III, dehydrogenation does not readily occur. Instead, Sc^+ can insert into one of the three terminal C–C bonds which makes the loss of CH_4 the most probable result. This is indeed what is observed, with the loss of CH_4 corresponding to ~57% of the total products observed in the case of 3,3-dimethyl-1-butene.

Reactions with Cyclic Alkenes. The reactions of Sc^+ with this last class of alkenes yield exclusively dehydrogenation processes, as seen in Table III. In the case of cyclopentene, single dehydrogenation is the major process observed with a minor amount of double dehydrogenation also observed. CID of the single dehydrogenation product $ScC_5H_6^+$ yields predominantly Sc^+–cyclopentadienyl and the bare metal ion at low kinetic energies with some additional fragmentation products appearing at higher energies (reactions 35–40). Although these reaction pathways are the same as reactions 29–34, the relative abundances differ significantly from the CID results obtained from $ScC_5H_6^+$ generated from the linear and branched alkenes.



Double dehydrogenations were the exclusive processes observed in the reaction of Sc^+ with both cyclohexene and 1-methylcyclohexene resulting in presumably the Sc^+–benzene and Sc^+–toluene ions, respectively. This is supported by CID results. CID of $ScC_6H_6^+$ generated from cyclohexene yields loss of C_6H_6 exclusively. Similarly, CID of $ScC_7H_8^+$ generated from 1-methylcyclohexene yields the loss of C_7H_8 exclusively. These results for Sc^+ can be compared to those obtained for Fe^+ and Co^+ which also showed double dehydrogenation as the major product with cyclohexene.[23]

The secondary reactions of these cyclic alkenes strongly mimic the primary reactions. Again, only dehydrogenations are observed. Sc^+–cyclopentadiene doubly dehydrogenates cyclopentene to form presumably the Sc^+–bis(cyclopentadienyl) complex (i.e. scandocenium). The Sc^+–bis(cyclopentadienyl) structure is supported by CID results which show the appearance of $ScC_5H_5^+$ as the major fragment ion. Likewise, the only reaction seen for Sc^+–benzene and Sc^+–toluene with cyclohexene and 1-methyl-1-cyclohexene are double dehydrogenations forming the Sc^+–bis(benzene) complex and the Sc^+–bis(toluene) complex, respectively. CID on the secondary product from cyclohexene yields sequential losses of C_6H_6 and, likewise, sequential losses of C_7H_8 fragments are observed for the toluene system supporting the bis(arene) structures.

Table IV. $ScC_4H_6^+$ Differentiation

$ScC_4H_6^+$ precursor	CID at ~44 eV neutral loss (%)	ion–molecule reactions	
		benzene	acetonitrile
linear butenes	$-C_4H_6$ (69) $-C_2H_4$ (15) $-H_2$ (16)	condensation (100%)	condensation (100%)
isobutene	$-C_4H_6$ (77) $-C_2H_4$ (15) $-H_2$ (8)	condensation (52%) dehydrogenation (48%)	condensation (54%) dehydrogenation (46%)
propene	$-C_4H_6$ (63) $-C_2H_4$ (29) $-H_2$ (8)	condensation (70%) dehydrogenation (30%)	condensation (66%) dehydrogenation (34%)

Isomer Differentiation. Throughout this study, a number of isomeric species have been observed. Three of these, $ScC_4H_6^+$, $ScC_4H_4^+$, and $ScC_4H_6^+$, have been the subject of further investigation. The methods used to attempt to differentiate the various isomers included CID, specific ion–molecule reactions, and H/D exchange experiments. In a number of cases, either a single method or a combintion of the above mentioned methods yielded evidence for the existence of unique isomeric species. Unfortunately, in other cases the results were not clearly distinguishable, and, therefore, isomer differentiation was not possible. In addition, the presence of mixtures of isomeric ions could not be elucidated or ruled out.

