ions (Fe, Co, Ni) decompose in the gas phase upon collisional activation both by symmetric ring cleavage (C_2H_4 elimination) and by dehydrogenation.[29,78,88,89,93,94] In addition, Rh^+ reacts with cyclobutane to generate $RhC_2H_4^+$ as one of the products, presumably by symmetric ring cleavage of an activated rhodacyclopentane species.[30] Finally, the reverse of the above ring expansion process (α-C–C bond cleavage) has been observed for nickelacyclohexanes in solution.[95] Hence, there is support for the ring expansion mechanism as well. It is quite likely, therefore, that both Schemes IV and V play a role in $RhC_2H_4^+$ formation in reaction 34.

Conclusions

The gas-phase chemistry of $RhCH_2^+$ is much richer than that for either $FeCH_2^+$ or $CoCH_2^+$.[27] For example, $RhCH_2^+$ reacts readily with both dihydrogen and methane, whereas the corresponding $FeCH_2^+$ and $CoCH_2^+$ species are inert. In addition, $RhCH_2^+$ yields additional products with both ethene and propene which are not observed for $FeCH_2^+$ and $CoCH_2^+$.

The methylene bond strength, $D^\circ(Rh^+-CH_2)$, was bracketed between 92 and 95 kcal/mol from which $D^\circ(Rh^+-CH_2) = 94 \pm 5$ kcal/mol is assigned. Structural studies clearly indicate that $RhCH_2^+$ consists of a methylidene–rhodium complex, **1**, instead of a hydrido–methylidyne species, **2**. In contrast, thermodynamic considerations suggest that $RhCH_3^+$ consists of a hydrido–methylidene complex, **4**, rather than the methyl species, **5**. In addition, α-hydride abstraction from $(CH_3)_2Rh^+$ appears to be quite facile. The activation barrier for reductive elimination of methane from $Rh(H)(CH_3)^+$ appears to be less than 5 kcal/mol.

The strong Rh^+-CH_2 bond should facilitate olefin methathesis; however, only a small amount is observed. The competing process for olefin metathesis is the facile rearrangement of rhodacyclobutane ion to coordinated propene by β-hydride elimination. This suggests that there is considerable puckering in the unsaturated rhodacyclobutane ring which favors β elimination.

In summary, $RhCH_2^+$ is a very reactive species in the gas phase. The limited results here clearly indicate that further work in this area is warranted.

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Reactions of $FeCH_3^+$ and $CoCH_3^+$ with Aliphatic Alkenes and Alkynes in the Gas Phase

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Abstract: The gas-phase reactions of $FeCH_3^+$ and $CoCH_3^+$ with a variety of alkenes and alkynes are described by using Fourier transform mass spectrometry (FTMS). $FeCH_3^+$ is unreactive with ethene, while $CoCH_3^+$ reacts with ethene to yield the allyl product $CoC_3H_5^+$. This reaction presumably proceeds by initial methyl migratory insertion into coordinated ethene to form a Co(propyl)$^+$ complex which subsequently dehydrogenates. Reactions with alkenes containing labile hydrogens α to the double bond proceed by initial elimination of methane to form an activated π-allyl complex which may subsequently decompose further. Both $FeCH_3^+$ and $CoCH_3^+$ undergo migratory insertion into coordinated butadiene generating a π-pentenyl complex which undergoes dehydrogenation. In addition, both $FeCH_3^+$ and $CoCH_3^+$ appear to insert into ethyne, generating a vinyl species which dehydrogenates to form $MC_3H_3^+$. These results suggest the following order for methyl migratory insertion into C–C multiple bonds: butadiene ~ ethyne > ethene. Decomposition of $M(C_5H_9)^+$ species proceeds by initial skeletal rearrangement to a linear structure followed by dehydrocyclization to generate M-c-$C_5H_5^+$. A stable Co(pentadienyl)$^+$ species was generated and is distinguishable from the corresponding Co(cyclopentenyl)$^+$ complex by H/D exchange with deuterium. Finally, D°(Fe$^+$–pentadienyl) is found to exceed 70 ± 6 kcal/mol and D°(Co$^+$–pentadienyl) exceeds 62 ± 5 kcal/mol.

Transition-metal alkyls[1] have been proposed as intermediates in a variety of important catalytic processes. For this reason transition-metal alkyls have been used as model compounds for homogeneous catalysis.[2] A particularly important process involving metal alkyls is the migratory insertion into carbon–carbon multiple bonds. For example, the catalytic arylation,[3] oligomerization,[4] Ziegler–Natta polymerization,[5] and (in some cases) carboalkoxylation[6] of olefins are believed to involve the insertion of metal–alkyl bonds into C–C double bonds. In addition, the catalytic trimerization[7,8] and (again, in some cases) the carboalkoxylation[6] of acetylenes are postulated to involve the insertion of metal–alkyl bonds into C–C triple bonds.

Due to the importance of these catalytic reactions, considerable effort has been devoted to the search for stoichiometric systems in which such insertions can be observed directly and studied. One such process which, though intensely investigated, still remains

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an enigma is the Ziegler–Natta polymerization of olefins.[5] This process has been proposed to proceed by direct transition-metal–alkyl insertion into olefin bonds,[9] metallacyclopentane intermediates,[10] as well as carbenoid species.[11,12] Olefin insertion into metal–alkyl bonds, typified by reaction 1, has received the most support, although this process has only recently been observed directly for ytterbium and lutetium complexes.[4a] Labeling studies

$$L_nM{-}CH_3 + CH_2{=}CH_2 \rightarrow L_nM{-}CH_2CH_2CH_3 \quad (1)$$

have shown that reaction 1 for ytterbium and lutetium is reversible.[4b] In addition, the reversible alkene insertion into a chelated Pt–alkyl bond has recently been observed.[13]

In the present study the gas-phase reactions of $FeCH_3^+$ and $CoCH_3^+$ with a series of aliphatic alkenes and alkynes are presented. The results are interpreted in terms of alkene and alkyne insertions into the metal–methyl bond as well as other competing processes. Previously, the reactions of both Co^+ [14] and Fe^+ [15] with olefins in the gas phase have been studied in detail. In addition, we have also studied the reactions of $FeCH_3^+$ and $CoCH_3^+$ with both aliphatic alkanes[16] and cyclic hydrocarbons.[17]

