σ-Bond Metathesis Reactions of Sc(CH₃)₂⁺ with Secondary C−H Bonds: Reactivity with Cyclohexane and Cyclopentane

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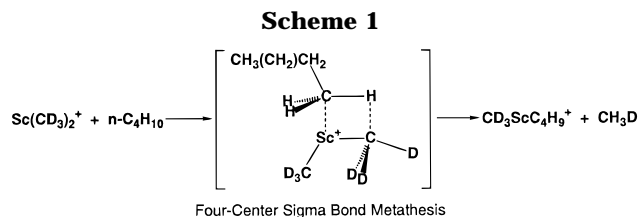
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Fourier transform ion cyclotron resonance mass spectrometry has been used to examine the σ-bond metathesis reactions of $Sc(CH_3)_2^+$ with the secondary C−H bonds of cyclohexane and cyclopentane. Methane elimination, accompanied by further dehydrogenation, is the initial and dominant reaction observed. These processes are facile at room temperature and involve little or no activation energy. Measured total bimolecular rate constants for the reaction of $Sc(CH_3)_2^+$ with cyclohexane and cyclopentane are 6.2×10^{-10} and 5.1×10^{-10} cm^3 s^{-1} molecule^{-1}, respectively. The total bimolecular rate constant for the reaction of Sc-$(CD_3)_2^+$ with cyclohexane is measured to be 6.6×10^{-10} cm^3 s^{-1} molecule^{-1}. In accordance with earlier theoretical predictions these metathesis reactions appear to proceed via an allowed four-center mechanism similar to that of a $2_\sigma + 2_\sigma$ cycloaddition. The observed gas phase reactivity is also compared to the liquid phase reactivity of similar complexes and the implications are discussed.

Introduction

Previous studies have observed σ-bond metathesis reactions for a variety of transition metal systems,[1−4] including scandium.[5] Exceptional reactivity has also been observed between $Sc(CD_3)_2^+$ and small alkanes in our laboratory.[6] In these gas phase reactions a four-center mechanism was invoked for metathesis reactions occurring at the metal center (see Scheme 1), in accord with the prediction of Steigerwald and Goddard that certain organometallic species containing an extremely acidic (in the Lewis sense) metal center should exhibit this kind of reactivity.[7] These metathesis reactions exhibited a high degree of site selectivity, with activation of the primary C−H bonds of a hydrocarbon being strongly favored relative to activation of the secondary and tertiary C−H bonds.[6] Similar positional reactivity has been observed in other studies.[4,5a,8,9]

Scheme 1

$$Sc(CD_3)_2^+ + n\text{-}C_4H_{10} \longrightarrow \left[\begin{array}{c} CH_3(CH_2)CH_2 \\ \end{array} \right] \longrightarrow CD_3ScC_4H_9^+ + CH_3D$$

Four-Center Sigma Bond Metathesis

Recent theoretical results suggest a thermodynamic explanation[10] of the preference for reaction at primary C−H bonds in the gas phase.[6,9] However, in the liquid phase the preference for reaction at primary C−H bonds has been attributed to steric effects.[5a] For example, in the liquid phase cyclohexane does not react with Cp*₂-Sc−CH₃,[11] but use of $^{13}CH_4$ shows that Cp*₂Sc−CH₃ will undergo methyl exchange.[5a] Though it would appear that reaction with cyclohexane is sterically hindered, it is possible that the observed reactivity could be controlled by other factors.

To examine this possibility, we have investigated the reaction of $Sc(CH_3)_2^+$ with simple compounds which do not possess primary C−H bonds, specifically cyclohexane and cyclopentane. Although $Sc(CH_3)_2^+$ is charged while Cp*₂Sc−CH₃ is not, both are formally d⁰ Sc(III) complexes and both undergo σ-bond metathesis,[5a,6] as would be expected of electron deficient systems.[7] In fact, Steigerwald and Goddard[7] performed their calculations

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(10) Perry, J. K.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1994,** *116,* 5013.
(11) Throughout this paper Cp* = η^5-C₅(CH₃)₅.

on the neutral Cl₂ScH system, but their results apply equally well to cationic scandium systems. In addition, even though $Sc(CH_3)_2^+$ may be more electrophilic than $Cp*_2Sc-CH_3$, theoretical calculations by Bauschlicher and Langhoff find that the $Sc-CH_3$ and Sc^+-CH_3 bond energies differ by only 4 kcal mol⁻¹ and that the $Sc-H$ and Sc^+-H bond energies differ by only 5 kcal mol⁻¹ (in both cases, the neutral species has the lower bond energy).[12] So it does not appear to be unreasonable to compare the reactivity of $Sc(CH_3)_2^+$ and $Cp*_2Sc-CH_3$ with cyclohexane. Compared with $Cp*_2Sc-CH_3$, there is little steric crowding around the metal center in $Sc(CH_3)_2^+$. Thus, if $Sc(CH_3)_2^+$ reacts with cyclohexane and cyclopentane, this would support the suggestion that steric factors are the main reason $Cp*_2Sc-CH_3$ (and similar compounds) does not react with secondary C−H bonds. If $Sc(CH_3)_2^+$ is not reactive with cyclohexane and cyclopentane, this would suggest that other (perhaps electronic or thermodynamic) factors control the reactivity toward secondary C−H bonds in both the gas and liquid phase.

