tagonal-bipyramidal geometry correspond to a d^2–d^2 closed-shell configuration. In Table III, we summarize the closed-shell requirements for different types of linear dinuclear transition-metal complexes. Complexes with electron counts more than the closed-shell requirements listed in Table III will have bent M–X–M structures. For complexes with electron counts less than or equal to the closed-shell requirements, linear M–X–M structures will be preferred.

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Chemistry of the Scandium–Benzyne Ion in the Gas Phase

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The gas-phase chemistry of Sc^+–benzyne with a wide variety of simple molecules is reported. The reactant ion, $ScC_6H_4^+$, was prepared from the dehydrogenation of benzene by Sc^+. $ScC_6H_4^+$ undergoes an unusual hydrogenation reaction with H_2 and D_2, as well as H/D exchange with the latter. Its reactions with a number of oxygen-containing species, XO, give ScO^+. The ability to form stable C_6H_4X neutral products from benzyne is a key factor in making this reaction exothermic. With the exception of methane, $ScC_6H_4^+$ reacts with all of the alkanes and alkenes studied to form a wide variety of product ions. A selected number of ions were subjected to more detailed structural study. Sc^+–styrene is formed from the reaction with ethane and propane. Sc^+–indane is also formed from the reaction with propane. The product ion $ScC_8H_{10}^+$ from *n*-butane is Sc^+–ethylbenzene. A prominent ion, $ScC_9H_7^+$, is formed from butadiene. Its frequent occurrence, unusual formulation, and resistance to fragmentation all indicate a high stability, with its structure most likely being that of the indenylscandium cation. $D°(Sc^+\text{–benzyne}) = 88 \pm 5$ kcal/mol was determined indirectly from the photodissociation threshold for loss of H_2 from Sc^+–benzene and from the observation that Sc^+ exothermically dehydrogenates benzene to form Sc^+–benzyne. Theoretical study indicates that the gas-phase structure is analogous to that of solid-phase mononuclear transition-metal–benzyne complexes observed crystallographically in which the metal center is coplanar with the benzyne ring and inserted symmetrically into the C–C triple bond forming a benzometallacyclopropene. The theoretical bond energy for the planar singlet $D°(Sc^+\text{–}C_6H_4) = 94$ kcal/mol is in good agreement with experiment.

Introduction

Benzyne is synthetically very useful because of its high reactivity with a wide variety of species.[1] But its high unsaturation also renders it somewhat elusive for isolation, and it has to be prepared in situ for synthetic purposes. The study of transition-metal–benzyne complexes is interesting because the highly unsaturated benzyne can be greatly stabilized by having its C–C triple bond serving as the coordinating site to the transition-metal center, thus partially compensating for the unsaturation. Some benzyne complexes have been synthesized and isolated in pure crystallized form.[2-4] Gas-phase transition-metal ions are well-known for their ability to undergo oxidative addition into the otherwise very stable C–C and C–H bonds of small hydrocarbons.[5] This, in combination with the thermodynamically driven tendency for benzyne ligand to lower its degree of unsaturation, provides an opportunity to examine the effect of the benzyne ligand on the reactivity of the metal center and vice versa. Recently we studied the chemistry of Fe^+–benzyne with a wide variety of small hydrocarbons in the gas phase.[6,7] In a typical reaction with an alkane, Fe^+ serves as a reaction initiating center via its ability to oxidatively add into C–C or C-H bonds, followed by migratory insertion of the resulting alkyl or hydrogen atom onto the benzyne ligand. Next, a β-hydrogen or alkyl is abstracted from the alkyl group and its coupling with the phenyl group and subsequent elimination of the resulting alkene ligand completes the reaction. A study of the reactions of Fe^+–benzyne with alkenes also suggests that the chemistry between them is initiated by the metal center.[7] Here we extend these studies to the reactivity of Sc^+–benzyne with some small hydrocarbons and oxygen-containing species in the gas phase, with the emphasis on determining reaction pathways and mechanisms.

Experimental Section

All experiments were performed on a prototype Nicolet FTMS-1000 Fourier transform mass spectrometer equipped with a 5.2-cm cubic trapping cell situated between the poles of a Varian 15-in. electromagnet maintained at 0.85 T.[8] The cell utilizes two stainless steel screens of 80% transmittance as the transmitter plates, permitting irradiation of the interior with a wide variety of light sources. Sc^+ was generated by focusing the beam of a Quanta Ray Nd:YAG laser (operated at 1.064 μm) onto a thin high-purity scandium target. Details of the laser desorption experiment are described elsewhere.[9]

All chemicals were obtained in high purity from commercial sources and used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensable gases. Sample pressures were measured with an uncalibrated Bayard–Alpert ionization gauge and were typically 4×10^{-6} Torr for reagents and 4×10^{-5} Torr for argon, which was used for collision-induced dissociation (CID) and for collisional cooling of reactant ions.

The reactant ion, $ScC_6H_4^+$, was prepared from the dehydrogenation reaction of Sc^+ with benzene and isolated by swept double-resonance ejection pulses before its reaction with a wide variety of different samples.[10] $ScC_6H_4^+$ reacts further with benzene to form the condensation products $Sc(C_6H_4)(C_6H_6)_n^+$ (n = 1, 2). To avoid this interference, benzene was pulsed in through a General Valve Corp. Series 9 pulsed solenoid valve, triggered simultaneously with the laser desorption of the Sc target. In this way, benzene filled the cell to a maximum pressure of 10^{-5} Torr in about 150 ms and was pumped away in about 300 ms by a 6-in. diffusion pump.[11]

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* To whom correspondence should be addressed at Purdue University.

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(2) Bennett, M. A.; Hambley, T. W.; Roberts, N. K.; Robertson, G. B. *Organometallics* **1985**, *4*, 1992.
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It is not absolutely certain that the $ScC_6H_4^+$ ion generated in reaction 1 has the benzyne structure. Sc^+ reacts with 1,5-hexadiyne to generate several products including a $ScC_6H_4^+$ ion. Collision-induced dissociation and selected ion–molecule reaction studies could not conclusively distinguish this ion from that produced in reaction 1. While this indicates that a ring-opened structure cannot be completely ruled out, we believe that there are a number of compelling reasons to suggest a benzyne structure. Early-transition-metal ions are known to undergo extensive dehydrogenation reactions with hydrocarbons presumably through mechanisms involving initial C–H insertion. It seems unlikely that a reaction with benzene would affect the C_6 backbone. A linear structure would be expected to yield a greater variety of products from collision-induced dissociation than that described in reactions 3 and 4. For example, the reaction of Sc^+ with 1,5-hexadyine yields several products, while its reaction with benzene yields only $ScC_6H_4^+$. Thus, we assume that this paper presents results on the Sc^+–benzyne ion and that possibly dehydrocyclization occurs in the reaction of Sc^+ with 1,5-hexadyne to generate the Sc^+–benzyne ion.

