= fulvene) upon collisional activation.

Conclusions

$FeCH_2^+$ and $CoCH_2^+$ react with cyclopropane and cyclobutane exclusively by initial insertion across a C–C bond generating an activated methylidene–metallacyclic species which decomposes via a variety of pathways. There is good evidence for ring expansion via migratory insertion of methylene into the metallacyclic ring system. Methylene/alkyl coupling has been implicated in another study involving the reactions of MCH_2^+ (M = Fe, Co) with aliphatic alkanes,[24] and this process is well supported in solution chemistry.[38-44] The ring-expansion product for reaction of MCH_2^+ with cyclobutane, reaction 15, generates M-c-$C_5H_6^+$.

With cyclopentane and cyclohexane, retention of the ring's integrity dominates the reactions. This suggests initial attack of C–H bonds and not C–C bonds. The difference in reaction mechanisms between small and large cyclic alkanes is attributed to the strong C–H bonds in cyclopropane and cyclobutane coupled with C–C bonds weakened by strain energy. Therefore, these weak C–C bonds are preferentially attacked. The C–C bonds in cyclopentane and cyclohexane have little or no strain energy and, therefore, are not as susceptible to attack relative to the C–H bonds. Similar behavior has been observed for reactions of MCH_3^+ (M = Fe and Co),[62] Fe^+[17,61], and Co^+[16,17] with cyclic alkanes where cyclopropane and cyclobutane are dominated by ring cleavages while cyclopentane and cyclohexane are dominated by retention of the ring's integrity.

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

Registry No. $FeCH_2^+$, 90143-30-9; $CoCH_2^+$, 76792-07-9; H_2, 1333-74-0; CH_4, 74-82-8; C_2H_4, 74-85-1; CH_2D_2, 676-55-1; $C_2H_2D_2$, 29060-53-5; $FeCD_2^+$, 93604-57-0; $CoCD_2^+$, 93604-58-1; cyclopropane, 75-19-4; cyclobutane, 287-23-0; cyclopentane, 287-92-3; cyclohexane, 110-82-7.

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Dynamics of Monoolefin–Metal Ion Complexes in the Gas Phase. Determination of the Number of Labile Hydrogens by Reaction with C_2D_4

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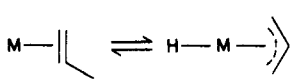
Abstract: H/D exchange reactions of organometallic ions with D_2 in the gas phase have proven valuable in determining the number of labile hydrogens in the complex. Unfortunately, many complexes are not observed to exchange with D_2. In this paper we demonstrate that C_2D_4 can extend the variety of complexes which may be studied. The propene complexes of Fe^+, Co^+, and Ni^+ which are unreactive with D_2 undergo 5 H/D exchanges with C_2D_4. These results are rationalized by invoking an equilibrium between the propene and hydrido-π-allyl species promoted by the activation afforded by ethene-d_4 coordination. The Rh(propene)$^+$ complex is observed to exchange all 6 hydrogens suggesting an additional mechanism involving a vinylic C–H bond insertion. In addition, this Rh(propene)$^+$ species undergoes multiple exchanges per C_2D_4 encounter in contrast to the M(propene)$^+$ species of Fe^+, Co^+, and Ni^+ which undergo only a single exchange per C_2D_4 encounter. The rate of the above exchanges falls into the order $Rh^+ > Co^+ > Fe^+ > Ni^+$. Rh(1,3-pentadiene)$^+$ undergoes 5 rapid exchanges with C_2D_4 while the corresponding iron and cobalt complexes yield 5 slow exchanges with no exchange observed for the nickel complex. No multiple exchanges occur for these pentadiene ions. The isomeric Rh(2-methylbutadiene)$^+$ species undergoes 5 slow exchanges with none observed for the iron, cobalt, and nickel species. M-c-$C_5H_6^+$ (M = Fe, Co, Ni) undergo 6 rapid exchanges with multiple exchanges predominating. The Rh-c-$C_5H_6^+$ species only undergoes one rapid exchange. Both Rh-c-$C_7H_8^+$ and Co-c-$C_7H_8^+$ generated from cycloheptatriene yield one slow exchange with C_2D_4 with none observed for Fe-c-$C_7H_8^+$ and Ni-c-$C_7H_8^+$.

The ability of transition-metal complexes to effect structural transformations in organic substrates constitutes a basic facet of organometallic chemistry. One such transformation which has received much attention is the metal-promoted isomerization of olefins.[1] Under hydride-free conditions, reversible insertion into an allylic carbon–hydrogen bond has been frequently invoked as the mechanism for catalytic isomerization of olefins, Scheme I,[2] and is supported by detailed stereocemical studies.[3-6] This mechanism is supported by detailed stereochemical studies.[3-6] In addition, the hydrido-π-allyl intermediate has been observed directly,[7,8] as well as in a dynamic equilibrium with the olefin complex,[8-10] eq 1. Therefore, the mechanism presented in Scheme



(1)

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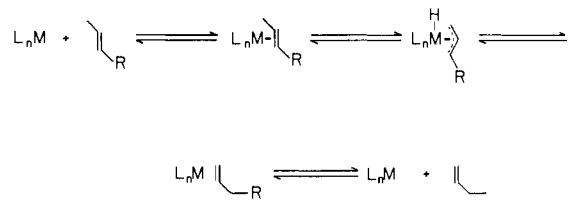
I for the isomerization of olefins under hydride-free conditions has gained general acceptance.

Scheme I



The above olefin isomerization requires that the metal complex contain an empty coordination site. An atomic transition metal

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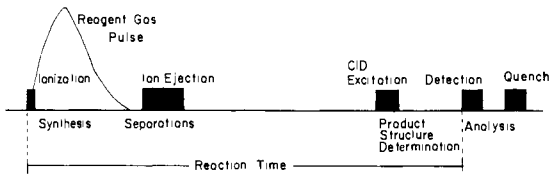
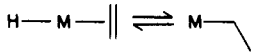


Figure 1. Sequence of events for pulsed valve addition of reagent gas for the FTMS experiment. See the Experimental Section for a more detailed explanation.

interacting with propene may, therefore, effect conversion to a hydrido-π-allyl complex, eq 1. Isolated monoolefin–metal ion complexes can readily be generated in the gas phase, either by electron impact on an appropriate organometallic complex[11] or by ion–molecule reactions.[12-14] Studying the dynamics of these ions is challenging since one does not have the luxury of such techniques as NMR, IR, ESR, X-ray, etc., to elucidate structures. Instead, gas-phase chemists must rely on chemical methods for probing ion structures and dynamics. Methods for probing ion structure in the gas phase are increasing and include isotopic labeling, collision-induced dissociation (CID), photodissociation, and specific ion–molecule reactions.

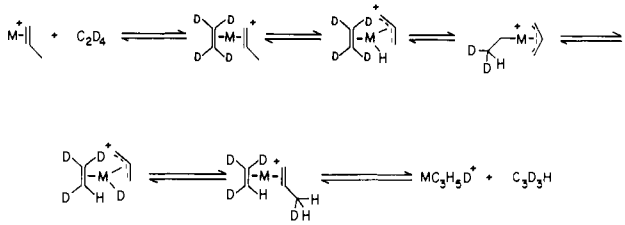
Reactions of transition-metal ions with a variety of organic species generates M(olefin)$^+$ species.[12-14] The structures of several M(olefin)$^+$ species (M = Fe, Co, Ni) have been the focus of recent investigations.[15-17] The results suggest formation of a rigid M(propene)$^+$ species with no evidence for a hydrido-π-allyl complex for Fe, Co, and Ni. H/D exchange with deuterium has been used to probe metal-hydride character in the gas phase.[18-20] Absence of H/D exchange for these species, however, does not rule out the presence of a metal-hydride since FeH$^+$ does not undergo exchange in the presence of deuterium.[20]

Ethene-d_4, however, should be an ideal reagent for probing transition-metal-hydride bonds in the gas phase since olefin insertion into transition-metal-hydride bonds is both rapid and reversible,[21,22] eq 2. The only requirement is that competing



(2)

Scheme II



reactions such as displacement, dehydrogenation, olefin oligomerization, etc., be slow relative to the insertion/elimination process. The results for the reactions of ethene-d_4 with a variety of M(olefin)$^+$ species (M = Fe, Co, Ni, and Rh) are presented and discussed.

