Gas-Phase Chemistry of $Sc(CH_3)_2^+$ with Alkenes: Activation of Allylic C-H Bonds by a d^0 System and the Migratory Insertion of C=C Bonds into Sc^+-CH_3 Bonds

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Abstract: The gas-phase chemistry of $Sc(CH_3)_2^+$ with alkenes was studied by Fourier transform mass spectrometry. The metal center on $Sc(CH_3)_2^+$ is d^0, providing an opportunity to study alternative mechanisms of C-C or C-H activation other than the most common one involving oxidative addition. The elimination of H_2 is observed in the reaction of $Sc(CH_3)_2^+$ with ethylene, and the product $ScC_4H_8^+$ further reacts with ethylene to form the dehydrogenation product, $ScC_6H_{10}^+$. Structure studies indicate that the $ScC_4H_8^+$ and $ScC_6H_{10}^+$ ions have a metal(methyl)(allyl) and metal-bisallyl structure, respectively, consistent with a proposed reaction mechanism involving the consecutive migratory insertion of ethylenes into the scandium-methyl bonds. In addition, theoretical calculations indicate that the metal(methyl)(allyl) structure is between 10 and 20 kcal/mol more stable than the metal(1-butene) isomer. $Sc(CH_3)_2^+$ reacts with propene to form predominantly $ScC_4H_8^+$ by loss of CH_4, with minor amounts of $ScC_3H_4^+$ and $ScC_4H_6^+$ also observed. $ScC_4H_6^+$ is formed as either the exclusive or the predominant product ion in the reactions of $Sc(CH_3)_2^+$ with butenes. $Sc(CH_3)_2^+$ reacts with cyclopentene to form predominantly $ScC_6H_8^+$ by losing CH_4 and H_2. The further reaction of $ScC_6H_8^+$ with cyclopentene forms scandocenium, $ScC_{10}H_{10}^+$. The reactions of cyclohexene and cycloheptene with $Sc(CH_3)_2^+$ are analogous to that of cyclopentene. Isotope labeling studies with $Sc(CD_3)_2^+$ and other structure studies indicate that all of the alkenes studied, with the exception of ethylene, react with $Sc(CH_3)_2^+$ via a multicentered σ-bond metathesis mechanism to activate allylic C-H bonds. Finally, the dehydrogenation reactions of Sc^+ with *n*-butane and neopentane were revisited, and a new mechanism is proposed for such chemistry in light of the new results from this study.

Introduction

One important aspect of gas-phase transition-metal ion chemistry which continues to be the focus of detailed study is the activation of C-C and C-H bonds in small hydrocarbons.[1-9] In general these reactions are initiated by the oxidative insertion of the metal center, facilitated by its low oxidation state and high degree of unsaturation. Alternative pathways to activate C-C or C-H bonds can be probed, however, when the metal center does not have the minimum of two unpaired valence electrons required for oxidative insertion. Thus far, such alternative pathways in the gas phase have received relatively little attention, despite the fact that there have been several examples in solution.[10-13] A few recent studies in the gas phase indicate that such processes could be of general significance. For example, both La^{2+} and Y^{2+} react with small alkanes despite their having a d^1 electronic structure, but still little is known about the mechanisms of such activation.[14,15] Another example is the formation of Cp_2ZrD^+ and CH_3D upon reacting $Cp_2ZrCH_3^+$ with D_2 in the gas phase.[16] This reaction was explained by a process involving a four-centered intermediate including the d^0 zirconium center, the methyl group, and the two deuterium atoms in D_2. Such a process has been termed σ-bond metathesis,[10-13] in analogy to the more common metathesis involving an alkene and a metal-carbene system. Although such a process is normally observed for d^0 systems, a recent study on the d^1 system, YCH_3^+,[17] indicates that for this case, activation of allylic C-H bonds by σ-bond metathesis is preferred over the better-known pathway of migratory insertion by C=C bonds into metal-carbon σ-bonds. Migratory insertion is a facile process involved in many known condensed-phase processes, such as alkene polymerization and Ziegler-Natta catalysis.[18]

Experimental Section

All experiments were performed on a prototype Nicolet FTMS-1000 Fourier transform mass spectrometer.[19] The instrument is equipped with a 5.2-cm cubic trapping cell situated between the poles of a Varian 15-in. electromagnet maintained at 0.9 T. The cell utilizes stainless steel screens with 80% transmittance as the transmitting plates, permitting the irradiation of the interior with various 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 target of scandium. Details of the laser desorption experiment are described elsewhere.[20,21]

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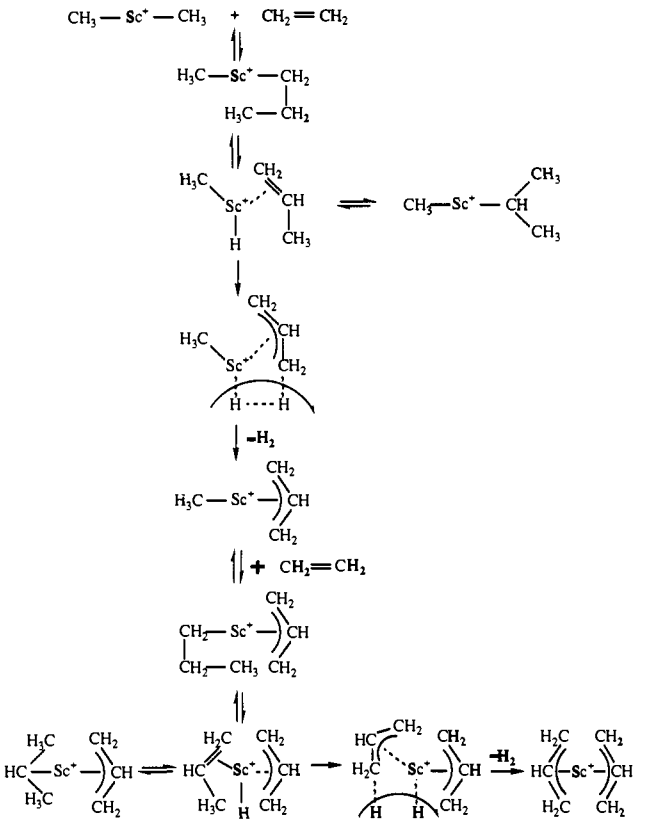
Scheme I