The product ion distributions are reproducible to ±10% absolute for primary product ions and ±15% for CID fragmentation ions. To ensure that the product branching ratios were collected primarily for ground state $ScC_6H_4^+$, a high background pressure of argon was maintained during the experiment to allow cooling of the reactant ions. Similar conditions have been found to be effective at cooling other early-transition-metal species.[12] However, a minor population of nonthermal species cannot be completely ruled out.[13,14]

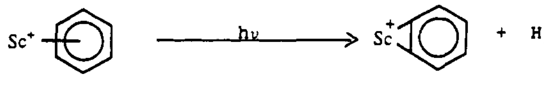
Several major primary product ion structures were investigated by collision-induced dissociation (CID) and ion–molecule reactions. Details of the CID experiments have been described previously.[15] The maximum translational energy of the ions is given in the laboratory frame and can be varied typically between 0 and 100 eV. The spread in kinetic energy is approximately 35% at 1 eV, 10% at 10 eV, and 5% at 30 eV.[16] Due to the multiple-collision conditions required to observe CID using FTMS, rearrangement can occur prior to dissociation, obscuring the structural information. CID of Sc^+–L with L being a hydrocarbon ligand often results in a wide variety of product ions characterized by a high degree of dehydrogenation and carbon skeleton cleavage, which are not very characteristic of the actual structure.[17] Thus, many of the structures proposed are discussed in terms of what is the most reasonable rather than what is proven.

$D°(Sc^+$–benzyne) was determined indirectly from the photodissociation threshold for the loss of H_2 from Sc^+–benzene. The details of the photodissociation experiments are described elsewhere.[18] $ScC_6H_6^+$ was isolated by swept double-resonance ejection pulses and trapped in a background of argon for 5 s. During this time, the ion was irradiated with light from a 2.5-kW Hg-Xe arc lamp, used in conjunction with a series of cutoff filters.

Results and Discussion

Unimolecular Chemistry of Sc^+–Benzyne. As mentioned earlier, Sc^+ can dehydrogenate benzene to form Sc^+–benzyne (reaction 1), suggesting $D°(Sc^+$–benzyne) ≥85 ± 2 kcal/mol or simply ≥ 83 kcal/mol.[19,20] It was not possible to use photodissociation on Sc^+–benzyne to determine $D°(Sc^+$–benzyne) directly because of the combination of insufficient light power from the arc lamp and absorption cross section in that energy range.[18] However, photodissociation of Sc^+–benzene, which is formed from the triple dehydrogenation of cyclohexane by Sc^+, yields the dehydrogenation product ion $ScC_6H_4^+$ (reaction 2). The threshold was determined to be at about 602 nm, corresponding to 48 ± 5 kcal/mol, given the experimental uncertainty. This, coupled with $D°(Sc^+$–benzene) = 49 ± 5 kcal/mol[21] gives $D°(Sc^+$–benzyne) = 86 ± 7 kcal/mol. However, taking the bond energy bracket from reaction 1 into consideration, we assign $D°(Sc^+$–benzyne) = 88 ± 5 kcal/mol. CID of $ScC_6H_4^+$ results in dissociation of the whole ligand from the metal center (reaction 3) and cleavage of the benzyne ligand (reaction 4). This is similar to the photodissociation processes observed for Fe^+–benzyne, while CID of the latter only results in ligand dissociation from the metal center.[6] It is interesting to note that CID on many of the primary product ions from Sc^+–benzyne reacting with alkanes and alkenes gives back $ScC_6H_4^+$, as well as its further fragmentation products, Sc^+ and $ScC_4H_2^+$, as will be seen later.


(1)


(2)

$$ScC_6H_4^+ \xrightarrow{\text{CID at 40 eV}} Sc^+ + C_6H_4 \qquad 39\% \qquad (3)$$

$$\longrightarrow ScC_4H_2^+ + C_2H_2 \qquad 61\% \qquad (4)$$

Detailed crystallographic studies of some mononuclear transition-metal–benzyne complexes have indicated that the metal center is coplanar with the benzyne ring and located symmetrically with respect to the C–C triple bond. This suggests contributions from the resonance structures of M–benzyne and benzometallacyclopropene.[2] Considering that $D°(Sc^+$–benzyne) = 88 ± 5 kcal/mol is substantially higher than $D°(Sc^+$–benzene) = 49 ± 5 kcal/mol,[21] it is reasonable to also postulate a coplanar structure for Sc^+–benzyne rather than a ring-centered structure. In fact detailed theoretical calculations fully support this assertion indicating that the stablest structure involves the insertion of singlet Sc^+ into the triple bond to form a benzometallacyclopropene species.[23] The theoretical binding energy of $D°(Sc^+–C_6H_4)$ = 94 kcal/mol is also in good agreement with experiment. Interestingly, a value of about 33 kcal/mol is calculated for both the planar triplet structure, if the bonding is forced to be electrostatic, and the π-type structure in which the Sc^+ is bound on top of the ring in analogy to the Sc^+–benzene ion. Using the same level of theory, the Sc^+–benzene binding energy is computed to be 41 kcal/mol. Thus, the error in these calculations is estimated to be up to 10 kcal/mol.


(5)

Unlike Fe^+–benzyne,[6] H_2 is observed to hydrogenate $ScC_6H_4^+$ to form Sc^+–benzene (reaction 5). This reaction indicates an upper limit on the Sc^+–benzyne bond strength of < 134 ± 7 kcal/mol, in accordance with the photodissociation results. This type of bimolecular reaction is extremely rare for a mononuclear metal center in the gas phase, with the only other reported example being the direct hydrogenation of $RhC_7H_6^+$.[22] As in that case, the Sc^+–benzene product ion in reaction 5 must be stabilized by an IR radiative relaxation process with some collisional stabilization also possible. General considerations that go into postu-

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(18) Hettich, R. L.; Jackson, T. C.; Stanko, E. M.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 5086.

(19) With use of ΔH_f(benzyne) = 440 ± 10 kJ mol^{-1} (105.2 ± 2.4 kcal/mol) from: Riveros, J. M.; Ingemann, S.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1991**, *113*, 1053.

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(23) The calculations are performed in a manner analogous to those in: Bauschlicher, C. W.; Langhoff, S. R. *J. Phys. Chem.* **1991**, *95*, 2278. Namely, the geometries are optimized at the self-consistent-field level in a double-ζ basis set and then the binding energies are computed in a double-ζ plus polarization basis set at the modified coupled pair functional level. More details of these calculations can be obtained by contacting C.W.B.

