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Generation and Decomposition of Group 8 Metal (Fe, Co, Ni) Ion Metallacycles in the Gas Phase

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Fe^+ decarbonylates cyclobutanone generating a stable metallacyclobutane ion. This metallacyclobutane ion does *not* react with olefins to yield metathesis products. Ni^+ and Co^+ do not generate stable metallacyclobutane ions by this process but rather form (propene)metal ion complexes. Stable metallacyclopentane ions are generated for Fe^+ and Ni^+, and they decompose by both symmetric ring cleavage and dehydrogenation. The dehydrogenation process proceeds by an initial 1,3-hydrogen atom shift generating a 1-butene complex followed by elimination of H_2. Metallacyclohexanes and metallacycloheptanes appear to decompose by initial 1,4- and 1,5-hydrogen atom shifts generating (1-pentene)- and (1-hexene)metal ion complexes, respectively, which then decompose.

Introduction

The formation and fragmentation of metallacycles is an important class of organotransition-metal reactions, since these processes are involved in a number of significant catalytic transformations. Olefin metathesis,[1-3] hydrocarbon cracking and isomerization,[4] epoxidation,[5] and deepoxidation[6] are all believed to proceed through the intermediacy of metallacyclobutanes. Metallacyclopentanes appear to be intermediates in a variety of olefin dimerization reactions.[7,8] Metallacyclohexanes and metallacycloheptanes, though important species to study, appear to have little relevance to catalysis. Several stable metallacycles have been synthesized and characterized by a variety of techniques. Studying the decomposition pathways of these metallacycles is important since they may be related to catalytic processes. Significant ligand and solvent effects are seen in these decompositions. For example, the mechanism of decomposition of nickelacyclopentanes in solution is strongly dependent on the coordination state of the metal.[9,10]

Studies involving metallacyclic species in the gas phase are particularly interesting since no solvent molecules are present. Hence, decomposition of naked gas-phase metallacyclic ions can provide fundamental information. Unfortunately, this area has remained virtually unexplored, due largely to instrumental limitations. Several recent instrumental advances, however, have now made these studies possible. Beauchamp et al.,[11] using both an ion cyclotron resonance (ICR) spectrometer and an ion beam instrument, have studied gas-phase metal ion–organic interactions and have postulated metallacyclic species as intermediates. Recently, we reported[12] the synthesis of stable metallacyclopentane ions in the gas phase by decarbonylation of cyclopentanone by Fe^+, Co^+, and Ni^+. This decarbonylation reaction suggested that a variety of stable metallacyclic ions including metallacyclobutane ions

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could be generated by decarbonylation of the appropriate cyclic ketones.

In this paper, we report on the generation and decomposition processes for gas-phase metallacyclic ions using Fourier transform mass spectrometry (FTMS). FTMS, the high performance daughter of ICR,[13] was first developed by Comisarow[14] and in general provides a number of real advantages over conventional ICR spectroscopy, including high mass range, high resolution, and rapid data acquisition times. As with conventional ICR, FTMS is capable of trapping ions for long periods (up to several seconds) which allows for ion–molecule reactions to occur. Reaction pathways can be probed by using the highly specific double-resonance technique.[13,14]

Collision-induced dissociation (CID) is a powerful technique for ion structure determination in the gas phase.[15] The CID technique simply consists of first isolating a particular ion by ejecting all unwanted ions[13,14] and then accelerating the ion into a collision gas, thereby imparting internal energy into the ion, which induces fragmentation. This essentially yields a mass spectrum of the precurser ion from which structural information can be obtained. Recently we reported the first examples of collision-induced dissociation using a Nicolet prototype FTMS-1000 mass spectrometer[16] and have since demonstrated its applicability to studies of metal–ion complexes.[12] This technique is used here to study the decomposition of gas-phase metallacyclic ions.

Experimental Section

The theory, instrumentation, and methodology of ion cyclotron resonance (ICR) spectroscopy[13] and Fourier transform mass spectrometry (FTMS)[14] have been discussed at length elsewhere. All experiments were performed by using a Nicolet prototype FTMS-1000 Fourier transform mass spectrometer previously described in detail[16] 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. High purity foils of the appropriate metals were attached to the opposite transmitter plate. Metal ions are generated by focusing the beam of a Quanta Ray Nd:YAG laser (frequency doubled to 530 nm) onto the metal foil. Details of the laser ionization technique have been described elsewhere.[17]

Chemicals were obtained commercially in high purity and used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensable gases. Deuterated cyclopentanone-$\alpha,\alpha,\alpha',\alpha'$-$d_4$ was synthesized according to the procedure of McNesby, Drew, and Gordon[18] by refluxing 9.0 mL of the ketone in the presence of 10.0 mL of D_2O containing 0.1 g of K_2CO_3 for 8–16 h in a closed system. Saturation of the water layer with K_2CO_3 was then followed by separation of the ketone layer, and the procedure was repeated eight times. Mass spectrometric analysis showed about 94% cyclopentanone-$\alpha,\alpha,\alpha',\alpha'$-$d_4$ and 6% cyclopentanone-α,α,α'-d_3. Sample pressures were on the order of 1 × 10^{-7} torr. Argon was used as the collision gas for the CID experiments at a total sample pressure of approximately 5 × 10^{-6} torr. A Bayard–Alpert ionization gauge was used to monitor pressure.