Furthermore, when a straight chain alkane reacts with $Sc(CD_3)_2^+$, competitive intramolecular reactivity occurs between the primary and secondary C−H bonds. Though we have observed that primary C−H bonds are more reactive than secondary C−H bonds toward $Sc(CD_3)_2^+$,[6] such observations only tell us about their *relative* reactivity toward $Sc(CD_3)_2^+$. Secondary C−H bonds might be rather nonreactive toward $Sc(CH_3)_2^+$ and provide little or no intramolecular competition with primary C−H bonds. Alternatively, secondary C−H bonds might be quite reactive toward $Sc(CH_3)_2^+$, but the more reactive primary C−H bonds still win the intramolecular competition for reaction with $Sc(CH_3)_2^+$. However, since cycloalkanes have *only* secondary C−H bonds, there are no primary bonds present to compete with the secondary bonds. Thus, the reactivity we observe between $Sc(CH_3)_2^+$ and cycloalkanes should shed light on the absolute reactivity of secondary C−H bonds, without intramolecular competition from primary C−H bonds.

Experimental Section

Reactions were investigated with Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry, of which a number of reviews are available.[13] In the Caltech instrument, a 1-in. cubic trapping cell is located between the poles of a Varian 15-in. electromagnet maintained at 1.0 T. Pressures were measured with a Schultz-Phelps ion gauge calibrated against an MKS 390 HA-00001SP05 capacitance manometer. The instrument at the University of Nice-Sophia Antipolis has the same specifications, except that pressures are measured with a Bayard-Alpert (BA) ionization gauge (Alcatel BN 111). The operation of the BA gauge has been described previously.[14] Uncertainties in the absolute pressure limit rate constants to an accuracy of ±20%. Cyclohexane and cyclopentane were obtained commercially from Aldrich and purified by freeze−pump−thaw cycling.

Sc⁺ ions were produced by laser ablation of a scandium metal target with a N₂ laser at 337.1 nm. The reactant ion

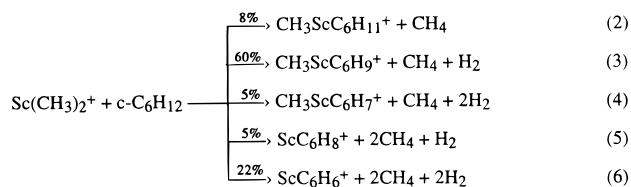was generated by reaction 1,[15] and unwanted ions were ejected

$$Sc^+ + CH_3CH_2CH_2CH_3 \rightarrow Sc(CH_3)_2^+ + CH_2CH_2 \quad (1)$$
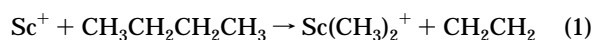
from the cell using double resonance techniques[16] and/or frequency sweep excitation.[17] Cyclohexane and cyclopentane were then added along with *n*-butane, and reactions due to the additional alkane were observed. In order to further elucidate reaction mechanisms and identify possible kinetic isotope effects, the reaction of isolated $Sc(CD_3)_2^+$ (made via reaction 1 using [1,1,1,4,4,4-D₆]-*n*-butane) with cyclohexane was examined. Rate constants were determined in a straightforward manner, from slopes of semilog plots of the decay of reactant ion abundance versus time, with various pressures of the neutral reactants.

Collision-induced dissociation (CID) experiments were also performed on the instrument in France. The CID experiments were performed in the multiple-collision regime using previously described methodologies.[18] Argon at a pressure of about 9.0×10^{-7} Torr was used as the collision gas. The collision energy was varied between 0 and 50 eV in the laboratory.

Results

Reaction with Cyclohexane. $Sc(CH_3)_2^+$ can react with cyclohexane as shown in reactions 2−6 (see Figure

$$Sc(CH_3)_2^+ + c\text{-}C_6H_{12} \begin{cases} \xrightarrow{8\%} CH_3ScC_6H_{11}^+ + CH_4 & (2) \\ \xrightarrow{60\%} CH_3ScC_6H_9^+ + CH_4 + H_2 & (3) \\ \xrightarrow{5\%} CH_3ScC_6H_7^+ + CH_4 + 2H_2 & (4) \\ \xrightarrow{5\%} ScC_6H_8^+ + 2CH_4 + H_2 & (5) \\ \xrightarrow{22\%} ScC_6H_6^+ + 2CH_4 + 2H_2 & (6) \end{cases}$$

1a). The main process observed with cyclohexane is the metathesis reaction 2 and the accompanying dehydrogenations of reactions 3 and 4. Reaction 5 is observed when the nascent product of reaction 3 eliminates methane, while reaction 6 is seen when the nascent product of reaction 5 loses hydrogen. Reaction 6 could also be observed when the nascent product of reaction 4 eliminates methane, but it is unlikely that such a process would occur (see the Discussion). When $Sc(CD_3)_2^+$ is reacted with cyclohexane, a nearly identical product distribution is seen (within experimental error). Additional metathesis reactions with a second cyclohexane molecule were not observed. To ensure that the products of reaction 5 and 6 are formed from the nascent product of reaction 3, CID experiments were performed on the isolated $CH_3ScC_6H_9^+$ ion (see Figure 1b). These experiments confirmed that excitation of $CH_3ScC_6H_9^+$ leads to the formation of $ScC_6H_8^+$ and $ScC_6H_6^+$. The CID of $CH_3ScC_6H_9^+$ also led to the formation of $CH_3ScC_6H_7^+$. For the reaction of $Sc(CH_3)_2^+$ with cyclohexane the total bimolecular rate constant $k = 6.2 \times 10^{-10}$ cm³ s⁻¹ molecule⁻¹ and the reaction efficiency $k/k_{Langevin} = 0.51$.[19,20] For the reaction of $Sc(CD_3)_2^+$ with cyclohexane the total bimolecular rate constant $k = 6.6 \times$