All chemicals were obtained in high purity from commercial sources and used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensible gases. Sample pressures were measured with an uncalibrated Bayard–Alpert type ionization gauge and were typically ~6 × 10^{-6} Torr for samples and ~4 × 10^{-5} Torr for background argon used for collision-induced dissociation.

Details of the collision-induced dissociation (CID) experiment have been described previously.[22,23] The laboratory collision energy can be varied typically in the range 0–150 eV (laboratory frame). The spread in kinetic energy depends on the average kinetic energy and is typically about 35% at 1 eV, 10% at 10 eV, and 5% at 30 eV.[24]

$Sc(CH_3)_2^+$ was prepared from the reaction of Sc^+ with *n*-butane.[25] *n*-Butane was introduced into the vacuum chamber through a General Valve Corporation Series 9 pulsed solenoid valve.[26] The pulsed reagent gas fills the chamber to a maximum pressure of about 10^{-5} Torr with about a 150-ms rise time and is pumped away by a high-speed 6-in. diffusion pump in about 400 ms. The reactant ion was then isolated by a swept double resonance experiment[27] and trapped in the background pressure of another reagent to study its chemistry. *1,1,1,4,4,4-d_6-n*-Butane purchased from MSD Isotopes with at least 98% isotope purity was used to prepare $Sc(CD_3)_2^+$ for the deuterium labeling experiments. The product ion distributions are reproducible to ±10% absolute for primary product ions and ±15% for CID fragmentation ions.

In the calculations on the relative stabilities of two $ScC_4H_8^+$ isomers, the geometries were fully optimized at the self-consistent-field (SCF) level. The second derivatives confirmed that the optimized structures are minima and not transition states. Using these SCF geometries, the binding energies were computed at the modified coupled-pair-functional (MCPF) level.[28] The basis sets were of valence double ζ quality. The (9s 5p)/[3s 2p] carbon and (scaled) (4s)/[2s] hydrogen basis sets are

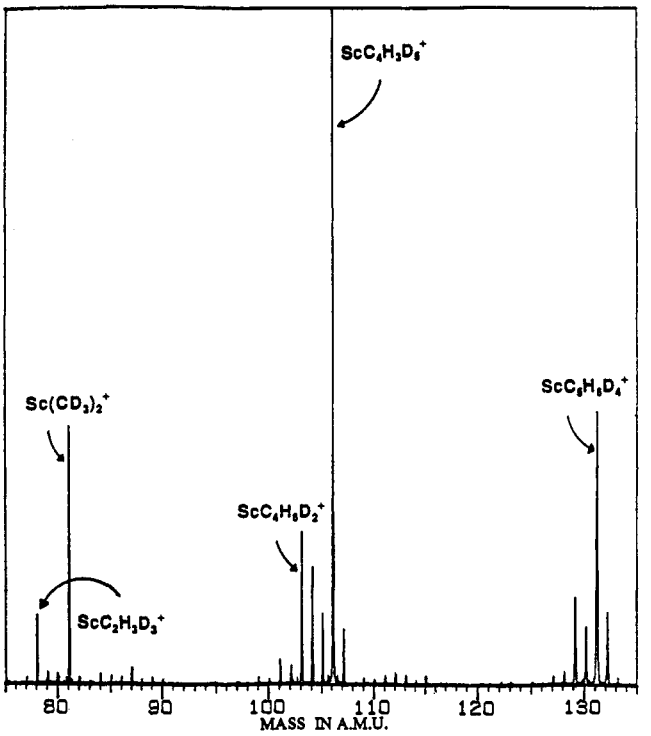


Figure 1. Primary and secondary reactions of $Sc(CD_3)_2^+$ with ethylene.

Table I. Branching Ratios for the Primary Reaction of $Sc(CD_3)_2^+$ with C_2H_4

product ion	percentage	product ion	percentage
$ScC_2H_3D_3^+$	21%	$ScC_4H_4D_4^+$	5%
$ScC_2H_2D_4^+$	<1%	$ScC_4H_3D_5^+$	69%
$ScC_2HD_5^+$	<1%	$ScC_4H_2D_6^+$	5%

those given by Dunning and Hay.[29] The (14s 11p 6d)/[8s 6p 4d] Sc basis set was derived from the set of Wachters[30] with two diffuse p and one diffuse d function added.[31] The small basis sets keep the calculations tractable but restrict the binding energies to qualitative accuracy. On the basis of previous studies,[32] it is expected that the binding energies will be about 7 kcal/mol too small for triplet states and about 15 kcal/mol too small for singlet states.

