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C-H Bond Activation and Cracking of Cyclohexane Using Mass Spectrometry

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C-H Bond Activation and Cracking of Cyclohexane Using Mass Spectrometry

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Abstract

Gas-phase mass spectrometry is used to study the C-H activation of cyclohexane by $[(\text{phen})M(X)]^+$ (where phen = 1,10-phenanthroline; M = Ni, Pd, or Pt; X = H or CH_3), forming the cyclohexyl species $[(\text{phen})M(c\text{-}C_6H_{11})]^+$. Collision-induced dissociation of this species and cyclohexane-induced ion molecule reactions result in ring opening followed by "cracking" of the hydrocarbon chain and dehydrogenation of the cyclohexyl ring. The catalytic nature of these processes enables the continual production of smaller hydrocarbons, such as ethylene and propylene, from ring opening/cracking as well as benzene, cyclohexene, and one, two, or three hydrogen molecules from dehydrogenation. The metal used largely determines which pathway is favored by a species, with Pt species preferring the dehydrogenation pathway over the ring opening/cracking pathway.
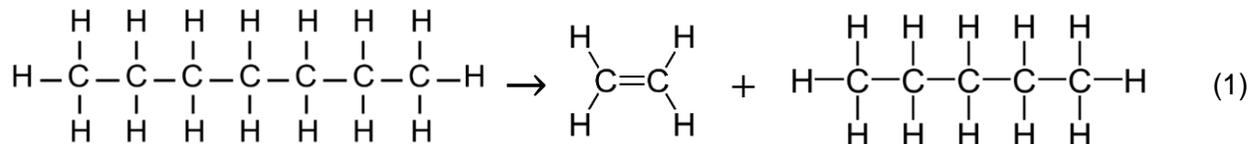
Introduction

  While C-H bonds in hydrocarbons were previously thought to be inert, recent research into the activation of C-H bonds confirms that this is not the case.[1] C-H rich compounds, such as biomass and fossil fuels, can be C-H activated to obtain the most beneficial form of these materials. C-H bond activation involves the cleavage of a C-H bond by a compound containing a metal, thus forming a species with a metal-carbon bond.[2] Often, hydrocarbons are an ideal source of C-H bonds.

  A major product from petroleum processing is naphtha, which is a mixture of hydrocarbons that contains both linear and cyclic molecules. A common model for cyclic hydrocarbons is cyclohexane (Figure 1) which is present in significant quantities in naphtha.[3] Cyclic hydrocarbons such as cyclohexane are transformed into high-commodity chemicals such as hydrogen, ethylene, and propylene by various processes.[4] Current methods to obtain such transformations involve temperatures well over 700°C and high pressures.[5]
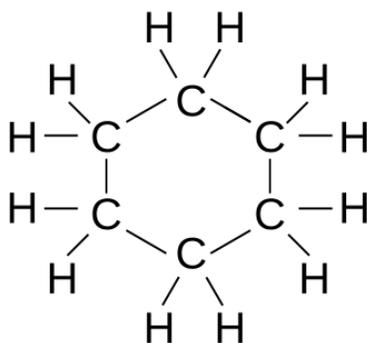

Figure 1: Structure of cyclohexane, a component of naphtha.

  One method of transforming hydrocarbons is cracking, in which a long hydrocarbon chain is broken down into shorter hydrocarbon chains by the breaking of C-C bonds. This process often produces alkenes, such as in Eq. 1 below where the cracking of heptane produces ethene and pentane.

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$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H \rightarrow \; \underset{\underset{H}{}}{\overset{\overset{H}{}}{C}}=\underset{\underset{H}{}}{\overset{\overset{H}{}}{C} } \;+\; H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H \tag{1}$$

In addition, dehydrogenation reactions also transform hydrocarbons by the loss of hydrogen molecules. For example, the dehydrogenation of cyclohexane produces benzene and three hydrogen molecules (Eq. 2).