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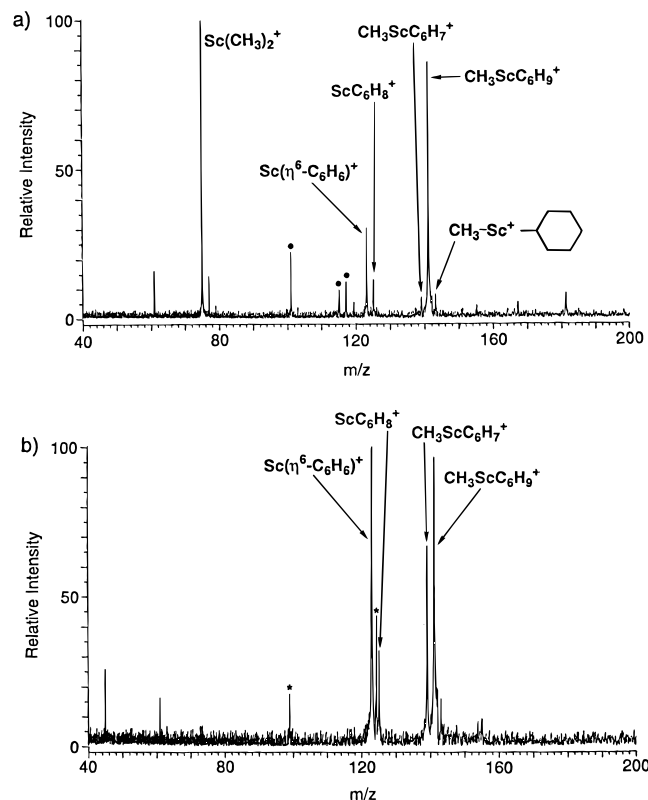
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(19) Collision rates are calculated using Langevin theory: Su, T.; Bowers, M. T. *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 1.

Figure 1. (a) Products of reaction of $Sc(CH_3)_2^+$ with cyclohexane. Spectra were taken 600 ms after isolation of $Sc(CH_3)_2^+$. The peaks above m/z 150 correspond to ScR_2^+, R = alkyl. Peaks at m/z 61, 77, and 79 correspond to ScO^+, CH_3ScOH^+, and $Sc(OH)_2^+$, respectively. Peaks at m/z 101, 115, and 117 correspond to $ScC_4H_8^+$, $CH_3ScC_4H_7^+$, and $CH_3ScC_4H_9^+$, respectively. These products (marked with bullets) result from reactions with the *n*-butane neutral. No products were observed above m/z 200. (b) Spectrum of products from the CID of isolated $CH_3ScC_6H_9^+$. For this spectrum the maximum energy in the laboratory frame of reference is 48 eV, corresponding to a center-of-mass collision energy of 10.6 eV. The peaks at m/z 99 and 124 (marked with asterisks) are due to electrical noise.

10^{-10} cm^3 s^{-1} molecule^{-1} and the reaction efficiency $k/k_{Langevin} = 0.55$.[19,20]

Reaction with Cyclopentane. $Sc(CH_3)_2^+$ reacts with cyclopentane as shown in reactions 7−10 (see

$$Sc(CH_3)_2^+ + c\text{-}C_5H_{10} \longrightarrow$$

$$\xrightarrow{10\%} CH_3ScC_5H_9^+ + CH_4 \quad (7)$$

$$\xrightarrow{60\%} CH_3ScC_5H_7^+ + CH_4 + H_2 \quad (8)$$

$$\xrightarrow{25\%} CH_3ScC_5H_5^+ + CH_4 + 2H_2 \quad (9)$$

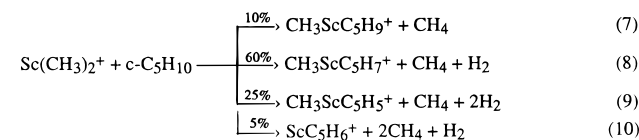$$\xrightarrow{5\%} ScC_5H_6^+ + 2CH_4 + H_2 \quad (10)$$

Figure 2). The main process observed with cyclopentane is the metathesis reaction 7 and the accompanying dehydrogenations (reactions 8 and 9). Reaction 10 is observed when the nascent product of reaction 8 eliminates methane. For the reaction of $Sc(CH_3)_2^+$ with cyclopentane the total bimolecular rate constant $k = 5.1 \times 10^{-10}$ cm^3 s^{-1} molecule^{-1} and the reaction efficiency $k/k_{Langevin} = 0.43$.[19,21]

