

The oxidation of carbon monoxide which is proposed in Scheme IV is noteworthy because it takes place at an appreciable rate ( $t_{1/2}$  ca. 20 min) at relatively low temperature (211 K) and significantly faster ( $t_{1/2}$  less than 1 min) at ice temperature. This is perhaps surprising in view of published reports on the reduction of cytochrome oxidase<sup>40</sup> or hemin<sup>41</sup> by carbon monoxide. However, the latter reactions take place in ferric-cupric or ferric systems, in contrast to the reaction in Scheme IV, which involves a ferryl ion. The ferryl ion, with the structure proposed, is well-suited to this reaction in two respects: It is able to accept two electrons at once, and it contains an oxygen atom which is not protonated.

**Electron-Transfer Pathways.** We conclude by noting one of the implications of the scheme describing the early electron-transfer events. This scheme involves the partitioning of the oxidase molecules into two distinct populations by transfer of the first electron from either  $\text{Fe}_a$  or  $\text{Cu}_A$ . The occurrence of this partitioning indicates that both  $\text{Cu}_A$ -to- $\text{Fe}_{a_3}$ / $\text{Cu}_B$  site and  $\text{Fe}_a$ -to- $\text{Fe}_{a_3}$ / $\text{Cu}_B$  site electron-transfer pathways are approximately equally competent at these temperatures. The similarity of the rates via the two paths indicates that one is not very much better than the other with respect to the distance of the transfer or the suitability of the intervening material.<sup>30</sup> The existence of two competent electron pathways to the dioxygen-reduction site may have implications for the mechanisms of energy conservation by

the oxidase. It is now well-established that the cytochrome oxidase-catalyzed transfer of electrons from cytochrome *c* to dioxygen is coupled to the active transport of protons across the mitochondrial membrane,<sup>4</sup> and it appears most likely that either  $\text{Fe}_a$  or  $\text{Cu}_A$  is involved in this proton pumping function. If, for example,  $\text{Cu}_A$  were the proton pump, then the  $\text{Fe}_a$ -to- $\text{Fe}_{a_3}$ / $\text{Cu}_B$  electron-transfer path would bypass the pump. Such a bypass mechanism might be important at steps in dioxygen reduction where the  $\text{Cu}_A$ -to- $\text{Fe}_{a_3}$ / $\text{Cu}_B$  transfer, which is linked to proton pumping, is relatively slow because these steps are not sufficiently exothermic. It has been suggested<sup>42</sup> that proton pumping might be uncoupled from electron transfer at some steps in the cytochrome oxidase reaction cycle. The existence of two competent electron-transfer pathways to the dioxygen-reduction site may reflect the need for this uncoupling.

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**Registry No.**  $\text{O}_2$ , 7782-44-7;  $\text{CO}$ , 630-08-0;  $\text{CO}_2$ , 124-38-9; cytochrome *c* oxidase, 9001-16-5; glycerol, 56-81-5; ethylene glycol, 107-21-1.

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## Reactions of $\text{CoCp}^+$ ( $\text{Cp} = \text{Cyclopentadienyl}$ ) with Hydrocarbons in the Gas Phase. Observation of Novel Skeletal Isomerizations/Dehydrocyclizations Resulting in Cobaltocenium Formation

D. B. Jacobson<sup>†</sup> and B. S. Freiser\*

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. Received March 26, 1985

**Abstract:** The gas-phase reactions of  $\text{CoCp}^+$  with a variety of hydrocarbons are described by using Fourier transform mass spectrometry (FTMS). All aliphatic alkanes larger than methane (except 2,2-dimethylpropane) are dehydrogenated by  $\text{CoCp}^+$  with no C-C bond cleavages observed. Collisional activation of  $\text{CoCp}(\text{olefin})^+$  species derived from  $\text{C}_5$  and  $\text{C}_6$  alkanes, as well as reactions of  $\text{CoCp}^+$  with isomeric pentenes and hexenes, are dominated by skeletal isomerization followed by dehydrocyclization forming cobaltocenium. Dehydrocyclization of linear  $\text{C}_5$  olefins is more facile than skeletal isomerization of branched  $\text{C}_5$  olefins. Reactions with cyclopropane and cyclobutane proceed by initial insertion across the strain-weakened C-C bonds. For cyclopropane, insertion into a C-C bond results in initial formation of a cobaltacyclobutane species which undergoes dehydrogenation exclusively. With cyclobutane, both dehydrogenation and symmetric ring cleavage occur for the cobaltacyclopentane species.  $\text{CoCp}^+$  reacts with cyclopentane and cyclohexane by attacking C-H bonds exclusively. Finally,  $D^\circ(\text{CoCp}^+-\text{Cp}) = 118 \pm 10$  kcal/mol and  $D^\circ(\text{Co}^+-\text{Cp}) = 85 \pm 10$  kcal/mol are assigned from the observed reactivities.

Atomic transition-metal ions have proven to be highly reactive in the gas phase. This has been demonstrated by several recent investigations on the reactions of gas-phase transition-metal ions with a variety of organic species using ion cyclotron resonance (ICR)<sup>1-4</sup> spectrometry, Fourier transform mass spectrometry (FTMS),<sup>5,6</sup> and ion beam techniques.<sup>7,8</sup> The first-row groups 8-10 transition-metal ions have received the most attention which has resulted in a good understanding of their reactions with a variety of simple hydrocarbons. In general, these atomic metal ions react with aliphatic alkanes by attacking C-C bonds predominantly.<sup>2,4d,6a,7a,b,8</sup>

The reactivity of organometallic fragment ions with hydrocarbons is particularly interesting since the intrinsic effect that

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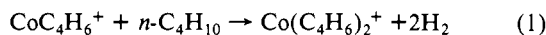
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<sup>†</sup> Current Address: 127-72 Noyes Laboratory, Department of Chemistry, California Institute of Technology, Pasadena, California 91125.

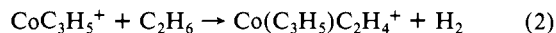
ligands have on metal ion reactivity can be studied. The metal-hydride ions ( $\text{FeH}^+$ ,  $\text{CoH}^+$ ,  $\text{NiH}^+$ ), for example, react with aliphatic alkanes by attacking C-H bonds.<sup>9</sup> The reactivity of  $\text{CoCH}_3^+$  is similar to that of  $\text{CoH}^+$  with aliphatic alkanes, whereas,  $\text{FeCH}_3^+$  is completely unreactive with aliphatic alkanes.<sup>10</sup> The carbene species,  $\text{FeCH}_2^+$  and  $\text{CoCH}_2^+$ , react with aliphatic alkanes by attacking C-H bonds predominantly with some C-C bond cleavages also observed.<sup>11</sup>

$\pi$ -Acid ligands such as olefins are important in organometallic chemistry. In the gas phase  $\text{M}(\text{alkene})^+$  ( $\text{M} = \text{Fe}, \text{Co}, \text{Ni}$ ) species, as well as the related  $\text{MCO}^+$  ions,<sup>12,13</sup> are observed to be unreactive with simple aliphatic alkanes. The conjugated diene-metal ion species ( $\text{M}$ -butadiene<sup>+</sup>,  $\text{M}$ -cyclopentadiene<sup>+</sup>, and  $\text{M}$ -cyclohexadiene<sup>+</sup> ( $\text{M} = \text{Fe}, \text{Co}$ )), however, react with alkanes by attacking C-H bonds resulting in the elimination of predominantly  $2\text{H}_2$ .<sup>6c,12</sup> For example,  $\text{Co}(\text{butadiene})^+$  reacts with *n*-butane by eliminating  $2\text{H}_2$  exclusively, reaction 1, resulting in formation of a bis(butadiene) complex.<sup>12</sup> The corresponding  $\text{Ni}(\text{diene})^+$  species



are unreactive with alkanes.<sup>6c,12</sup> The bis(ethene) $\text{M}^+$  species ( $\text{M} = \text{Fe}, \text{Co}, \text{Ni}$ ) are also unreactive toward alkanes.<sup>12</sup>

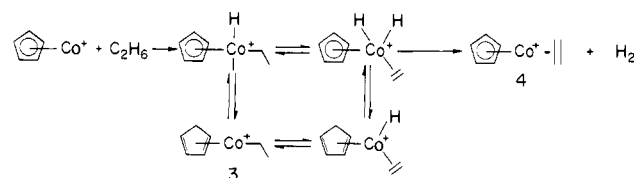
The allylic species,  $\text{M}(\text{C}_3\text{H}_5)^+$ , also react with alkanes by attacking C-H bonds for  $\text{M} = \text{Fe}, \text{Co},$  and  $\text{Ni}$ .<sup>10,12</sup> In fact,  $\text{CoC}_3\text{H}_5^+$  reacts readily with ethane to eliminate  $\text{H}_2$ , reaction 2, forming an allyl-ethene complex.<sup>10</sup> These allyl species appear to react more rapidly with alkanes than the corresponding  $\text{M}(\text{butadiene})^+$  species.



The  $\text{NiCp}^+$  ( $\text{Cp} = \text{cyclopentadienyl}$ ) species has been observed to react with aliphatic alkanes larger than ethane as well as cyclic alkanes by attacking C-H bonds.<sup>14,15</sup> The  $\text{M}(\text{benzene})^+$  species, however, are unreactive with alkanes.<sup>6c,12</sup> Although there are several other metal ion-ligand species to study, the above results indicate that closely related ligands can have dramatically different effects on metal ion reactivity in the gas phase.