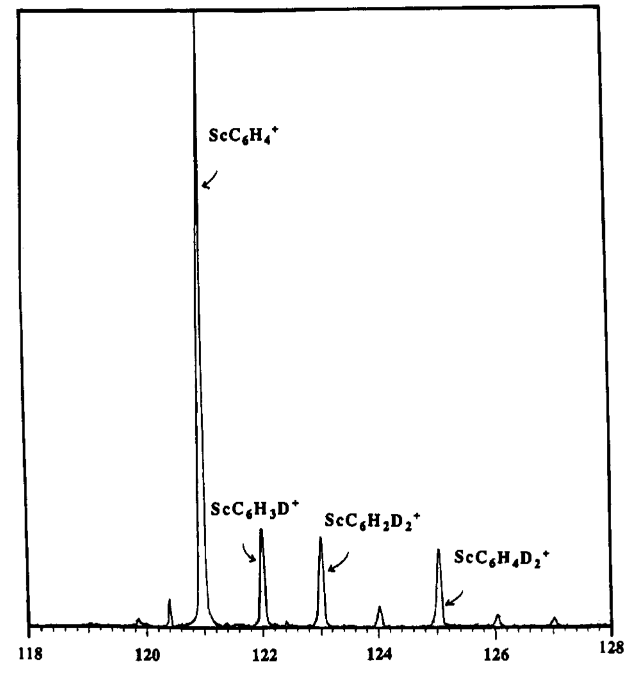
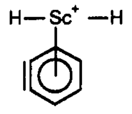


Figure 1. Reaction of Sc^+–benzyne with deuterium.

lating a mechanism for the hydrogenation reaction also relate to the reactions of Sc^+–benzyne with alkanes. It is conceivable that the reaction is initiated when Sc^+ inserts into the H–H bond. However, since the metallacyclopropene structure has a formal Sc(III) metal center with no remaining valence electrons, this would require the Sc^+ to migrate from its σ-bonding position to the less stable π configuration (structure I) to avoid an impossible +5 oxidation state. Alternatively, a four-centered intermediate II can be postulated. In either case, one of the two H atoms can then migrate to the benzyne ligand to form the hydrido–phenylscandium ion III. This, presumably, is the same intermediate formed when Sc^+ inserts into a benzene C–H bond in reaction 1. Coupling of the hydrogen and phenyl group completes the hydrogenation reaction.



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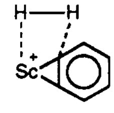
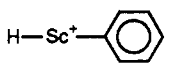


II



III

While intermediate I is reasonable, the known thermochemistry suggests that it may not be energetically feasible. Starting with Sc^+–benzyne and H_2, it requires an estimated 88 ± 5 kcal/mol plus 104 kcal/mol for a total of 192 ± 5 kcal/mol to generate the separated species Sc^+, benzyne, and 2 H. The energy regained in the bond-making process is 115 ± 3 kcal/mol to form ScH_2^+[24] and at most 50 kcal/mol to form the complex I for a total of 165 kcal/mol, suggesting that this species is *not* an intermediate in the hydrogenation process. Thus, the multicentered intermediate II, whose formation is necessarily lower in energy than the reactants by a minimum of the ion-induced dipole energy, appears to be a reasonable candidate. A similar argument can be made for alkanes despite the lower C–H and C–C bond energies.

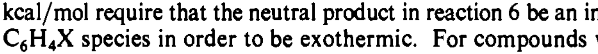
The reaction with D_2 indicates that H/D exchange is concurrent with reaction 5 (Figure 1). One interesting feature in Figure 1 is that the peak with one H/D exchange, $ScC_6H_3D^+$, and the one corresponding to two H/D exchanges, $ScC_6H_2D_2^+$, have very similar intensities. This is not expected from sequential single H/D exchange per reactive collision. To further probe this point, $ScC_6H_4^+$ was trapped in D_2 while $ScC_6H_3D^+$ was continuously ejected. $ScC_6H_2D_2^+$, although reduced in intensity, was still observed in this case, indicating that in fact both single and double H/D exchange per collision occur between $ScC_6H_4^+$ and D_2. Complete H/D exchange is possible for the benzyne ligand, but the peak for the fourth H/D exchange is of the same mass as the hydrogenation peak. However, all of the $ScC_6H_xD_{6-x}^+$ (x = 0–4) ions were observed upon extended trapping, confirming H/D exchange for all of the hydrogen atoms on the benzyne ligand. Finally, observation of H/D exchange provides evidence for the hydrido–phenyl intermediate discussed above.

Table I. Thermodynamic Data for the Reaction of $ScC_6H_4^+$ with XO

compd	$\Delta H_{reacn}(XO \rightarrow X + O)$, kcal/mol	reacn with $ScC_6H_4^+$
N_2O	40	no
C_2H_4O	85	yes
H_2O	117	yes
O_2	119	yes
CO_2	127	no
NO	151	yes
CO	257	no

Interestingly, $Sc(C_6H_4)(C_6H_6)^+$ from the condensation of $ScC_6H_4^+$ with benzene also undergoes hydrogenation, but at a somewhat faster rate, while no such reaction with H_2 is observed for $Sc(C_6H_4)(C_6H_6)_2^+$ under the same conditions. The same type of reactivity pattern with the number of benzene ligands present is observed for the reaction of these benzyne complexes with ethane. These results indicate that the presence of one benzene ligand stabilizes the hydrogenation product, as expected due to the greater number of degrees of freedom and, thus, the longer lifetime, while the second benzene ligand either electronically saturates the complex or sterically blocks the sites necessary for addition of H_2. This effect of "spectating" π-benzene ligands is interesting and merits further examination.

Reactions with Oxygen-Containing Species. ScO^+ is formed exclusively from the reactions of Sc^+–benzyne with H_2O, O_2, and NO (reaction 6) with the parentheses indicating that the identity of the neutral species is in most cases unknown. Reaction 6 is also observed as the predominant pathway for ethylene oxide, with $ScC_7H_6^+$ and $ScC_8H_6^+$ each accounting for about 10% of the reaction product ions, respectively. Examination of the thermochemistry involved reveals some interesting structural information on the neutral products. In particular, given the estimates $D°(Sc^+–O)$ = 161 ± 7 kcal/mol[25] and $D°(Sc^+–C_6H_4)$ = 88 ± 5 kcal/mol, oxygenated compounds in which $D°(X–O) > 85$ kcal/mol require that the neutral product in reaction 6 be an intact C_6H_4X species in order to be exothermic. For compounds with $D°(X–O) < 85$ kcal/mol, either an intact C_6H_4X or the separated species C_6H_4 and X are possible. This indicates that the neutral products generated from the reactions observed for reaction 6 in Table I from H_2O, O_2, and NO must be C_6H_4OH, C_6H_4O, and C_6H_4N, respectively. In the case of NO, for example, the total energy required to dissociate benzyne ligand from Sc^+–benzyne and to break NO into N and O amounts to 239 ± 5 kcal/mol. Given $D°(Sc^+–O)$ = 161 ± 7 kcal/mol, $D°(C_6H_4–N)$ = 78 ± 12 kcal/mol is required for reaction 6 to be exothermic. At the same level of theory used above for $D°(Sc^+–C_6H_4)$, C_6H_4–N is calculated to be bound by 65 kcal/mol in full support of experiment. Interestingly, the calculation also shows C_6H_4N to be planar with a three-membered N–C–C ring and with the N open shell in a π orbital as expected. The neutral product(s) generated from ethylene oxide may be either C_6H_4 and C_2H_4 or the intact C_8H_8. The absence of reaction 6 with N_2O and possibly CO_2 may be due to spin barriers.[26]



$$Sc^+C_6H_4 + XO \longrightarrow ScO^+ + (C_6H_4X) \quad (6)$$

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[24] Sunderlin, L.; Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.* **1987**, *109*, 178.

[25] Derived from IE(Sc) = 6.561 eV,[20] IE(ScO) = 6.6 ± 0.3 eV (Murad, E. *J. Geophys. Res.* **1978**, *83*, 5525), and $D°(Sc–O)$ = 7.01 ± 0.12 eV (Pedley, J. B.; Marshall, E. M. *J. Phys. Chem. Ref. Data* **1983**, *12*, 967).

