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Notes

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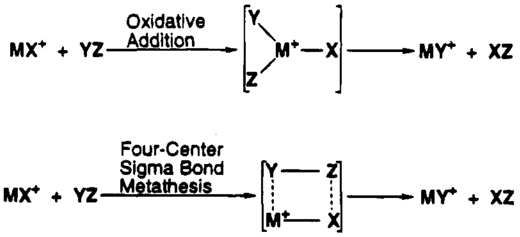
Summary: Fourier transform ion cyclotron resonance mass spectrometry is used to show that $Sc(CD_3)_2^+$ *reacts with saturated alkanes larger than ethane in the gas phase by a four center* σ*-bond metathesis reaction with methane elimination. These processes are facile at room temperature, involve little or no activation enery, and occur preferentially with primary carbon−hydrogen bonds.*

Introduction

Steigerwald and Goddard have predicted that the degenerate hydrogen exchange reaction of D_2 with transition metal complexes such as Cl_2MH (M = Sc, Ti, Ti^+) can occur via a four-center mechanism similar to $2_s + 2_s$ cycloaddition (Scheme 1). They found that these reactions can proceed at low energies with small barriers and that the barriers decreased as the Lewis acid character of the metal increased.[1] These predictions have interesting implications with regard to the reactivity of $Sc(CD_3)_2^+$ with alkanes. This ion has an extremely acidic metal center and should therefore be capable of reacting via a four-center mechanism. Also, since Sc^+ has only two valence electrons, it is capable of forming no more than two strong σ-bonds,[2,3] while oxidative addition mechanisms for reactions of $Sc(CD_3)_2^+$ with alkanes require the formation of four σ bonds (see Scheme 1). This suggests that $Sc(CD_3)_2^+$ must react via a four-center mechanism if it is to react at all.

Exceptional reactivity in other scandium complexes has also been observed. Thompson et al. have observed σ-bond metathesis reactions with permethylscandocene derivatives,[4a] and they invoked a four-center mechanism for this process. Huang et al. have observed σ-bond metathesis reactions of $Sc(CH_3)_2^+$ with alkenes,[4b] and such reactivity has also been observed in other transition metal systems.[4c,5−7] It might be thought that $Sc(CH_3)_2^+$ could exhibit such σ-bond metathesis reactions with alkanes. We have used labeled compounds to investigate the reactions of $Sc(CD_3)_2^+$ with small alkanes to see if any site selectivity is observed, as previous studies have found that attack can occur at both primary and secondary C−H bonds in hydrocarbons.[7−9] In this study we report the results of the reaction of $Sc(CD_3)_2^+$ with ethane, [2,2-D_2]propane, [1,1,1,4,4,4-D_6]-*n*-butane, and [2-D]isobutane.

Scheme 1



Experimental Section

Reactions were investigated with Fourier transform ion cyclotron resonance spectrometry (FT-ICR), of which a number of reviews are available.[10] 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. Uncertainties in the absolute pressure limit rate constants to an accuracy of ±20%. Labeled [2,2-D_2]propane (98% D), [1,1,1,4,4,4-D_6]-*n*-butane (98% D) and [2-D]isobutane (98% D) were obtained commercially from Merck, Sharp, and Dohme and purified by freeze−pump−thaw cycling.

Sc^+ ions were produced by laser ablation of a scandium metal target with a N_2 laser at 337.1 nm. The reactant ion was generated by reaction 1[2] and unwanted ions were ejected

