

## Formation and Decomposition of C<sub>3</sub> Metallacycles from Ethylene and Methylene on MoAl Alloy Thin Films

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**Abstract:** The reaction between adsorbed ethylene and methylene species has been investigated on a molybdenum–aluminum alloy grown from Mo(CO)<sub>6</sub> on a planar alumina film formed on a Mo(100) single crystal in ultrahigh vacuum. Di-σ-bonded ethylene reacts with carbene species, formed on the surface from methylene iodide, to form a C<sub>3</sub> metallacycle. This predominantly decomposes to yield propylene, while a smaller portion yields cross-metathesis products since <sup>12</sup>C<sup>13</sup>CH<sub>4</sub> is formed from reaction between <sup>13</sup>C<sub>2</sub>H<sub>4</sub> and <sup>12</sup>CH<sub>2</sub>. This work demonstrates for the first time that the reaction proceeds in heterogeneous phase via a C<sub>3</sub> metallacycle as proposed in the Hérisson-Chauvin mechanism.

### 1. Introduction

While the olefin metathesis reaction was first discovered on heterogeneous-phase catalysts,<sup>1–6</sup> insights into the reaction pathway came almost exclusively from studies on organometallic systems,<sup>7–24</sup> and confirmed the mechanism proposed by Hérisson and Chauvin.<sup>11</sup> The accepted mechanism involves the formation of a metallacycle from reaction between a carbene and a gas-phase alkene, where the reverse of this reaction yields metathesis products.

Heterogeneous olefin metathesis catalysts have been made by immobilizing organometallic compounds on oxides to form metathesis catalysts<sup>25–27</sup> so that homogeneous-phase pathways can be readily applied in these cases. However, there is less

direct evidence for the Hérisson-Chauvin pathway operating on heterogeneous catalysts. Handzlik et al. have performed a series of theoretical calculations to confirm the feasibility of Mo-alkylidene and metallacycle formation on heterogeneous catalysts,<sup>28–30</sup> and grafting methylene species from methylene iodide onto a heterogeneous catalyst resulted in a significant increase in metathesis rate.<sup>31</sup> Using surface science strategies, McBreen et al.<sup>32</sup> found facile cross-metathesis reactions between propylene and cyclopentylidene on a β-Mo<sub>2</sub>C surface, leading to the simultaneous isolation of surface methylidene and ethylidene, the two primary propagator species in the Hérisson-Chauvin mechanism for propylene metathesis. In these experiments, 2 × 10<sup>-8</sup> Torr of propylene was allowed to react with metal-alkylidene centers to mimic realistic gas–surface reaction conditions. It was suggested that steric hindrance and competing chemisorption of the olefin might inhibit the reaction for alkylidene groups situated directly on an extended planar surface. This work provided compelling evidence for metathesis proceeding via the Hérisson–Chauvin pathway, but the authors were not able to implicate a metallacyclic intermediate in this reaction.

Organic iodides have been extensively used to examine the surface chemistry of hydrocarbons on surfaces since these tend to decompose by scission of the C–I bonds at relatively low temperatures to deposit hydrocarbon moieties, along with chemisorbed iodine.<sup>33,34</sup> The chemistry of methyl<sup>35</sup> and methylene<sup>36</sup> species was studied on MoAl alloy thin films using this strategy, where it was found that, besides H<sub>2</sub> and methane

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formation, ethylene, ethane, propylene (from both iodomethane and diiodomethane), and butene (just from diiodomethane) are produced. These products were suggested to form via methylene insertion into alkyl-metal bonds, followed by  $\beta$ -hydride or reductive elimination reactions<sup>37,38</sup> suggesting that the molybdenum–aluminum alloys are extremely effective for catalyzing methylene insertion into surface-carbon single bonds. This implies that these surfaces may also be similarly active for methylene insertion into the carbon-surface bond of olefins to yield metallacycles.

Metallacycles have also been grafted onto a MoAl alloy surface by exposure to 1,3-diiodopropane.<sup>39</sup> It has been shown that these can decompose via an  $\eta^3$ -allylic intermediate to yield propylene as found on transition-metal surfaces.<sup>40</sup> More importantly, in the context of the Hérisson–Chauvin mechanism, an alternative decomposition pathway was found on the MoAl alloy that resulted in the evolution of ethylene and the deposition of carbenes on the surface.<sup>39</sup>

However, to fully confirm that metathesis proceeds in heterogeneous phase by the Hérisson–Chauvin pathway, it must be demonstrated that carbenes and alkenes react to form metallacycles and that they decompose similarly to the C<sub>3</sub> metallacycles grafted onto the surface from 1,3-diiodopropane, to evolve an alkene and deposit a carbene.