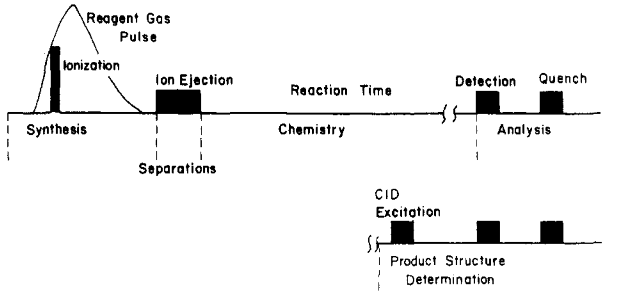
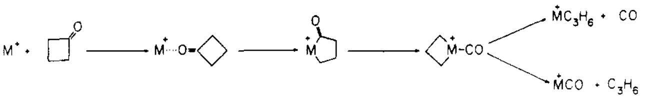


Figure 1. Sequence of events for pulsed valve addition of reagent gas for the FTMS experiment.

Scheme I



Details of the CID experiments have previously been discussed.[12,16,19,20] 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 ±5% absolute and are informative, yielding additional structural 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.[21]

Since FTMS is a single region spectrometer, all reagent gases are present in the same chamber. As a result, studying the chemistry of product ions with specific reagent gases can be complicated by reactions with the parent neutral gas. Addition of reagent gases through a pulsed valve can alleviate this problem.[22] The sequence of events using the pulsed valve are illustrated in Figure 1. Initially, a concurrent laser and valve pulse occurs. The pulsed reagent gas fills the vacuum chamber to a maximum pressure of ~10^{-5} torr and is pumped away by a high speed 5-in. diffusion pump in ~250 ms. This allows the metal ions to react with the pulsed reagent gas. The ions of interest are then isolated by swept double-resonance ejection[12-14] to remove all unwanted ions from the cell. These isolated ions are then reacted with a static pressure of a neutral gas without complicating reactions with the parent neutral. All secondary reactions were performed by using the pulsed valve technique.

Using an ion beam instrument, Beauchamp et al.[11a,c] reported that Co^+ undergoes an endothermic reaction with cyclopropane at 1-eV kinetic energy producing predominantly $CoCH_2^+$. No reactions were observed for laser desorbed Fe^+, Co^+, and Ni^+ with cyclopropane. Formation of MCH_2^+ from cyclopropane is roughly 7 kcal/mol endothermic for Co^+ and Ni^+, with Fe^+ being essentially thermoneutral.[23,24] The absence of reactivity toward cyclopropane is consistent with selecting laser formed metal ions with little or no electronic or kinetic excitation.

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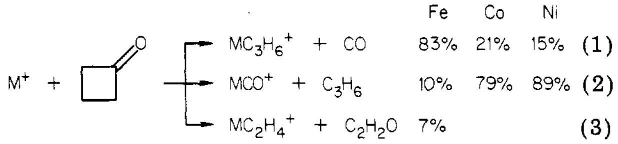
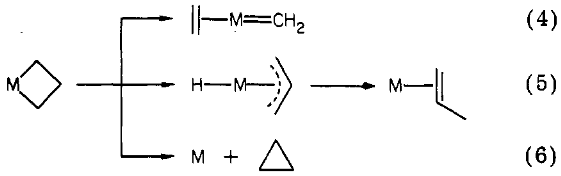
Results and Discussion

Metallacyclobutanes. Fe^+, Co^+, and Ni^+ react with cyclobutanone yielding the primary products listed in reactions 1–3. High resolution was used to distinguish the

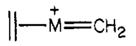


isobaric species $MC_3H_6^+$-$MC_2H_2O^+$ and $MC_2H_4^+$-MCO^+. A mechanism for formation of the products in reactions 1 and 2 is illustrated in Scheme I. Initially an activated complex is formed between the metal ion and cyclobutanone followed by insertion into an α-C–C bond. Carbonyl abstraction then occurs with competitive elimination of CO and C_3H_6. Scheme I suggests that the $MC_3H_6^+$ ions are initially formed as metallacyclobutane ions. Metallacyclobutanes decompose in solution by three basic routes:[25] (a) by conversion to a carbene olefin complex, process 4, (b) by hydride elimination, process 5, and



(c) by reductive elimination of cyclopropane, process 6. Hence, there are three possible structures for the $MC_3H_6^+$ ions formed in reaction 1: a metallacyclobutane, 1, a carbene ethene complex, 2, and a (propene)metal ion complex, 3.

