

# Reactions of $\text{FeCH}_2^+$ and $\text{CoCH}_2^+$ with Cyclic Alkanes in the Gas Phase

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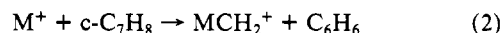
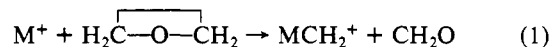
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**Abstract:** Gas-phase reactions of the title carbenes with cyclic alkanes with use of Fourier transform mass spectrometry (FTMS) are described. The metal-carbene reacts with both cyclopropane and cyclobutane by initial C-C bond insertion. The methyldiene-metallacyclobutane species produced from cyclopropane appears to decompose by three pathways: (1) cleavage of the metallacyclobutane ring (olefin metathesis), (2) ring expansion by carbene/alkyl coupling, and (3)  $\beta$ -hydride abstraction. With cyclobutane, an  $\text{MC}_5\text{H}_6^+$  ion is produced which consists of cyclopentadiene bound to the metal ion. For cyclopentane and cyclohexane, initial insertion into C-H bonds dominates generating  $\text{M}(\text{cyclic olefin})^+$  species. Small amounts of  $\text{M}(\text{C}_6\text{H}_8)^+$  and  $\text{M}(\text{C}_7\text{H}_8)^+$  were also produced from cyclopentane and cyclohexane, respectively, and are assigned as  $\text{M}(\text{MCP})^+$  (MCP = methylcyclopentadiene) and  $\text{M}(\text{tol})^+$  (tol = toluene).

The formation and fragmentation of metallacycles is important in organotransition-metal chemistry since these processes are involved in a number of key catalytic transformations. Olefin metathesis,<sup>1-3</sup> hydrocarbon cracking and isomerization,<sup>4</sup> epoxidation,<sup>5</sup> and deepoxidation<sup>6</sup> are all believed to proceed through the intermediacy of metallacyclobutanes. Metallacyclopentanes appear to be intermediates in a variety of olefin dimerization reactions.<sup>7,8</sup> Metal carbenes<sup>9</sup> represent another class of compounds important to the field of organotransition-metal chemistry and have been implicated as intermediates in olefin metathesis,<sup>1-3</sup> polymerization of olefins,<sup>10</sup> cyclopropane formation from olefins,<sup>11</sup> olefin homologation,<sup>12</sup> and metal-alkyl decompositions.<sup>13</sup> Studying the decomposition pathways of metallacycles as well as the chemistry of transition metal carbenes, therefore, may provide insight into catalytic pathways. Significant ligand and solvent effects are seen in these processes. For example, the mechanism of decomposition of nickelacyclopentanes in solution is strongly dependent on the coordination state of the metal.<sup>14,15</sup>

Studies involving metallacyclic species and metal carbenes in the gas phase are particularly interesting since no solvent molecules are present. Recently, reactions of the first-row group-8 transition-metal (Fe, Co, Ni) ions with cyclic alkanes were studied<sup>16,17</sup> with both dehydrogenation and ring cleavage observed. Dehydrogenation proceeds with retention of the ring's integrity.<sup>17</sup> Ring cleavage was proposed to proceed through metallacyclic intermediates.<sup>16,17</sup> Stable metallacyclobutane<sup>17b</sup> and metallacyclopentane<sup>17,18</sup> ions were generated by decarbonylation of cyclobutanone and cyclopentanone, respectively, and their decomposition processes studied.

Naked iron and cobalt carbene ions are produced from both ethylene oxide<sup>19</sup> and cycloheptatriene,<sup>20</sup> reactions 1 and 2.



Reactions of  $\text{FeCH}_2^+$  and  $\text{CoCH}_2^+$  with olefins<sup>23</sup> and aliphatic alkanes<sup>24</sup> have been studied in detail in the gas phase. Summarizing this work, reactions with simple olefins were dominated by metathesis products<sup>23</sup> while these metal carbenes were found to react with aliphatic alkanes predominantly by C-H bond insertion in contrast to the corresponding atomic metal ions which prefer C-C bond insertions.<sup>18,25</sup>

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- (20) This reaction was first reported for  $\text{Co}^+$ : Jacobson, D. B.; Byrd, G. D.; Freiser, B. S. *Inorg. Chem.* **1984**, *23*, 553. With use of the bond energies in ref 21 and the heats of formation in ref 22, formation of  $\text{FeCH}_2^+$  and  $\text{CoCH}_2^+$  from cycloheptatriene is calculated to be exothermic by  $29 \pm 5$  and  $16 \pm 7$  kcal/mol, respectively, assuming benzene as the neutral product.
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**Table I.** Distribution of Neutral(s) Lost in the Reaction of  $\text{FeCH}_2^+$  and  $\text{CoCH}_2^+$  with Cyclic Alkanes<sup>a</sup>

