Heteronuclear Diatomic Transition-Metal Cluster Ions in the Gas Phase. Reactions of CoFe$^+$ with Hydrocarbons

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Abstract: Reactions of CoFe$^+$ with several hydrocarbons in the gas phase by using Fourier transform mass spectrometry are described. No reaction is observed between CoFe$^+$ and cyclic (C_3–C_6) or acyclic (C_1–C_6) alkanes. CoFe$^+$ reacts with aliphatic alkenes containing a linear C_4 unit yielding predominantly dehydrogenation products. The only example where C–C bond cleavage is observed with aliphatic alkenes is for 3,3-dimethyl-1-butene which is a special case since it does not have β-hydrogens available for elimination upon olefin coordination. In this case, insertion into an allylic C–C bond occurs followed by a β-hydride shift resulting in methane elimination. Collisional activation of CoFe(olefin)$^+$ species containing a linear C_5 or C_6 chain undergoes facile dehydrocyclizations in analogy to what is observed on metal surfaces. Collisional activation of branched-olefin complexes indicates that skeletal isomerizations do not occur. Bis(cyclopentadienyl)CoFe$^+$ ions undergo facile elimination of either Co or Fe forming ferrocene and cobaltocene ions, respectively. The corresponding bis(benzene)CoFe$^+$ ions are much more stable with formation of Co(benzene)$_2$$^+$ and CoFe(benzene)$^+$ formed in low efficiency upon collisional activation.

Bare transition-metal clusters[1] are important in a variety of processes involving astronomy and homogeneous nucleation[2] and are of particular relevance as models for catalytic activity.[3] As a result, these clusters have been the focus of intense experimental[4,5] and theoretical[6] investigations. Several of these studies have been aimed at characterizing their physical properties such as structure, electronic character, binding energy, ionization potential, and electron affinity. Especially relevant to catalysis are studies involving the chemical properties of clusters, for example, reaction rate, mechanism, and thermochemistry. Such information, particularly if derived as a function of cluster size, is vital to efforts seeking to model catalytic processes.

Knudsen cell mass spectrometry[7] has yielded bond energies for most homonuclear transition-metal dimers. Matrix isolation techniques have been employed to generate and study dimers and larger clusters by using optical,[8] ESR,[9] and Mossbauer[10] spectroscopy. In addition, Smalley has recently developed an elegant and convenient technique for generating clusters of various sizes for gas-phase studies.[11] Armentrout and co-workers have also demonstrated the utility of using an ion beam instrument to determine the bond energy of dimer ions by measuring their collision-induced dissociation thresholds.[12]

Gas-phase ion techniques are ideally suited for studying size-selected metal cluster ions. To date these cluster ions have been generated by either electron impact[13] or multiphoton ionization,[14] typically on multinuclear carbonyl complexes. The former method has been employed, for example, to generate and study the gas-phase chemistry of Co$_2$$^+$[15] and Mn$_2$$^+$[15-17] by ion cyclotron resonance spectrometry and ion beam techniques.

Recently, we demonstrated a convenient technique for in situ synthesis of bare homonuclear and heteronuclear diatomic and triatomic transition-metal cluster ions in the gas phase using Fourier transform mass spectrometry–collision induced dissociation (FTMS-CID).[18] This technique involves a two-step process in which the first step is a gas-phase ion–molecule reaction between an atomic transition-metal ion and a transition-metal carbonyl in which one or more carbonyls are displaced.[19] Next, collisional activation of the resulting ion sequentially strips the remaining carbonyls from the complex ultimately producing the bare metal cluster ion. This cluster ion can be isolated, and its chemistry can then be studied.

Heteronuclear clusters can have unique characteristics compared to homonuclear clusters. For example, a diatomic cluster containing both a late and an early transition metal might have electron density polarized toward the late transition metal which could greatly modify its chemistry compared to the corresponding

homonuclear clusters. Recently, Klabunde and Imizu demonstrated that Mn–Co bimetallic dispersed dimers catalyze alkene

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hydrogenation at -60 °C at diffusion-controlled rates whereas the monometallic catalysts (Ni, Co, Fe, Mn, and Cr) show a greatly reduced activity.[20] Interestingly, in the case of the second transition series intermetallic, YPd, the electron density is predicted to be slightly polarized toward the Y atom and *not* the more electronegative Pd atom as would be commonly expected.[21]

In this paper we describe the nature of the heteronuclear diatomic cluster, FeCo$^+$, as well as its reactions with several simple hydrocarbons in the gas phase. This particular dimer was chosen for two reasons. First, the gas-phase chemistry of the atomic ions, Fe$^+$ and Co$^+$, has been studied in detail.[22-25] Second, since these metals are adjacent in the periodic table there should be little polarization of the electron density. The chemistry of early–late dimeric clusters such as TiFe$^+$, VFe$^+$, TiCo$^+$, VCo$^+$, etc., can then be compared with the CoFe$^+$ system.
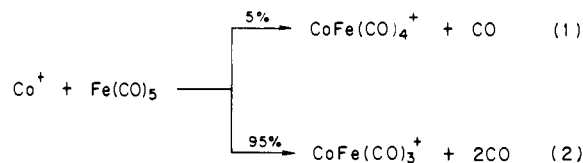
Experimental Section

The theory, instrumentation, and methodology of ion cyclotron resonance (ICR) spectrometry[26] and Fourier transform mass spectrometry (FTMS)[27] have been discussed at length elsewhere. All experiments were performed on a Nicolet prototype FTMS-1000 Fourier transform mass spectrometer previously described in detail[28] and equipped with a 5.2 cm cubic trapping cell situated between the poles of a Varian 15-in. electromagnet maintained at 0.9 T. The cell was constructed in our laboratory and includes a $^1/_4$ in. diameter hole in one of the transmitter plates which permits irradiation with various light sources. A high-purity cobalt foil was supported on the opposite transmitter plate. Cobalt ions were 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.[29]

Chemicals were obtained commercially in high purity and were used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensable gases. Fe(CO)$_5$ was introduced into the vacuum chamber at a static pressure of $\sim 3 \times 10^{-8}$ torr. The hydrocarbon reagents were added to bring the pressure to $\sim 1 \times 10^{-7}$ torr. Argon was used as the collision gas for collision-induced dissociation (CID) at a total pressure of $\sim 5 \times 10^{-6}$ torr. A Bayard-Alpert ionization gauge was used to monitor pressure.
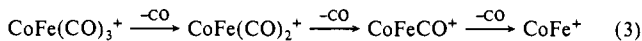
Details of the CID experiments have previously been discussed.[28,30,31] The collision energy of the ions can be varied (typically between 0 and

100 eV) from which plots of CID product ion intensities vs. ion kinetic energy can be made. These plots are reproducible to $\pm 5\%$ absolute and yield additional structural 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.[32]

CoFe$^+$ was generated and studied by the following procedure. Initially, laser desorbed cobalt ions react with Fe(CO)$_5$ by displacing one or two carbonyls, reactions 1 and 2. The product of reaction 2, CoFe-
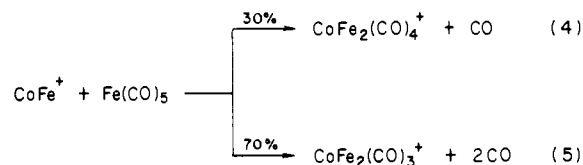

(CO)$_3{}^+$, was then isolated by swept double resonance ejection pulses[27] and accelerated to 31 eV kinetic energy causing the carbonyls to be sequentially eliminated from the cluster by inelastic collisions with the argon target gas, process 3. The CoFe$^+$ ions so generated were isolated

$$CoFe(CO)_3{}^+ \xrightarrow{-CO} CoFe(CO)_2{}^+ \xrightarrow{-CO} CoFeCO^+ \xrightarrow{-CO} CoFe^+ \quad (3)$$

and allowed to react with specific reagent gases, and the products of these reactions could be isolated and their structures probed by CID. Figure 1 illustrates each step pictorially for generation and reactions of CoFe$^+$ with 1-pentene.

In addition to reactions with the hydrocarbon reagent, CoFe$^+$ also reacts with Fe(CO)$_5$ by displacing one or two carbonyls, reactions 4 and 5. These reactions are much slower than the initial reaction of Co$^+$ with

Fe(CO)$_5$ and, therefore, do not present a problem. The CoFe$^+$ ions generated by process 3 undoubtedly are formed with a distribution of internal energies. The CID collision gas was maintained at a high pressure ($\sim 5 \times 10^{-6}$ torr) relative to the hydrocarbon reagent gas pressure ($\sim 1 \times 10^{-7}$ torr), therefore, in order to allow the excess energy to be dissipated by thermalizing collisions with argon prior to reaction.