This chemistry is demonstrated for the first time in the research reported here performed on MoAl alloy films grown on alumina deposited onto a Mo(100) single-crystal substrate in ultrahigh vacuum. Carbenes are grafted onto the surface using strategies similar to those described above by exposure of the surface to iodine-containing precursors, in this case methylene iodide. The rather unique activity of this surface for the insertion of carbenes into carbon-surface single bonds allows similar carbene insertion reactions into the C-surface bonds of ethylene to be explored using surface-sensitive techniques in ultrahigh vacuum.

## 2. Experimental Section

Temperature-programmed desorption (TPD) data were collected in an ultrahigh vacuum chamber operating at a base pressure of  $8 \times 10^{-11}$  Torr that has been described in detail elsewhere<sup>41–43</sup> where desorbing species were detected using a Dycor quadrupole mass spectrometer placed in line of sight of the sample. Temperature-programmed desorption spectra were collected at a heating rate of 10 K/s. This chamber was also equipped with a double-pass cylindrical mirror analyzer for collecting Auger spectra.

Infrared data were collected using a Bruker Equinox infrared spectrometer equipped with a liquid nitrogen cooled, mercury cadmium telluride detector operating at  $4 \text{ cm}^{-1}$  resolution and data were typically collected for 1000 scans. The complete light path was enclosed and purged with dry, CO<sub>2</sub>-free air.<sup>44,45</sup>

The Mo(100) substrate (1 cm diameter, 0.2 mm thick) was cleaned using a standard procedure, which consisted of argon ion bombardment (2 kV,  $1 \mu\text{A}/\text{cm}^2$ ) and any residual contaminants were removed by briefly heating to 2000 K in vacuo. The resulting Auger spectrum

showed no contaminants. Aluminum was deposited onto Mo(100) from a small heated alumina tube, which was enclosed in a stainless steel shroud to minimize contamination of other parts of the system.<sup>46</sup> Alumina thin films were formed by cycles of aluminum deposition—water vapor oxidation-annealing, until the Mo(100) features are completely obscured in the XP or Auger spectra.<sup>43</sup>

The formation and characterization of the MoAl alloy film has been extensively described.<sup>43</sup> Briefly, it is formed by adsorbing 5000 L of Mo(CO)<sub>6</sub> onto a dehydroxylated alumina film grown on a Mo(100) substrate held at 700 K to generate molybdenum carbide. This is then annealed to 1500 K to generate a surface MoAl alloy. During the annealing process, the deposited carbide reacts completely with the alumina substrate to desorb CO. Alloy formation is confirmed by X-ray photoelectron and Auger spectroscopies, where it is found that the binding energy of the deposited molybdenum, following annealing, is lower than that of pure metallic molybdenum.<sup>42,43</sup> The thickness of the alloy film, based on Auger electron probe depth analysis, is estimated to be 3–4 atomic layers and the atomic ratio of Mo and Al atoms in the near-surface region is  $\sim 1.6$ .<sup>35</sup>

Molybdenum hexacarbonyl (Aldrich, 99%), ethylene (Matheson, 99.5%), and diiodomethane (Aldrich, 99%) were transferred to glass vials, which were connected to the gas-handling line of the chamber and purified by repeated freeze–pump–thaw cycles, followed by distillation, and their purities were monitored using mass spectroscopy. These were dosed onto the surface via a capillary doser to minimize background contamination. The exposures in Langmuirs ( $1 \text{ langmuir} = 1 \times 10^{-6} \text{ Torr s}$ ) are corrected using an enhancement factor determined using temperature-programmed desorption (see ref 41 for a more detailed description of this procedure).