Results and Discussion

$Sc(CH_3)_2^+$ is reactive with all of the alkenes studied. For some alkenes, the two methyl groups seem to react independently, while for other alkenes, both methyl groups interact with each other.

Ethylene. $ScC_4H_8^+$ and $ScC_6H_{10}^+$ are observed as the only primary and secondary product ions, respectively, for the reaction of $Sc(CH_3)_2^+$ with ethylene, reactions 1 and 2. The reactions

$$Sc(CH_3)_2^+ + C_2H_4 \rightarrow ScC_4H_8^+ + H_2 \quad (1)$$

$$ScC_4H_8^+ + C_2H_4 \rightarrow ScC_6H_{10}^+ + H_2 \quad (2)$$

can each be explained by the migratory insertion of ethylene into the Sc^+–CH_3 bond, followed by H_2 elimination, as shown in Scheme I. CID on the primary product ion at 16 eV (laboratory) yields reactions 3–7. Scheme I predicts (methyl)(allyl)scandium

$$ScC_4H_8^+ \xrightarrow{CID} Sc^+ + (C_4H_8) \quad 5\% \quad (3)$$

$$\rightarrow ScC_3H_2^+ + CH_4 + H_2 \quad 5\% \quad (4)$$

$$\rightarrow ScC_3H_4^+ + CH_4 \quad 56\% \quad (5)$$

$$\rightarrow ScC_4H_4^+ + 2H_2 \quad 5\% \quad (6)$$

$$\rightarrow ScC_4H_6^+ + H_2 \quad 29\% \quad (7)$$

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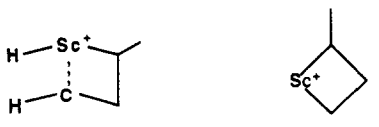
ion, structure I, as the structure for the primary product ion. The loss of CH_4 in reactions 4 and 5 is consistent with this structure.

I II

While CID does not provide conclusive structural information in this case, a deuterium labeling study sheds some light on both the product structures and the reaction mechanism. $Sc(CD_3)_2^+$ reacts with ethylene to give predominantly $ScC_4H_3D_5^+$, Figure 1. Table I lists the branching ratios for the primary product ions from the deuterated reaction. This ion then reacts with another ethylene molecule to produce $ScC_6H_6D_4^+$ as the predominant product ion in reaction 2. CID on the primary product ion, $ScC_4H_3D_5^+$, at 24 eV gives 83% loss of CD_3H and 17% loss of CD_4 for reaction 5, consistent with structure I. These labeling results also indicate that the hydrogen atom on the middle carbon of the allyl group is involved in methane elimination, suggesting that a Sc^+–allene structure, not Sc^+–propyne, is the most likely CID product ion in reaction 5. Taken as a whole, these results are consistent with the mechanism of consecutive migratory insertion depicted in Scheme I. It is interesting to note that a peak corresponding to $ScC_2H_3D_3^+$ emerges in Figure 1. This suggests a reversible rearrangement of (methyl)(propyl)scandium ion to (methyl)(isopropyl)scandium ion in analogy to a similar process observed for the reaction of YCH_3^+ with C_2D_4 to form YCD_3^+, as is outlined in Scheme I. The consecutive reactions of the two methyl groups by migratory insertion is particularly interesting considering that the elimination of a methane molecule after β-hydrogen abstraction could have occurred to give Sc^+(propene). Instead, H_2 elimination occurs. Because of the d^0 electronic structure on the Sc^+ center, dehydrogenation can only be explained by a multicentered σ-bond metathesis mechanism involving the metal, two hydrogen atoms, and the allyl group, Scheme I.[17]

To provide additional support for the proposed Structure I, $ScC_4H_8^+$ formed from the reaction of Sc^+ with *n*-butane was also studied. Upon reacting Sc^+ with *1,1,1,4,4,4-d*$_6$-*n*-butane in this study, 95% of the dehydrogenation occurs by HD elimination, along with 5% D_2 elimination also observed, ruling out 2,3-elimination. A simple 1,2-dehydrogenation by initial C–H bond insertion followed by β-hydrogen abstraction and subsequent H_2 elimination would result in both Sc(1-butene)$^+$, structure II, and Sc(2-butene)$^+$, respectively. Given the absence of 2,3-dehydrogenation, it seems unlikely that a simple 1,2-dehydrogenation process would account for this dehydrogenation product ion, strongly disfavoring structure II for the $ScC_4H_8^+$ ion formed from the reaction of Sc^+ with *n*-butane. Tolbert and Beauchamp first studied the chemistry of Sc^+ with alkanes and suggested its preference for 1,3-dehydrogenation processes.[25] They explained such a dehydrogenation pattern in the case of *n*-butane in terms of a four-centered concerted intermediate formed after initial Sc^+ insertion into one of the C–H bonds on the inner carbon atoms, structure III, which would then lose H_2 to give structure IV. CID