$$\bighexagon \; \longrightarrow \; \bigbenzene \; + 3\,H_2 \tag{2}$$
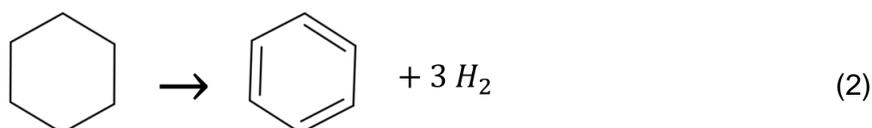
Cracking and dehydrogenation of hydrocarbons can be induced at lower temperatures and pressures using organometallic catalysts, which consist of a ligand, a metal, and an organic group. Mass spectrometry (MS) can be used to confirm such reactions by first ionizing the organometallic compound by electrospray ionization (ESI). During ESI, a high voltage is applied to the liquid sample to create an aerosol of ions. Following ionization, the species is reacted with a neutral reagent introduced separately into the system. Such reactions are known as ion-molecule reactions (IMR). Furthermore, applying energy and fragmenting the complexes in the reaction chamber is known as collision-induced dissociation (CID).[6] A scheme of the innerworkings of an MS is shown below in Figure 2.
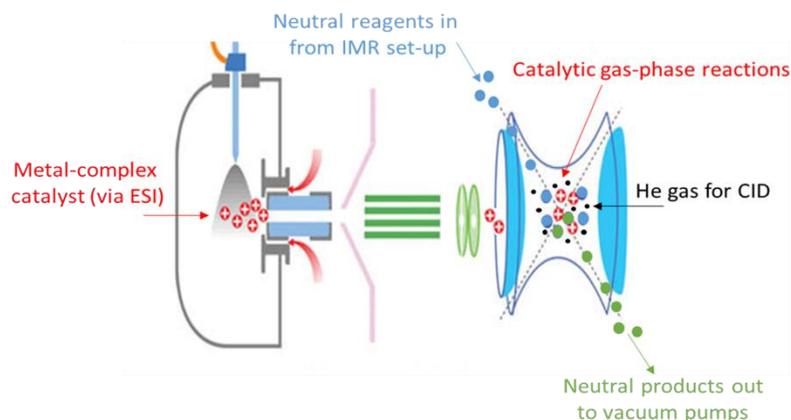
Figure 2: Mass spectrometer schematic.

In this research, an organometallic species containing 1,10-phenanthroline as the ligand, Ni, Pd, or Pt as the metal, and acetate or formate as the organic group is used to crack and dehydrogenate cyclohexane. As cyclohexane is a cyclic hydrocarbon, it also undergoes ring-opening, in which a C-C bond in the ring is broken, resulting in a linear hydrocarbon.

Methods

For the ligand in the organometallic compound, a 1 mg/mL solution of 1,10-phenanthroline was prepared in methanol. For the metal in the organometallic compound, a 1 mg/mL M(acetate)$_2$ solution (where M = Ni or Pd) in methanol was made. Additionally, a 25% formic acid solution was used. In order to synthesize an organometallic compound with acetate as the organic group, 100 µL of 1 mg/mL 1,10-phenanthroline, 100 µL of 1 mg/mL M(acetate)$_2$, and 800 µL of methanol were combined and mixed thoroughly. When formate was used as the organic group, 100 µL of 1 mg/mL 1,10-phenanthroline, 100 µL of 1 mg/mL M(acetate)$_2$, 100 µL of 25% acetic acid, and 700 µL of methanol were combined and mixed thoroughly. The organometallic complex formed using Pt as the metal was prepared following a procedure outlined in the literature[7]. This organometallic compound was then pumped into the Thermo LTQ Linear Ion Trap MS via a syringe pump at a flow rate of 5 µL/min and ionized using ESI.

In addition, this MS was specially modified to perform IMR. Cyclohexane was added to the helium bypass line which directly introduces it into the trap to react with isolated species. The resulting species were isolated, fragmented, and reacted appropriately.

