Ligand Effects on Transition-Metal Ion Reactivity: Primary and Secondary Reactions of Co^+ and Ni^+ with Alkenes

R. L. Hettich[†] and B. S. Freiser*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

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The primary reactions of Co^+ and Ni^+ with alkenes exhibit both C–H and C–C bond cleavages as well as direct condensation products. Both Co^+ and Ni^+ will dehydrogenate isobutene whereas Fe^+ is unreactive with isobutene. Structural investigations of $MC_4H_6^+$, generated from M = Co or Ni and isobutene, by collision-induced dissociation, ion–molecule reactions, and deuterium exchange indicate that this ion most likely is M^+–butadiene. Evidently, skeletal rearrangement to butadiene is favored over formation of trimethylenemethane. Allylic hydrogen shifts from the alkene to the metal ion are considerably more facile for Co^+ than for Ni^+, as evidenced by the amount of dehydrogenation observed in the primary and secondary reactions with alkenes. The secondary reactions of the metal ions are significantly different. $Co(alkene)^+$ reacts readily with alkenes, generating both ligand displacement and dehydrogenation products. Ligand coupling, presumably in the form of Diels–Alder reactions, is observed for Co^+ and not for Ni^+. $Ni(alkene)^+$ is essentially unreactive with alkenes, usually forming only condensation complexes.

Introduction

Atomic transition-metal ions are very reactive in the gas phase, exhibiting both C–H and C–C bond cleavages with alkanes.[1] Naturally, the effect that ligands have on metal ion reactivity is of considerable interest. Reactions of MH^+,[2] MCH_2^+,[3] MCH_3^+,[4] MOH^+,[5] and MO^+[6] (M = Fe and Co) with hydrocarbons have been examined. Each of these ligands appears to activate the metal ions for C–H bond insertions with alkanes. Cr^+ is unreactive in the gas phase, but $CrCl^+$ activates both C–C and C–H bonds of alkanes.[7] $M(alkene)^+$ and MCO^+ for M = Fe, Co, and Ni are unreactive with alkanes.[8] $Fe(diene)^+$ and $Co(diene)^+$ predominantly dehydrogenate alkanes, but $Ni(diene)^+$ is unreactive.[9] $NiCp^+$ and $CoCp^+$ (Cp = cyclopentadienyl) attack C–H bonds of alkanes while $M(benzene)^+$ is unreactive with alkanes.[10] Thus, as expected, ligands dramatically affect metal ion reactivity, but the details of this interaction are still not well understood.

The primary and secondary reactions of Fe^+ with alkenes have been reported,[11] and the presence of an alkene ligand was observed to influence the reactivity of Fe^+. The primary reactions of Co^+ with some alkenes have been examined[12] and were found to be quite similar to the reactions of iron. Cobalt reacts faster with hydrocarbons than does iron and is known to catalyze cycloaddition reactions in solution.[13] The secondary reactions of Ni^+ with hydrocarbons are very slow and appear to form predominantly condensation complexes.[8,9] The objective of this study is to examine how the presence of an alkene ligand affects the reactivities of Co^+ and Ni^+ in the gas phase.

Experimental Section

All experiments were performed by using a prototype Nicolet FTMS-1000 Fourier transform mass spectrometer[14] equipped with a 5.2-cm cubic trapping cell situated between the poles of a Varian 15-in. electromagnet maintained at 0.9 T. A 0.25-in. hole was drilled into one of the transmitter plates of the cell to permit irradiation with a laser. Co^+ and Ni^+ were generated by focussing the frequency-doubled beam (532 nm) of a Quanta Ray Nd:YAG laser onto the appropriate metal foil, which was supported on the opposite transmitter plate. Details of the laser ionization technique have been outlined.[15]

Chemicals were obtained commercially in high purity and used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensable gases. Sample pressures were on the order of 3×10^{-7} Torr. Argon was used at a total static pressure of 8×10^{-6} Torr to help thermalize any kinetically or internally excited ions and to act as a collision gas for collision-induced dissociation. However, the presence of some excited-state ions cannot be completely ruled out. A Bayard–Alpert ionization gauge was used to monitor pressure.

Details of the collision-induced dissociation (CID) experiment have been discussed.[16] The fragmentation of a given ion can be monitored as the collision energy of the ion is varied (typically between 0 and 70 eV). 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.[17] Since collision-induced dissociation in this application is a multiple-collision process, substantial ion rearrangement may precede fragmentation. Hence, this technique may not be very diagnostic for structural determinations of multiple-ligand ions.

Product ion intensities for primary reactions are reproducible to ±10%. Identification of secondary reactions was accomplished by using swept double-resonance pulses to isolate the ion of interest. These ions were then allowed to react with the parent reagent gas, and the ionic products were detected. The formulae of the neutral products are assigned on the basis of thermodynamic considerations. Parentheses are used where exact assignment of neutrals is ambiguous. Unless specified, a given isomer was reacted with the parent gas from which it was generated. For example, $CoC_5H_8^+$ formed from 1-hexene was further reacted with 1-hexene;

[†] Current address: Oak Ridge National Lab., P.O. Box 2008, Oak Ridge, TN 37831-6120.