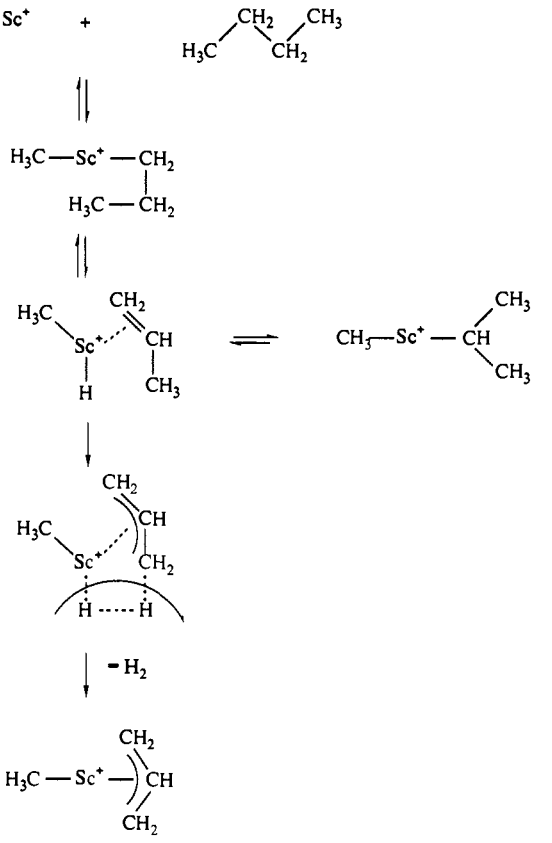


III IV

of the $ScC_4H_8^+$ ion formed from the reaction of Sc^+ with *n*-butane gives fragmentation patterns identical to that of the product ion from reaction 1 within experimental variations. These two ions also show identical reactivities with ethylene, propene, and benzene. For example, both ions from reaction 1 and from the reaction of Sc^+ with *n*-butane undergo reactions 8 and 9 with perdeuterated benzene. Thus, these results suggest that these two ions have

		Sc^+ + *n*-butane	rctn 1	
$ScC_4H_8 + C_6D_6 \longrightarrow$	$Sc(C_3H_4)(C_6D_6)^+ + CH_4$	30%	33%	(8)
$\longrightarrow$	$Sc(C_4H_6)(C_6D_6)^+ + H_2$	70%	67%	(9)

Scheme II



identical structure. In light of these results, we propose an alternative mechanism for the dehydrogenation of *n*-butane by Sc^+, Scheme II, in which the reaction proceeds by initial Sc^+ insertion into the CH_3–C_3H_7 bond. Note that this gives the same intermediate as in Scheme I after initial ethylene migratory insertion. This is followed by a β-hydrogen abstraction from the propyl group to Sc^+ and subsequent σ-bond metathesis to give (methyl)(allyl)scandium ion. Scheme II indicates a 1,2-dehydrogenation process, in contrast to 1,3-dehydrogenation proposed earlier.[25] However, it should be noted that when *1,1,1,4,4,4-d*$_6$-*n*-butane is used, we cannot distinguish between a 1,2- and 1,3-dehydrogenation process. The suggested preference for 1,3-dehydrogenation of Sc^+ was based on results from the deuterated *n*-butane, *2-d*-2-methylpropane, and *2,2-d*$_2$-propane. A 1,2-dehydrogenation via the mechanism proposed in Scheme II would still be consistent with the earlier observations. In the reaction of Sc^+ with the deuterated *n*-butane from this study, $ScC_2H_3D_3^+$ accounts for 26% of the scandium dimethyl product ions, along with 70% $ScC_2D_6^+$ and 4% $ScC_2HD_5^+$. This compares favorably with the 18% of $ScC_2H_3D_3^+$, 62% of $ScC_2D_6^+$, and less than 7% for any other scrambling product ions for the same reaction reported in the earlier study.[25] Such a high abundance of $ScC_2H_3D_3^+$ from the reaction of Sc^+ with *1,1,1,4,4,4-d*$_6$-*n*-butane again gives strong support for Schemes I and II. Scheme II predicts a $Sc(CD_3)(C_3H_3D_2)^+$ structure from the dehydrogenation reaction of Sc^+ with *1,1,1,4,4,4-d*$_6$-*n*-butane. This should have the same structure as the primary product from the reaction of $Sc(CD_3)_2^+$ with ethylene. This is verified by its reaction with ethylene, which results in the elimination of HD to give $ScC_6H_6D_4^+$, identical to the secondary reaction of $Sc(CD_3)_2^+$ with ethylene. Also, its reaction with propene results in the elimination of CHD_3, consistent with structure I, with the methyl group being perdeuterated, as will be obvious from the following discussion of the chemistry of $Sc(CH_3)_2^+$ with propene.

Finally, theoretical calculations were performed to provide further support for structure I. Insertion of Sc^+ into a C–C bond to form CH_3–Sc^+–allyl yields a singlet state. The computed energy for reductive elimination of 1-butene from this state is 38.7

kcal/mol. A bond energy of about 54 kcal/mol is predicted after accounting for limitations in the calculation. For Sc^+–1-butene, both the lowest triplet and singlet states were considered. The computed binding energies are 21.7 kcal/mol for the triplet and 17.6 kcal/mol for the singlet, leading to the best estimates of 29 and 33 kcal/mol, respectively. Both states of Sc^+–1-butene are, therefore, substantially less stable than CH_3–Sc^+–allyl. Although the calculations are qualitative in nature, the energy difference between structures I and II is sufficiently large that the calculations can be taken to support structure I over structure II.

