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Reactions of $FeCH_3^+$ and $CoCH_3^+$ with Cyclic Hydrocarbons in the Gas Phase

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Abstract: The gas-phase reactions of $FeCH_3^+$ and $CoCH_3^+$ with cyclic hydrocarbons (C_3 through C_6) were studied. Both $FeCH_3^+$ and $CoCH_3^+$ react with cyclopropane and cyclobutane by cleavage of the ring. For cyclopropane, insertion into a C–C bond results in initial formation of an ethyl–ethene complex which is in rapid equilibrium with the hydrido–bis(ethene) complex. Elimination of ethene then yields $MC_2H_5^+$ which appears to consist of a hydrido–ethene and an ethyl complex in equilibrium. Both $FeCH_3^+$ and $CoCH_3^+$ generate stable methyl–ethene complexes with cyclobutane. No reaction is observed for $FeCH_3^+$ with either cyclopentane or cyclohexane; however, $CoCH_3^+$ is reactive with retention of the integrity of the ring structures. A $Co\text{-}c\text{-}C_5H_7^+$ species is formed which undergoes two H/D exchanges with D_2. $Co\text{-}c\text{-}C_6H_7^+$ undergoes only one H/D exchange while no exchanges are seen for $Fe\text{-}c\text{-}C_6H_7^+$ with D_2. Products corresponding to protonated ferrocene and cobaltocene are generated and readily eliminate a hydrogen atom forming the respective metallocenes in high efficiency upon collisional activation. A lower limit of 84 and 66 kcal/mol is assigned to $D°(Co^+\text{-}c\text{-}C_5H_5)$ and $D°(Fe^+\text{-}c\text{-}C_5H_5)$, respectively.

Introduction

The importance of metallacyclic species in catalytic transformations has prompted several recent studies.[1-10] Few studies involving gas-phase metallacycles, however, have been performed.[11,12] Recently, the gas-phase reactions of the first row group 8 transition-metal ions with cyclic hydrocarbons have been studied in detail by Fourier transform mass spectrometry (FTMS)[12c] and by ion beam techniques.[11c] In these studies, no reaction was observed for ground-state Fe^+, Co^+, and Ni^+ with cyclopropane. With cyclobutane, only C–C bond cleavage processes were observed generating $MC_2H_4^+$ and $MC_4H_6^+$ ions. For cyclopentane and cyclohexane, both C–C and C–H bond cleavages were observed with C–H bond cleavage dominating.

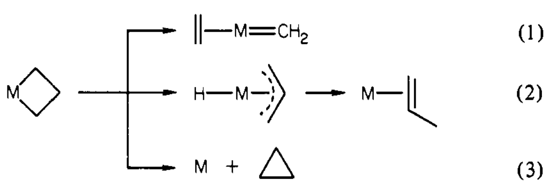
Initial insertion of a metal ion into a C–C bond of a cyclic alkane generates an activated metallacyclic species. Decomposition of these metallacyclic ions has yielded fundamental information on their fragmentation pathways in the absence of ligand and solvent perturbations. As seen in the previous paper in this issue, addition of a ligand (CH_3 or H) to the metal center may vastly alter its reactivity. In this paper we present the results of a study of the reactions of $FeCH_3^+$ and $CoCH_3^+$ with cyclic hydrocarbons.

Experimental Section

The theory, instrumentation, and methodology of ion cyclotron resonance (ICR) spectrometry[13] and Fourier transform mass spectrometry (FTMS)[14] have been discussed elsewhere. All experiments were performed by using a Nicolet prototype FTMS-1000 Fourier transform mass spectrometer previously described in detail.[15] A brief description appropriate for the present work is given in the Experimental Section of our related study of $FeCH_3^+$ and $CoCH_3^+$ with aliphatic alkanes.[16]

Results and Discussion

Reactions with Cyclopropane. Cyclopropane has the strongest C–H bonds (106.3 kcal/mol) of all the alkanes.[17] Due to ring strain, however, the C–C bonds are very weak and should be susceptible to metal insertion. Somewhat surprisingly, no reaction is seen for ground-state Fe^+ and Co^+ with cyclopropane. Insertion of the metal ion across a C–C bond of cyclopropane would generate an activated metallacyclobutane species. Metallacyclobutanes decompose by three basic routes:[18] (a) cleavage of the ring resulting in carbene formation (process 1), (b) β-elimination resulting in formation of propene (process 2), and (c) reductive elimination of cyclopropane (process 3). Decomposition by