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Table I. Product Distributions for the Dissociative Reactions of Co^+ with Alkenes

	percentage of neutral lost							
	H_2	$3H_2$	CH_4	C_2H_4	(C_2H_6)	C_3H_6	(C_3H_8)	C_4H_8
1-butene	100							
cis-2-butene	100							
trans-2-butene	100							
isobutene	96			4				
1-pentene	7		10	62		21		
trans-2-pentene	28		29	33		10		
2-methyl-1-butene	34		30	25		11		
2-methyl-2-butene	32		30	29		9		
3-methyl-1-butene	30		34	25		11		
1-hexene	7	6		3	9	73		2
trans-2-hexene	6	3	4	33	40	6		8
trans-3-hexene	4	3	8	32	30	10		13
2-methyl-1-pentene	2		8	83		1		6
2-methyl-2-pentene	20		43	16	2	9	5	5
3-methyl-2-pentene	7		54	13	14	3	5	4
4-methyl-1-pentene	4		8	2		86		
2,3-dimethyl-1-butene	17		46	11	10	4	7	5
2,3-dimethyl-2-butene	16		47	13	9	5	6	4
3,3-dimethyl-1-butene	14	2	57	11		6	7	3

Table II. Product Distributions for the Dissociative Reactions of Ni^+ with Alkenes

	percentage of neutral lost						
	H_2	CH_4	C_2H_4	(C_2H_6)	C_3H_6	(C_3H_8)	C_4H_8
1-butene	92	8					
cis-2-butene	100						
trans-2-butene	100						
isobutene	96	2	2				
1-pentene	4	4	69		23		
trans-2-pentene	11	47	31		11		
2-methyl-1-butene	28	33	32		7		
2-methyl-2-butene	18	36	35		11		
3-methyl-1-butene	17	39	36		8		
1-hexene	3	3	3	16	69		6
trans-2-hexene	8	1	34	40	4		13
trans-3-hexene	10	2	39	33	5		11
2-methyl-1-pentene	6	5	54	14	9	4	8
2-methyl-2-pentene	15	51	16	3	7	7	1
3-methyl-2-pentene	17	39	12	16	5	8	3
4-methyl-2-pentene	17	46	7	3	16	9	2
2,3-dimethyl-1-butene	9	45	12	13	8	10	3
2,3-dimethyl-2-butene	17	50	13	10	3	5	2
3,3-dimethyl-1-butene	7	51	14	4	10	12	2

$CoC_5H_8^+$ formed from 2-methyl-1-butene was further reacted with 2-methyl-1-butene.

Results and Discussion

Primary Reactions. Co^+ and Ni^+ react slowly with ethene and propene to produce exclusively the condensation complexes. Absence of formation of ethyne and propyne indicates that dehydrogenation of these alkenes is unfavorable, in contrast to results obtained for early-transition-metal ions.[18] Tables I and II summarize the primary dissociation reactions of Co^+ and Ni^+ with alkenes. Both linear butenes and isobutene are readily dehydrogenated by Co^+ and Ni^+, whereas alkenes larger than butene exhibit C–C and C–H bond cleavages in their reactions with these two metal ions. The primary reactions of Fe^+ with alkenes are quite similar to those of Co^+ and Ni^+, although Fe^+ will not dehydrogenate isobutene.[11] The results given in Table I are in good agreement with results given by Beauchamp and co-workers for the primary reactions of Co^+ with some C_4–C_6 alkenes.[12] Co^+ was observed to generate a greater abundance of dehydrogenated products than Ni^+, which suggests that the ability for allylic hydrogens to move from the alkene to the metal ion is greater for Co^+ than for Ni^+. Further discussions of the primary reactions of these metal ions will be given in the appropriate sections below.

Secondary Reactions. Larger alkenes are bound more strongly to M^+ than are smaller alkenes, as evidenced by the fact that larger alkenes will displace smaller alkenes. For example, the predominant process observed by reacting $Co(C_2H_4)^+$ with 1-butene is displacement of C_2H_4 (reaction 1). However, reaction 2 also occurs. Assuming $D^0(Co^+-C_2H_4) = 46 \pm 8$ kcal/mol and $D^0(Co^+-C_4H_6) \approx 56$ kcal/mol[19] requires that the neutral product which is lost is C_2H_6, not $C_2H_4 + H_2$, in order for reaction 2 to be exothermic.[20] Similar results are obtained for other alkene displacement reactions. Apparently, allylic hydrogen shifts from the alkene to the metal ion are rapid enough that alkane loss can compete with simple displacement. Both Fe^+ and Ni^+ also reveal alkane loss, but simple ligand displacement is much more predominant for these two metal ions. Reaction 2 is approximately 15 kcal/mol more

$$Co^+-C_2H_4 + 1\text{-butene} \xrightarrow{79\%} Co^+-C_4H_8 + C_2H_4 \qquad (1)$$

$$Co^+-C_2H_4 + 1\text{-butene} \xrightarrow{21\%} Co^+-C_4H_6 + C_2H_6 \qquad (2)$$

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[18] Sunderlin, L.; Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.* **1987**, *109*, 78.

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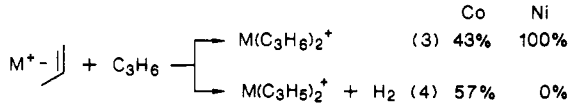
exothermic than reaction 1, but the greater intensity of the product of reaction 1 indicates that it is kinetically favored.

Reactions with Propene. Dehydrogenation competes with simple condensation in the secondary reactions of Co^+ with propene (reactions 3 and 4). Co^+ shows a higher percentage of the dehydrogenated product than does Ni^+ or Fe^+.[11] The secondary reaction of Ni^+ with propene yields only the condensation product $Ni(C_3H_6)_2^+$. These results agree well with earlier observations which indicated that allylic hydrogen shifts from a hydrocarbon onto a metal ion, followed by subsequent alkane or hydrogen elimination, are the most facile for Co^+, intermediate for Fe^+, and the least facile for Ni^+.[21]