To continue these studies we report here an extensive investigation of the reactions of  $\text{CoCp}^+$  with a variety of hydrocarbons

Scheme 1



in the gas phase using Fourier transform mass spectrometry (FTMS). The decomposition pathways of the product ions are probed by collisional activation.<sup>16</sup> The product ions  $\text{CpCoC}_6\text{H}_{10}^+$ ,  $\text{CpCoC}_6\text{H}_8^+$ , and  $\text{CpCoC}_6\text{H}_6^+$  have previously been reported in an ionized mixture of  $\text{CpCo}(\text{CO})_2$  and cyclohexene.<sup>17</sup>

### Experimental Section

The theory, instrumentation, and methodology of ion cyclotron resonance (ICR) spectrometry<sup>18</sup> and Fourier transform mass spectrometry (FTMS)<sup>19</sup> have been discussed elsewhere. All experiments were performed on a Nicolet prototype FTMS-1000 Fourier transform mass spectrometer previously described in detail<sup>20</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 includes a  $1/4$  in. diameter hole in one of the transmitter plates which permits irradiation with various light sources. A high-purity cobalt foil was supported on the opposite transmitter plate.  $\text{Co}^+$  was generated by focusing the beam of a Quanta Ray Nd:YAG laser (frequency doubled to 530 nm) onto the cobalt foil.<sup>4a,c</sup>

Chemicals were obtained commercially in high purity and used as supplied except for multiple freeze-pump-thaw cycles to remove non-condensable gases. Cyclopentadiene was prepared by thermally cracking dicyclopentadiene and distilling off the cyclopentadiene. Sample pressures were on the order of  $1 \times 10^{-7}$  torr. Argon was used as the collision gas for the collision-induced dissociation experiments at a total sample pressure of  $\sim 5 \times 10^{-6}$  torr. A Bayard-Alpert ionization gauge was used to monitor pressure.

Details of the CID experiments have previously been discussed.<sup>6b,20-22</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. ion kinetic energy can be made. These plots are reproducible to  $\pm 5\%$  absolute and yield additional structural and fragmentation information. The spread in 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>23</sup>

The  $\text{CoCp}^+$  ions were generated by reaction of  $\text{Co}^+$  with cyclopentadiene, reaction 3. The cyclopentadiene reagent gas was introduced



into the vacuum chamber through a General Valve Corp. Series 9 pulsed solenoid valve.<sup>24</sup> Both the laser and pulsed valve were triggered concurrently. The cyclopentadiene filled the vacuum chamber to a maximum pressure of  $\sim 10^{-3}$  torr and was pumped away by a high-speed 5-in. diffusion pump in  $\sim 250$  ms. The  $\text{CoCp}^+$  ions were then isolated by swept double resonance ejection pulses<sup>19</sup> and allowed to react with a static pressure of a reagent gas without complicating reactions with cyclopentadiene. The resulting product ion structures were probed by collisional activation.

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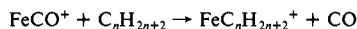
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$\text{FeC}_n\text{H}_{2n+2}^+$  formation, however, was observed in the source of an ion beam instrument at relatively high pressure and may, therefore, have been generated by the reaction of  $\text{Fe}^+$  with the alkane in a termolecular process or by reaction with excited  $\text{FeCO}^+$  formed upon ionization.

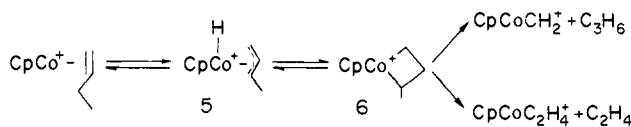
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**Table I.** Distribution of Neutral(s) Lost in the Reactions of CoCp<sup>+</sup> with Hydrocarbons<sup>a</sup>

hydrocarbon	condensa- tion	neutrals lost %											
		H·	H <sub>2</sub>	H <sub>2</sub> + H·	2H <sub>2</sub>	2H <sub>2</sub> + H·	CH <sub>4</sub> + H <sub>2</sub> + H·	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>4</sub> H <sub>6</sub>	C <sub>4</sub> H <sub>8</sub>	C <sub>5</sub> H <sub>8</sub>	(C <sub>5</sub> H <sub>9</sub> )
methane <sup>b</sup>													
ethane			100										
ethene <sup>b</sup>													
propane			100										
propene			100										
butane			86		14								
1-butene			76										
trans-2-butene			75						3	21			
cis-2-butene			77						3	22			
butadiene	100								3	20			
2-methylpropane			100										
2-methylpropene			77										
pentane			36		64				2	21			
1-pentene			76				24						
trans-1,3-pentadiene				100									
2-methylbutane			52		48								
2-methyl-1-butene			76				8					13	
3-methyl-1-butene			72				9		1	2		15	
2-methyl-2-butene			75				8		2	2		13	
2-methyl-1,3-butadiene	27			51					15	5	2		
2,2-dimethylpropane	100												
hexane			24		76								
1-hexene			60				40						
2,2-dimethylbutane			29		71								
2,3-dimethylbutane			37		63								
cyclopropane			100										
cyclobutane			51						49				
cyclopentane					100								
cyclopentene				100									
cyclopentadiene		100											
cyclohexane			70		30								
cyclohexene			9		65							15	11

<sup>a</sup>Reproducible to ±10% absolute. <sup>b</sup>No reaction observed.

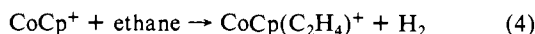
**Scheme II**

Reaction 3 may generate excited CoCp<sup>+</sup> if  $D^0$  (Co<sup>+</sup>-Cp) is greater than the energy required to convert cyclopentadiene to cyclopentadienyl and a hydrogen atom,  $79 \pm 1$  kcal/mol.<sup>25</sup> From this study a value of  $D^0$ (Co<sup>+</sup>-Cp) is assigned  $85 \pm 10$  kcal/mol, vide infra. Addition of a high pressure of argon ( $\sim 5 \times 10^{-6}$  torr) had little or no effect on either the reaction products observed or their distributions (Table I), suggesting that CoCp<sup>+</sup> was generated with little if any excess energy.

**Results and Discussion**

The reactions of CoCp<sup>+</sup> with a series of hydrocarbons are summarized in Table I. Reactions with alkanes are dominated by dehydrogenation as was observed previously for NiCp<sup>+</sup>.<sup>14,15</sup> CID of products derived from C<sub>5</sub> and C<sub>6</sub> alkanes, as well as reactions of CoCp<sup>+</sup> with C<sub>5</sub> and C<sub>6</sub> aliphatic olefins, however, yield a considerable amount of skeletal isomerization followed by dehydrocyclization generating CoCp<sub>2</sub><sup>+</sup>.

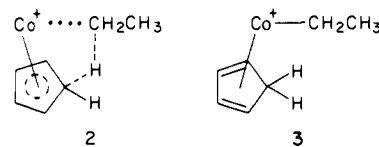
**C<sub>1</sub>-C<sub>3</sub> Aliphatic Hydrocarbons.** Methane is unreactive with CoCp<sup>+</sup>; however, ethane is readily dehydrogenated (reaction 4). Collisional activation of the product of reaction 4 yields facile



elimination of C<sub>2</sub>H<sub>4</sub> forming CoCp<sup>+</sup>. In addition, ethene is unreactive with CoCp<sup>+</sup>. These results suggest formation of an (ethene)(cyclopentadienyl) complex in reaction 4 and implies  $D^0$ (CpCo<sup>+</sup>-C<sub>2</sub>H<sub>4</sub>) > 33 kcal/mol.<sup>25</sup> This compares with  $D^0$ -

(Co<sup>+</sup>-C<sub>2</sub>H<sub>4</sub>)  $\sim 35$ -40 kcal/mol.<sup>7d</sup>

A crude mechanism for reaction 4 is outlined in Scheme I and involves initial addition across a C-H bond. This C-H insertion may only involve the metal (oxidative addition) forming 1 or may involve both the cyclopentadienyl ligand and the metal through intermediate 2 resulting in formation of 3. Corderman and



Beauchamp proposed that the reactions of NiCp<sup>+</sup> with alkanes may proceed by initial hydride abstraction.<sup>15</sup> The actual mechanism of C-H bond insertion may consist of a combination of these processes. The way in which metals break C-H and C-C bonds in hydrocarbons is a topic of current interest.<sup>26-30</sup> Finally, species

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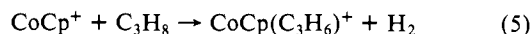
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(30) (a) Hoyano, J. K.; Graham, W. A. *J. Am. Chem. Soc.* **1982**, 104, 3723. (b) Jones, W. D.; Feher, F. J. *Organometallics* **1983**, 2, 562. (c) Watson, P. L. *J. Am. Chem. Soc.* **1983**, 105, 6491.

(25) Auxiliary thermochemical information taken from the following: Rosenstock, H. M.; Draxl, D.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem., Ref. Data. Suppl. 1* **1977**, 6. Heats of formation of organic radicals taken from the following: McMillen, D. G.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, 33, 493.

1 and 3 may be in dynamic equilibrium.<sup>31</sup>  $\beta$ -Hydride abstraction followed by reductive elimination of hydrogen generates (cyclopentadienyl)Co(ethene)<sup>+</sup> (4).

Propane reacts with CoCp<sup>+</sup> similarly to ethane (reaction 5).



