

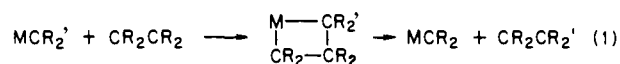
Reactions of FeCH_2^+ and CoCH_2^+ with Olefins in the Gas Phase. Studies Involving Olefin Metathesis

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Abstract: Reactions of the title carbenes with several olefins and alkynes are reported. Ethene reacts with MCH_2^+ yielding exclusively M^+ formation (C_3H_6 elimination). Reaction of ethene with MCD_2^+ yields the metathesis products FeCH_2^+ and CoCH_2^+ in 20% and 2% yields, respectively. Formation of the metathesis product MC_2H_4^+ dominates for propene with no MCH_2^+ produced from MCD_2^+ . Formation of MC_2H_4^+ is believed to proceed through an ethene-ethylidene intermediate that rearranges to a bis(ethene) complex followed by elimination of ethene. Absence of MCH_2^+ formation from reaction of MCD_2^+ with propene suggests that the alkene-alkylidene conversion is the key step in metathesis of olefins larger than ethene. Several other pathways compete with metathesis such as cyclopropanation, olefin homologation, dehydrogenation, and various C-C bond cleavages. Both carbenes react with butadiene, generating $\text{M-c-C}_3\text{H}_6^+$ and $\text{M-c-C}_3\text{H}_5^+$, implying $D^\circ(\text{Co}^+-\text{C}_3\text{H}_5) > 76 \pm 7$ kcal/mol and $D^\circ(\text{Fe}^+-\text{C}_3\text{H}_5) > 87 \pm 5$ kcal/mol. Finally, ethyne and propyne react with MCH_2^+ to yield M^+ as the only product.

Transition-metal-carbene-alkene complexes have been implicated as intermediates in a number of important catalytic transformations including the olefin metathesis reaction,¹ the cyclopropanation of alkenes,² and the Ziegler-Natta polymerization of alkenes.³ The olefin metathesis reaction¹ is proposed to proceed via interconversion of metal-carbene-alkene complexes and metallacyclobutanes, eq 1. This concept was originally



advanced by Herisson and Chauvin⁴ and has gained general acceptance.¹ The Herisson-Chauvin mechanism is supported by numerous studies on the reactions of metal-carbene complexes with olefins⁵ and by labeling experiments which show that the olefin metathesis reaction proceeds in a nonpairwise manner.⁶ Recently, a metallacyclobutane species was found to undergo olefin metathesis.⁷ Several side reactions may also compete with metathesis such as cyclopropanation^{2,8} and olefin homologation.⁹

There are several examples of both chelated¹⁰⁻¹⁵ and nonchelated^{16,17} metal-carbene-alkene complexes. Most of these complexes, however, do not take part in either olefin metathesis or cyclopropanation reactions. The only direct evidence for the conversion of a metal-carbene-alkene complex into a metallacyclobutane or a metallacyclobutane decomposition product is the recent discovery by Casey et al. of a series of (alkenyloxy)carbene complexes of tungsten which decompose to cyclopropanes.¹⁸

Studying reactions of olefins with metal-carbene ions in the gas phase provides a means for probing this interesting chemistry in the absence of ligand and solvent effects. Using ion cyclotron resonance (ICR) spectrometry,¹⁹ Stevens and Beauchamp studied the reactions of manganese- and iron-carbene ions in the gas phase.²⁰ They found that MnCH_2^+ produced metathesis products while $(\text{CO})_4\text{MnCH}_2^+$, $(\text{CO})_5\text{MnCH}_2^+$, $\text{CpFe}(\text{CO})_2\text{CH}_2^+$, and $\text{CpFe}(\text{CO})\text{CH}_2^+$ did not. These interesting results demonstrated that a bare metal-carbene, such as MnCH_2^+ , can undergo metathesis of alkenes and that the coordination state of the metal ion is important in the metathesis reaction in the gas phase.

Using an ion beam instrument, Beauchamp et al. have also determined that the metal ion-carbene bond energies, $D^\circ(\text{M}^+-\text{CH}_2)$, for the first row groups 8-10 transition-metal ions are on the order of 85-96 kcal/mol.²¹ Since strong metal-carbene bonds are a desirable feature for practical metathesis catalysts (fewer side reactions are possible), these first row groups 8-10 metal-carbene ions should produce metathesis products. In this paper the reactions of gas-phase FeCH_2^+ and CoCH_2^+ with a variety of olefins and alkynes are described. NiCH_2^+ was not studied

due to the difficulty in generating it in sufficient amounts. In accord with Beauchamp's earlier work with MnCH_2^+ and on the

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Table I. Distribution of Neutrals Lost in the Reactions of FeCH_2^+ and CoCH_2^+ with Olefins^a

olefin	carbene	neutrals lost, % ^b														
		H ₂ + H	H ₂	CH ₄	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₄	C ₃ H ₆	C ₃ H ₈	C ₄ H ₈	C ₄ H ₁₀	C ₅ H ₈	C ₅ H ₁₀	C ₆ H ₁₂	C ₇ H ₁₄
=	FeCH_2^+									100						
	CoCH_2^+									100						
=	FeCH_2^+		6			62					32					
	CoCH_2^+		15			54					31					
=	FeCH_2^+		7	18		38	2			14	1			20		
	CoCH_2^+		10	23		25	4			14				24		
=	FeCH_2^+		2	12		34				23				29		
	CoCH_2^+		3	18		40				18				21		
=	FeCH_2^+		2	14		49				25				10		
	CoCH_2^+		2	16		49				23				10		
=	FeCH_2^+		2	14		47				26				11		
	CoCH_2^+		9	15		47				20				9		
=	FeCH_2^+			6				45		12	2	21	3		11	
	CoCH_2^+			6		2	39		22	2	16				13	
=	FeCH_2^+			11		4	24		35	4	9	7		6		
	CoCH_2^+			10		4	28		37	4	8	2		7		
=	FeCH_2^+					2			2	20	41	3		22		10
	CoCH_2^+					3			2	25	43	2		19		6
=	FeCH_2^+			6		27	15		7	3	23	4		15		
	CoCH_2^+			9		13	18		17	8	20			15		
=	FeCH_2^+			5		18	35		5	6	14	8		9		
	CoCH_2^+			10		4	35		10	12	17			12		
=	FeCH_2^+			21		12	7		21	8	8	11		12		
	CoCH_2^+			19		18	13		23	14	6			7		
=	FeCH_2^+	6	20		2	22		5	4				41			
	CoCH_2^+	4	20		3	11		2	5				55			

^a Product distribution reproducible to $\pm 15\%$. ^b Empirical formula of neutrals lost. See text.

