Competition between C–C and C–H Activation in Reactions of Neutral Yttrium Atoms with Cyclopropane and Propene

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I. Introduction

The development of organometallic catalysts for the conversion of naturally abundant hydrocarbon feedstocks to more useful forms is a long-sought goal in organometallic chemistry. The activity of such catalysts is quite sensitive to the electronic structure of the transition metal center and to ligand and solvent effects.1–5 Although the cleavage or “activation” of C–H bonds in solution phase inorganic chemistry is now quite well-known, the analogous process involving C–C bonds has remained elusive.6

To better understand how electronic structure controls transition metal reactivity, reactions of transition metal atoms and cations with hydrocarbons have been studied, both experimentally and theoretically. In reactions of transition metal cations, both C–H and C–C bond activation is quite well-known.5–8 Calculations have demonstrated that for cation reactions, barrier heights for C–C insertion are comparable to or even lower than those for C–H insertion.8 For example, reactions of Fe+, Co+, and Ni2+ with propane led to methane elimination via C–C insertion, as well as to molecular hydrogen elimination following C–H insertion.

The potential energy barriers for insertion of neutral second-row transition metal atoms into C–H and C–C bonds are considerably larger than those for cations.9 For ethane, because the potential energy barrier heights for C–H insertion are much larger than those for C–H insertion,9,10 no evidence for this process was observed in our previous studies.11,12 The fundamental difference between C–H and C–C insertion for saturated hydrocarbons such as ethane has been rationalized in terms of differences in the directionality of the relevant orbitals.13 For

insertion into a C–H bond, the spherical orbital of a H atom may participate in multicenter metal–ligand bonding, leading to lower transition-state energies than those for insertion into the highly directional C–C bond.10,13

For cyclopropane, calculations indicate that barriers for insertion into the strained C–C bonds lie lower in energy than C–H insertion barriers for certain transition metal systems including Y and Mo.9 Insertions into the C–H and C–C bonds are expected to be the rate-limiting steps in cyclopropane reactions with C–H insertion leading to formation of YCH2H + H2 and C–C insertion leading to YCH2 + CH4 (Figure 1).9,14 We have recently presented a report focusing on the branching ratios between C–C and C–H activation of cyclopropane by Y, Zr, Nb, and Mo.14 In that work, we observed a direct correlation between the product branching ratios and the calculated relative potential energy barrier heights for C–C and C–H insertion.14

We use the term “C–C activation” to describe any reaction leading to C–C bond fission in which the hydrocarbon is broken into two smaller hydrocarbon products with one hydrocarbon bound to the metal. It is important to note that C–C activation does not necessarily require true C–C insertion. As will be shown in this paper, the reaction of Y with propene leads to formation of YCH2 + CH4. The mechanism involves addition to the C=C bond followed by H atom migration and C–C bond fission, rather than by true C–C insertion.

There have been several experimental and theoretical studies of reactions of neutral transition metal atoms with propene leading to C–H activation (i.e., elimination of H2). In a combined experimental and theoretical effort, Carroll and coworkers reported that both ethene and propene undergo bimolecular reaction with second-row transition metal atoms.9 By monitoring the depletion of Y in a fast-flow reactor, Carroll et
al. observed effective bimolecular rate constants at 298 K of $k_1 = 8.2 \times 10^{-12}$ and $143 \times 10^{-12}$ cm$^3$ s$^{-1}$ for ethene and propene, respectively. The origin of the very large difference in reactivity of the two molecules was not determined. Subsequently, Porembski and Weisshaar studied the reactions in a flow cell and directly observed H$_2$ elimination in room-temperature experiments, demonstrating that H$_2$ elimination occurs in Y atom reactions with ethene and propene even at a mean collision energy of 0.9 kcal/mol. There were considerable similarities between the reaction mechanisms for Y and Zr atoms. For both Y and Zr, the presence of deuterium isotope effects in ethene reactions demonstrated that the mechanism involved initial formation of $\pi$-complexes, which subsequently underwent C--H insertion forming HMC$_2$H$_3$. The lowest pathway to H$_2$ elimination involved concerted molecular elimination over a multicanter transition state, rather than a stepwise mechanism involving H$_2$MC$_2$H$_5$. More recently, Bayse has shown that such multicanter transition states are also important in H$_2$ elimination in Y + H$_2$CO reactions.

In this paper, we present a study of the reactions of Y with cyclopropane and propene. Rather surprisingly, we have found that C--C activation, leading to formation of YCH$_2$ + C$_2$H$_4$, is significant even for propene reactions, particularly at higher collision energies. We have also observed some similarity between Y reactions with propene and cyclopropane. In both cases, competition between C--C activation forming YCH$_2$ + C$_2$H$_4$ and C--H activation forming YCH$_2$H$_2$ + H$_2$ was observed. At the highest collision energies, an additional C--H activation channel producing YH$_2$ + C$_3$H$_4$ was also observed.