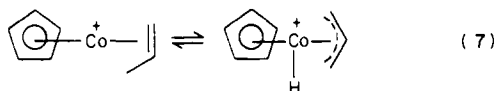
Collisional activation of this species yields facile elimination of C<sub>3</sub>H<sub>6</sub> forming CoCp<sup>+</sup>, suggesting formation of a (propene)(cyclopentadienyl) species. Interestingly, propene reacts slowly ( $k \sim 10^{-11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) with CoCp<sup>+</sup> to eliminate H<sub>2</sub> (reaction 6). This reaction is followed by rapid displacement of C<sub>3</sub>H<sub>4</sub> by propene



to generate CoCp(C<sub>3</sub>H<sub>6</sub>)<sup>+</sup>. Both CoCp(C<sub>3</sub>H<sub>4</sub>)<sup>+</sup> and the displacement product, CoCp(C<sub>3</sub>H<sub>6</sub>)<sup>+</sup>, yield CoCp<sup>+</sup> readily upon collisional activation by elimination of C<sub>3</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub>, respectively.

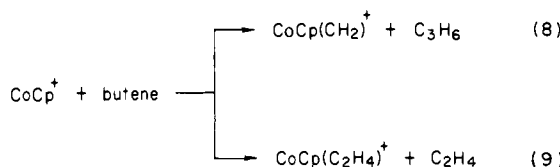
CoCpC<sub>3</sub>H<sub>4</sub><sup>+</sup>, generated in reaction 6, may consist of either propyne or allene bound to the CoCp<sup>+</sup> moiety. Reaction 6 implies  $D^\circ(\text{CpCo}^+-\text{propyne}) > 40 \text{ kcal/mol}$  and  $D^\circ(\text{CpCo}^+-\text{allene}) > 41 \text{ kcal/mol}$ .<sup>25</sup> Absence of CoCp(ethyne)<sup>+</sup> formation from ethene vide supra, however, is evidence against formation of CoCp(propyne)<sup>+</sup> in reaction 6<sup>32</sup> and suggests that CoCp(allene)<sup>+</sup> is actually formed. The rapid displacement of C<sub>3</sub>H<sub>4</sub> by propene implies  $D^\circ(\text{CoCp}^+-\text{propene}) > 41 \text{ kcal/mol}$ .

The activation afforded by ethene coordination to Co(propene)<sup>+</sup> has been shown to effect  $\beta$ -hydride shifts generating hydrido- $\pi$ -allyl metal ion complexes in the gas phase.<sup>33</sup> Furthermore, oxidative addition across allylic C-H bonds is well supported in solution-phase studies.<sup>34</sup> The activation afforded by propene coordination may, therefore, induce the equilibrium in reaction 7.



If this equilibrium is rapid, as it appears it may be,<sup>31</sup> then the rate-limiting step is abstraction of the central hydrogen of the allyl resulting in dehydrogenation. Direct formation of CoCp(propyne)<sup>+</sup> in reaction 6, however, cannot be ruled out. Furthermore, it is possible that CoCp<sup>+</sup> may effect isomerization of allene to propyne.<sup>35</sup> Finally, the absence of dehydrogenation of CoCp(propene)<sup>+</sup> upon collisional activation is simply due to the frequency factor for dehydrogenation being much lower than that for direct cleavage of propene.

**C<sub>4</sub> Aliphatic Hydrocarbons.** Butane and 2-methylpropane undergo dehydrogenation exclusively with CoCp<sup>+</sup>. Although dehydrogenation dominates for the butene isomers, significant amounts of C-C bond cleavage products are also observed (reactions 8 and 9). Butadiene yields only condensation with CoCp<sup>+</sup>



to generate CoCp(C<sub>4</sub>H<sub>6</sub>)<sup>+</sup>. In addition, collisional activation of

(31) Co(cyclopentadiene)<sup>+</sup> appears to be in rapid equilibrium with the corresponding (hydrido)(cyclopentadienyl)Co<sup>+</sup> species. See, for example, ref 6c and 33.

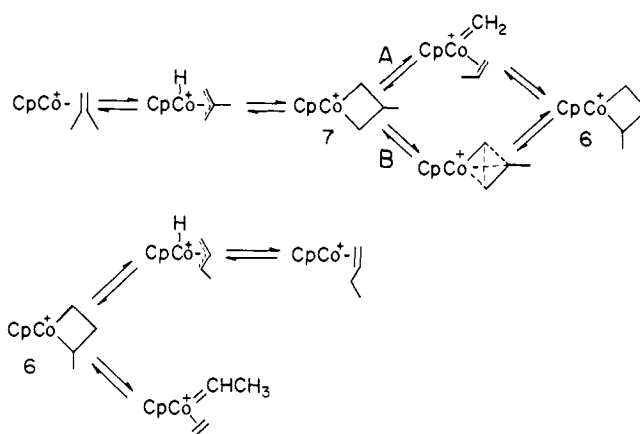
(32) Formation of CoCp(ethyne)<sup>+</sup> from CoCp<sup>+</sup> and ethene only requires  $D^\circ(\text{CoCp}^+-\text{ethyne}) > 41.5 \text{ kcal/mol}$ .<sup>25</sup>

(33) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 72.

(34) (a) Tulip, T. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4201. (b) Scherman, E. O.; Schreiner, P. R. *J. Chem. Soc., Chem. Commun.* **1978**, 223. (c) Ephritikhin, M.; Green, M. L. H.; Mackenzie, R. E. *J. Chem. Soc., Chem. Commun.* **1976**, 619. (d) Bonneman, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 736. (e) Byrne, J. W.; Blasser, H. U.; Osborn, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 3817.

(35) The photochemical isomerization of allene to cyclopropene and propyne has been observed. See, for example: (a) Chapman, O. L. *Pure Appl. Chem.* **1975**, 511. (b) Steinmetz, M. G.; Mayers, R. T.; Yang, J.-C. *J. Am. Chem. Soc.* **1982**, *104*, 3518.

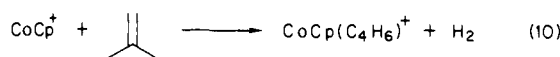
Scheme III



CoCp(C<sub>4</sub>H<sub>6</sub>)<sup>+</sup> generated from reactions with butane, butene isomers, or butadiene with CoCp<sup>+</sup> yields elimination of C<sub>4</sub>H<sub>6</sub> as the only fragmentation at low kinetic energy with some Co<sup>+</sup> observed at high energy.

The above results clearly indicate that the C-C bond cleavage reactions 8 and 9 occur prior to dehydrogenation. These C-C bond cleavages may proceed through metallacyclobutane intermediates as shown in Scheme II for 1-butene. Initial butene coordination is followed by formation of the hydrido- $\pi$ -allyl complex (5).<sup>36</sup> Conversion of 5 to 6 has been proposed as an initiation step in olefin metathesis.<sup>37</sup> The reverse process (conversion of metallacyclobutanes to metal-olefin species through hydrido- $\pi$ -allyl intermediates) is supported by numerous solution-phase studies.<sup>37-39</sup> The metallacyclobutane, 6, can decompose by eliminating either C<sub>3</sub>H<sub>6</sub> or C<sub>2</sub>H<sub>4</sub> (olefin metathesis)<sup>40-42</sup> with C<sub>3</sub>H<sub>6</sub> loss dominating over C<sub>2</sub>H<sub>4</sub> loss. A similar mechanism has been proposed for elimination of C<sub>3</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub> for reactions of Fe(butadiene)<sup>+</sup> with linear butenes in the gas phase.<sup>6b</sup> Conversion of isobutene to CH<sub>2</sub> and propene requires  $D^\circ(\text{CpCo}^+-\text{CH}_2) > 101 \text{ kcal/mol}$ .<sup>25</sup> Since  $D^\circ(\text{Co}^+-\text{CH}_2) = 85 \pm 7 \text{ kcal/mol}$ ,<sup>43</sup> addition of a cyclopentadienyl ligand must enhance the Co<sup>+</sup>-CH<sub>2</sub> bond strength. Finally, formation of CpCo(butadiene)<sup>+</sup> from CoCp<sup>+</sup> and butane implies  $D^\circ(\text{CpCo}^+-\text{butadiene}) > 57 \text{ kcal/mol}$ .<sup>25</sup> For comparison,  $D^\circ(\text{Co}^+-\text{butadiene})$  has previously been found to be less than  $52 \pm 4 \text{ kcal/mol}$ .<sup>44</sup>

Dehydrogenation of 2-methylpropene by CoCp<sup>+</sup>, reaction 10, may proceed directly, generating a trimethylene methane complex.



Alternatively, CoCp<sup>+</sup> may effect isomerization of 2-methylpropene to a linear C<sub>4</sub> unit prior to dehydrogenation. CoCpC<sub>4</sub>H<sub>6</sub><sup>+</sup> formed both in reaction 10 and from linear butenes yields similar CID spectra with elimination of C<sub>4</sub>H<sub>6</sub> occurring exclusively at low collision energy with no fragmentation of the C<sub>4</sub>H<sub>6</sub> unit. This observation by itself, however, does not distinguish a CoCp(tri-

(36) It seems reasonable to speculate that dehydrogenation from the 1-methallyl species in Scheme II probably occurs primarily via the anti isomer rather than the syn (shown) isomer. The interconversion of these two isomers, however, can occur through allyl-butene interconversion by reversible hydride shifts.