M^+-CH_2 bond dissociation energies, metathesis reactions are observed for FeCH_2^+ and CoCH_2^+ with alkenes along with a variety of other pathways.

Experimental Section

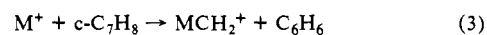
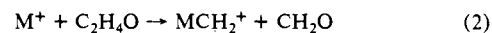
The theory, instrumentation, and methodology of ion cyclotron resonance (ICR) spectrometry¹⁹ and Fourier transform mass spectrometry (FTMS)²² have been discussed elsewhere. All experiments were performed by using a Nicolet prototype FTMS-1000 Fourier transform mass spectrometer previously described in detail²³ and equipped with a 5.2-cm³ trapping cell situated between the poles of a Varian 15-in. electromagnet maintained at 0.9 T. The cell was constructed in our laboratory and includes a 1/4 in. diameter hole in one of the transmitter plates which permits irradiation with various light sources. High-purity foils of the appropriate metals were supported on the opposite transmitter plate. Metal ions are generated by focusing the beam of a Quanta Ray Nd: YAG laser (frequency doubled to 530 nm) onto a metal foil. Details of the laser ionization technique have been described elsewhere.²⁴

Chemicals were obtained commercially in high purity and used as supplied except for multiple freeze-pump-thaw cycles to remove non-condensable gases. $\text{C}_2\text{D}_4\text{O}$ (>98 atom % D) and 1-butene-1,1-*d*₂ (>96 atom % D) were obtained from MSD Isotopes, Merck Chemical Division. Sample pressures were on the order of 1×10^{-7} torr. Argon was used as the collision gas for the collision-induced dissociation (CID) experiments at a total sample pressure of approximately 5×10^{-6} torr. A Bayard-Alpert ionization gauge was used to monitor pressure.

Details of the CID experiments have previously been discussed.^{23,25,26} 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 $\pm 5\%$ 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.²⁷

The MCH_2^+ ions were generated by reacting laser desorbed Fe^+ and Co^+ with ethylene oxide²⁸ or cycloheptatriene,²⁹ reactions 2 and 3. The



carbenes generated in reactions 2 and 3 gave identical results (within $\pm 15\%$) for reactions with alkenes (Table I). Labeled metal-carbene (MCD_2^+) was formed by reaction with deuterated ethylene oxide. The carbene reagent gas (ethylene oxide or cycloheptatriene) was introduced into the vacuum chamber through a General Valve Corp. Series 9 pulsed solenoid valve.³⁰ 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 ~ 250 ms. The MCH_2^+ (MCD_2^+) ions are then isolated by swept double-resonance ejection techniques²² and allowed to react with a static pressure of a reagent gas without complicating reactions with ethylene oxide or cycloheptatriene. The products resulting from reactions with the static reagent gas can be isolated by additional swept ejection pulses to allow their further chemistry to be studied or their CID spectra to be obtained.

Results and Discussion

Reactions with Ethene. Both FeCH_2^+ and CoCH_2^+ react rapidly with ethene, yielding exclusively C_3H_6 elimination, reaction

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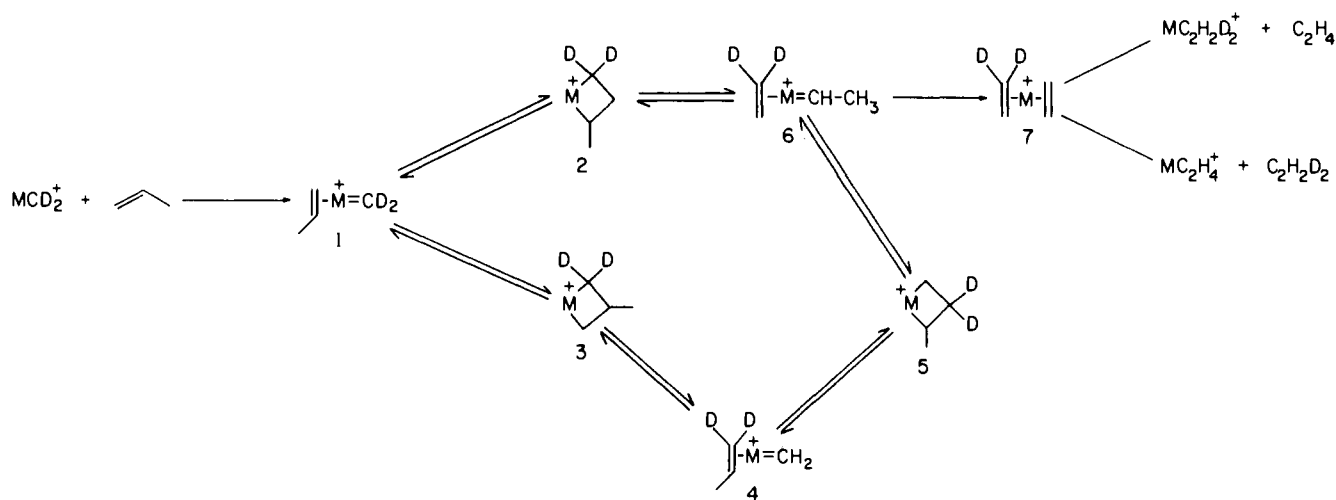
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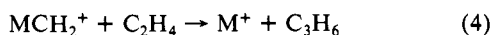
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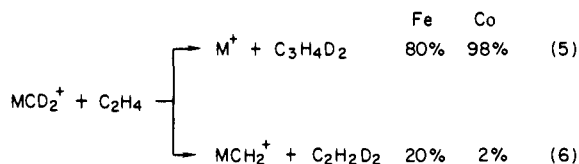
Scheme I



4. The neutral product in this reaction may consist of either cyclopropane or propene. Formation of propene is thermally more



favorable than cyclopropane.³¹ For CoCH₂⁺, both propene and cyclopropane formation are exothermic, while only propene formation is exothermic for Fe⁺.³² Reaction with MCD₂⁺ yields both the bare metal ion and unlabeled carbene (olefin metathesis), reactions 5 and 6. The small amount of metathesis, reaction 6,



suggests that cyclopropanation and olefin homologation are favored over metathesis.