Experimental Section

The theory, instrumentation, and methodology of ion cyclotron resonance (ICR) spectrometry[23] and Fourier transform mass spectrometry (FTMS)[24] have been discussed at length elsewhere. All experiments were performed on a Nicolet prototype FTMS-1000 Fourier transform mass spectrometer previously described in detail[25] and equipped with a 5.2 cm cubic trapping cell situated between the poles of a Varian 15-in. electromagnet maintained at 0.9 T. The cell was constructed in our laboratory and includes a $^1/_4$-in.-diameter hole in one of the transmitter plates which permits irradiation with various light sources. High-purity foils of the appropriate metals were supported on the opposite transmitter plate. Metal ions 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.[14a]

Chemicals were obtained commercially in high purity and were used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensable gases. C_2D_4 (>99 atom % D) was obtained from MSD Isotopes, Merck Chemical Division. Sample pressures were on the order of 1–5 $\times$ 10^{-7} torr. Argon was used as the collision gas for the collision-induced dissociation experiments at a total pressure of $\sim$5 $\times$ 10^{-6} torr. A Bayard-Alpert ionization gauge was used to monitor pressure.

Since FTMS is a single region mass spectrometer, all reagent gases are present in the same chamber. As a result, studying the chemistry of product ions with specific reagent gases can be complicated by reactions with the parent neutral gas. Addition of reagent gases through a pulsed valve can alleviate this problem.[26] The M(olefin)$^+$ ions were generated by reacting laser desorbed metal ions with the appropriate organic species pulsed into the vacuum chamber. The sequence of events using the pulsed valve for reagent gas addition is illustrated in Figure 1. Initially, a concurrent laser (metal ionization) and valve pulse occurs. The pulsed reagent gas fills the vacuum chamber to a maximum pressure of $\sim$$10^{-5}$ torr and is pumped away by a high-speed 5-in. diffusion pump in $\sim$250 ms. Both primary and secondary reactions with the pulsed reagent gas can occur in this time period, depending on the nature and the amount of reagent pulsed into the vacuum chamber. The M(olefin)$^+$ ions are then isolated by swept double resonance ejection techniques[24] and allowed

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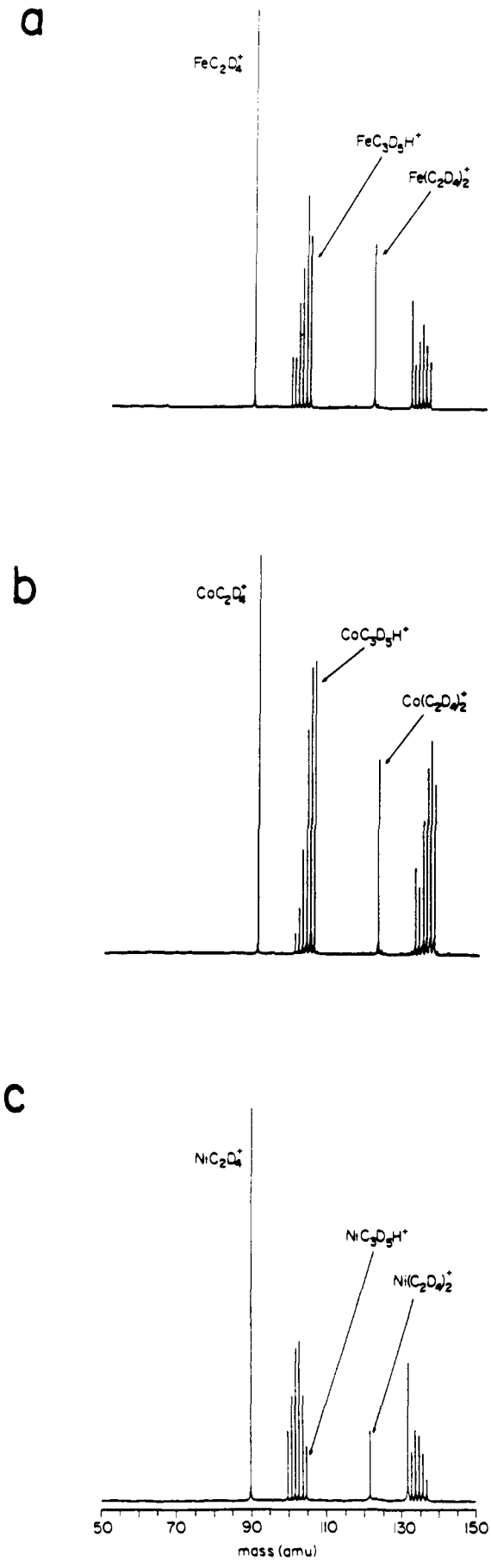

Figure 2. Mass spectra obtained when $MC_3H_6^+$ ions formed in reaction 4 are isolated and trapped in the presence of 2.5×10^{-7} torr of C_2D_4 for 2.0 s: (a) $FeC_3H_6^+$; (b) $CoC_3H_6^+$; (c) $NiC_3H_6^+$.

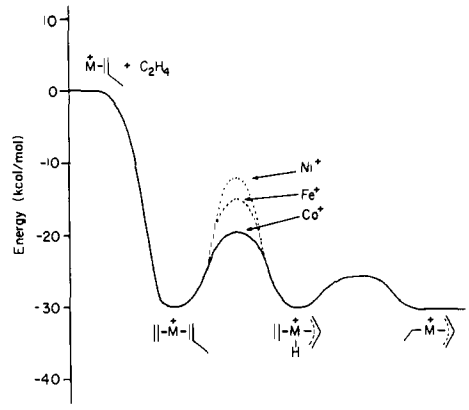

Figure 3. Simplified reaction coordinate diagram for H/D exchange of $M(prop)^+$ ions (M = Fe, Co, Ni) with C_2D_4.

to react with a static pressure of a second reagent gas without complicating reactions with the precursor organic. The products resulting from reactions with the static reagent gas can be isolated by additional swept ejection pulses to allow their collisional activation spectra to be obtained.

Details of the CID experiments have previously been discussed.[25,27,28] The collision energy of the ions can be varied (typically between 0 and 100 eV) from which plots of CID product ion intensities vs. kinetic energy can be made. These plots are reproducible to ±5% absolute and 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.[29]

Results and Discussion

$MC_3H_6^+$ and $MC_4H_8^+$. $MC_3H_6^+$ ions (M = Fe, Co, Ni) have been synthesized from a variety of hydrocarbons, reactions 3–5,[13,14b,15] and may consist of $M(propene)^+$ (**1**), $M(hydrido\text{-}\pi\text{-}allyl)^+$

$$M^+ + C_3H_8 \rightarrow MC_3H_6^+ + H_2 \quad (3)$$

$$M^+ + n\text{-}C_5H_{12} \rightarrow MC_3H_6^+ + C_2H_6 \quad (4)$$

$$M^+ + 1\text{-}C_5H_{10} \rightarrow MC_3H_6^+ + C_2H_4 \quad (5)$$

(**2**), or both in rapid equilibrium. Detailed structural studies, however, suggest that they consist predominantly of $M(propene)^+$, structure **1**, in the ground state.[15,17]

All three $MC_3H_6^+$ ions undergo 5 H/D exchanges with C_2D_4 in contrast to D_2 where no exchanges occur. Since these exchanges are relatively slow, both ligand displacement and condensation, reactions 6 and 7, compete with H/D exchange. Figure 2 shows

$$MC_3H_6^+ + C_2D_4 \rightarrow MC_2D_4^+ + C_3H_6 \quad (6)$$

$$MC_3H_6^+ + C_2D_4 \rightarrow M(C_3H_6)C_2D_4^+ \quad (7)$$

the spectra obtained when $M(C_3H_6)^+$ ions, generated in reaction 4, are trapped in the presence of C_2D_4 under identical conditions. As can be seen in Figure 2, H/D exchange is more facile for $CoC_3H_6^+$ than for either $FeC_3H_6^+$ or $NiC_3H_6^+$. Continuous ejection of $MC_3H_5D^+$ results in complete absence of all subsequent exchanges. This indicates that only one H/D exchange occurs for each interaction with C_2D_4.