(37) (a) Reference 34c. (b) Adams, G. J. A.; Davies, S. G.; Ford, K. A.; Ephritikhine, M.; Todd, P. E.; Green, M. L. H. *J. Mol. Catal.* **1980**, *15*. (c) Curtis, M. D.; Fotinor, N. A. *J. Organomet. Chem.* **1984**, *272*, 43.

(38) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.

(39) (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.

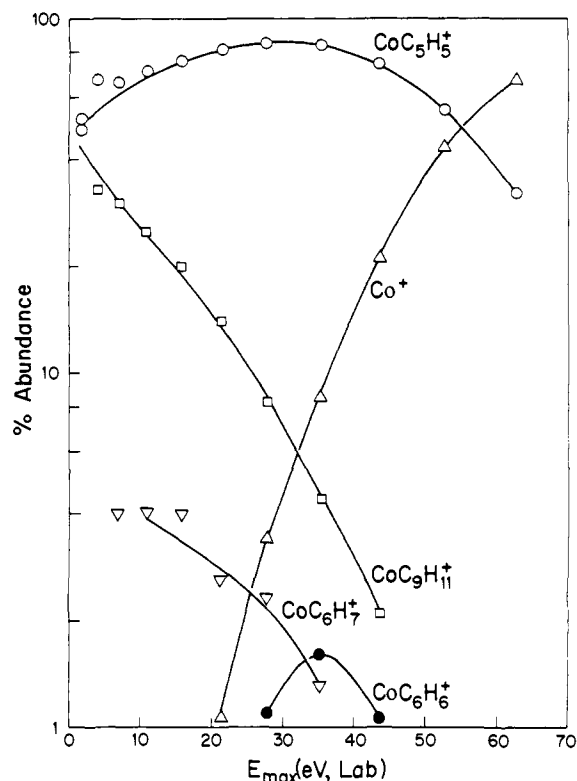
(40) Herrison, J. L.; Chauvin, Y. *Makromol. Chem.* **1970**, *141*, 161.

(41) For recent reviews on olefin metathesis see: (a) Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449. (b) Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1. (c) Katz, T. J. *Adv. Organomet. Chem.* **1977**, *16*, 283. (d) Grubbs, R. H. "Comprehensive Organometallic Chemistry"; Wilkinson, G., Ed.; Pergamon Press: Oxford, England, **1982**; Vol. 8, p 5.

(42) (a) Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 6449. (b) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 2605.

(43) Armentrout, P. B.; Beauchamp, J. L. *J. Chem. Phys.* **1981**, *74*, 2819.

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

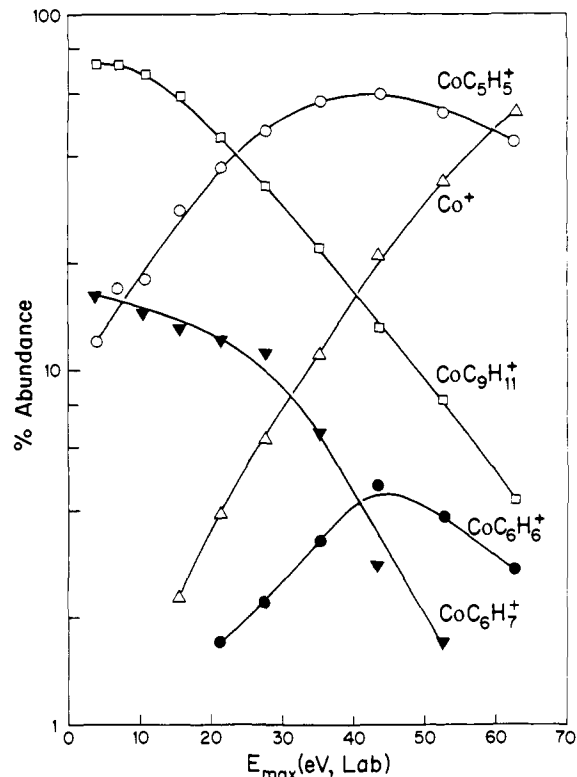


**Figure 1.** Variation of CID product ion abundances as a function of kinetic energy for  $\text{CpCoC}_4\text{H}_8^+$  formed from  $\text{CpCo}^+$  and 2-methylpropene.

methylenemethane)<sup>+</sup> species from a  $\text{CoCp}(\text{butadiene})^+$  complex. Atomic cobalt cations have been observed to predominantly dehydrogenate 2-methylpropene<sup>7c</sup> (reaction 11). Structural studies



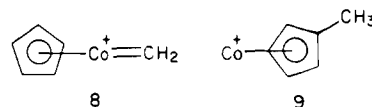
on  $\text{CoC}_4\text{H}_6^+$  formed in reaction 11 indicate that it consists of butadiene bound to  $\text{Co}^+$  rather than trimethylenemethane and, therefore, that considerable rearrangement has occurred in the carbon framework.<sup>45</sup> A mechanism for the skeletal rearrangement of 2-methylpropene by  $\text{CoCp}^+$  is outlined in Scheme III.<sup>46</sup> A similar mechanism has previously been proposed for the isomerization of 2-methylpropene to linear butene on metal surfaces.<sup>47</sup> This mechanism involves initial formation of the metallacyclobutane species 7 by hydride shifts in analogy to that in Scheme II. Isomerization of 7 to 6 may occur by either route A or B. Route A finds analogy with the mechanism of olefin metathesis<sup>40,41</sup> and has previously been proposed for reactions of  $\text{CoCH}_2^+$  with olefins in the gas phase.<sup>42b</sup> Isomerization by path B finds analogy with platinacyclobutane systems.<sup>48-51</sup> If the isomerization in Scheme III was not occurring for  $\text{CoCp}^+$ , then no elimination of  $\text{C}_2\text{H}_4$  should be observed. Since nearly identical product dis-



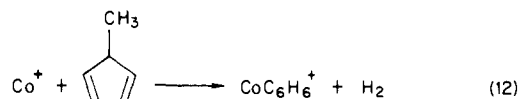
**Figure 2.** Variation of CID product ion abundances as a function of kinetic energy for  $\text{CpCoC}_4\text{H}_8^+$  formed from  $\text{CpCo}^+$  and *n*-butane.

tributions are observed for reactions of  $\text{CoCp}^+$  with all four butene isomers, however, it is likely that the isomerization in Scheme III is indeed occurring.

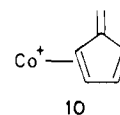
$\text{CoCpCH}_2^+$  formed in reaction 8 does *not* undergo H/D exchange with deuterium.  $\text{Co-c-C}_6\text{H}_7^+$ , however, undergoes one rapid exchange with deuterium.<sup>44</sup> Collisional activation of  $\text{CoCpCH}_2^+$  yields facile elimination of H<sup>•</sup> forming  $\text{CoC}_6\text{H}_6^+$  with some  $\text{Co}^+$  observed at high energy in analogy to that for  $\text{Co-c-C}_6\text{H}_7^+$ .<sup>44</sup> Thus, the  $\text{CoC}_6\text{H}_7^+$  ions formed in reaction 8 consist of either a  $\text{Co}(\text{Cp})(\text{CH}_2)^+$  structure, 8, or a  $\text{Co}(\text{methylcyclopentadienyl})^+$  structure, 9. Ring expansion by methylene insertion



into both cyclic alkanes<sup>52</sup> and cyclic alkenes<sup>53</sup> occurs for reactions with  $\text{CoCH}_2^+$  in the gas phase. It is possible, therefore, for ring expansion to occur by methylene insertion into the cyclopentadienyl group of 8 upon collisional activation forming  $\text{Co-c-C}_6\text{H}_7^+$ , which can subsequently eliminate a hydrogen atom to form  $\text{Co}(\text{benzene})^+$ . Since  $\text{Co}^+$  reacts with methylcyclopentadiene by dehydrogenation, reaction 12, it is also possible that 9 can eliminate



a hydrogen atom to form  $\text{Co}(\text{fulvene})^+$  (10).



The distribution of CID fragment ion abundances as a function of collision energy for  $\text{CpCo}(\text{C}_4\text{H}_8)^+$  formed from 2-methyl-

(45) Hettich, R. L.; Jacobson, D. B.; Freiser, B. S., unpublished results.

(46) This mechanism was first proposed by Armentrout et al. (ref 7c) as a possible scheme for the dehydrogenation of 2-methylpropene by  $\text{Co}^+$ .

(47) (a) Peter, A.; Clarke, J. K. A. *J. Chem. Soc., Faraday Trans. 1* **1976**, 72, 1201. (b) Garin, F.; Gault, F. G. *J. Am. Chem. Soc.* **1975**, 97, 4466. (c) Amir-Ebrahimi, V.; Gault, F. G. *J. Chem. Soc., Faraday Trans. 1* **1980**, 76, 1735. (d) Amir-Ebrahimi, V.; Choplin, A.; Parayre, P.; Gault, F. G. *Nouv. J. Chim.* **1980**, 4, 431. (e) O'Donohoe, C.; Clark, J. K. A.; Rooney, J. J. *J. Chem. Soc., Faraday Trans 1* **1980**, 76, 345.

(48) (a) Puddephatt, R. J.; Quyser, M. A.; Tipper, C. F. H. *J. Chem. Soc., Chem. Commun.* **1976**, 626. (b) Perkins, D. C. L.; Puddephatt, R. J.; Tipper, C. F. H. *J. Organomet. Chem.* **1978**, 154, C16. (c) Al Essa, R. J.; Puddephatt, R. J.; Tipper, C. F. H.; Thompson, P. J. *J. Organomet. Chem.* **1978**, 157, C40. (d) Al Essa, R. J.; Puddephatt, R. J.; Quyser, M. A.; Tipper, C. F. H. *J. Am. Chem. Soc.* **1979**, 101, 364.