| cyclic alkane     | carbene           | neutral(s) lost |               |               |               |                            |                             |                        |                        |                        |                        |                        |                           |                           |                           |
|-------------------|-------------------|-----------------|---------------|---------------|---------------|----------------------------|-----------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|---------------------------|---------------------------|---------------------------|
|                   |                   | $\text{H}_2$    | $2\text{H}_2$ | $3\text{H}_2$ | $\text{CH}_4$ | $\text{CH}_4 + \text{H}_2$ | $\text{CH}_4 + 2\text{H}_2$ | $\text{C}_2\text{H}_4$ | $\text{C}_2\text{H}_6$ | $\text{C}_3\text{H}_6$ | $\text{C}_3\text{H}_8$ | $\text{C}_4\text{H}_8$ | $\text{C}_5\text{H}_{10}$ | $\text{C}_6\text{H}_{12}$ | $\text{C}_7\text{H}_{14}$ |
| $\triangle$       | $\text{FeCH}_2^+$ | 8               |               |               |               |                            |                             | 67                     |                        |                        |                        | 25                     |                           |                           |                           |
|                   | $\text{CoCH}_2^+$ | 33              |               |               |               |                            |                             | 35                     |                        |                        |                        | 32                     |                           |                           |                           |
| $\square$         | $\text{FeCH}_2^+$ |                 | 10            |               | 6             |                            |                             | 26                     |                        | 21                     |                        |                        | 37                        |                           |                           |
|                   | $\text{CoCH}_2^+$ |                 | 18            |               | 18            |                            |                             | 24                     |                        | 13                     |                        |                        | 27                        |                           |                           |
| $\text{pentagon}$ | $\text{FeCH}_2^+$ |                 | 3             |               |               | 82                         |                             |                        |                        |                        |                        |                        |                           | 15                        |                           |
|                   | $\text{CoCH}_2^+$ |                 | 10            |               |               | 78                         |                             |                        | 2                      | 6                      |                        |                        |                           | 4                         |                           |
| $\text{hexagon}$  | $\text{FeCH}_2^+$ |                 |               | 2             |               | 6                          | 80                          |                        |                        |                        |                        |                        |                           |                           | 12                        |
|                   | $\text{CoCH}_2^+$ |                 |               | 8             | 2             | 23                         | 60                          |                        |                        |                        | 3                      | 2                      |                           |                           | 2                         |

<sup>a</sup> Product distribution reproducible to  $\pm 10\%$ .

Here, we study in detail the reactions of  $\text{FeCH}_2^+$  and  $\text{CoCH}_2^+$  with cyclic alkanes using Fourier transform mass spectrometry (FTMS).  $\text{NiCH}_2^+$  was not studied due to the difficulty in generating it in sufficient quantities. Structures of product ions were probed by collision-induced dissociation (CID),<sup>26</sup> specific ion-molecule reactions, and H/D exchanges using deuterium.

### Experimental Section

The theory, instrumentation, and methodology of ion cyclotron resonance (ICR) spectroscopy<sup>27</sup> and Fourier transform mass spectrometry (FTMS)<sup>28</sup> have been discussed elsewhere. All experiments were performed on a Nicolet prototype FTMS-1000 Fourier transform mass spectrometer previously described in detail<sup>29</sup> and equipped with a 5.2-cm cubic trapping cell situated between the poles of a Varian 15-in electromagnet maintained at 0.9 T. The cell was constructed in our laboratory and utilizes 80% neutral density screens as the transmitter plates which permit irradiation with various light sources. High-purity foils of the appropriate metals were attached to the opposite transmitter screen. Metal ions are generated by focusing the beam of a Quanta Ray Nd:YAG laser (frequency doubled to 530 nm) onto a metal foil. Details of the laser ionization technique have been described elsewhere.<sup>30</sup>

Chemicals were obtained commercially in high purity and used as supplied except for multiple freeze-pump-thaw cycles to remove non-condensable gases.  $\text{C}_2\text{D}_4\text{O}$  (>98 atom % D) was obtained from MSD Isotopes, Merck Chemical Division. Sample pressures were on the order of  $1 \times 10^{-7}$  torr. Argon was used as the collision gas for the collision-induced dissociation (CID) experiments at a pressure of approximately  $5 \times 10^{-6}$  torr. A Bayard-Alpert ionization gauge was used to monitor pressure.

Details of the CID experiments have previously been discussed.<sup>18,29,31,32</sup> The collision energy of the ions can be varied (typically between 0 and 100 eV) from which plots of CID product ion intensities vs. kinetic energy can be made. These plots are reproducible to  $\pm 5\%$  absolute and yield additional structural information. The spread of ion kinetic energies is dependent on the total average kinetic energy and is approximately 35% at 1 eV, 10% at 10 eV, and 5% at 30 eV.<sup>33</sup>

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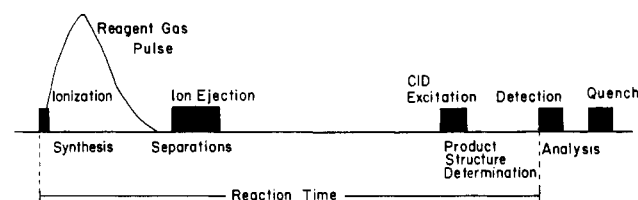
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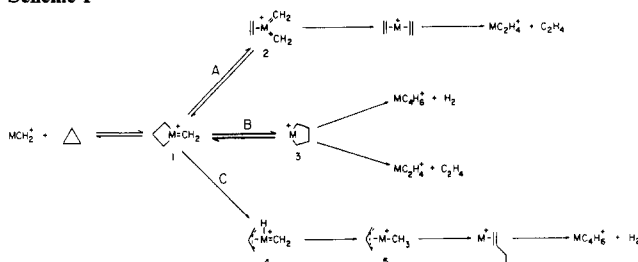
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**Figure 1.** Sequence of events for pulsed valve addition of reagent gas for the FTMS experiment. See Experimental Section for a more detailed explanation.