Table II. Product Distributions (%) from the Reactions of $ScC_6H_4^+$ with Alkanes

product	CH_4	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	n-C_5H_{12}	neo-C_5H_{12}
$ScC_4H_6^+$				7	3	3	6
$ScC_4H_8^+$				3	6		
$ScC_5H_8^+$						1	
$ScC_5H_{10}^+$						1	26
$ScC_6H_6^+$		23	4	2		6	
$ScC_7H_6^+$				2	3	1	
$ScC_7H_8^+$			5	1	4	1	
$ScC_8H_6^+$		15					
$ScC_8H_8^+$		62	59	16	4	16	
$ScC_8H_{10}^+$				35	18	4	
$ScC_9H_8^+$			5	5	6	7	
$ScC_9H_{10}^+$			27	8	11	16	
$ScC_9H_{12}^+$						16	
$ScC_{10}H_{10}^+$				2	8	1	15
$ScC_{10}H_{12}^+$				19	37	5	53
$ScC_{11}H_{10}^+$						1	
$ScC_{11}H_{12}^+$						21	

Table III. Comparison of the Product Distributions (%) from the Reactions of Sc^+ and $ScC_6H_4^+$ with Alkanes

alkane	neutral(s) lost	Sc^{+a}	$ScC_6H_4^{+b}$
CH_4		no reacn	no reacn
C_2H_6	2 H_2	29	15
	H_2	71	62
	C_2H_4		23
C_3H_8	C_3H_6		4
	C_2H_4		5
	CH_4	27	59
	2 H_2		5
	H_2	73	27
n-C_4H_{10}	C_2H_6		16
	C_2H_4	28	35
	CH_4, H_2	2	5
	CH_4		8
	2 H_2	16	2
	H_2	54	19
i-C_4H_{10}	C_3H_8		3
	C_3H_6		4
	C_2H_6		4
	C_2H_4	5	18
	CH_4, H_2		6
	CH_4		11
	2 H_2	9	8
	H_2	86	37
n-C_5H_{12}	C_5H_{10}		6
	C_3H_8		16
	C_3H_8, H_2		4
	C_2H_6, H_2		7
	C_2H_6		16
	C_2H_4	51	16
	CH_4, H_2	13	1
	CH_4	9	5
	2 H_2	8	21
	H_2	19	
neo-C_5H_{12}	CH_4, H_2	15	15
	CH_4	14	53
	H_2	71	

[a] Results taken from: Wise, M. B. Ph.D. Thesis, Purdue University, 1984. [b] Results taken from Table II. Does not include C_6 neutral losses or products having less than 3% relative intensity.

Reactions with Alkanes. With the exception of methane, all of the other alkanes studied react readily with Sc^+–benzyne to form a wide variety of product ions, as shown in Table II. Compared to the chemistry of $FeC_6H_4^+$ with alkanes, $ScC_6H_4^+$ seems to give less of the corresponding hydrogenation product ion $ScC_6H_6^+$ except with ethane, which does not give $FeC_6H_6^+$ from $FeC_6H_4^+$.[6] In addition, a comparison of the chemistry of $ScC_6H_4^+$ to that of Sc^+ (Table III) indicates that a wider variety of products are observed mainly involving C–C bond cleavage for the benzyne species.[27]

Table IV. CID (%) on $ScC_8H_8^+$ from Different Reactions[a]

from ion–molecule reacn $ScC_6H_4^+ + C_2H_6$		from displacement reacn $ScC_2H_2^+ + C_8H_8$ (styrene)		from displacement reacn $ScC_2H_2^+ + C_8H_8$ (COT)	
$ScC_6H_4^+ + C_2H_4$	61	$ScC_6H_4^+ + C_2H_4$	64	Sc^+	22
$ScC_8H_6^+ + H_2$	39	$ScC_8H_6^+ + H_2$	36	$ScC_5H_5^+ + C_3H_3$	40
				$ScC_8H_6^+ + H_2$	20
				$ScC_8H_7^+ + H^\bullet$	18

[a] All data obtained at 30-eV laboratory energy.

One of the conceivable structures for $ScC_8H_8^+$ from the reaction with ethane is Sc^+(benzyne)(ethylene). This ion reacts with benzene to form the condensation product $Sc(C_8H_8)(C_6H_6)^+$, exclusively. CID on the condensation product ion eliminates C_6H_6 exclusively at 7 eV, indicating that the structure is not Sc^+(benzyne)(ethylene)(benzene), since an ion of this structure should competitively eliminate benzene and ethylene, with the latter being highly favored. Table IV compares the CID spectra of $ScC_8H_8^+$ ions from the reaction of $ScC_6H_4^+$ with ethane to those generated by the displacement reactions of styrene and cyclooctatriene (COT) with Sc^+–acetylene. As can be seen, there is excellent agreement with the Sc^+–styrene species, while Sc^+–COT can be ruled out with reasonable certainty. CID on $ScC_8H_8^+$ from the reaction with propane gives the same CID pattern as that from ethane. In addition, Sc^+ reacts with styrene to give 46% $ScC_6H_4^+$ and 54% $ScC_8H_6^+$. These results all suggest the structure of Sc^+–styrene. However, the possibility of Sc^+–benzocyclobutene, which is the analogous product ion from the reaction of $FeC_6H_4^+$ with ethane,[6] cannot be simply ruled out. Unfortunately, a known structure of Sc^+–benzocyclobutene, and subsequently its CID spectra, could not be obtained because of the absence of a commercial source of benzocyclobutene. To further probe this structure, $ScC_6D_4^+$, prepared from perdeuterated benzene, was reacted with ethane and the product ion $ScC_8H_4D_4^+$ was isolated. If benzocyclobutene is the correct structure, then cleavage of the cyclobutene ring to lose ethylene upon CID is expected to result in all four deuterium atoms retained on the Sc^+–benzyne fragment. If styrene is the correct structure, however, the ligand should have one H and one D atom on the neighboring positions of the vinyl group, with both having the same opportunity to be eliminated with the vinyl group. Upon CID of $ScC_8H_4D_4^+$ at 32 eV, $ScC_6D_4^+$ and $ScC_6HD_3^+$ account for 64% and 36% of the Sc^+–benzyne fragment, respectively, supporting the Sc^+–styrene structure. The unequal intensities might be due to an isotope effect during the fragmentation step, favoring H over D elimination as expected. Or, less likely, they could indicate a mixture of the styrene and benzocyclobutene structures.

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(26) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Chem. Phys.* **1982**, *76*, 2449.

(27) Tolbert, M.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 8117.