Results and Discussion

Bonding in CoFe$^+$. The bond energy of CoFe$^+$ has been bracketed[18a] as $D°(Co^+-OH) = 71 \pm 3$ kcal/mol[33] $> D°(Co^+-benzene) > D°(Co^+-Fe) > D°(Co^+-CH_3CN) > D°(Co^+-CH_3) = 61 \pm 4$ kcal/mol[34] from which $D°(Co^+-Fe) = 66 \pm 7$ kcal/mol and $\Delta H_f°(CoFe^+) = 315.5 \pm 7$ kcal/mol were assigned.[35] $D°(Fe^+-Co)$ is very nearly identical with $D°(Co^+-Fe)$ due to the slight difference in the ionization potential of Fe (IP $= 7.87$ eV) and Co (IP $= 7.86$ eV).[35] A predicted Co–Fe bond energy of 31 kcal/mol has been reported.[36] Using eq 6, together

$$IP(CoFe) = D°(Co-Fe) + IP(Co) - D°(Co^+-Fe) \quad (6)$$

with the predicted Co–Fe bond energy, yields a calculated IP for CoFe $= 6.34$ eV which compares with an experimental IP for Fe$_2$ $= 5.90 \pm 0.2$ eV.[37] Finally, CID of CoFe$^+$ yields both Co$^+$ and Fe$^+$ in roughly a 2:1 ratio at kinetic energies in excess of 50 eV.[38]

Since Fe$_2$ is isoelectronic with CoFe$^+$, it may serve as a model for understanding the bonding. Fe$_2$ has been the focus of a number

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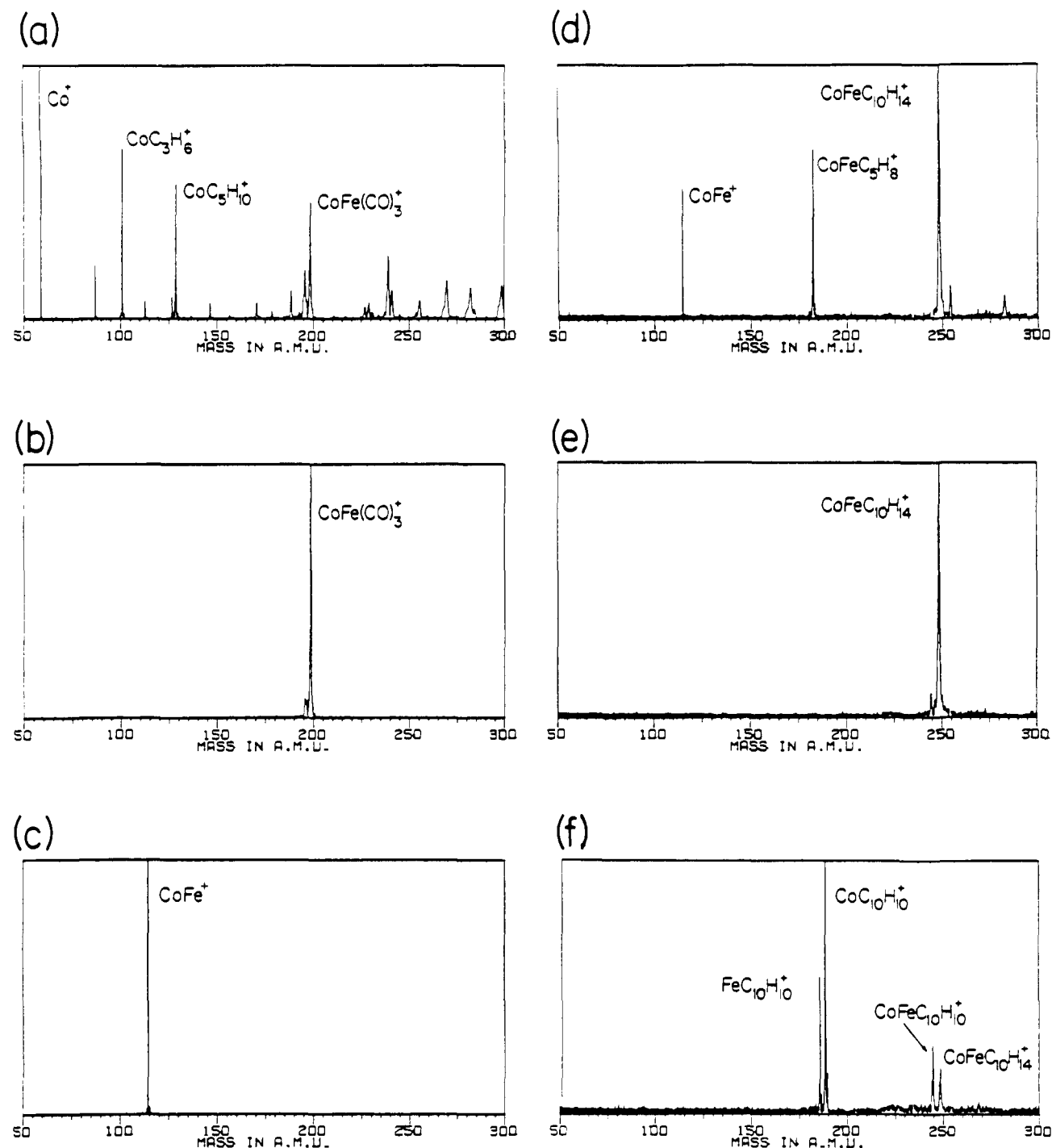
Figure 1. (a) Mass spectrum obtained when laser desorbed Co^+ is trapped with a 2:1 mixture of 1-pentene and $Fe(CO)_5$ ($P \sim 1 \times 10^{-7}$ torr) in the presence of 5×10^{-6} torr of argon for 300 ms. (b) Same as part a except all ions other than $CoFe(CO)_3^+$ have been ejected from the cell by swept double resonance ejection pulses. (c) Same as part b except following isolation, $CoFe(CO)_3^+$ is accelerated to 31 eV and allowed to undergo collision-induced dissociation for 40 ms followed by isolation of the resulting $CoFe^+$ species. Over 80% of the original $CoFe(CO)_3^+$ has been converted to $CoFe^+$. (d) Same as part c except an additional 600-ms trap allows $CoFe^+$ to react with 1-pentene. (e) Same as part d except $CoFeC_{10}H_{14}^+$ has been isolated. (f) Same as part e except $CoFeC_{10}H_{14}^+$ is accelerated to 22 eV of kinetic energy with the fragmentations detected. Each individual spectrum has been normalized to the most intense peak.

of detailed theoretical calculations[6c,39] and spectroscopic measurements[10,40-42] which suggest that the ground state is $^7\Delta_u{}^{6c}$ arising from interaction between two iron atoms each in the $^5F(3d)^7(4s)^1$ state. This configuration together with the highly localized nature of the 3d orbitals reveal that the chemical bond between Fe atoms

is a single bond almost entirely due to the $4s\sigma$ molecular orbital.[6c] Similar calculations on $NiFe$,[6f] Ni_2,[6] $NiCu$,[6d] Co_2,[6k] and $Cu_2{}^{61}$ indicate that they all contain a single bond due essentially to a $4s\sigma$ molecular orbital. The bonding of $CoFe^+$, therefore, probably also consists of a single bond composed primarily of 4s character.

$CoFe^+$ may be considered either as Fe^+ interacting with Co or Co^+ interacting with Fe since they have essentially identical IP's.[35] The former can easily be envisioned as having a single bond of $4s\sigma$ character formed from interaction of ground-state Co $(^4F(3d)^8(4s)^1)$ with the ground state of Fe^+ $(^6D(3d)^6(4s)^1)$. In the latter case interaction of ground-state Fe $(^5D(3d)^6(4s)^2)$ with

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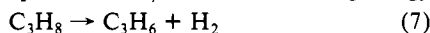(42) NcNab, T. K.; Mickliz, H.; Barrett. P. H. *Phys. Rev. B.* **1971**, *4*, 3787.

the ground state of Co^+ ($^3F(3d)^8$) could result in formation of a single bond of $4s\sigma$ character. Alternatively, an iron atom in the $^5F(3d)^7(4s)^1$ state could form a single bond of $4s\sigma$ character with Co^+ in the $^5F(3d)^7(4s)^1$ state in analogy to that for Fe_2.[6c] For $CoFe^+$, bonding between d electrons may be of even less importance than that for neutral CoFe since the positive charge will tend to contract and stabilize the 3d orbitals. A full understanding of the bonding in $CoFe^+$, however, must await detailed theoretical calculations and spectroscopic measurements.