### Scheme I



The  $\text{MCH}_2^+$  ions were generated by reacting laser desorbed  $\text{Fe}^+$  and  $\text{Co}^+$  with ethylene oxide<sup>19</sup> or cycloheptatriene,<sup>20</sup> reactions 1 and 2. The carbenes generated in reactions 1 and 2 gave identical results (within experimental error) for reactions with the cyclic alkanes, Table I. Furthermore, the addition of a high pressure of argon ( $\sim 5 \times 10^{-6}$  torr) had little effect on the product distributions in Table I. This suggests that the  $\text{M(R)}^+$  ( $\text{R} = \text{carbene}$ ) ions formed in reactions 1 and 2 contain little excess internal energy. Labeled carbene ( $\text{MCD}_2^+$ ) was formed by reaction with deuterated ethylene oxide. The carbene reagent gas (ethylene oxide or cycloheptatriene) was introduced into the vacuum chamber through a General Valve Corp. series 9 pulsed solenoid valve.<sup>34</sup> The sequence of events with use of the pulsed valve for addition of a reagent gas is illustrated in Figure 1. Initially, a concurrent laser (metal ionization) and valve pulse occurs. The pulsed reagent gas fills the vacuum chamber to a maximum pressure of  $\sim 10^{-5}$  torr and is pumped away by a high-speed 5-in diffusion pump in  $\sim 250$  ms. The  $\text{MCH}_2^+$  ( $\text{MCD}_2^+$ ) ions are then isolated by swept double resonance ejection techniques<sup>28</sup> and allowed to react with a static pressure of a reagent gas without complicating reactions with ethylene oxide or cycloheptatriene. The products resulting from reactions with the static reagent gas can be isolated by additional swept ejection pulses to allow their further chemistry to be studied or their CID spectra to be obtained. The distributions of neutral(s) lost in the primary reactions of  $\text{MCH}_2^+$  and  $\text{MCD}_2^+$  are summarized in Tables I and II, respectively.

### Results and Discussion

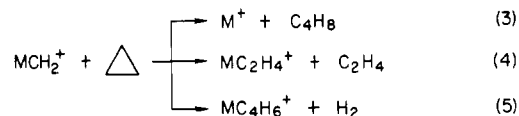
**Cyclopropane.** Cyclopropane yields three products with  $\text{FeCH}_2^+$  and  $\text{CoCH}_2^+$ , reactions 3–5. The ratio for dehydrogenation, reaction 5, with  $\text{MCD}_2^+$  for total scrambling is 15:12:1 for

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Table II. Distribution of Neutral(s) Lost in the Reaction of  $\text{FeCD}_2^+$  and  $\text{CoCD}_2^+$  with Cyclic Alkanes<sup>a</sup>

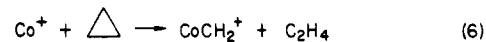
| cyclic alkane     | carbene           | neutral(s) lost |             |              |               |              |                           |               |                         |                                      |                                       |
|-------------------|-------------------|-----------------|-------------|--------------|---------------|--------------|---------------------------|---------------|-------------------------|--------------------------------------|---------------------------------------|
|                   |                   | $\text{H}_2$    | $\text{HD}$ | $\text{D}_2$ | $2\text{H}_2$ | $\text{H}_2$ | $\text{D}_2 + \text{H}_2$ | $3\text{H}_2$ | $\text{CH}_2\text{D}_2$ | $\text{CH}_2\text{D}_2 + \text{H}_2$ | $\text{CH}_2\text{D}_2 + 2\text{H}_2$ |
| $\triangle$       | $\text{FeCD}_2^+$ | 3               | 3           |              |               |              |                           |               |                         |                                      |                                       |
|                   | $\text{CoCD}_2^+$ | 19              | 14          | <1           |               |              |                           |               |                         |                                      |                                       |
| $\square$         | $\text{FeCD}_2^+$ |                 | 4           |              | 3             |              |                           |               |                         |                                      |                                       |
|                   | $\text{CoCD}_2^+$ |                 | 8           |              | 8             |              |                           |               |                         |                                      |                                       |
| $\text{pentagon}$ | $\text{FeCD}_2^+$ |                 | 8           |              | 3             |              |                           |               |                         |                                      |                                       |
|                   | $\text{CoCD}_2^+$ |                 | 9           |              | 9             |              |                           |               |                         |                                      |                                       |
| $\text{hexagon}$  | $\text{FeCD}_2^+$ |                 |             |              |               |              |                           |               |                         |                                      |                                       |
|                   | $\text{CoCD}_2^+$ |                 |             |              |               |              |                           |               |                         |                                      |                                       |

<sup>a</sup> Product distribution reproducible to  $\pm 10\%$ .

$\text{H}_2\text{:HD:D}_2$ . This is roughly the distribution observed for  $\text{MCD}_2^+$  (Table II), indicating that considerable scrambling occurs prior to dehydrogenation. Elimination of ethene as  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2\text{D}_2$  occurs in roughly equal amounts with  $\text{MCD}_2^+$ .

Both  $\text{FeCH}_2^+$  and  $\text{CoCH}_2^+$  react with aliphatic alkanes predominantly by C-H bond insertion.<sup>24</sup> Cyclopropane has the strongest C-H bonds ( $106.3 \pm 0.3$  kcal/mol)<sup>35</sup> of all the alkanes. Due to ring strain, however, the C-C bonds are very weak and should be susceptible to metal insertion. A mechanism for reaction of  $\text{MCH}_2^+$  with cyclopropane is presented in Scheme I and involves metal insertion into the weak C-C bond of cyclopropane forming an activated methylidene-metallacyclobutane species (**1**), which can decompose by several pathways. Elimination of  $\text{C}_2\text{H}_4$  ( $\text{C}_2\text{H}_2\text{D}_2$ ) can proceed by routes A and B while dehydrogenation can occur by routes B and C. Route A involves initial ring cleavage generating a bis(methylidene)-ethene complex **2**. Coupling of the methylenes in **2** is followed by ethene elimination. Elimination of roughly equal amounts of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2\text{D}_2$  with  $\text{MCD}_2^+$  requires methylene coupling to be rapid with respect to ethene elimination.