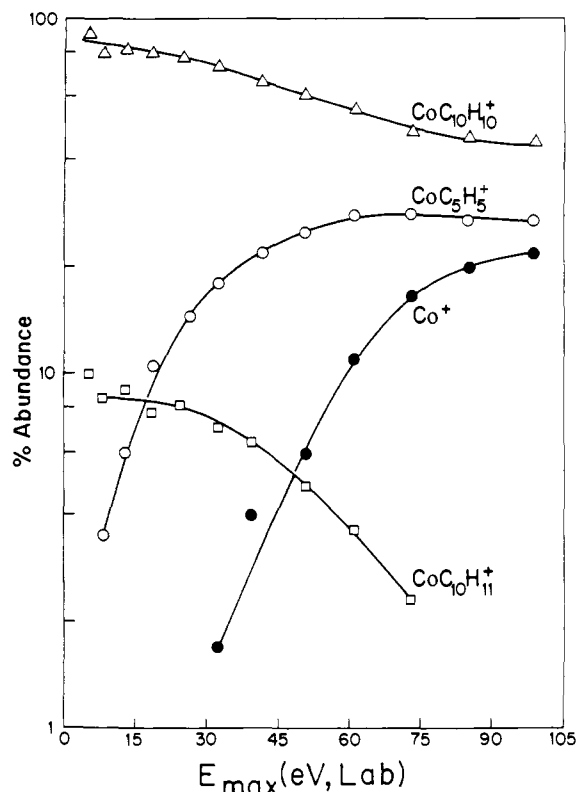
(49) Johnson, T. H. *J. Org. Chem.* **1979**, 44, 1356.

(50) Casey, C. P.; Scheck, D. M.; Shusterman, A. J. *J. Am. Chem. Soc.* **1979**, 101, 4233.

(51) Puddephatt, R. J. "Inorganic Chemistry: Toward the 21st Century"; American Chemical Society: Washington, D.C., 1983; ACS Symposium Series 211, Chapter 24.

(52) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, 107, 67.

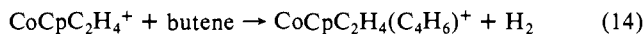
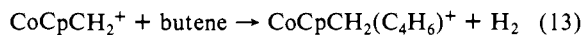
(53) Jacobson, D. B.; Freiser, B. S., unpublished results.



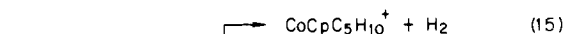
**Figure 3.** Variation of CID product ion abundances as a function of kinetic energy for  $\text{CpCoC}_5\text{H}_8^+$  formed in reaction 16.

propane and *n*-butane is shown in Figures 1 and 2, respectively. Although Figures 1 and 2 agree qualitatively, they differ quantitatively. The dehydrogenation in Figure 2 occurs with a higher efficiency than that in Figure 1. In addition, direct cleavage of  $\text{C}_4\text{H}_8$  is much more dominant in Figure 1 than in Figure 2. These results suggest that the rate-determining step for reaction of  $\text{CoCp}^+$  with 2-methylpropene is skeletal isomerization as shown in Scheme III. For comparison, CID of  $\text{Co}(2\text{-methylpropene})^+$  in our FTMS yields only elimination of  $\text{C}_4\text{H}_8$  with no dehydrogenation.<sup>6a</sup> This underscores the effect a cyclopentadienyl ligand has in promoting the skeletal isomerization of 2-methylpropene by  $\text{Co}^+$  in the gas phase. This may in part be due to the lifetime of the activated ion being increased by the presence of a Cp group.

Both  $\text{CoCpCH}_2^+$  and  $\text{CoCpC}_2\text{H}_4^+$  generated in reactions 8 and 9, respectively, undergo rapid secondary reactions with all four butene isomers resulting predominantly in dehydrogenation (reactions 13 and 14).

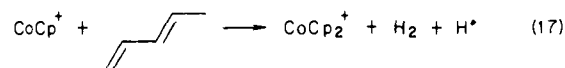


**$\text{C}_5$  Aliphatic Hydrocarbons.** Pentane yields exclusively dehydrogenation products with  $\text{CoCp}^+$  (reactions 15 and 16). Collisional activation of either product yields facile dehydrogenations



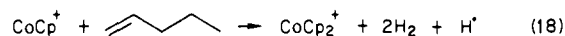
resulting in formation of  $\text{CoC}_{10}\text{H}_{10}^+$  with no C–C bond cleavages observed (Figure 3). Subsequent decomposition of the above  $\text{CoC}_{10}\text{H}_{10}^+$  species yields elimination of  $\text{C}_5\text{H}_5$  and  $\text{C}_{10}\text{H}_{10}$  in low efficiency. These results suggest that dehydrocyclizations forming cobaltocenium<sup>54</sup> occur readily for  $\text{CoCp}(\text{linear pentene})^+$  species.<sup>55,56</sup>  $\text{CoCp}^+$  reacts similarly with 1-pentene and *trans*-1,3-

pentadiene to yield exclusively dehydrogenations forming  $\text{CoCpC}_5\text{H}_8^+$  and  $\text{CoCp}_2^+$ , respectively. Again,  $\text{CoCpC}_5\text{H}_8^+$  yields facile formation of  $\text{CoCp}_2^+$  upon collisional activation. The fact that  $\text{CoCp}^+$  yields exclusively  $\text{CoCp}_2^+$  with *trans*-1,3-pentadiene, reaction 17, indicates that 1-pentene can be dehydrogenated to

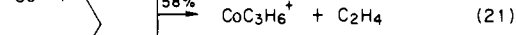
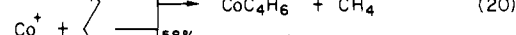
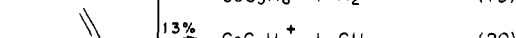
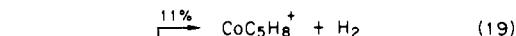


1,3-pentadiene followed by dehydrocyclization. The absence of formation of  $\text{CoCp}(\text{C}_5\text{H}_6)^+$  with *trans*-1,3-pentadiene and 1-pentene is consistent with facile elimination of H $\cdot$  forming  $\text{CoCp}_2^+$ .<sup>44</sup>

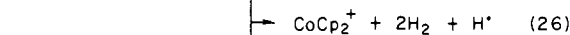
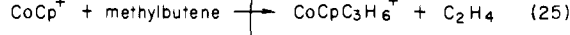
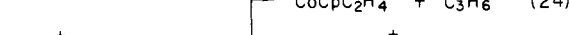
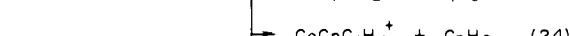
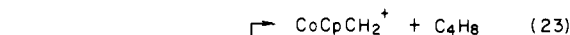
Observation of reaction 18 implies  $D^\circ(\text{CpCo}^+-\text{Cp}) > 115$  kcal/mol.<sup>25</sup> This compares with  $D^\circ(\text{Co}^+-\text{Cp}) > 84 \pm 4$  kcal/mol.<sup>44</sup>



Atomic cobalt cations react with 1-pentene predominantly by yielding C–C bond cleavage products<sup>7c</sup> (reactions 19–22). These reactions are dominated by insertion across the weak allylic C–C bond yielding  $\text{CoC}_3\text{H}_6^+$  and  $\text{CoC}_2\text{H}_4^+$ . This result again demonstrates the effect a cyclopentadienyl ligand has on  $\text{Co}^+$  reactivity.

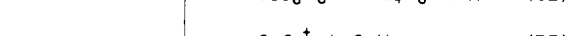
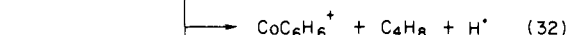
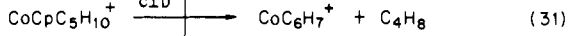
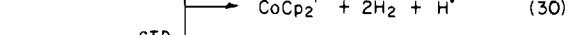
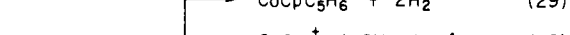
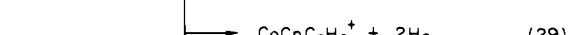
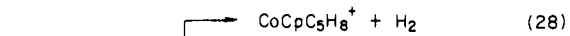


$\text{CoCp}^+$  yields dehydrogenations exclusively with 2-methylbutane. In contrast to 1-pentene, the three methylbutene isomers yield significant amounts of C–C bond cleavages (reactions 23–25),



although dehydrogenations (reactions 26 and 27) dominate. The C–C bond cleavages are reminiscent of the reactions of  $\text{CoCp}^+$  with the butene isomers and may proceed by processes similar to those presented in Scheme II for 1-butene.

Collisional activation of  $\text{CoCpC}_5\text{H}_{10}^+$ , formed from 2-methylbutane, yields the following losses:



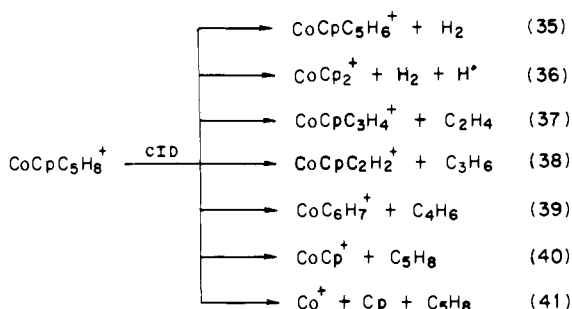
(55) Dehydrocyclization forming  $\text{CoCp}^+$  has previously been observed in the gas phase for CID of  $\text{CoC}_5\text{H}_9^+$  formed from  $\text{CoCH}_3^+$  and *n*-pentane. See ref 10.