While it is reasonably established that the product ions from both reaction 1 and from the dehydrogenation reaction of Sc^+ with *n*-butane have structure I, the evidence also points to the tendency of structure I to rearrange to structure II under collisional activation or upon its reaction with a neutral reactant. For example, CID at 22 eV on the product ion in reaction 9 from both sources gives $ScC_4H_6^+$ as the only product, suggesting the competitive elimination between a 1,3-butadiene ligand and a benzene ligand. The detachment of the benzene ligand as the only process observed is consistent with an earlier study and with $D^0(Sc^+$–butadiene) > $D^0(Sc^+$–benzene).[33] Thus, this suggests that upon the influence of an incoming benzene ligand, the ion with an initial structure I rearranges into one with structure II, which then loses a hydrogen molecule. Also, reactions 6 and 7 suggest that upon activation, rearrangement of I by coupling the methyl and the allyl ligand readily occurs to give Sc^+–butene, structure II, which subsequently undergoes dehydrogenation. Finally, CID at 24 eV on the product ion from reaction 8 from both sources of $ScC_4H_8^+$ gives exclusive formation of $ScC_3H_4^+$, suggesting the competitive elimination between a benzene and an allene ligand. The tendency of structure I to lose a methane molecule to give Sc^+–allene is also evident from reaction 5.

Propene. Reactions 10–13 were observed for $Sc(CH_3)_2^+$ with propene. A migratory insertion by the C=C moiety into

$$Sc(CH_3)_2^+ + C_3H_6 \rightarrow ScC_3H_4^+ + 2CH_4 \quad 8\% \quad (10)$$

$$\rightarrow ScC_4H_6^+ + CH_4 + H_2 \quad 12\% \quad (11)$$

$$\rightarrow ScC_4H_8^+ + CH_4 \quad 80\% \quad (12)$$

Sc^+—CH_3 is again plausible and may be used to explain most of the primary products. Upon reacting $Sc(CD_3)_2^+$ with propene, reaction 11 gives $ScC_4H_4D_2^+$ and reaction 12 yields $ScC_4H_5D_3^+$, exclusively, the latter suggesting the retention of one deuterated methyl group. If the reaction proceeds by migratory insertion, the intermediates expected would be CD_3–Sc^+–$CH(CH_3)CH_2CD_3$ and CD_3–Sc^+–$CH_2CH(CH_3)(CD_3)$. Subsequent elimination of a methane molecule arising from the methyl group and a β-hydrogen would result in both $Sc(CH_2CHCH_2CD_3)^+$ and $Sc(CH_3CHCHCD_3)^+$ from CD_3–Sc^+–$CH(CH_3)CH_2CD_3$, while CD_3–Sc^+–$CH_2CH(CH_3)(CD_3)$ would yield $Sc(CH_2C(CH_3)CD_3)^+$. Such a mechanism involves a CD_3H elimination and is certainly consistent with the observed isotope distribution of reaction 12. However, a brief examination of the secondary reactions with $Sc(CD_3)_2^+$ as the reactant ion points to the functioning of an alternative mechanism. Reactions 13 and 14 were observed upon reacting another propene molecule with $ScC_4H_8^+$ from reaction 12. $ScC_6H_{10}^+$ is formed exclusively in reaction 13 upon

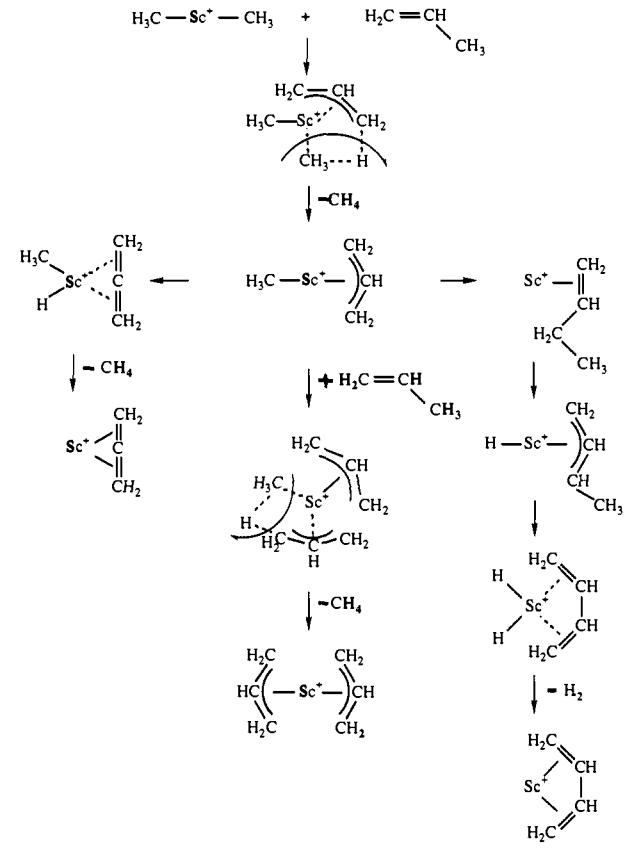
$$ScC_4H_8^+ + C_3H_6 \rightarrow ScC_6H_{10}^+ + CH_4 \quad 88\% \quad (13)$$

$$\rightarrow ScC_7H_{12}^+ + H_2 \quad 12\% \quad (14)$$

reacting propene with $Sc(CD_3)(C_3H_5)^+$ generated from $Sc(CD_3)_2^+$ in reaction 12. It is highly unlikely for any of the potential migratory insertion product ions mentioned above, namely, $Sc(CH_2CHCH_2CD_3)^+$, $Sc(CH_3CHCHCD_3)^+$, and $Sc(CH_2C(CH_3)CD_3)^+$, to give such exclusive CD_3H elimination.