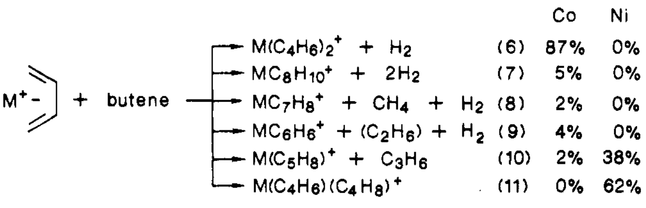


CID of the product of reaction 3 yields sequential loss of C_3H_6, suggesting a bis(propene) structure. Dehydrogenation is not observed in the CID of $Co(C_3H_6)_2^+$, indicating that no ligand coupling occurs in this case. $Co(C_3H_5)_2^+$, the product of reaction 4, was examined by CID and ligand displacement. CID energy >60 eV is required before fragmentation is observed, and then the fragmentation is characterized by rearrangement reactions, forming predominantly $CoC_6H_6^+$ and $CoC_3H_4^+$. These rearrangement reactions imply that ligand coupling can occur between the two C_3H_5 ligands upon activation. CH_3CN will displace alkenes and butadiene from Co^+ (since $D^0(Co^+-CH_3CN) > 61$ kcal/mol[22] exceeds most $D^0(Co^+-\text{alkene})$); however, CH_3CN will not displace any ligand from $Co(C_3H_5)_2^+$. The results stated above suggest that the product of reaction 4 may be Co^+–(bis(allyl)). The formation of Co^+–cyclohexene as the product of reaction 4, which would imply coupling of the propene ligands, can be ruled out by the ligand displacement reaction outlined above.

Reactions with Butenes. Both Co^+ and Ni^+ react with linear butenes to form predominantly $M(C_4H_6)^+$ (reaction 5), which presumably is a butadiene bound to the metal.

$$M^+ + \text{linear butene} \rightarrow MC_4H_6^+ + H_2 \quad (5)$$

The secondary reactions of Co^+ and Ni^+ with linear butenes (reactions 6–11) indicate that dehydrogenation is the major product observed for Co^+, whereas Ni^+ reveals carbene abstraction and simple condensation. All of the neutral losses were determined by mass balance and by assuming reaction exothermicity using the appropriate heats of formation from ref 20. In reaction 9 the C_2H_6 is in parentheses since $C_2H_4 + H_2$ is also thermodynamically possible. CH_3CN will sequentially displace two C_4H_6 units from $Co(C_4H_6)_2^+$, suggesting that the product of reaction 6 consists of two butadienes bound to the metal. CID of $Co(C_4H_6)_2^+$, shown in Figure 1, generates several products including $CoC_8H_{10}^+$, $CoC_8H_8^+$, $CoC_7H_8^+$, $CoC_6H_6^+$, $CoC_4H_6^+$, and Co^+. CID results indicate that $CoC_6H_6^+$ is Co^+–benzene. These product ions are probably generated via a Diels–Alder reaction between the two butadienes following collisional activation (reactions 12–15). CID of $Fe(C_4H_6)_2^+$, generated by a secondary reaction of Fe^+ with 1-butene, also yields $FeC_6H_6^+$, which was postulated to occur via a Diels–Alder reaction.[11]



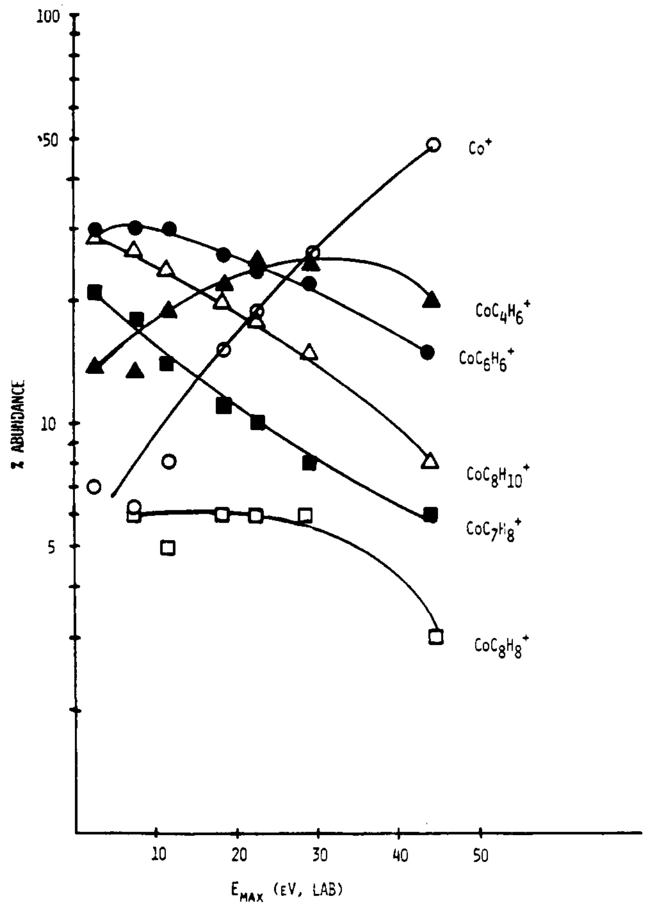
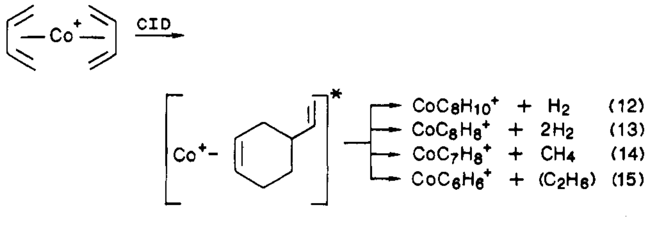
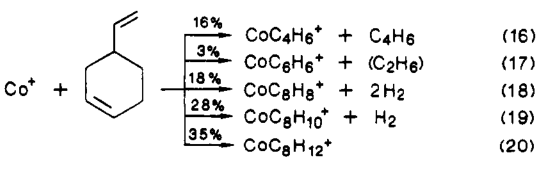


Figure 1. Collision-induced dissociation product ion intensities vs ion kinetic energy for $Co(C_4H_6)_2^+$ generated from reaction 6. The product ion intensities are normalized to 100%. Although the products are observed at low energies, they are not present at 0 eV.



In order to investigate the Diels–Alder mechanism mentioned above, the dissociative reactions of Co^+ with 4-vinylcyclohexene were examined (reactions 16–20).