(56) Dehydrocyclizations on metal surfaces are commonly observed. See, for example: (a) Anderson, J. R. *Adv. Catal.* **1973**, *23*, 1. (b) reference 45. (c) Csicsery, S. M. *Adv. Catal.* **1979**, *28*, 293. (d) Zoltan, P. *Adv. Catal.* **1980**, *29*, 272. (e) Bragin, O. V.; Krasavin, S. A. *Russ. Chem. Rev.* **1983**, *52*, 625.

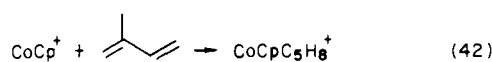
(57) (a) Clark, D. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6774. (b) Pederson, S. F.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 7483. (c) Edwards, D. S.; Biondi, L. V.; Ziller, J. W.; Churchill, M. R.; Schrock, R. R. *Organometallics* **1983**, *2*, 1505.

(58) (a) Foley, P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 2732. (b) Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713. (c) Tulip, T. H.; Thorn, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 2448.

Processes 28–30 dominate at low to moderate kinetic energy with process 33 dominating at high energy. Formation of  $\text{CoCp}_2^+$ , reaction 30, does not occur with nearly the facility of that for CID of  $\text{CoCpC}_5\text{H}_{10}^+$  formed from *n*-pentane. CID of  $\text{CoCpC}_5\text{H}_8^+$  formed from the methylbutene isomers and 2-methylbutane yields



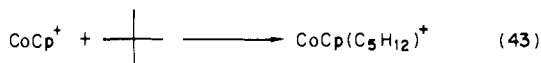
processes 35–41. Processes 36 and 40 dominate at low energy with process 40 dominating at high energy. Again, formation of  $\text{CoCp}_2^+$  does not occur with the facility of that for CID of  $\text{CoCp}(\text{linear pentene})^+$ . Finally, reaction of  $\text{CoCp}^+$  with 2-methylbutadiene yields predominantly  $\text{CoCp}_2^+$ ; however, significant amounts of  $\text{CoCpC}_5\text{H}_8^+$  (condensation) are also observed (reaction 42). CID of this  $\text{CoCpC}_5\text{H}_8^+$  is identical with that for



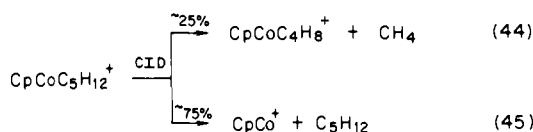
$\text{CoCpC}_5\text{H}_8^+$  formed from the methylbutene isomers. Observation of the condensation reaction 42 underscores the fact that skeletal isomerization is not as facile for 2-methylbutadiene as dehydrocyclization is for *n*-pentadienes. CID of  $\text{CoCp}_2^+$  formed in reactions 26, 30, and 36 yields elimination of  $\text{C}_5\text{H}_5$  and  $\text{C}_{10}\text{H}_{10}$  in low efficiency suggesting formation of cobaltocenium.<sup>59</sup>

It is interesting that CID of  $\text{CoC}_{10}\text{H}_{13}^+$  formed in reaction 13 yields *no*  $\text{CoC}_{10}\text{H}_{10}^+$  and indicates that not all  $\text{CoC}_{10}\text{H}_n^+$  ( $n > 11$ ) isomers can rearrange upon collisional activation to form cobaltocenium.

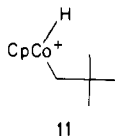
$\text{CpCo}^+$  yields only slow condensation with 2,2-dimethylpropane (reaction 43). Collisional activation of this product yields elim-



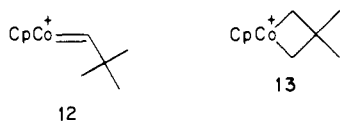
ination of  $\text{CH}_4$  and  $\text{C}_5\text{H}_{12}$  (reactions 44 and 45) at low ( $\sim 1$  eV) kinetic energy with only  $\text{C}_5\text{H}_{12}$  elimination occurring above 30 eV kinetic energy. This indicates that  $\text{CpCo}^+$  can insert across



the terminal C–H bond of 2,2-dimethylpropane to form **11**. Absence of dehydrogenation suggests that  $\alpha$ -hydride and  $\gamma$ -hydride



abstractions forming **12** and **13**, respectively, do not occur. Both  $\alpha$ -C–H bond insertions<sup>57</sup> and  $\gamma$ -C–H bond insertions<sup>58</sup> have been observed for neopentyl complexes.



(59)  $\beta$ -Methyl transfers have been observed in solution-phase organometallic chemistry. Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471.

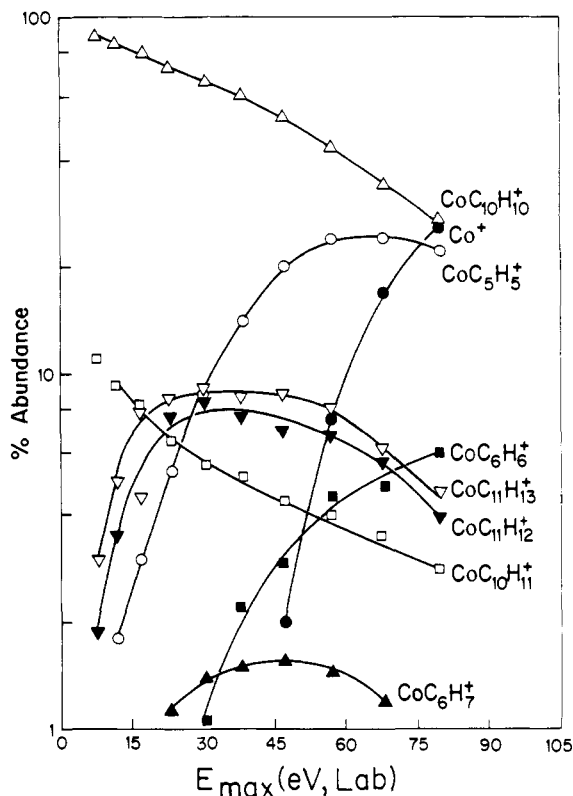
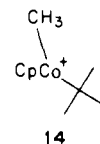


Figure 4. Variation of CID product ion abundances as a function of kinetic energy for  $\text{CpCoC}_6\text{H}_{10}^+$  formed in reaction 46.

The elimination of  $\text{CH}_4$ , process 44, suggests that  $\beta$ -methyl migration can occur;<sup>59</sup> however, it is not nearly as facile as  $\beta$ -hydride abstraction. In addition, formation of **11** implies that  $D^\circ(\text{CpCo}^+-\text{H}) + D^\circ(\text{Cp}(\text{H})\text{Co}^+-\text{CH}_2\text{C}(\text{CH}_3)_3) > 100$  kcal/mol.<sup>25</sup>

It is possible that reaction 44 actually proceeds by insertion across a C–C bond. However, C–C bond insertion forming **14** could result in either  $\text{C}_4\text{H}_{10}$  elimination or  $\text{CH}_4$  elimination by



alkyl migration onto the cyclopentadienyl ring<sup>60</sup> followed by an exo hydrogen [1,5] sigmatropic shift.<sup>61</sup> Furthermore, since  $\text{CH}_4$  loss is not observed for reaction 43,  $D^\circ(\text{CpCo}^+-\text{CH}_3) + D^\circ(\text{Cp}(\text{CH}_3)\text{Co}^+-\text{C}(\text{CH}_3)_3) < D^\circ(\text{CH}_3-\text{C}(\text{CH}_3)_3) = 84.1 \pm 1$  kcal/mol<sup>25</sup> is implied. For comparison,  $D^\circ(\text{Co}^+-2(\text{CH}_3))$  appears to exceed 96 kcal/mol.<sup>62</sup>

**Reactions with  $\text{C}_6$  Hydrocarbons.** As with the above alkanes,  $\text{CoCp}^+$  reacts with the hexane isomers to yield exclusively dehydrogenations. Figure 4 shows a plot of CID fragment ion abundances vs. kinetic energy for  $\text{CpCoC}_6\text{H}_{10}^+$  generated in reaction 46. The dominant loss is  $\text{CH}_4 + \text{H}^*$  forming  $\text{CoC}_{10}\text{H}_{10}^+$



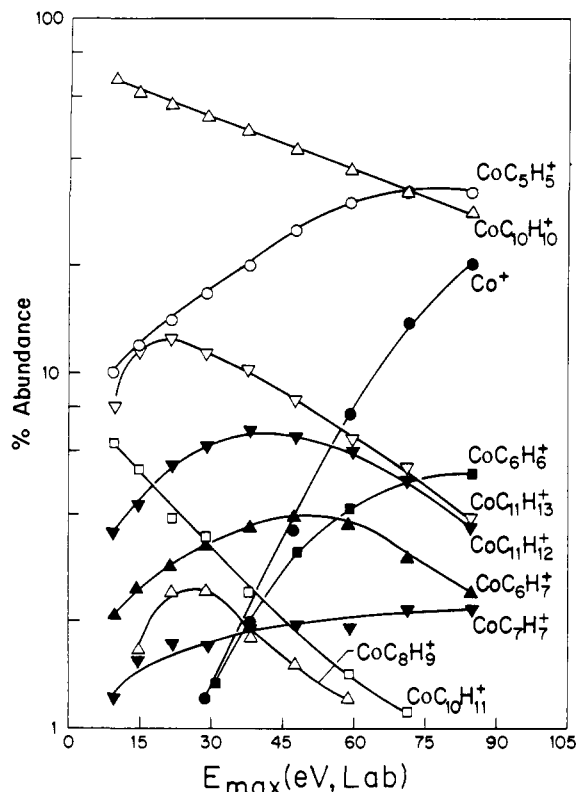
which, subsequently, yields a CID spectrum characteristic of cobaltocenium.<sup>54</sup> There is also a small amount of  $\text{CoC}_{11}\text{H}_{13}^+$  ( $\text{H}_2$

(60) Methylation incorporation into the cyclopentadienyl ring of  $\text{FeCp}^+$ ,  $\text{CoCp}^+$ , and  $\text{NiCp}^+$ , generating substituted cyclopentadienyl-metal ion complexes, has been observed previously in the gas phase. See, for example: (a) Corderman, R. R.; Beauchamp, J. L. *Inorg. Chem.* **1978**, *17*, 68. (b) Jones, R. W.; Staley, R. H. *Int. J. Mass Spectrom Ion Phys.* **1981**, *39*, 35.