In the accompanying paper, we present results of experimental studies of reactions of Y with four butene isomers. These studies confirm some of the mechanistic details inferred here and provide additional mechanistic insight. In particular, we propose that the large yield of YCH$_2$ + C$_2$H$_4$ from Y + propene results from the unfavorable nature of $\beta$-H migration necessary for the competing reaction pathways leading to C--H activation (YC$_3$H$_4$ + H$_2$ and YH$_2$ + C$_3$H$_4$). In reactions involving butenes, on the other hand, $\beta$-H migration is favorable, causing a dramatic shift in branching ratios, C--H activation being dominant and C--C activation being a minor channel.

II. Experimental Section

The reactions were studied using a rotatable source crossed molecular beams apparatus. The Y beam was produced by laser ablation from a 0.25-in. diameter rod (99% purity, Alfa Aesar) using the 532 nm output of a Nd:YAG laser (Continuum Surelite, 15mJ). A piezo-electrically actuated pulsed valve delivered an inert carrier gas that entrained the Y atoms into a supersonic expansion. The metal beam was collimated by a skimmer and a defining aperture and was temporally refined by a slotted chopper wheel before entering the main collision chamber held at or below 10$^{-6}$ Torr. The electronic state populations of the Y beam were previously characterized using laser-induced fluorescence spectroscopy, confirming the presence of only the two spin–orbit levels of the ground a$^2D_J$ (s$^2d^1$) electronic state.

A molecular beam was generated by expanding a dilute (10–20%) mixture of C$_3$H$_6$ in an inert carrier gas. The beam was collimated by a skimmer before intersecting the Y beam at 90°. Neutral products were detected 24.1 cm away by photoionization using 157 nm F$_2$ excimer radiation (Lambda Physik LPX 220i) followed by mass selection and ion detection. The time-of-flight (TOF) spectra of the products were obtained by scanning the trigger of the excimer laser with respect to time zero for reaction, as defined by the chopper wheel. By rotating the two molecular beams with respect to the fixed detector, TOF spectra were recorded at various laboratory angles. Product lab angular distributions were obtained by integrating TOF spectra for each channel at 2° increments.

The product scattering distribution, $I(E, \theta)$, was assumed to be separable into the center-of-mass (CM) product translational energy, $P(E)$, and angular, $T(\theta)$, distributions. For reactions involving intermediate complexes with lifetimes far in excess of their rotational periods, as in the reactions reported here, this is a reasonable assumption. These distributions were used with the known experimental parameters (flight distances, aperture sizes, etc.) to simulate the raw TOF and angular distribution data using the forward convolution technique. The CM distributions were iteratively adjusted until agreement between simulations and experimental data was obtained.

III. Results and Analysis

A. Yttrium + Cyclopropane: $E_{\text{coll}} = 18.5$ kcal/mol. For both C$_3$H$_6$ reactant isomers, several competing product channels were observed:

\[
\begin{align*}
\text{Y} & \text{(a$^2D_J$; 5s$^2d^1$)} + \text{C}_3\text{H}_6 \rightarrow \text{YCH}_2 + \text{C}_2\text{H}_4 \quad (1) \\
& \quad \rightarrow \text{YC}_3\text{H}_4 + \text{H}_2 \quad (2) \\
& \quad \rightarrow \text{YH}_2 + \text{C}_3\text{H}_4 \quad (3) \\
& \quad \rightarrow \text{Y} + \text{C}_3\text{H}_6 \quad (4)
\end{align*}
\]

In the accompanying paper, we present results of experimental studies of reactions of Y with four butene isomers. These studies confirm some of the mechanistic details inferred here and provide additional mechanistic insight. In particular, we propose that the large yield of YCH$_2$ + C$_2$H$_4$ from Y + propene results from the unfavorable nature of $\beta$-H migration necessary for the competing reaction pathways leading to C--H activation (YC$_3$H$_4$ + H$_2$ and YH$_2$ + C$_3$H$_4$). In reactions involving butenes, on the other hand, $\beta$-H migration is favorable, causing a dramatic shift in branching ratios, C--H activation being dominant and C--C activation being a minor channel.

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Collisions of Y with cyclopropane were studied at $E_{\text{coll}} = 9.4 - 36.8$ kcal/mol (Table 1). The competition between YCH$_2^+$ and YC$_3$H$_4^+$ was monitored at various laboratory angles by alternating scans at $m/e = 103$ (YCH$_2^+$) and 129 (YC$_3$H$_4^+$). A Newton diagram in velocity space (Figure 2) depicts the relationship between the lab and CM reference frames for $E_{\text{coll}} = 18.5$ kcal/mol. Reaction products scatter radially from the tip of the CM velocity vector, $V_{\text{CM}}$, with a maximum allowed velocity (shown as circles) determined by reaction energetics and conservation of linear momentum. As anticipated from energy and momentum conservation, the YCH$_2$ products were scattered over a wider lab angular range than the YC$_3$H$_4$ products because of the heavier recoiling counter-fragment (C$_2$H$_4$ vs. H$_2$, respectively). The $m/e = 103$ data has been corrected for a small contribution from fragmentation of YC$_3$H$_4$. Representative TOF spectra are shown at indicated lab angles in Figure 3.