Both Fe⁺ and Co⁺ decarbonylate cyclobutanone, reaction 7. The proposed mechanism of this reaction suggests that, at least initially, a metallacyclobutane ion is formed.³³ Structural studies

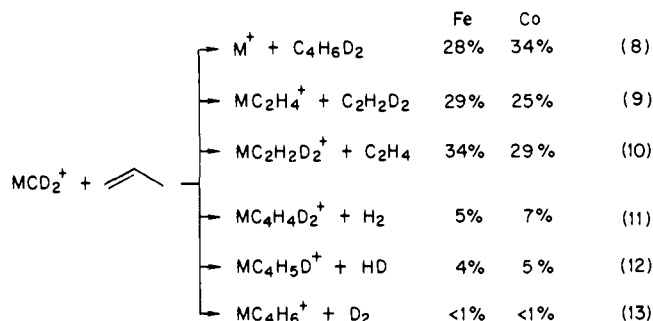


on CoC₃H₆⁺ generated by reaction 7 were consistent with formation of a Co(propene)⁺ species; however, FeC₃H₆⁺ appeared to consist predominantly of a stable ferracyclobutane ion.³³ The ferracyclobutane ion formed in reaction 7 eliminates predominantly cyclopropane upon reaction with C₂D₄. In addition a small amount of FeC₂H₄⁺ and FeC₂D₂H₂⁺ is also observed with no evidence for rearrangement of the ferracyclobutane ion to Fe(propene)⁺.³⁴ The latter products are presumably generated by reversible conversion of the ferracyclobutane ion to a metal-carbene-alkene species induced by the activation afforded by ethene-d₄ coordination. These results indicate that isolated cobaltacyclobutane ions undergo facile rearrangement to Co(propene)⁺ by β-hydride abstraction whereas the corresponding ferracyclobutane ions ap-

parently do not rearrange to Fe(propene)⁺. Rearrangement of metallacyclobutanes to metal-olefin complexes via hydrido-π-allyl intermediates is well supported in solution-phase studies.³⁵⁻³⁷

The minor amount of metathesis product observed for CoCD₂⁺ in reaction 6 is consistent with facile conversion of cobaltacyclobutane ion to Co(propene)⁺ followed by elimination of propene or possibly cyclopropane, reaction 5. The dominance of Fe⁺ formation in reaction 5 suggests that propene elimination is competitive with olefin metathesis, reaction 6. This result is surprising considering that the ferracyclobutane ion apparently does not rearrange to Fe(propene)⁺ as discussed above. Alternatively, elimination of cyclopropane, which is calculated to be 9 ± 5 kcal/mol endothermic³², could occur by formation of FeCH₂⁺ with excess internal energy in reactions 2 and 3. Addition of a high pressure of argon (~5 × 10⁻⁶ torr), however, had no effect on the product distribution in reactions 5 and 6 for FeCD₂⁺, indicating that excited FeCH₂⁺ is not involved in cyclopropane formation in reaction 5. Finally, the actual Fe⁺-carbene bond strength may be less than the previously reported value of 96 ± 5 kcal/mol.²¹ Elimination of cyclopropane in reaction 5 coupled with formation of FeCH₂⁺ in reaction 2 would bracket D(Fe⁺-CH₂) between 77 and 87 kcal/mol.³¹

Reactions with Propene and Isobutene. The neutral losses for the reactions of MCH₂⁺ with propene and isobutene are summarized in Table I. Formation of the metathesis product MC₂H₄⁺ dominates for propene with smaller amounts of M⁺ and MC₄H₆⁺ also produced. Propene reacts with MCD₂⁺ to yield the products in reactions 8-13 with no MCH₂⁺ formed.



A mechanism for the formation of the products in reactions 9 and 10 is presented in Scheme I. Initially, the olefin coordinates to the carbene, forming an activated complex 1. Since there is

(31) Supplementary thermochemical information taken from: Rosenstock, H. M.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data. Suppl.* **1977**, *6*, No. 1. ΔH_f^o(CH₂) taken as 92.4 kcal/mol from: Chase, M. W.; Curnutt, J. L.; Prophet, H.; McDonald, R. A.; Syverund, A. N. *J. Phys. Chem. Ref. Data, Suppl.* **1975**, *4*, No. 1. ΔH_f^o(c-C₃H₅) taken as 57.9 ± 1.5 kcal/mol from: McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(32) Formation of propene and cyclopropane from CoCH₂⁺ and ethene is exothermic by 15 and 2 kcal/mol, respectively. Propene formation is 4 kcal/mol exothermic and cyclopropane formation is 9 kcal/mol endothermic for FeCH₂⁺ and ethene. These values are calculated by using the bond dissociation energies given in ref 21 and heats of formation from ref 31.

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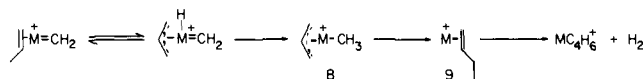
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Table II. Distribution of Neutrals Lost in Reactions of FeCD_2^+ and CoCD_2^+ with C_4 Olefins^a

olefin	carbene	neutrals lost, %												
		H_2	HD	CH_4	CH_3D	CH_2D_2	C_2H_4	$\text{C}_2\text{H}_3\text{D}$	$\text{C}_2\text{H}_2\text{D}_2$	$\text{C}_2\text{H}_4\text{D}_2$	C_3H_6	$\text{C}_3\text{H}_5\text{D}$	$\text{C}_3\text{H}_4\text{D}_2$	$\text{C}_5\text{H}_8\text{D}_2$
	FeCD_2^+	5	4	18					39		14			20
	CoCD_2^+	7	6	11	6	3	3	7	16	4	4	5	7	21
	FeCD_2^+	2		2	3	7			41		24			21
	CoCD_2^+	2		4	5	12	8	6	21		13	2	5	22
	FeCD_2^+	2		3	4	8	47						25	11
	CoCD_2^+	4		4	4	7	45	3	2		2		20	9
	FeCD_2^+	2		3	4	10	48						23	10
	CoCD_2^+	12		3	4	7	48	3	1			1	16	5
	FeCH_2^+	1		8	2		1	2	41		25	2		18
	CoCH_2^+	2		12	4	3	8	6	23		16	3	6	17

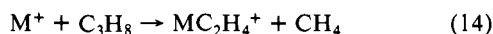
^a Product distribution reproducible to $\pm 15\%$.