Thermodynamically, the neutral product in reaction 17 could be either C_2H_6 or $C_2H_4 + H_2$. Some of the primary products react further with the parent to produce Co^+–(4-vinylcyclohexene) by ligand displacement. CID of Co^+–(4-vinylcyclohexene) reproduced the CID spectrum of $Co(C_4H_6)_2^+$ from reaction 6 exactly (including the small peak corresponding to $CoC_7H_8^+$), verifying this ligand coupling mechanism. Surprisingly, reaction of Co^+ with

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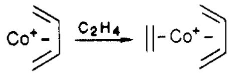
[21] Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 72.
[22] Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 4623.

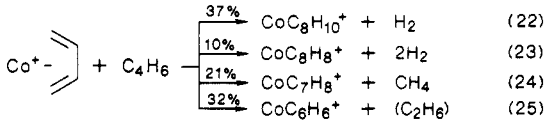
4-vinylcyclohexene does not yield $CoC_7H_8^+$, but CID of Co^+–(4-vinylcyclohexene) does produce this ion. In summary, the Co^+–(bis(butadiene)) rearranges to Co^+–(vinylcyclohexene) after CID excitation.

$Co(C_4H_6)^+$ reacts with ethylene and propene to produce only the condensation complexes, as shown for ethylene in reaction 21. CID of this ion revealed exclusive cleavage of C_2H_4 to yield $Co(C_4H_6)^+$ with no $CoC_6H_6^+$ observed, indicating that a Diels–Alder reaction does not occur in this case. Interestingly, even though the product of reaction 21 should be an ideal system for a Diels–Alder reaction, there is apparently a significant barrier to the process and the differences in $D^0(Co^+–C_2H_4)$ and $D^0(Co^+–C_4H_6)$ are great enough that elimination of the weakest ligand (C_2H_4) occurs instead of Diels–Alder coupling. Furthermore, $CoC_2H_4^+$ reacts with C_4H_6 by simple ligand displacement (and not by Diels–Alder coupling), forming $CoC_4H_6^+$.



(21)

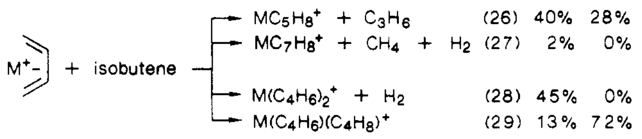
Secondary reaction of Co^+ with butadiene results in four products, shown in reactions 22–25. These reactions



further verify the Diels–Alder mechanism suggested in reactions 12–15. The intensities of the products observed in reactions 22–25 correlate with the percentages of fragments formed in the CID of $Co(C_4H_6)_2^+$ at ~7 eV, shown in Figure 1. Condensation of C_4H_6 onto $CoC_4H_6^+$ provides about 2.4 eV (56 kcal/mol) of internal energy (due to $D^0(Co^+–C_4H_6)^{19}$). Collisional activation of $CoC_4H_6^+$ at ~7 eV translational energy corresponds to a center-of-mass energy of ~1.8 eV and provides roughly the same amount of internal energy.

CID of $Ni(C_5H_8)^+$ from reaction 10 produces primarily $NiC_3H_6^+$ and Ni^+ with some $NiC_2H_2^+$ also observed. Apparently, reaction 10 occurs for Ni^+ by coupling the ligands together, resulting in carbene abstraction and incorporation into the butadiene ligand, followed by elimination of propene. This $NiC_5H_8^+$ complex rapidly reacts with butene to form the condensation product $Ni(C_5H_8)(C_4H_8)^+$. CID of the condensation product formed by reaction 11 of $NiC_4H_6^+$ with butene produces $NiC_4H_6^+$, $NiC_4H_8^+$, and Ni^+, suggesting that this ion probably is Ni^+–(butadiene)(butene), with no coupling of the ligands observed in this case.

$MC_4H_6^+$, formed from M^+ and 1-butene, undergoes several reactions with isobutene (reactions 26–29).



$CoC_4H_6^+$ reacts primarily by propene elimination and dehydrogenation (reactions 26 and 28), whereas propene elimination and condensation dominate for $NiC_4H_6^+$. Interestingly, the reactions of $NiC_4H_6^+$ with isobutene are quite similar to the reactions of $NiC_4H_6^+$ with linear butenes. The $Co(C_4H_6)_2^+$ produced in reaction 28 gives an identical CID spectrum to the $Co(C_4H_6)_2^+$ from reaction 6. The product of reaction 26 for Co^+ will dehydrogenate isobutene once more.

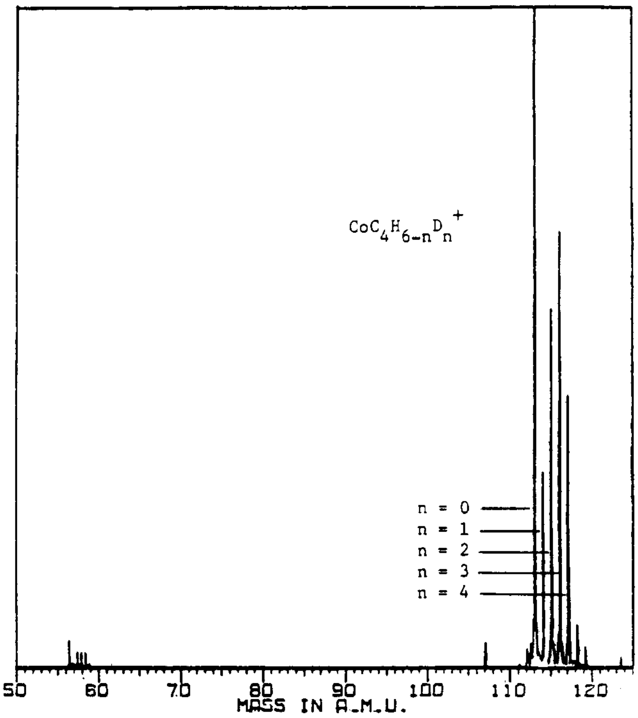


Figure 2. The deuterium exchange pattern for the reaction of $CoC_4H_6^+$, generated by reaction 5, with C_3D_6.