Bis(alkylidene) complexes have been prepared and studied<sup>36-38</sup> and lend support to the bis-methylidene pathway proposed. Also of relevance is the observation that kinetically excited  $\text{Co}^+$  ions react with cyclopropane to yield predominantly  $\text{CoCH}_2^+$ ,<sup>16,19</sup> reaction 6. This reaction is believed to proceed through initial



oxidative addition of  $\text{Co}^+$  across a C-C bond followed by rearrangement to a methylidene-ethene complex which eliminates ethene. In addition,  $\text{FeCD}_2^+$  and  $\text{CoCD}_2^+$  react with ethene resulting in formation of  $\text{MCH}_2^+$ ,<sup>23</sup> reaction 7. This reaction



probably proceeds by interconversion of the metal methylidene-ethene with metallacyclobutane (olefin metathesis).<sup>1-3</sup>

Incorporation of methylene into the metallacyclobutane ring of **1** generates the ring-expansion product **3**, a metallacyclopentane. Methylene incorporation (migratory insertion) of an alkyl has also been implicated for reactions of  $\text{MCH}_2^+$  ( $\text{M} = \text{Fe}, \text{Co}$ ) with aliphatic alkanes in the gas phase.<sup>24</sup> Migratory insertion of an alkyl to an alkylidene is well supported in solution for cationic alkylidene/alkyl complexes.<sup>38-44</sup> In those studies the alkylidene/alkyl insertions were facilitated by a positive charge on the metal center. It has been suggested that the positive charge renders the unsaturated carbon center electrophilic and accelerates a migratory insertion which is best regarded as a migration of the alkyl group with its bonding electron pair onto the unsaturated carbon.<sup>44</sup> Such a process is analogous to the well-characterized

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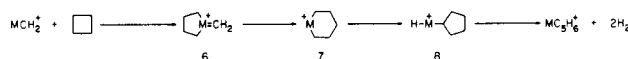
(42) (a) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984.

(b) Thorn, D. L. *Organometallics* **1982**, *1*, 879.

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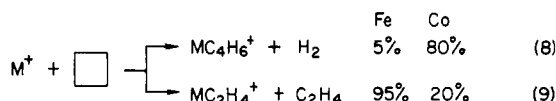
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## Scheme II



alkyl/carbonyl migratory insertions.<sup>45</sup>

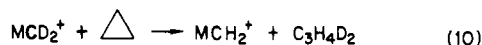
Metallacyclopentanes decompose in solution by symmetric ring cleavage resulting in formation of ethene, by  $\beta$ -hydride elimination producing butene and by reductive elimination of cyclobutane-1,3c,14,15,46-48. Stable metallacyclopentane ions have been synthesized in the gas phase by decarbonylation of cyclopentanone<sup>17,15</sup> by  $\text{Fe}^+$  and  $\text{Ni}^+$ . These metallacyclopentane ions decompose upon collisional activation both by symmetric ring cleavage ( $\text{C}_2\text{H}_4$  elimination) and by dehydrogenation. Labeling studies in the gas phase indicated that symmetric ring cleavage occurred with no H/D scrambling; however, dehydrogenation proceeded with considerable scrambling.<sup>17</sup> Absence of H/D scrambling for symmetric ring cleavage indicates that H/D scrambling occurs only after rearrangement to a structure different than metallacyclopentane, presumably a linear butene complex.<sup>49</sup> Finally,  $\text{Fe}^+$ <sup>17</sup> and  $\text{Co}^+$ <sup>16,17</sup> react with cyclobutane, yielding the products in reactions 8 and 9. These reactions are proposed to proceed



through metallacyclopentane intermediates and suggest that dehydrogenation is much more facile for cobaltacyclopentane ions than for ferracyclopentane ions.

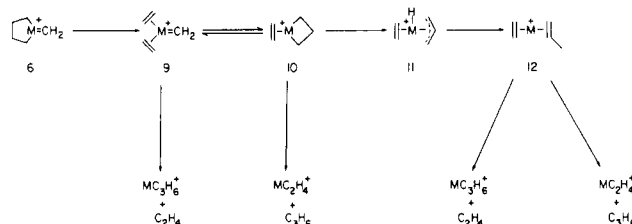
Dehydrogenation may also proceed by  $\beta$ -hydride abstraction from 1 (route C, Scheme I). Rearrangement of metallacyclobutanes to metal olefin complexes via hydride- $\pi$ -allyl intermediates has been proposed in solution-phase studies.<sup>38,50,51</sup>  $\beta$ -Hydride abstraction is followed by formation of a methyl-allyl intermediate 5. C-C bond formation generates an activated linear butene complex which can undergo considerable H/D scrambling prior to dehydrogenation.<sup>49</sup> Dehydrogenation by route C is probably more likely to occur for cobalt than for iron since cobaltacyclobutane ions readily rearrange to  $\text{Co}(\text{prop})^+$  (prop = propene) in the gas phase and ferracyclobutane ions do not.<sup>17b,52</sup>

Finally, the thermoneutral reaction 10 occurs for  $\text{FeCD}_2^+$  but not for  $\text{CoCD}_2^+$ . This probably proceeds via an equilibrium

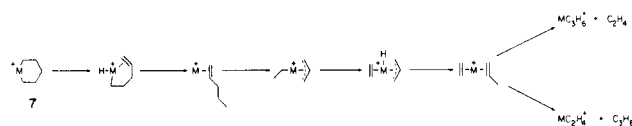


between species 1 and 2 in Scheme I with reductive elimination of cyclopropane from 1. Observation of reaction 10 implies that rearrangement of the bis(methylidene)-ethene complex, 2, to the methylidene-metallacyclobutane species, 1, is competitive with methylene coupling of intermediate 2 forming  $\text{M}(\text{eth})_2^+$  (eth = ethene) for iron. Alternatively, species 1 and 3 in Scheme I may be in equilibrium. There is strong evidence that a nickelacyclohexane complex undergoes  $\alpha$ -C-C bond cleavage forming a