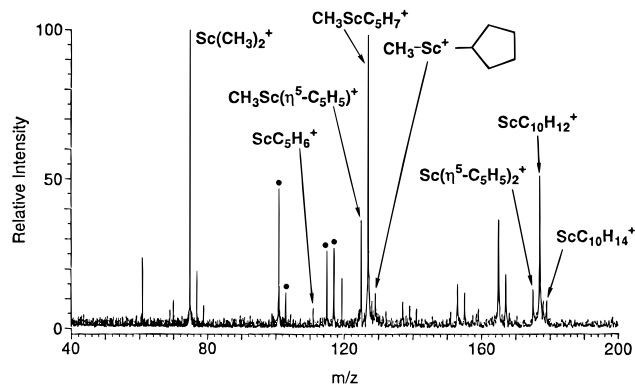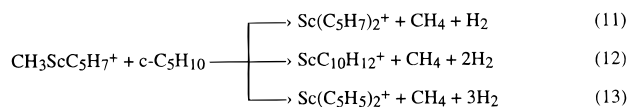Furthermore, the product of reaction 8 can subsequently undergo σ-bond metathesis and accompanying

Figure 2. Products of reaction of $Sc(CH_3)_2^+$ with cyclopentane. Spectra were taken 840 ms after isolation of $Sc(CH_3)_2^+$. The main peaks between m/z 135 and 170 correspond to ScR_2^+, R = alkyl. Peaks at m/z 61, 77, and 79 correspond to ScO^+, CH_3ScOH^+, and $Sc(OH)_2^+$, respectively. Peaks at m/z 101, 103, 115, and 117 correspond to $ScC_4H_8^+$, $ScC_4H_{10}^+$, $CH_3ScC_4H_7^+$, and $CH_3ScC_4H_9^+$, respectively. These products (marked with bullets) result from reactions with the *n*-butane neutral.

dehydrogenation with a second cyclopentane, as shown in reactions 11−13. In principle, the ionic products of

$$CH_3ScC_5H_7^+ + c\text{-}C_5H_{10} \longrightarrow$$

$$\longrightarrow Sc(C_5H_7)_2^+ + CH_4 + H_2 \quad (11)$$

$$\longrightarrow ScC_{10}H_{12}^+ + CH_4 + 2H_2 \quad (12)$$

$$\longrightarrow Sc(C_5H_5)_2^+ + CH_4 + 3H_2 \quad (13)$$

reactions 7 and 9 could undergo the same reactions, but since the $CH_3ScC_5H_7^+$ product of reaction 8 predominates, we only show its specific reactions. A rate constant was not derived for this process. Such reactivity was not observed with cyclohexane.

Discussion

Overview. In this study σ-bond metathesis reactions involving secondary C−H bonds are observed to occur with cyclohexane and cyclopentane, where a methyl group of $Sc(CH_3)_2^+$ is replaced by either a cyclohexyl or cyclopentyl group. Subsequent dehydrogenation of the metathesis product is observed with both cyclohexane and cyclopentane. With cyclohexane, a second methane is eventually eliminated leading to the formation of $Sc(\eta^6\text{-}C_6H_6)^+$. $Sc(\eta^6\text{-}C_6H_6)^+$ has also been previously observed in the reaction of Sc^+ with cyclohexane.[22] In general, metathesis reactions can proceed via an oxidative addition/reductive elimination pathway or via a four-center intermediate. Since Sc^+ has only two valence electrons with which to form strong σ bonds,[15,23] we favor a four-center mechanism for these metathesis reactions (as shown in Scheme 1 for the reaction with *n*-butane). The high kinetic efficiencies observed indicate low barriers for these metathesis reactions, in accordance with the predictions of Steigerwald and Goddard.[7]

To investigate the possible presence of kinetic isotope effects, we also used $[1,1,1,4,4,4\text{-}D_6]$-*n*-butane to generate $Sc(CD_3)_2^+$, which we then allowed to react with cyclohexane. The total bimolecular rate constants

(20) For cyclohexane, the polarizability $\alpha = 10.87$ Å^3: Stuart, H. A. *Landolt-Börnstein Zahlenwerte und Funktionen*, Eucken, A., Hellwege, K. H., Eds.; Springer-Verlag: Berlin, 1951; Vol. 1, Part 3.
(21) For cyclopentane, the polarizability $\alpha = 9.15$ Å^3: Applequist, J.; Carl, J. R.; Fung, K.-K. *J. Am. Chem. Soc.* **1972**, *94*, 2952.

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(23) Beauchamp, J. L.; van Koppen, P. A. M. *Energetics of Organometallic Species*; Simoes, J. A. M., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992.

measured with each ion differed slightly ($k_H/k_D = 0.94$), indicating that a small but measurable isotope effect exists in this system. This is a slightly larger isotope effect than seen previously with straight chain alkanes, and the deuterium-labeled system has the larger rate constant, consistent with previous observations.[6,9]

Small amounts of ScO⁺, CH₃ScOH⁺, and Sc(OH)₂⁺ are observed from the reaction of Sc(CH₃)₂⁺ with trace amounts of water in the background gas. These ions have been observed previously.[6,9] Though the ion at m/z 61 is assigned to be ScO⁺, it could also correspond to Sc(CH₄)⁺. However, the absence of any shift in this peak when Sc(CD₃)₂⁺ was used confirms the assignment as ScO⁺.