Results

Initially, [(phen)M(OOCX)]$^+$ (top left ion in Figure 3) was formed by reacting 1,10-phenanthroline, M(acetate)$_2$, and, in the case of X = H, acetic acid (where M = Ni, Pd, or Pt and X = H or CH$_3$). This aqueous solution was introduced into the MS via a syringe pump. Isolation and CID on this species saw the loss of CO$_2$, forming [(phen)M(X)]$^+$ (top middle ion in Figure 3, herein referred to as **1-M**). The introduction of cyclohexane via the IMR line saw the C-H bond activation of cyclohexane by **1-M**, forming [(phen)M(C$_6$H$_{11}$)]$^+$ (top right ion in Figure 3, herein referred to as **2-M**).
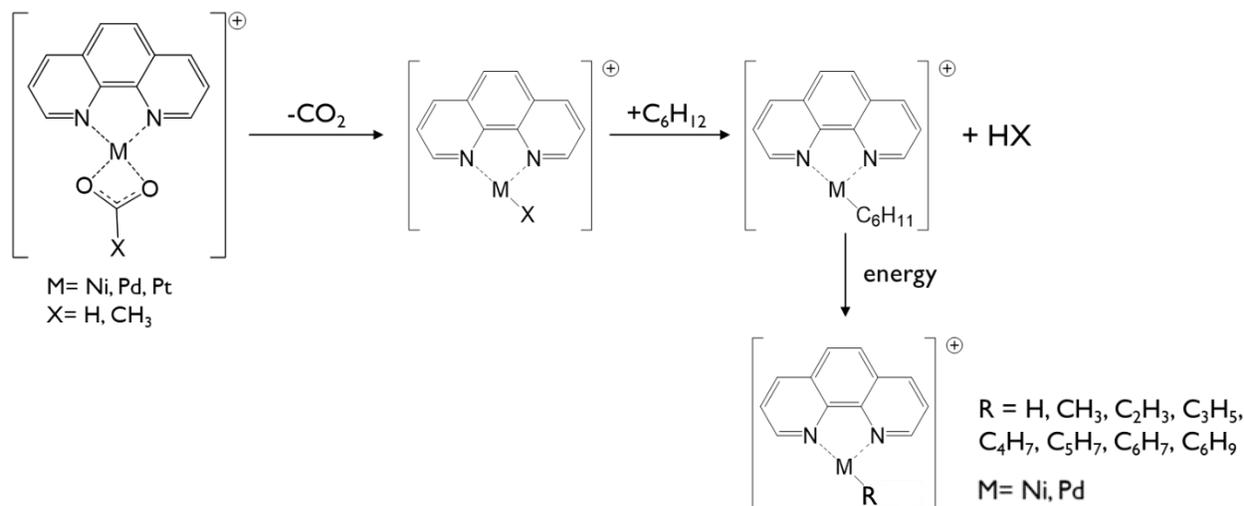

Figure 3: Formation of reactive organometallic species.

A mass spectrum for the IMR of cyclohexane with **1-Pd** is shown below in Figure 4. **1-Pd** was isolated at m/z 287 and allowed to react with cyclohexane (being introduced into the cell via the IMR line). The presence of a peak at m/z 369 indicates the formation of **2-Pd**, as well as the

loss of H_2. This phenomenon, along with the decarboxylation of $[(phen)M(XCO_2)]^+$, was observed using Ni, Pd, or Pt as the metal ion as well as using CH_3 (from acetate) as the X group.
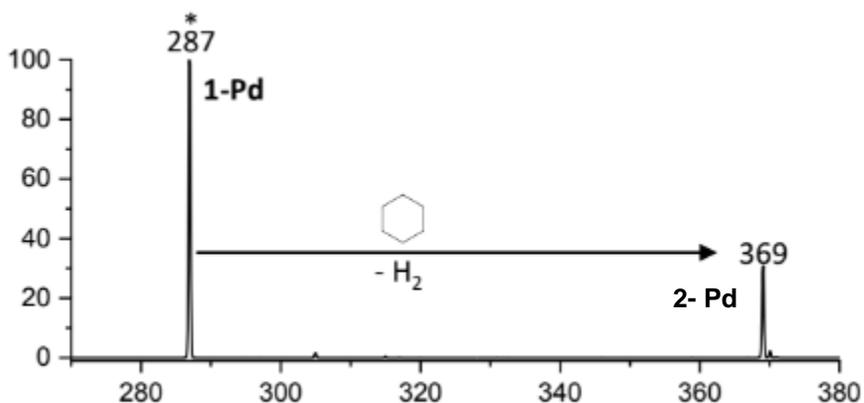

Figure 4: Mass spectrum for IMR of **1-Pd** with cyclohexane, forming **2-Pd**.