Scheme II



little or no barrier for rearrangement of metallacyclobutanes to the corresponding olefin-alkylidene species,³⁸ intermediates 1–5 are believed to be in rapid equilibrium. Formation of the ethylidene species 6, however, is followed by rapid and irreversible conversion to a coordinated ethene species, 7, which can eliminate either C_2H_4 or $\text{C}_2\text{H}_2\text{D}_2$. It is the ethylidene to ethene rearrangement which accounts for the significant increase in metathesis of propene over ethene. Rearrangement of alkylidene species to coordinated olefins has been observed previously in solution and is a termination reaction in olefin metathesis.^{39,40} Such a rearrangement has been reported to be facile for cationic alkylidene complexes.⁴¹

Propene displaces C_2H_4 and $\text{C}_2\text{H}_2\text{D}_2$ exclusively from the MC_2H_4^+ and $\text{MC}_2\text{H}_2\text{D}_2^+$ species generated in reactions 9 and 10 (no metathesis products are generated). Furthermore, the CID spectra of these ions are identical (same peaks, intensities, and energy dependence within experimental error) with that for MC_2H_4^+ produced in reaction 14. These results are consistent

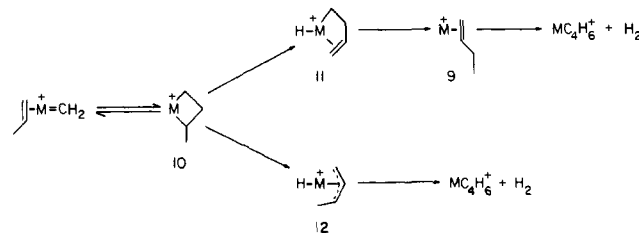


with rearrangement of ethylidene to ethene as shown in Scheme I. The various methylene-olefin and metallacyclobutane species are apparently in rapid equilibrium. Formation of the ethylidene species 6, however, is followed by rapid and irreversible conversion to a coordinated ethylene. The dominance of MC_2H_4^+ formation from propene and MCH_2^+ requires that the competing processes such as cyclopropanation and β -hydride elimination are slow relative to the metal-carbene-alkene/metallacyclobutane equilibrium. The absence of MCH_2^+ from MCD_2^+ may indicate that in Scheme I, structure 2 is more stable than structure 3 and that structure 4 may not be formed.

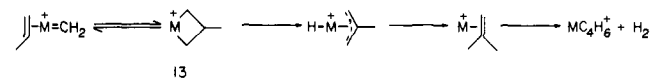
Formation of $\text{M}(\text{ethene})^+$ from MCH_2^+ and propene requires $D^\circ(\text{Co}^+-\text{ethene}) > 13$ kcal/mol and $D^\circ(\text{Fe}^+-\text{ethene}) > 24$ kcal/mol.^{21,23} Bond energies of Fe^+ and Co^+ to alkenes appear to be in the range of 35–45 kcal/mol and,⁴² therefore, metathesis forming $\text{M}(\text{ethene})^+$ is exothermic.

Dehydrogenation and C_4H_8 elimination compete with metathesis of propene. Dehydrogenation may proceed by β -hydrogen abstraction from the carbene-propene species to form 8, a methyl-allyl complex (Scheme II). Coupling of methyl to a terminal carbon of the allyl group generates a metal-butene

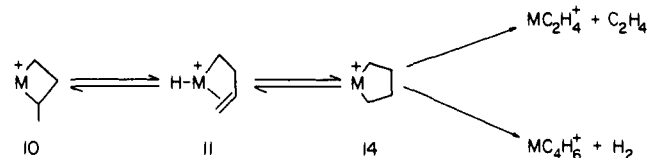
Scheme III



Scheme IV



Scheme V



species, 9, that readily eliminates hydrogen.⁴³ An alternative mechanism is presented in Scheme III and involves initial formation of the metallacyclobutane species 10. β -Hydrogen transfer from the methyl group forms 11 which readily converts to 9, essentially a 1,4-hydrogen atom shift. A more direct dehydrogenation process would involve β -hydride abstraction from the central methylene carbon, forming a hydrido-1-methyl species 12 which eliminates hydrogen (Scheme III). H/D scrambling has been observed for reactions of Fe^+ and Co^+ with 1-butene-1,1- d_2 ^{43b} and is proposed to proceed by an equilibrium between the hydrido- π -allyl species and linear butene prior to dehydrogenation. Complete scrambling would result in 54% H_2 , 43% HD, and 3% D_2 elimination. This is roughly the distribution of H_2 , HD, and D_2 losses seen in reactions 11–13, suggesting that considerable H/D scrambling occurs prior to dehydrogenation. Dehydrogenation by β -hydride abstraction from the metallacyclobutane species 13, forming an activated isobutene species, Scheme IV, may also be involved in dehydrogenation for CoCH_2^+ but probably does not occur for FeCH_2^+ .⁴⁴ Elimination of C_4H_8 to form M^+ in reaction 8 may proceed by both olefin homologation and by cyclopropanation. Formation of both methylcyclopropane and 1-butene is exothermic for cobalt by 6 and 12 kcal/mol, respectively, while methylcyclopropane formation is endothermic by 5 kcal/mol for iron with 1-butene formation being roughly 4 kcal/mol exothermic.^{21,31} Each of these values for iron would be

(38) Rappe, A. K.; Upton, T. H. *Organometallics* **1984**, *3*, 1440.

(39) Schrock, R. R.; "Inorganic Chemistry: Toward the 21st Century"; American Chemical Society: Washington, DC, 1983; ACS Symp. Ser. No. 211; Chapter 25.

(40) (a) Casey, C. P.; Loren, D. A.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2533. (b) Schrock, R. R.; Sharp, P. R. *J. Organomet. Chem.* **1979**, *171*, 43.