Studying the chemistry of gas-phase organometallic fragment ions has proven to yield a variety of information on the fundamental processes which can occur in the absence of complicating ligand and solvent perturbations. For example, both naked cobaltacyclobutane and nickelacyclobutane cations were shown to undergo facile conversion to coordinated propene (presumably through the intermediacy of hydrido–π-allyl species),[18-20] whereas the naked ferracyclobutane cations did not undergo this rearrangement.[21a] Furthermore, reaction of the ferracyclobutane ion with ethene-d_4 yields nearly exclusively C_3H_6 displacement (reaction 2) with only a trace (<5%) of C_2H_4 and $C_2H_2D_2$ eliminations (reactions 3 and 4).[21b] Recent calculations suggest that there is no activation barrier for the interconversion of metallacyclobutanes with the corresponding olefin–alkylidene species.[22]

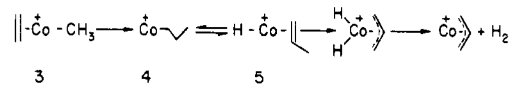
$$FeC_3H_6^+ + C_2D_4 \rightarrow FeC_2D_4^+ + C_3H_6 \quad (2)$$

$$FeC_3H_6^+ + C_2D_4 \rightarrow FeC_3H_2D_4^+ + C_2H_4 \quad (3)$$

$$FeC_3H_6^+ + C_2D_4 \rightarrow FeC_3H_4D_2^+ + C_2H_2D_2 \quad (4)$$

The small amount of C_2H_4 and $C_2H_2D_2$ eliminations (reactions 3 and 4), therefore, suggest that the ferracyclobutane ion is more stable than the corresponding (ethene)(methylidene)Fe^+ species.

Scheme I



As these results demonstrate, a variety of fundamental information about organometallic chemistry can be derived from studying the chemistry of organometallic fragment ions in the gas phase.

Experimental Section

The theory, instrumentation, and methodology of ion cyclotron resonance (ICR) spectrometry[23] and Fourier transform mass spectrometry (FTMS)[24] have been discussed elsewhere. All experiments were performed on a Nicolet prototype FTMS-1000 Fourier transform mass spectrometer previously described in detail[25] 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 supported on the opposite transmitter plate. Metal ions are generated by focussing the beam of a Quanta Ray Nd:YAG laser (frequency doubled to 530 nm) onto a metal foil.[26]

Chemicals were obtained commercially in high purity and used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensable gases. CD_3I (>99.5% D) and C_2D_4 (>99.5% D) were obtained from MSD isotopes (Merck Chemical Division). Hydrocarbon sample pressures were on the order of 1×10^{-7} torr. Argon was used as the collision gas for the collision-induced dissociation (CID) experiments at a total sample pressure of $\sim 5 \times 10^{-6}$ torr.[27] A Bayard–Alpert ionization gauge was used to monitor pressure.

Details of the CID experiments have previously been discussed.[15a,25,28-30] 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 ±5% absolute and yield 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.[31]

The MCH_3^+ ions were formed by reaction of Fe^+ and Co^+ with methyl iodide, reaction 5.[32] The methyl iodide reagent gas was introduced into

$$M^+ + CH_3I \rightarrow MCH_3^+ + I \quad (5)$$

the vacuum chamber through a General Valve Corp. Series 9 pulsed solenoid valve.[33] Both the laser and the valve are pulsed concurrently. The pulsed reagent gas fills the vacuum chamber to a maximum pressure of $\sim 10^{-5}$ torr and is pumped away by a high-speed 5-in. diffusion pump in ~250 ms. The MCH_3^+ ions are then isolated by swept double resonance ejection techniques[24,34] and allowed to react with a static pressure

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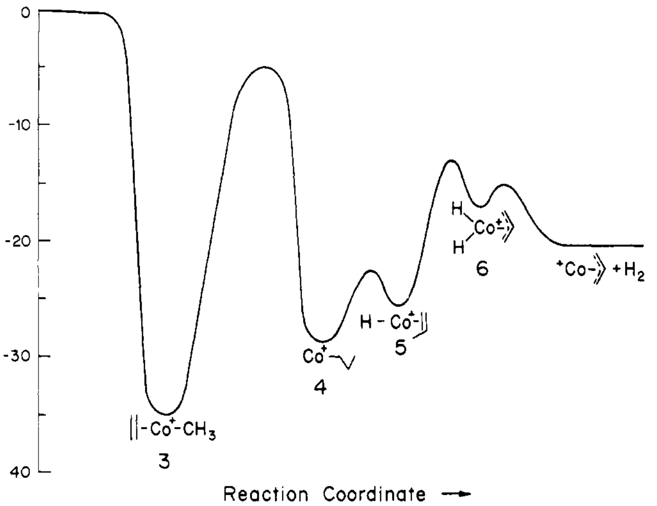


Figure 1. Reaction coordinate diagram for the dehydrogenation of ethene by $CoCH_3^+$. The vertical axis is in kcal/mol.

of a hydrocarbon without complicating reactions with methyl iodide. Product structures were probed by CID, and reaction sequences were delineated by using the highly specific double resonance technique.[24]

Results and Discussion

Reactions with Ethylene. The MCH_3^+ ions have been shown to consist of a rigid metal–methyl structure **1** and not a hydrido–methylidene structure **2**.[16,35] Ethene reacts readily with

$$\overset{+}{\mathrm{M}}\mathrm{{-}CH_3} \qquad \mathrm{H{-}}\overset{+}{\mathrm{M}}\mathrm{{=}CH_2}$$

1 **2**

$CoCH_3^+$ resulting in H_2 elimination, reaction 6, while no reaction is observed with $FeCH_3^+$. The CID spectra of this $CoC_3H_5^+$ ion are identical (same peaks, intensities, and energy dependence)

$$CoCH_3^+ + C_2H_4 \rightarrow CoC_3H_5^+ + H_2 \qquad (6)$$

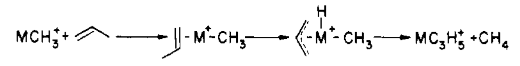
within experimental error to those for $CoC_3H_5^+$ produced in reaction 7, suggesting formation of Co(allyl)$^+$ in reaction 6.[16] Reaction 6 can best be explained by invoking initial migratory

$$CoCH_3^+ + C_3H_8 \rightarrow CoC_3H_5^+ + CH_4 + H_2 \qquad (7)$$

insertion of the methyl to the coordinated ethene to form **4** which dehydrogenates to form Co(allyl)$^+$, Scheme I.

The insertion of an olefin into a metal–alkyl bond has often been postulated but not observed directly.[36] In some cases it has been inferred from the isolation of secondary products which derive from the initial insertion product via such processes as β-hydrogen elimination[37] or further olefin insertion.[38] Only recently has direct insertion of an olefin into a metal–alkyl bond been observed for ytterbium and lutetium complexes.[4a] These insertions are related to the well-known insertion of olefins into metal–hydrogen bonds.[39,40] Other metal–alkyl migratory insertions are also known, including the well-characterized carbonyl/alkyl,[41] alkylidene/alkyl,[42–44] and nitrosyl/alkyl[45] insertions.