An alternative pathway for methane elimination after the initial migratory insertion step to form CD_3–Sc^+–$CH(CH_3)CH_2CD_3$, however, can also be postulated. β-hydrogen abstraction from the CH_3 group by the metal center and a subsequent σ-bond metathesis involving the metal center, the hydrogen atom on the metal center, and the CD_3 group on the resulting 1-butene ligand, in much the same manner as H_2 elimination in Scheme I, would yield the metal–allyl structure I. However, no such CD_3H elimination is possible after a β-hydrogen abstraction from the CH_2 group, which should be as likely as that from the CH_3 group. In contrast, H_2 elimination via σ-bond metathesis involving the metal center, the hydrogen atom on the metal center, and an allylic hydrogen atom should be competitive with such a CD_3H elimination after a β-hydrogen abstraction from the CH_3 group. Furthermore, H_2 would be the exclusive elimination product after a β-hydrogen abstraction from the CH_2 group. The absence of dehydrogenation from the primary reaction of $Sc(CH_3)_2^+$ with propene provides strong evidence against such a process. Moreover, a similar process for CD_3–Sc^+–$CH_2CH(CH_3)(CD_3)$, the other intermediate after migratory insertion, would only give H_2 and HD elimination, although one might make an argument in this case that CD_3–Sc^+–$CH(CH_3)CH_2CD_3$ formation is favored over that of CD_3–Sc^+–$CH_2CH(CH_3)(CD_3)$ based on steric or thermodynamic factors.

Scheme III



Instead, the results suggest the σ-bond metathesis mechanism shown in Scheme III. In this mechanism, the allylic C–H bond is activated via a multicentered intermediate, resulting in CH_4 elimination. It is likely that the reaction is exothermic and the excess energy can cause additional dehydrogenation and CH_4 elimination, reactions 10 and 11. The most likely dehydrogenation pathway is the coupling between the methyl group and the allyl group to form a Sc^+–butene intermediate, structure II, which then undergoes dehydrogenation. The observation of $ScC_4H_4D_2^+$ from reaction 11 with $Sc(CD_3)_2^+$ as the reactant ion is also consistent with such a pathway. Finally, $ScC_7H_{10}D_2^+$ and $ScC_7H_9D_3^+$ account for ~40% and ~60% of the product ions formed in reaction 14, respectively, consistent with the migratory insertion of propene and subsequent dehydrogenation. Scheme III again predicts structure I for the $ScC_4H_8^+$ ion produced in reaction 12. This is supported by the fact that this ion behaves in an identical manner to that produced in reaction 1 in its CID and its reactions with ethylene, propene, and benzene, respectively.

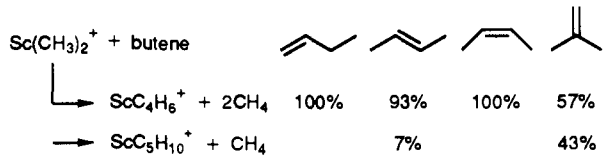
(33) Lech, L. M.; Freiser, B. S. *Organometallics* **1988**, *7*, 1948.

Table II. Product Branching Ratios from the Reactions of Butenes with $ScC_4H_8^+$ from Different Sources

		origin of $ScC_4H_8^+$		
neutral	product ion	$Sc(CH_3)_2^+ + C_2H_4$	$Sc(CH_3)_2^+ + C_3H_6$	$Sc^+ + n$-butane
1-butene	$ScC_4H_6^+$	11	15	15
	$ScC_7H_{12}^+$	73	68	69
	$ScC_8H_{12}^+$	8	9	7
	$ScC_8H_{14}^+$	8	8	9
cis-2-butene	$ScC_4H_6^+$	13	17	11
	$ScC_7H_{12}^+$	77	72	72
	$ScC_8H_{12}^+$	4	5	7
	$ScC_8H_{14}^+$	6	6	10
trans-2-butene	$ScC_4H_6^+$	8	11	14
	$ScC_7H_{12}^+$	75	70	69
	$ScC_8H_{12}^+$	4	5	4
	$ScC_8H_{14}^+$	13	14	13
isobutene	$ScC_7H_{12}^+$	93	91	88
	$ScC_8H_{14}^+$	7	9	12

It is expected that structure I would also react with other alkenes via both σ-bond metathesis and migratory insertion, similar to reactions 13 and 14. Accordingly, Table II lists the product ions from the reactions of the butenes with $ScC_4H_8^+$ formed from reaction 1, reaction 12, and from the reaction of Sc^+ with *n*-butane. The identical reactivities within experimental error again support their common structure. The major product ion in all of these reactions, $ScC_7H_{12}^+$, is the expected product ion from a mechanism of σ-bond metathesis.

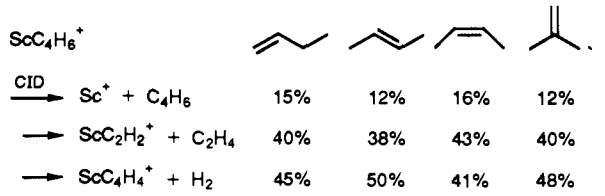
Butenes. $ScC_4H_6^+$ is formed as either the exclusive or the predominant product in the reactions of $Sc(CH_3)_2^+$ with the butenes, reactions 15 and 16. The corresponding reaction of