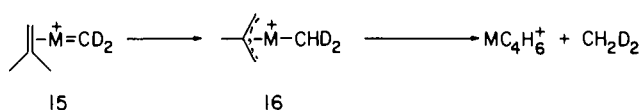
(41) Hatton, W. G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6157.

(42) (a) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6628. (b) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7492.

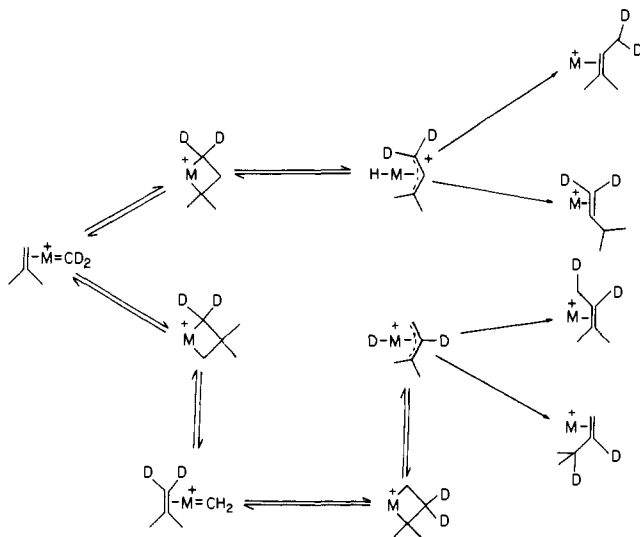
(43) Metal ions react with linear butenes eliminating H_2 nearly exclusively; see: (a) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6624. (b) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7484.

(44) Co^+ reacts with isobutene predominantly by elimination of H_2 ; see ref 41a. Fe^+ does not react with isobutene; see ref 41b.

Scheme VI



Scheme VII



more exothermic if $D^\circ(\text{Fe}^+-\text{CH}_2)$ were lower than the reported value of 96 kcal/mol as discussed above.

Alternatively, since β -hydride transfers are often rapid and reversible, ring expansion of the metallacyclobutane intermediate **10** may occur, Scheme V. The metallacyclopentane **14** can then decompose by symmetric ring cleavage or dehydrogenation.^{45,46} This could also account for reactions 8–13. The ring expansion process in Scheme V, however, has never been observed in solution, although the reverse reaction has been observed for some catalytic alkene dimerization reactions.⁴⁷ Furthermore, gas-phase cobaltacyclopentane ions appear to decompose predominantly by dehydrogenation.⁴⁶ Therefore, ring expansion is not believed to be involved in the formation of the products in reactions 8–13.

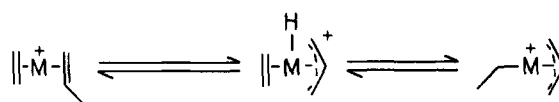
A richer chemistry is observed for isobutene than for propene, Table I. Elimination of C₂H₄ and C₃H₆ with the unlabeled carbenes corresponds to metathesis products, generating MC₃H₆⁺ and MC₂H₄⁺, respectively. The MC₃H₆⁺ and MC₂H₄⁺ ions consist of propene and ethene bound to the metal. Scheme I predicts elimination of C₂H₂D₂ and C₃H₆ for MCD₂⁺ to be the sole metathesis products. While this is observed for FeCD₂⁺, significant H/D scrambling occurs for CoCD₂⁺, Table II. This scrambling suggests that a more complicated mechanism than that presented in Scheme I is necessary to account for the reaction of isobutene with CoCH₂⁺. Loss of methane as CH₄ occurs exclusively for FeCD₂⁺ and also dominates for CoCD₂⁺, Table II. This indicates that methane elimination by two sequential β -hydride abstractions from **15** as shown in Scheme VI does not occur. More likely a coupling of methyl to 2-methylallyl in **16**

(45) Metallacyclopentanes in solution decompose by symmetric ring cleavage, dehydrogenation, and reductive elimination of cyclobutane; see for example: (a) ref 18b. (b) Grubbs, R. H.; Miyashita, A. "Fundamental Research in Homogeneous Catalysis"; Tsutsui, M., Ed.; Plenum Press: New York, 1979; Vol. 3, p 151. (c) Braterman, P. S. *J. Chem. Soc., Chem. Commun.* **1979**, 70. (d) McKinney, R. J.; Thorn, D. L.; Hoffman, R.; Stockis, A. *J. Am. Chem. Soc.* **1981**, *103*, 2595. (e) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521. (f) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529. (g) Diversi, P.; Ingrosso, G.; Lucherini, A. *J. Chem. Soc., Chem. Commun.* **1978**, 735. (h) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 4451.

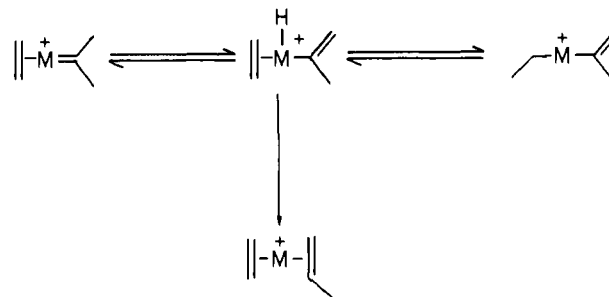
(46) Gas-phase metallacyclopentane ions (iron and cobalt) decompose by symmetric ring cleavage and dehydrogenation; see, for example: (a) Reference 26. (b) Reference 33. (c) Reference 42. (d) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 5197.

(47) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5451.

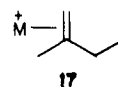
Scheme VIII



Scheme IX



occurs, generating a 2-methyl-1-butene species, **17**, with the labeled methyl group occupying the terminal position. Complex **17**



contains an internal energy equivalent to the metal-olefin bond strength (roughly 40 kcal/mol). Complex **17** can then decompose by eliminating H₂, CH₄, C₂H₄, and C₃H₆.⁴³ Methane elimination may also proceed subsequent to processes outlined in Scheme VII where an activated methylbutene is again formed.