The efficiencies ($k_{reaction}/k_{collision}$) for the reaction of Sc(CH₃)₂⁺ with cyclohexane and cyclopentane differ by about 20%, with cyclohexane exhibiting the larger kinetic efficiency. The higher kinetic efficiency seen for the reaction of Sc(CH₃)₂⁺ with cyclohexane can be accounted for by the deeper potential well which results from the larger polarizability of cyclohexane.[20,21] This makes it easier to overcome any intrinsic barrier to σ-bond metathesis. These results are consistent with previous observations of Sc(CD₃)₂⁺ reacting with straight chain hydrocarbons[6] and reminiscent of the reactions of Co⁺ with hydrocarbons, where larger hydrocarbons deepen the electrostatic potential well for the Co⁺–alkane adduct. This provides greater chemical activation to the system, which facilitates overcoming the barrier to bond insertion.[24]

Comparison of Gas Phase and Liquid Phase Reactivity. Previous gas phase[6,9] and liquid phase[5a] work involving σ-bond metathesis processes with scandium have shown a preference for reaction at primary C–H bonds. In the liquid phase, this preference has been attributed to steric effects resulting from the bulky Cp* ligands bound to scandium. However, in the gas phase the Sc(CH₃)₂⁺ ion exhibits the same preference.

Recent theoretical results suggest that the exchange reaction Sc⁺–R + R′–H → Sc⁺–R′ + R–H (R = small alkanes) should be approximately thermoneutral in the gas phase.[10] However, alkyl groups larger than ethyl can bend around and interact further with the Sc⁺ metal center via an ion-polarization interaction. This additional interaction will further stabilize the Sc⁺ metal center but can only occur if primary C–H bonds are attacked. Thermodynamic considerations can, therefore, explain the observed preference Sc(CH₃)₂⁺ shows for reacting with primary C–H bonds.[6,9] Since there is no steric crowding around Sc(CH₃)₂⁺, the thermodynamic explanation is the only way to rationalize this preference for reaction at primary C–H bonds in the gas phase.

Thus, when a straight chain alkane reacts with Sc(CH₃)₂⁺, the primary and secondary sites intramolecularly compete with each other. This competition is usually won by the primary site. Unfortunately, this tells us nothing of the absolute reactivity of secondary C–H bonds toward σ-bond metathesis reactions. All it shows is that primary sites are more reactive. However, both cyclohexane and cyclopentane contain only secondary C–H bonds and both exhibit high kinetic efficiencies in their reactions with Sc(CH₃)₂⁺. This shows that

secondary C–H bonds are *not* thermodynamically forbidden from reacting. In fact, secondary C–H bonds are very reactive toward σ-bond metathesis, but primary C–H bonds are even more reactive. The preference to react at primary C–H bonds is simply a reflection that the intrinsic barrier to primary C–H bond activation is lower than the intrinsic barrier to secondary C–H bond activation.

What implications does this have for the liquid phase reactivity of Cp*₂Sc–CH₃ toward C–H bonds? Our present results show that the preference of Sc(CH₃)₂⁺ to react with primary C–H bonds in the gas phase does not imply that secondary C–H bonds will not react when no primary C–H bonds are present. This observation supports the view that it is steric effects in the liquid phase that modify the potential energy surface so as to render Cp*₂Sc–CH₃ unreactive toward cyclohexane.[5a]

Reaction Energetics. The product distributions from the reaction of cyclohexane with Sc(CH₃)₂⁺ and the CID of CH₃ScC₆H₉⁺ exhibit an interesting and subtle feature. Very little CH₃ScC₆H₇⁺ is seen in the direct reaction of Sc(CH₃)₂⁺ with cyclohexane, while a large amount is produced by CID of CH₃ScC₆H₉⁺. However, Sc(η⁶-C₆H₆)⁺ and ScC₆H₈⁺ are observed to form in both cases. To explore this point further, we have constructed a reaction coordinate diagram (see Figure 3) for the processes shown in reactions 2–6. Thermochemical values relevant to this work are shown in Tables 1 and 2. The necessary values were mostly obtained directly from the literature or calculated from other literature values in a straightforward manner. However, some had to be estimated as follows.

For Sc–(η⁶-C₆H₆)⁺, Lech and Freiser[22] found from bracketing experiments that the bond energy was 53 ± 5 kcal mol⁻¹. However, recent work by Meyer et al.[28] has determined the Ti–(η⁶-C₆H₆)⁺ and V–(η⁶-C₆H₆)⁺ bond energies to be 62 and 56 kcal mol⁻¹, respectively. This suggests that the Sc–(η⁶-C₆H₆)⁺ bond energy may be slightly higher than 53 kcal mol⁻¹. Thus, we estimate the Sc–(η⁶-C₆H₆)⁺ bond energy to be approximately 60 kcal mol⁻¹.