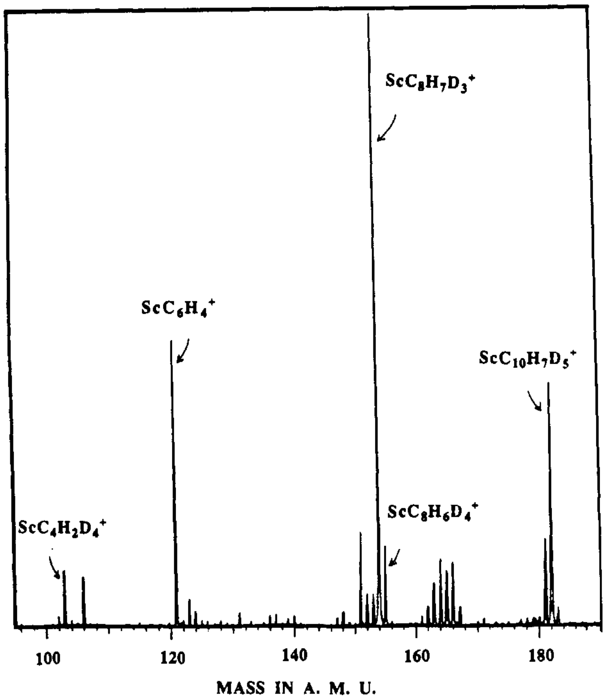


Figure 2. Reaction of Sc^+–benzyne with (1,1,1,4,4,4-D_6)-*n*-butane.

$ScC_8H_{10}^+$ is the most abundant product ion generated from *n*-butane. There are two reasonable structures for this species, Sc^+–*o*-xylene and Sc^+–ethylbenzene. This product ion is particularly interesting when compared with the chemistry of Sc^+ itself. In the reactions with alkanes larger than propane, Sc^+ forms a series of dialkyl product ions having the structure R_1–Sc^+–R_2, with CH_3–Sc^+–CH_3 for *n*-butane in particular. Beauchamp and co-workers explained the formation of this "unusual" product on the basis of the d^1s^1 electronic structure of Sc^+ by a mechanism where the reaction is initiated by Sc^+ insertion into the CH_3–C_3H_7 bond.[27] This is followed by a β-methyl abstraction from the propyl group to the metal center and subsequent ethylene elimination to yield $Sc(CH_3)_2^+$. If the same initial site is preferred for the reaction of $ScC_6H_4^+$ with *n*-butane, the reaction could proceed further by the migration of the methyl group to the benzyne ligand. The abstraction of a β-methyl group from the propyl group and its subsequent coupling with the *o*-methylphenyl ligand and ensuing ethylene elimination would give Sc^+–*o*-xylene. When the $ScC_8H_{10}^+$ ion from *n*-butane is subjected to CID, single and double dehydrogenation, as well as cleavage of the ligand is observed. For example, reactions 7–12 occur at a CID energy of 33 eV.

$$ScC_8H_{10}^+ \longrightarrow Sc^+ + (C_8H_{10}) \quad 3\% \qquad (7)$$

$$\longrightarrow ScC_6H_4^+ + (C_2H_6) \quad 10\% \qquad (8)$$

$$\longrightarrow ScC_7H_4^+ + CH_4 + H_2 \quad 8\% \qquad (9)$$

$$\longrightarrow ScC_7H_6^+ + CH_4 \quad 17\% \qquad (10)$$

$$\longrightarrow ScC_8H_6^+ + 2H_2 \quad 16\% \qquad (11)$$

$$\longrightarrow ScC_8H_8^+ + H_2 \quad 46\% \qquad (12)$$

Unfortunately, known structures of Sc^+–*o*-xylene and Sc^+–ethylbenzene could not be generated, since attempts to prepare these ions, including the generally softer ligand-exchange method, resulted in dehydrogenation of ethylbenzene and *o*-xylene. When $ScC_6D_4^+$ is reacted with *n*-butane and the resulting $ScC_8H_6D_4^+$ is isolated and subjected to CID at 33 eV, $ScC_6HD_3^+$ and $ScC_6D_4^+$ account for 38% and 62% of the fragment ion intensity in reaction 8, respectively. The same argument applied to the aforementioned ethane case supports the ethylbenzene structure over the *o*-xylene structure. Further evidence against the *o*-xylene structure comes from the reaction of $ScC_6H_4^+$ with (1,1,1,4,4,4-D_6)-*n*-butane. Figure 2 shows that there is no peak corresponding to $ScC_8H_4D_6^+$, as would be expected for the Sc^+–*o*-xylene structure. A simple mechanism can be proposed to explain the formation of Sc^+–ethylbenzene from *n*-butane (Scheme I). According to this mechanism, $ScC_8H_6D_4^+$ should be the expected main product ion. While this peak is indeed observed, surprisingly, the main peak corresponds to the formation of $ScC_8H_7D_3^+$. Thus, a reversible step has to be incorporated in Scheme I to explain the observed isotope distribution. Additionally, the reversible scrambling must occur much faster than the migratory insertion of the hydrogen atom from the metal center to the ethylphenyl ligand and there should be a significant isotope effect favoring H migration over that of D.

Scheme I

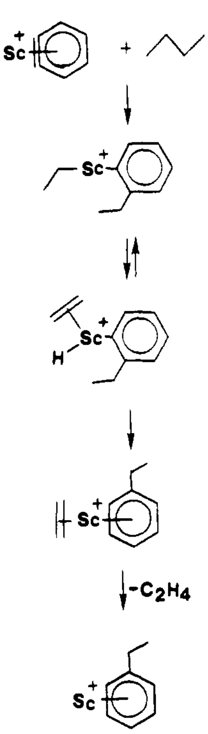


Table V. CID (%) on $ScC_9H_{10}^+$ from the Reaction of $ScC_6H_4^+$ with Propane

ion	energy, eV 15	30	48
Sc^+	1	3	4
$ScC_2H_2^+$	1	1	1
$ScC_3H_2^+$	1	2	3
$ScC_3H_4^+$	3	4	4
$ScC_4H_2^+$	1	3	5
$ScC_4H_6^+$	1	1	1
$ScC_5H_4^+$		2	3
$ScC_6H_4^+$	12	16	18
$ScC_6H_6^+$	1	2	4
$ScC_7H_4^+$		2	4
$ScC_7H_6^+$	28	22	20
$ScC_7H_8^+$	8	7	6
$ScC_9H_6^+$	5	7	7
$ScC_9H_7^+$	4	6	7
$ScC_9H_8^+$	34	22	13

The product ion, $ScC_9H_{10}^+$, formed from the reaction with propane is interesting because, in the case of $FeC_6H_4^+$, the $FeC_9H_{10}^+$ ion was found to consist of a mixture of several structures.[6] Upon CID of $ScC_9H_{10}^+$, a wide variety of fragment ions were observed, as listed in Table V for several different CID energies. Although the CID results are not very informative for its structure, the reaction with deuterated propane, (2,2-D_2)-propane, provides some very interesting insight. As is shown in Figure 3, the predominant peak for the product ion has the two deuterium atoms retained, $ScC_9H_8D_2^+$, indicating that the hydrogen atoms eliminated come from the terminal carbon atoms. Of the various conceivable structures for this ion, Sc^+–indane is the only one consistent with these labeling results. The fragment ion $ScC_9H_7^+$ in Table V is very characteristic of the indene system, as will be discussed later. Unfortunately, attempts to synthesize