The significant amount of H/D scrambling for CoCD₂⁺ may be accounted for by invoking rapid reversible hydrogen shifts for activated Co(propene)(ethene)⁺ species as shown in Scheme VIII prior to olefin elimination.⁴⁸ Alternatively, scrambling could occur during the alkylidene/vinyl transformations illustrated in Scheme IX, but this does not appear to be involved since reaction of CoCD₂⁺ with propene should also result in scrambling but does not in reactions 9 and 10. Furthermore, reaction of MCD₂⁺ with propene forms a bis(ethene) species that has no labile β -hydrogens available for scrambling as Scheme VIII requires. Therefore, it appears that the H/D scrambling must proceed by processes similar to that outlined in Scheme VIII.

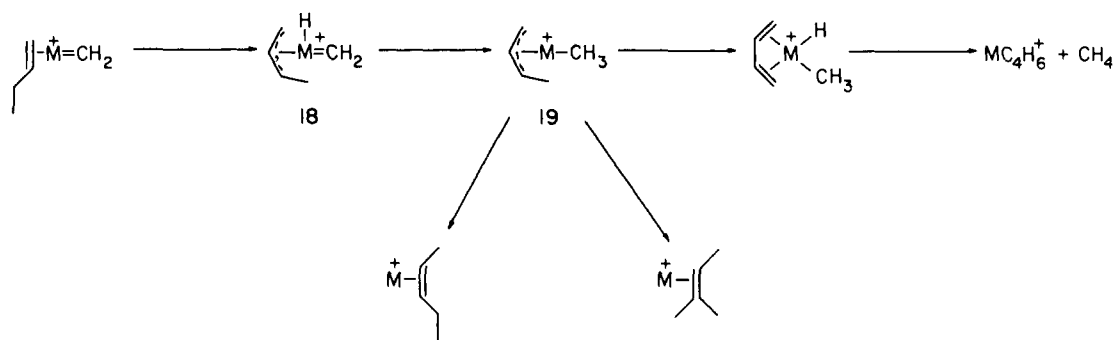
Lack of MCH₂⁺ formation in reactions of MCD₂⁺ with propene or isobutene suggests that conversion of alkylidene ligands to coordinated olefins is the key step in olefin metathesis for olefins larger than ethene. Stevens and Beauchamp^{20b} reported that MnCH₂⁺ reacts with the olefins C₂D₄, CH₃CHCH₂, and (C-D₃)₂CCD₂ to yield the new carbene species MnCD₂⁺, MnCHCH₃⁺, and MnC(CD₃)₂, respectively. No MnCD₂⁺ was produced from (CD₃)₂CCD₂. These results again can be interpreted by invoking alkylidene to olefin conversion as the key step in metathesis of the larger olefins.

Reactions with Linear Butenes. Both the iron- and cobalt-carbenes react with linear butenes predominantly by cleavage of the butene C-C framework, Tables I and II. This is in contrast to reactions with the bare metal ions where only dehydrogenation occurs, presumably generating a butadiene-metal ion complex.⁴³ Unlike isobutene, elimination of methane as CD₂H₂ dominates for reactions with MCD₂⁺ with some CH₃D and CH₄ elimination also observed. This suggests that methane elimination proceeds predominantly via two sequential β -hydride shifts as shown in Scheme X for 1-butene. The H/D scrambling (CH₃D and CH₄ eliminations) may proceed by the mechanism in Scheme X where the methyl-allyl complex **19** is in equilibrium with the carbene-hydrido-allyl species **18**. CoCH₃⁺ and FeCH₃⁺ species were found to retain a rigid metal-methyl structure,⁴⁹ however, suggesting that complexes **18** and **19** are not in equilibrium. Alternatively, the methyl group in **19** may couple to the allyl ligand, generating

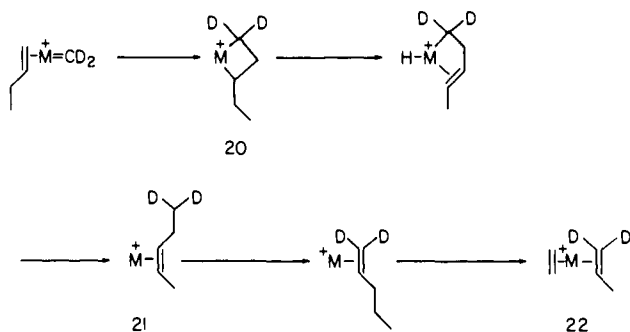
(48) The equilibrium in Scheme VIII is more facile for Co⁺ than Fe⁺; see, for example ref 34.

(49) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 3891.

Scheme X



Scheme XI



either a 2-pentene or a 2-methyl-1-butene species. H/D scrambling may then occur prior to methane elimination.

Elimination of C_3H_6 and C_2H_4 corresponds to the metathesis products. Scheme I predicts the formation of $MC_3H_6^+$ and $MC_2H_2D_2^+$ as the metathesis products for both reactions of MCD_2^+ with 1-butene and MCH_2^+ with 1-butene-1,1- d_2 which are observed, Table II. Reaction of MCD_2^+ with 1-butene-1,1- d_2 yields predominantly formation of $MC_2D_4^+$ and $MC_3H_6^+$ as the metathesis products, and reactions of MCD_2^+ with *cis*- and *trans*-2-butene yield predominantly $MC_3H_4D_2^+$ and $MC_2H_4^+$ as the metathesis products, as predicted in Scheme I. Again, some H/D scrambling occurs for cobalt but not for iron and may proceed by a process similar to that illustrated in Scheme VIII. The small amount of H/D scrambling for the reaction of $FeCH_2^+$ with 1-butene-1,1- d_2 is probably due to impure labeling.