The first isomer studied was $ScC_4H_6^+$ generated as the dehydrogenation product from the linear butenes (reaction 10) or isobutene, and in the secondary reactions with propene (reaction 9). The results are summarized in Table IV. The CID of these isomers all show losses of C_4H_6, C_2H_4, and H_2 with approximately the same ratios. However, the existence of at least two different isomers is supported by ion–molecule reactions with benzene and acetonitrile. $ScC_4H_6^+$ generated from the linear butenes only showed condensation with both benzene and acetonitrile, while $ScC_4H_6^+$ generated from isobutene and propene was observed to lose H_2 in its reactions with both benzene and acetonitrile as well as yield the corresponding condensation products.

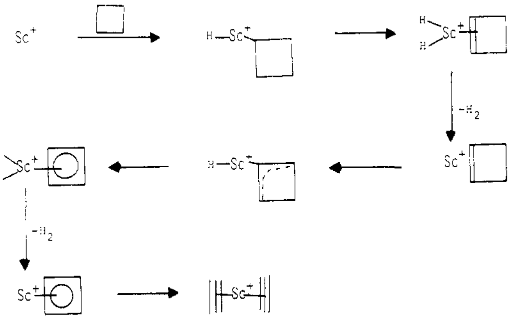
H/D exchange experiments were also performed on these isomers by using C_3D_6 as the deuteriating reagent. $ScC_4H_6^+$ generated from the linear butenes gave four rapid exchanges followed by two slower exchanges which sup-

Table V. $ScC_4H_4^+$ Differentiation

$ScC_4H_4^+$ precursor	CID at 20 eV neutral loss (%)	ion-molecule reactions: *hydrogen cyanide* neutral loss (%)	ion-molecule reactions: *acetonitrile* neutral loss (%)
1,3-butadiene	$-C_4H_4$ (21) $-C_2H_2$ (28) $-H_2$ (51)	$-C_2H_2$ (9) $-H_2$ (70) cond[a] (21)	$-C_2H_2$ (8) $-H_2$ (22) cond[a] (70)
ethene	$-C_4H_4$ (24) $-C_2H_2$ (14) $-H_2$ (62)	$-C_2H_2$ (10) $-H_2$ (71) cond[a] (19)	$-C_2H_2$ (8) $-H_2$ (24) cond[a] (68)
cyclobutane	$-C_4H_4$ (29) $-C_2H_2$ (71) $-H_2$ (0)	$-C_2H_2$ (20) $-H_2$ (80) cond[a] (0)	$-C_2H_2$ (22) $-H_2$ (39) cond[a] (39)

[a] Cond = condensation.

Scheme III



ports the butadiene structure. Isobutene yielded six very slow exchanges which differs from the linear butenes. H/D exchange could not successfully be performed on $ScC_4H_6^+$ generated from propene due to a small product ion signal and difficulty in initially isolating an unscrambled $ScC_4H_6^+$ species. The $ScC_4H_6^+$ generated from isobutene and propene apparently are very similar if not identical. The possibility of a mixture also exists.

The next isomer studied, $ScC_4H_4^+$, can be generated from three different precursors: ethene, cyclobutane, and butadiene. The results are given in Table V and indicate that $ScC_4H_4^+$ generated from cyclobutane is clearly different than the ions generated from ethene and butadiene. The results for $ScC_4H_4^+$ generated from ethene and 1,3-butadiene, however, are more ambiguous. The CID spectra for $ScC_4H_4^+$ generated from the three neutral precursors are shown in Figure 1. The curves represent a visual fit through the data. The most striking difference observed is that, while the ions from ethene and butadiene lose H_2, those from cyclobutane do not. This result provides evidence for at least two stable $ScC_4H_4^+$ isomers. Although the CID spectra from ethene and butadiene are similar, they differ in that C_2H_2 loss is a more dominant process at lower energies for the species generated from butadiene. In fact it is surprising that C_2H_2 loss is least from the species one would most expect to observe it, namely, from ethene. This suggests, however, that the C_4H_4 ligand generated from ethene is predominantly coupled and in the form of a single ligand as discussed below.