## Scheme III



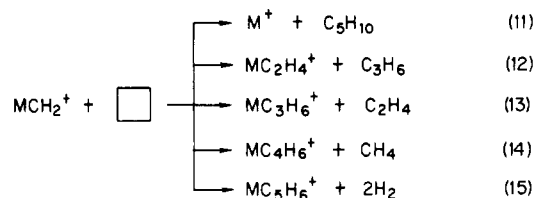
## Scheme IV



methylidene-metallacyclopentane species in solution.<sup>53</sup>

Formation of the bare metal ions (elimination of  $\text{C}_4\text{H}_8$ ) may proceed by reductive elimination of cyclobutane or linear butene. Elimination of butadiene +  $\text{H}_2$  or two ethenes are both thermally unfavorable.<sup>54</sup>

**Cyclobutane.** Both  $\text{FeCH}_2^+$  and  $\text{CoCH}_2^+$  yield five products with cyclobutane, reactions 11-15. The product of reaction 15,



$\text{MC}_5\text{H}_6^+$ , yields elimination of  $\text{C}_5\text{H}_6$  as the only fragmentation upon collisional activation. In addition, this product undergoes six H/D exchanges with  $\text{D}_2$ . These results are indicative of  $\text{M}(\text{CP})^+$  (CP = cyclopentadiene) species.<sup>17</sup> A mechanism for formation of  $\text{M-c-C}_5\text{H}_6^+$  in reaction 15 is outlined in Scheme II. Initially, the carbene oxidatively inserts into a C-C bond of cyclobutane generating an activated methylidene-metallacyclopentane species 6. Incorporation of methylene into the metallacyclic ring generates the ring-expansion product 7 followed by rearrangement to a hydrido-cyclopentyl complex 8 which eliminates  $2\text{H}_2$  forming  $\text{M-c-C}_5\text{H}_6^+$ . The reverse of the above ring expansion process ( $\alpha$ -C-C bond cleavage) has been observed for nickelacyclohexanes in solution.<sup>53</sup> Roughly equal amounts of  $2\text{H}_2$  and  $\text{H}_2 + \text{HD}$  elimination are observed with  $\text{MCD}_2^+$ , Table II. Observation of this ring-expansion process for cyclobutane lends support to the ring expansion described above for cyclopropane.

Methane elimination, reaction 14, probably proceed by two sequential  $\beta$ -hydride shifts from intermediate 6 forming  $\text{M}(\text{but})^+$  (but = butadiene). CID on the product of reaction 14 yields  $\text{C}_4\text{H}_6$  elimination as the only fragmentation consistent with  $\text{M}(\text{but})^+$  species.<sup>32</sup>

Elimination of  $\text{C}_3\text{H}_6$  and  $\text{C}_2\text{H}_4$ , reactions 12 and 13, corresponds to C-C bond cleavage of the cyclobutane ring. With  $\text{MCD}_2^+$ , elimination of  $\text{C}_2\text{H}_4$  and  $\text{C}_3\text{H}_4\text{D}_2$  dominates with considerable scrambling seen for cobalt, Table II. A mechanism for these losses is presented in Scheme III. Irreversible symmetric ring cleavage of 6 generates the bis(ethene)-methylidene complex 9.<sup>55</sup> Intermediate 9 can eliminate  $\text{C}_2\text{H}_4$  or rearrange to an ethene-me-

(45) For a general review of CO insertion reactions see: Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299.

(46) (a) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521. (b) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529.

(47) Diversi, P.; Ingrosso, G.; Lucherini, A. *J. Chem. Soc., Chem. Commun.* **1978**, 735.

(48) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 4451.

(49) Considerable H/D scrambling occurs for reaction of  $\text{Fe}^+$  and  $\text{Co}^+$  with 1-butene-1,1- $d_2$  in the gas phase, presumably proceeding through the interconversion of hydrido- $\pi$ -allyl and linear butene-metal ion species. See for example ref 32.

(50) (a) Cushman, B. M.; Brown, D. B. *J. Organomet. Chem.* **1978**, *152*, C42. (b) Johnson, T. H.; Cheng, S. J. *J. Am. Chem. Soc.* **1979**, *101*, 5277.

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(53) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 7418.

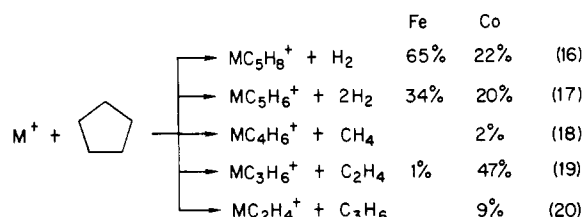
(54) Elimination of  $2\text{C}_2\text{H}_4$  is endothermic by 15.8 kcal/mol for  $\text{FeCH}_2^+$  and 4.8 kcal/mol for  $\text{CoCH}_2^+$  with butadiene +  $\text{H}_2$  also endothermic by 17.2 kcal/mol for  $\text{FeCH}_2^+$  and 6.2 kcal/mol for  $\text{CoCH}_2^+$ . Elimination of 1-butene is exothermic by 9.1 kcal/mol for  $\text{FeCH}_2^+$  and 20.1 kcal/mol for  $\text{CoCH}_2^+$  and cyclobutane elimination is also exothermic by 2.8 kcal/mol for  $\text{FeCH}_2^+$  and 13.8 kcal/mol for  $\text{CoCH}_2^+$ . These calculations use the bond energies in ref 21 and the heats of formation in ref 22.

(55) Symmetric ring cleavage of ferracyclopentane and cobaltacyclopentane ions to form bis(ethene) complexes is irreversible in the gas phase. See for example ref 17.

tallacyclobutane species **10**. Intermediate **10** can reductively eliminate cyclopropane<sup>56</sup> as well as undergo interconversion with intermediates **9** and **11**. Complex **11** can readily rearrange to the bis(olefin) species **12**, which can eliminate either  $\text{C}_2\text{H}_4$  or  $\text{C}_3\text{H}_6$ .