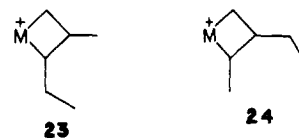
An anomaly exists for the H/D scrambling products for reactions of $CoCD_2^+$ with 1-butene and $CoCH_2^+$ with 1-butene-1,1- d_2 where formation of $CoC_2H_4^+$ dominates over $CoC_2H_3D^+$ and $CoC_3H_4D_2^+$ dominates over $CoC_3H_5D^+$ (the opposite is expected). This suggests that other mechanisms are involved in the C-C bond cleavages besides that presented in Scheme I. Since rearrangement of cobaltacyclobutane ions to coordinated alkenes is facile, conversion of the metallacyclobutane **20** to the pentene complex **21** may occur (Scheme XI). This activated pentene species can rearrange to a 1-pentene-1,1- d_2 complex by reversible β -hydride shifts followed by insertion into an allylic C-C bond,⁵⁰ generating the activated ethene-propene species **22**, which eliminates either C_2H_4 or $C_3H_4D_2$. The abundant dehydrogenation of *cis*-2-butene by $CoCH_2^+$ is also surprising but may be related to the favorable geometry for H_2 elimination.⁵¹

Reactions with C_5 and C_6 Olefins. Reactions of the metal-carbenes with larger olefins are difficult to interpret due to the large number of products formed by the numerous pathways available for decomposition. Formation of $MC_4H_6^+$ dominates for reactions of MCH_2^+ with 1-pentene with significant amounts of $MC_3H_6^+$ and $MC_2H_4^+$ also produced, whereas for *trans*-2-

pentene, $MC_4H_6^+$ and $MC_3H_6^+$ dominate, Table I. The neutral losses for reactions with MCD_2^+ for both 1-pentene and *trans*-2-pentene are summarized in Table III.

Formation of $MC_2H_4^+$ and $MC_4H_8^+$ from 1-pentene correspond to metathesis products, Scheme I, with the latter product retaining sufficient internal energy to dehydrogenate, producing $MC_4H_6^+$. Reactions with MCD_2^+ should yield $MC_2H_2D_2^+$ and $MC_4H_6^+$ ⁵² as the metathesis products and they dominate as shown in Table III.

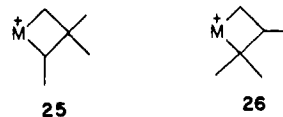
For *trans*-2-pentene, formation of $MC_2H_4^+$, $MC_3H_6^+$, and $MC_4H_6^+$ ⁵² all correspond to metathesis products with two different metallacycles involved, **23** and **24**. Complex **23** can rearrange



to a bis(propene) species, resulting in formation of $MC_3H_6^+$, while complex **24** rearranges to an ethene-butene species that can decompose, forming predominantly $MC_4H_6^+$ and some $MC_2H_4^+$. Reaction with a labeled carbene generates predominantly $MC_3H_6^+$, $MC_3H_4D_2^+$, $MC_2H_4^+$, and $MC_4H_4D_2^+$ which are the expected products of olefin metathesis.

Reaction of MCH_2^+ with 1-hexene yields predominantly $MC_4H_6^+$,⁵² $MC_3H_6^+$, and $MC_2H_4^+$ (Table I). Reaction of 1-hexene with bare metal ions generates predominantly $MC_3H_6^+$, presumably proceeding through insertion into an allylic C-C bond.⁵⁰

A variety of products are generated in the reactions of methylbutenes with MCH_2^+ (Table I) and MCD_2^+ (Table III). Reactions of the bare metal ions Fe^+ and Co^+ with the methylbutenes are complicated and not well understood, with isomerizations apparently taking place prior to decomposition.⁴³ Simple metathesis (Scheme I) with 3-methyl-1-butene yields an ethene-isobutene complex with the label on ethene. Reaction with labeled carbene yields predominantly $M(\text{ethene})^+$ as $MC_2H_2D_2^+$ and $M(\text{isobutene})^+$ as $MC_4H_8^+$ (Table III) as predicted for metathesis in Scheme I. Metathesis with 2-methyl-1-butene is similar; however, an ethene-linear butene species is formed with the label predominantly on ethene. Some H/D scrambling can occur in the ethene-linear butene complex by reversible β -hydride shifts prior to ethane elimination, forming $MC_4H_6^+$, $MC_4H_5D^+$, and $MC_4H_4D_2^+$. The large abundance of $CoC_4H_4D_2^+$ (Table III) vs. $CoC_4H_5D^+$ suggests that another mechanism, such as that presented in Scheme XI for 1-butene, may be involved. Two metallacyclobutane species are formed with 2-methyl-2-butene, **25** and **26**, which can participate in metathesis. Complex **25** can



(50) Cobalt and iron cations react with 1-pentene and 1-hexene predominantly by insertion into allylic C-C bonds; see, for example: ref 43.

(51) β -hydride abstraction from *cis*-2-butene produces a hydrido-1-methylallyl species which should consist predominantly in the anti form. It seems reasonable to speculate that dehydrogenation probably occurs primarily via the anti isomer and not via the syn isomer.

(52) Initially, metathesis produces an activated $MC_4H_8^+$ species which subsequently dehydrogenates if the ligand consists of linear butene. See, for example: ref 43.

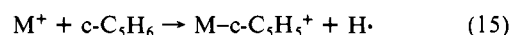
Table III. Distribution of Neutrals Lost in Reaction of FeCD₂⁺ and CoCD₂⁺ with C₃ and C₆ Olefins^a

olefin	carbene	neutrals lost, % ^b																								
		CH ₂ D ₂	C ₂ H ₄	C ₂ H ₃ D	C ₂ H ₂ D ₂	C ₂ H ₂ D ₂	C ₂ H ₆	C ₃ H ₄ D	C ₃ H ₄ D ₂	C ₃ H ₆	C ₃ H ₅ D	C ₃ H ₅ D ₂	C ₃ H ₆ D	C ₃ H ₆ D ₂	C ₃ H ₈	C ₃ H ₇ D	C ₃ H ₇ D ₂	C ₄ H ₆ D	C ₄ H ₆ D ₂	C ₄ H ₈ D ₂	C ₅ H ₁₀	C ₅ H ₈ D ₂	C ₅ H ₁₀ D ₂	C ₆ H ₁₀ D ₂	C ₆ H ₁₂ D ₂	
	FeCD ₂ ⁺	5				10	4	35																		
	CoCD ₂ ⁺	4				13	10	21																		
	FeCD ₂ ⁺	10	2			15	7	5																		
	CoCD ₂ ⁺	6	3	1		16	11	6																		
	FeCD ₂ ⁺					3																				
	CoCD ₂ ⁺					2																				
	FeCD ₂ ⁺	5				28	1	14																		
	CoCD ₂ ⁺	8	1	3		16	5	11																		
	FeCD ₂ ⁺	6	1			12	5	27																		
	CoCD ₂ ⁺	10	4	2		14	11	17																		
	FeCD ₂ ⁺	15	14			2	2	6																		
	CoCD ₂ ⁺	18	23			5	5	3																		

^a Product distributions are reproducible to ±15%. ^b Empirical formula of neutrals lost. See text.