To further probe the structures of the isomeric $ScC_4H_4^+$ ions, ion-molecule reactions with hydrogen cyanide and acetonitrile were studied. With hydrogen cyanide, three products were observed for $ScC_4H_4^+$ generated from ethene and 1,3-butadiene (reactions 41–43). For $ScC_4H_4^+$ generated from cyclobutane, reaction 41 was not observed. It

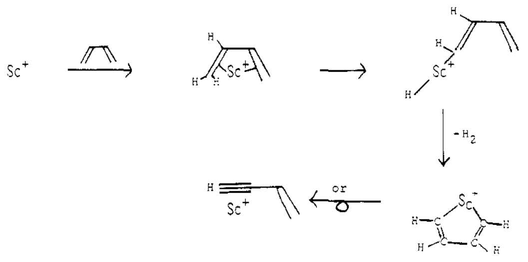
$$ScC_4H_4^+ + HCN \longrightarrow Sc(C_4H_4)(HCN)^+ \qquad (41)$$
$$ScC_4H_4^+ + HCN \longrightarrow Sc(C_5H_3N)^+ + H_2 \qquad (42)$$
$$ScC_4H_4^+ + HCN \longrightarrow Sc(C_2H_2)(HCN)^+ + C_2H_2 \qquad (43)$$

is interesting that H_2 loss is observed (reaction 42), whereas it is not observed in the CID spectra. Thus, in agreement with the CID experiments, these results also differentiate $ScC_4H_4^+$ generated from cyclobutane from that generated from ethene and 1,3-butadiene. The product ion distribution for the latter two species, once again, are not significantly different enough to claim that they are unique isomers. However, the small amount of C_2H_2 loss (10%) for $ScC_4H_4^+$ generated from ethene is further evidence for a single ligand species. When the $ScC_4H_4^+$ isomers were allowed to react with acetonitrile, three products were observed (reactions 44–46). Again, only subtle differences

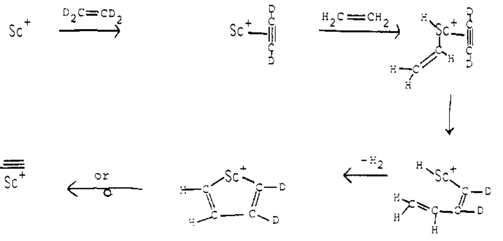
$$ScC_4H_4^+ + CD_3CN \longrightarrow Sc(C_4H_4)(CD_3CN)^+ \qquad (44)$$
$$ScC_4H_4^+ + CD_3CN \longrightarrow Sc(C_4H_2)(CD_3CN)^+ + H_2 \qquad (45)$$
$$ScC_4H_4^+ + CD_3CN \longrightarrow Sc(C_2H_2)(CD_3CN)^+ + C_2H_2 \qquad (46)$$

in the reactivity of these ions were observed. Condensation of acetonitrile (reaction 44) is by far the predominant process. The fact that loss of C_2H_2 again seems to be more favorable for cyclobutane, 22% compared to 8% for both ethene and butadiene, supports a bis(acetylene) structure for at least a portion of the population of this ion and a one ligand structure for the other two isomers. H/D exchange experiments were attempted on the $ScC_4H_4^+$ isomers but proved to be inconclusive. Other reagents used included benzene, pyridine, and ammonia. In each case loss of C_2H_2 was greatest for $ScC_4H_4^+$ generated from cyclobutane. However, no other striking differences in products or product ion distributions were observed. Finally, photodissociation experiments yield evidence for the existence of two distinct isomers. Figure 2 shows the results of trapping each isomer for five seconds while irradiating them at 370 nm (77 kcal/mol). Each of the isomers show the same losses as in the CID experiment, except for cyclobutane which also shows a loss of H_2 which is absent in its CID spectrum. The cyclobutane case once again shows a greater occurrence of C_2H_2 loss than do ethene or butadiene, and the data for ethene and butadiene are remarkably similar. A mechanism for the formation of the bis(acetylene) species generated from cyclobutane is shown in Scheme III. This mechanism invokes C–H insertions and a sequence of β-hydrogen shifts that are typical of Sc^+ chemistry. The great ring strain is alleviated by decomposition of the four-member ring into two acetylene ligands. A possible mechanism for the formation of