1



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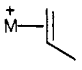
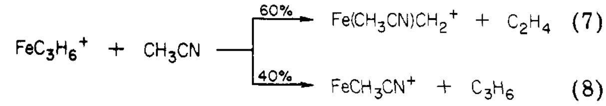


3

Acetonitrile reacts with $FeC_3H_6^+$, generated in reaction 1, to yield both C_2H_4 and C_3H_6 elimination (reactions 7 and 8). Interestingly, CID on the $Fe(CH_3CN)CH_2^+$ species



yields loss of CH_3CN exclusively, indicating that the carbene has remained intact. In constrast to this result, carbene has been observed to incorporate into the butadiene ligand of $Fe(C_4H_6)CH_2^+$.[20] Only C_3H_6 displacement, process 8, is observed for both $CoC_3H_6^+$ and $NiC_3H_6^+$ ions formed in reaction 1. Both 2-methylpropene and ethene displace C_3H_6 exclusively from the $MC_3H_6^+$ ions generated in reaction 1, and carbon monoxide is unreactive.

Metal ion–propene complexes can be synthesized directly by reaction 9. Simple displacement of C_3H_6 by

$$M^+ + \text{propane} \rightarrow MC_3H_6^+ + H_2 \qquad (9)$$

acetonitrile, 2-methylpropene, and ethene is the only process observed for M(propene)$^+$ for all three metals, and again M(propene)$^+$ complexes are unreactive with carbon monoxide.

A plot of ion intensity vs. kinetic energy for CID of $FeC_3H_6^+$ generated in reaction 1 is shown in Figure 2. Loss of C_3H_6 dominates over C_2H_4 loss at all kinetic energies studied with the greatest dominance occurring at low energy. Both $CoC_3H_6^+$ and $NiC_3H_6^+$ ions formed in reaction 1 yield exclusively C_3H_6 elimination in their CID spectra at all kinetic energies studied. M(propene)$^+$ species simply lose C_3H_6 as the only CID fragment.[12]

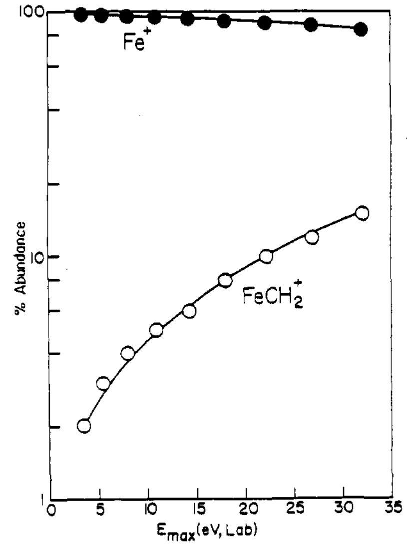


Figure 2. Variation of CID product intensities vs. kinetic energy for $FeC_3H_6^+$ ions generated in reaction 1.

Ligand exchange results for 2-methylpropene and ethene indicate that the $MC_3H_6^+$ ions generated in reaction 1 contain an intact C_3H_6 unit, either a metallacyclobutane species, 1, or a (propene)metal ion complex, 3. Reaction of acetonitrile with $FeC_3H_6^+$ along with the CID results (Figure 2) are evidence for formation of an ion having a structure different than the Fe(propene)$^+$ complex. These results provide fairly conclusive evidence for a metallacyclobutane complex, 1, since elimination of ethene would be expected to dominate at high collision energies for an ethene–carbene complex, 2. CID and ligand exchange reactions for $CoC_3H_6^+$ and $NiC_3H_6^+$ ions generated in reaction 1 are identical with the M(propene)$^+$ species.

In summary, it appears that a stable ferracyclobutane ion is formed by reaction 1 that decomposes at low energy by processes 5 and 6 and at high energy also by process 4. The corresponding cobalta- and nickelacyclobutanes, initially formed in reaction 1, however, appear to retain sufficient internal energy for rearrangement to a propene complex, process 5, prior to structural studies. Rearrangement of metallacyclobutane species to a (propene)-metal species requires formation of a π-allyl hydrido intermediate. The degree of puckering of the metallacyclobutane ring is believed to be important in this process.[25] The smaller the dihedral angle (greater puckering), the more favorable hydride transfer becomes. Hence, the ferracyclobutane may be nearly planar while the cobalta- and nickelacyclobutanes may have significant puckering. As mentioned above, Beauchamp et al.[11a,c] have reported that kinetically excited Co^+ reacts with cyclopropane yielding predominantly $CoCH_2^+$. Presumably, this proceeds via initial insertion into a C–C bond forming a cobaltacyclobutane intermediate that decomposes by process 4. Process 5 may also be occurring since conversion of cyclopropane to propene is 8 kcal/mol exothermic. This would result in regeneration of Co^+ and could not be monitored.