Scheme II



Although ethene insertion into the Co–CH_3^+ bond is not observed directly, the product is strongly suggestive of initial migratory insertion as shown in Scheme I vide supra. Reaction of ethene with $CoCD_3^+$ yields dehydrogenation as H_2(26%), HD(64%), and D_2(10%). This is close to the predicted H_2:HD:D_2 ratio of 2:4:1 for complete scrambling prior to dehydrogenation. This scrambling can be rationalized by invoking a rapid equilibrium between **4** and **5** in Scheme I, which has previously been suggested for reaction of CoD^+ with propene,[46] providing further evidence for the initial migratory insertion. In a related study, $CH_3TiCl_2^+$ reacts with ethene in the gas phase to form $C_3H_5TiCl_2^+$,[47] presumably an allylic species. Both the $CoC_3H_5^+$ and $C_3H_5TiCl_2^+$ species are unreactive with ethene, suggesting that dehydrogenation may, therefore, be viewed as a possible termination mechanism for Ziegler–Natta olefin polymerization.

A crude reaction coordinate diagram for dehydrogenation of ethene by $CoCH_3^+$ is shown in Figure 1. Ethene coordination results in formation of species **3** which has roughly 35 kcal/mol excess energy.[48] Migratory insertion of ethene into the Co–methyl bond generates **4** which retains ~28 kcal/mol excess energy.[49] Sequential β-hydride shifts resulting in dehydrogenation yield $CoC_3H_5^+$. This overall process is roughly 22 kcal/mol exothermic.[51] Conversion of **4** to **5** appears to have a small activation energy relative to **5** to **6** conversion. This is based on several lines of evidence. First, olefin insertion into metal–hydride bonds is both rapid and reversible[52] and, therefore, has low activation barriers (~5 kcal/mol).[53] Further indication of the low barrier for conversion of **4** to **5** is the dominance of H_2 elimination for reaction of CoD^+ with propene.[46] A larger barrier for conversion of **5** to **6** is assigned because H/D exchange of Co(propene)$^+$ with C_2D_4 is slow.[19b] No $CoCH_2D^+$ or $CoCHD_2^+$ is observed for reaction of $CoCD_3^+$ with ethene which could be generated by β-methyl abstraction from the H/D scrambled alkyl species **4**.

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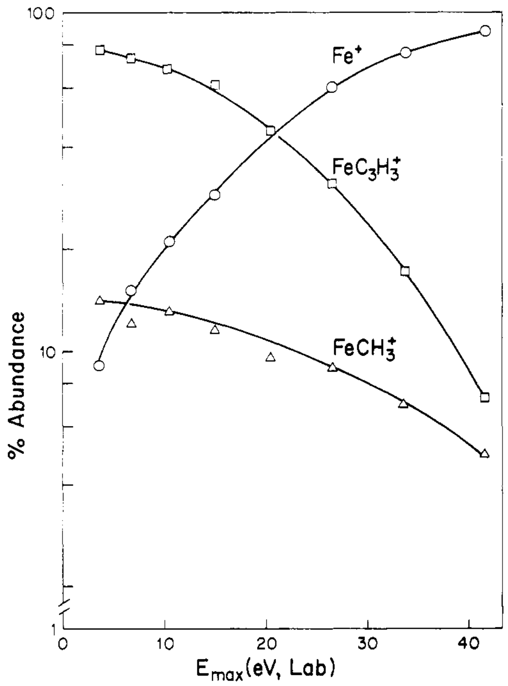


Figure 2. Variation of CID product ion intensities as a function of kinetic energy for $FeC_3H_5^+$ formed in reaction 8.

This suggests that the barrier for β-methyl abstraction from **4** is greater than the overall barrier for dehydrogenation from **4**. Hence, the barrier for migratory insertion of ethene into the Co^+–methyl bond is assigned as ~25–35 kcal/mol. Absence of reaction 6 for both $FeCH_3^+$ and $FeCD_3^+$ with ethene implies an activation barrier for ethene insertion into $Fe–CH_3^+$ in excess of ~35 kcal/mol. Reaction of FeH^+ with propene yields approximately 17% $FeCH_3^+$.[46] This can best be explained by invoking a β-methyl abstraction from an Fe(*n*-propyl)$^+$ intermediate which places an upper limit for migratory insertion of ethene into $Fe^+–CH_3$ of ~55 kcal/mol.[54]

β-Alkyl transfers have previously been proposed for reaction of Fe^+ with labeled alkanes.[55] The larger barrier for β-methyl abstraction from the M(*n*-propyl)$^+$ species vide supra coupled with the lower barrier for β-H abstractions from M(alkyl)$^+$ species, however, suggests that other processes may indeed be responsible for the products in that study.

Finally, α-hydride abstractions from metal–alkyls have been observed in solution.[56,57] No H/D exchanges, however, were observed for reactions of MCD_3^+ (M = Fe and Co) with ethene[58] to yield MCD_2H^+, $MCDH_2^+$, and MCH_3^+ ions. This suggests that activation by ethene coordination (~35 kcal/mol) is not sufficient to induce α-hydride abstraction from the MCD_3^+ species. Therefore, there is a substantial barrier to α-hydride abstraction for MCH_3^+.

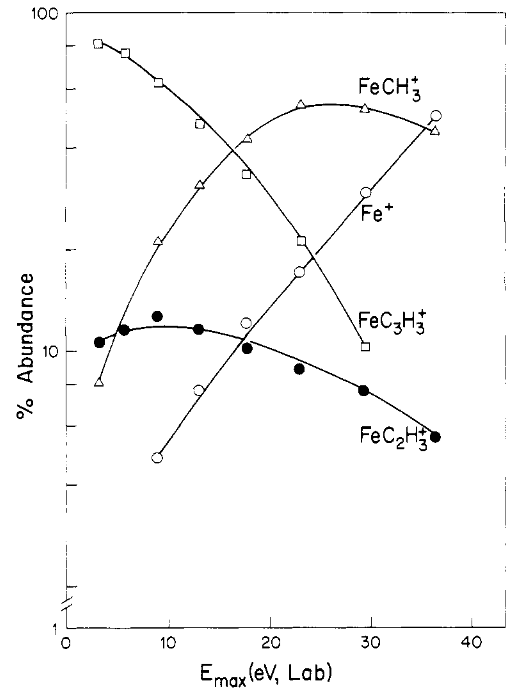
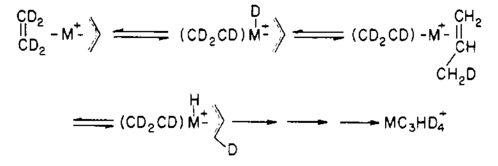
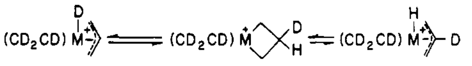


Figure 3. Variation of CID product ion intensities as a function of kinetic energy for $FeC_4H_7^+$ formed in reaction 9.