The solid-line simulations included in Figures 2 and 3 were generated using the CM translational energy, $P(E)$, and angular distributions, $T(\theta)$, used to simulate data from collisions of Y + cyclopropane at $E_{\text{coll}} = 18.5$ kcal/mol. Arrows indicate maximum allowed translational energy for formation of two distinct product isomers.

The solid-line simulations included in Figures 2 and 3 were generated using the CM translational energy, $P(E)$, and angular, $T(\theta)$, distributions shown in Figure 4. The maximum allowed translational energy for formation of the two possible YC$_3$H$_4$ isomers, Y−allene and Y−propyne, are denoted by arrows on the energy axis of the $P(E)$. With the use of the calculated energetics for Y−propyne formation along with $E_{\text{coll}}$ and $P(E) = 14.0$ kcal/mol, the average fraction of available energy deposited as translational energy ($f_T$) was 0.34. Reductive elimination of ethene was best fit with a $P(E)$ peaking closer to zero translational energy (Figure 4), such that the fraction of energy appearing in translation was $f_T = 0.18$. For both product

### Table 1: Experimental Conditions for Y-Atom Beam

<table>
<thead>
<tr>
<th>$E_{\text{coll}}$ (^a)</th>
<th>carrier gas</th>
<th>velocity (^b)</th>
<th>fwhm (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.6</td>
<td>pure Ne</td>
<td>1410</td>
<td>150</td>
</tr>
<tr>
<td>18.5</td>
<td>50% Ne/50% He</td>
<td>1690</td>
<td>190</td>
</tr>
<tr>
<td>29.5</td>
<td>pure He</td>
<td>2480</td>
<td>310</td>
</tr>
<tr>
<td>36.8</td>
<td>50% He/50% H$_2$</td>
<td>2930</td>
<td>420</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$E_{\text{coll}}$ (^a)</th>
<th>carrier gas</th>
<th>velocity (^b)</th>
<th>fwhm (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.3</td>
<td>pure Ne</td>
<td>1380</td>
<td>130</td>
</tr>
<tr>
<td>15.8</td>
<td>50% Ne/50% He</td>
<td>1680</td>
<td>190</td>
</tr>
<tr>
<td>25.2</td>
<td>pure He</td>
<td>2430</td>
<td>310</td>
</tr>
<tr>
<td>28.8</td>
<td>50% He/50% H$_2$</td>
<td>2570</td>
<td>350</td>
</tr>
<tr>
<td>43.2</td>
<td>pure H$_2$</td>
<td>3290</td>
<td>470</td>
</tr>
</tbody>
</table>

\(^a\) Values in kcal/mol. \(^b\) Values in m/s.

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**Figure 2.** Newton diagram in velocity space for Y + cyclopropane at $E_{\text{coll}} = 18.5$ kcal/mol. Larger solid circle corresponds to maximum velocities for YCH$_2$ products, while smaller solid circle and smaller dotted circle correspond to maximum velocities for Y−propyne and Y−allene products, respectively. Lab angular distributions for YCH$_2$ (■) and YC$_3$H$_4$ (○) were recorded under identical collision conditions. Solid-line fits to lab angular distributions were generated using CM distributions in Figure 4.

**Figure 3.** Sample TOF spectra recorded at indicated lab angles for YCH$_2$ (left) and YC$_3$H$_4$ (right) products from collisions of Y + cyclopropane at $E_{\text{coll}} = 18.5$ kcal/mol (open points). Solid-line fits were generated using CM distributions in Figure 4.

**Figure 4.** CM translational energy distributions, $P(E)$, and angular distributions, $T(\theta)$, used to simulate data from collisions of Y + cyclopropane at $E_{\text{coll}} = 18.5$ kcal/mol. Arrows indicate maximum allowed translational energy for formation of two distinct product isomers.
channels, the best-fit CM angular distributions are symmetric about $\theta = 90^\circ$.\textsuperscript{21,22}

The ratios of reaction cross sections for competing product channels may be derived from the relative signal levels if the relative ionization cross sections for the products are known. Because the 157 nm photoionization cross sections for YCH\textsubscript{2}, Y-propyne, and Y-allene are not known, experiments were performed using electron impact ionization, which may be calibrated, as discussed in section III.D. These studies indicated that the ratio of YCH\textsubscript{2} to YC\textsubscript{3}H\textsubscript{4} 157 nm photoionization cross sections is approximately unity. Determination of the branching ratio also requires explicit consideration of fragmentation during ionization. We recorded TOF spectra at all $m/e$ values at which signal was observed and scaled the parent ion ratio accordingly. The fraction of the total product signal sampled within the detector solid angle depends on the radius of the scattering sphere in the CM reference frame. The appropriate Jacobian transformations to account for this dependence on the scattering radius are included in the forward convolution calculations used to simulate the experimental data. By scaling the normalized simulations to the experimental data, the product branching ratio at $E_{\text{coll}} = 18.5$ kcal/mol, $\phi_{\text{YCH}_2}/\phi_{\text{YCH}_4}$, was determined to be 1.09:1.00.