Following MS isolation of **2-M**, CID on the ion caused cracking to occur and $[(phen)M(R)]^+$ (where R = H, CH_3, C_2H_3, C_3H_5, C_4H_7, C_5H_7, C_6H_7, C_6H_9 and M = Ni, Pd) to be formed (bottom right ion in Figure 3). Thus, both dehydrogenation (loss of H_2 and $2H_2$) and cracking (breaking of C-C bonds in a hydrocarbon chain) occur when Ni or Pd is used as the metal in the reactive organometallic species.

The dehydrogenation and cracking of **2-Pd** is shown in Figure 5 below. The peak at m/z 369 corresponds to **2-Pd**. CID on this species yields products that correspond to the bottom left ion in Figure 3 above.
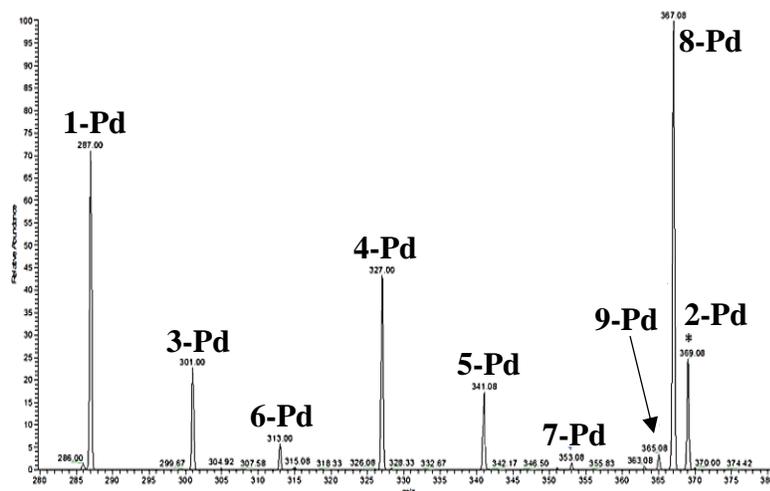
Figure 5: Mass spectrum for CID on **2-Pd** forming $[(phen)Pd(R)]^+$ (where R = H, CH_3, C_2H_3, C_3H_5, C_4H_7, C_5H_7, C_6H_7, C_6H_9).

A cycle is created by isolating each ring-opening peak in Figure 5, possibly doing CID on that peak, and performing IMR with cyclohexane to reform **2-Pd**. For example, in Figure 6 below, CID on $[(phen)Pd(C_3H_5)]^+$ (herein referred to as **4-Pd**) results in the formation of **1-Pd** and $[(phen)Pd(CH_3)]^+$ (herein referred to as **3-Pd**). Reacting each of these products with cyclohexane results in **2-Pd** formation, completing the catalytic cycle.
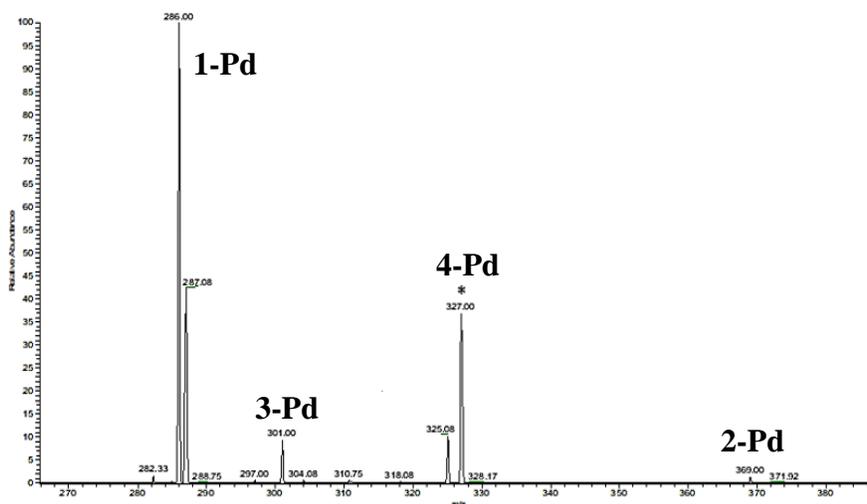

Figure 6: Mass spectrum for CID on **4-Pd** forming **1-Pd** and **3-Pd**.