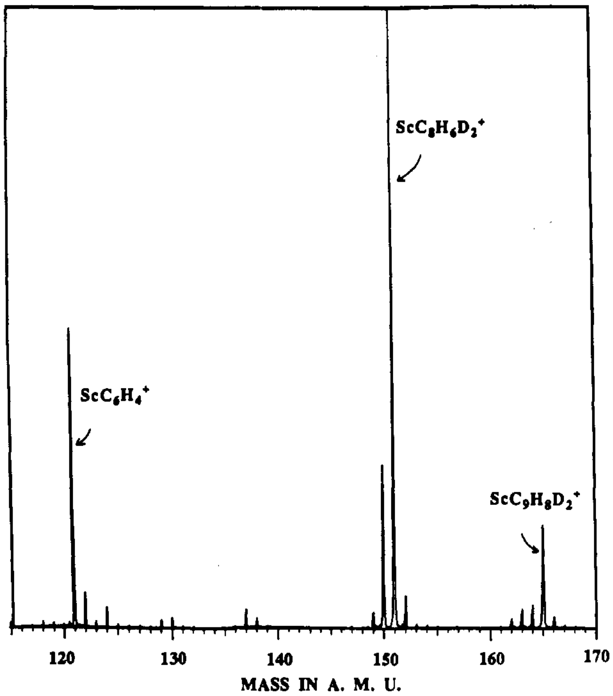
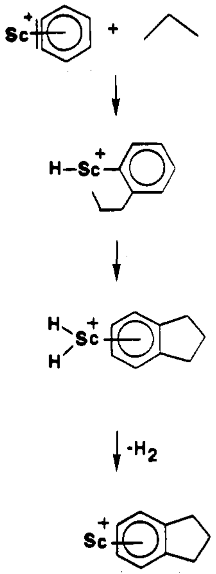
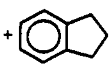


Figure 3. Reaction of Sc^+–benzyne with (2,2-D_2)propane.

Scheme II



a known structure of Sc^+–indane for CID studies proved unsuccessful. When Sc^+ is reacted with indane, however, reactions 13–19 are all observed as significant pathways, Table V. Taken

Sc^+ + 

$\longrightarrow ScC_6H_4^+ + C_3H_6$ 6% (13)

$\longrightarrow ScC_7H_4^+ + C_2H_6$ (or $C_2H_4 + H_2$) 5% (14)

$\longrightarrow ScC_7H_6^+ + C_2H_4$ 61% (15)

$\longrightarrow ScC_7H_8^+ + C_2H_2$ 9% (16)

$\longrightarrow ScC_9H_6^+ + 2H_2$ 4% (17)

$\longrightarrow ScC_9H_7^+ + H_2 + H\cdot$ 3% (18)

$\longrightarrow ScC_9H_8^+ + H_2$ 12% (19)

together, the Sc^+–indane structure is consistent with the results, and Scheme II is proposed to explain its formation from the reaction with propane.

Finally, benzyne ions can be prepared for the other two group 3 cations from the dehydrogenation of benzene by yttrium and lanthanum ions. For the reaction with propane, $YC_6H_4^+$ gives product ions very similar to that of $ScC_6H_4^+$, but at a somewhat slower rate, while the reaction for $LaC_6H_4^+$ is negligible under similar conditions. This decrease in reactivity going from Sc^+ to La^+ has been observed before for other types of ligands.[28]

Table VI. Product Distributions (%) from the Reactions of $ScC_6H_4^+$ with Alkenes

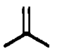
product	=						
$ScC_4H_6^+$			91	97	41	50	
$ScC_6H_6^+$			9	3			
$ScC_7H_6^+$		14			3		
$ScC_7H_8^+$		22					
$ScC_8H_6^+$	100	6					
$ScC_8H_8^+$					7		
$ScC_9H_7^+$					7		75
$ScC_9H_8^+$		58			27		
$ScC_{10}H_6^+$							5
$ScC_{10}H_8^+$					6	30	20
$ScC_{10}H_{10}^+$					9	20	

Table VII. CID (%) on $ScC_8H_6^+$ from Different Reactions[a]

	from ion–molecule reacn $ScC_6H_4^+ + C_2H_4$	from displacement reacn $ScC_2H_2^+ + C_8H_6$ (phenylacetylene)
Sc^+	14	22
$ScC_4H_2^+ + C_4H_4$	23	20
$ScC_6H_4^+ + C_2H_2$	60	53
$ScC_8H_4^+ + H_2$	3	5

[a] All data obtained at 56-eV laboratory energy.

Reactions with Alkenes. Studies on the reactions of $FeC_6H_4^+$ with small alkenes demonstrated very interesting chemistry varying significantly with the alkene size.[7] Thus, it is also of interest to study and compare the chemistry of Sc^+–benzyne with small alkenes. All of the alkenes studied react with Sc^+–benzyne (Table VI). As was observed for the alkanes, $ScC_6H_4^+$ yields a greater variety of products involving C–C bond cleavage than does Sc^+, which yields predominantly dehydrogenation products with alkenes.[29]

The only product ion formed from the reaction of Sc^+–benzyne with ethylene is $ScC_8H_6^+$. CID on the product ion yields $ScC_6H_4^+$ at 11 eV. Again, both Sc^+ and $ScC_4H_2^+$ appear upon increasing the CID energy. This CID pattern is certainly consistent with the bisligand structure Sc^+(benzyne)(acetylene). However, $ScC_8H_6^+$ reacts with benzene to yield the condensation product ion, $Sc(C_8H_6)(C_6H_6)^+$, exclusively, which undergoes CID by eliminating C_6H_6 to give back $ScC_8H_6^+$. This ion in turn fragments further to give $ScC_6H_4^+$ within the energy range studied (11–35 eV). The lack of competitive elimination of acetylene with benzene tends to exclude Sc^+(benzyne)(acetylene) as the structure and implies that C_8H_6 exists as an integral ligand. One of the most likely structures is Sc^+–phenylacetylene. Another structure, Sc^+–benzocyclobutadiene, although much less stable and less likely, cannot be simply ruled out. CID on the known structure of Sc^+–phenylacetylene, prepared from the displacement reaction of phenylacetylene with Sc^+–acetylene, gives the same CID pattern within experimental error (Table VII). CID at 33 eV on $ScC_8H_2D_4^+$ obtained by reacting $ScC_6D_4^+$ with ethylene yields 69% $ScC_6D_4^+$ and 31% $ScC_6D_3H^+$ for the Sc^+–benzyne fragment. The same argument applied for the Sc^+–styrene case indicates a Sc^+–phenylacetylene structure rather than the benzocyclobutadiene structure.

Sc^+–benzyne reacts with propene to give reactions 20–23. The product ion structures in reactions 21 and 20 are presumably

$ScC_6H_4^+ + C_3H_6 \longrightarrow ScC_7H_6^+ + C_2H_4$ 14% (20)

$\longrightarrow ScC_7H_8^+ + C_2H_2$ 22% (21)

$\longrightarrow ScC_8H_6^+ + CH_4$ 6% (22)

$\longrightarrow ScC_9H_8^+ + H_2$ 58% (23)

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(28) Huang, Y.; Wise, M. B.; Jacobson, D. B.; Freiser, B. S. *Organometallics* **1987**, *6*, 346.