For CH₃Sc–(η³-C₆H₉)⁺ one might expect the Sc⁺–(η³-C₆H₉)⁺ bond energy to be intermediate between the bond energies of Sc–(η⁴-C₆H₈)⁺ and Sc–(η²-C₆H₁₀)⁺. But prior work by Huang et al.[5b] has found that CH₃Sc–(η³-C₃H₅)⁺ is approximately 15 kcal mol⁻¹ more stable than Sc⁺–(1-butene). Assuming that the bond energy of Sc⁺–(1-butene) is 45 kcal mol⁻¹ (similar to the bond energy of 47 kcal mol⁻¹ for Sc⁺–(2-butene) calculated from known heats of formation[25]), we can then calculate from known thermochemistry[25] that the bond energy of CH₃Sc–(η³-C₆H₉)⁺ is approximately 75 kcal mol⁻¹. As this value seems a bit high, we estimate the value of the CH₃Sc–(η³-C₆H₉)⁺ bond energy to be 70 kcal mol⁻¹, which is slightly larger than the Sc–(η⁴-C₆H₈)⁺ bond energy. Furthermore, we would expect CH₃Sc–(η⁵-C₆H₇)⁺ to exhibit parallel behavior and have a bond

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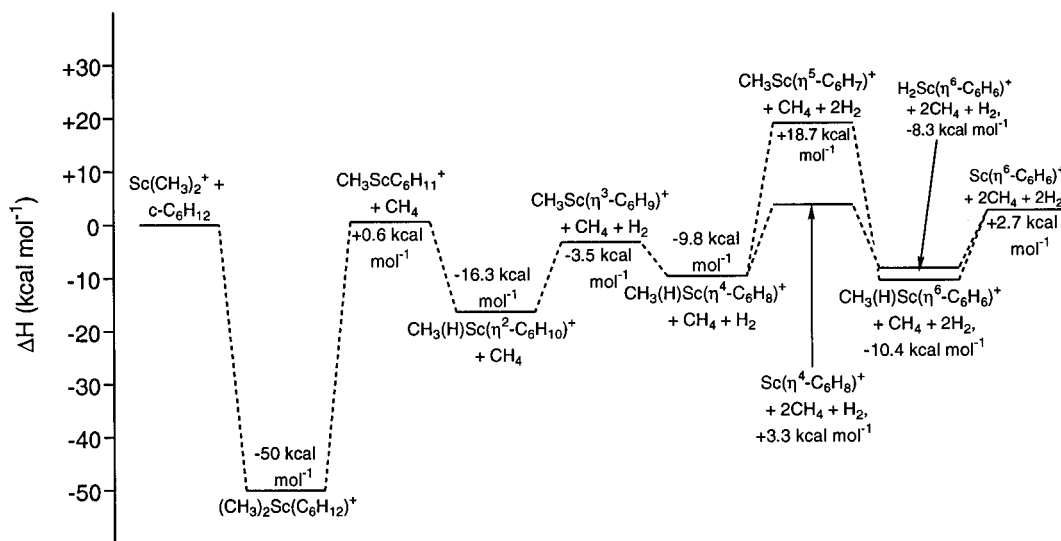(29) Kemper, P. R.; Bushnell, J.; van Koppen, P.; Bowers, M. T. *J. Phys. Chem.* **1993**, *97*, 1810.

Figure 3. Illustration of reaction energetics for processes resulting from interaction of cyclohexane with $Sc(CH_3)_2^+$. The relative energies are derived from the thermochemistry given in Tables 1 and 2. Some of the values have significant uncertainties (see text for discussion). Note the comparatively high energy required to reach $CH_3Sc(\eta^5\text{-}C_6H_7)^+$, which prevents the formation of $CH_3(H)Sc(\eta^6\text{-}C_6H_6)^+$. Because of this, $CH_3ScC_6H_9^+$ will preferentially lose methane to form $ScC_6H_8^+$.

Table 1. Gas Phase Heats of Formation at 298 K for Chemical Species Relevant to This Work[a,b]

species	$\Delta H^{\circ}_{f,298}$ (kcal mol^{-1})	species	$\Delta H^{\circ}_{f,298}$ (kcal mol^{-1})
CH$_4$	$-17.8(0.1)$	C$_6$H$_6$	$+19.8(0.1)$
CH$_3$	$+35.1(0.2)^c$	CH$_3$Sc$^+$-C$_6$H$_{11}$	$+180.9(8)^g$
H	$+52.1(0.1)$	CH$_3$Sc$^+$-$(\eta^3$-C$_6$H$_9)$	$+176.8(9)^g$
Sc$^+$	$+241(5)$	Sc$^+$-$(\eta^4$-C$_6$H$_8)$	$+201.4(8)^d$
ScCH$_3^+$	$+217(6)^d$	CH$_3$Sc$^+$-$(\eta^5$-C$_6$H$_7)$	$+199(10)^g$
Sc(CH$_3$)$_2^+$	$+192(7)^e$	Sc$^+$-$(\eta^6$-C$_6$H$_6)$	$+200.8(8)^d$
ScH$^+$	$+237(5)^d$	(CH$_3$)$_2$Sc$^+$-(C$_6$H$_{12}$)	$+112.5(10)^h$
ScH$_2^+$	$+230(6)^e$	(CH$_3$)(H)Sc$^+$-$(\eta^2$-C$_6$H$_{10}$)	$+164(9)^i$
c-C$_6$H$_{12}$	$-29.5(0.1)$	(CH$_3$)(H)Sc$^+$-$(\eta^4$-C$_6$H$_8$)	$+170.5(10)^i$
c-C$_6$H$_{11}$	$+13.9(1)^c$	(CH$_3$)(H)Sc$^+$-$(\eta^6$-C$_6$H$_6$)	$+169.9(10)^i$
c-C$_6$H$_{10}$	$-1.1(0.1)$	H$_2$Sc$^+$-$(\eta^6$-C$_6$H$_6$)	$+189.8(9)^h$
c-C$_6$H$_9$	$+29.8(1)^f$		