Scheme IV



Scheme V



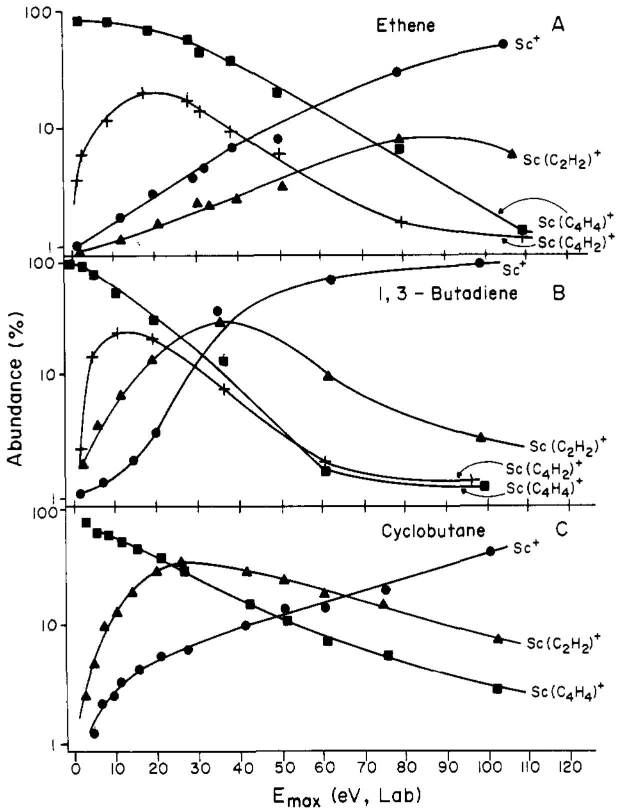


Figure 1. CID product ion intensities vs ion kinetic energy for $ScC_4H_4^+$ isomers generated from (a) ethene (b) 1,3-butadiene, and (c) cyclobutane.

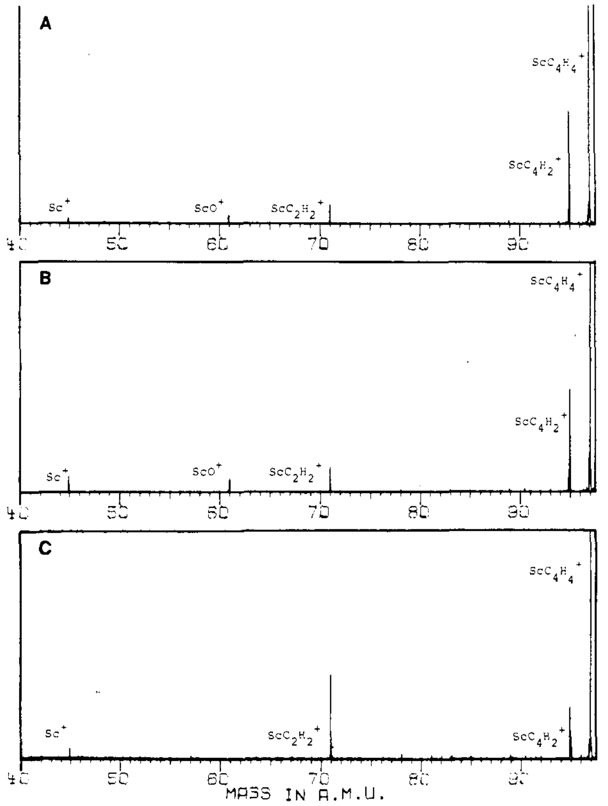


Figure 2. Photodissociation spectra (using 370-nm light) of $ScC_4H_4^+$ isomers generated from (a) ethene, (b) 1,3-butadiene, and (c) cyclobutane. Note: the presence of ScO^+ arises from background oxygen in the system.