## 3. Results

Figure 1(a) displays a series of 41 amu (propylene) temperature-programmed desorption (TPD) traces collected following the adsorption of ethylene and then diiodomethane on the alloy surface. For comparison, the 41 amu (propylene) desorption trace obtained following exposure of 5 L of CH<sub>2</sub>I<sub>2</sub> alone is also displayed (taken from ref 36) where only a small amount of propylene is found to desorb at  $\sim 300$  K. Propylene, in the latter case, forms via methylene insertion, where a portion of adsorbed CH<sub>2</sub> species hydrogenate to form surface CH<sub>3</sub> moieties followed by CH<sub>2</sub> insertion into the methyl-metal bonds. Facile  $\beta$ -hydride elimination results in olefin formation.<sup>36</sup> When the surface is precovered by ethylene, the 41 amu (propylene) profiles exhibit two states; a weak state at  $\sim 220$  K and a much broader and intense one at  $\sim 330$ -K state. By comparing the desorption at various masses with the mass spectrometer ionizer fragmentation pattern of pure C<sub>3</sub> hydrocarbons, including propylene, cyclopropane and propane as well as oxygenates, measured with the same mass spectrometer, it is found that the 330-K state is due entirely to propylene desorption (see Supporting Information). The desorption of propylene at  $\sim 330$  K is characteristic for the decomposition of C<sub>3</sub> metallacycles.<sup>39</sup> However, no 220-K features were detected in these desorption spectra. Thus, to elucidate the nature of the 220-K desorption state, propylene (41 amu) desorption spectra were collected by dosing in the reverse order, that is by exposing the alloy to 5 L C<sub>2</sub>H<sub>4</sub> followed by various exposures to CH<sub>2</sub>I<sub>2</sub>. The results of Figure 1b reveal that the 220-K state appears only after the CH<sub>2</sub>I<sub>2</sub> exposure exceeds 5 L. Since this is identical to the temperature at which molecular CH<sub>2</sub>I<sub>2</sub> desorbs,<sup>36</sup> this indicates that this feature is an artifact due to CH<sub>2</sub>I<sub>2</sub> reacting within the mass spectrometer

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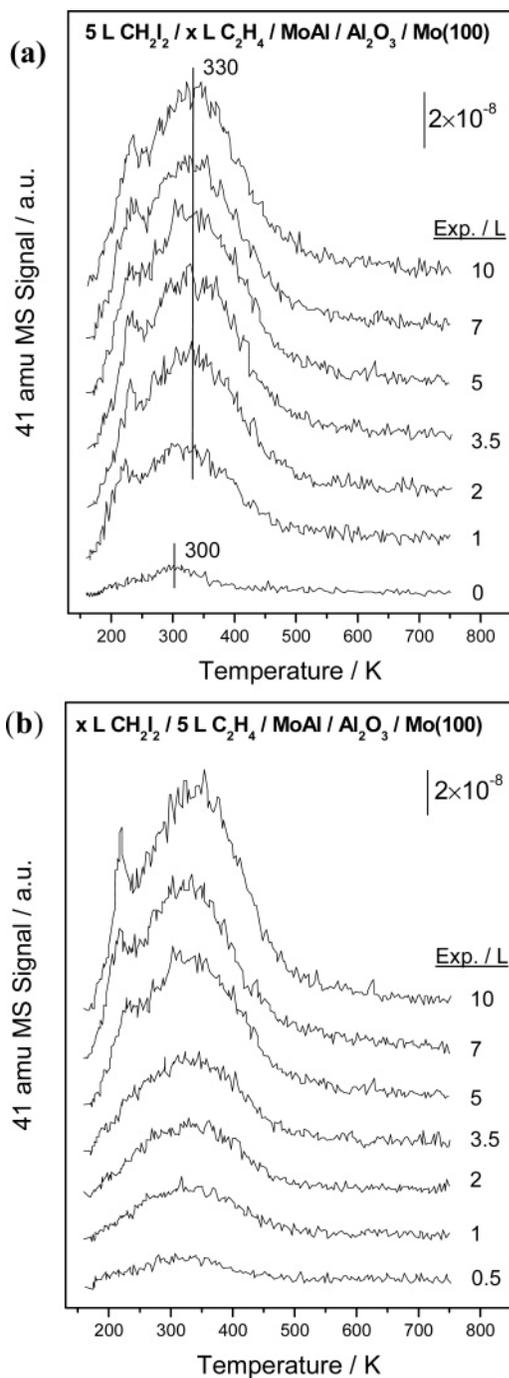
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**Figure 1.** Temperature-programmed desorption spectra collected using a heating rate of 10 K/s showing (a) the 41 amu (propylene) signals following exposure of a MoAl alloy to various amounts of ethylene followed by exposure to 5 L of methylene iodide, where the ethylene exposures are indicated adjacent to the corresponding spectrum. Note that the spectrum for an ethylene exposure of 0 L corresponds to methylene iodide alone adsorbed on the surface. The spectra (b) show the effect of varying the methylene iodide exposure where the surface was initially exposed to 5 L of ethylene followed by various amounts of methylene iodide, where methylene iodide exposures are indicated adjacent to the corresponding spectrum.

ionizer. It is also evident that the order of adsorption affects the propylene yield implying that CH<sub>2</sub>I<sub>2</sub> may block surface sites for ethylene adsorption.