A mechanism for exchange is presented in Scheme II with a general reaction coordinate diagram shown in Figure 3. Initially ethene-d_4 coordinates to the metal–propene complex forming a species with approximately 30 kcal/mol excess energy.[30] This activation effects reversible β-hydride shifts resulting in H/D

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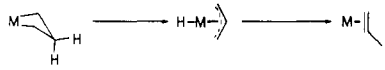
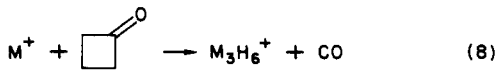
Scheme III



exchange. Formation of metal π-allyl hydride species is well documented in solution.[7,8] A stable $HFe(CO)_3(\eta^3\text{-}C_3H_5)$ has recently been observed in the low-temperature photochemistry of $Fe(CO)_4(C_3H_6)$ in an inert matrix.[31] In addition, $HNi(\eta^3\text{-}C_3H_5)L$, L = $P(C_6H_5)_3$ or PF_3, has been prepared at low temperature with the PF_3 complex in dynamic equilibrium with the corresponding nickel(0)–η^2-propene complex between −40 and −50 °C.[9] Olefin insertion into transition-metal-hydride bonds is both rapid and reversible[21,22] and has been invoked in gas-phase studies.[20,32,33]

Since olefin insertion into metal-hydride bonds is both rapid and reversible,[21,22] the activation barrier for this process is assigned as less than 5 kcal/mol.[34] The slowness of these exchanges must, therefore, be due to a barrier for conversion of ethene–propene to an ethene–hydride–allyl species. Since H/D exchange is slowest for nickel it is assigned the highest barrier while cobalt has the lowest barrier with iron intermediate. This barrier can be interpreted in terms of a double potential well similar to that for gas-phase nucleophilic displacements.[35] This interpretation is also consistent with the absence of multiple exchanges per C_2D_4 encounter.

Decarbonylation of cyclobutanone by Fe^+, Co^+, and Ni^+ generates $MC_3H_6^+$ ions, reaction 8, together with a number of other



$$M^+ + \square{=}O \rightarrow M_3H_6^+ + CO \qquad (8)$$

products.[36] The proposed mechanism for this reaction suggests that the $MC_3H_6^+$ ions are initially formed as metallacyclobutane ions[36] (**3**). CID studies, coupled with ion–molecule reactions,

3

indicated formation of a stable ferracyclobutane ion in reaction 8 while the corresponding $NiC_3H_6^+$ and $CoC_3H_6^+$ species appeared to have rearranged to propene complexes prior to structural studies.

Both $NiC_3H_6^+$ and $CoC_3H_6^+$ produced in reaction 8 yield essentially identical results to their corresponding propene species with $C_2\mathbf{D}_4$. This clearly indicates that the initially formed metallacyclobutane ions have rearranged to M(propene)$^+$ species by β-hydride abstraction, Scheme III. Rearrangement of metallacyclobutanes to metal olefin complexes via hydrido-π-allyl intermediates has been proposed in solution-phase studies.[37–39] $FeC_3H_6^+$ generated in reaction 8 yields rapid displacement of C_3H_6 with ethene-d_4, reaction 9, with a small amount of $FeC_3H_2D_4^+$

$$FeC_3H_6^+ + C_2D_4 \rightarrow FeC_2D_4^+ + C_3H_6 \qquad (9)$$

and $FeC_3H_4D_2^+$ also observed. The complete absence of H/D exchange with C_2D_4 indicates formation of a stable ferracyclobutane ion in reaction 8 which reductively eliminates *cyclopropane* rather than undergo rearrangement by β-hydride elimination. Observation of cyclopropane displacement implies an upper limit for the binding energy of trimethylene to Fe^+ of 97 kcal/mol.[40,41] This compares with $D°(Fe^+\text{–}CH_3) = 69 \pm 5$ kcal/mol.[42] Since ring strain in 4-membered metallacycles is often found to be small,[43] the binding energy of Fe^+–(2R) should not exceed 97 kcal/mol substantially. Fe^+ has been observed to decarbonylate acetone,[14a] reaction 10, implying $D°(Fe^+\text{–}(2CH_3)) > 96$ kcal/mol.[41,44]

$$Fe^+ + \text{acetone} \rightarrow Fe(CH_3)_2^+ + CO \qquad (10)$$

The degree of puckering of the metallacyclobutane ring is believed to be important for facile β-hydride abstraction (Scheme III).[45] The smaller the dihedral angle (greater puckering), the more favorable hydride transfer becomes. Hence, the ferracyclobutane ions may be nearly planar while the cobaltacyclobutane and nickelacyclobutane ions may have significant puckering. In addition, $D°(M^+\text{–}CH_3)$ is greater for Fe^+ than for either Co^+ or Ni^+[42] which should help stabilize the ferracyclobutane ions relative to the cobalta- and nickelacyclobutane ions.

Several stable group 8 metallacyclobutanes have been synthesized in solution.[46–48] Thermal degradation of platinacyclobutanes at relatively high temperature produces cyclopropanes and propenes by competitive reductive elimination and β-hydride elimination.[49] Thermal degradation of nickelacyclobutanes yields predominantly reductive elimination and β-hydride elimination with some C–C bond cleavage products also observed.[48] Significantly, nickelacyclobutane in solution appears to be in equilibrium with the olefin-coordinated nickel–carbene complex, but this apparently does not occur in the gas phase. A stable iron–carbene–olefin complex has been synthesized in solution and found not to react to give cyclopropane.[50]

Neopentane reacts with Fe^+, Co^+, and Ni^+ to produce $MC_4H_8^+$ exclusively, reaction 11. Detailed structural studies indicate that

$$M^+ + \text{neo-}C_5H_{12} \rightarrow MC_4H_8^+ + CH_4 \qquad (11)$$

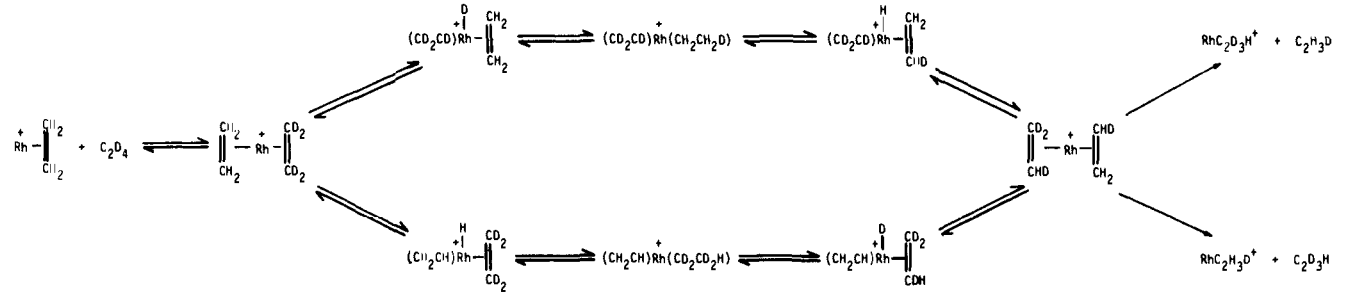
these ions consist of isobutene bound to the metal.[15,17] Furthermore, the only fragmentation observed in FTMS–CID is elimination of C_4H_8. This suggests that dehydrogenation forming a metal ion–trimethylene methane complex or rearrangement to a linear butene followed by dehydrogenation is difficult.[51] Surprisingly, Co^+ reacts with isobutene yielding predominantly $CoC_4H_6^+$,[52] reaction 12, while both Fe^+ and Ni^+ only yield the