Reactions with Alkanes. $CoFe^+$ is completely inert toward both cyclic (C_3–C_6) and acyclic (C_1–C_6) alkanes. The homonuclear diatomic ion, Co_2^+, has also been reported to be unreactive with alkanes.[15a] These results are in contrast to the corresponding atomic ions, Fe^+ and Co^+, which are highly reactive toward alkanes in the gas phase with both C–H and C–C bond insertions observed.[15a,21-25,31,34]

Correlation of experimental metal ion–hydrogen and metal ion–methyl bond strengths with electronic promotion energies (3d → 4s) of the metal ions indicates that the metal orbital involved in bonding consists primarily of 4s character for the first-row transition-metal ions.[43] Similar conclusions were reached for the neutral metal hydrides, ScH through FeH.[44] Preliminary calculations on FeH^+ indicate that the hybridization of the metal orbital involved in the Fe^+–H bond is 75% s, 11% p, and 14% d.[45]

Since the bonding in $CoFe^+$ probably consists predominantly of $4s\sigma$ character, oxidative addition of an alkane should result in a weakening of the $CoFe^+$ bond. The net result is that the bond of a hydrogen atom or an alkyl to the $CoFe^+$ dimer is weaker than that to the atomic ions, Fe^+ and Co^+. Absence of reaction with 2-methylpropane implies that $D°(CoFeCH_3^+-i-C_3H_7) + D°-(CoFe^+-CH_3) < D°(CH_3-i-C_3H_7) = 85$ kcal/mol and $D°(Co-FeH^+-t-C_4H_9) + D°(CoFe^+-H) < D°(H-t-C_4H_9) = 93$ kcal/mol.[46] For comparison, the binding energy of two methyls to Fe^+ and Co^+ appears to exceed 96 kcal/mol.[48]

Alternatively, the inert behavior toward acyclic alkanes may be due to a weak olefin bond. For example, dehydrogenation of propane, reaction 7, requires 30 kcal/mol.[35] The binding energy
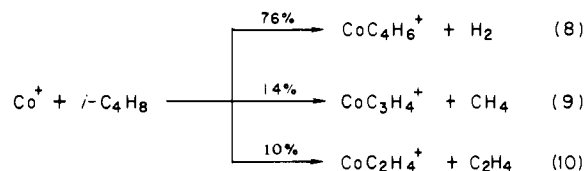
$$C_3H_8 \rightarrow C_3H_6 + H_2 \qquad (7)$$

of olefins to Co^+ and Fe^+ appears to be in the range of 35–45 kcal/mol.[22b,25] If the binding energy of olefins to the $CoFe^+$ dimer is less than 30 kcal/mol, then the inert behavior would be due to the overall process of alkane dehydrogenation being endothermic. We feel, however, that the binding energy of olefins to $CoFe^+$ is probably similar to that for the atomic ions, Fe^+ and Co^+, and therefore attribute the inert behavior to the initial oxidative addition process being unfavorable. Similar arguments may hold for the homonuclear dimer, Co_2^+.

In a related study, matrix-isolated iron dimers in solid CH_4 at 10–12 K were found neither to react thermally (10–50 K) nor react photochemically (400–580 nm) with CH_4.[49] On the other hand, Fe atoms photoexcited at 300 nm are highly reactive toward CH_4 at 12 K, leading to the oxidative-addition product CH_3FeH.[50] It is interesting to note that the 300-nm excitation corresponds to the $3d^74s^1 \leftarrow 3d^64s^2$ of atomic iron.[51] Small nickel crystallites have been observed to react with alkanes at low temperatures with

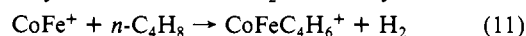atomic nickel being unreactive.[52] Interestingly, Co_2CO^+[53] and Co_2Fe^+[18b] both react with alkanes in the gas phase predominantly by attacking C–H bonds.

Reactions with Olefins. Aliphatic C_2–C_4 Olefins. No reaction is observed for ethene, propene, 2-methylpropene, and butadiene with $CoFe^+$. Atomic iron cations are also unreactive with these olefins.[54] In addition, atomic cobalt cations have been found to be unreactive with the above olefins except for 2-methylpropene where reactions 8–10 are observed.[55] Structural studies on the

$$Co^+ + i\text{-}C_4H_8 \begin{cases} \xrightarrow{76\%} CoC_4H_6^+ + H_2 & (8) \\ \xrightarrow{14\%} CoC_3H_4^+ + CH_4 & (9) \\ \xrightarrow{10\%} CoC_2H_4^+ + C_2H_4 & (10) \end{cases}$$

dehydrogenation product, reaction 8, indicate that it consists of butadiene bound to cobalt rather than trimethylene methane and, therefore, that considerable rearrangement has occurred in the carbon framework.[56] The absence of dehydrogenation of 2-methylpropene by $CoFe^+$ indicates that dehydrogenation forming trimethylene methane or rearrangement to a linear structure is unfavorable.

The simplest olefins which react with $CoFe^+$ are the linear butenes which yield elimination of H_2 exclusively, reaction 11.

$$CoFe^+ + n\text{-}C_4H_8 \rightarrow CoFeC_4H_6^+ + H_2 \qquad (11)$$

This reaction probably proceeds by initial insertion across an allylic C–H bond forming $CoFe(H)(C_4H_7)^+$. A second β-hydride shift onto the cluster with subsequent reductive elimination of hydrogen results in formation of $CoFe(butadiene)^+$. Oxidative addition across an allylic C–H bond is well supported in solution-phase studies[57] and has been implicated in several gas-phase studies.[22b,23,25,31,58] This reactivity with linear butenes can be attributed to several factors. First, the allylic C–H bond is relatively weak (82–86 kcal/mol).[47] Second, the allylic bond to Co^+ is strong, $D°(Co^+-\eta^3-C_3H_5) > 71$ kcal/mol.[59] In addition, the bonding of an η^3-allyl to a metal involves predominantly metal orbitals of d character[60] and, therefore, should not substantially weaken the 4s molecular orbital between the two metals. The bonding of allylic species to metal dimers can vary and involve only one metal, a bridging η^3-allyl interaction,[61] or formation of a σ–π bridged system.[62,63] Absence of reaction with ethene, propene, and isobutene can be attributed to the lack of a linear C_4 chain containing β-hydrogens available for dehydrogenation generating an alkadiene unit.

Collisional activation of $CoFeC_4H_6^+$, formed in reaction 11, causes facile elimination of C_4H_6 with some Co^+ and Fe^+ also observed at high energy. Absence of additional fragmentations is consistent with butadiene bound to the cluster vide supra. The bonding of butadiene to the cluster can be quite complex with either one or both metals interacting with the butadiene ligand.

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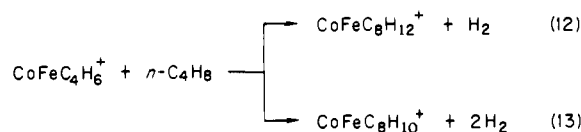
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Table I. Distribution of Neutral(s) Lost for the Primary Reactions of CoFe$^+$ with Olefins and for the Secondary Reactions of FeCoL$^+$ Species[a]