The propylene yield from an ethylene-covered surface is substantially larger than with CH<sub>2</sub>I<sub>2</sub> alone (Figure 1a) demonstrating that ethylene is involved in the formation of propylene.

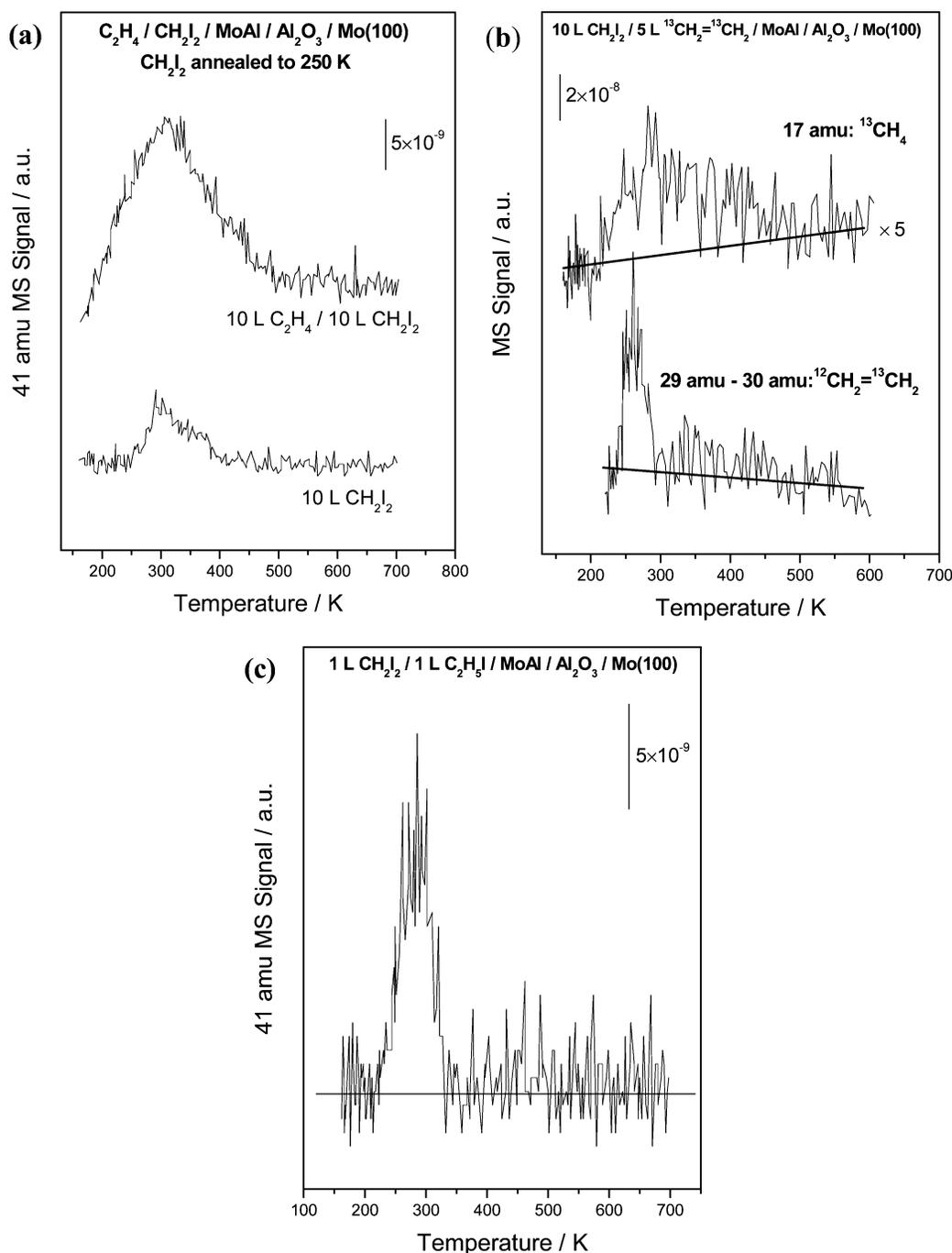
To explore this chemistry further, experiments were performed using <sup>13</sup>CH<sub>2</sub>=<sup>13</sup>CH<sub>2</sub>/CH<sub>2</sub>I<sub>2</sub> and <sup>12</sup>CH<sub>2</sub>=<sup>12</sup>CH<sub>2</sub>/CD<sub>2</sub>I<sub>2</sub>. The desorption profiles at 43 amu (due to <sup>13</sup>C<sub>2</sub><sup>12</sup>CH<sub>6</sub> or <sup>12</sup>C<sub>3</sub>H<sub>4</sub>D<sub>2</sub>, respectively, see Supporting Information) mimic those at 41 amu shown in Figure 1. This clearly demonstrates that both ethylene and diiodomethane are involved in propylene formation, although the 43 amu signal in the latter case may contain a small contribution from H–D scrambling products.