Fe^+ is unreactive with isobutene,[11] but both Co^+ and Ni^+ will dehydrogenate isobutene (reaction 30). Interestingly,

$$M^+ + \text{isobutene} \rightarrow MC_4H_6^+ + H_2 \qquad (30)$$

$$M = Co, Ni$$

the presence of C_4H_6 on M^+ activates carbene abstraction (reactions 10 and 26). Beauchamp has proposed a mechanism for reaction 30 with Co^+ involving a metallacyclobutane, possibly forming Co^+–butadiene.[12] Deuterium exchange, CID, and ion–molecule reactions were used to probe the structure of the product of reaction 30.

CID of $MC_4H_6^+$ generated by either reaction 5 or reaction 30 are identical and reveal exclusive loss of C_4H_6 to regenerate M^+. $MC_4H_6^+$, generated from M^+ and 1-butene in reaction 5, undergoes sequential deuterium exchange with C_3D_6 (reaction 31), revealing four fast exchanges and

$$MC_4D_nH_{6-n}^+ + C_3D_6 \rightarrow MC_4D_{n+1}H_{5-n}^+ + C_3D_5H \qquad (31)$$

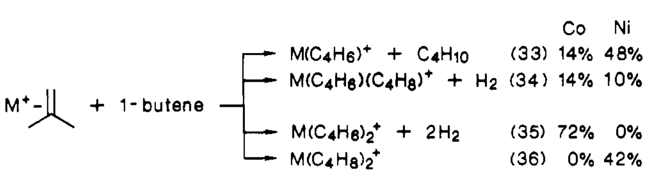
$$n = 0–5$$

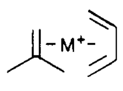
two slow exchanges. Figure 2 shows an example of the deuterium exchange pattern for $CoC_4H_6^+$. This same pattern is observed for $FeC_4H_6^+$ generated from Fe^+ and 1-butene. Continuous ejection of $MC_4H_5D^+$ does not quench the appearance of $MC_4H_4D_2^+$, indicating that more than one deuterium can be exchanged per collision. $MC_4H_6^+$ from M^+ and isobutene (reaction 30) undergoes the identical deuterium exchange pattern, with four fast and two slow exchanges. Finally, $MC_4H_6^+$, generated from M^+ and isobutene, undergoes the same secondary reactions with isobutene as are shown in reactions 26–29. Thus, the results obtained by CID, ion–molecule reactions, and deuterium exchange suggest that $MC_4H_6^+$ for M = Co and Ni from both reactions 5 and 30 have the same structure, presumably M^+–butadiene.

Co^+ and Ni^+ react with neopentane to form $M^+–C_4H_8$ (reaction 32), which has been identified as M^+–isobutene.[23]

(32)

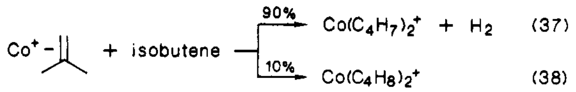
Reactions 33–36 show the reaction of M^+–isobutene with 1-butene. In order for reaction 33 to be exothermic, C_4H_{10} must be the neutral lost.[20] This eliminates the possibility of initially liberating H_2 to form $M(C_4H_6)(C_4H_8)^+$ and then splitting off the weaker ligand, C_4H_8. Reaction 34 is probably the dehydrogenation of the 1-butene to a butadiene, generating structure I. This complex can then eliminate H_2 in the same manner as reaction 28. CID of $Co(C_4H_6)_2^+$ produced in reaction 35 is the same as the CID of $Co(C_4H_6)_2^+$ produced in reactions 6 and 28, suggesting a bis(butadiene) structure.



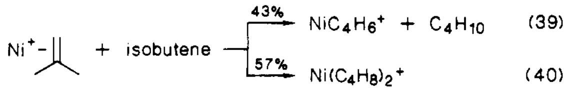


I

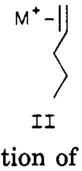
Reaction of Co^+–isobutene with isobutene yields two products (reactions 37 and 38). CID of $Co(C_4H_7)_2^+$ from reaction 37 indicates a tightly bound complex, yielding only rearrangements at high energy. In addition, CH_3CN will not displace any ligand from $Co(C_4H_7)_2^+$, suggesting that the product of reaction 37 may be Co^+–(bis(methylallyl)). Reactions 37 and 38 are probably similar to reactions 3 and 4.



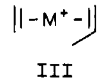
The reaction of Ni^+–isobutene with isobutene yields both alkane loss and condensation (reactions 39 and 40) but no H_2 loss, which is consistent with the results of the reaction of $NiC_3H_6^+$ with propene.



Reactions with Linear Pentenes. The secondary reactions of 1-pentene and *trans*-2-pentene are remarkably similar, suggesting that reversible allylic hydrogen shifts can interconvert the two structures. Small olefins bound to M^+ are displaced by larger olefins. For example, both $MC_2H_4^+$ and $MC_3H_6^+$ react with pentene to form predominantly $MC_5H_{10}^+$ (a small amount of $MC_5H_8^+$ is also formed, implying that C_3H_8 is the neutral lost). Two isomeric structures, II and III, can be postulated for $MC_5H_{10}^+$. Reaction of either $MC_2H_4^+$ or $MC_3H_6^+$ with pentene yields presumably structure II due to simple ligand displacement. Isomers II and III have been differentiated by using ion–molecule reactions and CID,[23] as well as photodissociation.[24] The ion of structure II can easily rearrange to structure III upon activation, as indicated by the prominent losses of C_2H_4 and C_3H_6 in the primary reactions of M^+ with pentene (Tables I and II).