The data for nonreactively scattered Y atoms recorded at $m/e$ 89 (Figure 5) exhibit typical features for impulsive inelastic scattering without appreciable long-lived complex formation.\textsuperscript{11,12} At all lab angles, the fast scattering peak ($\sim 150$ $\mu$s) dominates. In the CM reference frame, the recoiling Y atoms were forward scattered as seen in the $T(\theta)$. The TOF spectra recorded approaching $\theta = 0^\circ$ became increasingly unreliable because of contributions from the atomic beam. Consequently, the uncertainty in the $T(\theta)$ increases for CM angles $\theta < 50^\circ$, as demonstrated by the gray shaded area included in Figure 5. By comparing $\langle P(E) \rangle$ to $E_{\text{coll}}$, it was found that $\sim 31\%$ of the initial kinetic energy was converted into cyclopropane internal energy.

**B. Yttrium + Cyclopropane: Dependence on $E_{\text{coll}}$.** The product branching ratios were measured as a function of $E_{\text{coll}}$ (Figure 6). It was found that for $E_{\text{coll}} \geq 19$ kcal/mol, formation of YCH\textsubscript{2} became dominant. The CM distributions for these two product channels were found to be qualitatively similar at all $E_{\text{coll}}$ studied. Product at $m/e$ 129 (YC\textsubscript{3}H\textsubscript{4})\textsuperscript{+} was observed at $E_{\text{coll}}$ as low as 9.4 kcal/mol. At this $E_{\text{coll}}$, production of YCH\textsubscript{2} could not be confirmed because of background signal from YO mass overflow. At $E_{\text{coll}} = 36$ kcal/mol, a third minor product channel, YH\textsubscript{2} + C\textsubscript{3}H\textsubscript{4} (recorded at $m/e$ 91) was observed with a signal level 25 times smaller than that for YC\textsubscript{3}H\textsubscript{4}. With the use of the best-fit $P(E)$ with the energetics for YH\textsubscript{2} + allene formation, $f_\text{r}$ was 0.15.

**C. Yttrium + Propene: $E_{\text{coll}} = 25.2$ kcal/mol.** Formation of YCH\textsubscript{2} and YC\textsubscript{3}H\textsubscript{4} was observed for the propene reaction. The experimental data recorded at $m/e$ 129 at $E_{\text{coll}} = 25.2$ kcal/mol were similar to that observed for Y + cyclopropane at $E_{\text{coll}} = 18.5$ kcal/mol, and are therefore not shown. By considering the difference in enthalpies of formation for propene and cyclopropane, we find that these two data sets correspond to nearly the same total energy above the product asymptotes.\textsuperscript{9} The TOF spectra at $m/e$ 103, corresponding to YCH\textsubscript{2}\textsuperscript{+}, (Figure 7) were recorded with a similar amount of averaging as those shown in Figure 3 and have been corrected to account for a minor contribution from fragmentation of YC\textsubscript{3}H\textsubscript{4} as discussed below.

The solid-line fits shown in Figure 7 were generated using the CM distributions shown in Figure 8. For YCH\textsubscript{2}, $\langle P(E) \rangle$ =

\[
\langle P(E) \rangle = \frac{1}{E_{\text{coll}}} \int_{0}^{E_{\text{coll}}} P(E) \, dE
\]

Figure 5. Sample TOF spectra (top) recorded at indicated lab angles for nonreactive scattering of Y atoms from collisions with cyclopropane at $E_{\text{coll}} = 18.5$ kcal/mol (open points) and CM distributions (bottom) used to generate solid-line simulations to the TOF data. Shaded area in the $T(\theta)$ indicates range of distributions that give acceptable fits to the data.

Figure 6. Product branching ratio, $\phi_{\text{YCH}_2}/\phi_{\text{YCH}_4}$, for reactions of Y + cyclopropane as a function of $E_{\text{coll}}$.