C–I bond scission in methylene iodide occurs sequentially where an intermediate CH<sub>2</sub>I<sub>(ads)</sub> species persists on an ethylene precovered surface up to ~220 K (see below), but where iodine removal is complete by ~250 K.<sup>36</sup> To establish that ethylene has reacted with a surface carbene (CH<sub>2</sub>(ads)), the carbene was formed by exposing an alloy surface to 10 L of CH<sub>2</sub>I<sub>2</sub> and then heating to 250 K, and the sample then exposed to 10 L of ethylene at 150 K. The resulting 41 amu TPD spectrum is displayed in Figure 2(a). The spectrum for CH<sub>2</sub>I<sub>2</sub> alone, also annealed to 250 K, is displayed for comparison. Propylene desorbs at ~330 K, identical to the data of Figure 1 demonstrating that propylene forms in those cases by a reaction between ethylene and adsorbed CH<sub>2</sub>. Note the absence of the 220-K feature in this case.

It has been demonstrated previously that C<sub>3</sub> metallacycles can decompose to form ethylene and methylene species (which desorb as methane), a central step in the Hérisson-Chauvin metathesis mechanism.<sup>39</sup> However, this reaction cannot be probed when metallacycles are formed from *normal* ethylene and diiodomethane, since the signals due to any reaction products (ethylene and methane) will be obscured by the initial reactants. TPD experiments were therefore performed by allowing isotopically labeled ethylene (<sup>13</sup>C<sub>2</sub>H<sub>4</sub>) to react with normal CH<sub>2</sub>I<sub>2</sub> to follow this reaction. Figure 2b displays the resulting 29 amu (<sup>12</sup>C<sup>13</sup>CH<sub>4</sub>) desorption trace following adsorption of 5 L of <sup>13</sup>C<sub>2</sub>H<sub>4</sub> with 10 L of <sup>12</sup>CH<sub>2</sub>I<sub>2</sub>, where the 29-amu contribution from <sup>13</sup>C<sub>2</sub>H<sub>4</sub> has been subtracted. A clear peak is evident at ~270 K. The reliability of the subtraction protocol was tested using the 26-amu fragment of propylene compared to the 41 amu parent peak. Also shown in Figure 2b is the corresponding 17 amu (<sup>13</sup>CH<sub>4</sub>) desorption trace demonstrating the formation of methane in a broad feature centered at ~300 K due to the hydrogenation of <sup>13</sup>CH<sub>2</sub>. Note that methane is not formed from <sup>13</sup>C<sub>2</sub>H<sub>4</sub> at this temperature,<sup>47</sup> and is not due to <sup>12</sup>-CH<sub>2</sub> hydrogenation. On the basis of the integrated intensities of the <sup>12</sup>C<sup>13</sup>CH<sub>4</sub> and propylene signals (Figures 1a and b) the selectivity to ethylene formation is estimated to be ~30%.