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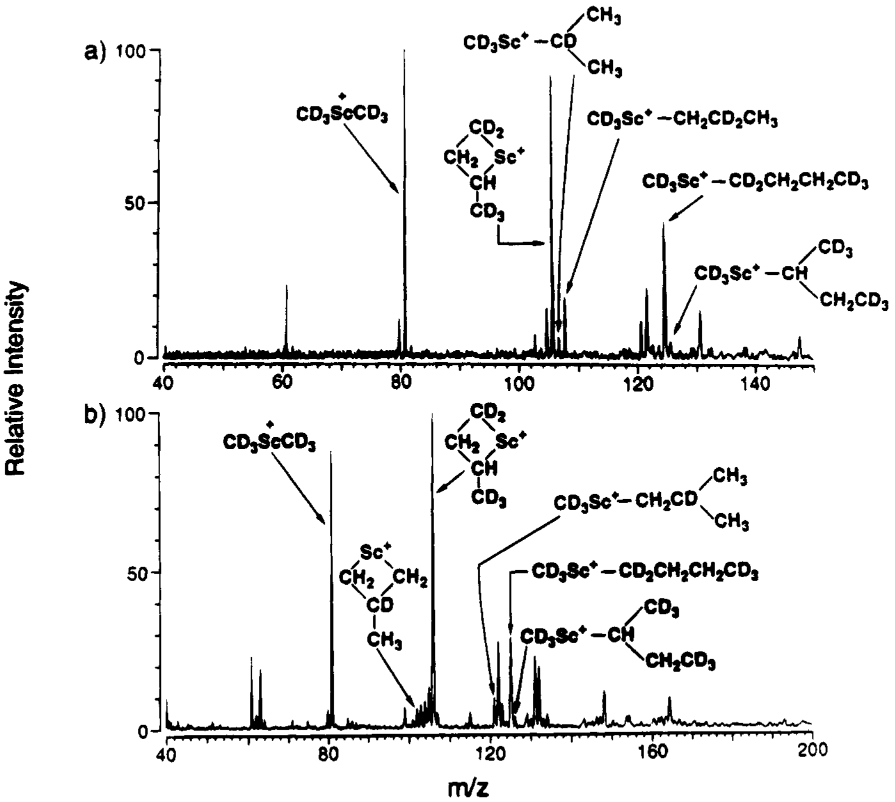


Figure 1. (a) Products of the reaction of $Sc(CD_3)_2^+$ with propane-*2,2-d₂* and *n*-butane-*1,1,1,4,4,4-d₆*. Spectra were taken 140 ms after the isolation of $Sc(CD_3)_2^+$. The main peaks above *m/z* 130 correspond to ScR_2^+, R = alkyl. The peaks at *m/z* 61 and 79 correspond to ScO^+ and $Sc(OH)_2^+$, respectively. (b) Products of the reaction of $Sc(CD_3)_2^+$ with isobutane-*2-d* and *n*-butane-*1,1,1,4,4,4-d₆*. Spectra were taken 400 ms after the isolation of $Sc(CD_3)_2^+$. The main peaks above *m/z* 130 correspond to ScR_2^+, R = alkyl. The peaks at *m/z* 61 and 63 correspond to ScO^+ and $ScOH_2^+$, respectively.

from the cell using double resonance techniques[11] and/or frequency sweep excitation.[12] Reactions of isolated $Sc(CD_3)_2^+$ were first examined with labeled *n*-butane. Methane, ethane, labeled propane, or labeled isobutane was then added along with the labeled *n*-butane, and reactions due to the additional alkane were observed. In order to determine if any kinetic isotope effects were present, the reaction of isolated $Sc(CH_3)_2^+$ (made via reaction 1 using unlabeled *n*-butane) with unlabeled *n*-butane 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.

$$Sc^+ + CD_3CH_2CH_2CD_3 \rightarrow Sc(CD_3)_2^+ + CH_2CH_2 \quad (1)$$

Results

Reaction with Methane. The thermoneutral exchange reaction of $Sc(CD_3)_2^+$ with CH_4 (reaction 2) was not observed. For reaction 2 we estimate that $k \le 1 \times 10^{-11}$ cm³ s⁻¹ molecule⁻¹.

$$Sc(CD_3)_2^+ + CH_4 \rightarrow D_3C{-}Sc^+{-}CH_3 + CD_3H \quad (2)$$

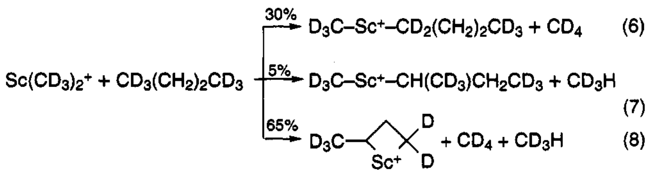
Reaction with Ethane. The only process observed is reaction 3. For reaction 3 $k = 4.7 \times 10^{-11}$ cm³ s⁻¹ molecule⁻¹ and the reaction efficiency $k/k_{\mathrm{Langevin}} = 0.045$.

$$Sc(CD_3)_2^+ + CH_3CH_3 \rightarrow D_3C{-}Sc^+{-}CH_2CH_3 + CD_3H \quad (3)$$

Reaction with Propane. The main process observed with the labeled propane is the metathesis reaction 4. Reaction 5 is a minor pathway (see Figure 1a). For the reaction of $Sc(CD_3)_2^+$ with labeled propane the total bimolecular rate constant $k = 1.5 \times 10^{-10}$ cm³s⁻¹ molecule⁻¹ and the reaction efficiency $k/k_{\mathrm{ADO}} = 0.14$.[13]

$$Sc(CD_3)_2^+ + CH_3CD_2CH_3 \begin{cases} \xrightarrow{90\%} D_3C{-}Sc^+{-}CH_2CD_2CH_3 + CD_3H & (4) \\ \xrightarrow{10\%} D_3C{-}Sc^+{-}CD(CH_3)_2 + CD_4 & (5) \end{cases}$$