Figure 7. Sample TOF spectra recorded at indicated lab angles for YCH\textsubscript{2} products from collisions of Y + propene at $E_{\text{coll}} = 25.2$ kcal/mol (open points). Solid-line simulations were generated from CM distributions shown in Figure 8. Dashed line indicates overflow contribution from YO contamination in the Y atomic beam.
3.18 kcal/mol, giving $f_1 = 0.23$. The $T(\theta)$, however, was identical to that shown in Figure 4 for the cyclopropane reaction. At small lab angles (\(\Theta \lesssim 8^\circ\)), an additional fast component (i.e., short flight times) appears in the TOF spectra due to YO overflow signal. Dashed lines shown in the TOF spectra at 6° and 8° were obtained by fitting data recorded at \(mle\ 105\) (the source of the overlap) and have been scaled accordingly. The product branching ratio, $\phi_{YCH_2}/\phi_{YC_3H_4}$, at $E_{coll} = 25.2$ kcal/mol was 0.48:1.00.

The minor YH$_2$ + C$_2$H$_4$ channel was observed for the propene reaction at $E_{coll} = 28.8$ kcal/mol, as shown in Figure 9. For YH$_2$, $P(E) = 3.7$ kcal/mol, which yields $f_1 = 0.32$. The $T(\theta)$ was strongly polarized with $T(0^\circ)/T(90^\circ) = 12.46$. The YH$_2$ channel was 45 times weaker than for YC$_3$H$_4$ at $E_{coll} = 28.8$ kcal/mol.

The TOF spectra recorded at \(mle\ 89\) (Figure 10), corresponding to nonreactive Y + propene collisions, are distinctly different from corresponding data obtained for cyclopropane. At wider lab angles, the slower peak (~175 \(\mu\)s) becomes more intense than the fast peak. This behavior is very similar to that seen previously in our studies of reactions of transition metal atoms with C$_2$H$_4$, C$_2$H$_2$, and carbonyl-containing species such as H$_2$CO, and clearly results from decay of $\pi$-complexes back to reactants. As in the previous studies, data was simulated using two separate $P(E)$ and $T(\theta)$ combinations (Figure 10). In one combination (shown on the right), $T(\theta)$ was constrained to forward-backward symmetry, corresponding to long-lived complexes that survive many rotational periods prior to decay back to reactants. A second forward-scattered $T(\theta)$ corresponds to direct nonreactive collision events that do not persist for time scales longer than their rotational periods.

D. Yttrium + Propene: Dependence on Collision Energy.

At $E_{coll} = 12.3$ kcal/mol, formation of YC$_3$H$_4$ + H$_2$ was observed (Figure 11). Weak signal was also observed at \(mle\ 103\), the mass corresponding to YCH$_3$+, but comparison of the data recorded at \(mle\ 103−129\) at this $E_{coll}$ revealed that the weak \(mle\ 103\) signal originates primarily from fragmentation of YC$_3$H$_4$ during photoionization. The intensity of fragmentation signal at \(mle\ 103\) was 3.6% of the parent ion signal (\(mle\ 129\)). The same value was obtained at $E_{coll} = 10.4$ kcal/mol and was used to correct the YCH$_2$ data at all $E_{coll}$. The best-fit $P(E)$ (Figure 11 bottom) indicated that $f_1 = 0.46$. The product flux distributions for the two major product channels, YC$_3$H$_4$ and YCH$_2$, are shown in Figure 12.

For reaction with propene, YCH$_2$ product was clearly observed at $E_{coll} \geq 15.8$ kcal/mol. The complete set of lab angular distributions recorded for reactions of Y + propene at different collision energies is shown in Figure 13. Although an increase in the relative amount of YCH$_2$ formed was observed as $E_{coll}$ increased, YC$_3$H$_4$ formation was always dominant. The reaction with propene was also studied using electron impact ionization at $E_{coll} = 31.2$ kcal/mol. Because much longer averaging was required for each TOF, data were only recorded at the CM laboratory angle (\(\Theta_{CM} = 14^\circ\)) and one angle outside
the range of YC$_3$H$_4$ scattering ($\Theta = 20^\circ$). Figure 14 shows the data recorded for the YCH$_2$ and YC$_3$H$_4$ parent ion signals. The solid-line fits were generated using CM distributions obtained from analysis of data obtained at the same $E_{\text{coll}}$ recorded using 157 nm photoionization. To fit the $m/e_{103}$ data, it was evident that fragmentation from YC$_3$H$_4$ must be considered. The dotted-line fit at 14$^\circ$ represents this fragmentation, while the dashed line indicates the YCH$_2$ signal from ethene elimination. The raw branching ratio, YCH$_2$/YC$_3$H$_4$, was 0.80:1.00. Using electron impact ionization, we relate the ionization cross section, $\sigma_{\text{ion}}$ (Å$^2$), to the molecular polarizability, $\alpha$ (in Å$^2$), using the empirical formula$^{26}$

$$\sigma_{\text{ion}} = 36\sqrt{\alpha} - 18 \quad (5)$$

The molecular polarizabilities for YC$_3$H$_4$ and YCH$_2$ were calculated by adding the Y atomic polarizability to the propyne and carbene polarizabilities. Using eq 5, we found $\sigma_{\text{ion}}$ to be 163 and 176 Å$^2$ for YCH$_2$ and YC$_3$H$_4$, respectively. The branching ratio as corrected to include the relative ionization cross sections was $\phi_{\text{YCH}_2}/\phi_{\text{YC}_3\text{H}_4} = 0.74:1.00$. This is shown in Figure 15 (A), along with the values obtained using 157 nm photoionization (■). The agreement of these separate measurements shows that the ratio of 157 nm photoionization cross sections for the competing product channels is approximately unity.