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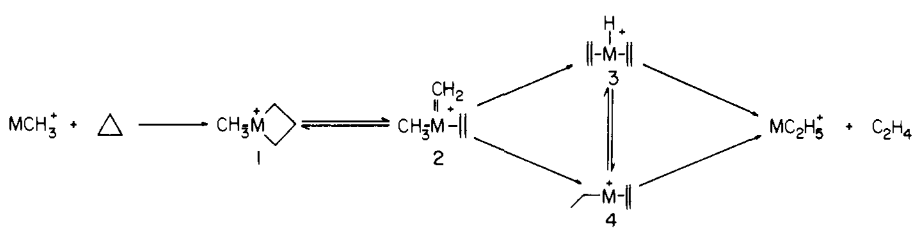
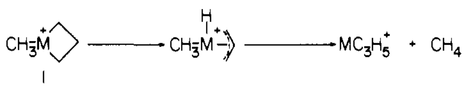
Scheme I



Scheme II



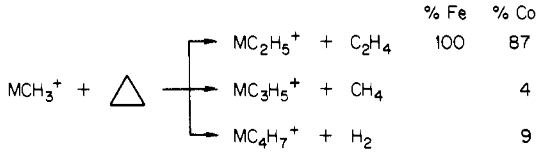
process 1 resulting in ethene elimination is endothermic for reaction of Fe^+ and Co^+ with cyclopropane.[19,20] Conversion of cyclopropane to propene is, however, 8-kcal/mol exothermic and, therefore, the M(propene)$^+$ formed from cyclopropane in process 2 contains 8 kcal/mol more internal energy than required for M^+–propene bond cleavage. As a result, any M(propene)$^+$ so generated will decompose yielding the bare metal ion. Process 3, cyclopropanation, is thermoneutral for cyclopropane and results in regeneration of the bare metal ion. Hence, Fe^+ and Co^+ probably do insert into the C–C bonds of cyclopropane; however, the only energetically accessible processes result in regeneration of the metal ions.

Armentrout and Beauchamp[11a,c] have demonstrated that kinetically excited Co^+ reacts with cyclopropane producing predominantly $CoCH_2^+$ (reaction 4). This reaction is believed to

(4)

proceed through initial oxidative addition of Co^+ across a C–C bond forming a cobaltacyclobutane ion. This is followed by rearrangement to a carbene–ethene complex as in process 1 with elimination of ethene.

While Fe^+ and Co^+ do not react with cyclopropane, $FeCH_3^+$ and $CoCH_3^+$ yield reactions 5–7. Nearly complete H/D scrambling is observed for $MC_2H_5^+$ generated from MCD_3^+ (reactions 8–11), where the deuterium distribution for total scrambling is given in parentheses. A mechanism for the formation of the $MC_2H_5^+$ ions is presented in Scheme I. Initial oxidative addition across a C–C bond of cyclopropane generates the metallacyclobutane intermediate **1**. The metallacyclobutane intermediate **1** may be in equilibrium with the ethene–carbene complex **2** (olefin metathesis),[1-3] however, conversion to the hydrido–bis(ethene) complex **3** or the ethyl–ethene complex **4** is irreversible. Rapid equilibrium between the ethyl–ethene complex **4** and the hydrido–bis(ethene) complex can account for the observed H/D scrambling. Elimination of ethene generates $MC_2H_5^+$. The driving force for this reaction appears to be the coupling of carbene to methyl.[21]



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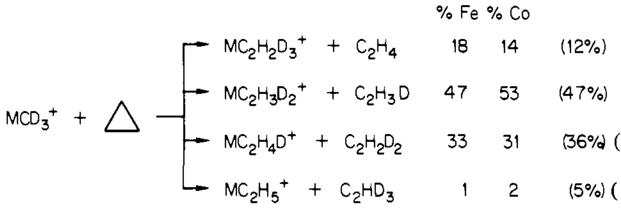

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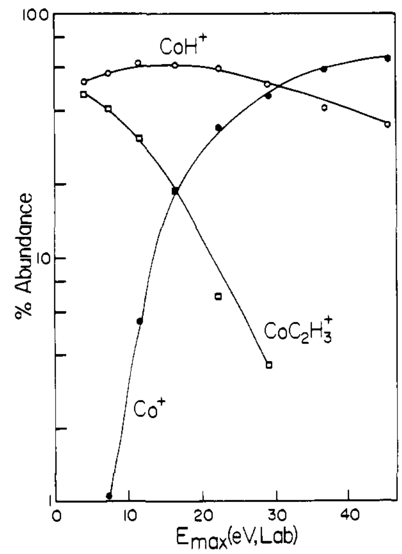

Figure 1. Distribution of CID product intensities vs. kinetic energy for $CoC_2H_5^+$ ions formed in reaction 5.