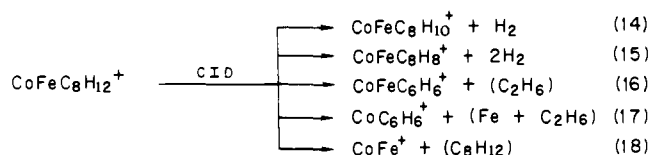| olefin	primary reactions			secondary reactions		
	neutral(s)	ion	rel %	neutral(s)	ion	rel %
ethene		no reaction				
propene		no reaction				
2-methylpropene		no reaction				
1-butene	H_2	$CoFeC_4H_6^+$	100	H_2	$CoFeC_8H_{12}^+$	60
				$2H_2$	$CoFeC_8H_{10}^+$	40
cis-2-butene	H_2	$CoFeC_4H_6^+$	100	H_2	$CoFeC_8H_{12}^+$	58
				$2H_2$	$CoFeC_8H_{10}^+$	42
trans-2-butene	H_2	$CoFeC_4H_6^+$	100	H_2	$CoFeC_8H_{12}^+$	61
				$2H_2$	$CoFeC_8H_{10}^+$	39
1,3-butadiene		no reaction				
1-pentene	H_2	$CoFeC_5H_8^+$	100	$2H_2$	$CoFeC_{10}H_{14}^+$	100
trans-1,3-pentadiene	H_2	$CoFeC_5H_6^+$	100	$2H_2$	$CoFeC_{10}H_{10}^+$	17
				$(Fe + 2H_2)$	$CoC_{10}H_{10}^+$	56
				$(Co + 2H_2)$	$FeC_{10}H_{10}^+$	27
1-hexene	H_2	$CoFeC_6H_{10}^+$	58	$2H_2$	$CoFeC_{12}H_{18}^+$	30
				$3H_2$	$CoFeC_{12}H_{16}^+$	45
				$(C_3H_6 + H_2)$	$CoFeC_9H_{14}^+$	25
	$2H_2$	$CoFeC_6H_8^+$	42	$2H_2$	$CoFeC_{12}H_{16}^+$	100
2-methyl-1-butene	H_2	$CoFeC_5H_8^+$	100	H_2	$CoFeC_{10}H_{16}^+$	34
				$2H_2$	$CoFeC_{10}H_{14}^+$	66
3-methyl,-1,3-butadiene		no reaction				
3,3-dimethyl-1-butene	CH_4	$CoFeC_5H_8^{+ \, b}$	100			
2,3-dimethyl-1-butene	H_2	$CoFeC_6H_{10}^+$	100	H_2	$CoFeC_{12}H_{20}^+$	25
				$2H_2$	$CoFeC_{12}H_{18}^+$	75
cyclopentene	H_2	$CoFeC_5H_6^+$	100	$2H_2$	$CoFeC_{10}H_{10}^+$	49
				$(Fe + 2H_2)$	$CoC_{10}H_{10}^+$	30
				$(Co + 2H_2)$	$FeC_{10}H_{10}^+$	21
cyclopentadiene		$CoFeC_5H_6^+$	55	$(Fe + H_2)$	$CoC_{10}H_{10}^+$	73
				$(Co + H_2)$	$FeC_{10}H_{10}^+$	27
	H_2	$CoFeC_5H_4^+$	45	Fe	$CoC_{10}H_{10}^+$	68
				Co	$FeC_{10}H_{10}^+$	32
1-methylcyclopentene	H_2	$CoFeC_6H_8^+$	22	$3H_2$	$CoFeC_{12}H_{12}^+$	100
	$2H_2$	$CoFeC_6H_6^+$	78	$2H_2$	$CoFeC_{12}H_{12}^+$	100
cyclohexene	$2H_2$	$CoFeC_6H_6^+$	88	$2H_2$	$CoFeC_{12}H_{12}^+$	100
	$(Fe + 2H_2)$	$CoC_6H_6^+$	12			
1-methylcyclohexene	$2H_2$	$CoFeC_7H_8^+$	90	$3H_2$	$CoFeC_{14}H_{14}^+$	85
				$2H_2$	$CoFeC_{14}H_{16}^+$	15
	$(Fe + 2H_2)$	$CoC_7H_8^+$	10			
benzene	Fe	$CoC_6H_6^+$	100			
toluene	Fe	$CoC_7H_8^+$	100			
cycloheptatriene	(CoH)	$FeC_7H_7^+$	23			
	Co	$FeC_7H_8^+$	13			
	Fe	$CoC_7H_8^+$	64			
norbornadiene	C_2H_2	$CoFeC_5H_6^+$	74	$(Fe + C_2H_4)$	$CoC_{10}H_{10}^+$	80
				$(Co + C_2H_4)$	$FeC_{10}H_{10}^+$	20
	$(Fe + C_2H_2)$	$CoC_5H_6^+$	6			
	Fe	$CoC_7H_8^+$	20			

[a] Product distribution reproducible to ±10%. [b] No secondary reactions observed.

Surprisingly, $CoFeC_4H_6^+$ generated in reaction 11 yields elimination of H_2 and $2H_2$ upon interaction with a second linear butene, reactions 12 and 13. A perusal of Table I reveals that

$$CoFeC_4H_6^+ + n\text{-}C_4H_8 \longrightarrow CoFeC_8H_{12}^+ + H_2 \quad (12)$$
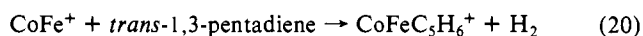$$\longrightarrow CoFeC_8H_{10}^+ + 2H_2 \quad (13)$$

the secondary reactions, in general, result in elimination of more hydrogens than those for the primary reactions. Apparently the presence of an olefin ligand activates the cluster toward olefins. The product of reaction 12 may simply consist of two butadienes bound to the cluster in some fashion. Elimination of $2H_2$, reaction 13, may proceed by a coupling of the two ligands.

CID of $CoFeC_8H_{12}^+$ yields a richer fragmentation pattern than that for $CoFeC_4H_6^+$ with processes 14–18 observed. At low

$$CoFeC_8H_{12}^+ \xrightarrow{CID}$$
$$\longrightarrow CoFeC_8H_{10}^+ + H_2 \quad (14)$$
$$\longrightarrow CoFeC_8H_8^+ + 2H_2 \quad (15)$$
$$\longrightarrow CoFeC_6H_6^+ + (C_2H_6) \quad (16)$$
$$\longrightarrow CoC_6H_6^+ + (Fe + C_2H_6) \quad (17)$$
$$\longrightarrow CoFe^+ + (C_8H_{12}) \quad (18)$$

energy, formation of $CoFeC_6H_6^+$ dominates, with $CoC_6H_6^+$ and $CoFe^+$ dominating at high kinetic energy. The dehydrogenation processes 14 and 15 account for only a minor amount of the overall fragmentation intensities at all kinetic energies. Formation of $CoFeC_6H_6^+$ may involve an initial Diels–Alder cycloaddition of bis(butadiene)$CoFe^+$ generating a 4-vinylcyclohexene complex, followed by reversible β-hydride shifts resulting in elimination of C_2H_4 and H_2 producing CoFe(benzene)$^+$. Observation of an abundant $CoC_6H_6^+$ signal at high kinetic energy is consistent with benzene formation in reaction 16.[18a] The above Diels–Alder cycloaddition has been modeled for CID of bis(butadiene)Fe^+ which results in $FeC_6H_6^+$ formation.[54]

Aliphatic C_5 and C_6 Olefins. CoFe$^+$ reacts with 1-pentene and trans-1,3-pentadiene, yielding exclusively elimination of H_2, reactions 19 and 20. This is in contrast to reactions of Co$^+$ and

$$CoFe^+ + 1\text{-pentene} \rightarrow CoFeC_5H_8^+ + H_2 \quad (19)$$

$$CoFe^+ + trans\text{-}1,3\text{-pentadiene} \rightarrow CoFeC_5H_6^+ + H_2 \quad (20)$$

Fe$^+$ with 1-pentene where C–C bond cleavages dominate, presumably by facile insertion into an allylic C–C bond.[31,54,55,64] In addition, both Co$^+$ and Fe$^+$ react with trans-1,3-pentadiene,
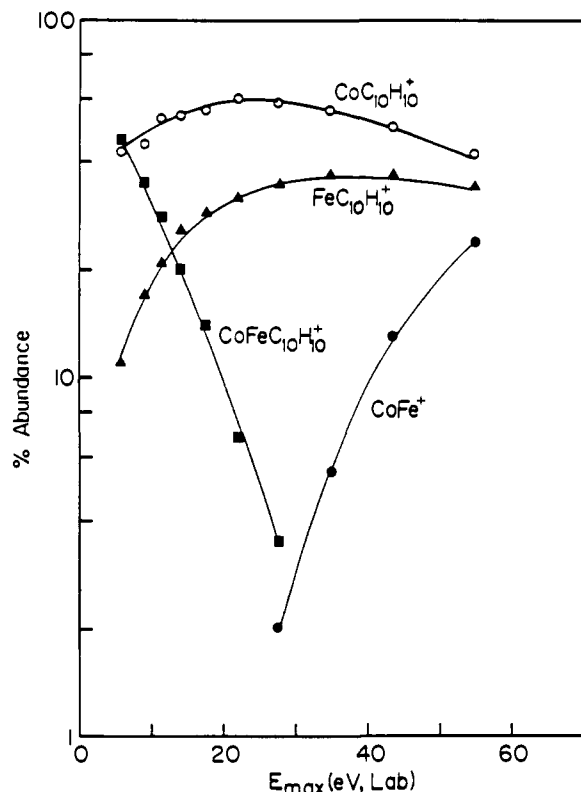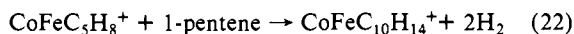
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Figure 2. Variation of CID product ion intensities as a function of kinetic energy for $CoFeC_{10}H_{14}^+ \cdot$ generated in reaction 22.