IV. Discussion
A. Nonreactive Scattering in Cyclopropane and Propene Reactions. For Y + cyclopropane, the forward peaking of the Y angular distribution (Figure 5) is similar to that reported
The absence of initial direct C–C bond insertion. Bergman and co-workers studied the reaction of C₅(CH₃)₅RhCO with many alkanes and cycloalkanes. For example, Bergman reactions of unsaturated transition metal complexes in solution in cyclopropane have been implicated as intermediates in reactions of unsaturated transition metal complexes in solution with many alkanes and cycloalkanes. For example, Bergman and co-workers studied the reaction of C₅(CH₃)₅RhCO with hydrocarbons including cyclopropane at low temperatures in solution. In their experiment, the photolytically generated unsaturated C₅(CH₃)₅RhCO complex was found to insert spontaneously into the C–H bond of cyclopropane. When the sample was warmed, the kinetically favored C–H insertion complex was found to undergo rearrangement to the more thermodynamically favorable C–C inserted metallacyclobutane complex. Detailed kinetic studies revealed that the mechanism involves reductive elimination from the C–H complex, forming the weakly bound σ-complex, which then underwent C–C insertion. The absence of initial direct C–C insertion was attributed to steric effects imposed by the bulky ligands on the metal complex.

For bare transition metal atom reactions with hydrocarbons such as cyclopropane, the small local minimum corresponding to σ-bound complexes should be no deeper than several kilocalories per mole. At the relatively high collision energies of our experiment, the small σ-binding energies, comparable to those in van der Waals species, cannot support σ-bound complexes for time scales greater than their rotational periods. Therefore, for Y + cyclopropane, C–C and C–H bond insertion are direct processes without initial σ-complex formation. Insertion into cyclopropane C–H and C–C bonds has been reported previously in reactions of transition metal complexes in solution, cation reactions in gas-phase guided beam experiments, and neutral transition metal atoms in low-temperature matrices.

The reaction dynamics are quite different for Y + propene. The wide angle nonreactive scattering (Figure 10) with a slow approach of initially formed complexes decay back to reactants rather than forming chemical products. The approach of neutral metal atoms in low-temperature matrixes is no significant contribution from formation of long-lived intermediates decay back to reactants. The approach of a neutral metal atom toward the strained C–C bond is sometimes considered analogous to metal–olefin interactions, in which the strained σ C–C orbital (HOMO) and the σ* orbital (LUMO) interact with the metal atom. One might, therefore, anticipate formation of a σ-complex prior to C–H or C–C insertion. Indeed, such σ-complexes involving either C–H or C–C bonds in cyclopropane have been implicated as intermediates in reactions of unsaturated transition metal complexes in solution with many alkanes and cycloalkanes. For example, Bergman and co-workers studied the reaction of C₅(CH₃)₅RhCO with hydrocarbons including cyclopropane at low temperatures in solution. In their experiment, the photolytically generated unsaturated C₅(CH₃)₅RhCO complex was found to insert spontaneously into the C–H bond of cyclopropane. When the sample was warmed, the kinetically favored C–H insertion complex was found to undergo rearrangement to the more thermodynamically favorable C–C inserted metallacyclobutane complex. Detailed kinetic studies revealed that the mechanism involves reductive elimination from the C–H complex, forming the weakly bound σ-complex, which then underwent C–C insertion. The absence of initial direct C–C insertion was attributed to steric effects imposed by the bulky ligands on the metal complex.

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Reactions of Y with Cyclopropane and Propene


metathesis reaction involves the addition of ethene to a metal carbene, forming a metallacyclobutane, that is, the exact reverse of the mechanism proposed here. In Figure 1, a possible intermediate along the reaction pathway, CH2YC3H4, is included. To assess the possibility that this species can be accessed, consider the reverse reaction, addition of a metal carbene to ethene. The electronic configuration of YCH2 (5s14d2) can readily add to the ethene double bond to form a CH2YC3H4 complex through a barrierless transition state. This complex is strongly bound with respect to ethylene loss, suggesting that it represents a true local minimum on the reaction coordinate. The small translational energy release (f = 0.18) observed for ethylene loss and the large yield of YCH2 is consistent with a loose transition state for loss of ethylene from the metallacyclobutane.