Roughly equal amounts of  $\text{C}_2\text{H}_4$  and  $\text{C}_3\text{H}_6$  elimination occur for  $\text{FeCH}_2^+$ . This suggests that these eliminations probably proceed predominantly from intermediates **9** and **10** instead of from **12**. Conversion to intermediate **12** would result in considerably more  $\text{C}_2\text{H}_4$  elimination than  $\text{C}_3\text{H}_6$ <sup>18,32,57</sup> since smaller olefins are bound more weakly than larger olefins to cationic metal centers in the gas phase and, therefore, the smaller olefin will be preferentially cleaved.<sup>58</sup> For  $\text{CoCH}_2^+$  the ratio of  $\text{C}_2\text{H}_4$  to  $\text{C}_3\text{H}_6$  elimination is roughly 2:1. Furthermore, considerable H/D scrambling is observed with  $\text{CoCD}_2^+$ . This scrambling can be rationalized by invoking reversible  $\beta$ -hydride shifts in **12** prior to olefin elimination.<sup>59</sup>

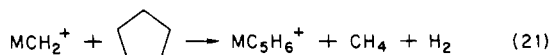
$\text{Fe}^+$  and  $\text{Co}^+$  react with cyclopentane to yield the products in reactions 16–20.<sup>16,17</sup> The C–C bond cleavages, reactions 18–20,



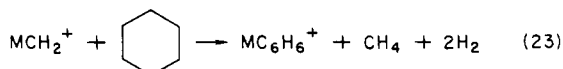
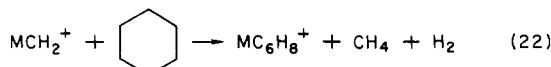
are believed to proceed by initial formation of an activated metallacyclohexane intermediate **7** which subsequently rearranges to a  $\text{M}(\text{l-pent})^+$  (pent = pentene) species via a 1–4 hydrogen atom shift<sup>17</sup> which ultimately decomposes predominantly by insertion into an allylic C–C bond, Scheme IV.<sup>18,32,57</sup> This mechanism predicts formation of  $\text{M}(\text{C}_5\text{H}_4)(\text{C}_3\text{H}_4\text{D}_2)^+$  (50%),  $\text{M}(\text{C}_2\text{H}_2\text{D}_2)(\text{C}_3\text{H}_6)^+$  (17%), and  $\text{M}(\text{C}_2\text{H}_3\text{D})(\text{C}_3\text{H}_5\text{D})^+$  (33%) which should decompose, yielding products with varying amounts of deuterium due to H/D scrambling prior to olefin elimination.<sup>59</sup> This is clearly not seen for iron carbene; however, some scrambling is seen for cobalt carbene. Therefore, the C–C bond cleavages appear to proceed predominantly by Scheme III with some also occurring by Scheme IV for cobalt carbene.

Formation of  $\text{Co}^+$  in reaction 11 by elimination of cyclopentane, cyclopentene +  $\text{H}_2$ , and butadiene + methane is exothermic while formation of  $\text{Fe}^+$  in reaction 11 is only exothermic for elimination of cyclopentane.<sup>60</sup>

**Cyclopentane and Cyclohexane.** The neutral losses for the reactions of cyclopentane and cyclohexane with  $\text{MCH}_2^+$  and  $\text{MCD}_2^+$  are dominated by retention of the ring's integrity in contrast to the smaller cyclic alkanes where ring cleavages dominate. Structural studies indicate that  $\text{M-c-C}_5\text{H}_6^+$  is generated in reaction 21 and that  $\text{M-c-C}_6\text{H}_8^+$  and  $\text{M-c-C}_6\text{H}_6^+$  are formed



in reactions 22 and 23. Similar behavior has been observed for



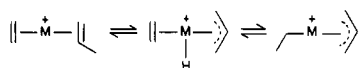
reactions of the bare transition-metal ions ( $\text{Fe}^+$  and  $\text{Co}^+$ ) with

(56) Grubbs, R. H. *Inorg. Chem.* **1979**, *18*, 2623.

(57) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6624.

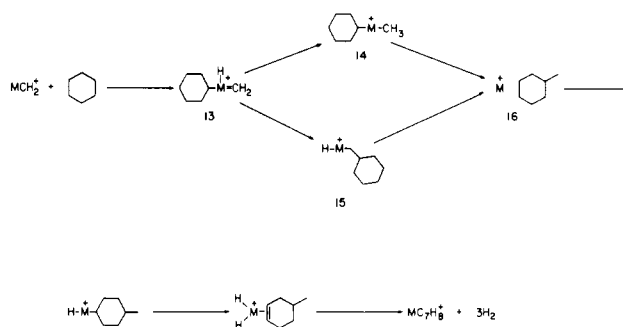
(58) Kappes, M. M.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 1813.

(59) The following equilibrium has been observed for  $\text{Fe}^+$ ,  $\text{Co}^+$ , and  $\text{Ni}^+$  in the gas phase. See ref 52.



(60) On the basis of the bond energies in ref 21 and heats of formation in ref 22.

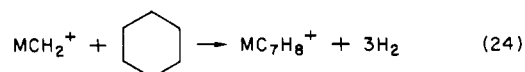
Scheme V



cyclic alkanes where ring cleavages dominate for cyclobutane while cyclopentane and cyclohexane predominantly yield retention of the ring's integrity.<sup>16,17,61</sup> This difference in chemistry for larger cyclic alkanes is attributed to the relatively weak C–H bonds ( $94.5 \pm 1$  kcal/mol for cyclopentane and  $95.5 \pm 1$  kcal/mol for cyclohexane)<sup>35b</sup> and the fact that the C–C bonds have little or no strain energy.

A small amount of C–C bond cleavage occurs for  $\text{CoCH}_2^+$  with cyclopentane and cyclohexane, but none occurs for  $\text{FeCH}_2^+$ . These cleavages probably result from initial insertion into a C–C bond generating an activated methyldiene–metallacyclic species which subsequently decomposes. The mode of decomposition of these activated methyldiene–metallacyclic complexes is probably quite complex with several decomposition channels available.