yielding exclusively elimination of C_2H_2 and C_3H_6 generating $MC_3H_6^+$ and $MC_2H_2^+$, respectively.[56] The reactivity of the dimer, therefore, is quite different than that of the respective atomic cations.
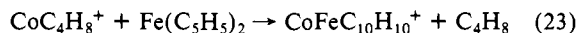
$CoFeC_5H_8^+$, generated in reaction 19, undergoes facile elimination of H_2 upon collisional activation with C_5H_8 elimination dominant at high kinetic energy. CID of $CoFeC_5H_6^+$, formed in reaction 20, yields an efficient elimination of C_5H_6 with some Co^+ and Fe^+ observed at high energy. These results can be rationalized by invoking an initial dehydrogenation forming (1,3-pentadiene)$CoFe^+$ (reaction 19) which subsequently undergoes a dehydrocyclization,[65] generating formally a (cyclopentadiene)$CoFe^+$ complex. Dehydrocyclization has previously been proposed for CID of $CoC_5H_9^+$, generated in reaction 21, resulting in formation of Co(cyclopentadienyl)$^+$ upon elimination of $2H_2$.[59]

$$CoCH_3^+ + n\text{-}C_5H_{12} \rightarrow CoC_5H_9^+ + CH_4 + H_2 \quad (21)$$

$CoFeC_5H_8^+$, formed in reaction 19, yields exclusively elimination of $2H_2$ with 1-pentene, reaction 22. CID on $CoFeC_{10}H_{14}^+$

$$CoFeC_5H_8^+ + 1\text{-pentene} \rightarrow CoFeC_{10}H_{14}^+ + 2H_2 \quad (22)$$

yields facile formation of $CoFeC_{10}H_{10}^+$, $CoC_{10}H_{10}^+$, and $FeC_{10}H_{10}^+$ with some $CoFe^+$ and no $CoFeC_{10}H_{12}^+$ observed, Figure 2. As can be seen in Figure 2, $CoC_{10}H_{10}^+$ and $FeC_{10}H_{10}^+$ dominate at high energy in roughly a 2:1 ratio. These results can be interpreted by invoking dehydrocyclizations generating bis-(cyclopentadienyl)$CoFe^+$ which eliminates either metal forming cobaltocene and ferrocene cations. This hypothesis is supported by CID of $CoFeC_{10}H_{10}^+$, generated in reaction 23, which forms

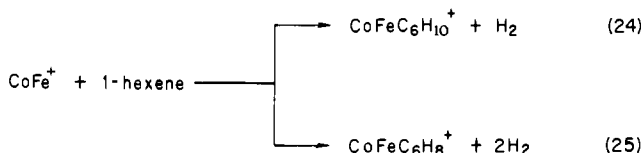$$CoC_4H_8^+ + Fe(C_5H_5)_2 \rightarrow CoFeC_{10}H_{10}^+ + C_4H_8 \quad (23)$$

$CoC_{10}H_{10}^+$ and $FeC_{10}H_{10}^+$ in roughly a 2:1 ratio at high energy.[66]

Reaction of $CoFeC_5H_6^+$ with *trans*-1,3-pentadiene can be interpreted as above with dehydrocyclization generating bis(cyclopentadienyl)$CoFe^+$, cobaltocene$^+$, and ferrocene$^+$. The structure of the above bis(cyclopentadienyl)$CoFe^+$ ions may consist of CoFe sandwiched between the cyclopentadienyl rings, structure **1**. Bridging cyclopentadienyl ligands have been reported for Pd_2,[67,68] $PdPt$,[69] and Pt_2[70] complexes.

1

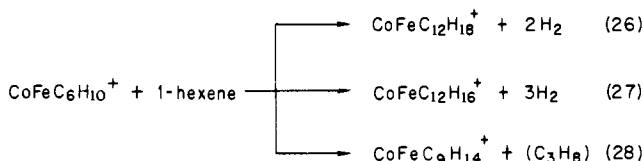$CoFe^+$ yields dehydrogenation products with 1-hexene, reactions 24 and 25, in analogy with 1-pentene. Again, this is in contrast

$$CoFe^+ + 1\text{-hexene} \begin{cases} \longrightarrow CoFeC_6H_{10}^+ + H_2 \quad (24) \\ \longrightarrow CoFeC_6H_8^+ + 2H_2 \quad (25) \end{cases}$$
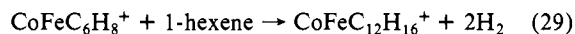
to Fe^+ and Co^+ which form predominantly C–C bond cleavage products.[31,54,55,64] Collisional activation of either product results in facile dehydrogenations, generating $CoFeC_6H_6^+$ with $CoC_6H_6^+$ observed at high energy. These results are consistent with dehydrocyclization[65] forming CoFe(benzene)$^+$ which eliminates Fe forming Co(benzene)$^+$.[18a]

$CoFeC_6H_{10}^+$ undergoes both dehydrogenation and C–C bond cleavages with 1-hexene, reactions 26–28. The C–C bond cleavage, reaction 28, is surprising since 1-pentene only yields dehydroge-

$$CoFeC_6H_{10}^+ + 1\text{-hexene} \begin{cases} \longrightarrow CoFeC_{12}H_{18}^+ + 2H_2 \quad (26) \\ \longrightarrow CoFeC_{12}H_{16}^+ + 3H_2 \quad (27) \\ \longrightarrow CoFeC_9H_{14}^+ + (C_3H_8) \quad (28) \end{cases}$$

nation with $CoFeC_5H_8^+$, reaction 22. Reaction 28 may proceed by initial insertion across an allylic C–C bond, resulting in elimination of C_3H_6 by β-hydride shifts, in analogy to reactions of Fe^+ and Co^+ with 1-hexene,[31,54,55,64] followed by dehydrogenation. $CoFeC_6H_8^+$, formed in reaction 25, yields dehydrogenation as the only product with 1-hexene, reaction 29.

$$CoFeC_6H_8^+ + 1\text{-hexene} \rightarrow CoFeC_{12}H_{16}^+ + 2H_2 \quad (29)$$

CID of both $CoFeC_{12}H_{18}^+$ and $CoFeC_{12}H_{16}^+$, formed in reactions 26, 27, and 29, result in dehydrogenations ultimately forming $CoFeC_{12}H_{12}^+$ in high efficiency. No other fragmentations are observed. Collisional activation may induce dehydrocyclizations, generating bis(benzene)$CoFe^+$. Absence of elimination of cobalt or iron at high kinetic energy suggests that bis(benzene)$CoFe^+$ is a much more stable complex than bis(cyclopentadienyl)$CoFe^+$, which as mentioned above readily eliminates cobalt or iron, generating ferrocene$^+$ and cobaltocene$^+$.[66] The above bis(benzene)$CoFe^+$ complex may consist of a structure similar to that proposed for bis(cyclopentadienyl)$CoFe^+$ with the benzene rings bridging the Co–Fe nucleus. Binuclear palladium complexes containing two benzene rings sandwiching the Pd–Pd unit have been prepared and characterized.[71]

(65) For recent reviews on dehydrocyclization in the presence of metal-containing catalysts see: (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.* **1983**, *52*, 625.
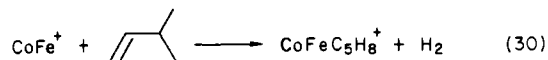
(66) Jacobson, D. B.; Freiser, B. S., *Organometallics*, in press.

(67) (a) Werner, H.; Tune, D.; Parker, G.; Jrygerm C.; Brauer, D. J. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 185. (b) Kuhn, A.; Werner, H. *J. Organomet. Chem.* **1979**, *179*, 421.

(68) (a) Werner, H.; Kraus, H. J. *J. Chem. Soc., Chem. Commun.* **1979**, 814. (b) Werner, H.; Kraus, H. J. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 948.

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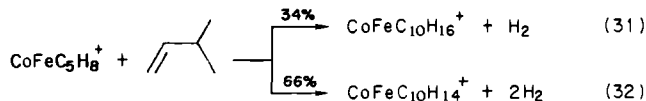
3-methyl-1-butene eliminates H_2 exclusively upon interaction with CoFe⁺, reaction 30. Both Fe⁺ and Co⁺ yield predominantly

$$CoFe^+ + \text{(structure)} \longrightarrow CoFeC_5H_8^+ + H_2 \qquad (30)$$

C–C bond cleavages.[54,55] Collisional activation of $CoFeC_5H_8^+$ results in facile elimination of C_5H_8 as the only fragmentation at low energy, forming CoFe⁺ with both Co⁺ and Fe⁺ observed at high energy.
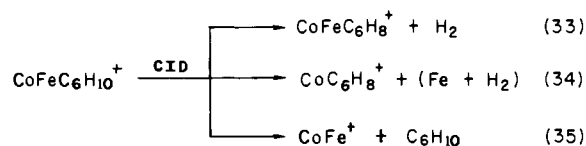
Absence of dehydrogenation forming $CoFeC_5H_6^+$ indicates that skeletal isomerization to a linear pentadiene does not occur. The absence of reaction of CoFe⁺ with 2-methyl-1,3-butadiene indicates that the product of reaction 30 may indeed consist formally of isoprene bound to CoFe⁺.