Several stable group 8 metallacyclobutanes have been synthesized in solution.[26-28] Thermal degradation of

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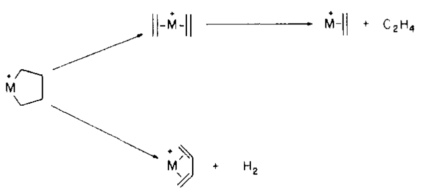
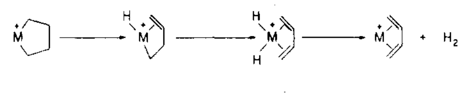
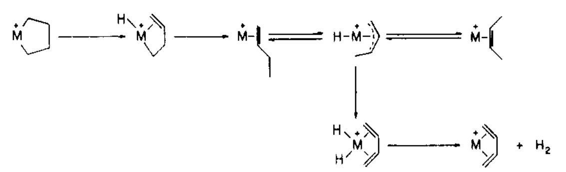
Scheme II



Scheme III

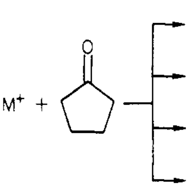


Scheme IV



platinacyclobutanes at relatively high temperature produces cyclopropane and propene from competitive reductive elimination and β-hydride elimination.[29] Thermal degradation of nickelacyclobutanes yields predominantly reductive elimination and β-hydride elimination with some C–C bond cleavage products also observed.[28] Significantly, the nickelacyclobutane in solution appears to be in equilibrium with the olefin-coordinated nickel–carbene complex, but this apparently does not occur in the gas phase.

Metallacyclopentanes. Metallacyclopentanes decompose in solution by symmetric ring cleavage resulting in formation of ethene, by β-hydride elimination producing butene and by reductive elimination of cyclobutane.[1,3c,9,10,30–32] Stable metallacyclopentanes have previously been synthesized in the gas phase by decarbonylation of cyclopentanone[12] by Fe^+ and Ni^+ along with three other products, reactions 10–13.



	Fe	Co	Ni	
$MC_5H_6O^+ + H_2$	11%	5%	0%	(10)
$MC_4H_8^+ + CO$	30%	8%	39%	(11)
$MC_4H_6^+ + CO + H_2$	49%	82%	48%	(12)
$MC_2H_4^+ + C_2H_4 + CO$	10%	5%	13%	(13)

The metallacyclopentanes produced in reaction 11 decompose upon collisional activation both by symmetric ring cleavage (C_2H_4 elimination) and by dehydrogenation (Scheme II).[12,33] The latter result implies that the product of reaction 12 is probably formed by sequential loss of CO forming the metallacyclopentane followed by dehydrogenation instead of loss of CH_2O. Dehydrogenation of the metallacyclopentanes may simply involve two sequential hydride shifts as shown in Scheme III or a 1,3-hydrogen atom shift may occur generating a (linear butene) metal ion complex which readily dehydrogenates as shown in Scheme IV. The mechanism for dehydrogenation of gas-phase metallacyclopentanes was probed by using cyclopentanone-α,α,α′,α′-d_4. Decarbonylation, reaction 11, then produces the deuterated metallacyclopentane 4.

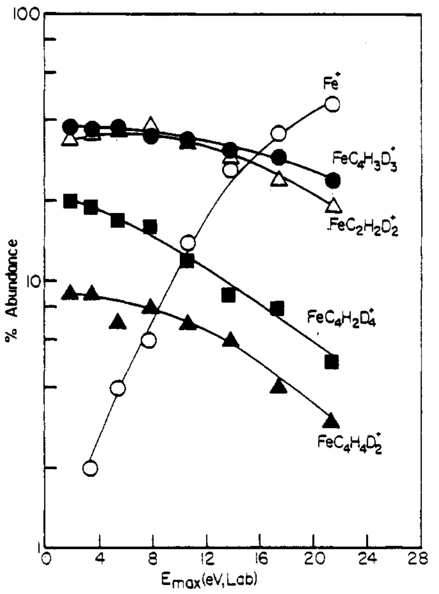


Figure 3. Variation of CID product intensities vs. kinetic energy for $FeC_4H_4D_4^+$ ions generated by decarbonylation of cyclopentanone-α,α,α′,α′-d_4 by Fe^+.