(61) Spangler, C. W. *Chem. Rev.* **1976**, *76*, 187.

(62) This is based on the observation that  $\text{Co}^+$  decarbonylates acetone in the gas phase, presumably forming  $\text{Co}(\text{CH}_3)_2^+$ : Halle, L. F.; Crowe, W. E.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1984**, *3*, 1694.

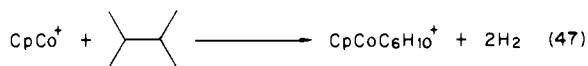
(63) (a) Barron, Y.; Maire, G.; Muller, J. M.; Gault, F. G. *J. Catal.* **1966**, *5*, 428. (b) Barron, Y.; Cornet, D.; Maire, M.; Gault, F. G. *J. Catal.* **1963**, *2*, 152. (c) Paul, Z.; Tetenyi, P. *Acta Chim. Acad. Sci. Hung.* **1972**, *72*, 227.



**Figure 5.** Variation of CID product ion abundances as a function of kinetic energy for  $\text{CpCoC}_6\text{H}_{10}^+$  formed in reaction 47.

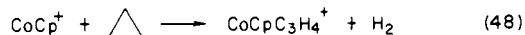
elimination) and  $\text{CoC}_{11}\text{H}_{12}^+ + \text{H}_2 + \text{H}\cdot$  elimination with *no*  $\text{CoC}_{11}\text{H}_{11}^+$  formation. These results suggest that dehydrocyclization of a linear  $\text{C}_6$  chain by  $\text{CoCp}^+$  producing a cyclopentadienyl species is more favorable than benzene formation. Formation of  $\text{CoC}_{11}\text{H}_{12}^+$  is surprising since  $\text{CoC}_{11}\text{H}_{11}^+$  (a (cyclopentadienyl)(benzene) $\text{Co}^+$ ) is expected if dehydrocyclization forming benzene occurs, *vide infra*. Dehydrocyclization of linear  $\text{C}_6$  and  $\text{C}_7$  alkanes to methylcyclopentanes has been observed on metal surfaces.<sup>63</sup>

The variation of CID product ion abundances as a function of kinetic energy for  $\text{CoCpC}_6\text{H}_{10}^+$  formed in reaction 47 is shown in Figure 5. The CID efficiency for  $\text{CoCp}_2^+$  formation is not quite as high as that for  $\text{CpCoC}_6\text{H}_{10}^+$  formed in reaction 46.



However, the formation of  $\text{CoC}_{10}\text{H}_{10}^+$  dominates and it appears to consist of cobaltocenium. In addition, however, two new ions are observed,  $\text{CoC}_7\text{H}_7^+$  and  $\text{CoC}_8\text{H}_9^+$ .

**Reactions with Cyclic Hydrocarbons.**  $\text{CoCp}^+$  reacts slowly with cyclopropane resulting in dehydrogenation reaction 48. Since cyclopropane has the strongest C–H bonds (106.3 kcal/mol)<sup>64</sup>



of all of the alkanes and weak C–C bonds (due to ring strain),<sup>65</sup> the C–C bonds are susceptible to attack. Insertion across the C–C bond results in formation of **15**, a chemically activated metallacyclobutane species. Simple olefin metathesis<sup>40–42</sup> would result

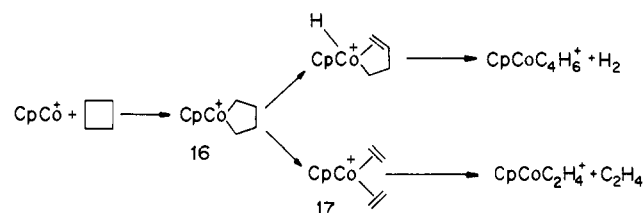


15

(64) Baghal-Vayjooee, M. H.; Benson, S. W. *J. Am. Chem. Soc.* **1979**, *101*, 6471.

(65) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976; p 273. Strain energies are (kcal/mol) the following:  $\text{C}_3\text{H}_6$ , 27.6;  $\text{C}_4\text{H}_8$ , 26.2;  $\text{C}_5\text{H}_{10}$ , 6.3;  $\text{C}_6\text{H}_{12}$ , 0.2.

#### Scheme IV

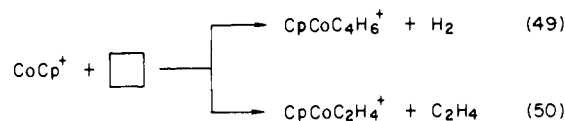


in  $\text{CpCoCH}_2^+$  formation ( $\text{C}_2\text{H}_4$  elimination); however, this is not observed even though it is thermally more favorable than  $\text{CH}_2$  abstraction from the butene isomers, *vide supra*.<sup>25</sup>

Apparently, intermediate **15** undergoes conversion to  $\text{CpCo}(\text{propene})^+$  by  $\beta$ -hydride shifts. This species can then eliminate propene or undergo dehydrogenation. The slow rate of dehydrogenation, reaction 48, is due to the propene dehydrogenation by  $\text{CoCp}^+$  and not to the rearrangement to  $\text{CpCo}(\text{propene})^+$  from **15**.

Finally, it is interesting to note that in a recent solution study by Janowicz and Bergman,<sup>66</sup> the reaction of an unsaturated iridium complex with cyclopropane resulted in exclusive insertion into the strong C–H bond. A similar mechanism for the cobalt system would avoid the metallacyclobutane intermediate altogether, which would also explain the lack of metathesis-like chemistry. We believe, however, that this route is highly improbable.

Cyclobutane reacts rapidly with  $\text{CoCp}^+$  yielding both dehydrogenation and C–C bond cleavage (reactions 49 and 50). No



secondary reactions are observed. Both products yield facile formation of  $\text{CoCp}^+$  upon collisional activation which is indicative of  $\text{CpCo}(\text{butadiene})^+$  and  $\text{CpCo}(\text{ethane})^+$ , *vide supra*.

A mechanism for formation of the products in reactions 49 and 50 is presented in Scheme IV and involves initial insertion across a C–C bond forming the metallacyclopentane species, **16**. Intermediate **16** decomposes by either dehydrogenation forming  $\text{CpCo}(\text{C}_4\text{H}_6)^+$  or symmetric ring cleavage forming  $\text{CpCoC}_2\text{H}_4^+$ . Metallacyclopentanes decompose in solution by symmetric ring cleavage resulting in ethene formation, by  $\beta$ -hydride elimination producing butene, and by reductive elimination of cyclobutane.<sup>67</sup>

The coordination state of a metal may have a significant effect on the mechanism of decomposition of metallacycles. For example, the decomposition pathways of nickelacyclopentanes in solution are strongly dependent on the coordination state of the metal.<sup>68,69</sup> Atomic cobalt cations react with cyclobutane in the gas phase to yield 95% dehydrogenation and 5% ethene elimination.<sup>66,7d</sup> Addition of a methyl ligand to  $\text{Co}^+$  enhances decomposition by symmetric ring cleavage over dehydrogenation, where at least 62% of the reaction processes proceed by symmetric ring cleavage.<sup>44</sup> Therefore, addition of a ligand such as  $\text{CH}_3$  or  $\text{c-C}_5\text{H}_5$  favors decomposition by symmetric ring cleavage over dehydrogenation.

It is possible that complexes **16** and **17** may be in dynamic equilibrium (reaction 51). Metallacyclopentanes have been synthesized in solution by olefin dimerization reactions.<sup>70–73</sup> In

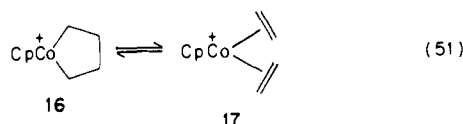
(66) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929.

(67) (a) Casey, C. P.; Scheck, D. M.; Shusterman, A. J. "Fundamental Research in Homogeneous Catalysis"; Tsutsui, M., Ed.; Plenum Press: New York, 1979; Vol. 3, p 141. (b) Grubbs, R. H.; Miyashita, A. "Fundamental Research in Homogeneous Catalysis"; Tsutsui, M., Ed.; Plenum Press: New York, 1979; Vol. 3, p 151.