Formation of YCH2 + C2H4 is thermodynamically less favorable than production of YC3H4 + H2. However, 1,1-H2 elimination from the sp3-hybridized carbon atoms in the metallacyclobutane complex will likely encounter large potential energy barriers. Therefore, H2 elimination would require H atom migration or reductive elimination by passage back over the high C–C insertion barrier. For transition metal atom reactions under collision-free conditions, reductive elimination would lead to reformation of reactants with essentially no probability of getting trapped in the shallow σ-complex well. These considerations, in addition to a large body of inorganic literature, indicate that C2H4 rather than H2 elimination is the dominant decay pathway following C–C insertion. This leads us to believe that the metallacyclobutane complex decays exclusively to YCH2 + C2H4. Similarly, C–H insertion in cyclopropane leads to efficient H2 elimination. Because the rate-limiting steps for both C–C and C–H activation reactions are the initial insertion processes and because interconversion between C–C and C–H insertion complexes is not likely to compete with molecular elimination forming products, we conclude that the branching ratio between YCH2 and YC3H4 in the cyclopropane experiments is the branching ratio for initial C–C to C–H insertion. This is supported by our previous experiments in which the MCH2/MC3H4 branching ratios for Y, Nb, Zr, and Mo reactions with cyclopropane were correlated to the relative barrier heights for C–C and C–H insertion rather than to the thermodynamics of product formation.

D. YCH2 + H2 and YH2 + C2H4 from the Propene Reaction. Our finding that the reaction Y + propene → YCH2 + H2 was observed at all collision energies is certainly not surprising in light of the fact that Porembski and Weisshaar observed H2 elimination at a mean collision energy of only 0.9 kcal/mol. We observe YCH2 signal from the propene reaction to be 15 times more intense than that from cyclopropane at Ecollision = 12 kcal/mol. Clearly the reactivity of propene results from the large capture cross section for formation of π-complexes, a process that has been shown theoretically to proceed for Y + ethene with no significant potential energy barrier. This contrasts the situation for reactions of alkanes including cyclopropane that must be initiated by direct insertion over relatively tight transition states.

As already noted, it has been known for some time that the reaction rate constant is much larger for propene than for ethene at room temperature. To date, however, no definitive explanation for this behavior has been offered. It has been pointed out that the larger density of states for the metal π-complex resulting from the presence of a methyl group in propene will lead to increased complex lifetimes relative to those for ethene. This increased lifetime could increase the probability of termolecular stabilization in the flow-cell experiments. However, in those experiments, it was concluded that the Y + ethene and propene reactions were bimolecular, not termolecular, and H2 products have been observed. In the absence of collisional stabilization, the branching ratio for decay of complexes to products relative to decay back to reactants depends on the total energy and the nature of the transition states for the competing processes, independent of well depth and lifetime of the common complex. Thus the increased density of states in propene relative to ethene cannot explain the greater rate constant for propene relative to ethene. Because steric hindrance should be greater for propene, these considerations would lead to the conclusion that propene should be less reactive, not more reactive, than ethene.

We have previously studied the reactions of several second-row transition metal atoms, including Y, with ethene. To understand why propene is more reactive than ethene, we have measured the branching ratios for decay of π-complexes to products relative to that for decay back to reactants. This measurement was accomplished by including all reactive contributions with explicit inclusion of fragmentation effects upon 157 nm photoionization. The nonreactive scattering channel was evaluated by monitoring wide angle signal appearing at long flight times (Figure 10) for each reactant system. We find that the ratio for propene and butene is larger than that for ethene by nearly an order of magnitude. This indicates that the potential energy barrier for the rate-limiting step in the reaction must be substantially smaller for propene and butene than for ethene. Because the potential energy barriers for insertion of the metal center into the vinylic C–H bonds in each system should not differ appreciably, we conclude that the large difference in reactivity must result from the presence of one or two methyl groups in the propene and butene reactants, respectively. The methyl groups apparently open up an important low-energy reaction pathway that was not available in the ethene reactions.

Reactions of ethene, propene, and butenes are initiated by formation of π-complexes. For ethene, reaction involves C–H insertion into one of the four relatively strong sp3-hybridized C–H bonds. In the case of propene (and the butenes), although C–H insertion into an sp2 C–H bond can occur, the alternative process involving insertion into the weaker sp3-hybridized methyl C–H bonds is also possible. The potential energy barrier for insertion of a free ground-state Y(s2d1) atom into the C–H bond of ethane is large (20 kcal/mol). This is primarily associated with the inert gaslike s2 repulsion of the ground-state atomic configuration (e.g., s2d4 for Y). However, formation of the ground-state Y–propene π-complex leads to considerable electronic rearrangement at the metal center with considerable rehybridization to s2d2 electronic character, substantially decreasing the barrier height for intramolecular β-C–H insertion into the methyl C–H bonds in propene. The much greater reactivity of propene inferred from our experiments and those of Carroll strongly suggests that this barrier height must be substantially smaller than that for insertion into sp3-hybridized vinylic C–H bonds. The observation of a substantial deuterium isotope effect observed by Porembski and Weisshaar for reactions of ethene but not those of propene also strongly suggests that the C–H insertion barrier following π-complex formation is substantially smaller for propene than for ethene.