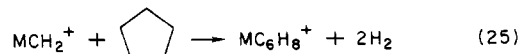
As with cyclopropane and cyclobutane, dehydrogenation products are also observed for cyclopentane and cyclohexane. Reaction with cyclohexane yields only one dehydrogenation product, reaction 24. Complete retention of the label is seen for



$\text{MCD}_2^+$ . Collisional activation of  $\text{CoC}_7\text{H}_8^+$  yields only  $\text{C}_7\text{H}_8$  elimination. The  $\text{FeC}_7\text{H}_8^+$  intensity was too low to allow for it to be studied.  $\text{M(tol)}^+$  yields elimination of  $\text{C}_7\text{H}_8$  as the only fragmentation upon collisional activation. CID of authentic  $\text{M(CH)}^+$  ( $\text{CH}$  = cycloheptatriene) and  $\text{M(NB)}^+$  ( $\text{NB}$  = norbornadiene) species ( $\text{M} = \text{Fe}, \text{Co}$ ) yield elimination of  $\text{C}_2\text{H}_2$ ,  $\text{C}_3\text{H}_6$ ,  $\text{C}_6\text{H}_6$ , and  $\text{C}_7\text{H}_8$ . In addition, some  $\text{H}^+$  elimination from  $\text{Fe(CH)}^+$  is also observed. These results are consistent with formation of  $\text{M(tol)}^+$  in reaction 24.

A mechanism for formation of  $\text{M(tol)}^+$  in reaction 24 is presented in Scheme V and involves initial oxidative addition across a C–H bond forming **13**. Intermediate **13** rearranges to **14** and **15** which undergo reductive elimination forming a metal ion–methylcyclohexane species **16**. Oxidative addition across a C–H bond is followed by elimination of  $3\text{H}_2$  forming  $\text{M(tol)}^+$ . This mechanism also predicts retention of the label with  $\text{MCD}_2^+$ . In addition to elimination of  $3\text{H}_2$ , intermediate **16** may also lose methane forming  $\text{M(CH)}^+$  ( $\text{CH}$  = cyclohexene) which can undergo subsequent dehydrogenations.<sup>17a</sup>

Dehydrogenation of cyclopentane by  $\text{MCH}_2^+$  yields  $\text{MC}_6\text{H}_8^+$ , reaction 25, with complete retention of label observed for  $\text{MCD}_2^+$ .



Again, the intensity of the iron analogue was too low for it to be studied. CID of  $\text{CoC}_6\text{H}_8^+$  yields dehydrogenation forming  $\text{CoC}_6\text{H}_6^+$  in high efficiency along with  $\text{C}_6\text{H}_8$  elimination.  $\text{CoC}_6\text{H}_6\text{D}_2^+$ , generated from  $\text{CoCD}_2^+$ , yields dehydrogenation by eliminating  $\text{H}_2$  ( $\sim 60\%$ ) and  $\text{HD}$  ( $\sim 40\%$ ). These results are consistent with formation of  $\text{M(MCP)}^+$  ( $\text{MCP}$  = methylcyclopentadiene) in reaction 25 by a mechanism similar to that presented in Scheme V for  $\text{MC}_7\text{H}_8^+$  formation from cyclohexane. Dehydrogenation of  $\text{CoC}_6\text{H}_8^+$  would then generate  $\text{Co(ful)}^+$  (ful

(61) Byrd, G. D.; Burnier, R. C.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 3565.

= fulvene) upon collisional activation.

### Conclusions

$\text{FeCH}_2^+$  and  $\text{CoCH}_2^+$  react with cyclopropane and cyclobutane exclusively by initial insertion across a C-C bond generating an activated methyldiene-metallacyclic species which decomposes via a variety of pathways. There is good evidence for ring expansion via migratory insertion of methylene into the metallacyclic ring system. Methylene/alkyl coupling has been implicated in another study involving the reactions of  $\text{MCH}_2^+$  ( $\text{M} = \text{Fe}, \text{Co}$ ) with aliphatic alkanes,<sup>24</sup> and this process is well supported in solution chemistry.<sup>38-44</sup> The ring-expansion product for reaction of  $\text{MCH}_2^+$  with cyclobutane, reaction 15, generates  $\text{M-c-C}_5\text{H}_6^+$ .

With cyclopentane and cyclohexane, retention of the ring's integrity dominates the reactions. This suggests initial attack of C-H bonds and not C-C bonds. The difference in reaction mechanisms between small and large cyclic alkanes is attributed to the strong C-H bonds in cyclopropane and cyclobutane coupled with C-C bonds weakened by strain energy. Therefore, these weak C-C bonds are preferentially attacked. The C-C bonds in cy-

clopentane and cyclohexane have little or no strain energy and, therefore, are not as susceptible to attack relative to the C-H bonds. Similar behavior has been observed for reactions of  $\text{MCH}_3^+$  ( $\text{M} = \text{Fe}$  and  $\text{Co}$ ),<sup>62</sup>  $\text{Fe}^{+17,61}$ , and  $\text{Co}^{+16,17}$  with cyclic alkanes where cyclopropane and cyclobutane are dominated by ring cleavages while cyclopentane and cyclohexane are dominated by retention of the ring's integrity.

**Acknowledgment** is made to the Division of Chemical Sciences in the Office of Basic Energy Sciences in the United States Department of Energy (DE-AC02-80ER10689) for supporting this research and to the National Science Foundation (CHE-8310039) for supporting advances in FTMS methodology.