An alternative propylene-formation pathway could involve the initial formation of ethyl species by reaction between ethylene and surface hydrogen, followed by methylene insertion into the metal-ethyl bond to form surface propyl species, yielding propylene by β-hydride elimination. This is rather unlikely since ethylene hydrogenates on the alloy surface at ~270 K,<sup>47</sup> so that at ~330 K (the propylene desorption maximum, Figures 1 and 2), the ethyl coverage will be vanishingly small. However, to confirm this conjecture, 1 L of C<sub>2</sub>H<sub>5</sub>I was adsorbed on the MoAl alloy surface prior to exposure to 1 L of CH<sub>2</sub>I<sub>2</sub>, both at 150 K. The resulting 41 amu (propylene) desorption spectrum is displayed in Figure 2c. Propylene desorbs at ~285 K with a yield larger than that due to methylene iodide

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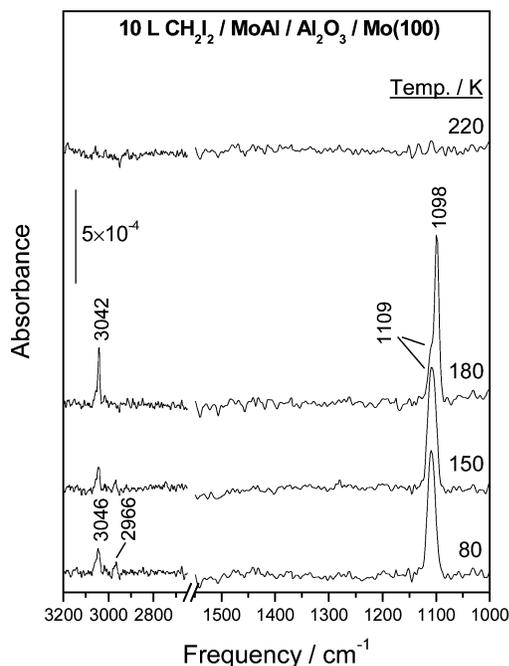
**Figure 2.** Temperature-programmed desorption spectra collected using a heating rate of 10 K/s, (a) monitoring 41 amu (propylene) following adsorption of 10 L of methylene iodide and annealing to 250 K to form a methylene species, followed by exposure to 10 L of ethylene to this surface. Part (b) displays the spectra obtained following adsorption of 5 L of  $^{13}\text{C}_2\text{H}_4$  followed by 10 L of  $^{12}\text{CH}_2\text{I}_2$ , monitoring 17 ( $^{12}\text{CH}_4$ ) and 29 amu ( $^{12}\text{C}^{13}\text{CH}_4$ ) where contributions from molecular ethylene have been subtracted, and (c) shows the 41 amu (propylene) spectrum following exposure to 1 L of  $\text{C}_2\text{H}_5\text{I}$  followed by 1 L  $\text{CH}_2\text{I}_2$ .

alone,<sup>36</sup> and at a lower temperature (compare with Figure 1a) indicating that the 330 K features in Figure 1 are not due to reaction of an intermediate propyl species.

The decomposition of diiodomethane on the MoAl was investigated using reflection–absorption infrared spectroscopy (RAIRS). The alumina substrate has an intense and broad longitudinal optical mode feature at  $\sim 930\text{ cm}^{-1}$  preventing meaningful data from being collected below  $1000\text{ cm}^{-1}$ . Figure 3 displays the infrared spectra of 10 L of  $\text{CH}_2\text{I}_2$  adsorbed on the alloy surface at 80 K (thus forming a multilayer<sup>36</sup>) and after annealing to various temperatures, where the annealing

temperatures are displayed adjacent to the corresponding spectrum. Following adsorption at 80 K, features are detected at  $3046$  and  $2966\text{ cm}^{-1}$  in the C–H stretching region. By comparison with the infrared spectrum of gas-phase diiodomethane,<sup>48</sup> the  $3046\text{ cm}^{-1}$  feature is assigned to  $\nu_a(\text{CH}_2)$  and the  $2966\text{ cm}^{-1}$  feature to a  $\nu_s(\text{CH}_2)$  mode. At lower frequencies, the only detectable peak is an intense  $\omega(\text{CH}_2)$  mode at  $1109\text{ cm}^{-1}$ . These frequencies are very close to those of gaseous  $\text{CH}_2\text{I}_2$ , suggesting that the molecule is only slightly