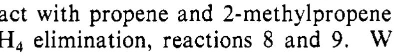
Scheme III



Scheme IV



Reactions with Propene and 2-Methylpropene. $FeCH_3^+$ and $CoCH_3^+$ react with propene and 2-methylpropene to yield exclusively CH_4 elimination, reactions 8 and 9. With MCD_3^+, methane is eliminated exclusively as CD_3H. These results indicate


(8)


(9)

that allylic hydrogen abstraction from alkenes resulting in methane elimination and formation of π-allyl complexes (Scheme II) is much more facile than insertion of the olefin into the metal–methyl bond. The formation of hydrido–π-allyl metal complexes is well supported in solution[59,60] and matrix isolation studies[61] and has precedent in the gas-phase metal ion work.[21b,62] Finally, $CH_3Co(PPh_3)_3$ has been observed to react with 2,3-dimethyl-2-butene and 1-hexene, resulting in methane elimination and formation of π-allyl cobalt complexes.[63]

The variation of product ion abundances as a function of kinetic energy for CID of $FeC_3H_5^+$ and $FeC_4H_7^+$ formed in reactions 8 and 9 are shown in Figures 2 and 3, respectively. The CID spectra of $CoC_3H_5^+$ (reaction 8) and $CoC_4H_7^+$ (reaction 9) are identical (same peaks, intensities, and energy dependence within experi-

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[54] This is based on $D°(Fe^+–H) = 59 \pm 5$ kcal/mol from the following: Halle, L. F.; Klein, F. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 2543. $D°(Fe^+–CH_3) = 69 \pm 5$ kcal/mol from ref 35b; and the heats of formation are from ref 50. Again, $D°$(Fe$^+$–*n*-propyl) is assumed to ~2 kcal/mol greater than $D°(Fe^+–CH_3)$.

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[58] FeD^+ and CoD^+ react rapidly with ethene to yield FeH^+ and CoH^+, respectively. (a) Halle, L. F.; Klein, F. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 2543. (b) Reference 46.

[59] (a) Tulip, T. H.; Ibers, J. H. *J. Am. Chem. Soc.* **1979**, *101*, 4201. (b) Scherman, E. O.; Scheiner, P. R. *J. Chem. Soc., Chem. Commun.* **1978**, 223.

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[63] D'yachkovskii, F. S.; Khrushch, N. E.; Shilov, A. E. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1970**, *40*, 1712.

Table I. Distribution of Neutral(s) Lost for Reactions of $FeCH_3^+$ and $CoCH_3^+$ with Aliphatic Olefins

olefin	MCH_3^+	H_2	$2H_2$	CH_4	H_2 + CH_4	$2H_2$ + CH_4	C_2H_4	CH_4 + C_2H_4	C_2H_6	C_2H_6 + H_2	C_2H_6 + $2H_2$	CH_4 + C_3H_6
		% neutral(s) lost										
ethene	$FeCH_3^{+a}$											
	$CoCH_3^+$	100										
propene	$FeCH_3^+$			100								
	$CoCH_3^+$			100								
2-methylpropene	$FeCH_3^+$			100								
	$CoCH_3^+$			100								
1-butene	$FeCH_3^+$			100								
	$CoCH_3^+$			100								
1,3-butadiene	$FeCH_3^+$	93	7									
	$CoCH_3^+$	10	75				15					
1-pentene	$FeCH_3^+$				100							
	$CoCH_3$				87	6		7				
1-hexene	$FeCH_3^+$			18	39			32		9		2
	$CoCH_3^+$			12	20	4		50	2	3	3	6
2-methyl-1-butene	$FeCH_3^+$			64	27			9				
	$CoCH_3^+$			55	25			20				
3-methyl-1-butene	$FeCH_3^+$			59	33			8				
	$CoCH_3^+$			45	33			22				
2-methyl-2-butene	$FeCH_3^+$			66	28			6				
	$CoCH_3^+$			48	34			18				
2,3-dimethyl-1-butene	$FeCH_3^+$			48	30			6				16
	$CoCH_3^+$			30	37	11		4				18
2,3-dimethyl-2-butene	$FeCH_3^+$			56	23			7				14
	$CoCH_3^+$			36	35	7		6				16
3,3-dimethyl-1-butene	$FeCH_3^+$			7	12			6	72			3
	$CoCH_3^+$			11	13	6		50	7	5		8

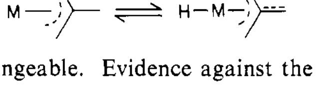
[a] No reaction observed.

mental error) with that for Co(allyl)$^+$ and Co(2-methallyl)$^+$ [16] and are also very similar to that for the corresponding iron species.

Both $MC_3H_5^+$ and $MC_4H_7^+$ species are unreactive with ethene. $FeC_3H_5^+$ undergoes 4 slow H/D exchanges with ethene-d_4, whereas $CoC_3H_5^+$ undergoes 5 slow exchanges. A mechanism for the exchanges for $FeC_3H_5^+$ is outlined in Scheme III and involves initial insertion across a vinylic C–H bond. This is followed by exchange of the 4 terminal allylic hydrogens with the central hydrogen unexchangeable. A similar mechanism has been invoked for observation of 4 exchanges of a CpRh(allyl)$^+$ species with D_2.[64] Both Fe(allyl)$^+$ and Co(allyl)$^+$ yield no exchanges with D_2. A mechanism for exchange of the 5th central allyl hydrogen for $CoC_3H_5^+$ is presented in Scheme IV and involves formation of a cobaltacyclobutane intermediate which undergoes reformation of a hydridoallyl species. Conversion of hydrido–π-allyl complexes to metallacyclobutanes has been proposed as an initiation step for olefin metathesis.[65,66] The reverse process is well supported in solution-phase studies.[18,19,65]