$$Co^+ + \text{iso-}C_4H_8 \rightarrow CoC_4H_6^+ + H_2 \qquad (12)$$

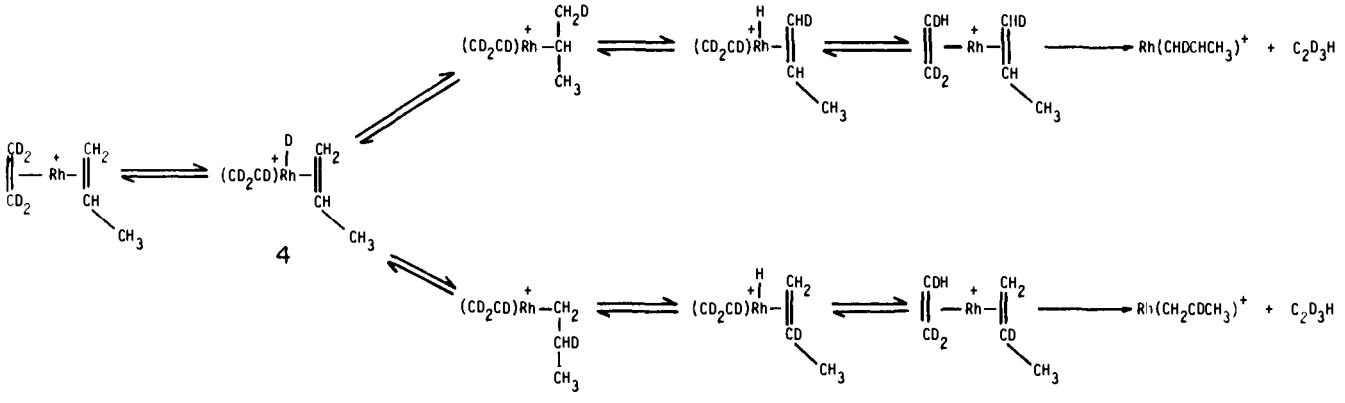
condensation product $MC_4H_8^+$. Structural studies on $CoC_4H_6^+$ indicate that it consists of butadiene bound to cobalt suggesting

(31) Mitchner, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 1065.
(32) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 3900.
(33) Halle, L. F.; Klein, F. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 2543.
(34) Kazlauskas, R. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 6005.
(35) (a) Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219. (b) Asubiojo, O. I.; Brauman, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 3715.
(36) Jacobson, D. B.; Freiser, B. S. *Organometallics* **1984**, *3*, 513.
(37) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.
(38) Cushman, B. M.; Brown, D. B. *J. Organomet. Chem.* **1978**, *152*, C42.
(39) (a) Ephritikhine, M.; Green, M. L. H.; Mackenzie, R. F. *J. Chem. Soc., Chem. Commun.* **1976**, 619. (b) Adam, G. J. A.; Davies, S. E.; Ford, K. A.; Ephritikhine, M.; Todd, P. F.; Green, M. L. H. *J. Mol. Catal.* **1980**, 15.
(40) This is calculated by using $D°(Fe^+\text{–}C_2H_4) = 37$ kcal/mol and the heats of formation in ref 41.
(41) Heats of formation taken from: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data Suppl.* **1977**, *6*. $\Delta H_f°$(trimethylene) = 72 kcal/mol from: Doering, W. von E. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5279.
(42) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6501.
(43) Moore, S. S.; DiCosimo, R.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 948.
(44) Heats of formation of organic radical species are taken from: McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.
(45) Grubbs, R. H. "Comprehensive Organometallic Chemistry"; Wilkinson, G., Ed.; Pergamon Press: Oxford, England, 1982; Vol. 8, p 533.
(46) Puddephatt, R. J.; Quyser, M. A.; Tipper, C. F. H. *J. Chem. Soc., Chem. Commun.* **1976**, 626.
(47) Foley, P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 2737.
(48) Miyashita, A.; Grubbs, R. H. *Tetrahedron Lett.* **1981**, *22*, 1255.
(49) Johnson, T. H.; Cheng, S. S. *J. Am. Chem. Soc.* **1979**, *101*, 5277.
(50) Priester, W.; Rosenblum, M. J. *J. Chem. Soc., Chem. Commun.* **1978**, 26.
(51) Linear butenes are readily dehydrogenated by Fe^+, Co^+, and Ni^+ in the gas phase forming M(butadiene)$^+$ species. See, for example, ref 28 and 52.
(52) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6624.

Scheme IV



Scheme V



that in this case considerable rearrangement has occurred prior to dehydrogenation.[53]

Ethene reacts with $MC_4H_8^+$ (M = Fe, Co, Ni), generated in reaction 11, by both ligand displacement and condensation, reactions 13 and 14. Ligand displacement is not as prominent here

$$MC_4H_8^+ + C_2H_4 \rightarrow MC_2H_4^+ + C_4H_8 \quad (13)$$

$$MC_4H_8^+ + C_2H_4 \rightarrow M(C_4H_8)(C_2H_4)^+ \quad (14)$$

as for M(propene)$^+$, since larger olefins are bound more strongly to metal ion centers than smaller olefins.[15,54] Despite the competitive reactions, up to 8 hydrogens in the $MC_4H_8^+$ ions generated in reaction 11 undergo exchange with ethene-d_4 in agreement with what is predicted from Scheme II. In addition, only a single exchange occurs upon each encounter with ethene-d_4. Again no exchange occurs with D_2.

$RhC_3H_6^+$, generated in reaction 3, undergoes 5 H/D exchanges with deuterium.[18] These H/D exchanges were rationalized by proposing a rapid equilibrium between the propene and hydrido-π-allyl species. Exchange occurs with the hydrido-π-allyl complex followed by H/D scrambling by reversible conversion to the propene species. This interpretation is consistent with one unique and unexchangeable hydrogen and suggests that $RhC_3H_6^+$ formed in reaction 3 consists of Rh(propene)$^+$ in dynamic equilibrium with $HRh(\eta^3\text{-}C_3H_5)^+$.

Ethene reacts with $RhC_3H_6^+$ yielding both displacement and dehydrogenation products, reactions 15 and 16. In addition,

$$RhC_3H_6^+ + C_2H_4 \rightarrow RhC_2H_4^+ + C_3H_6 \quad (15)$$

$$RhC_3H_6^+ + C_2H_4 \rightarrow RhC_5H_8^+ + H_2 \quad (16)$$

$RhC_2H_4^+$ generated from ethane undergoes a subsequent slow reaction with ethene yielding exclusively the dehydrogenation product, $RhC_4H_6^+$. Surprisingly, all six hydrogens in $RhC_3H_6^+$ are exchanged with ethene-d_4, Figure 4. $RhC_2H_4^+$ undergoes a small amount of H/D exchange with ethene-d_4, but ligand displacement dominates. This exchange may be explained by initial oxidative addition across a vinylic C–H or C–D bond followed by reversible hydride shifts and elimination of ethene,

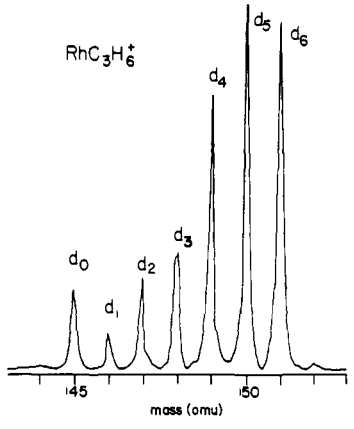


Figure 4. Partial mass spectrum obtained when $RhC_3H_6^+$, generated in reaction 3, is isolated and trapped in the presence of 1.5×10^{-7} torr of C_2D_4 for 2.0 s.