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The complete network of reactivity for cycles involving **1-M** and **3-M** is shown below in Figure 7. Dashed arrows represent IMR and solid arrows represent CID. All spectra obtained experimentally, such as those in Figures 5 and 6, support the formation of the cycles depicted in Figure 7. All species fragment or react with cyclohexane to form **2-Pd**, whether through one or more steps.

Figure 7: Catalytic cycle involving **1-Pd** and **3-Pd**.

Three different metals were used in these reactions: Ni, Pd, and Pt. While varying the metal had no significant impact of forming the organometallic species, it did alter whether dehydrogenation or ring opening/cracking was favored. Ni and Pd species readily underwent dehydrogenation and ring opening/cracking. However, Pt species almost exclusively underwent dehydrogenation (see loss of C_4H_6 in Figure 8a below for an exception). Cracking of **2-Pt** results in a third dehydrogenation reaction, whereas cracking of **2-Ni** or **2-Pd** resulted in only two

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dehydrogenations. The IMR of $[(phen)Pt(C_6H_5)]^+$ (herein referred to as **10-Pt**) with cyclohexane results in the completion of the Pt catalytic cycle and the formation of benzene.

Mass spectra indicating a Pt dehydrogenation catalytic cycle are shown below in Figure 8. In Figure 8a, the base peak at m/z 455 corresponds to loss of H_2 when **2-Pt** is cracked. The resulting species, $[(phen)Pt(C_6H_9)]^+$ (herein referred to as **8-Pt**), is then isolated and fragmented in Figure 8b, resulting in a peak at m/z 453 corresponding to a second loss of H_2. The resulting species, $[(phen)Pt(C_6H_7)]^+$ (herein referred to as **9-Pt**), is then isolated and fragmented in Figure 8c, resulting in a peak at m/z 451 corresponding to a third loss of H_2. The resulting species, **10-Pt**, is then isolated and reacted with cyclohexane in Figure 8d, resulting in a peak at m/z 457 corresponding to formation of **2-Pt**, completing the catalytic cycle.
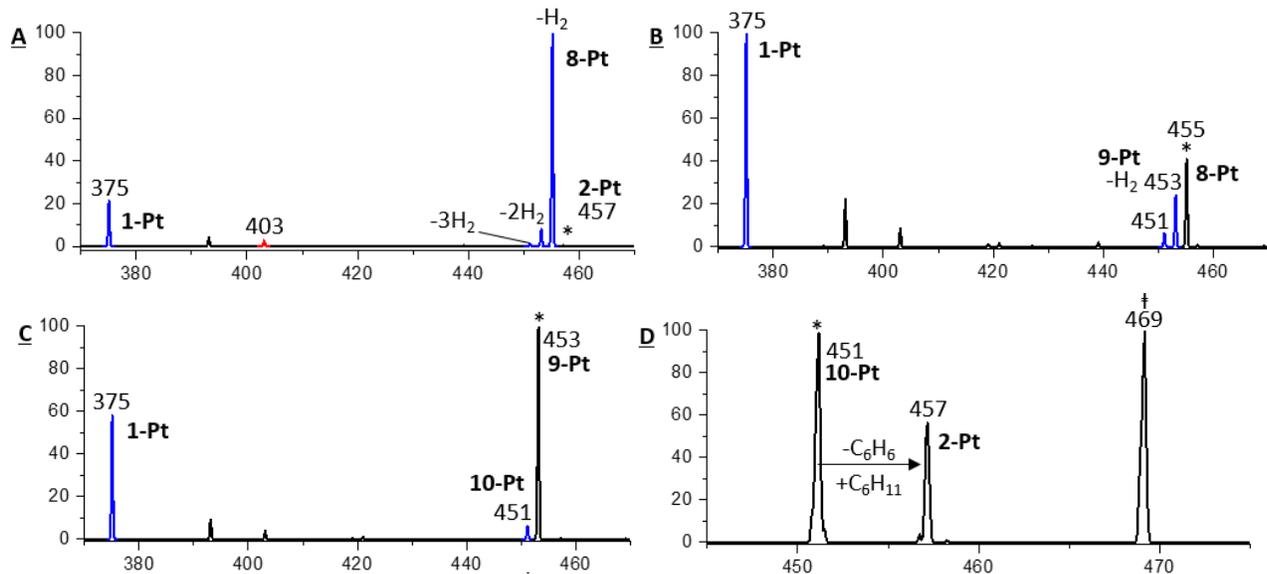