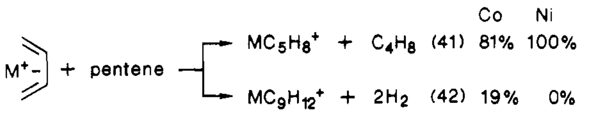


II



III

Two reactions are observed between $M(C_4H_6)^+$ and pentene (reactions 41 and 42). These results are surprisingly and inexplicably different than reactions 6–10 for $M(C_4H_6)^+$ and butene. Interestingly, a comparison of reactions 10 and 41 suggests that the $MC_5H_8^+$ product ions in reaction 41 may be formed by two different mechanisms for Co^+ and Ni^+. Whereas ligand coupling to form C_5H_8 seems reasonable for Ni^+ in analogy to reaction 10, most likely dehydrogenation of pentene to form pentadiene occurs for Co^+. As discussed below, however, the dehydrogenation mechanism for Ni^+ may also be important. In either case butene can be eliminated (once again, C_4H_8 must be the neutral lost in order for reaction 41 to be exothermic), or for Co^+, double dehydrogenation involving ligand coupling can generate the product of reaction 42.



Reaction of $CoC_5H_8^+$ with pentene produces only the doubly dehydrogenated product (reaction 43). CID of $CoC_{10}H_{14}^+$ yields additional dehydrogenation as well as

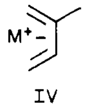
$$CoC_5H_8^+ + \text{pentene} \rightarrow CoC_{10}H_{14}^+ + 2H_2 \qquad (43)$$

$CoC_6H_6^+$ formation, suggesting ligand coupling in the form of Diels–Alder reactions. $NiC_5H_8^+$ is unreactive with pentenes, forming only the condensation product at high pressures.

M^+–pentene, generated by ligand displacement, reacts with pentene to form a variety of products, as shown in reactions 44–48. CID of $CoC_{10}H_{16}^+$ produces predominantly $CoC_6H_6^+$, which was identified as Co(benzene)$^+$, indicating that ligand coupling occurs for this ion. CID of $NiC_{10}H_{20}^+$ and $Ni(C_3H_6)(C_5H_{10})^+$ reveal simple ligand cleavages, indicating that ligand coupling is unfavorable for these ions.

			Co	Ni
$M(C_5H_{10})^+$ + pentene	$\rightarrow M(C_3H_6)(C_5H_{10})^+ + C_2H_4$	(44)	29%	6%
	$\rightarrow M(C_2H_4)(C_5H_{10})^+ + C_3H_6$	(45)	11%	2%
	$\rightarrow MC_5H_8^+ + C_5H_{12}$	(46)	12%	33%
	$\rightarrow MC_{10}H_{16}^+ + 2H_2$	(47)	29%	8%
	$\rightarrow MC_{10}H_{20}^+$	(48)	19%	51%

Reactions with Methylbutenes. Primary reaction of M^+ with 2- and 3-methylbutene produces a large percentage of the dehydrogenated product, which probably exists as structure IV shown below. Reactions 49 and 50 of $CoC_5H_8^+$ with the methylbutenes reveal ligand coupling to form substituted benzenes, implying that the isoprene unit is present to allow Diels–Alder coupling. The same products are formed in the reactions of $MC_4H_6^+$ with the methylbutenes as were formed in reactions 41 and 42. CID of $CoC_9H_{12}^+$ generates dehydrogenation products as well as $CoC_7H_8^+$ and $CoC_6H_6^+$. CID of $CoC_{10}H_{14}^+$ from reaction 50 yields dehydrogenation and formation of $CoC_8H_{10}^+$, $CoC_7H_8^+$, and $CoC_6H_6^+$, which are all possible from a Diels–Alder reaction. As expected, $NiC_5H_8^+$ is unreactive with the methylbutenes, forming only the condensation complex at high pressures. The parent ion $CoC_5H_{10}^+$, generated by ligand displacement, reacts with the methylbutene to produce three products (reactions 51–53).



IV

$CoC_5H_8^+$ + methylbutene	$\xrightarrow{18\%} CoC_{10}H_{16}^+ + H_2$	(49)
	$\xrightarrow{82\%} CoC_{10}H_{14}^+ + 2H_2$	(50)

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[23] Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 5197.

$$\mathrm{CoC_5H_{10}^+ + methylbutene} \xrightarrow{28\%} \mathrm{CoC_5H_8^+ + C_5H_{12}} \quad (51)$$

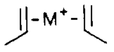
$$\xrightarrow{60\%} \mathrm{CoC_{10}H_{16}^+ + 2H_2} \quad (52)$$

$$\xrightarrow{12\%} \mathrm{CoC_{10}H_{14}^+ + 3H_2} \quad (53)$$

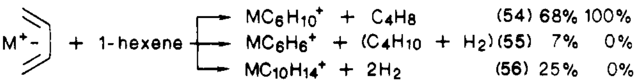
$NiC_5H_8^+$ is the only product obtained by reacting $NiC_5H_{10}^+$ with methylbutene. The product ions in reactions 52 and 53 are probably formed by ligand coupling in direct analogy to the structures of the ions formed in reactions 49 and 50.

Reactions with Linear Hexanes. The major primary product of M^+ with 1-hexene is $MC_3H_6^+$. As expected, secondary reaction of this ion with 1-hexene results in displacement of C_3H_6 to give $MC_6H_{12}^+$, which probably exists as structure V. Another isomer, structure VI, can be postulated for $MC_6H_{12}^+$. The ease of converting the ion of structure V to VI upon activation can be observed in the primary reactions of M^+ with hexene, which reveal propene elimination to form $MC_3H_6^+$ as the predominant product (see Tables I and II). Structures V and VI have been distinguished by ion–molecule reactions and photodissociation.[23,24]


V


VI

The reactions of $MC_4H_6^+$ with hexene are shown in reactions 54–56. The hexene is probably initially dehydrogenated to a hexadiene, followed by butene elimination or by coupling with the butadiene to yield a substituted cyclohexadiene. Note that $MC_5H_8^+$ is not observed, indicating a significant change in mechanism for the reaction of $NiC_4H_6^+$ with butene (reaction 10) relative to the reaction of $NiC_4H_6^+$ with hexene (reaction 54). Formation of $CoC_6H_6^+$ in reaction 55 is energetically possible if either (C_4H_{10} + H_2) or (C_4H_8 + $2H_2$) are the neutrals lost.[20] $CoC_6H_{10}^+$ reacts with linear hexenes to generate four products (reactions 57–60). $NiC_6H_{10}^+$ is unreactive with linear hexenes.