(68) (a) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 2418. (b) Grubbs, R. H.; Miyashita, A.; Liu, M.; Burk, P. L. *J. Am. Chem. Soc.* **1977**, *99*, 3863. (c) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 7416.

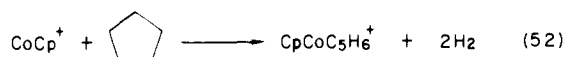
(69) (a) Braterman, P. S. *J. Chem. Soc., Chem. Commun.* **1979**, 70. (b) Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952. (c) McKinney, R. J.; Thorn, D. L.; Hoffmann, R.; Stockis, A. *J. Am. Chem. Soc.* **1981**, *103*, 2595.





addition bis(ethene) complexes have been observed to be in dynamic equilibrium with the corresponding metallacyclopentanes in solution.<sup>74</sup> Gaseous bis(ethene) $\text{Co}^+$  ions, however, were found *not* to be in equilibrium with cobaltacyclopentane ions.<sup>75</sup> Although the equilibrium in reaction 51 was not studied directly, it seems reasonable to assume that it does not occur based on the large abundance of ethene elimination in reaction 50.

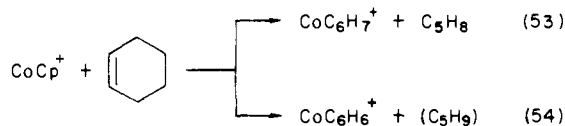
$\text{CoCp}^+$  reacts with cyclopentane by attacking C-H bonds exclusively (reaction 52). This product undergoes facile elimination



of  $\text{H}\cdot$  forming  $\text{CoC}_{10}\text{H}_{10}^+$  upon collisional activation. CID of this  $\text{CoC}_{10}\text{H}_{10}^+$  species indicates formation of cobaltocenium. The  $\text{CoC}_{10}\text{H}_{11}^+$  formed in reaction 52 can, therefore, be considered simply as protonated cobaltocene. Interestingly, CID of  $\text{Co-c-C}_5\text{H}_6^+$  only produces  $\text{C}_5\text{H}_6$  elimination with no elimination of  $\text{H}\cdot$  to produce  $\text{CoC}_5\text{H}_5^+$  observed.<sup>66,75</sup>  $\text{CoCp}^+$  reacts with both cyclopentene and cyclopentadiene to produce  $\text{CoC}_{10}\text{H}_{10}^+$  exclusively.

Absence of  $\text{CoCp}_2^+$  formation in reaction 52 implies an upper limit for  $D^\circ(\text{CoCp}^+-\text{Cp})$  of 128 kcal/mol,<sup>25</sup> and reaction 18 implies  $D^\circ(\text{CoCp}^+-\text{Cp}) > 115$  kcal/mol. An appearance potential measurement previously suggested  $D^\circ(\text{CoCp}^+-\text{Cp}) \sim 180$  kcal/mol.<sup>76</sup> The use of appearance potentials for deducing thermodynamic information is susceptible to large errors with the actual values being upper limits.  $D^\circ(\text{Co}^+-\text{Cp})$  has previously been reported to exceed  $84 \pm 4$  kcal/mol.<sup>44</sup> Using IP of  $\text{CoCp}_2 = 5.56$  eV<sup>76</sup> and  $\Delta H_f(\text{CoCp}_{2(g)}) = 67$  kcal/mol<sup>78</sup> yields  $D^\circ(\text{Co}^+-(2\text{Cp})) = 203$  kcal/mol. It appears, therefore, that  $D^\circ(\text{Co}^+-\text{Cp})$  cannot exceed  $84 \pm 4$  kcal/mol by much and is, therefore, assigned as  $85 \pm 10$  kcal/mol while  $D^\circ(\text{CoCp}^+-\text{Cp})$  is assigned as  $118 \pm 10$  kcal/mol. For comparison,  $D^\circ(\text{FeCp}-\text{Cp}) = 91 \pm 3$  kcal/mol and  $D^\circ(\text{Fe}-\text{Cp}) = 51 \pm 3$  kcal/mol.<sup>79</sup>

Reactions with cyclohexane and cyclohexene are dominated by dehydrogenation. In addition, reactions 53 and 54 are observed for cyclohexene. The product of reaction 53 undergoes one rapid



H/D exchange with deuterium and also readily eliminates  $\text{H}\cdot$  upon

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

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(73) (a) Fraser, A. R.; Bird, P. H.; Bezman, S. A.; Shapley, J. R.; White, R.; Osborn, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 597. (b) Cassar, L.; Easton, P. E.; Halpeen, J. *J. Am. Chem. Soc.* **1970**, *92*, 3515. (c) Catl, J.; Haines, R. J.; Leigh, G. *J. Chem. Soc., Chem. Commun.* **1972**, 1203. (d) Fellman, J. D.; Rupprecht, G. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5099. (e) Porri, L. *Tetrahedron Lett.* **1974**, 11, 879.

(74) (a) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 1300. (b) McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1977**, *99*, 3519.

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(78) Chipperfield, J. R.; Sneyd, J. C. R.; Webster, D. E. *J. Organomet. Chem.* **1979**, *178*, 177.

(79) Lewis, K. E.; Smith, G. P. *J. Am. Chem. Soc.* **1984**, *106*, 4650.

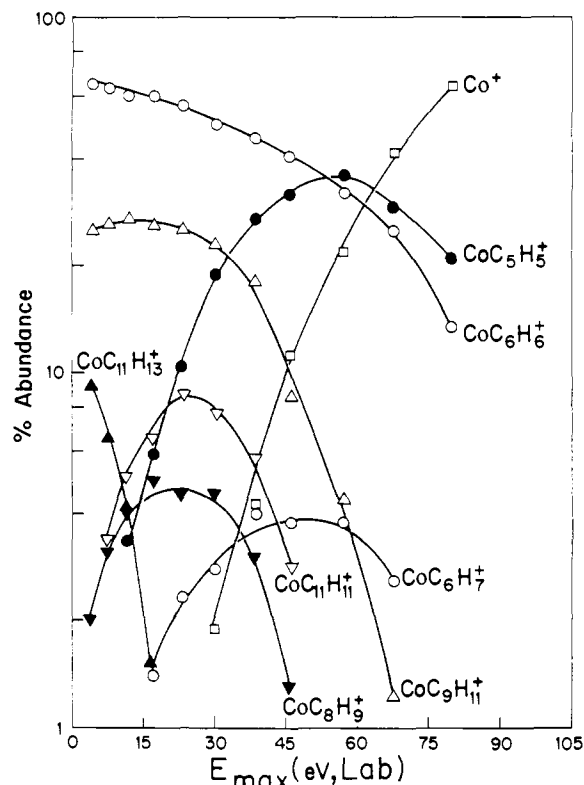


Figure 6. Variation of CID product ion abundances as a function of kinetic energy for  $\text{CpCoC}_6\text{H}_{10}^+$  formed from  $\text{CpCo}^+$  and cyclohexane.

collisional activation to form  $\text{CoC}_6\text{H}_6^+$ . These results suggest formation of  $\text{Co-c-C}_6\text{H}_7^+$  in reaction 53.<sup>44</sup> Elimination of  $\text{C}_5\text{H}_9$  in reaction 54 as  $\text{c-C}_5\text{H}_9$  and  $\text{H}\cdot$  is calculated to be endothermic by  $37 \pm 6$  kcal/mol while elimination of  $\text{c-C}_5\text{H}_9$  is roughly thermoneutral.<sup>80</sup> Reaction 54, therefore, proceeds by elimination of a cyclopentyl radical and not cyclopentene plus a hydrogen atom.

CID of  $\text{Co}(\text{Cp})(\text{benzene})^+$  generated from  $\text{CoCp}^+$  and cyclohexene yields exclusively benzene elimination consistent with  $D^\circ(\text{Co}^+-\text{benzene}) = 70 \pm 4$  kcal/mol<sup>80</sup>  $< D^\circ(\text{Co}^+-\text{Cp}) = 85 \pm 10$  kcal/mol. CID of  $\text{CoCp}(\text{C}_6\text{H}_{10})^+$ , generated from cyclohexane, is dominated by  $\text{CoC}_6\text{H}_6^+$  formation with *no*  $\text{CoC}_{10}\text{H}_{10}^+$  formation observed (Figure 6). This is in contrast to CID of  $\text{CoCp}(\text{C}_6\text{H}_{10})^+$  formed from the hexane isomers and demonstrates that cyclohexane cannot undergo isomerization to a cyclopentene species.

## Conclusions

$\text{CoCp}^+$  reacts with aliphatic alkanes by attacking C-H bonds. The reactivity resembles that of  $\text{Co}(\text{allyl})^+$  toward alkanes.<sup>10</sup> The facile induced skeletal isomerizations of aliphatic olefins containing 5 carbons or more followed by dehydrocyclizations is unique for gas-phase transition-metal-ion chemistry. The effect particular ligands have on metal ion reactivity toward hydrocarbons is at present not well understood. Clearly, additional work in this area should prove to be both stimulating and enlightening.

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(80) This calculation is based on  $D^\circ(\text{Co}^+-\text{Cp}) = 85 \pm 10$  kcal/mol (this paper),  $D^\circ(\text{Co}^+-\text{benzene}) = 70 \pm 4$  kcal/mol (D. B. Jacobson and B. S. Freiser, unpublished results), and the heats of formation in ref 25.