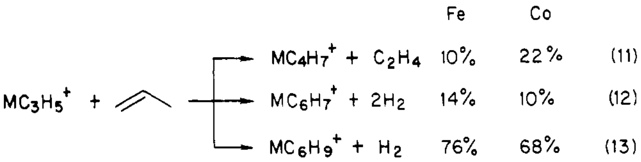
Scheme III predicts that dehydrogenation of ethene by the M(allyl)$^+$ species producing an (ethyne)M(allyl)$^+$ complex may be competitive with the H/D exchanges. The fact that this is not observed suggests that the overall process is endothermic, implying $D°(M(allyl)^+–C_2H_2) < 43$ kcal/mol.[50] For comparison $D°(Co(allyl)^+–C_2H_4)$ exceeds 33 kcal/mol.[16]

Both $FeC_4H_7^+$ and $CoC_4H_7^+$ produced in reaction 9 undergo 7 slow H/D exchanges with ethene-d_4 while no exchanges are seen with D_2. These exchanges may be occurring by processes analogous to that for $M(C_3H_5)^+$ in Scheme III. Alternatively, the following equilibrium may contribute to the exchanges where the hydride species undergoes exchange. Both processes yield all seven hydrogens exchangeable. Evidence against the equilibrium in reaction 10 is twofold. First, Co$^+$ dehydrogenates 2-methylpropene to produce exclusively the rearrangement product Co(butadiene)$^+$ [67] while Fe$^+$ is unreactive with 2-methylpropane.[15a] Second, the H/D exchanges for both $M(C_3H_5)^+$ and $M(C_4H_7)^+$ species are slow and occur at roughly the same rate. Therefore, the H/D exchanges for the $MC_4H_7^+$ ions are believed to proceed by processes similar to those outlined in Scheme III.



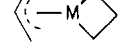
(10)

In contrast to ethylene, $MC_3H_5^+$ ions are reactive with propene.

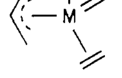


(11)
(12)
(13)

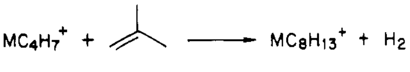
Reaction 11 may proceed by reversible β-hydride shifts resulting in formation of the metallacyclobutane species 6 similar to that for Scheme IV. The metallacyclobutane species can then rearrange to an ethylene–methylidene complex, 7, followed by ethylene elimination (olefin metathesis).[68] The driving force for ethylene elimination in reaction 11 may be an irreversible methylene coupling to the allyl. Olefin metathesis has been observed for reactions of $FeCH_2^+$ and $CoCH_2^+$ with olefins in the gas phase.[69] The dehydrogenation reactions 12 and 13 may proceed by an initial coupling of the ligands forming a metal–cyclohexyl species which subsequently dehydrogenates. In contrast to the above results, 2-methylpropene yields exclusively dehydrogenation with $MC_4H_7^+$ (formed in reaction 9), reaction 14.



6



7



(14)

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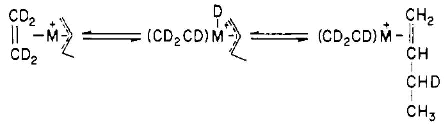
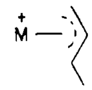
Scheme V



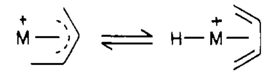
Reaction with 1-Butene and 1,3-Butadiene. Both $FeCH_3^+$ and $CoCH_3^+$ react with 1-butene to yield exclusively elimination of methane (Table I). Methane is eliminated exclusively as CD_3H for reaction of MCD_3^+ with 1-butene generating $MC_4H_7^+$ for which Scheme II predicts structure **8**. Collisional activation of $FeC_4H_7^+$ formed from 1-butene yields elimination of C_2H_4, C_4H_6, and C_4H_7 with C_4H_6 elimination dominating at intermediate to high energy. This fragmentation pattern is distinguishable from that for $FeC_4H_7^+$ produced in reaction 9 (Figure 3). The CID spectra for $CoC_4H_7^+$ produced above is identical (same peaks, intensities, and energy dependence within experimental error) with that for Co(1-methallyl)$^+$ reported previously.[16] Elimination of C_4H_6 probably proceeds through a hydrido–butadiene intermediate. Complete absence of H· loss generating $FeC_4H_6^+$ implies $D°(Fe^+\text{–butadiene}) < D°(Fe^+\text{–H}) = 59 \pm 5$ kcal/mol.[54] A photodissociation threshold near 570 nm has been observed for process 15,[70] implying $D°(Fe^+\text{–butadiene}) \sim 50 \pm 5$ kcal/mol which is consistent with the above CID results. For comparison, $D°(Co^+\text{–butadiene}) < D°(Co^+\text{–H}) = 52 \pm 4$ kcal/mol.[16,35a]



8

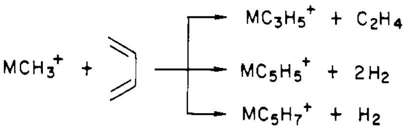
$$FeC_4H_6^+ + h\nu \rightarrow Fe^+ + C_4H_6 \qquad (15)$$

Co(1-methallyl)$^+$ undergoes 5 slow H/D exchanges with D_2. This can be rationalized by invoking the following equilibrium, where exchange occurs with the hydrido–butadiene species. The corresponding Fe(1-methallyl)$^+$ species does not undergo exchange with D_2. This observation, however, does not rule out the equilibrium in reaction 16 since not all iron–hydride species undergo exchange.[46,58] With ethene-d_4, the $MC_4H_7^+$ species undergoes 5 rapid exchanges followed by 2 slower exchanges. The 5 rapid exchanges can proceed by the equilibrium in reaction 16. The two slow subsequent exchanges may proceed by the process outlined in Scheme V.



(16)

1,3-Butadiene reacts readily with the MCH_3^+ species to yield reactions 17–19. Reaction 19 dominates for $FeCH_3^+$ with reaction 18 dominating for $CoCH_3^+$. The $MC_5H_7^+$ ions readily dehydrogenate upon collisional activation to form $MC_5H_5^+$. CID of $MC_5H_5^+$, generated either from CID of $MC_5H_7^+$ or by reaction 18, yields only C_5H_5 elimination in low effeciency, suggesting formation of M(cyclopentadienyl)$^+$. These results suggest initial insertion of methyl into butadiene to form **9**, a linear pentenyl species[72] which subsequently undergoes dehydrocyclization to generate M(cyclopentadienyl)$^+$. Dehydrocyclization of a Co(pentenyl)$^+$ species to form Co(cyclopentadienyl)$^+$ has previously been observed in the gas phase.[16]



(17)
(18)
(19)

9

It is interesting to note that migratory insertion of a methyl into ethene does *not* occur for iron vide supra. The above methyl insertion into butadiene, however, may be driven by the additional energy afforded by butadiene coordination vs. ethene coordination (~50 kcal/mol vs. ~35 kcal/mol).