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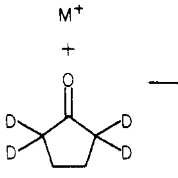
Formation of the (butadiene)metal ion complex, as in reaction 12, generates products with varying degrees of deuteration, as shown in reactions 14–16. In addition, a plot of fragment ion abundances vs. ion kinetic energy for CID of $FeC_4H_4D_4^+$ (the stable metallacyclopentane 4) is shown in Figure 3. Dehydrogenation via losses of H_2, HD, and D_2 are observed along with loss of $C_2H_2D_2$. Similar results were obtained for CID of the $NiC_4H_4D_4^+$ metallacyclic species, but, unfortunately, the $CoC_4H_4D_4^+$ ion could not be isolated for its CID spectra to be studied. The deuterium losses in reactions 15 and 16 and in Figure 3 probably proceed via the 1,3-hydrogen shift mechanism outlined in Scheme IV since dehydrogenation by Scheme III requires loss of H_2 exclusively. In addition, Scheme IV predicts that significant amounts of H_2 loss should also be observed: however, H_2 loss by Scheme III is probably also occurring. Loss of $C_2H_2D_2$ as the only CID C–C bond cleavage product for the deuterated metallacyclopentane species indicates that hydrogen scrambling occurs only after rearrangement to a structure different than metallacyclopentane, presumably a linear butene complex. All three metal ions react with 1-butene-*1,1*-d_2 resulting in H_2 (~65%), HD (~32%), and D_2 (~3%) elimination.[20] The deuterium losses clearly indicate that reversible β-hydride transfers are occurring for (linear butene) metal ion com-



	Fe	Co	Ni	
$MC_4H_2D_4^+ + CO + H_2$	48%	44%	48%	(14)
$MC_4H_3D_3^+ + CO + HD$	38%	40%	33%	(15)
$MC_4H_4D_2^+ + CO + D_2$	14%	16%	19%	(16)

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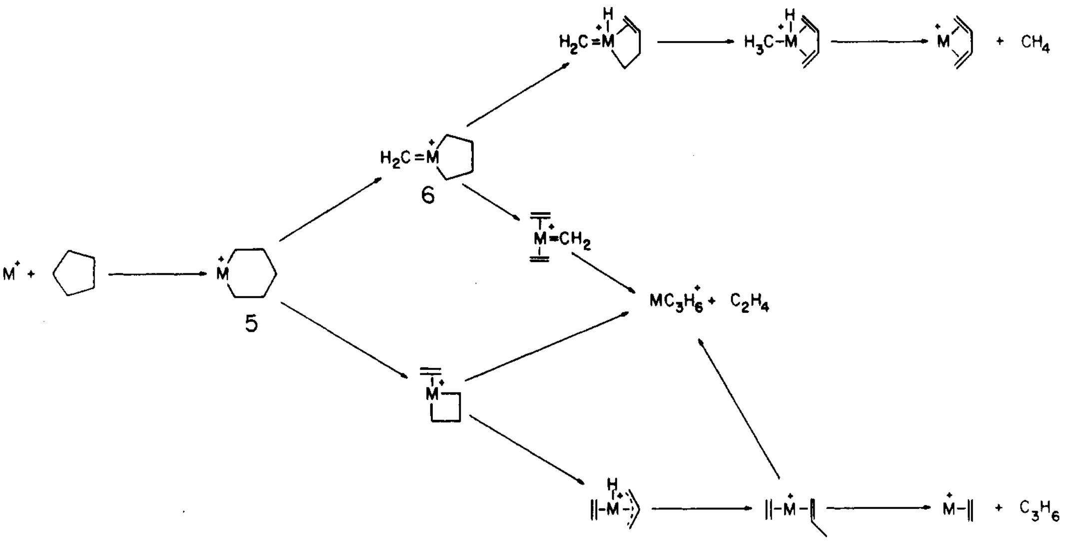
Table I. Percentages of Neutrals Lost in the Primary Reactions of Fe^+, Co^+, and Ni^+ with Cyclopentane and Cyclohexane[a]

hydrocarbon	M^+	neutrals lost							
		H_2	$2H_2$	$3H_2$	CH_4	H_2 CH_4	C_2H_4	C_2H_6 $(H_2 + C_2H_4)$	C_3H_6
cyclopentane	Fe	65	34				1		
	Co	22	20		2		47		9
	Ni	57	13				27		3
cyclohexane	Fe	63	24	13					
	Co	33	37	7		1	1	1	20
	Ni	65	25						10

[a] Data taken from ref 42.

Scheme V

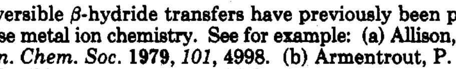


plexes prior to dehydrogenation.[34] In summary, these gas phase metallacyclopentane ions decompose losing H_2 by both Schemes III and IV, along with symmetric ring cleavage (Scheme II).