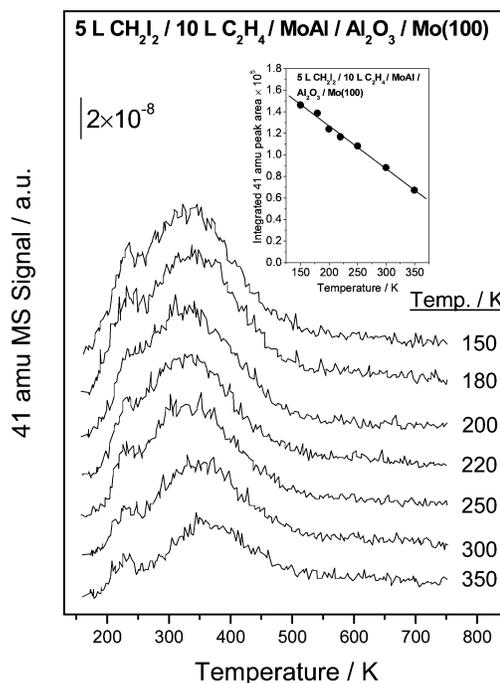
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**Figure 3.** Reflection-absorption infrared spectra of 10 L of methylene iodide adsorbed on a MoAl alloy at 80 K and heated to various temperatures, where the annealing temperatures are displayed adjacent to the corresponding spectrum.

perturbed upon adsorption. The spectra remain unchanged when the sample is annealed to 150 K. However, when the surface is heated to 180 K, the intensity of the  $\nu_a(\text{CH}_2)$  mode increases significantly and shifts slightly to 3042  $\text{cm}^{-1}$ , while the  $\nu_s(\text{CH}_2)$  mode attenuates. In the low-frequency region, the intensity of the 1109  $\text{cm}^{-1}$  feature decreases while an intense new feature appears at 1098  $\text{cm}^{-1}$ . The surface species giving rise to the intense 3042 and 1098  $\text{cm}^{-1}$  features could be either  $\text{CH}_{2(\text{ads})}$  or  $\text{CH}_2\text{I}_{(\text{ads})}$ . Since  $\text{CH}_{2(\text{ads})}$  modes are extremely weak,<sup>49</sup> these features are assigned to  $\text{CH}_2\text{I}_{(\text{ads})}$ . This notion is corroborated by the observation that  $\text{CH}_3\text{I}$  desorbs from an alloy surface at high  $\text{CH}_2\text{I}_2$  exposures, indicating that the C–I bond cleaves in a stepwise manner.<sup>36</sup> This is also supported by XPS measurements where it is found that extensive C–I bond cleavage occurs at 200 K and above.<sup>36</sup> All features due to molecular  $\text{CH}_2\text{I}_2$  and  $\text{CH}_2\text{I}_{(\text{ads})}$  diminish when the surface is annealed to 220 K suggesting complete dissociation of C–I bonds to form carbenes, in accordance with previous XPS measurements.<sup>36</sup> The results, in connection with previous XPS data, confirm that methylene species are present on the surface on a MoAl surface heated to  $\sim 250$  K, confirming that the reaction products observed in Figure 2a are formed by reaction between ethylene and methylene species.

Figure 4 presents TPD results (at 41 amu, propylene) for 10 L of  $\text{C}_2\text{H}_4$  adsorbed at 150 K and annealed to various temperatures before cooling to 150 K, then exposing to 5 L of  $\text{CH}_2\text{I}_2$ , where the annealing temperatures are displayed adjacent to the corresponding spectra. The resulting propylene desorption yield is plotted as a function of annealing temperature as an inset to Figure 4 showing that the propylene yield decreases linearly with annealing temperatures up to 350 K, where only the area under the  $\sim 330$ -K state is measured. Since  $\pi$ -bonded ethylene desorbs below 200 K, whereas di- $\sigma$ -bonded ethylene



**Figure 4.** Temperature-programmed desorption spectra collected at a heating rate of 10 K/s collected at 41 amu (propylene) following exposure to 10 L of ethylene at 150 K, where the sample is heated to various temperatures, and the annealing temperatures are indicated adjacent to the corresponding spectrum. The sample was then allowed to cool to 150 K and exposed to 5 L of methylene iodide, following which the spectrum was recorded. Shown as an inset is the relative propylene yield as a function of annealing temperature.

is stable at much higher temperatures,<sup>47</sup> this indicates that propylene is formed by reaction with di- $\sigma$ -bonded ethylene.