Table VI. $ScC_5H_6^+$ Differentiation

$ScC_5H_6^+$ precursor	CID at 60 eV neutral loss (%)	H/D exchange
branched butenes[a]	-H• (14) $-H_2$ (1) $-C_2H_2$ (9) $-C_2H_3$ (9) $-C_2H_4$ (27) $-C_5H_6$ (40)	six very slow exchanges
cyclopentene	-H• (42) $-H_2$ (19) $-C_2H_2$ (1) $-C_2H_3$ (4) $-C_2H_4$ (10) $-C_5H_6$ (24)	one fast followed by five slower exchanges

[a] The branched butenes represent the acyclic isomer. CID results here are from $ScC_5H_6^+$ generated from 2-methyl-1-butene.

a monoligand species from the reaction with butadiene is given in Scheme IV. Since the data collected on the $ScC_4H_4^+$ isomers generated from butadiene and ethene do not unambiguously differentiate between these two isomers, a mechanism for the reaction of Sc^+ with ethene producing the same product as the reaction with butadiene is proposed in Scheme V and invokes a migratory insertion of acetylene into a Sc^+–alkylidene bond. Next, concerted loss of H_2 and ring closure result in the formation of the same product ion proposed in the reaction with 1,3-butadiene (Scheme IV). In addition, exclusive loss of H_2 and absence of the H/D exchange products ScC_2HD^+ and $ScC_2H_2^+$ in the reaction of $ScC_2D_2^+$ with C_2H_4 support initial insertion into a C–H bond in the incoming ethylene and the absence of a reversible bis(alkylidene) intermediate.

Another species whose isomers can be readily differentiated is $ScC_5H_6^+$. The cyclic species (generated presumably by dehydrogenation of cyclopentene) shows major differences in both CID results and H/D exchange experiments compared to the acyclic species (dehydrogenation product of 2-methyl-1-butene). The CID results for the acyclic species shows a higher degree of fragmentation, i.e. formation of $ScC_3H_4^+$, $ScC_3H_3^+$, and $ScC_3H_2^+$, than does the cyclic species. In addition, the H/D exchange results for the acyclic species shows six slow exchanges with C_2D_4, whereas the cyclic species exhibits one rapid exchange followed by five slow exchanges. The latter behavior is characteristic of the hydrido–cyclopentadienyl structure.[23] These results can be found in Table VI. In general agreement with the CID results, photodissociation of the cyclic species yields considerably less fragmentation than does the acyclic species. Surprisingly, no significant differences were detected between the $ScC_5H_6^+$ ions generated from the branched butenes or the linear pentenes using any of the techniques mentioned above.

Thermochemistry. It is possible to extract thermochemical data from the FTMS experiment. The heats of formation of acetylene and ethene and the fact that Sc^+ dehydrogenates ethene yields $D°(Sc^+\text{–acetylene}) > 41.7$ kcal/mol.[18] Likewise, it is possible to derive lower limits on all of the Sc^+–ligand bond energies formed through the reactions of Sc^+ with the various alkenes studied. In order to successfully bracket the Sc^+–ligand bond energy, however, first a known Sc^+–ligand bond strength is needed. Second, it must be possible to form and isolate this Sc^+–ligand complex in our system. Beauchamp and Tolbert reported $D°(Sc^+\text{–}CH_3) = 65 \pm 5$ kcal/mol and $D°(Sc^+\text{–}H) = 54 \pm 4$ kcal/mol.[6] In a more recent study, Armentrout and co-workers, using slightly more sensitive instrumentation determined $D°(Sc^+\text{–}CH_3) = 59.0 \pm 3$ kcal/mol and $D°(Sc^+\text{–}H) = 56.2 \pm 2$ kcal/mol.[19] A variety