A possible complication in this study is that the metallacyclopentane ions may be in equilibrium with bis(ethene)metal ion complexes, process 17. This equilibrium

 (17)

could easily account for the deuterium losses in reactions 15 and 16 and also for the CID results. Metallacyclopentanes have been synthesized in solution by olefin dimerization reactions.[7,8,32,35-38] In addition, the equilibrium in reaction 17 has been observed in solution.[39,40] Bis(ethene)metal ion complexes have been generated by reaction of (ethene) metal (+) with cyclobutane, process 18, for Fe^+, Co^+, and Ni^+.[41] Loss of C_2H_4 and C_4H_8 are the only fragments observed in the CID spectra of the bis(ethene) complexes generated in reaction 18. If the equilibrium in reaction 17 was occurring in the gas phase, then some dehydrogenation producing $MC_4H_6^+$ ions would be expected in the CID spectra but this is not observed. Therefore, the equilibrium between bis(ethene) and metallacyclopentanes apparently does not occur in the gas phase for Fe^+, Co^+, and Ni^+.

 (18)

$$MC_2H_4^+ + \square \longrightarrow M(C_2H_4)_2^+ + C_2H_4 \quad (18)$$

Metallacyclohexanes and Metallacycloheptanes. There have been few studies on the decomposition of metallacyclohexanes[1a,3c,30,32,42] and metallacycloheptanes[30,32] in solution. Miyashita and Grubbs[1a,3c,42] have studied the decomposition of nickelacyclohexanes and titanacyclohexanes and reported that they decompose by C–C bond cleavage yielding predominantly ethene and methane, some butene, and little or no propene. Labeling studies indicated that α-C–C bond cleavage of the ring seemed to occur more often than β-C–C bond cleavage. In contrast to this, platinacycloheptanes decompose yielding 1- and 2-hexenes exclusively in solution.[30,32]

No stable metallacyclohexanes and metallacycloheptanes could be generated by decarbonylation of the appropriate cyclic ketones in the gas phase. However, Co^+ and Ni^+ react with cyclopentane and cyclohexane yielding C–C bond cleavage products along with dehydrogenation products while Fe^+ yields dehydrogenation products exclusively (Table I). The results in Table I are in excellent agreement with those previously reported for Co^+ using an ion beam instrument[11c] and for Fe^+, Co^+, and Ni^+ formed by electron impact on the appropriate organometallic species.[43] Dehydrogenation proceeds with re-

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(34) Reversible β-hydride transfers have previously been postulated for gas-phase metal ion chemistry. See for example: (a) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998. (b) Armentrout, P. B.; Beauchamp, J. L. *Ibid.* **1981**, *103*, 784. (c) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963. (d) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1976**, *98*, 7445. (e) Reference 20.

(35) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 7416.

(36) Chatt, J.; Haines, R. J.; Leigh, G. J. *J. Chem. Soc., D.* **1972**, 1203.

(37) Porri, L. *Tetrahedron Lett.* **1974**, *11*, 879.

(38) Fellman, J. D.; Rupprecht, G. A.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5099.

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

(40) Stockis, A.; Hoffman, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952.

(41) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7492.

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

(43) Kalmbach, K. A.; Ridge, D. P.; Peake, D.; Gross, M. L., presented at the 31st American Society for Mass Spectrometry metting, 1983.

Scheme VI

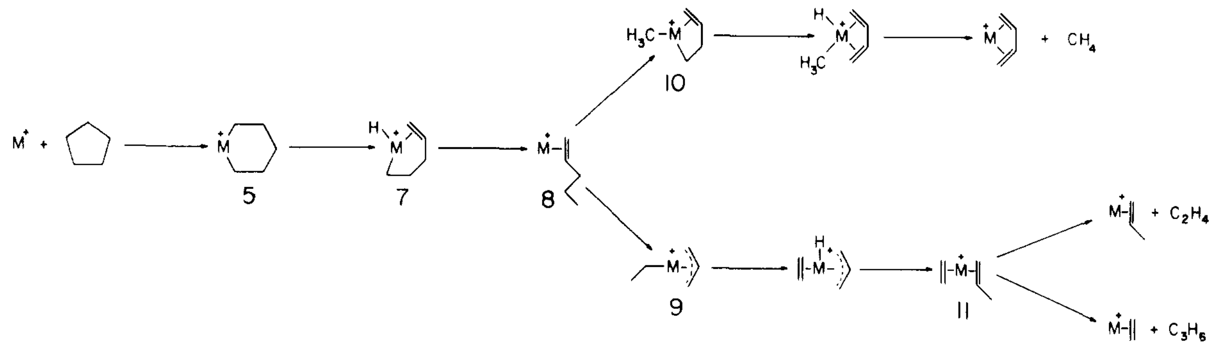
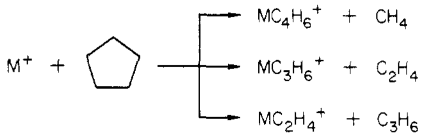