Reaction with *n*-Butane. Reactions 6–8 are observed with labeled *n*-butane (see Figure 1a). Unlabeled *n*-butane shows the same product distribution, but without labeling we are unable to differentiate between the *n*-butyl and *s*-butyl products. It is postulated that reaction 8 occurs when the vibrationally excited product of reaction 6 has enough energy for a second intramolecular metathesis reaction, resulting in the metallacycle product. For the reaction of $Sc(CD_3)_2^+$ with labeled



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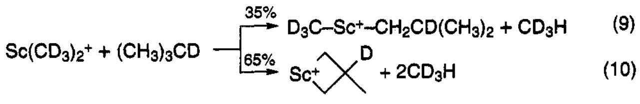
n-butane the total bimolecular rate constant $k = 4.4 \times 10^{-10}$ cm^3 s^{-1} molecule^{-1} and the reaction efficiency $k/k_{\rm ADO}$ is 0.39.[13] For the reaction of $Sc(CH_3)_2^+$ with unlabeled n-butane the total bimolecular rate constant $k = 4.3 \times 10^{-10}$ cm^3 s^{-1} molecule^{-1} and the reaction efficiency $k/k_{\rm ADO}$ is 0.37.[13]

Reaction with Isobutane. Reactions 9 and 10 are observed with labeled isobutane (see Figure 1b). Reaction 10 occurs when the vibrationally excited product of reaction 9 has enough energy for a second metathesis reaction to yield the metallacyle product. For the reaction of $Sc(CD_3)_2^+$ with labeled isobutane the total bimolecular rate constant $k = 4.3 \times 10^{-10}$ cm^3 s^{-1} molecule^{-1} and the reaction efficiency $k/k_{\rm ADO}$ is 0.37.[13]



Discussion

With ethane, propane, n-butane, and isobutane σ-bond metathesis reactions occur where a methyl group of $Sc(CD_3)_2^+$ is replaced by either an ethyl, propyl, n-butyl, or isobutyl group. Indeed, in the reaction with n-butane and isobutane, the n-butyl and isobutyl groups appear to undergo a second intramolecular σ-bond metathesis reaction (reactions 8 and 10) and form a four-membered metallacycle. The metathesis reactions could proceed via an oxidative addition/reductive elimination pathway or via a four-center intermediate (see Scheme 1). Again, since Sc^+ has only two valence electrons with which to form strong σ bonds,[2,3] we favor a four-center mechanism for these metathesis reactions. The high kinetic efficiencies observed indicate low barriers for these metathesis reactions, in accordance with the predictions of Steigerwald and Goddard.[1]

All of the labeled hydrocarbons we used contained hydrogen at their primary positions except the labeled n-butane, which was deuterated at its primary positions. Since the deuterium labels of n-butane could affect the measured total bimolecular rate constant, we observed the reaction of $Sc(CH_3)_2^+$ with unlabeled n-butane to see if kinetic isotope effects were present. The total bimolecular rate constants measured for labeled and unlabeled n-butane were practically identical (k_H/k_D = 0.98). Thus we conclude that little or no isotope effect exists.

The rate constants for the reaction of $Sc(CD_3)_2^+$ with n-butane and isobutane are almost the same and are about 2.9 times as large as that for the reaction with propane. In contrast, ethane is only $^1/_{10}$th as reactive as the butanes and methane is not observed to react at all with $Sc(CD_3)_2^+$. The latter observation agrees with the theoretical predictions of Perry and Goddard[14] that the degenerate metathesis reaction of methane with $Sc(CH_3)_2^+$ has a net barrier of approximately 12 kcal mol^{-1}. The higher kinetic efficiencies seen for the reactions of $Sc(CD_3)_2^+$ with the butanes and propane can be accounted for by the deeper potential wells which result from the increased polarizabilities of the larger alkanes. This makes it easier to overcome the intrinsic barrier to σ-bond metathesis. These results are reminiscent of the reactions of Co^+ with hydrocarbons, where larger hydrocarbons deepen the electrostatic potential well for the Co^+—alkane adduct, more strongly binding the alkane to Co^+ and lowering the barrier to bond insertion below the energy of the reactants[9,15] (see Figure 2).