We propose the mechanism for C–H activation of propene illustrated in Figure 16. Formation of a π-complex is followed by insertion into a methyl C–H bond, leading to formation of HYCH2CH2. This species may be represented by several resonance structures: Two involve a single Y–C bond with
Atoms; such complexes tend to be much less kinetically stable in inorganic literature, is well-known to be the primary decomposition of the central carbon atom, known as "allyl-type structure. Transfer of the single hydrogen atom from the Y–complex to YCH2, or alternatively to Y forming H2YCH3, which subsequently decomposes by simple ligand loss to give YH2 + CH4.

Figure 16. Proposed reaction mechanism (top) for Y + propene. Addition to the C≡C bond leads to formation of a π-complex, followed by intramolecular insertion into a methyl C–H bond. Three resonance structures may be written for the resulting allyl hydride complex. The bottom panel shows the mechanism for C–H activation of propene. Decay of the allyl hydride complex may proceed via migration of the lone vinyl H atom (β-H migration). Migration may proceed toward the Y–H moiety via a MCTS, forming YC3H4 + H2, or alternatively to Y forming H2YCH3, which subsequently decomposes by simple ligand loss to give YH2 + CH4.

Figure 17. Possible mechanism for C–C activation involving formation of a π-complex followed by direct sp3–sp3 C–C insertion. This mechanism is ruled out on the basis of the much larger potential energy barrier for C–C insertion relative to C–H insertion from the π-complex.

Figure 18. Mechanism for C–C activation of propene. Decay of the allyl hydride complex may proceed via migration of the metal-bound H atom to the β-carbon atom in the allyl moiety (i.e., reverse β-H migration), leading to formation of the same metallacyclobutane complex implicated in the Y + cyclopropane reaction. The dynamically most favorable decay pathway is to YCH2 + CH4.

CH3YCH2H2 which can decay to YCH2 + C2H4 products. Again with the reasonable assumption made that all propene reactions originate from a common π-complex, the product branching ratio φCH2/φCH4 is the ratio of the rate for C–H insertion (kcc) to that for C–H insertion (kci) from the initial π-complex. Thus Rice–Ramsperger–Kassel–Marcus (RRKM) theory may be used to calculate kcc(E)kci(E). As has been described in detail,40 we have carried out RRKM calculations and, not surprisingly, have found that the large yields of YCH2 + C2H4 require that the largest potential energy barrier along the reaction coordinate cannot be significantly larger than that for H2 elimination. Therefore, the potential energy barrier for C–C insertion cannot significantly exceed that for C–H insertion. However, theoretical calculations9,10 and molecular orbital arguments13 always indicate that C–C insertion barriers are significantly larger than those for C–H insertion, except in systems containing ring strain. For us to successfully model the observed branching ratios, which become nearly 1:1 at the highest collision energies, would require a C–C insertion barrier that is nearly identical to that for the C–H bond, which is not a likely possibility. Thus the sp3–sp3 C–C insertion mechanism shown in Figure 17 cannot be a primary mechanism for YCH2 formation in the Y + propene reaction.

We believe that in the propene reaction the large yield of YCH2 + C2H4 results from a mechanism very similar to that for production of YH2 + C2H4 and YC3H4 + H2. However, theoretical calculations9,10 and molecular orbital arguments13 always indicate that C–C insertion barriers are significantly larger than those for C–H insertion, except in systems containing ring strain. For us to successfully model the observed branching ratios, which become nearly 1:1 at the highest collision energies, would require a C–C insertion barrier that is nearly identical to that for the C–H bond, which is not a likely possibility. Thus the sp3–sp3 C–C insertion mechanism shown in Figure 17 cannot be a primary mechanism for YCH2 formation in the Y + propene reaction.

E. YCH2 + C2H4 Formation from Propene Reactions. The observation of YCH2 + ethylene from the Y + propene reaction illustrates the cleavage of an unstrained C≡C bond in a neutral metal–hydrocarbon reaction. We were quite surprised that the YCH2 yield is nearly as large as that for YC3H4 at high collision energies, despite the much less favorable thermodynamics for this channel (Figure 1). We now consider possible mechanisms for intramolecular rearrangement of the initially formed Y–propene π-complex to YCH2 + C2H4. One possible mechanism involves immediate insertion into the sp3–sp3 C–C bond adjacent to the oxidized C≡C bond in the Y–propene complex, as shown in Figure 17. The resulting Y(CH3)(CH=CH2) intermediate could further rearrange via α-C–H insertion to form YCH2(H)(CH=CH2). Transfer of an H atom then gives

YH2 + H2.
\[ \text{References and Notes} \]