**Registry No.**  $\text{FeCH}_2^+$ , 90143-30-9;  $\text{CoCH}_2^+$ , 76792-07-9;  $\text{H}_2$ , 1333-74-0;  $\text{CH}_4$ , 74-82-8;  $\text{C}_2\text{H}_4$ , 74-85-1;  $\text{CH}_2\text{D}_2$ , 676-55-1;  $\text{C}_2\text{H}_2\text{D}_2$ , 29060-53-5;  $\text{FeCD}_2^+$ , 93604-57-0;  $\text{CoCD}_2^+$ , 93604-58-1; cyclopropane, 75-19-4; cyclobutane, 287-23-0; cyclopentane, 287-92-3; cyclohexane, 110-82-7.

(62) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, 106, 3900.

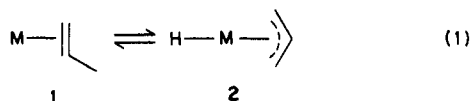
## Dynamics of Monoolefin-Metal Ion Complexes in the Gas Phase. Determination of the Number of Labile Hydrogens by Reaction with $\text{C}_2\text{D}_4$

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Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. Received May 29, 1984

**Abstract:** H/D exchange reactions of organometallic ions with  $\text{D}_2$  in the gas phase have proven valuable in determining the number of labile hydrogens in the complex. Unfortunately, many complexes are not observed to exchange with  $\text{D}_2$ . In this paper we demonstrate that  $\text{C}_2\text{D}_4$  can extend the variety of complexes which may be studied. The propene complexes of  $\text{Fe}^+$ ,  $\text{Co}^+$ , and  $\text{Ni}^+$  which are unreactive with  $\text{D}_2$  undergo 5 H/D exchanges with  $\text{C}_2\text{D}_4$ . These results are rationalized by invoking an equilibrium between the propene and hydrido- $\pi$ -allyl species promoted by the activation afforded by ethene- $d_4$  coordination. The  $\text{Rh}(\text{propene})^+$  complex is observed to exchange all 6 hydrogens suggesting an additional mechanism involving a vinylic C-H bond insertion. In addition, this  $\text{Rh}(\text{propene})^+$  species undergoes multiple exchanges per  $\text{C}_2\text{D}_4$  encounter in contrast to the  $\text{M}(\text{propene})^+$  species of  $\text{Fe}^+$ ,  $\text{Co}^+$ , and  $\text{Ni}^+$  which undergo only a single exchange per  $\text{C}_2\text{D}_4$  encounter. The rate of the above exchanges falls into the order  $\text{Rh}^+ > \text{Co}^+ > \text{Fe}^+ > \text{Ni}^+$ .  $\text{Rh}(1,3\text{-pentadiene})^+$  undergoes 5 rapid exchanges with  $\text{C}_2\text{D}_4$  while the corresponding iron and cobalt complexes yield 5 slow exchanges with no exchange observed for the nickel complex. No multiple exchanges occur for these pentadiene ions. The isomeric  $\text{Rh}(2\text{-methylbutadiene})^+$  species undergoes 5 slow exchanges with none observed for the iron, cobalt, and nickel species.  $\text{M-c-C}_5\text{H}_6^+$  ( $\text{M} = \text{Fe}, \text{Co}, \text{Ni}$ ) undergo 6 rapid exchanges with multiple exchanges predominating. The  $\text{Rh-c-C}_5\text{H}_6^+$  species only undergoes one rapid exchange. Both  $\text{Rh-c-C}_7\text{H}_8^+$  and  $\text{Co-c-C}_7\text{H}_8^+$  generated from cycloheptatriene yield one slow exchange with  $\text{C}_2\text{D}_4$  with none observed for  $\text{Fe-c-C}_7\text{H}_8^+$  and  $\text{Ni-c-C}_7\text{H}_8^+$ .

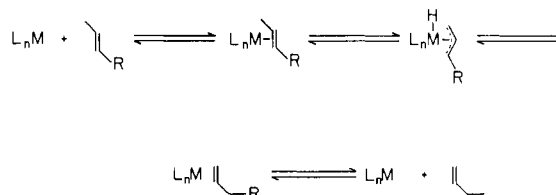
The ability of transition-metal complexes to effect structural transformations in organic substrates constitutes a basic facet of organometallic chemistry. One such transformation which has received much attention is the metal-promoted isomerization of olefins.<sup>1</sup> Under hydride-free conditions, reversible insertion into an allylic carbon-hydrogen bond has been frequently invoked as the mechanism for catalytic isomerization of olefins, Scheme I,<sup>2</sup> and is supported by detailed stereochemical studies.<sup>3-6</sup> This mechanism is supported by detailed stereochemical studies.<sup>3-6</sup> In addition, the hydrido- $\pi$ -allyl intermediate has been observed directly,<sup>7,8</sup> as well as in a dynamic equilibrium with the olefin complex,<sup>8-10</sup> eq 1. Therefore, the mechanism presented in Scheme



I for the isomerization of olefins under hydride-free conditions has gained general acceptance.

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### Scheme I



The above olefin isomerization requires that the metal complex contain an empty coordination site. An atomic transition metal

(1) For reviews of transition-metal-catalyzed olefin isomerizations see: (a) Tolman, C. A. "Transition Metal Hydrides"; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; pp 271-312. (b) Hubert, A. J.; Reimlinger, H. *Synthesis* **1970**, 2, 405. (c) Davies, N. R. *Rev. Pure Appl. Chem.* **1967**, 17, 83. (d) Orchin, M. *Adv. Catal. Rel. Subj.* **1966**, 16, 1.

(2) (a) Manuel, T. A. *J. Org. Chem.* **1962**, 27, 3941. (b) Emerson, G. F.; Pettit, R. *J. Am. Chem. Soc.* **1962**, 84, 4591. (c) Harrod, J. F.; Chalk, A. J. *J. Am. Chem. Soc.* **1966**, 88, 3491.

(3) (a) Green, M.; Hughes, R. P. *J. Chem. Soc., Dalton Trans.* **1976**, 1907. (b) Green, M. *Ann. N.Y. Acad. Sci.* **1977**, 295, 160.