Reaction 6 may proceed by β-hydride abstraction from the methyl–metallacyclobutane species resulting in elimination of methane (Scheme II). Recently, β-elimination (process 2) was found to be considerably more facile for cobaltacyclobutane ions than for ferracyclobutane ions,[12d] and this is consistent with the absence of reaction 6 for $FeCH_3^+$. Reaction 7 probably proceeds via incorporation of methyl into the C_3H_6 framework followed by dehydrogenation.

The variation of fragment ion abundance vs. kinetic energy for CID of $CoC_2H_5^+$ generated in reaction 5 is shown in Figure 1. Elimination of H_2, C_2H_4, and C_2H_5 is all observed. Formation of CoH^+ may proceed by both direct loss of C_2H_4 and sequential elimination of H_2 and C_2H_2. In contrast, the corresponding $FeC_2H_5^+$ species eliminates C_2H_4 at low energy with some C_2H_5 loss observed at high energy. In addition, the $MC_2H_5^+$ ions react with water resulting in displacement of C_2H_4 (reaction 12).

$$MC_2H_5^+ + H_2O \rightarrow M(H_2O)H^+ + C_2H_4 \qquad (12)$$

Finally, $CoC_2H_5^+$ undergoes five H/D exchanges in the presence of excess deuterium, while no exchanges are observed for $FeC_2H_5^+$. Not all metal hydride species are observed to undergo H/D ex-

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[19] This process is calculated to be 7-kcal/mol endothermic for Co^+ and 4-kcal/mol exothermic for Fe^+ using $D°(Co^+–CH_2) = 85 \pm 7$ kcal/mol from ref 11a. $D°(Fe^+–CH_2) = 96 \pm 5$ kcal/mol from: Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6501.

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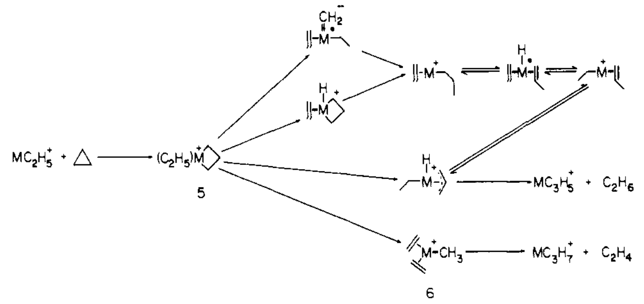
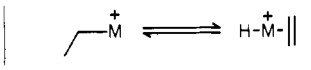
Scheme III

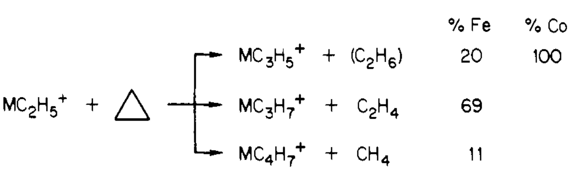


change. For example, FeD^+ does not undergo exchange with H_2.[22] Thus, despite lack of H/D exchange for $FeC_2H_5^+$, these results indicate that the ethyl complex is in equilibrium with the hydrido–ethene species (process 13).[23]



(13)

$FeC_2H_5^+$ generated in reaction 5 yields three products with cyclopropane (reactions 14–16), whereas $CoC_2H_5^+$ yields only



(14)

(15)

(16)