Figure 8: Mass spectra corresponding to the dehydrogenation catalytic cycle for Pt.

The complete network of the dehydrogenation catalytic cycles involving Ni, Pd, and Pt is shown below in Figure 9. The cycle from **1-M** to **2-M** to **8-M** to **9-M** and back to **1-M** holds true when M = Ni, Pd, Pt. The third dehydrogenation branching off from **9-M** to **10-M** and back to **2-**

M is true only when M = Pt. All spectra obtained experimentally, such as those in Figure 8, support

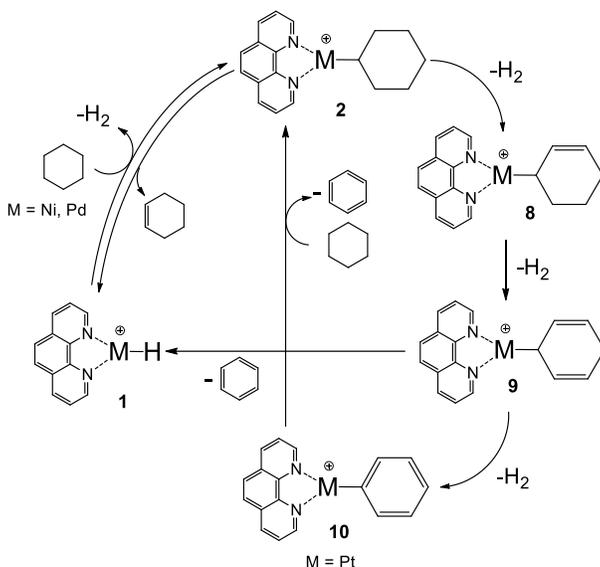the formation of the cycles depicted in Figure 9.

Figure 9: Dehydrogenation catalytic cycles where Pt undergoes a third dehydrogenation.

Conclusion

Mass spectrometry was used to study the ring-opening/cracking and dehydrogenation of

cyclohexane using organometallic catalysis. Using Ni or Pd as the metal component of the catalyst

created cracking catalytic cycles. The cracking of $[(phen)M(C_6H_{11})]^+$ (where M = Ni or Pd)

yielded species that reacted with cyclohexane, or, upon further cracking, formed species with

shorter hydrocarbon chains that reacted with cyclohexane to reform $[(phen)M(C_6H_{11})]^+$.

Furthermore, the use of Ni or Pd produced a dehydrogenation catalytic cycle with two incremental

losses of hydrogen molecules. The use of Pt yielded a similar cycle, but included a third loss of

hydrogen, along with a subsequential reaction with cyclohexane and loss of benzene. Regardless

of whether Ni, Pd, or Pt was used, the respective dehydrogenation cycle was closed by the

formation of $[(phen)M(C_6H_{11})]^+$ (where M = Ni, Pd, or Pt), which was produced initially. Overall,

the use of organometallic catalysis to induce ring-opening, cracking, and dehydrogenation of

cyclohexane produced chemically favorable molecules, such as hydrogen and ethene, and created

a catalytic cycle to enable the constant production of such molecules, providing an alternative to current processes used in the petroleum industry.

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