		Co	Ni
$MC_6H_{10}^+ + C_4H_8$	(54)	68%	100%
$MC_6H_6^+ + (C_4H_{10} + H_2)$	(55)	7%	0%
$MC_{10}H_{14}^+ + 2H_2$	(56)	25%	0%

$$\mathrm{CoC_6H_{10}^+ + 1\text{-}hexene} \xrightarrow{39\%} \mathrm{CoC_6H_6^+ + (C_6H_{14} + H_2)} \quad (57)$$

$$\xrightarrow{20\%} \mathrm{CoC_{12}H_{18}^+ + 2H_2} \quad (58)$$

$$\xrightarrow{21\%} \mathrm{CoC_{12}H_{20}^+ + H_2} \quad (59)$$

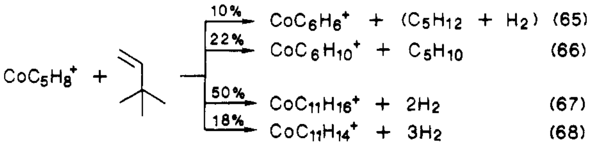
$$\xrightarrow{20\%} \mathrm{CoC_{12}H_{22}^+} \quad (60)$$

Primary reaction of *trans*-2-hexene with M^+ produces $MC_4H_8^+$. Secondary reaction of this ion with 2-hexene shows simple displacement of C_4H_8 to give $MC_6H_{12}^+$ (some $MC_6H_{10}^+$ is also observed), suggesting that the $MC_4H_8^+$ is probably M(butene)$^+$, and not $M(C_2H_4)_2^+$. Reaction of M^+–hexene, formed by ligand displacement, with hexene indicates the ease of propene elimination, reaction 62.

$MC_6H_{12}^+$ + 1-hexene →

		Co	Ni
$MC_6H_{10}^+ + C_6H_{14}$	(61)	13%	38%
$MC_9H_{18}^+ + C_3H_6$	(62)	42%	42%
$MC_{12}H_{20}^+ + 2H_2$	(63)	25%	0%
$MC_{12}H_{24}^+$	(64)	20%	20%

Reactions with Dimethylbutenes. Methane loss to generate $MC_5H_8^+$ is the predominant product in the primary reactions of M^+ with the dimethylbutenes. Structure IV is the most reasonable assignment for $MC_5H_8^+$ in this case. Four products are formed in the reactions of $CoC_5H_8^+$ with 3,3-dimethyl-1-butene (reactions 65–68).



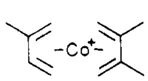
$$\xrightarrow{10\%} \mathrm{CoC_6H_6^+ + (C_5H_{12} + H_2)} \quad (65)$$

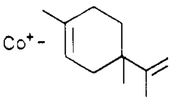
$$\xrightarrow{22\%} \mathrm{CoC_6H_{10}^+ + C_5H_{10}} \quad (66)$$

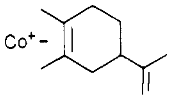
$$\xrightarrow{50\%} \mathrm{CoC_{11}H_{16}^+ + 2H_2} \quad (67)$$

$$\xrightarrow{18\%} \mathrm{CoC_{11}H_{14}^+ + 3H_2} \quad (68)$$

Reaction of $NiC_5H_8^+$ with the dimethylbutenes generates only $NiC_6H_{10}^+$. Interestingly, the reaction of $CoC_5H_8^+$ with 2,3-dimethyl-1-butene yields predominantly reactions 66 and 67 in roughly equal intensities with only a trace of reaction 68 observed. Formation of $CoC_6H_6^+$ (reaction 65) is also observed for linear hexenes and may imply that 3,3-dimethyl-1-butene undergoes skeletal rearrangement with Co^+ to form a linear structure. Further evidence for the occurrence of a Diels–Alder reaction as the mechanism for ligand coupling is provided by considering reactions 67 and 68 for the different dimethylbutene isomers. Hydrogen migration can occur between $CoC_5H_8^+$ and the dimethylbutene leading to a $Co(C_5H_{10})(C_6H_{10})^+$ species which can eliminate C_5H_{10} (reaction 66). Alternatively, H_2 elimination followed by a Diels–Alder reaction for VII (from 2,3-dimethyl-1-butene) would generate either structure VIII or IX. Clearly, structure VIII cannot liberate $2H_2$ to conjugate the ring so reaction 68 would not be observed in this case. Any Diels–Alder reaction between $CoC_5H_8^+$ and 3,3-dimethyl-1-butene would allow $3H_2$ loss to occur, forming ultimately a substituted benzene (reaction 68).


VII


VIII


IX

Reactions with Methylpentenes. The primary and secondary reactions of M^+ with the methylpentenes are very similar to reactions with linear hexenes, except $CoC_6H_6^+$ is not observed in these reactions. As a result of this similarity, only the differences between the hexenes and the methylpentenes are outlined in the following section. Reaction of M^+ with the methyl-2-pentenes yields more dehydrogenation than with the other methylpentenes. This may be a reflection of the fact that several reversible allylic hydrogen shifts are necessary for alkane elimination from the methyl-2-pentenes.