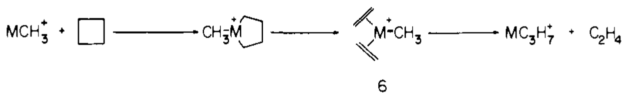
$CoC_3H_5^+$ (reaction 14). This is in contrast to the MCH_3^+ reactions described above. The reactive $MC_2H_5^+$ species may be either the ethyl complex or the hydrido–ethene structure; however, the ethyl species is probably the more reactive form. A mechanism for formation of $MC_3H_5^+$ and $MC_3H_7^+$ is presented in Scheme III and involves initial insertion into a C–C bond of cyclopropane forming intermediate **5**. Cleavage of the ring forming a carbene species followed by a β-hydrogen shift from the C_2H_5 portion results in formation of a bis(ethene)–methyl complex **6**. Elimination of C_2H_4 yields $MC_3H_7^+$ which may dehydrogenate generating $MC_3H_5^+$. Alternatively, $MC_3H_5^+$ may be formed by insertion of CH_2 into the C_2H_5 ligand generating a propyl–ethene species. Reductive elimination of ethane then occurs by sequential β-hydrogen shifts from the propyl ligand. The propyl–ethene intermediate may also be generated by insertion of hydrogen directly into the metallacyclobutane ring. Another route to $MC_3H_5^+$ formation involves β-hydrogen abstraction from the metallacyclobutane ring followed by elimination of C_2H_6. This latter process seems unlikely for $FeC_2H_5^+$ since the corresponding process for $FeCH_3^+$ is not observed. Other mechanisms may also be involved in $MC_3H_5^+$ formation. Formation of $FeC_4H_7^+$ probably involves some form of C–C bond formation between the ligands prior to CH_4 elimination.

The CID spectra of $CoC_3H_5^+$ produced in reaction 14 are identical (same peaks, intensities, and energy dependence within experimental error) with that for Co(allyl)$^+$.[16] The intensity of the corresponding $FeC_3H_5^+$ was too low for its structure to be studied by CID; however, it probably also consists of Fe(allyl)$^+$. CID of $FeC_3H_7^+$ formed in reaction 15 yields predominantly C_2H_4 elimination ($FeCH_3^+$ formation) with *no* dehydrogenation generating $FeC_3H_5^+$ observed. In addition, water displaces C_2H_4 from these $FeC_3H_7^+$ ions (reaction 17). These results are consistent

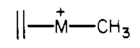
$$FeC_3H_7^+ + H_2O \rightarrow Fe(CH_3)(H_2O)^+ + C_2H_4 \qquad (17)$$

with formation of a methyl–ethene complex 7 in reaction 15. This

Scheme IV



structure is distinguishable from M(propyl)$^+$ ions which upon collisional activation lose predominantly H_2.[16,24]

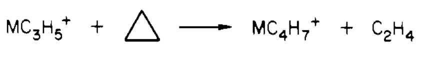


$$||-\overset{+}{M}-CH_3$$

7

$CoCH_3^+$ reacts with ethene to form $CoC_3H_5^+$ exclusively, while no reaction is seen for $FeCH_3^+$. This indicates that a methyl–ethene intermediate is not involved in $FeC_3H_5^+$ formation in reaction 14, but it may be involved in $CoC_3H_5^+$ formation.

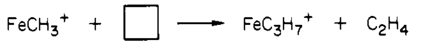
The product of reaction 14, $MC_3H_5^+$, generates only one product with cyclopropane (reaction 18). This may be formed



(18)

by a process similar to Scheme I whereby $MC_3H_5^+$ inserts into a C–C bond of cyclopropane followed by ring cleavage and C_2H_4 elimination. Unfortunately, structural studies on $MC_4H_7^+$ were inconclusive due to its low abundance. Incorporation of carbene into the C_3H_5 framework, however, seems likely.

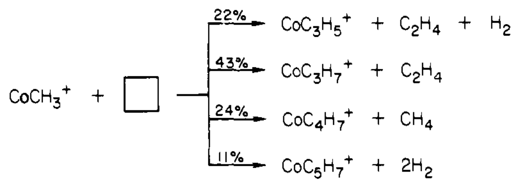
Reactions with Cyclobutane. $FeCH_3^+$ reacts with cyclobutane yielding only one ion, $FeC_3H_7^+$ (reaction 19). $FeCD_3^+$ yields complete retention of the lable in the ion product when reacted with cyclobutane. Water reacts with the product of reaction 19



(19)

by displacing C_2H_4 in analogy to reaction 17. Water also displaces C_2H_4 from $FeC_3H_4D_3^+$, generated by reaction of $FeCD_3^+$ with cyclobutane. Furthermore, $FeC_3H_7^+$ yields $FeCH_3^+$ in high yield upon collisional activation with no $FeC_3H_5^+$ observed. These results indicate that a methyl–ethene complex **7** is formed in reaction 19. A mechanism for reaction 19 is presented in Scheme IV. Initially, $FeCH_3^+$ oxidatively inserts into a C–C bond forming a metallacyclopentane intermediate. Symmetric ring cleavage occurs followed by elimination of C_2H_4 forming $FeC_3H_7^+$.[25] This $FeC_3H_7^+$ ion is unreactive with cyclobutane.