Reactions with 1-Pentene and 1-Hexene. Reactions of $CoCH_3^+$ and $FeCH_3^+$ with 1-pentene are dominated by $MC_5H_7^+$ formation, reaction 20. With MCD_3^+, methane is eliminated as CD_3H exclusively with no deuterium observed in the ion product. This reaction presumably proceeds by the mechanism outlined in Scheme II for propene, generating an activated M(pentenyl)$^+$ species **9** which subsequently dehydrogenates. This is in contrast to reactions of the corresponding atomic metal ions with 1-pentene where insertion into the allylic C–C bond dominates the chemistry.[14,15] Therefore, addition of a methyl group on Fe^+ or Co^+ dramatically affects their reactivities with larger olefins. This same effect has been observed with $CoCp^+$ (Cp = cyclopentadienyl) where only dehydrogenations are observed with 1-pentene.[74] Formation of $CoC_3H_5^+$ from $CoCH_3^+$ and 1-pentene (Table I) presumably proceeds by initial methane elimination followed by C_2H_4 elimination. The evidence for this is twofold. First, reaction with $CoCD_3^+$ yields no lable in the ionic product. Second, $CoC_3H_5^+$ is observed in the CID spectra of $CoC_5H_9^+$ formed in reaction 21.[16]

(20)

$$CoCH_3^+ + n\text{-pentane} \rightarrow CoC_5H_9^+ + CH_4 + H_2 \qquad (21)$$

$CoC_5H_7^+$ formed in reaction 20 undergoes 7 slow H/D exchanges with deuterium while no exchanges are observed for $FeC_5H_7^+$. These results clearly distinguish the $CoC_5H_7^+$ species from Co-c-$C_5H_7^+$ which undergoes only 2 H/D exchanges with deuterium.[17] The $MC_5H_7^+$ species formed in reaction 20 are, therefore, believed to consist of M(pentadienyl)$^+$ species. Several stable pentadienyl–metal complexes are known;[75,76] however, they are not nearly as numerous as the corresponding cyclopentadienyl analogues. The molecular orbitals of pentadienyl and cyclopentadienyl systems are quite analogous[77] and, in terms of energy considerations, the open system could turn out to possess even stronger metal–ligand bonds. The 7 H/D exchanges for Co(pentadienyl)$^+$ are surprising since Co(allyl)$^+$ does *not* undergo exchange with deuterium.[16] These exchanges may proceed by initial oxidative addition of deuterium to cobalt followed by a variety of reversible hydride migrations.

Both $MC_5H_7^+$ ions produced in reaction 20 undergo facile dehydrogenation to form $MC_5H_5^+$ upon collisional activation with some M^+ observed at high energy. CID of this $MC_5H_5^+$ is identical with that of "authentic" M(cyclopentadienyl)$^+$ species

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(70) Jackson, T. C.; Hettich, R. L.; Freiser, B. S., unpublished results.

(71) M-c-$C_5H_5^+$ ions produced by electron impact on ferrocene and by reaction of Fe^+ and Co^+ with monomeric cyclopentadiene lose C_5H_5 as the only fragmentation in low efficiency upon collisional activation. Jacobson, D. B.; Freiser, B. S., unpublished results.

(72) $CH_3Co(PPh_3)_3$ reacts with 1,3-butadiene presumably forming $(PPh_3)_2$Co(pentenyl). See, for example, ref 63.

(73) Dehydrocyclizations have been observed on metal surfaces. (a) Anderson, J. R. *Adv. Catal.* **1973**, *23*, 1. (b) Clarke, J. K. A.; Rooney, J. J. *Adv. Catal.* **1976**, *25*, 125. (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. Engl. Transl.* **1983**, *52*, 625.

(74) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.*, in press.

(75) (a) Mahler, J. E.; Pettit, R. *J. Am. Chem. Soc.* **1962**, *84*, 1511. (b) Giannini, U.; Pellino, E.; Lachi, M. P. *J. Organomet. Chem.* **1968**, *12*, 551. (c) Rienacker, R.; Yoshiura, H. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 677. (d) Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 678. (e) Yasuda, H.; Yamauchi, M.; Nakamura A.; Sei, T.; Kai, Y.; Yasuoka, N. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1089.

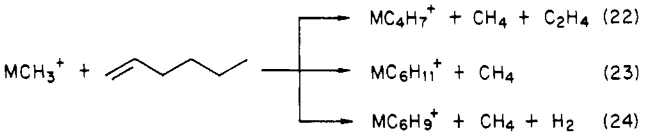
(76) (a) Wilson, D. R.; DiLullo, A. A.; Ernst, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 5928. (b) Wilson, D. R.; Lui, J.-Z.; Ernst, R. D. *J. Am. Chem. Soc.* **1982**, *104*, 1120. (c) Lui, J.-Z.; Ernst, R. D. *J. Am. Chem. Soc.* **1982**, *104*, 3737. (d) Wilson, D. R.; Ernst, R. D.; Cymbaluk, T. H. *Organometallics* **1983**, *2*, 1220. (e) Stahl, L.; Ernst, R. D. *Organometallics* **1983**, *2*, 1229.

(77) Streitwieser, A., Jr. "Molecular Orbital Theory for Organic Chemists"; Wiley: New York, 1961.

where direct loss of C_5H_5 in low efficiency is the only cleavage observed.[71] These results suggest that M(pentadienyl)$^+$ species undergo a facile dehydrocyclization to generate M(cyclopentadienyl)$^+$.[73]

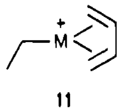
Formation of M(pentadienyl)$^+$ in reaction 20 implies $D°$(Fe–pentadienyl) > 70 ± 6 kcal/mol and $D°$(Co$^+$–pentadienyl) > 62 ± 5 kcal/mol.[78] This compares with $D°$(Fe$^+$–cyclopentadienyl) > 87 ± 6 kcal/mol[69] and $D°$(Co$^+$–cyclopentadienyl) = 85 ± 5 kcal/mol.[74]

Reaction of MCH_3^+ with 1-hexene yields a richer chemistry than with 1-pentene (Table I), but upon close examination it can be easily explained. The dominant process is $MC_4H_7^+$ formation, reaction 22. With MCD_3^+, no lable appears in the ionic product. The CID spectra of these $MC_4H_7^+$ ions are identical (same peaks, intensities, and energy dependence) within experimental error with that for M(1-methallyl)$^+$ species vide supra. Finally, reactions 23 and 24 proceed with complete loss of lable in the ionic product with MCD_3^+.