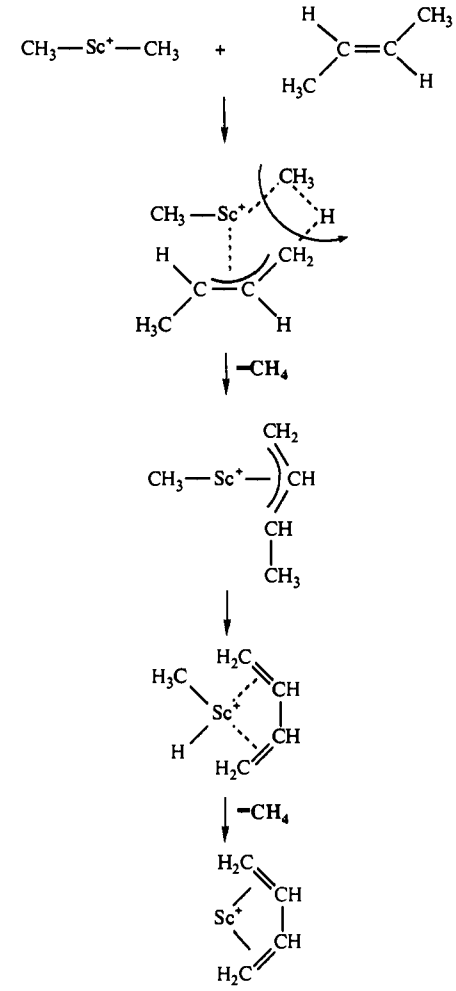
$Sc(CD_3)_2^+$ yields the exclusive loss of $2CD_3H$ in reaction 15 and CD_3H in reaction 16, indicating that the methyl groups are lost directly from the metal center. Reactions 15 and 16 can be rationalized by initial methane elimination through σ-bond metathesis. Excess internal energy can then lead to the loss of the second molecule of methane. Supporting this latter supposition is the fact that the $ScC_5H_{10}^+$ species from reaction 16 with isobutene undergoes facile loss of CH_4 to form $ScC_4H_6^+$ upon its CID. While the $ScC_4H_6^+$ from the linear butenes is expected to be Sc^+–butadiene, structure V, as shown in Scheme IV, Sc^+–trimethylenemethane, structure VI, is expected for isobutene.

The difference in the reactivity of *cis*-2-butene and *trans*-2-butene may be due to stereochemical factors. As depicted in Scheme IV for *trans*-2-butene, initial elimination of a methane molecule by σ-bond metathesis would give methyl-Sc^+-1-methylallyl. Because of the η^3 bond between the metal and the allyl group, the spatial position between the metal and the hydrogen attached to the allyl carbon bearing the methyl group is effectively frozen. The migration of this hydrogen to the metal center would have somewhat different energetics for *cis*- and *trans*-2-butene because of the different spatial distance of the hydrogen atom relative to the metal center. The results listed in reactions 15 and 16 suggest that such a process is more favorable for *cis*-2-butene than for *trans*-2-butene.

CID at 40 eV was performed on the $ScC_4H_6^+$ species arising from the various butenes in reaction 15, yielding reactions 17–19.



Scheme IV

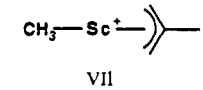


In agreement with an earlier study, these results indicate that structure V and structure VI give almost identical CID fragmentation patterns.[29] Fortunately, ion–molecule chemistry may

V VI

be used to distinguish these two ions. For example, the $ScC_4H_6^+$ ion from 1-butene and *cis*- and *trans*-2-butene all give condensation as the exclusive product with C_6D_6. Only the $ScC_4H_6^+$ ion from isobutene gives 28% dehydrogenation to produce $Sc(C_4H_4)(C_6D_6)^+$ and 72% condensation to form $Sc(C_4H_6)(C_6D_6)^+$, consistent with structure VI, as was demonstrated in the earlier study.[31]

The dehydrogenation reaction of Sc^+ with neopentane provided an important piece of evidence for the 1,3-dehydrogenation pattern because of its lack of 1,2-hydrogens.[25] Adaptation of Scheme II to this system indicates that the Sc(methyl)(2-methylallyl) ion, structure VII, should be formed. This should also be the primary

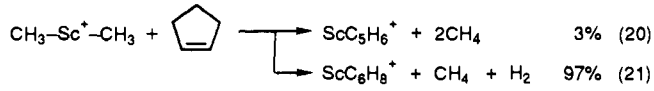


VII

product ion from the reaction of $Sc(CH_3)_2^+$ with isobutene in reaction 16. This is indeed the case. For example, the ion $ScC_5H_{10}^+$, both from reaction 16 with isobutene and from the reaction of Sc^+ with neopentane, reacts with another isobutene molecule to give $ScC_8H_{14}^+$, or $Sc(C_4H_7)_2^+$, as expected from consecutive σ-bond metathesis. Also, both react with C_6D_6 to give $Sc(C_4H_6)(C_6D_6)^+$, in analogy to reaction 8.