Four products are seen in the reactions of $CoCH_3^+$ with cyclobutane (reactions 20–23). The product of reaction 21,



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(23)

$CoC_3H_7^+$, reacts with water by displacement of C_2H_4 and, in addition, $CoCD_3^+$ generates a $CoC_3H_4D_3^+$ product similar to that for $FeCD_3^+$ with water displacing only C_2H_4. Hence, the $CoC_3H_7^+$ structure is concluded to be the same as that for $FeC_3H_7^+$, a methyl–ethene complex 7, and can be formed by the process outlined in Scheme IV. This is in contrast to $CoC_3H_7^+$ produced from propane where an intact C_3 ligand is bound to Co^+ consisting of either a propyl or a hydrido–propene complex.[16] $CoC_3H_5^+$, produced in reaction 20, may be generated by initial formation

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(22) Carlin, T. J.; Sallans, L.; Cassady, C. J.; Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.*, **1983**, *105*, 6230.

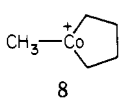
(23) Further evidence for this equilibrium is that H/D exchange is seen for reactions of FeH^+ with C_2D_4 and for MD^+ (M = Fe, Co, Ni) with C_2H_4; see, for example, ref. 21. Also see: Halle, L. F.; Klein, F. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* in press.

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

(25) Metallacyclopentanes decompose in solution by symmetric ring cleavage, by β-hydride elimination, and by reductive elimination of cyclobutane. (b) Grubbs, R. H.; Miyashita, A. "Fundamental Research in Homogeneous Catalysis"; Tsutsui, M., Ed.; Plenum Press: New York, 1979; Vol. 3, p 151. (c) Grubbs, R. H., Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 2418. (c) Grubbs, R. H.; Miyashita, A.; Liu, M.; Burk, P. L. *Ibid.* **1977**, *99*, 3863. (d) Grubbs, R. H.; Miyashita, A. *Ibid.* **1978**, *100*, 7416. (e) Braterman, P. S. *J. Chem. Soc., Chem. Commun.* **1979**, 70. (f) Mckinney, R. J.; Thorn, D. L.; Hoffmann, R.; Stockis, A. *J. Am. Chem. Soc.* **1981**, *103*, 2595. (g) McDermott, J. X.; White, J. F.; Whitesides, G. M. *Ibid.* **1976**, *98*, 6521. (h) McDermott, J. X.; Wilson, M. E., Whitesides, G. M. *Ibid.* **1976**, *98*, 6529.

of $CoC_3H_7^+$ (structure **7**). If **7** retains sufficient internal energy, then dehydrogenation can occur forming a Co(allyl)$^+$ complex.

$CoC_4H_7^+$, formed in reaction 22, may be generated by initial formation of intermediate **8**. β-Hydride transfer results in CH_4



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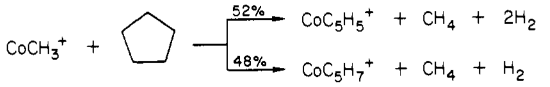
9

loss leaving **9** which probably rearranges to a methallyl complex by a β-hydride shift.[25] Loss of CD_3H is observed when $CoCD_3^+$ is used providing further evidence for this mechanism. Formation of $CoC_5H_7^+$ probably proceeds through incorporation of CH_3 into the carbon framework followed by dehydrogenations.

Both Fe^+ and Co^+ react with cyclobutane by initial insertion into a C–C bond generating an activated metallacyclopentane species.[11c,12c,d] This activated species decomposes by symmetric ring cleavage (C_2H_4 elimination) and dehydrogenation. For Co^+, dehydrogenation dominates over ethene loss 80% to 20% in contrast to Fe^+ where ethene elimination dominates over dehydrogenation 95% to 5%. Addition of a methyl ligand to Fe^+ or Co^+ appears to enhance decomposition by symmetric ring cleavage over dehydrogenation as exemplified by $CoCH_3^+$, where at least 62% of the reaction processes proceed by symmetric ring cleavage, and $FeCH_3^+$, where 100% of the reaction proceeds in this fashion.

Secondary reactions are seen for both $CoC_3H_5^+$ and $CoC_4H_7^+$. Both react with cyclobutane by abstracting C_2H_4. This probably proceeds through oxidative addition across a C–C bond, symmetric ring cleavage, and elimination of C_2H_4.