Scheme IV. Five H/D exchanges for $RhC_3H_6^+$ may proceed by the mechanism presented in Scheme II for the first row group 8 metal ion–propene species. A mechanism for exchange of the sixth (unique) hydrogen is presented in Scheme V. Initial oxidative addition across a vinylic C–D bond forms **4** which can undergo both Markovnikov (path A) and anti-Markovnikov (path B) insertion. Markovnikov addition leaves the central hydrogen unexchanged; however, anti-Markovnikov addition would render the central (unique) hydrogen exchangeable. Anti-Markovnikov addition should be favored due to steric considerations.[55]

Double resonance indicates that a considerable amount of multiple exchange occurs with each ethene-d_4 encounter, Figure 5, in contrast to the first row group 8 metal ion–propene species where only a single exchange is observed per collision with ethene-d_4. This appears to be a manifestation of the apparent dynamic equilibrium between the propene and hydrido-π-allyl species of rhodium (low activation barrier for this process).

(53) Hettich, R. L.; Jacobson, D. B.; Freiser, B. S., unpublished results.
(54) Kappas, M. M.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 1813.
(55) (a) Yagupsky, M.; Wilkinson, G. *J. Chem. Soc. A* **1970**, 941. (b) Hallman, P. S.; McGarvey, B. R.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 3143. (c) O'Connor, C.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 2665. (d) Burnett, M. G.; Morrison, R. J. *J. Chem. Soc. A* **1971**, 2325.

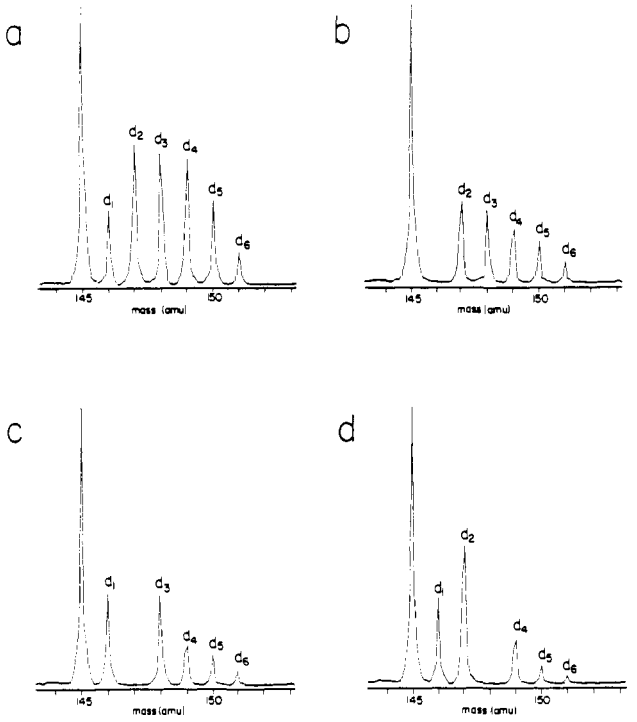


Figure 5. (a) Partial mass spectrum obtained when $RhC_3H_6^+$, generated in reaction 3, is trapped in the presence of 1.5×10^{-7} torr of C_2D_4 for 750 ms. (b–d) Same conditions as part a but with continuous ejection of either (b) $RhC_3H_5D^+$, (c) $RhC_3H_4D_2^+$, or (d) $RhC_3H_3D_3^+$ throughout the 750-ms trap.

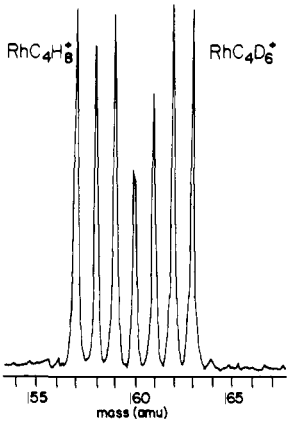


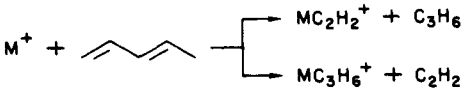
Figure 6. Mass spectrum obtained when $RhC_4H_8^+$, generated in reaction 16, is isolated and trapped in the presence of 2.0×10^{-7} torr of C_2D_4 for 3.0 s.

$RhC_4H_8^+$, generated in reaction 17, undergoes 8 exchanges with deuterium[18] and ethene-d_4. With deuterium the only process

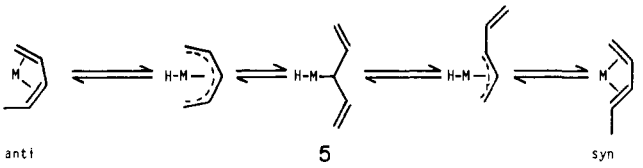
$$Rh^+ + \text{iso-}C_4H_{10} \rightarrow RhC_4H_8^+ + H_2 \qquad (17)$$

observed is H/D exchange. Ethene-d_4, however, yields dehydrogenation as well as exchange. No further exchange occurs after dehydrogenation. Figure 6 shows the spectrum observed after exchange and dehydrogenation are complete. Dehydrogenation probably proceeds by elimination of ethane rather than H_2 + ethene. The dehydrogenation product may consist of either trimethylene methane bound to rhodium or rearrangement to a linear butene may occur prior to dehydrogenation. The $RhC_4H_8^+$ also undergoes a facile dehydrogenation upon collisional activation.

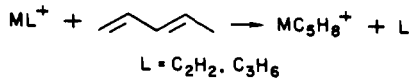
$MC_5H_8^+$. $MC_5H_8^+$ ions (M = Fe, Co, Ni) are generated in a two-step process. First, *trans*-1,3-pentadiene yields the products in reactions 18 and 19 which then subsequently react with



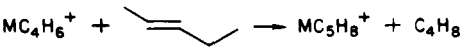
Scheme VI



trans-1,3-pentadiene by simple ligand displacement, reaction 20. $MC_5H_8^+$ can also be generated by initial reaction with 1-butene



forming $MC_4H_6^+$. $MC_4H_6^+$ reacts with *trans*-2-pentene yielding predominantly $MC_5H_8^+$ by reaction 21. The $MC_5H_8^+$ ions are



produced by pulsing in a mixture of 1-butene and *trans*-2-pentene. The products of reactions 20 and 21 yield essentially identical CID spectra indicating that they have the same structure, presumably M(1,3-pentadiene)$^+$.

Ethene-d_4 reacts with both $FeC_5H_8^+$ and $CoC_5H_8^+$, produced in reactions 20 and 21, yielding 5 slow H/D exchanges. The only competing reaction is condensation, reaction 22. No H/D exchange is seen for $NiC_5H_8^+$ produced in reactions 20 and 21 with condensation generating $Ni(C_5H_8)C_2D_4^+$ being the only process observed. This $Ni(C_5H_8)C_2D_4^+$ species loses C_2D_4 in high ef-

$$MC_5H_{8-n}D_n^+ + C_2D_4 \rightarrow M(C_5H_{8-n}D_n)C_2D_4^+ \qquad (22)$$
$$n \leq 5$$

ficiency upon collisional activation with no evidence for H/D scrambling seen in any of the fragments. $RhC_5H_8^+$ produced in reaction 23 undergoes 5 rapid H/D exchanges with ethene-d_4. Only a single exchange occurs per C_2D_4 encounter for $RhC_5H_8^+$, $FeC_5H_8^+$, and $CoC_5H_8^+$.

$$Rh^+ + n\text{-}C_5H_{12} \rightarrow RhC_5H_8^+ + 2H_2 \qquad (23)$$

Transition-metal complexes effect isomerization of *cis*-1,3-pentadienes to *trans*-1,3-pentadienes in solution.[56–58] The thermodynamic driving force for this isomerization is the relief of repulsion between anti substituents and the metal. The mechanism for this isomerization, first proposed by Nelson et al.,[58b] is presented in Scheme VI and involves initial insertion into an allylic C–H bond. Rearrangement to intermediate **5** is the key to this isomerization and allows free rotation of both vinyl groups. The allyl group (η^3) can reform with either syn or anti stereochemistry according to the orientation of the second vinyl group at the time of formation. Dynamic syn ⇌ anti exchange-isomerization is particularly well established for palladium(II) complexes[59] but is also known for rhodium.[60] Intermediate **5** should be the highest energy species in the overall isomerization.[58b]

A mechanism for the 5 H/D exchanges is outlined is Scheme VII for the syn (most stable) complex. Coordination of ethene-d_4

(56) (a) Mahler, J. E.; Kocklar, R.; Pettit, R. *J. Org. Chem.* **1964**, *29*, 3620. (b) Pettit, R.; Emerson, G. F.; Mahler, J. E. *J. Chem. Educ.* **1963**, *40*, 175. (c) Kockar, R. K.; Pettit, R. *J. Organomet. Chem.* **1966**, *6*, 272.