The secondary reactions of $CoFeC_5H_8^+$ with 3-methyl-1-butene yield dehydrogenations exclusively, reactions 31 and 32. Col-

$$CoFeC_5H_8^+ + \text{(structure)} \left\{ \begin{array}{l} \xrightarrow{34\%} CoFeC_{10}H_{16}^+ + H_2 \qquad (31) \\ \xrightarrow{66\%} CoFeC_{10}H_{14}^+ + 2H_2 \qquad (32) \end{array} \right.$$

lisional activation of both $CoFeC_{10}H_{16}^+$ and $CoFeC_{10}H_{14}^+$ results in sequential dehydrogenations ultimately forming $CoFeC_{10}H_{10}^+$ in low efficiency. Absence of any $CoC_{10}H_{10}^+$ and $FeC_{10}H_{10}^+$ formation indicates that rearrangement to cyclopentadienyl ligands has not occurred upon collisional activation.

2,3-Dimethyl-1-butene reacts similarly to 3-methyl-1-butene with dehydrogenation forming $CoFeC_6H_{10}^+$ occurring exclusively. Collisional activation of this ion yields the following fragmentations

$$CoFeC_6H_{10}^+ \xrightarrow{CID} \left\{ \begin{array}{l} \longrightarrow CoFeC_6H_8^+ + H_2 \qquad (33) \\ \longrightarrow CoC_6H_8^+ + (Fe + H_2) \qquad (34) \\ \longrightarrow CoFe^+ + C_6H_{10} \qquad (35) \end{array} \right.$$

Dehydrogenation may generate a tetramethylene ethane bridged FeCo⁺ complex, structure **2**. There are several examples of

2

2,2'-linked bis(allyl) bridging ligands known for diiron complexes.[72] Formation of $CoC_6H_8^+$ may proceed by either elimination of H_2 followed by loss of iron or by elimination of FeH_2.[73] Since $D°(Co^+-\eta^3-C_3H_5) > 71$ kcal/mol[59] and $D°(Co^+-Fe) < 71$ kcal/mol, complex **2** can eliminate iron.

The secondary reactions of $CoFeC_6H_{10}^+$ with 2,3-dimethyl-1-butene result in formation of $CoFeC_{12}H_{20}^+$ ($-H_2$, 25%) and $CoFeC_{12}H_{18}^+$ ($-2H_2$, 75%). As the complexity of the reacting linear butene isomers increases, so does the $2H_2/H_2$ elimination ratio for the secondary reactions. Collisional activation of $CoFeC_{12}H_{20}^+$ and $CoFeC_{12}H_{18}^+$ results in sequential dehydrogenations ultimately forming $CoFeC_{12}H_{12}^+$. Since skeletal isomerization does not occur for the 3-methyl-1-butene system vide supra, it is doubtful that it occurs here generating bis-(benzene)CoFe⁺.

(70) (a) Werner, H.; Kuhn, A.; Burschka, C. *Chem. Ber.* **1980**, *113*, 2291. (b) Werner, H.; Kuhn, A. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 412.
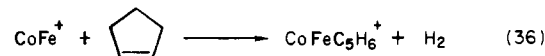
(71) (a) Allegra, G.; Immirzi, A.; Porri, L. *J. Am. Chem. Soc.* **1965**, *87*, 1394. (b) Allegra, G.; Casagrande, G. T.; Immirzi, A.; Porri, L.; Vitulli, G. *J. Am. Chem. Soc.* **1970**, *92*, 289.

(72) (a) Nakamura, A.; Kim. P. J.; Hagihara, N. *J. Organomet. Chem.* **1965**, *3*, 480. (b) Otsuka, S.; Nakamura, A.; Tuni, K. *J. Chem. Soc. A* **1968**, 2248. (c) Otsuka, S.; Nakamura, A.; Tuni, K. *J. Chem. Soc. A* **1971**, 154. (d) King, R. B.; Harmon, C. A. *J. Organomet. Chem.* **1975**, *86*, 239. (e) Sadeh, S.; Gaoni, Y. *J. Organomet. Chem.* **1975**, *93*, C31. (f) Howell, J. A. S.; Lewis, J.; Matheson, T. W.; Russell, D. R. *J. Organomet. Chem.* **1975**, *99*, C55.
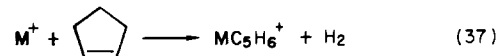
(73) FeH⁺ has been reported to undergo hydride abstraction in the gas phase, presumable forming FeH₂. The results suggest $\Delta H°_f(FeH_2) < 77.5$ kcal/mol. Halle, L. F.; Klein, F. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 2543.

3,3-Dimethyl-1-butene reacts relatively slowly with CoFe⁺ generating $CoFeC_5H_8^+$ (CH_4 elimination) exclusively. CID of this ion results in facile elimination of C_5H_8 at low collision energy with some Co⁺ and Fe⁺ observed at high energy. Absence of dehydrogenation indicates that this product consists formally of 2-methyl-1,3-butadiene bound to CoFe⁺. This reaction probably proceeds by initial insertion into an allylic C–C bond of the coordinated olefin followed by β-hydride abstraction resulting in methane elimination. The slow nature of this reaction indicates that insertion into allylic C–C bonds is not nearly as facile as insertion into allylic C–H bonds. No secondary reactions of $CoFeC_5H_8^+$ with 3,3-dimethyl-1-butene are observed. This indicates that the $CoFeC_5H_8^+$ complex cannot effect allylic C–C bond cleavage from a coordinated 3,3-dimethyl-1-butene.

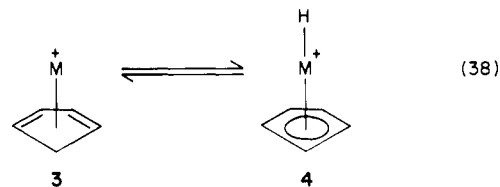**Cyclic C_5 to C_7 Olefins.** CoFe⁺ dehydrogenates cyclopentene forming $CoFeC_5H_6^+$, reaction 36. Collisional activation results

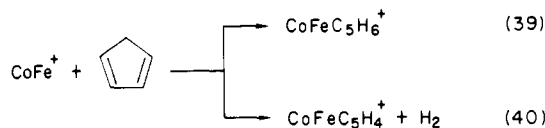$$CoFe^+ + \text{(pentagon)} \longrightarrow CoFeC_5H_6^+ + H_2 \qquad (36)$$

in efficient elimination of C_5H_6 with some Co⁺ and Fe⁺ observed at high energy. These CID results are identical (same peaks, intensities, and energy dependence within experimental error) with CID of $CoFeC_5H_6^+$ formed in reaction 20, providing further evidence for dehydrocyclization generating formally CoFe(cyclopentadiene)⁺ in reaction 20. FTMS-CID of $FeC_5H_6^+$ and $CoC_5H_6^+$, generated in reaction 37, yields elimination of C_5H_6

$$M^+ + \text{(pentagon)} \longrightarrow MC_5H_6^+ + H_2 \qquad (37)$$

as the only fragmentation.[25] Observation of 6 H/D exchanges with D_2[25] together with CID of $FeC_5H_6^+$ in a sector instrument[75] suggest that these $MC_5H_6^+$ ions consist of a cyclopentadiene complex, **3**, in dynamic equilibrium with the hydrido–cyclopentadienyl species, **4**.

$$\text{(38)}$$

3   **4**

Since fragmentations from CID in FTMS occur predominantly from multiple collisions with the target gas, direct fragmentations from a particular species may not always be sampled but rather processes with low-frequency factors, i.e., rearrangements. $CoFeC_5H_6^+$ ions generated in reactions 20 and 36 may, therefore, actually consist of a hydrido–cyclopentadienyl structure which, upon collisional activation, rearranges to a cyclopentadiene structure that then eliminates C_5H_6. Evidence for this is that monomeric cyclopentadiene reacts slowly with CoFe⁺, generating the condensation product, $CoFeC_5H_6^+$, as well as the dehydrogenation product, $CoFeC_5H_4^+$, reactions 39 and 40. Reaction

$$CoFe^+ + \text{(structure)} \left\{ \begin{array}{l} \longrightarrow CoFeC_5H_6^+ \qquad (39) \\ \longrightarrow CoFeC_5H_4^+ + H_2 \qquad (40) \end{array} \right.$$
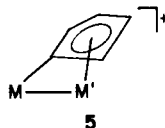
40 apparently proceeds through a hydrido–cyclopentadienyl intermediate which upon dehydrogenation probably generates a bridging $\eta^1:\eta^5$-C_5H_4–cyclopentadienyl complex, **5**. Complexes containing a bridging $\eta^1:\eta^5$-C_5H_4–cyclopentadienyl ligand have been characterized for dinuclear complexes of the early transition metals.[76]
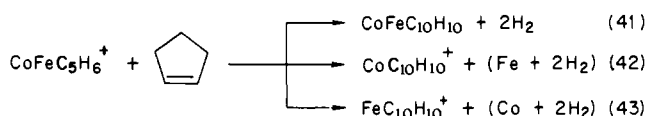
(74) Deleted in press.