The above results can be rationalized by invoking initial formation of M(hexenyl)$^+$, **10**, by elimination of methane as in Scheme II for propene. This is followed by either dehydrogenation or C_2H_4 elimination. Ethene elimination may proceed by initial insertion into the C–C bond adjacent to the terminal C–C bond to form **11** which can subsequently eliminate ethene. This C–C bond insertion is analogous to the allylic C–C bond insertion of Fe$^+$ and Co$^+$ with 1-pentene and 1-hexene.[14,15]

10



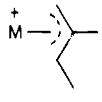
11

Reactions with Methylbutenes and Dimethylbutenes. Reactions with the methylbutenes are dominated by $MC_5H_9^+$, $MC_5H_7^+$, and $MC_3H_5^+$ formation, reactions 25–27. Again, no lable is seen in the ionic products with MCD_3^+ as a consequence of the mechanism in which initial methane elimination occurs to form **12**. The $CoC_5H_7^+$ ions formed in reaction 26 appeared to undergo 7 H/D exchanges with deuterium. This study was complicated, however, by both the low relative intensity of the initial $CoC_5H_7^+$ signal and the H/D exchange of the $CoC_5H_9^+$ species. These results suggest that intermediate **12** undergoes skeletal rearrangement to a linear pentenyl species prior to dehydrogenation.

$$MCH_3^+ + \text{methylbutene} \rightarrow MC_5H_9^+ + CH_4 \quad (25)$$

$$\rightarrow MC_5H_7^+ + CH_4 + H_2 \quad (26)$$

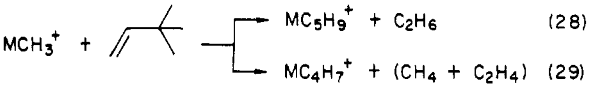
$$\rightarrow MC_3H_5^+ + CH_4 + C_2H_4 \quad (27)$$



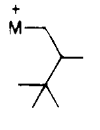
12

CID of $MC_5H_9^+$ produced in reaction 25 yields elimination of H_2, $2H_2$, and C_2H_4. Collisional activation of $MC_5H_7^+$ formed in reaction 26 generates $MC_5H_5^+$ in high efficiency with some M$^+$ observed at high energies in analogy with M(pentadienyl)$^+$ ions described above.

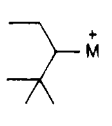
Reactions with 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene are very similar to that for the methylbutenes. 3,3-Dimethyl-1-butene yields unique reactivity as expected since it has no labile hydrogens α to the double bond. Reaction 28 dominated for $FeCH_3^+$, whereas reaction 29 dominated for $CoCH_3^+$. $FeCD_3^+$ results in elimination of ethane as $C_2D_3H_3$ with no lable observed in the ionic product. This suggests that initial olefin coordination is followed by insertion into an allylic C–C bond, resulting in reductive elimination of ethane, presumably forming **12**. Structural studies are consistent with formation of **12** in reaction 28.



The small amount of $CoC_5H_9^+$ produced in reaction 28 suggests that insertion into an allylic C–C bond is not competitive with other processes. As with ethene, the reaction of $CoCH_3^+$ with 3,3-dimethyl-1-butene may proceed by initial migratory insertion of methyl into the olefin, resulting in formation of either **13** or **14** which subsequently decompose. This predicts that reaction of $CoCD_3^+$ should yield some incorporation of lable into the final ionic product which is observed.



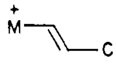
13



14

Reactions with Ethyne and Propyne. Ethyne reacts with MCH_3^+ to yield dehydrogenation exclusively, reaction 30. Collisional activation of this product results in exclusive elimination of C_3H_3 to form M$^+$, suggesting formation of an intact C_3 unit. Dehydrogenation with MCD_3^+ proceeds with an H_2:HD:D_2 ratio of approximately 1:8:4 which is close to the random scrambling ratio of 1:6:3. These results can be rationalized by invoking initial insertion of ethyne into the metal–methyl bond to form **15**, a vinyl complex, which subsequently dehydrogenates. The insertion of acetylene into metal–alkyl bonds to form vinyl complexes is well supported in solution.[79-81]

$$MCH_3^+ + C_2H_2 \rightarrow MC_3H_3^+ + H_2 \quad (30)$$



15

Ethyne reacts with the $MC_3H_3^+$ species to yield predominantly M$^+$ (~95%) and $MC_5H_5^+$ (~5%), reactions 31 and 32. The intensity of the $MC_5H_5^+$ product, unfortunately, was too low to allow for structural characterization; however, it seems reasonable that reactions 31 and 32 result in cyclopentadienyl formation.

$$MC_3H_3^+ + C_2H_2 \rightarrow M^+ + C_5H_5 \quad (31)$$

$$\rightarrow MC_5H_5^+ \quad (32)$$

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[78] These calculations used $D°$(Fe$^+$–CH$_3$) = 69 ± 5 kcal/mol from ref 35b, $D°$(Co$^+$–CH$_3$) = 61 ± 4 kcal/mol from ref 35a, and the heats of formation in ref 50.

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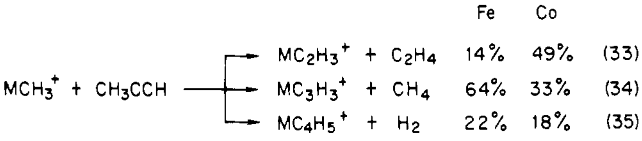
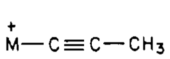
Observation of reactions 30 and 31 yields $\Delta H_f(\mathrm{FeC_3H_3^+}) = 293 \pm 13$ kcal/mol and $\Delta H_f(\mathrm{CoC_3H_3^+}) = 298 \pm 15$ kcal/mol from which $D°(\mathrm{Fe^+{-}C_3H_3}) = 92 \pm 15$ kcal/mol and $D°(\mathrm{Co^+{-}C_3H_3}) = 89 \pm 17$ kcal/mol are derived, assuming formation of a cyclopropenyl.[50,78] Formation of cyclopentadienyl complexes from tungstenacyclobutadiene complexes and dialkylacetylenes has recently been observed.[84] Finally, electron impact on organometallic species containing cyclopentadienyl ligands yields, among other products, $\mathrm{MC_3H_3^+}$, indicating that the reverse of this reaction can occur.[85] A stable metallacyclobutadiene complex has recently been characterized for tungsten.[82] In addition, tungstenacyclobutadiene complexes have been shown to undergo isomerization through an η^3-cyclopropenyl species.[83]