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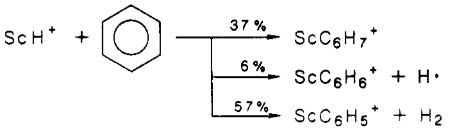
[23] Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7492.

of ab initio techniques have also been used[24] yielding a theoretical bond dissociation energy, $D°(Sc^+–H)$, that is in good agreement with the experimental results. Both the $Sc^+–CH_3$ and $Sc^+–H$ ions are products of endothermic reactions of Sc^+ with ethane, whereas generally only exothermic processes are monitored in our experiment. MCH_3^+ can be formed by the exothermic reaction of CH_3I with the later transition metal ions such as Fe^+ and Co^+,[25] but this reaction is not observed for the early transition metals. A new experiment which has recently been developed for the FTMS,[16] however, provides a method of forming and studying product ions that result from endothermic reactions in analogy to the ion-beam experiment. With use of this methodology, $Sc^+–H$ was formed by accelerating Sc^+, immediately after its formation, and then allowing it to react with ethane. Isolation of the $Sc^+–H$ ion was accomplished by carefully ejecting the remaining Sc^+ and using an RF sweep to eject all ions higher in mass than the $Sc^+–H$.

With this accomplished, an attempt to bracket $D°(Sc^+–\text{benzene})$ was made. The Sc^+–benzene system was chosen because it has previously been shown in our laboratory that Sc^+ reacts with cyclohexane to form Sc^+–benzene indicating $D°(Sc^+–\text{benzene}) > 49.25$ kcal/mol.[18] To bracket $D°(Sc^+–\text{benzene})$, benzene was allowed to react with the isolated $Sc^+–H$ resulting in three products (reactions 47–49). CID of the product of reaction 47 yields $Sc^+–H$ exclusively, which suggests, although not conclusively,[26] that the $Sc^+–H$ bond strength is stronger than the Sc^+–benzene bond strength. The appearance of reaction 48 is apparently a result of a small amount of endothermic reaction and suggests that $D°(Sc^+–H)$ is only about 1 or 2 kcal/mol stronger than $D°(Sc^+–\text{benzene})$. Thus, these results indicate 49.25 kcal/mol $< D°(Sc^+–\text{benzene}) < 56.2 \pm 2$ kcal/mol, from which a value $D°(Sc^+–\text{benzene}) = 53 \pm 5$ kcal/mol is assigned. This is in excellent agreement with photodissociation experiments yielding $D°(Sc^+–\text{benzene}) = 50 \pm 5$ kcal/mol.[27] An upper limit of 368 kcal/mol was calculated for $\Delta H_f(ScC_6H_5)^+$ generated in reaction 49. Benzene has proven to be a useful ligand displacement reagent,[28] as further exemplified in this study. In particular, benzene was observed to displace acetylene from $ScC_2H_2^+$ (generated from ethene) (reaction 50), indicating that 56.2 ± 2 kcal/mol $> D°(Sc^+–\text{benzene}) > D°(Sc^+–C_2H_2) > 41.7$ kcal/mol. This value is considerably, and at this time inexplicably, lower than a previously reported value for $D(Sc^+–C_2H_2) = 78$ kcal/mol[19] but is comparable to a reported value of $D°(V^+–C_2H_2) = 51$ kcal/mol.[29] In a similar experiment butadiene was found to displace benzene (reaction 51), thus indicating $D°(Sc^+–C_4H_6) > 49.2$ kcal/mol. Supporting this result is the observation that (benzene)(butadiene)Sc^+ undergoes collision-induced dissociation to lose predominantly benzene. It is perhaps surprising that a formally six-electron donor, benzene, is displaced in favor of butadiene and, in contrast, benzene appears to be bound somewhat more strongly than butadiene for Fe^+ and Co^+.[14,30] The explanation for these interesting results awaits a detailed theoretical treatment.