(75) Peake, D. A.; Gross, M. L.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 4307.

(76) (a) Pez, G. P. *J. Am. Chem. Soc.* **1976**, *98*, 8072. (b) Guggenberger, L. J. *Inorg. Chem.* **1973**, *12*, 294. (c) Baker, E. C.; Raymond, K. N.; Marks, T. J.; Watcher, W. A. *J. Am. Chem. Soc.* **1974**, *96*, 7586.

5

CoFeC$_5$H$_6$$^+$, generated in reaction 36, yields the following products with cyclopentene
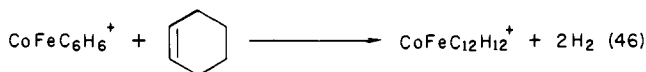

More CoFeC$_{10}$H$_{10}$$^+$ is produced with cyclopentene than with *trans*-1,3-pentadiene (Table I) and is related to the difference in the stabilities of *trans*-1,3-pentadiene and cyclopentene.[35] CID of CoFeC$_{10}$H$_{10}$$^+$, generated in reaction 41, is identical (same peaks, intensities, and energy dependence within experimental error) with that for CoFeC$_{10}$H$_{10}$$^+$ formed in reaction 23.[66] The products in reactions 39 and 40 yield formation of FeC$_{10}$H$_{10}$$^+$ and CoC$_{10}$H$_{10}$$^+$ exclusively with cyclopentadiene. The CID spectra of these ions are consistent with formation of ferrocene and cobaltocene ions.[77] Formation of FeC$_{10}$H$_{10}$$^+$ and CoC$_{10}$H$_{10}$$^+$ from CoFeC$_5$H$_4$$^+$ indicates that the integrity of the C$_5$ ring has been retained in reaction 40.

In contrast to cyclopentane, cyclohexene yields two products with CoFe$^+$, reactions 44 and 45. Reaction 45 is calculated to
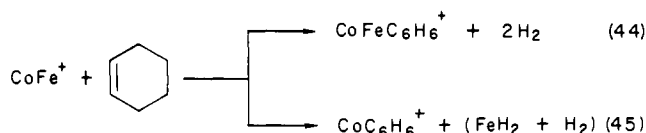
be endothermic by $\sim$16 kcal/mol with the neutral losses being an iron atom plus 2H$_2$.[78] If FeH$_2$ and H$_2$ are the neutral losses, however, this reaction becomes exothermic by $\sim$6 kcal/mol.[78] CID of CoFeC$_6$H$_6$$^+$ yields CoC$_6$H$_6$$^+$ in high efficiency with some Co$^+$ observed at high energy.

CoFeC$_6$H$_6$$^+$, generated in reaction 44, yields elimination of 2H$_2$ exclusively with cyclohexene, reaction 46. Collisional activation

of CoFeC$_{12}$H$_{12}$$^+$ yields an inefficient formation of CoC$_{12}$H$_{12}$$^+$ and CoFeC$_6$H$_6$$^+$ in roughly equal amounts with a small amount of CoC$_6$H$_6$$^+$ observed at high energy. These results are consistent with formation of a bis(benzene)CoFe$^+$ complex discussed earlier. Finally, observation of roughly equal amounts of CoC$_{12}$H$_{12}$$^+$ and CoFeC$_6$H$_6$$^+$ in the CID spectra implies roughly equal binding of Fe and benzene in the bis(benzene)CoFe$^+$ complex.

1-Methylcyclopentene yields formation of CoFeC$_6$H$_8$$^+$ and CoFeC$_6$H$_6$$^+$ with CoFe$^+$, reactions 47 and 48. Both products

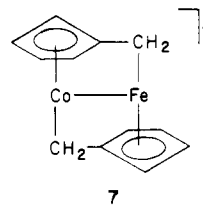
react with a second 1-methylcyclopentene, generating CoFeC$_{12}$H$_{12}$$^+$ exclusively. Collisional activation of CoFeC$_6$H$_6$$^+$, formed in reaction 48, results in facile formation of CoC$_6$H$_6$$^+$ with both CoFe$^+$ and Co$^+$ observed at high energy. CID of CoFeC$_{12}$H$_{12}$$^+$ formed from 1-methylcyclohexene yields CoC$_{12}$H$_{12}$$^+$ as the only fragmentation in low efficiency. Absence of
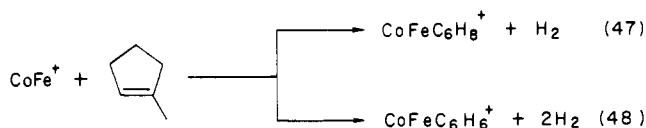
CoFeC$_6$H$_6$$^+$ and CoC$_6$H$_6$$^+$ in the CID spectra is evidence against isomerization to benzene. Hence, these products probably consist of fulvene bound to CoFe$^+$. Several stable metal–fulvene complexes are known.[79] In addition, dinuclear iron compounds containing a bridging fulvene are also known.[80] The structure of the CoFeC$_{12}$H$_{12}$$^+$ ions may, therefore, consist of **7**.

7

The primary reactions of 1-methylcyclohexene with CoFe$^+$ are similar to those for cyclohexene with reactions 49 and 50 observed.

CID of CoFeC$_7$H$_8$$^+$ yields facile formation of CoC$_7$H$_8$$^+$ with some Co$^+$ produced at high energy. This is indicative of a (toluene)-CoFe$^+$ species since toluene reacts with CoFe$^+$ exclusively by displacement of iron. Formation of CoC$_7$H$_8$$^+$ in reaction 50 probably proceeds by elimination of FeH$_2$ + H$_2$ since elimination of an iron atom plus 2H$_2$ is calculated to be $\sim$22 kcal/mol endothermic.[78]

The secondary reactions of CoFeC$_7$H$_8$$^+$, generated in reaction 49, yield dehydrogenations, reactions 51 and 52. CID of

CoFeC$_{14}$H$_{16}$$^+$ yields CoFeC$_{14}$H$_{14}$$^+$ and CoC$_{14}$H$_{14}$$^+$. Collisional activation of CoFeC$_{14}$H$_{14}$$^+$ results in facile elimination of iron, forming CoC$_{14}$H$_{14}$$^+$ with no further fragmentations observed. In addition, CID of the CoC$_{14}$H$_{14}$$^+$ so generated yields no fragmentations, indicating that it is very stable. Although other possibilities exist, the CoC$_{14}$H$_{14}$$^+$ ion may consist of two bridged benzene rings, structure **8**. This structure is analogous to the bridged metallocenes.[81]

8

Norbornadiene yields three products with CoFe$^+$, reactions 53–55. Collisional activation of CoFeC$_5$H$_6$$^+$ and CoC$_5$H$_6$$^+$ yields efficient elimination of C$_5$H$_6$, indicating formation of cyclopentadiene in reactions 53 and 54. Formation of CoFeC$_5$H$_6$$^+$ and CoC$_5$H$_6$$^+$ from norbornadiene probably proceeds simply by

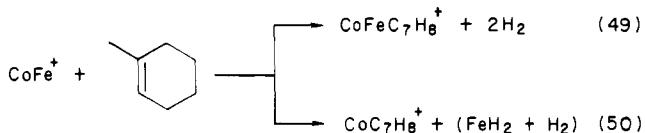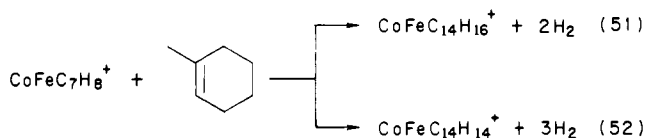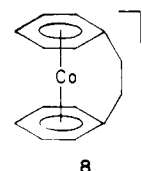(77) These ions lose C$_5$H$_5$ and 2C$_5$H$_5$ in low efficiency upon collisional activation as do ferrocene and nickelocene ions generated by electron impact on ferrocene and nickelocene.

(78) This is calculated by using the heats of formation in ref 35 for cyclohexene, benzene, and iron(g). $\Delta H°_f$(CoFe$^+$) = 315 $\pm$ 7 kcal/mol from ref 18a. $\Delta H°_f$(Co$^+$–benzene) = 230 kcal/mol with use of $D°$(Co$^+$–benzene) = 70 kcal/mol. $\Delta H°_f$(FeH$_2$) < 77.5 kcal/mol from ref 71.

(79) (a) Behrens, U.; Wiess, E. *J. Organomet. Chem.* **1975**, *96*, 399. (b) Behrens, U. *J. Organomet. Chem.* **1979**, *182*, 89. (c) Ceccon, D.; Benozzi, D. *J. Organomet. Chem.* **1980**, *185*, 231.