Reactions with propyne are more complex with processes 33–35 observed. Reaction of $\mathrm{MCD_3^+}$ yields elimination of methane exclusively as $\mathrm{CD_3H}$ with no lable observed in the ionic product. The ionic product in reaction 34 may consist of an alkynyl species **16** in analogy to a process which has been observed previously for cobalt–methyl complexes in solution.[86] Since the acetylinic C–H bond in propyne is strong ($\sim 132 \pm 5$ kcal/mol)[50] and the alkyl C–H bond is much weaker ($\sim 89 \pm 2$ kcal/mol),[50] however, it seems more likely that abstraction of the alkyl C–H hydrogen actually occurs, resulting in formation of either M(cyclopropenyl)$^+$ or a metallacyclobutadiene complex. Evidence for this is that both $\mathrm{MC_3H_3^+}$ ions produced in reactions 30 and 34 yield identical CID spectra.



$$\mathrm{MCH_3^+ + CH_3CCH} \longrightarrow \begin{array}{llll} & & \text{Fe} & \text{Co} \\ \to \mathrm{MC_2H_3^+ + C_2H_4} & & 14\% & 49\% \quad (33) \\ \to \mathrm{MC_3H_3^+ + CH_4} & & 64\% & 33\% \quad (34) \\ \to \mathrm{MC_4H_5^+ + H_2} & & 22\% & 18\% \quad (35) \end{array}$$



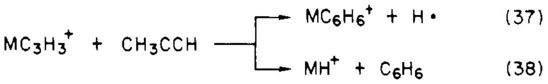
$$\overset{+}{\mathrm{M}}\mathrm{{-}C{\equiv}C{-}CH_3}$$

16

Reactions 33 and 35 probably proceed by initial migratory insertion to form an M(vinyl)$^+$ complex which subsequently eliminates either $\mathrm{C_2H_4}$ or $\mathrm{H_2}$. CID of $\mathrm{MC_2H_3^+}$ formed in reaction 33 yields both $\mathrm{C_2H_2}$ elimination ($\mathrm{MH^+}$ formation) and $\mathrm{C_2H_3}$ elimination. This implies $D°(\mathrm{Fe^+{-}C_2H_2}) < D°(\mathrm{Fe^+{-}H}) = 59 \pm 5$ kcal/mol[54] and $D°(\mathrm{Co^+{-}C_2H_2}) < D°(\mathrm{Co^+{-}H}) = 52 \pm 4$ kcal/mol.[35]

$\mathrm{MC_2H_3^+}$ formed in reaction 33 undergoes a secondary reaction with propyne to yield predominantly $\mathrm{MC_5H_5^+}$, reaction 36. CID of this species is consistent with formation of M-c-$\mathrm{C_5H_5^+}$. Reaction of $\mathrm{CoC_3H_3^+}$ with propyne yields exclusively $\mathrm{CoC_6H_6^+}$ (reaction 37), whereas $\mathrm{FeC_3H_3^+}$ yields both $\mathrm{FeC_6H_6^+}$ as well as $\mathrm{FeH^+}$ with propyne (reactions 37 and 38). CID suggests formation of a metal–benzene complex in reaction 37. Finally, taken together these results suggest that a cyclohexadienyl intermediate is involved in the formation of the products in reactions 37 and 38.[17]

$$\mathrm{MC_2H_3^+ + CH_3CCH \rightarrow MC_5H_5^+ + H_2} \qquad (36)$$



$$\mathrm{MC_3H_3^+ + CH_3CCH} \longrightarrow \begin{array}{ll} \to \mathrm{MC_6H_6^+ + H\cdot} & (37) \\ \to \mathrm{MH^+ + C_6H_6} & (38) \end{array}$$

Conclusions

Reactions of metal–methyl ions with olefins containing a labile hydrogen α to the double bond are dominated by methane elimination, resulting in formation of a π-allyl complex. This π-allyl complex can undergo further decomposition provided it retains sufficient internal energy. In addition, $\mathrm{CoCH_3^+}$ is able to undergo migratory insertion into ethene to form a Co(propyl)$^+$ complex which eliminates hydrogen, whereas $\mathrm{FeCH_3^+}$ is unreactive with ethene. These differences arise because the barrier for migratory insertion of ethene into the Co$^+$–methyl bond is between $\sim$25 and $\sim$35 kcal/mol, whereas for Fe$^+$–methyl is between $\sim$35 and $\sim$55 kcal/mol. In contrast both $\mathrm{FeCH_3^+}$ and $\mathrm{CoCH_3^+}$ readily insert into butadiene to generate a pentenyl complex which subsequently dehydrogenates. In addition, both $\mathrm{MCH_3^+}$ ions appear to undergo rapid insertion into ethyne to form vinyl complexes. These results suggest the following order for methyl insertion: butadiene $\sim$ ethyne > ethene.

Decomposition of $\mathrm{M(C_5H_9)^+}$ species proceeds by facile skeletal rearrangement to a linear structure followed by dehydrogenation and dehydrocyclization to generate M-c-$\mathrm{C_5H_5^+}$ ions. H/D exchanges using deuterium distinguished a Co(pentadienyl)$^+$ species from a Co(cyclopentenyl)$^+$ species. $D°(\mathrm{Fe^+}$–pentadienyl) is found to exceed 70 ± 6 kcal/mol and $D°(\mathrm{Co^+}$–pentadienyl) exceeds 62 ± 5 kcal/mol. This compares with $D°(\mathrm{Fe^+}$–cyclopentadienyl) > 87 ± 6 kcal/mol[69] and $D°(\mathrm{Co^+}$–cyclopentadienyl) = 85 ± 5 kcal/mol.[74]

Finally, these results demonstrate that addition of a methyl ligand to Fe$^+$ and Co$^+$ dramatically affects their reactivity with olefins. Whereas reactions of the atomic ions with $\mathrm{C_5}$ and $\mathrm{C_6}$ olefins are dominated by C–C bond cleavages, the reactions with $\mathrm{MCH_3^+}$ proceed predominantly by retention of the olfein's framework.

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

Registry No. $\mathrm{FeCH_3^+}$, 90143-29-6; $\mathrm{CoCH_3^+}$, 76792-06-8; ethyne, 74-86-2; propyne, 74-99-7; ethene, 74-85-1; propene, 115-07-1; 2-methylpropene, 115-11-7; 1-butene, 106-98-9; 1,3-butadiene, 106-99-0; 1-pentene, 109-67-1; 1-hexene, 592-41-6; 2-methyl-1-butene, 563-46-2; 3-methyl-1-butene, 563-45-1; 2-methyl-2-butene, 513-35-9; 2,3-dimethyl-1-butene, 563-78-0; 2,3-dimethyl-2-butene, 563-79-1; 3,3-dimethyl-1-butene, 558-37-2.

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