Reactions with Cyclopentane and Cyclopentene. No reaction is observed for $FeCH_3^+$ with cyclopentane, while $CoCH_3^+$ generates two products with cyclopentane (reactions 24 and 25).



(24)

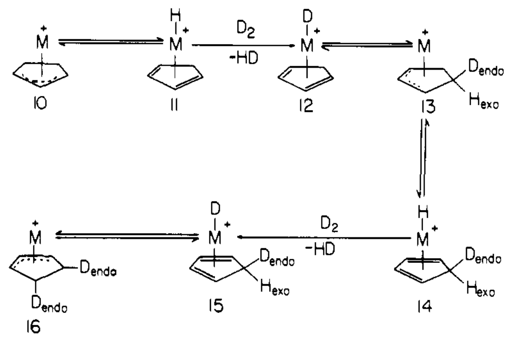
(25)

$CoCD_3^+$ reacts with complete loss of the label from the ion products. The product of reaction 24 loses C_5H_5 as the only fragmentation under collisional activation in relatively low efficiency. The product of reaction 25 readily dehydrogenates at low collision energy with some loss of C_5H_7 observed at high collision energies. These results indicate that Co(cyclopentadienyl)$^+$ and Co(cyclopentenyl)$^+$ are generated in reactions 24 and 25, respectively.[12c,d] Observation of reactions 24 and 25 implies $D°$ (Co^+-c-C_5H_5) > 84 kcal/mol and $D°$ (Co^+-c-C_5H_7) > 65 kcal/mol.[20] Co^+ reacts with cyclopentane both by C–H bond insertion (42%) and C–C bond insertion (58%) while Fe^+ reacts predominantly by C–H bond insertion.[11c,12c,d] The effect of the additional CH_3 group on reactivity is analogous to what was observed for the aliphatic alkanes. $CoCH_3^+$ inserts exclusively into C–H bonds of cyclopentane, and $FeCH_3^+$ is unreactive.

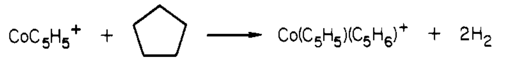
Two H/D exchanges are observed for Co-c-$C_5H_7^+$ in the presence of excess deuterium, while none are seen for Co-c-$C_5H_5^+$. A proposed mechanism for H/D exchange with Co-c-$C_5H_7^+$ is presented in Sheme V and invokes a rapid equilibrium between the cyclopentenyl complex **10**, and the hydrido–cyclopentadiene complex **11**. Oxidative addition of deuterium to **11** is followed by reductive elimination of HD forming **12**. Transfer of the deuterium to the ring forms the monodeuterated cyclopentenyl species **13**, with the deuterium in the endo position. Complex **13** is in rapid equilibrium with **12** and **14**. Addition of deuterium to **14** followed by elimination of HD results in the second exchange. Although complexes **15** and **16** are in rapid equilibrium, no further exchanges are possible since only the endo deuteriums are available for transfer to the metal. This suggests that an η^3 to η^1 fluxionality of the cyclopentenyl ligand is not occurring since this would result in scrambling of the endo/exo positions. This result is in contrast to Fe-c-$C_5H_6^+$ and Co-c-$C_5H_6^+$ where complete exchange is observed.[12c,d]

A rhodium allyl complex has been observed to undergo H/D exchange with deuterium.[26] Here, deuterium was postulated to oxidatively add to rhodium and transfer to the ligand, followed by reductive elimination of HD. Four exchanges were observed for the Rh(allyl)$^+$ complex. If a similar mechanism was occurring for the $CoC_5H_7^+$ species, then all seven hydrogens should be exchangeable. In addition, no H/D exchanges are observed for Co(allyl)$^+$.[16]

Scheme V

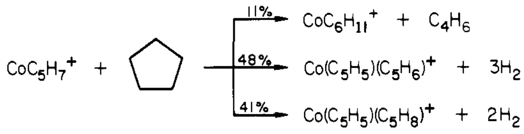


The product of reaction 24, $CoC_5H_5^+$, reacts with cyclopentane yielding only one product (reaction 26). In a related study,



(26)

Ni-c-$C_5H_5^+$ has been reported to dehydrogenate cyclopentane yielding both $Ni(C_5H_5)(C_5H_8)^+$ (49%) and $Ni(C_5H_5)(C_5H_6)^+$ (51%).[26] $CoC_5H_7^+$, produced in reaction 25, yields three products with cyclopentane (reactions 27–29).