(29) Lech, L. M.; Freiser, B. S. *Organometallics* **1988**, *7*, 1949.

Table VIII. CID (%) on $ScC_9H_8^+$ from Different Reactions[a]

	from ion-molecule reacn $ScC_6H_4^+ + C_3H_6$	from condensation reacn $Sc^+ + C_9H_8$ (indene)
$Sc^+ + C_9H_8$	16	19
$ScC_5H_4^+ + C_4H_4$	5	1
$ScC_6H_6^+ + C_3H_2$	5	1
$ScC_7H_4^+ + C_2H_4$	9	14
$ScC_7H_6^+ + C_2H_2$	22	19
$ScC_9H_6^+ + H_2$	16	19
$ScC_9H_7^+ + H^\bullet$	27	27

[a] All data obtained at 40-eV laboratory energy.

toluene and dehydrogenated toluene, respectively. Upon reaction of $ScC_7H_8^+$ from reaction 21 with styrene, the condensation product $Sc(C_7H_8)(C_8H_8)^+$ at m/z 241 is formed. Subsequent CID on the condensation product at 21 eV collision energy yields approximately 22% $ScC_7H_8^+$, 70% $ScC_8H_8^+$, and 8% $ScC_8H_6^+$, suggesting competitive elimination of intact C_7H_8 and C_8H_8 ligands. The condensation product at m/z 241 was also prepared by the reaction sequence 24 and 25. CID on this ion gives the

$$\mathrm{Sc^+ + methylcyclohexane \longrightarrow Sc^+\text{-}toluene + 3H_2} \qquad (24)$$

$$\mathrm{Sc^+\text{-}toluene + styrene \longrightarrow Sc(C_7H_8)(C_8H_8)^+} \qquad (25)$$

identical results described above. These data support a Sc^+–toluene structure for the $ScC_7H_8^+$ product ion in reaction 21. If, for example, the structure of this ion had been $Sc(benzene)CH_2^+$, which would arise if reaction 21 was a simple carbene abstraction, the loss of C_6H_6 would have been observed in the CID experiments. Finally, Fe^+–toluene is the only product ion from the reaction of Fe^+–benzyne with propene.[7]

CID on $ScC_9H_8^+$ from reaction 23 at 48 eV gives a number of product ions (reactions 26–32). The fragment in reaction 32

$$\mathrm{ScC_9H_8^+ \longrightarrow Sc^+ + (C_9H_8)} \qquad 16\% \qquad (26)$$

$$\mathrm{\longrightarrow ScC_5H_4^+ + (C_4H_4)} \qquad 5\% \qquad (27)$$

$$\mathrm{\longrightarrow ScC_6H_6^+ + C_3H_2} \qquad 5\% \qquad (28)$$

$$\mathrm{\longrightarrow ScC_7H_4^+ + C_2H_4} \qquad 9\% \qquad (29)$$

$$\mathrm{\longrightarrow ScC_7H_6^+ + C_2H_2} \qquad 22\% \qquad (30)$$

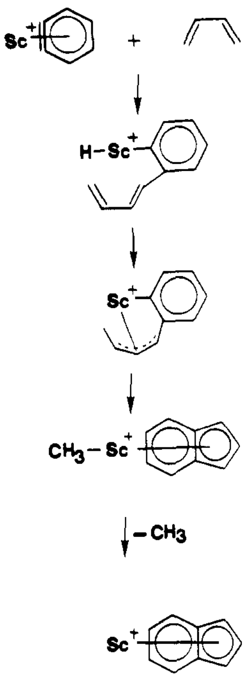
$$\mathrm{\longrightarrow ScC_9H_6^+ + H_2} \qquad 16\% \qquad (31)$$

$$\mathrm{\longrightarrow ScC_9H_7^+ + H^\bullet} \qquad 27\% \qquad (32)$$

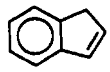
is most unusual in its formulation of an odd number of hydrogen atoms, and it will be discussed in more detail later. Both products in reactions 31 and 32 are observed when Sc^+ reacts with indene. In addition, the $ScC_9H_8^+$ condensation product from the reaction of Sc^+ with indene gives the same CID fragmentation pattern within experimental error (Table VIII). All these results suggest the likelihood of a Sc^+–indene structure for the product ion in reaction 23.

Both *cis*- and *trans*-2-butene react very similarly with Sc^+–benzyne to give mostly $ScC_4H_6^+$, presumably Sc^+–butadiene, and a minor amount of Sc^+–benzene. Both reactions probably proceed via initial Sc^+ interaction with an allylic C–H bond in a multicentered process to form the (methylallyl)phenylscandium cation. Subsequent hydrogen abstraction from the methyl group and its coupling with the phenyl group give Sc^+(butadiene)(benzene). With $D°(Sc^+\text{–butadiene}) > D°(Sc^+\text{–benzene})$, the competitive elimination of the benzene ligand is favored. As can be seen in Table VI, the reaction with 1-butene gives several more product ions than 2-butene. If the reaction with 1-butene only proceeds via initial Sc^+ interaction with the allylic C–H bond, as in the case of 2-butene, this should give the same product ions as 2-butene. The additional product ions observed, therefore, suggest that Sc^+ attacks some other reactive sites, such as the allylic C–C or terminal C–H bond. Again, here the unusual $ScC_9H_7^+$ product is observed.

Scheme III



The reaction with butadiene is very interesting because of the prominent $ScC_9H_7^+$ as its major product ion. Its frequent occurrence and unusual formulation suggest a high stability for this species. No reaction or H/D exchange is observed with H_2, D_2, and C_2D_4, despite its high degree of unsaturation. The high stability is also evident from the lack of fragmentation up to a CID energy of 75 eV under our experimental conditions, in sharp contrast with the usual high efficiency of dissociation for other Sc^+–hydrocarbon ions. Similarly, $ScC_9H_7^+$ generated in reaction 18 undergoes no discernible CID fragmentations under the same conditions. Structure IV seems to be consistent with such a high stability. A study by Gross and co-workers indicated that a wide variety of precursor ions can fragment and rearrange to the indenyl structure in structure IV.[30] When Sc^+ reacts with indene, reactions 33–35 occur. Again, the ion from reaction 34 does not

$$\mathrm{Sc^+ +}$$  $$\mathrm{\longrightarrow ScC_9H_6^+ + H_2} \qquad 27\% \qquad (33)$$

$$\mathrm{\longrightarrow ScC_9H_7^+ + H^\bullet} \qquad 54\% \qquad (34)$$

$$\mathrm{\longrightarrow ScC_9H_8^+} \qquad 19\% \qquad (35)$$

dissociate well under our CID conditions, supporting the assignment of structure IV. Finally, a somewhat speculative mechanism (Scheme III) is proposed to explain the formation of structure IV from the reaction with butadiene.

IV

Conclusion

Sc^+–benzyne displays some interesting chemistry with the neutral species used in this study. It not only undergoes hydrogenation with H_2 and D_2 but also gives H/D exchange with the latter. $ScC_6H_4^+$ can undergo oxygen abstraction with certain oxygen-containing species XO to give ScO^+. Interestingly, thermodynamic considerations indicate that the ability to form a stable C_6H_4X compound with benzyne is a key factor in determining the occurrence of such a reaction.