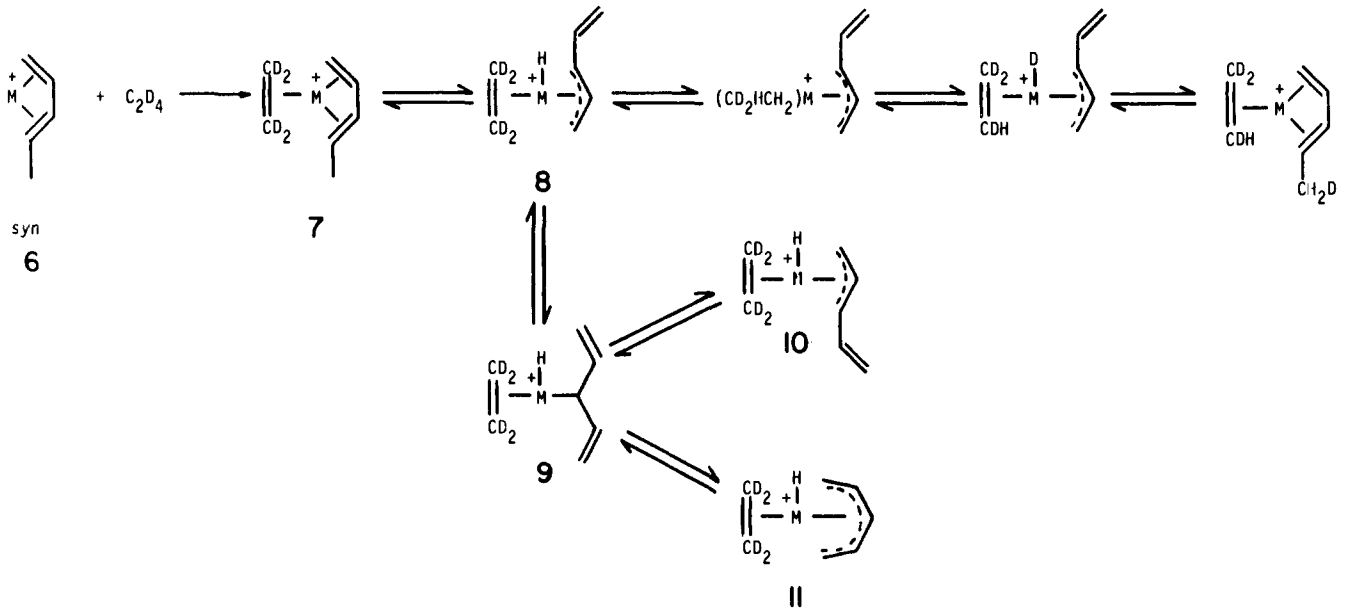
(57) Birch, A. J.; Cross, P. E.; Lewis, J.; White, D. A.; Wild, J. *J. Chem. Soc. A* **1968**, 332.

(58) (a) Nelson, S. M.; Sloan, M.; Drew, M. G. B. *J. Chem. Soc., Dalton Trans.* **1973**, 2195. (b) Arthurs, M.; Sloan, M.; Drew, M. G. B.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1975**, 794. (c) Arthurs, M.; Regan, C. M.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1980**, 2053.

(59) (a) Tibbetts, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1970**, *92*, 3010. (b) Hughes, R. P.; Powell, J. *J. Am. Chem. Soc.* **1972**, *94*, 7723. (c) Guthrie, D. J. S.; Nelson, S. M. *Coord. Chem. Rev.* **1972**, *8*, 139.

(60) (a) Powell, J.; Shaw, B. L. *J. Chem. Soc. A* **1968**, 583. (b) Volger, H. C.; Vrieze, K. *J. Organomet. Chem.* **1967**, *9*, 527. (c) Vogler, H. C.; Vreize, K. *J. Organomet. Chem.* **1968**, *13*, 479.

Scheme VII



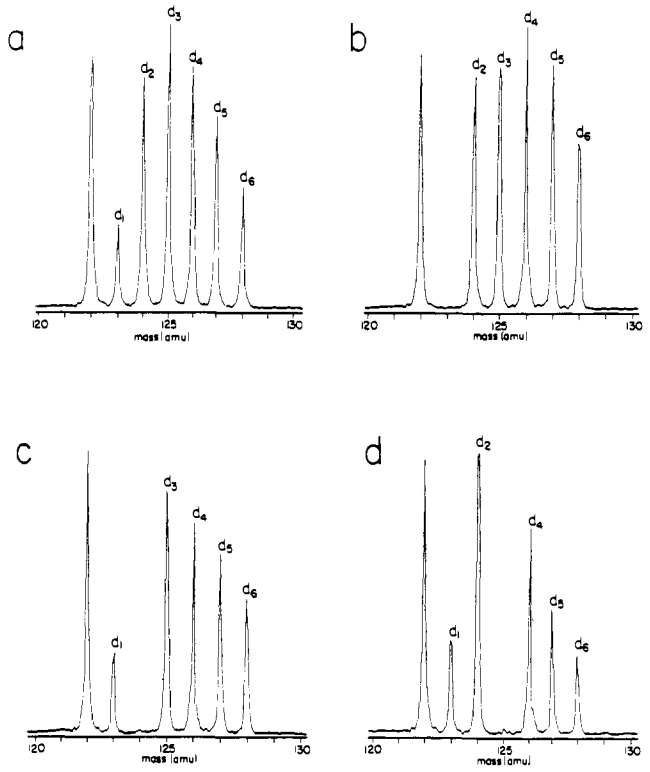
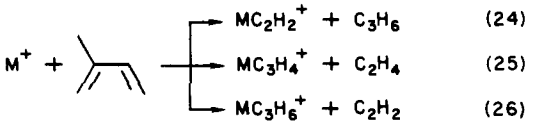


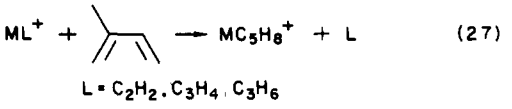
Figure 7. (a) Mass spectrum obtained when Fe-c-$C_5H_6^+$ is trapped in the presence of 1.5×10^{-7} torr of C_2D_4 for 750 ms. (b–d) Same conditions as part a but with continuous ejection of either (b) $FeC_5H_5D^+$, (c) $FeC_5H_4D_2^+$, or (d) $FeC_5H_3D_3^+$ throughout the 750-ms trap.

to **6** forms **7** with roughly 30 kcal/mol of excess internal energy.[30] This activation effects insertion into an allylic C–H bond forming **8**. Reversible hydride shifts result in up to 3 exchanges in the terminal methyl group. Rearrangement of **8** to **9**, however, equilibrates the two vinyl groups. Intermediate **9** can rearrange to the syn species **8** and **10** or to the anti species **11**. These rearrangements allow for all 5 terminal hydrogens in **6** to be exchangeable. The π molecular orbitals of pentadienyl and cyclopentadienyl systems are quite analogous,[61] and in terms of energy considerations the open system could turn out to possess even stronger metal–ligand bonds. Therefore, intermediate **11** may represent a potential minimum in the overall energy surface. There are several examples of pentadienyl ligands in transition-metal chemistry.[62]