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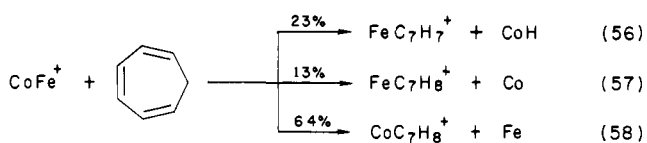
(81) (a) Rinehart, K. L.; Frerichs, A. K.; Kittle, P. A.; Westman, L. F.; Gustafson, D. H.; Pruett, R. L.; Mc Mahon, J. E. *J. Am. Chem. Soc.* **1960**, *82*, 4111. (b) Laing, M. B.; Trueblood, K. N. *Acta. Crystallogr.* **1965**, *19*, 373. (c) Hillman, M.; Gordon, B.; Weiss, A. J.; Guzikowski, A. P. *J. Organomt. Chem.* **1978**, *155*, 77. (d) Lentzner, H. L.; Watts, W. E. *J. Chem. Soc., Chem. Commun.* **1970**, *26*. (e) Eilbracht, P. *Chem. Ber.* **1976**, *109*, 3136. (f) Eilbracht, P.; Mayser, U.; Tiedtke, G. *Chem. Ber.* **1980**, *113*, 1420.

$$CoFeC_5H_6^+ + C_2H_2 \quad (53)$$
$$CoC_5H_6^+ + (FeC_2H_2) \quad (54)$$
$$CoC_7H_8^+ + Fe \quad (55)$$
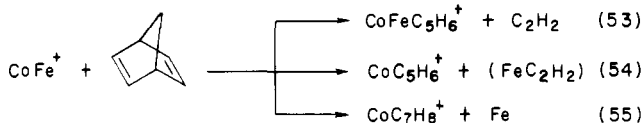
a retro-Diels–Alder reaction followed by loss of acetylene and Fe(acetylene), respectively. Both Co^+[82] and Fe^+[83] react with norbornadiene, generating predominantly $MC_5H_6^+$. CID of $CoC_7H_8^+$ formed in reaction 55 yields predominantly $CoC_5H_6^+$ at low kinetic energy which is in accord with CID of authentic Co(norbornadiene)$^+$. Displacement of iron by norbornadiene is surprising since the conjugated dienes, butadiene and cyclopentadiene, do not displace iron from $CoFe^+$. This suggests that the nonconjugated diene, norbornadiene, is bound strongly to Co^+, i.e., $D^\circ(Co^+-\text{norbornadiene}) > D^\circ(Co^+-Fe) = 66 \pm 7 \text{ kcal/mol}$.[18a]

The product of reaction 53, $CoFeC_5H_6^+$, yields formation of $CoC_{10}H_{10}^+$ and $FeC_{10}H_{10}^+$ exclusively with norbornadienes. CID of these $MC_{10}H_{10}^+$ ions is indicative of metallocene ions.[77]

Cycloheptatriene generates exlusively cleavage of the Co–Fe$^+$ bond, reactions 56–58. Cycloheptatriene reacts with Fe$^+$, yielding

$$\xrightarrow{23\%} FeC_7H_7^+ + CoH \quad (56)$$
$$\xrightarrow{13\%} FeC_7H_8^+ + Co \quad (57)$$
$$\xrightarrow{64\%} CoC_7H_8^+ + Fe \quad (58)$$

$FeC_7H_7^+$ as one of the products, reaction 59. CID of $FeC_7H_7^+$ produced in reactions 56 and 59 generates $C_7H_7^+$ exclusively.

$$Fe^+ + \longrightarrow FeC_7H_7^+ + H\cdot \quad (59)$$
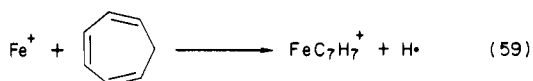
These $C_7H_7^+$ ions are unreactive with toluene, providing evidence against a benzyl ion which readily undergoes methylene transfer, reaction 60.[84] Hence, the above results suggest formation of

$$C_6H_5CH_2^+ + \longrightarrow C_8H_9^+ + C_6H_6 \quad (60)$$
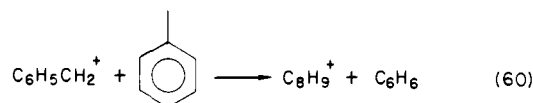
Fe(cycloheptatrienyl)$^+$ in reactions 56 and 59. In addition, the low IP of cycloheptatrienyl (6.24 eV)[35] is consistent with the absence of any Fe$^+$ in the above CID spectra of $FeC_7H_7^+$.[38] CID of $FeC_7H_8^+$ and $CoC_7H_8^+$, produced in reactions 57 and 58, are identical (same peaks, intensities, and energy dependence within experimental error) with those for authentic Fe(cycloheptatriene)$^+$ and Co(cycloheptatriene)$^+$. This indicates that $D^\circ(Fe^+-\text{cyclo-heptatriene})$ and $D^\circ(Co^+-\text{cycloheptatriene})$ both exceed $D^\circ(Co^+-Fe) = 66 \pm 7 \text{ kcal/mol}$.[18a]

Conclusions

The gas-phase chemistry of the dimer, CoFe$^+$, differs greatly from the corresponding atomic metal ions, Co$^+$ and Fe$^+$. Whereas Co$^+$ and Fe$^+$ react readily with alkanes predominantly by C–C bond insertions,[15a,21,25,31,34] CoFe$^+$ is unreactive with alkanes. Surprisingly, both Co_2CO^+[53] and the trimer $FeCo_2^+$[18b] react readily with alkanes predominantly by attacking C–H bonds. The CoFe$^+$ dimer reacts with aliphatic alkenes containing a linear C_4 unit, yielding predominantly dehydrogenation products and, again, is in contrast to the corresponding atomic ions which yield pre-

dominantly C–C bond cleavage products.[54,55] The only example where C–C bond cleavage occurs with aliphatic alkenes is for 3,3-dimethyl-1-butene which is a special case since it does not have labile hydrogens α to the double bond available for elimination. Instead, an allylic C–C bond insertion occurs followed by a β-hydride abstraction resulting in methane elimination.

A significant finding in these studies is that decomposition of linear C_5 and C_6 olefin cluster species yields facile dehydrocyclizations. Dehydrocyclizations forming C_5 and C_6 cyclic hydrocarbons are common for metal surfaces[65] and have previously been observed in the gas phase for collisional activation of Co-(pentenyl)$^+$.[59] CID of branched C_5 and C_6 olefin cluster complexes indicate that skeletal isomerization to linear C_5 and C_6 olefins does not occur whereas such processes can be effected by metal surfaces.[65]

As seen in Table I, the secondary reactions typically result in a greater amount of dehydrogenation thatn that for the primary reactions. Addition of an olefin ligand, therefore, apparently activates the cluster for dehydrogenation. In a related study addition of a carbonyl to Co_2^+ was found to activate it toward alkanes.[53]

The synthesis of bare anionic clusters by an analogous process to that for the positive clusters has thus far proven fruitless. For example, negative atomic metal ions react readily with neutral metalcarbonyls, resulting in elimination of a carbonyl, reaction 61.[85] Decomposition of the resulting $MM(CO)_{x-1}^-$ anion by

$$M^- + M(CO)_x \rightarrow MM(CO)_{x-1}^- + CO \quad (61)$$
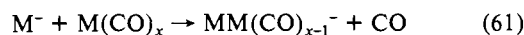
collisional activation yields facile elimination of a neutral metal followed by sequential carbonyl losses.[85] This suggests that the dinuclear anion can be thought of as an $M(CO)_{x-1}^-$ anion *weakly bound to a metal atom*. Decomposition of negative dimers containing additional carbonyls may lead to formation of bare dimeric anions. Collisional activation of $Fe_2(CO)_6^-$, generated in reaction 62,[86] however, yields sequential carbonly eliminations forming

$$Fe(CO)_3^- + Fe(CO)_5 \rightarrow Fe_2(CO)_6^- + 2CO \quad (62)$$
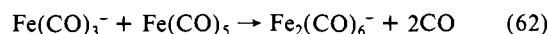
$Fe_2(CO)_4^-$ which then loses an iron atom. Several alternative sources for generation of bare anionic clusters in the gas phase are currently being pursued.

In addition to CoFe$^+$, a variety of other homonuclear and heteronuclear cluster ions are currently being studied. These include dimers, trimers, and tetramers.

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(83) Jacobson, D. B.; Freiser, B. S., unpublished results.
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(86) The gas-phase anionic chemistry of Fe(CO)$_5$ has previously been studied. (a) Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1971**, *93*, 4924. (b) Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 4808. (c) Dunbar, R. C.; Ennever, J. F.; Fackler, J. P. *Inorg. Chem.* **1973**, *12*, 2734. (d) Wronka, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 67.