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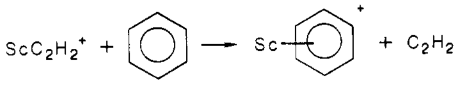

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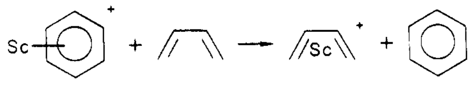

(51)

Conclusions

The results of this study point to a preference for dehydrogenation processes in the reactions of Sc^+ with various linear, branched, and cyclic olefins. These processes may be exclusive single or multiple dehydrogenations, or losses of H_2 can occur in conjunction with losses of small alkanes. This is consistent with the previously reported reactions of Sc^+ with hydrocarbons[6] in which single and double dehydrogenations were the predominant processes that were observed (73% of the total products in the reaction with propane, 59% for the reactions with *n*-butane, and 82% for the reaction with isobutane) and is also consistent with the trend for dehydrogenation demonstrated by other early first-row transition metals.[4,5] A significant difference in the reactions of Sc^+ with alkenes is the absence of dialkyl products which were observed for Sc^+ with alkanes.[6] For example, Sc^+ reacts with *n*-butane to generate $Sc(CH_3)_2^+$. The analogous species were not observed in reactions with alkenes. The results for Sc^+ are also quite different from those obtained for the groups 8–10 transition metals where a strong preference for C–C bond cleavage reactions was observed.[12]

The results of this study also imply that Sc^+ is more reactive than Fe^+ or Co^+. For example, Sc^+ dehydrogenates ethene and propene and Fe^+ and Co^+ do not. This difference may be due to the fact that the bond energies of acetylene and allene to Sc^+ are stronger than those to Fe^+ and Co^+.

CID, ion–molecule reactions, and H/D exchange experiments were used to suggest at least two isomers each for $ScC_4H_6^+$, $ScC_4H_4^+$, and $ScC_5H_6^+$. There was some evidence for a third $ScC_4H_4^+$ isomer, but, due to lack of significant differences, an absolute assignment could not be made.

Finally, this work further demonstrated the cability of FTMS for studying endothermic reactions, which proved to be a valuable aid in bracketing $D°(Sc^+–\text{benzene})$.

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) and the National Science Foundation (CHE-8612234) for supporting the advancement of FTMS methodolgy.

Registry No. C_2H_4, 74-85-1; C_3H_6, 115-07-1; (*Z*)-C_4H_8, 590-18-1; (*E*)-C_4H_8, 624-64-6; $CH_2{=}C(CH_3CH_2CH_3$, 563-46-2; C_6H_6, 71-43-2; $CH_2{=}CHCH{=}CH_2$, 106-99-0; $\overline{CH_2CH_2CH_2CH_2}$, 287-23-0; Sc^+, 14336-93-7; Fe^+, 14067-02-8; Co^+, 16610-75-6; 1-pentene, 109-67-1;

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trans-2-pentene, 646-04-8; 1-hexene, 592-41-6; *trans*-2-hexene, 4050-45-7; *trans*-3-hexene, 13269-52-8; 1-heptene, 592-76-7; 2-methylpropene, 115-11-7; 3-methyl-1-butene, 563-45-1; 2-methyl-2-butene, 513-35-9; 2-methyl-1-pentene, 763-29-1; 3-methyl-1-pentene, 760-20-3; 4-methyl-1-pentene, 691-37-2; 2-methyl-2-pentene, 625-27-4; 3-methyl-2-pentene, 922-61-2; 4-methyl-2-pentene, 4461-48-7; 2,3-dimethyl-1-butene, 563-78-0; 3,3-dimethyl-1-butene, 558-37-2; 2,3-dimethyl-2-butene, 563-79-1; cyclopentene, 142-29-0; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; isobutene, 115-11-7.