All of the alkanes studied, with the exception of methane, react readily with $ScC_6H_4^+$. Its reaction with ethane gives both the hydrogenation product $ScC_6H_6^+$ and Sc^+–styrene, the latter also being formed from the reaction with propane. Sc^+–indane is, presumably, the main contributing structure for the $ScC_9H_{10}^+$ ion formed from the reaction with propane. The product ion $ScC_8H_{10}^+$, formed from the reaction with *n*-butane, is proposed

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(30) Dass, C.; Gross, M. L. *Org. Mass Spectrom.* **1983**, *18*, 542.

to be Sc^+–ethylbenzene rather than Sc^+–*o*-xylene. This suggests initial cleavage of the central C–C bond, in contrast to bare Sc^+, where preference for the terminal C–C bond is observed.

All of the alkenes studied also react with $ScC_6H_4^+$ to give a variety of product ions. Its reaction with ethylene appears to give Sc^+–phenylacetylene, exclusively. One of the frequently observed ions in this study is $ScC_9H_7^+$. Its unusual formulation and low CID efficiency all indicate a high stability for this ion, with its structure most likely being that of indenylscandium ion.

Acknowledgement is made by B.S.F. to the Division of Chemical Sciences in the Office of Basic Sciences in the United States Department of Energy (Grant DE-FG02-87ER13766) for supporting this research and to the National Science Foundation (Grant CHE-8920085) for continued support of FTMS methodology. M.S. gratefully acknowledges the Fulbright Fund for fellowship support.

Registry No. Sc^+, 14336-93-7; C_6H_6, 71-43-2; $ScC_6H_6^+$, 107494-94-0; ScC_6H_4, 135865-29-1; ScO^+, 134627-16-0; CH_4, 74-82-8; C_2H_6, 74-84-0; C_3H_8, 74-98-6; *n*-C_4H_{10}, 106-97-8; *i*-C_4H_{10}, 75-28-5; *n*-C_5H_{12}, 109-66-0; *neo*-C_5H_{12}, 463-82-1.

Contribution from the Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6226,
and Chemistry Department, University of Virginia, Charlottesville, Virginia 22901

Matrix Infrared Spectra of HCl Complexes with UF_6, WF_6, and MoF_6

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Received December 20, 1990

HCl complexes with UF_6, WF_6, and MoF_6 were prepared in solid argon at 12 K. The FTIR spectrum of UF_6/HCl contained a doublet at 2850.6 and 2849.7 cm^{-1} due to the hydrogen-bonded UF_6–HCl complex. In contrast, the HCl interaction with WF_6, as well as MoF_6 produced two distinctly different 1:1 complexes. The 2862.1-cm^{-1} absorption due to the antihydrogen-bonded complex, WF_6–ClH, was slightly more intense than the 2866.2-cm^{-1} absorption of the hydrogen-bonded complex, WF_6–HCl. The frequencies and relative intensities of the absorptions for the MoF_6 complexes with HCl were very similar to those of their WF_6 counterparts.

Introduction

Hydrogen bonds and Lewis acid–base interactions play important roles in determining the intermolecular structures and the properties of weak complexes. The possibility of direct competition between these two means of intermolecular binding has been the focus of several recent investigations.[1-6] The Cl_2 and ClF complexes with HF serve as prime examples of this competition. Even though the molecular beam electric resonance studies[1,2] have only detected the Cl_2–FH and FCl–FH complexes, the most recent ab initio calculations[3] have shown that the hydrogen-bonded complexes, Cl_2–HF and ClF–HF, are only slightly less stable than their antihydrogen-bonded counterparts. These theoretical results have been confirmed by a matrix infrared investigation[4] of HF complexes with Cl_2 and ClF. In this matrix IR study, complexes with both structural arrangements were characterized because the matrix cage quickly quenches internal energy and prevents rearrangement. In contrast to the HF complexes, a matrix IR investigation[5] on HCl complexes with Cl_2 and ClF detected only the hydrogen-bonded complexes, Cl_2–HCl and ClF–HCl.

The most recent case of direct competition between hydrogen bonding and Lewis acid–base interactions involved a matrix IR investigation[6] on HF complexes with UF_6, WF_6, and MoF_6. While the UF_6–HF complex was more stable than the UF_6–FH complex, HF complexes with WF_6 and MoF_6 preferred the antihydrogen-bonded arrangements. The characterization of the HF complexes with metal hexafluorides can be corroborated by substituting HCl for HF since the larger covalent radius of chlorine in HCl should significantly reduce the preference for antihydrogen-bonded complexes. The present study reports the infrared observation and characterization of HCl complexes with UF_6, WF_6, and MoF_6.

Experimental Section

The apparatus and spectroscopic techniques for the hydrogen halide experiments with the metal hexafluorides in solid argon at 12 K have been described in detail earlier.[4] Samples of UF_6, WF_6, MoF_6 (Oak Ridge National Laboratory), HCl (Matheson), and DCl (MSD Isotopes) were condensed at 77 K and evacuated to remove any volatile impurities. HCl and DCl were codeposited from passivated stainless-steel manifolds. Samples were diluted between 100/1 and 200/1 mol ratios with argon (Air Products) and deposited on a CsI window at total rates of 14–17 mmol/h for 3.3–3.8 h. In order to promote further aggregation of the HCl, each matrix was annealed to 25 K for 10 min and then recooled to 12 K. Finally, each matrix was warmed to 30 K for an additional 10 min and then cooled back to 12 K. IR spectra were obtained before, during, and after the sample codeposition as well as after the matrix annealings. All spectra were recorded on a Nicolet 7199 FTIR spectrometer at resolutions ranging from 0.24 to 1.0 cm^{-1}.

Results

Matrix infrared observations of UF_6, WF_6, and MoF_6 complexes with HCl and DCl will be described in turn.

Uranium Hexafluoride. A series of uranium hexafluoride experiments were conducted with hydrogen chloride at different concentrations in argon at 12 K. After the most concentrated samples were deposited, the spectrum in Figure 1a shows absorptions due to the HCl monomer (labeled HCl, Q and P bands), dimer (labeled D), and trimer (labeled T); these band positions are in agreement with earlier matrix IR studies.[7,8] Absorptions for the N_2–HCl and $N_2(HCl)_2$ complexes[8] (labeled N and M, respectively) were also observed. Due to the small HF and DF impurities in the hexafluoride sample, absorptions due to the HF–HCl and HCl–DF complexes[9] were also detected at 2834.5, 2832.5, and 2807.2 cm^{-1}. A new product absorption at 2850.5 cm^{-1} (labeled ν_s) appeared as a shoulder of the P branch of HCl. The spectra at a resolution of 0.24 cm^{-1} clearly revealed that this new shoulder was actually a doublet at 2850.6 and 2849.7 cm^{-1}. In addition, weak product absorptions were observed at 2827.2 and 2805.0 cm^{-1} (labeled ν_{sa} and ν_{sb}, respectively). No perturbed UF_6 modes were observed. The spectrum in Figure 1b exhibits the effect of annealing the matrix to 30 K for 10 min. While the

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