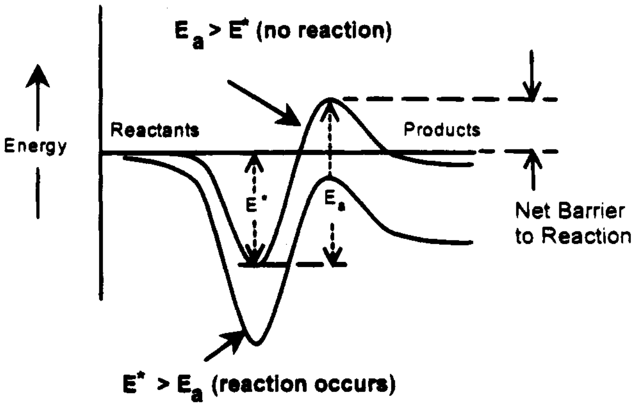


Figure 2. Schematic of a general potential energy surface showing how the initial electrostatic potential well can affect the height of a barrier relative to the energy of the reactants. Deepening the initial electrostatic well can lower the barrier to reaction below the energy of the reactants. The upper curve would be appropriate for the reaction of $Sc(CD_3)_2^+$ with methane, which is predicted to have a barrier of 12 kcal mol^{-1}.[14] The lower curve would correspond to the reaction with ethane, propane, and the isomeric butanes.

Site specificity was observed for the reactions of $Sc(CD_3)_2^+$ with propane, n-butane, and isobutane (see Figure 1). For propane and n-butane, the initial metathesis reactions (reactions 4–7) show a marked preference for attack at primary rather than secondary C—H bonds. For isobutane the initial metathesis reaction (reaction 9) occurs *only* at primary C—H bonds. No attack is seen at the tertiary site. These are interesting results considering that secondary and tertiary C—H bonds are weaker than primary C—H bonds.[16] For $Sc(CH_3)_2^+$, steric effects are not likely to be important at the uncrowded metal center, even in the four-center transition state for σ-bond metathesis. Perry and Goddard[14] have recently presented a theoretical study of the reactions of $Sc(CH_3)_2^+$ with alkanes and found that the differences in bond strengths for Sc^+—R for the series R = CH_3, C_2H_5, i-C_3H_7, and t-C_4H_9 match closely the differences in bond strengths for H—R. This suggests that the exchange reaction $Sc^+—R + R'—H \rightarrow Sc^+—R' + R—H$ should be thermoneutral for this series. However, alkyl groups larger than ethyl are able to bend around and interact with the Sc^+ center. The additional interaction or "solvation" with the alkyl group further stabilizes the Sc^+ center by about 3 kcal mol^{-1} in the case of the n-propyl substituent.[14] This stabilization explains the observed preference for reaction at primary sites with the larger alkanes in this investigation. While reaction at the secondary position of propane is thermoneutral, reaction at the primary position is exothermic by approximately 5 kcal mol^{-1}. Reaction at

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primary C—H bonds may also be favored by the structure of the most stable Sc^+—alkyl adduct. Perry et al. have found that the Co^+—propane adduct is more stable when it exhibits η^4 coordination to the two primary carbons than when it exhibits η^2 coordination to the secondary carbon.[15] $Sc(CH_3)_2^+$ may show a similar behavior when it forms an adduct with propane.

Our results in this system contrast with results obtained by Weinberg and Sun,[8] who find that in the case of propane reacting with a Pt surface attack at secondary C—H bonds is preferred over attack at primary C—H bonds. However, reactions of iridium complexes in solution[7] and Co^+ with propane[9] in the gas phase have shown a preference for attack at primary C—H bonds.

Though numerous examples of four-center σ-bond metathesis reactions have been documented,[4-7] to our knowledge the present results comprise the first example of alkanes showing such reactivity with such a comparatively simple metal complex and the first case where a larger alkyl group replaces a smaller alkyl group at the metal center. Previous studies[4-7] used experimentally measured equilibrium constants for σ-bond metathesis reactions to evaluate relative metal—X bond strengths for a series of complexes. This method of evaluating relative metal—X bond strengths may also prove to be useful in the present system for evaluating *absolute* Sc^+—R bond strengths, since the absolute value of the Sc^+—CH_3 and CH_3Sc^+—CH_3 bond energies are known.[17] It might also prove possible to extend these experiments to different series of ligands and different metals. We are currently conducting experiments in our laboratory along these lines.

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