Table II. Comparison of the Percentages of C-C Bond Cleavage Products for Primary Reactions of Co^+ and Ni^+ with 1-Pentene, 1-Hexene, Cyclopentane, and Cyclohexane[a]

hydrocrabon	M^+	neutrals lost				
		CH_4	C_2H_4	C_2H_6 (H_2 + C_2H_4)	C_3H_6	C_4H_8
1-Pentene	Co	7	71		22	
	Ni	3	73		24	
cyclopentane	Co	3	81		16	
	Ni		90		10	
1-hexene	Co	2	3	9	82	4
	Ni	2	2	9	82	5
cyclohexane	Co	4	4	4	88	
	Ni	...	...	...	100	

[a] Data for alkenes taken from ref 12b.

tention of the ring's integrity.[41] The C–C bond cleavage products, reactions 19–21, may be explained by mechanisms similar to those put forward by Grubbs and Miyashita for decomposition of titanacyclohexanes and nickelacyclohexanes.[1a,3c,42] As shown in Scheme V for cyclopentane, loss of methane is proposed to proceed by an initial α-C–C bond cleavage from **5** to form intermediate **6**. As discussed above for metallacyclopentanes, sequential hydride shifts and reductive elimination of methane yields a (butadiene)metal ion complex. Loss of ethene may occur by either an α- or a β-C–C bond cleavage as shown in Scheme V. Loss of C_3H_6 presumably occurs via β-C–C bond cleavage. Armentrout and Beauchamp[11c] have proposed this mechanism to account for the C–C bond cleavage products for reaction of Co^+ with cyclopentane.



(19)
(20)
(21)

An alternative mechanism for the losses of CH_4, C_2H_4, and C_3H_6 from cyclopentane is presented in Scheme VI and invokes an initial 1,4-hydrogen atom shift generating a (1-pentene)metal ion complex, **8**. This is analogous to the mechanism proposed for dehydrogenation of metallacyclopentanes outlined in Scheme IV. Decomposition of (olefin)metal (+) complexes has been studied recently in the gas phase both by ion–molecule reactions[12,20,44] and by CID.[12,20] In these studies, oxidative addition of an allylic C–C bond or a terminal C–C bond is postulated to initially occur for 1-pentene generating complexes **9** and **10** in Scheme VI, respectively. β-Hydride shifts result in formation of a bis(olefin) complex, **11**, in the former and a butadiene complex (CH_4 loss) in the latter. The bis(olefin) complex then preferentially eliminates ethene as shown in Scheme VI.[12,20,44,45] This mechanism is particularly appealing since the distribution of CH_4, C_2H_4, and C_3H_6 losses are in excellent agreement with results for reactions with 1-pentene (Table II) and CID of (1-pentene)metal ion complexes.[12,20]

In addition to the C–C bond cleavages, a small amount of H_2 elimination (~5% total primary product distribution) for Co^+ reacting with with 1-pentene is observed; however, no dehydrogenation is seen for CID of (1-pentene)metal ion complexes.[12] This difference between CID and ion–molecule reactions has been attributed to the nature of the two processes. FTMS–CID fragmentations are, for the most part, the result of multiple collisions.[12,19,20] Therefore, the ions gain internal energy in increments with the result being that rearrangements may occur prior to dissociation. Other factors are probably also involved.[12b] Conversion of cyclopentane to 1-pentene requires 13.5 kcal/mol;[24] therefore, (1-pentene)metal ion complexes formed from cyclopentane will contain 13.5 kcal/mol less internal energy than those formed from reaction of the metal ion with 1-pentene. The $M(C_2H_4)(C_3H_6)^+$ ions (structure **11**, Scheme VI) formed from cyclopentane and 1-pentene will also have this energy difference. Smaller olefins are cleaved preferentially from bis(olefin) complexes since they are not bound as strongly, and the ratio of C_2H_4 to C_3H_6 loss from structure **11** decreases with increasing internal energy.[12,20,45] Observation of a greater C_2H_4 to C_3H_6 loss ratio for cyclopentane relative to 1-pentene (Table II) is, therefore, consistent with the energetics.