An isomeric $MC_5H_8^+$, M(2-methylbutadiene)$^+$, can be compared with the linear pentadienes. Again, $MC_5H_8^+$ ions (M = Fe, Co, Ni) are generated in a two-step process by reaction with 2-methylbutadiene in a manner analogous to that for *trans*-1,3-pentadiene described above. Condensation with ethene-d_4 is the



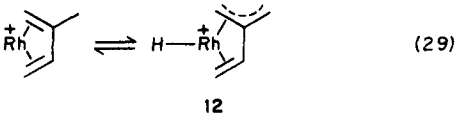
only process observed for the $MC_5H_8^+$ ions generated in reaction 27 forming $M(C_5H_8)C_2D_4^+$. CID of this ion yields facile elim-



ination of C_2D_4 indicating no scrambling has occurred. Rh(2-methylbutadiene)$^+$ is generated directly by reaction with 2-methylbutane, reaction 28. This $RhC_5H_8^+$ ion undergoes 5 slow

$$Rh^+ + \text{2-methylbutane} \rightarrow RhC_5H_8^+ + 2H_2 \quad (28)$$

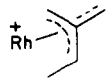
H/D exchanges with ethene-d_4. These exchanges can be rationalized by invoking the equilibrium in reaction 29. Reversible



rearrangement to the substituted trimethylene methane, complex **13**, would result in 7 exchangeable hydrogens and, therefore, its formation is apparently unfavorable. An alternative explanation for these exchanges for rhodium is to invoke a slow isomerization to linear 1,3-pentadiene followed by exchange. The above results

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

(62) (a) Pettit, R.; Mahler, J. E. *J. Am. Chem. Soc.* **1962**, *84*, 1511. (b) Giannini, U.; Pellina, E.; Lachi, M. P. *J. Organomet. Chem.* **1968**, *12*, 551. (c) Riennacker, R.; Yoshiura, H. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 677. (d) Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 678. (e) Yasuda, H.; Yamauchi, M.; Nakamura, A.; Sei, T.; Kai, Y.; Yasuoka, N. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1089. (f) Wilson, D. R.; DiLullo, A. A.; Ernst, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 5928. (g) Wilson, D. R.; Ernst, R. D.; Cymbaluk, T. H. *Organometallics* **1983**, *2*, 1220.



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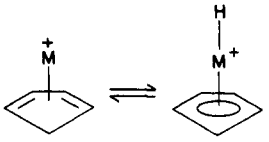
indicate that insertion into an allylic C–H bond of 2-methylbutadiene and isomerization to linear 1,3-pentadiene do not occur for Fe^+, Co^+, and Ni^+. For Rh^+, formation of **12** or rearrangement to 1,3-pentadiene, if it occurs, appears to be slow.

M-c-$C_5H_6^+$ and M-c-$C_7H_8^+$. M-c-$C_5H_6^+$ ions (M = Fe, Co, Ni, Rh) are produced directly from cyclopentene, reaction 30.

$$M^+ + c\text{-}C_5H_8 \rightarrow MC_5H_6^+ + H_2 \qquad (30)$$

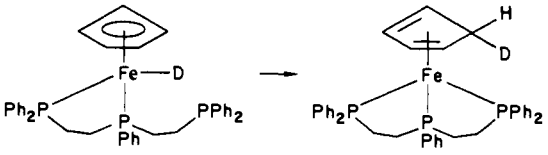
Both Fe-c-$C_5H_6^+$ and Co-c-$C_5H_6^+$ undergo six H/D exchanges in the presence of excess deuterium, with no exchanges observed for Ni-c-$C_5H_6^+$ and Rh-c-$C_5H_6^+$.[18,19] The first exchange is slow (~1/20 that of the Langevin collision rate) for both Fe-c-$C_5H_6^+$ and Co-c-$C_5H_6^+$ with the second exchange occurring much more slowly than the first for both ions. These results were interpreted by invoking an equilibrium between the cyclopentadiene complex, **14**, and the hydrido-cyclopentadienyl complex, **15**. The first H/D



(31)

14 15

exchange then occurs by interaction of deuterium with **15**. Although complexes **14** and **15** are in rapid equilibrium, the incorporated deuterium will remain unscrambled in the endo position. H/D scrambling can occur via *exo*-hydrogen [1,5] sigmatropic shifts (thermally allowed in the ground state[63]), which are known to occur rapidly at room temperature in labeled cyclopentadiene,[64] allowing for the remaining hydrogens to be exchanged. The *exo*-hydrogen [1,5] sigmatropic shift appears to be the rate-limiting step for the second and subsequent exchanges in the gas phase. Complex **16** undergoes slow exchange of D with the ring hydrogen atoms at 20 °C implying an *exo*-hydrogen sigmatropic shift in **17** formed by D transfer.[65]



16 17

There is good evidence for the equilibrium in reaction 31 from CID experiments. CID on Fe-c-$C_5H_6^+$ with use of a sector instrument at 8 keV produces predominantly $FeC_5H_5^+$ and Fe^+ in roughly a 2:1 ratio.[17b] In FTMS–CID, however, elimination of C_5H_6 is the only fragmentation observed.[19] These differences are due to the nature and amount of energy deposited into the ions by these two techniques. Dissociation in a sector instrument at 8 keV is due primarily to a single collision and often favors direct cleavage products which yield a "snapshot" of the ground-state ions. In FTMS, dissociation primarily results from multiple collisions with the target prior to fragmentation.[27,28] Each individual collision imparts internal energy into the ion with the net effect that the ions gain internal energy in a stepwise manner. This allows the ions to rearrange to structure **14** prior to fragmentation.

Ethene-d_4 reacts with M-c-$C_5H_6^+$ (M = Fe, Co, Ni) formed in reaction 30 yielding 6 rapid H/D exchanges. In addition, multiple exchanges per C_2D_4 predominate for all three M-c-$C_5H_6^+$ ions, Figure 7. The rapid initial and subsequent exchanges are a result of the activation afforded by ethene coordination, ~30

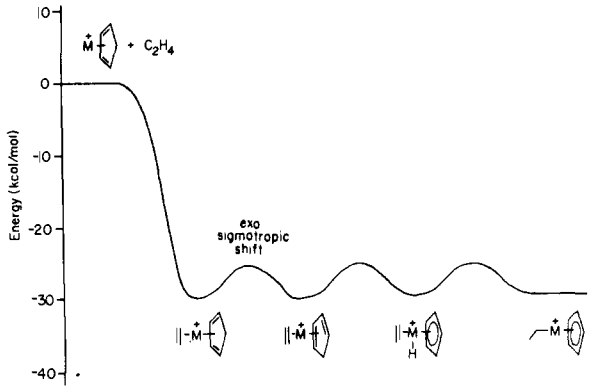


Figure 8. Simplified reaction coordinate diagram for H/D exchange of M-c-$C_5H_6^+$ (M = Fe, Co, Ni) with C_2D_4.