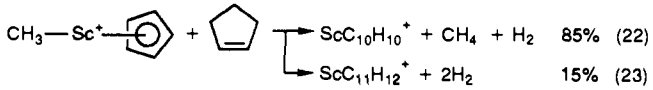
Cyclic Alkenes. YCH_3^+ activates allylic C–H bonds in both acyclic and cyclic alkenes.[17] This is also true for $Sc(CH_3)_2^+$. Reactions 20 and 21 were observed upon reacting $Sc(CH_3)_2^+$ with

cyclopentene. Both products may be easily explained according



to the aforementioned σ-bond metathesis mechanism. After the initial elimination of CH_4 from the multicentered intermediate, it can either eliminate another methane molecule to give Sc^+–cyclopentadiene, reaction 20, or undergo dehydrogenation to give (methyl)(cyclopentadienyl)scandium ion, reaction 21. Upon CID at 20 eV on the product ion from reaction 21, $ScC_5H_5^+$ is observed exclusively, supporting this structure since $D^\circ(Sc^+–CH_3) < D^\circ(Sc^+–\text{cyclopentadienyl})$ is expected.[34] The predominance of reaction 21 may be attributed to the high stability expected for the product ion in reaction 21. Upon reacting $Sc(CD_3)_2^+$ with cyclopentene, $ScC_5H_6^+$ is again observed as the only product ion for reaction 20, while $ScC_6H_5D_3^+$ is observed for the product ion in reaction 21, exclusively. These results strongly support the above mechanisms. CID on $ScC_6H_5D_3^+$ at 19 eV gives only $ScC_5H_5^+$, excluding any H/D scrambling during the competitive eliminations.

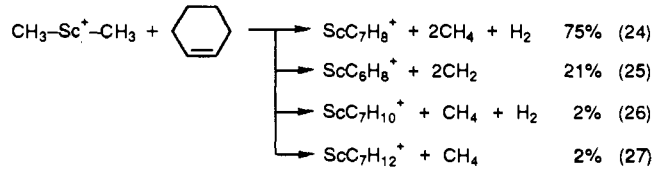
(Methyl)(cyclopentadienyl)scandium ion is another d^0 electronic system, and it is also expected to participate in an additional σ-bond metathesis step with cyclopentene. This is indeed the case, as shown in reaction 22. The product ion in reaction 22 is formed



from additional dehydrogenation after initial σ-bond metathesis, suggesting a scandocenium ion structure. Upon isolating $(CD_3)Sc(C_5H_5)^+$ from the reaction of $Sc(CD_3)_2^+$ with cyclopentene and reacting it with another cyclopentene molecule, no deuterium retention is observed for the product ion in reaction 22, while $ScC_{11}H_9D_3^+$ is the sole product ion for reaction 23. The absence of deuterium retention for reaction 22 is consistent with the formation of scandocenium.

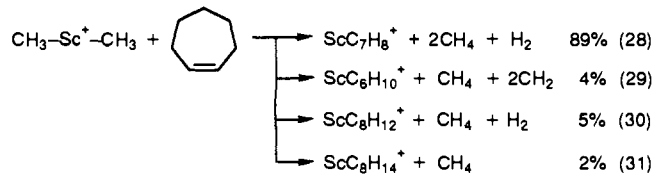
The product ion in reaction 23 can best be explained by the migratory insertion of the C=C bond of cyclopentene into the $C_5H_5Sc^+–CH_3$ bond, followed by sequential dehydrogenation. The labeling study, which gives exclusively $ScC_{11}H_9D_3^+$ for reaction 23, is consistent with such a mechanism. The fact that only σ-bond metathesis is observed for the primary reaction and both this and migratory insertion are observed for the secondary reaction is particularly interesting because it can only be traced to the different roles of the methyl and cyclopentadienyl groups. Neither of them appears to actively participate in the reaction, but they obviously exert effects on the reaction patterns. A similar case was also observed in reaction 14.

Reactions 24–27 were observed for cyclohexene. This reactivity



is similar to the *cis*-2-butene and cyclopentene cases where consecutive elimination of methane molecules dominates, resulting in the loss of both methyl groups from the metal center. However, the minor product ions in reactions 26 and 27 still suggest the retention of a single methyl group and the σ-bond metathesis mechanism predicts (methyl)(cyclohexadienyl)scandium and (methyl)(cyclohexenyl)scandium ion for the product ions in reactions 26 and 27, respectively. It should be noted that the products in reactions 26 and 27 can also be explained by a mechanism of migratory insertion.

Finally, the reaction of cycloheptene is very similar to that of cyclohexene with mainly just consecutive methane eliminations, reactions 28–31.



Conclusion

The gas-phase chemistry of $Sc(CH_3)_2^+$ with a variety of alkenes has proven to be quite interesting. As one of the low-valence electronic species we have studied, $Sc(CH_3)_2^+$ exhibits a unique reactivity. Since the most common reaction pathway, oxidative addition, is ruled out due to the d^0 electronic state of $Sc(CH_3)_2^+$, alternative pathways are proposed. For the reaction with ethylene, the migratory insertion of ethylene into the $Sc^+–CH_3$ bond takes place first and then the elimination of the hydrogen proceeds via a multicentered transition state. The reaction mechanisms with propene and butenes are different from that with ethylene. They begin with a multicentered transition state, followed by σ-bond metathesis to eliminate methane. The allylic C–H bonds in the cyclic alkenes are also activated by $Sc(CH_3)_2^+$, with cyclopentene, cyclohexene, and cycloheptene all exhibiting similar reaction patterns.

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(34) While $D^0(Sc^+–Cp)$ has not been reported, Cp rings are known to bond strongly with transition metal centers. For example, $D^0(Fe^+–Cp) = 88 \pm 7$ kcal/mol has been reported by Huang and Freiser: Huang, Y.; Freiser, B. S. *J. Am. Chem. Soc.* **1990**, *112*, 5086. Thus, $D^0(Sc^+–Cp)$ is expected to be higher than the 59 ± 3 kcal/mol reported for $D^0(Sc^+–CH_3)$ by Sunderlin et al.: Sunderlin, L. S.; Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.* **1987**, *109*, 78.