$MC_3H_6^+$ is the major product from M^+ and 4-methyl-1-pentene. Displacement of propene is the only reaction of $MC_3H_6^+$ with 4-methyl-1-pentene (reaction 69).

$$\mathrm{MC_3H_6^+ + C_6H_{12} \rightarrow MC_6H_{12}^+ + C_3H_6} \quad (69)$$

$MC_6H_{12}^+$ from reaction 69 reacts with 4-methyl-1-pentene to generate $MC_9H_{18}^+$ as the major product (reaction 70),

$$\mathrm{MC_6H_{12}^+ + C_6H_{12} \rightarrow MC_9H_{18}^+ + C_3H_6} \quad (70)$$

verifying the ease of propene elimination for 4-methyl-2-pentene (in this case, propene elimination could come from either ligand).

M^+ reacts with 2-methyl-1-pentene to form primarily $MC_4H_8^+$, which is most likely M^+–isobutene based on a scheme previously outlined for reaction of M^+ with al-

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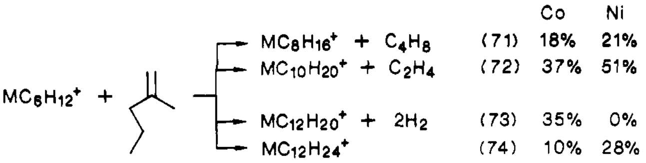
[24] Hettich, R. L.; Freiser, B. S., in preparation.

kenes.[11] $MC_4H_8^+$ reacts with 2-methyl-1-pentene to displace C_4H_8 yielding only $MC_6H_{12}^+$, which further reacts with 2-methyl-1-pentene to generate four products (reactions 71–74). The elimination of C_4H_8 or C_2H_4 (reactions 71 and 72) verify the ability of Co^+ to rearrange 2-methyl-1-pentene to Co^+–(isobutene)(ethylene).



Comparison of Fe^+, Co^+, and Ni^+ Reactivities. The primary reactions of Fe^+, Co^+, and Ni^+ with alkenes are very similar, exhibiting both C–C and C–H bond cleavages. Interestingly, both Co^+ and Ni^+ dehydrogenate isobutene, whereas only condensation occurs for Fe^+.[11] This fact may be a reflection of the somewhat stronger $D^0(M^+\text{–alkene})$ for M = Co and Ni or due to the ease of forming nickela- and cobaltacyclobutane complexes, which appear to be necessary for the dehydrogenation of isobutene. Each of these metal ions also yield condensation complexes with alkenes larger than butene. These condensation complexes most likely consist of a rearranged form of the alkene coordinated to the metal ion.

Initial coordination of the alkene to the metal ion probably occurs through the π-bond of the alkene. This fact is supported by the observation that most of the products formed result from allylic C–C and C–H bond insertions. The fact that more dehydrogenation is observed for the primary and secondary reactions of Co^+ relative to either Fe^+ or Ni^+ indicates that allylic hydrogen shifts from the alkene to the metal ion and subsequent elimination of H_2 is the most facile for Co^+, intermediate for Fe^+, and the least facile for Ni^+.

The secondary reactions for these ions reveal remarkable differences. $Co(alkene)^+$ ions react readily with alkenes, yielding both ligand displacement and dehydrogenation reactions. Ligand coupling, evidently in the form of Diels–Alder reactions, is very pronounced for Co^+. Ligand coupling occurs to a limited extent for Fe^+ and is basically nonexistent for Ni^+. Interestingly, while Ni^+ is fairly reactive with alkenes, $Ni(alkene)^+$ is essentially unreactive with alkenes. The presence of an alkene or diene on Ni^+ drastically reduces the reactivity, and simple condensations are often the only products observed for the secondary reactions of Ni^+ with alkenes.

Further experimental and theoretical investigations will certainly be required to understand these differences in reactivity. However, simplistic consideration of possible electronic structures for these ions can yield valuable insight for the observed reactivities. If an alkene ligand is bound to a metal ion primarily through electron donation of the alkene π-cloud into an empty 4s orbital of the metal ion, then the ability of the metal ion to form an s^0d^n electronic state and the number of resulting unpaired d electrons will influence further reactivity. For example, coordination of an alkene to Ni^+, which has an s^0d^9 ground electronic state, would leave one unpaired d electron. Hence, the ability of the Ni^+–alkene complex to react by oxidative addition would be greatly diminished, which is consistent with the observations of the secondary reactions of Ni^+. In contrast, both Fe^+–alkene and Co^+–alkene complexes bound in this manner would still have at least two or more unpaired d electrons available for oxidative additions and their secondary reactions should be readily observed, which is indeed the case.

Acknowledgement is made to the Division of Chemical Sciences in the Office of Basic Energy Sciences in the United States Department of Energy (DE-FG02-87ER13766) for supporting this research and to the National Science Foundation (CHE-8612234) for continued support of the FTMS. We wish to thank D. B. Jacobson for many helpful discussions. R.L.H. would like to thank the American Cyanamid Co. for providing fellowship support.

Registry No. $Co(C_4H_6)_2^+$, 122174-45-2; $CoC_4H_6^+$, 122174-46-3; $CoC_6H_6^+$, 102307-50-6; Co^+, 16610-75-6; Ni^+, 14903-34-5; 1-butene, 106-98-9; *cis*-2-butene, 106-98-9; *trans*-2-butene, 624-64-6; isobutene, 115-11-7; 1-pentene, 109-67-1; *trans*-2-pentene, 646-04-8; 2-methyl-1-butene, 563-46-2; 2-methyl-2-butene, 513-35-9; 3-methyl-1-butene, 563-45-1; 1-hexene, 592-41-6; *trans*-2-hexene, 4050-45-7; *trans*-3-hexene, 13269-52-8; 2-methyl-1-pentene, 763-29-1; 2-methyl-2-pentene, 625-27-4; 3-methyl-2-pentene, 922-61-2; 4-methyl-1-pentene, 691-37-2; 2,3-dimethyl-1-butene, 563-78-0; 2,3-dimethyl-2-butene, 563-79-1; 3,3-dimethyl-1-butene, 558-37-2; ethene, 74-85-1; propene, 115-07-1.