#### 4. Discussion

Previous work to graft C<sub>3</sub> metallacycles onto MoAl alloy surfaces by reaction with 1,3-diiodopropane (DIP) has demonstrated that they predominantly decompose via an  $\eta^3$ -allylic intermediate to desorb propylene at  $\sim 330$  K, whereas a smaller portion decomposes to evolve both ethylene (at  $\sim 280$  K) and methane from hydrogenation of the resulting methylene species.<sup>39</sup> The detection of propylene in a feature centered at  $\sim 330$  K from reaction between methylene species and ethylene (Figures 1 and 2a) and ethylene formation at  $\sim 280$  K (Figure 2b), are consistent with a reaction pathway involving the intermediate formation of a metallacycle. The data of Figure 2a confirms that reaction occurs between the carbene formed from methylene iodide and the results of Figure 2b are consistent with both the decomposition products (ethylene and methane) and reaction temperatures from the decomposition of C<sub>3</sub> metallacycles formed from DIP.<sup>39</sup> The data of Figure 2b demonstrate that ethylene metathesis has occurred since the <sup>12</sup>C originally in the carbene has been incorporated into the ethylene that is produced. Finally, the data of Figure 2c indicate that reaction has not proceeded via methylene insertion into an ethyl species. The data of Figure 4a implicate di- $\sigma$ -bonded ethylene as the reactant to the formation of propylene, where it is found that, even after an ethylene-covered surface is annealed to 350 K (to remove all  $\pi$ -bonded ethylene<sup>47</sup>), substantial propylene is formed.

These results indicate that olefin metathesis proceeds on the MoAl alloy by reaction between adsorbed di- $\sigma$ -bonded ethylene

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and carbene species. These form a stable metallacyclic intermediate since the propylene formation kinetics from both the reaction between ethylene and methylene iodide (Figure 1) and between ethylene and  $\text{CH}_2(\text{ads})$  (Figure 2a) are identical to the decomposition kinetics of the  $\text{C}_3$  metallacycle grafted onto the surface by reaction with 1,3-diiodopropane.<sup>39</sup> The correspondence between the decomposition kinetics of the grafted metallacycle and that formed by reaction between ethylene and the carbene also implies that the rate of metallacycle formation is fast and that metallacycle decomposition is the rate-limiting step to the formation of propylene or ethylene. Recent density functional theory (DFT) calculations for reactions between a molybdenum-carbene complex and ethylene show a similar effect, with an almost isothermic formation of the ethylene adduct, and a low activation barrier to the formation of a stable metallacyclobutane in a trigonal bipyrimidal conformation.<sup>51</sup> Only a small number of DFT calculations have been carried out for heterogeneous catalysts.<sup>28–30</sup> While these calculations are for  $\text{Mo}=\text{CH}_2$  species attached to oxide surfaces and therefore not necessarily directly relevant to the MoAl alloy, they reveal a significant activation barrier to the formation of a metallacycle of greater than 35 kcal/mol. Notable is that DFT calculations for both homogeneous<sup>51–55</sup> and heterogeneous catalysts<sup>28–30</sup> find  $\pi$ -coordination to the metal center, in contrast to the activity of di- $\sigma$ -bonded ethylene found here. Clearly, di- $\sigma$ -bonded ethylene reacts with the carbene on the MoAl alloy surface to form a metallacycle. A possible explanation for this disparity may be that the heat of adsorption of  $\pi$ -bonded ethylene is lower than

the activation energy for metallacycle formation, and so desorbs before it has had a chance to react.

To show that the reaction proceeds catalytically, ideally it should be demonstrated that the carbene formed by metallacycle decomposition further reacts with ethylene and undergo additional cross metathesis. Unfortunately, this is not possible since the metallacycle predominantly decomposes to form propylene and any remaining carbenes hydrogenate to yield methane (Figure 2b). Nevertheless, the catalytic cycle is evident from the results presented here, since a carbene reacts with ethylene to form metallacycle, which then reacts to form ethylene and regenerates the carbene.

## 5. Conclusions

These results taken together demonstrate that di- $\sigma$ -bonded ethylene reacts with carbene species to form a stable  $\text{C}_3$  metallacyclic intermediate. This predominantly decomposes to yield propylene, whereas a smaller portion yields cross-metathesis products since  $^{12}\text{C}^{13}\text{CH}_4$  is formed from reaction between  $^{13}\text{C}_2\text{H}_4$  and  $^{12}\text{CH}_2$ . Although similar chemistry to this has been found previously in UHV on carbide surfaces, as far as we are aware, this work demonstrates for the first time that the reaction proceeds in heterogeneous phase via a  $\text{C}_3$  metallacycle as proposed in the *Hérisson–Chauvin mechanism*.

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**Supporting Information Available:** Temperature-programmed desorption data showing that propylene is formed by reaction between ethylene and methylene iodide. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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