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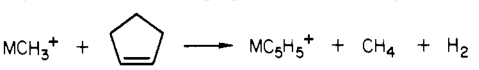
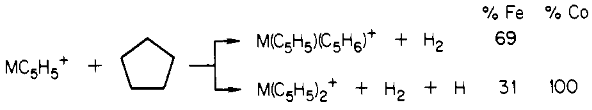
(29)

Both $CoCH_3^+$ and $FeCH_3^+$ form one product with cyclopentene (reaction 30). Observation of reaction 30 implies $D°(Fe^+\text{-c-}C_5H_5)$ > 66 kcal/mol.[20] Loss of C_5H_5 in low efficiency is the only CID



(30)

fragmentation, which is consistent with formation of M-c-$C_5H_5^+$ ions.[12c] The M-c-$C_5H_5^+$, generated in reaction 30, forms two products with cyclopentene (reactions 31 and 32). Only reaction

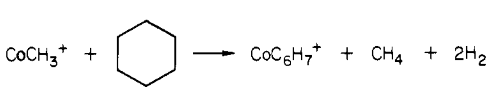


(31)

(32)

31 was observed for $FeC_5H_5^+$ when 5 × 10^{-6} torr of argon collision gas was added to the system; however, little effect was seen for $CoC_5H_5^+$. Apparently the $Fe(C_5H_5)(C_5H_6)^+$ ions formed with enough internal energy to decompose by elimination of H· are sufficiently long lived to permit collisional stabilization. The products of reactions 26, 28, and 31 can be considered simply as protonated metallocenes. Loss of a hydrogen atom is the dominant fragment observed in high efficiency for CID of both $M(C_5H_5)(C_5H_6)^+$ ions forming $M(C_5H_5)_2^+$ along with some loss of C_5H_6 and $C_{10}H_{11}$. This is in contrast to M-c-$C_5H_6^+$ species which only yield loss of C_5H_6 under collisional activation.[12c,27]

Reactions with Cyclohexane and Cyclohexene. Only one product is seen in the reaction of $CoCH_3^+$ with cyclohexane (reaction 33). Again, no reaction is seen for $FeCH_3^+$. However, both $FeCH_3^+$



(33)

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[27] Jacobson, D. B.; Byrd, G. D.; Freiser, B. S. *Inorg. Chem.* **1984**, *23*, 553–557.

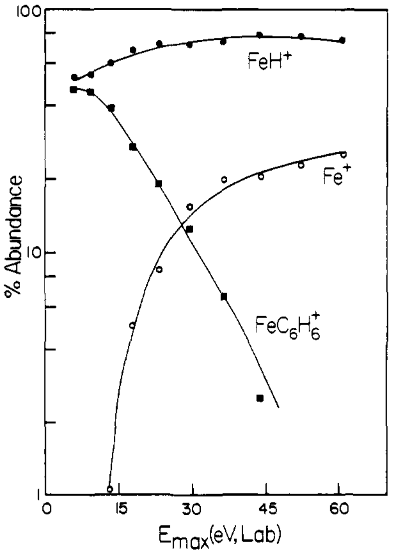
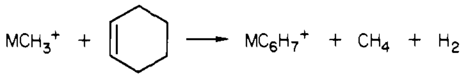


Figure 2. Distribution of CID product intensities vs. kinetic energy for $FeC_6H_7^+$ ions generated in reaction 34.

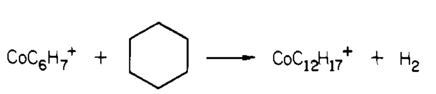
and $CoCH_3^+$ react with cyclohexene generating $MC_6H_7^+$ as the only product (reaction 34). Both $CoC_6H_7^+$ ions generated in reactions 33 and 34 undergo a single rapid H/D exchange with deuterium, while no exchange is seen for the $FeC_6H_7^+$ ions.