^{a} Uncertainties are in parentheses. ^{b} Unless otherwise noted, all values come from ref 25. ^{c} Reference 26. ^{d} Derived from the equation $\Delta H^{\circ}_{f,298}(ScX^+) = \Delta H^{\circ}_{f,298}(Sc^+) + \Delta H^{\circ}_{f,298}(X) - D^{\circ}_{298}(Sc^+-X)$. The appropriate bond energy is taken from Table 2. ^{e} Derived from the equation $\Delta H^{\circ}_{f,298}(ScX_2^+) = \Delta H^{\circ}_{f,298}(ScX^+) + \Delta H^{\circ}_{f,298}(X) - D^{\circ}_{298}(XSc^+-X)$. The appropriate bond energy is taken from Table 2. ^{f} Derived from the measured bond energy of the allyl hydrogen to cyclohexene, using the equation $\Delta H^{\circ}_{f,298}(c\text{-}C_6H_9) = \Delta H^{\circ}_{f,298}(c\text{-}C_6H_{10}) - \Delta H^{\circ}_{f,298}(H) + D^{\circ}_{298}(\text{cyclohexenyl-allyl H})$. The appropriate bond energy is taken from Table 2. ^{g} Derived from the equation $\Delta H^{\circ}_{f,298}(XSc\text{-}Y^+) = \Delta H^{\circ}_{f,298}(ScX^+) + \Delta H^{\circ}_{f,298}(Y) - D^{\circ}_{298}(XSc\text{-}Y^+)$. The appropriate bond energy is taken from Table 2. ^{h} Derived from the equation $\Delta H^{\circ}_{f,298}(X_2Sc\text{-}Y^+) = \Delta H^{\circ}_{f,298}(ScX_2^+) + \Delta H^{\circ}_{f,298}(Y) - D^{\circ}_{298}(X_2Sc\text{-}Y^+)$. The appropriate bond energy is taken from Table 2. ^{i} Derived from the equation $\Delta H^{\circ}_{f,298}((X)(Y)Sc\text{-}Z^+) = \Delta H^{\circ}_{f,298}(ScX^+) + \Delta H^{\circ}_{f,298}(Y) + \Delta H^{\circ}_{f,298}(Z) - D^{\circ}_{298}(XSc\text{-}Y^+) - D^{\circ}_{298}((X)(Y)Sc\text{-}Z^+)$. The appropriate bond energy is taken from Table 2.

Table 2. Gas Phase Bond Energies at 298 K for Chemical Species Relevant to This Work[a]

species	D°_{298} (kcal mol^{-1})	species	D°_{298} (kcal mol^{-1})
c-C$_6$H$_{11}$-H	$95.5(1)^b$	Sc$^+$-C$_5$H$_9$	$50(5)^e$
c-C$_6$H$_9$-allyl H	$83(1)^c$	Sc$^+$-$(\eta^6$-C$_6$H$_6$)	$60(7)^f$
c-C$_6$H$_7$-allyl H	$73(5)^b$	Sc$^+$-$(\eta^5$-C$_6$H$_7$)	$65(7)^g$
c-C$_5$H$_9$-H	$94.5(1)^b$	Sc$^+$-$(\eta^4$-C$_6$H$_8$)	$65(7)^h$
HSc$^+$-H	$59(4)^d$	Sc$^+$-$(\eta^3$-C$_6$H$_9$)	$70(7)^i$
Sc$^+$-H	$56(2)^d$	Sc$^+$-$(\eta^2$-C$_6$H$_{10}$)	$45(5)^j$
CH$_3$Sc$^+$-CH$_3$	$60(5)^d$	Sc$^+$-C$_6$H$_{11}$	$50(5)^e$
Sc$^+$-CH$_3$	$59(3)^d$	Sc$^+$-C$_6$H$_{12}$	$50(7)^k$

^{a} Uncertainties are in parentheses. ^{b} Reference 26. ^{c} Estimated assuming a resonance stabilization energy of approximately 12 kcal mol^{-1} for an allyl hydrogen.[26] ^{d} Reference 27. ^{e} Estimated from Perry and Goddard's[10] theoretical bond energy of 36.9 kcal mol^{-1} for a secondary carbon bonded to Sc$^+$. We have included a correction of approximately 15 kcal mol^{-1}, since Perry and Goddard's calculated Sc$-$CH$_3$ bond energy is 15 kcal mol^{-1} lower than the experimentally determined value.[27] ^{f} References 22 and 28. See discussion in text. ^{g} See discussion in text. ^{h} Estimated utilizing the facts that butadiene will displace benzene from Sc(η^6-C$_6$H$_6$)$^+$ in the gas phase and that CID of Sc(η^4-C$_4$H$_6$)(η^6-C$_6$H$_6$)$^+$ leads predominantly to the loss of benzene.[22] ^{i} Reference 5b. See discussion in text. ^{j} Estimated to be similar to the bond energy of 47 kcal mol^{-1} for Sc$-$(2-butene)$^+$. The bond energy of Sc$-$(2-butene)$^+$ is calculated using values for the heats of formation from ref 25. ^{k} Estimated utilizing refs 24 and 29. See discussion in text.

energy slightly larger than that for Sc$-(\eta^6$-C$_6$H$_6)^+$. Therefore, we estimate the CH$_3$Sc$-(\eta^5$-C$_6$H$_7)^+$ bond energy to be 65 kcal mol^{-1}.