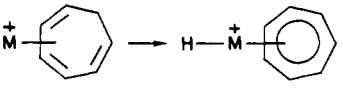
kcal/mol.[30] This activation facilitates not only formation of a hydrido-cyclopentadienyl species but also H/D scrambling by exo [1,5] sigmatropic shifts in cyclopentadiene. The activation barrier for a sigmatropic shift is 23.6 kcal/mol for cyclopentadiene.[64] Metal ion coordination along with the excess energy due to ethene coordination is sufficient to effect rapid *exo*-hydrogen [1,5] sigmatropic shifts for cyclopentadiene. A general reaction coordinate diagram is shown in Figure 8 for these exchanges. The important features in this diagram are the low barriers to *exo*-hydrogen [1,5] sigmatropic shift and to reversible conversion of the ethene–cyclopentadiene and ethene–hydrido–cyclopentadienyl species. These low barriers are suggested by the significant amount of multiple exchanges per C_2D_4 encounter. The lifetime of the ethene–cyclopentadiene complex should be greater than that of the ethene–propene complex described above which would also favor multiple exchange. In contrast to the above M-c-$C_5H_6^+$ ions, Rh-c-$C_5H_6^+$ only undergoes a single rapid exchange with ethene-d_4. This result can be rationalized if the hydrido–cyclopentadienyl species is much more stable than the corresponding cyclopentadiene complex. Finally, the rhodium complex, **18**, undergoes complete exchange of the hydride and ethene hydrogens with D_2O in CD_3NO_2 at −20 °C with no exchange of ring hydrogens observed suggesting the following equilibrium.[66]

$$[Rh(h)(C_2H_4)(C_5H_5)(PMe_3)]^+ \rightleftharpoons [Rh(C_2H_5)(C_5H_5)(PMe_3)]^+$$

M-c-$C_7H_8^+$ ions are generated by reaction with cycloheptene, reaction 32. Both Rh-c-$C_7H_8^+$ and Co-c-$C_7H_8^+$ undergo a single slow exchange with C_2D_4. No exchange occurs for either Ni-

$$M^+ + c\text{-}C_7H_{12} \rightarrow MC_7H_8^+ + 2H_2 \qquad (32)$$

c-$C_7H_8^+$ or Fe-c-$C_7H_8^+$. Observation of only one slow exchange indicates that conversion from the cycloheptatriene complex, **19**, to the hydrido–cycloheptatrienyl complex, **20**, is not very favorable for Co^+ and Rh^+ and does not occur at all for Ni^+ and Fe^+. In addition, H/D scrambling by sigmatropic shifts does not appear to occur for Co-c-$C_7H_8^+$ and Rh-c-$C_7H_8^+$.



(33)

19 20

Conclusions

H/D exchange using deuterium has proven valuable in studying the dynamics of gas-phase metal–olefin complexes.[18,19,67] Unfortunately, only a handful of complexes have been observed to undergo exchange with deuterium. Ethene-d_4, however, proves to be a far superior reagent for studying the above dynamics. With deuterium, little excess energy is imparted into the complexes;

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however, ethene coordination activates the complex by the ML^+–ethene bond energy. This activation can effect β-hydride shifts generating hydrido–metal complexes. For exchange to take place the metal–olefin complex must be coordinatively unsaturated. In addition, the metal–olefin complex must be reasonably stable, and competing reactions such as displacement, dehydrogenation, condensation, olefin oligomerization, etc., must be slow relative to the insertion/elimination process, reaction 2. Ethene-d_4 yielded excellent results for M(propene)$^+$ and M(isobutene)$^+$ for M = Fe, Co, and Ni and M(1,3-pentadiene)$^+$, M(2-methylbutadiene)$^+$, M(cyclopentadiene)$^+$, and M(cycloheptatriene)$^+$ for M = Fe, Co, Ni, and Rh. Only for Rh(propene)$^+$ and Rh(isobutene)$^+$ is deuterium superior to ethene-d_4 for H/D exchange due to complicating processes with ethene. For M(propene)$^+$ species the rate of exchange with ethene-d_4 was found to decrease in the following order: $Rh^+ > Co^+ > Fe^+ > Ni^+$. It is interesting to note that more H/D scrambling has been observed for reactions of Co^+ with selectively deuterated alkanes than for either Fe^+ or Ni^+.[13,68]

The dynamics of a variety of metal–ligand species, where the ligand is not an olefin, may also be studied. For example, $MOCH_3^+$ ions are generated by reaction with methyl nitrite, reaction 34.[69] Collisional activation yields elimination of CH_2O

$$M^+ + CH_3ONO \rightarrow MOCH_3^+ + NO \quad (34)$$

$$M = Fe, Co, Ni$$

(68) Houriet, R.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1983**, *2*, 1818.

in high efficiency, indicating that the ion has rearranged to a hydrido–formaldehyde complex prior to fragmentation. The hydrido–formaldehyde species may, however, be in dynamic equilibrium with the methoxy species, eq 35. The product of

$$H\text{-}M^+\text{-}OCH_2 \rightleftharpoons M^+OCH_3 \quad (35)$$

reaction 34 undergoes three rapid H/D exchanges with ethene-d_4.[69] This clearly indicates that the equilibrium in reaction 35 is occurring.

Propene-d_6 may be a useful reagent for investigating dynamic H/D exchanges for metal–olefin complexes which contain no labile hydrogens. For example, M(butadiene)$^+$ and M(trimethylene methane)$^+$ complexes could be studied. The butadiene complex should undergo only 4 exchanges, whereas all 6 hydrogens should be exchangeable in the trimethylene methane species.

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Registry No. C_2D_4, 683-73-8; *n*-C_5H_{12}, 109-66-0; neo-C_5H_{12}, 463-82-1; C_2H_4, 74-85-1; iso-C_4H_{10}, 75-28-5; c-C_5H_8, 142-29-0; c-C_7H_{12}, 628-92-2; H_2, 1333-74-0; Fe^+, 14067-02-8; Co^+, 16610-75-6; Ni^+, 14903-34-5; Rh^+, 20561-59-5; cyclobutanone, 1191-95-3; *trans*-1,3-pentadiene, 2004-70-8; 1-butene, 106-98-9; *trans*-2-pentene, 646-04-8; 2-methylbutadiene, 78-79-5; 2-methylbutane, 78-78-4.

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Methyl Substituent Effects in the Gas-Phase Acidities of Halosubstituted Oxygen Acids. A Realignment with Substituent Effects in Solution

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Abstract: The gas-phase acidities of a number of chloro-, bromo-, and trifluoromethyl-substituted carboxylic acids and alcohols have been measured by using pulsed electron beam high-pressure mass spectrometry and in several cases pulsed ion cyclotron resonance spectroscopy. The results show that in situations where a methyl group is substituted (at sp^3 carbon) in a carboxylic acid or alcohol, a net acid weakening effect is observed. This is in contrast to normal aliphatic carboxylic acids and alcohols where methyl substitution leads to an increase in acid strength. The reversal of the methyl substituent effect is interpreted as due to a diminished charge-induced polarization stabilization in the species substituted with electronegative groups.

Brauman and Blair's discovery[1] of the gas-phase aliphatic alcohol acidity order (*t*-C_4H_9OH > *iso*-C_3H_7OH > C_2H_5OH > CH_3OH > H_2O) was a landmark event in the interpretation of intrinsic alkyl substituent effects.[1] This ordering, which is an exact reversal of that observed in aqueous solution,[2] demonstrated for the first time that alkyl groups have the ability to stabilize negative charge via a through-space polariation interaction. With more quantitative data, Taft has shown that while alkyl groups do in fact exert substantial destabilizating, field/inductive effects in alkoxide anions, these are overwhelmed by the stabilizing ion-induced polarization interaction which may be from three to seven times greater in magnitude.[3] This type of net anionic stabilization is observed for other acidic functional groups as well. For example, $CH_3CH_2CO_2H$ has a gas-phase acidity 1.2 kcal/mol greater than CH_3CO_2H, and $CH_3CH_2C{\equiv}CH$ is 1.3 kcal/mol more acidic than $CH_3C{\equiv}CH$.[4] However, when methyl for hydrogen substitution occurs at the sp^2 or sp carbon an overall acid weakening effect is observed. For example, CH_3CO_2H is 3.3 kcal/mol less acidic than HCO_2H and $CH_3C{\equiv}CH$ is 4.2 kcal/mol less acidic than $HC{\equiv}CH$.[4] These latter results have been intepreted, using perturbation molecular orbital theory, as being due to a stabili-

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