Ortho-Chelated Arylrhodium(I) Complexes. X-ray Structure of $\mathrm{Rh^I[C_6H_3(CH_2NMe_2)_2}$-*o*,*o*′-*C*,*N*](COD)

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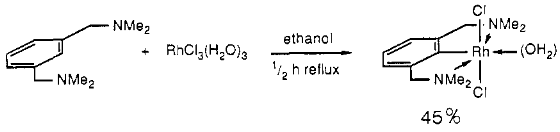
The reaction of $\mathrm{Li}_n[\mathrm{C_6H_3(CH_2NMe_2)}$-*o*-R-*o*′$]_n$ with $[\mathrm{RhCl(diene)}]_2$ yields the ortho-chelated arylrhodium(I) complexes $\mathrm{Rh[C_6H_3(CH_2NMe_2)}$-*o*-R-*o*′](diene) (R = $\mathrm{CH_2NMe_2}$, diene = COD (**1a**) or NBD (**1b**); diene = COD, R = Me (**2**) or H (**3**)). The solid-state structure of **1a** was determined by a single-crystal X-ray diffraction study. $\mathrm{C_{20}H_{31}N_2Rh}$: triclinic, space group $P\bar{1}$, with lattice parameters $a = 10.169$ (1) Å, $b = 13.036$ (1) Å, $c = 14.688$ (2) Å, $\alpha = 79.54$ (1)°, $\beta = 77.04$ (1)°, $\gamma = 79.53$°; $V = 1845.6$ (4) Å^3, $Z = 4$; D(calcd) = 1.448 g cm^{-3}. Refinement with 4696 observed reflections converged at $R = 0.0395$. The structure of **1a** consists of a rhodium(I) center that has a square-planar coordination comprising the two double bonds of COD and a C atom and one of the N atoms of the monoanionic aryl ligand. In solution compounds **1** and **2** exhibit dynamic behavior which involves a reversible dissociation of the Rh–N bond and rotation of the aryl moiety around Rh–C. This process, which generates a highly unsaturated T-shaped 14 electron species, is accompanied by the relief of steric repulsions within the complex. Complex **1** reacts with a range of electrophilic reagents leading to Rh–C bond breakage (HX, X = acac, Cl, Br, OAc, OH, OMe, L-alanyl; $\mathrm{MX}_n\mathrm{L}_m$, $\mathrm{SnMe_2Br_2}$, $\mathrm{NiBr_2(PBu_3)_2}$, $\mathrm{ZrCl_4}$, $\mathrm{PdCl_2(NCPh)_2}$, $\mathrm{HgCl_2}$, $\mathrm{PtBr_2(COD)}$, and $[\mathrm{IrCl(COD)}]_2$). A redox reaction of **1** with AgX (X = OAc, $\mathrm{NO_3}$) leads to the formation of $\mathrm{Rh^{III}X_2[C_6H_3(CH_2NMe_2)_2}$-*o*,*o*′$]\mathrm{(H_2O)}$.

Introduction

Recently we reported on the syntheses of $\mathrm{Rh^{III}Cl_2[C_6H_3(CH_2NMe_2)_2}$-*o*,*o*′$]\mathrm{(H_2O)}$ via direct metalation of *m*-$\mathrm{(Me_2NCH_2)_2C_6H_4}$ with $\mathrm{RhCl_3(H_2O)_3}$ (eq 1).[1v] The high



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stability of this organometallic complex and its derivatives shows the stabilizing influence that the "built-in" ligands in the organo group have on the metal–carbon bond. In the special case of bis-ortho chelation, a terdentate monoanionic aryl ligand like $[\mathrm{C_6H_3(CH_2NMe_2)_2}$-*o*,*o*′$]$ encapsulates the complexed metal to some extent but still leaves enough distinctly positioned sites for the resulting complex to serve as a model compound for the study of elementary reaction processes. In this respect the use of organo, but also nonorgano,[2] terdentate ligands has been extensively exploited by us[1] and others[3-6] and has produced many unprecedented results. The chemistry of nickel(II) and platinum(II) $[\mathrm{C_6H_3(CH_2NMe_2)_2}$-*o*,*o*′$]$ complexes has greatly improved our understanding of the elementary steps in electron-transfer processes between d^8 metal complexes and electrophiles like alkyl halides and halogens.[1] These results prompted us to also develop the chemistry of

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