Experimental work by Kemper et al.,[29] Hill et al.,[30] and Armentrout and co-workers[31] in conjunction with theoretical work by Perry et al.[24] has demonstrated that the complexation energies between transition metal cations and alkanes are significantly larger than one

might have anticipated. For example, Kemper et al. found that the Co$^+\cdot$2C$_2$H$_6$ molecular complex has a total binding energy of about 55 kcal mol^{-1}.[29] Cyclohexane is more polarizable than ethane, but due to its ring shape cyclohexane can only interact through three of its hydrogen atoms; so we might expect the binding energy of Sc$^+$ and cyclohexane to be similar to the binding energy of two ethanes to Co$^+$. Thus, we estimate a bond energy of 50 kcal mol^{-1} for (CH$_3$)$_2$Sc$^+-$C$_6$H$_{12}$.

The reaction coordinate diagram shown in Figure 3 assumes a stepwise sequential reaction mechanism for the eventual dehydrogenation of cyclohexane to benzene. The initial step is adduct formation with cyclohexane, leading to the σ-bond metathesis of reaction 2. The next step could then be one of two paths: dehydrogenation of the cyclohexyl ring (reaction 3) or a second

(30) Hill, Y. D.; Freiser, B. S.; Bauschlicher, C. W. *J. Am. Chem. Soc.* **1991**, *113*, 1507.

(31) (a) Schultz, R. H.; Armentrout, P. B. *J. Am. Chem. Soc.* **1991**, *113*, 729. (b) Schultz, R. H.; Armentrout, P. B. *J. Phys. Chem.* **1992**, *96*, 1662.

intramolecular metathesis reaction (reaction 14). As

$$CH_3ScC_6H_{11}{}^+ \rightarrow Sc(C_6H_{10})^+ + CH_4 \qquad (14)$$
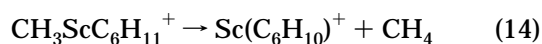
shown in Figure 3, the dehydrogenation of the cyclo-hexyl ring is achieved by moving through an η^2 π-com-plex (via a β-hydride transfer) with the subsequent elimination of H_2. Since no $Sc(C_6H_{10})^+$ is observed, we conclude that reaction 14 does not occur.

This mechanistic pattern continues in a stepwise sequence. After the initial σ-bond metathesis, β-hydride transfer leads to an intermediate species, which then eliminates either H_2 or methane until the final product $Sc(\eta^6\text{-}C_6H_6)^+$ is reached. From Figure 3, we see that most species involved in reactions 2−6 are below or just slightly above the energy of the reactants. However, $CH_3Sc(\eta^5\text{-}C_6H_7)^+$ is seen to be energetically quite unfa-vorable when compared with the reactants. Thus, very little $CH_3(H)Sc(\eta^6\text{-}C_6H_6)^+$ (which can only be reached from $CH_3Sc(\eta^5\text{-}C_6H_7)^+$) will form without any external activation, and $CH_3ScC_6H_9{}^+$ will preferentially elimi-nate methane (instead of H_2) to form $ScC_6H_8{}^+$. Fur-thermore, we see that the product of reaction 6 must then arise from dehydrogenation of $ScC_6H_8{}^+$, since almost no $CH_3ScC_6H_7{}^+$ is produced. On the other hand, if enough excitation energy is supplied through pro-cesses such as CID, then it will be possible to form significant amounts of $CH_3ScC_6H_7{}^+$. Such behavior was in fact observed.

Comparison of the Behavior of Cyclohexane and Cyclopentane. After the initial metathesis reactions, an interesting difference between the reactivity of CH_3-$ScC_6H_9{}^+$ and $CH_3ScC_5H_7{}^+$ is observed. With CH_3-$ScC_6H_9{}^+$, only subsequent dehydrogenation leading eventually to the formation of $Sc(\eta^6\text{-}C_6H_6)^+$ is seen. In contrast to the reactivity of $CH_3ScC_6H_9{}^+$, $CH_3ScC_5H_7{}^+$ will undergo a second metathesis reaction with a second cyclopentane molecule (eliminating the remaining meth-yl group) and subsequently dehydrogenate to form the observed products, including $Sc(\eta^5\text{-}C_5H_5)_2{}^+$ (i.e., scan-docenium). We should note that scandocenium has been observed previously as a product of the reaction of Sc^+ with cyclopentene,[22] but in our system it is generated from a ligated Sc^+ metal center and a saturated hydrocarbon. Apparently, the dehydrogenation of CH_3-$ScC_6H_9{}^+$ is more facile than the dehydrogenation of CH_3-$ScC_5H_7{}^+$. Subsequent collisions of $CH_3ScC_6H_9{}^+$ with cyclohexane may lead to dehydrogenation rather than a second σ-bond metathesis reaction.