(34)

Observation of only one H/D exchange for Co-c-$C_6H_7^+$ suggests that it may be frozen as a hydrido–benzene complex, or that hydrogen scrambling by sigmatropic shifts does not occur for cyclic C_6H_7 bound to Co^+ in contrast to Co-c-$C_5H_6^+$[12c,27] where six H/D exchanges are observed to occur. Loss of H· (or D· for the H/D exchange product) along with some Co^+ formation are the only CID fragmentations observed for the $CoC_6H_7^+$ ($CoC_6H_6D^+$) ions. This implies that $D°(Co^+\text{-c-}C_6H_6) > D°(Co^+\text{–}H) = 52 \pm 4$ kcal/mol.[28] This lower limit is substantiated by the fact that benzene displaces H· exclusively from CoH^+.[21] CID of $FeC_6H_7^+$ yields loss of H·, C_6H_6, and C_6H_7 (Figure 2). Elimination of both H· and C_6H_6 suggests that $D°(Fe^+\text{-c-}C_6H_6) \sim D°\ (Fe^+\text{–}H) = 58 \pm 5$ kcal/mol.[19] FeD^+ reacts with benzene yielding $FeC_6H_6^+$ (31%), $FeC_6H_5D^+$ (52%), and the condensation product $FeC_6H_6D^+$ (17%).[22]

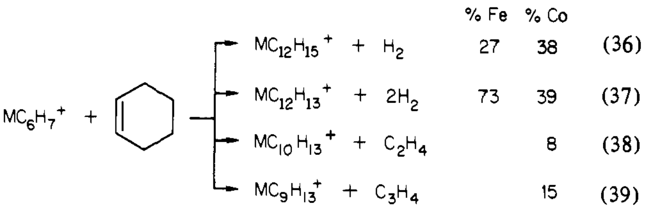
The product of reaction 33, $CoC_6H_7^+$, reacts with cyclohexane yielding H_2 loss exclusively (reaction 35). In addition, the



(35)

deuterated $CoC_6H_6D^+$ reacts with cyclohexane with complete loss of the label. CID of $CoC_{12}H_{17}^+$ yields predominantly formation of $CoC_6H_6^+$ with some Co^+ seen at high energies.

Cyclohexene reacts with the products of reaction 34 yielding reactions 36–39. The product of reaction 37 can be interpreted simply as a protonated dibenzene metal complex. In contrast



to CID of $M(C_5H_5)(C_5H_6)^+$ discussed above, no H· loss is observed for CID of the product of reaction 37 with formation of $MC_6H_6^+$ dominating.

Conclusions

Both $FeCH_3^+$ and $CoCH_3^+$ react with cyclopropane by initial insertion into a C–C bond; however, the corresponding bare metal ions are unreactive with cyclopropane.[11c,12c] The inert behavior of the bare metal ions is attributed to processes which result only in regeneration of the metal ion rather than the lack of C–C bond insertion. Cyclobutane reacts with $FeCH_3^+$ and $CoCH_3^+$ exclusively by initial insertion into C–C bonds. These results are in contrast to aliphatic alkanes and cyclic alkanes larger than cyclobutane where only C–H bond insertion is observed for $CoCH_3^+$, and $FeCH_3^+$ is unreactive. Insertion into the C–C bonds of cyclopropane and cyclobutane is attributed to the weakness of the C–C bonds, arising from ring strain, making them more susceptible to attack.

$FeCH_3^+$ reacts with cyclobutane generating a metallacyclopentane species which decomposes exclusively by symmetric ring cleavage, and this same process dominates for $CoCH_3^+$. The corresponding bare metal ions yield more dehydrogenation products than the metal–methyl ions suggesting that addition of a methyl ligand to metallacyclopentane ions favors decomposition by symmetric ring cleavage over dehydrogenation.

CID and specific ion–molecule reactions were able to yield valuable information on several ion structures. For example, a methyl–ethene complex was distinguishable from a propyl complex. Several secondary reactions are also observed. Of particular interest is the formation of the protonated metallocenes in reactions 26, 28, and 31. CID of these ions yielded elimination of a hydrogen atom forming metallocene ions. Loss of H· may be related to the inherent stability of metallocene ions. In contrast to this behavior, M-c-$C_5H_6^+$ ions lose exclusively C_5H_6 upon CID while protonated bis(benzene) complexes lose (C_6H_7) to form $MC_6H_6^+$. Finally, lower limits of 84 and 66 kcal/mol are assigned to $D°(Co^+\text{-c-}C_5H_5)$ and $D°(Fe^+\text{-c-}C_5H_5)$, respectively.

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Registry No. $FeCH_3^+$, 90143-29-6; $CoCH_3^+$, 76792-06-8; cyclopropane, 75-19-4; cyclobutane, 287-23-0; cyclopentane, 287-92-3; cyclopentene, 142-29-0; cyclohexane, 110-82-7; cyclohexene, 110-83-8.

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