Co^+ and Ni^+ react with cyclohexane producing both C–C bond cleavage products and dehydrogenation products while Fe^+ again yields exclusively dehydrogenation products (Table I). As with cyclopentane, dehydrogenation proceeds with retention of the ring's integrity.[41] Loss of C_3H_6 is the only C–C bond cleavage product for Ni^+ while CH_4, C_2H_4, C_2H_6 (C_2H_4 + H_2), and C_3H_6 losses are seen for Co^+ with predominant C_3H_6 loss (Table II). These C–C

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

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

bond cleavages for cyclohexane may be viewed similarly to those for cyclopentane in Scheme VI. Initially, the metal ion inserts into a C–C bond generating a metallacycloheptane followed by a 1,5-hydrogen atom shift forming an activated (1-hexene)metal ion complex. This species then decomposes by insertion into an allylic C–C bond followed by β-hydride shifts generating a bis(propene) complex that eliminates propene. CH_4, C_2H_4, and C_2H_6 (C_2H_4 + H_2) losses for Co^+, observed as minor products, may proceed by insertion into C–C bonds further removed from the double bond. Alternatively, reversible hydride shifts resulting in conversion of 1-hexene into 2- or 3-hexene prior to insertion into an allylic C–C bond may occur.[34] The distribution of C–C bond cleavage products are in excellent agreement with results for reactions with 1-hexene (Table II). Furthermore, CID of stable (1-hexene)nickel(+) complexes result in C_3H_6 loss as the only C–C bond cleavage product.[12] Conversion of cyclohexane to 1-hexene requires 19.5 kcal/mol.[24] Again, the difference between reactions with cyclohexane and 1-hexene may also be attributed to the difference in energy of the (1-hexene)metal ion complexes. Alternatively, however, processes similar to those presented in Scheme V may be involved.

Conclusions

Fe^+ decarbonylates cyclobutanone generating a stable metallacyclobutane ion (at least 60% has this structure), reaction 1. This ion decomposes at low energies by either β-hydride transfer or reductive elimination of cyclopropane. At high energies, decomposition by initial rearrangement to a carbene ethene complex followed by elimination of ethene becomes competitive with the above processes. This ferracyclobutane ion does not react with olefins to give metathesis products. Rosenblum has reported the synthesis of an iron carbene alkene complex[46] which does not react to give either cyclopropane or metathesis like products.

Both Ni^+ and Co^+ decarbonylate cyclobutanone, reaction 1, generating unstable metallacyclobutane intermediates that appear to undergo β-hydride transfer forming metal ion–propene complexes. The apparent difference between the stabilities of the metallacyclobutanes to rearrange to propene complexes suggests that the cobalta- and nickelacyclobutane ions may have significant puckering of the ring while the ferracyclobutane ions may be nearly planar. The energies of the π-allyl hydrido intermediates may also play an important role in the stability of these metallacyclobutane ions.

Metallacyclopentane ions appear to decompose by both symmetric ring cleavage and dehydrogenation processes (Scheme II). Labeling studies indicate that dehydrogenation proceeds by both Schemes III and IV.

The metallacyclohexanes appear to also decompose by an initial 1,4-hydrogen atom shift generating an activated (1-pentene)metal ion complex (Scheme VI). This 1-pentene complex then decomposes yielding predominantly ethene and propene losses with some methane loss also observed for Co^+. This mechanism is particularly appealing since the distribution of CH_4, C_2H_4, and C_3H_6 losses are in excellent agreement with results for reactions with 1-pentene[12,20,44] (Table II) and CID of (1-pentene)metal ion complexes.[12,20] Losses of CH_4, C_2H_4, and C_3H_6 may also be adequately explained by the mechanism put forward by Miyashita and Grubbs[1a,3c,43] for decomposition of titanacyclohexanes and nickelacyclohexanes (Scheme V).

Further evidence for decomposition of the metallacyclohexanes by Scheme VI lies in the results for the metallacycloheptanes. Ni^+ reacts with cyclohexane producing only one C–C bond cleavage product, loss of C_3H_6. Scheme VI predicts that the nickelacycloheptane would first undergo rearrangement by a 1,5-hydrogen atom shift producing a (1-hexene)nickel ion complex. CID of (1-hexene)Ni^+ complexes yields loss of C_3H_6 as the only C–C bond cleavage fragment.[12] For Co^+, loss of C_3H_6 also dominates as predicted by Scheme VI and observed for CID on (1-hexene)Co^+ species.[12b] These results together with the cyclopentane results provide strong evidence that decomposition of gas-phase metallacyclohexane and metallacycloheptane ions proceed by the mechanism outlined in Scheme VI.

Acknowledgment is made to the Division of Chemical Sciences in the Office of Basic Energy Sciences in the U.S. Department of Energy (DE-AC02-80ER10689) for supporting this research and the National Science Foundation (CHE-8002685) for providing funds for the purchase of the FTMS.

Registry No. Fe^+, 14067-02-8; Co^+, 16610-75-6; Ni^+, 14903-34-5; cyclopentane, 287-92-3; cyclohexane, 110-82-7; 1-pentene, 109-67-1; 1-hexene, 592-41-6; cyclobutanone, 1191-95-3; propane, 74-98-6; cyclopentanone, 120-92-3; cyclopentanone-*2,2,5,5-d_4*, 3997-89-5.

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(46) Priester, W.; Rosenblum, M. *J. Chem. Soc., Chem. Commun.* **1978**, 26.