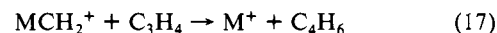
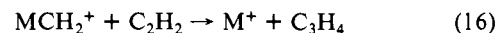
rearrange to an ethene-isobutene species with the label on isobutene. Complex **26** rearranges to a bis(propene) species. These processes are consistent with the neutral losses listed in Table III.

Reactions with Butadiene, Ethyne, and Propyne. The neutral losses for reactions of MCH₂⁺ with butadiene are summarized in Table I. Formation of MC₃H₄⁺ and MC₂H₄⁺ corresponds to metathesis products, Scheme I. Reactions with labeled metal-carbene yields MC₃H₄⁺ and MC₂H₂D₂⁺. Dehydrogenation generates MC₃H₆⁺ which loses exclusively C₃H₆ upon collisional activation. Furthermore, these MC₃H₆⁺ ions undergo six H/D exchanges with deuterium with the second exchange occurring considerably slower than the first. The above CID and H/D exchange results are identical with that for Fe-c-C₅H₆⁺ and Co-c-C₅H₆⁺ ions.^{33,42b} The M-c-C₅H₆⁺ species is probably formed by initial cyclization, forming an activated M(cyclopentene)⁺ species which eliminates hydrogen. The activated M-c-C₅H₆⁺ generated above can eliminate a hydrogen atom, forming M-c-C₅H₅⁺. Evidence for this process is that Fe⁺ and Co⁺ react with cyclopentadiene generating M-c-C₅H₅⁺ exclusively, reaction 15, and that CID of MC₅H₅⁺, formed either from carbene and butadiene or from reaction 15, yields only C₅H₅ loss in low efficiency.⁵³ Formation of M-c-C₅H₅⁺ from butadiene and MCH₂⁺



implies $D^0(\text{Co}^+ - c-C_5H_5) > 76 \pm 7$ kcal/mol and $D^0(\text{Fe}^+ - c-C_5H_5) > 87 \pm 5$ kcal/mol while from cyclopentadiene (reaction 15) requires $D^0(M^+ - c-C_5H_5)$ to exceed 71 kcal/mol.^{21,31} The large abundance of M⁺ produced from butadiene and MCH₂⁺ probably proceeds predominantly by elimination of cyclopentene from the activated M(cyclopentene)⁺ species.^{21,31}

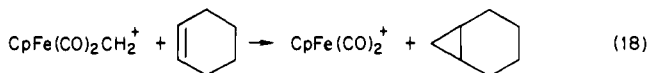
Ethyne and propyne only yield M⁺ with MCH₂⁺, reactions 16 and 17. The neutral product in reaction 16 may consist of either



allene or propyne with cyclopropene formation being endothermic.^{21,31}

Conclusions

The bare metal-carbenes FeCH₂⁺ and CoCH₂⁺ react with olefins yielding metathesis products. Reaction of MCD₂⁺ with ethene generates the metathesis products FeCH₂⁺ and CoCH₂⁺ in low yield. With propene and MCD₂⁺, formation of the metathesis products MC₂H₄⁺ and MC₂H₂D₂⁺ dominates with no MCH₂⁺ formed. These results suggest that conversion of the intermediate alkene-alkylidene species to a bis(alkene) species is the key step in metathesis of olefins larger than ethene. Structural studies indicate that alkylidene-to-alkene conversion occurs in all cases. Formation of functionalized alkylidenes should also be favored over methylene species since they can better stabilize cationic centers.⁵⁴ Beauchamp and Stevens^{20b} observed similar results where MnCH₂⁺ reacts with CD₂C(CD₃)₂ yielding MnC(CD₃)₂⁺ and no MnCD₂⁺. Their findings can be rationalized by invoking alkylidene-alkene rearrangement as the key step in metathesis. No metathesis was observed for (CO)₄MnCH₂⁺ and (CO)₅MnCH₂⁺. They also studied the reactions of CpFe(CO)₂CH₂⁺ and CpFe(CO)CH₂⁺ with olefins and no metathesis was observed; however, the carbene-transfer reaction 18 was observed.^{20a} For CpFe(CO)CH₂⁺ only displacement of CH₂CO



by cyclohexene occurs. These results suggest that the coordination

(53) M-c-C₅H₅⁺ ions produced by electron impact on ferrocene and by reaction of Fe⁺ and Co⁺ with cyclopentadiene lose C₃H₅ as the only fragmentation in low efficiency upon collisional activation. Jacobson, D. B.; Freiser, B. S., unpublished results.

(54) It has been argued that the major chain carrying species in the metathesis of terminal olefins is the functionalized alkylidene instead of the methylene species. Casey, C. P.; Tuinstra, H. E. *J. Am. Chem. Soc.* **1978**, *100*, 2270.

state of the metal ion as well as the nature of the ligands present are important in metathesis. Finally, these results suggest a bracketing for $D^\circ(\text{Fe}^+-\text{CH}_2)$ between 77 and 87 kcal/mol which is somewhat lower than the previously reported value of 96 ± 5 kcal/mol obtained by using ion beam techniques.²¹

We are currently studying the reactions of FeCH_2^+ and CoCH_2^+ with a variety of alkanes, cyclic alkanes, cyclic polyenes, and several other simple molecules such as N_2 , O_2 , CO , CO_2 , etc.

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Registry No. FeCH_2^+ , 90143-30-9; CoCH_2^+ , 76792-07-9; FeCD_2^+ , 93604-57-0; CoCD_2^+ , 93604-58-1; ethene, 74-85-1; propene, 115-07-1; 2-methylpropene, 115-11-7; 1-butene, 106-98-9; *trans*-2-butene, 624-64-6; *cis*-2-butene, 590-18-1; 1-pentene, 109-67-1; *trans*-2-pentene, 646-04-8; 1-hexene, 592-41-6; 3-methyl-1-butene, 563-45-1; 2-methyl-1-butene, 563-46-2; *trans*-2-methyl-2-butene, 513-35-9; 1,3-butadiene, 106-99-0; 1-butene-1,1-*d*₂, 26119-76-6; ethyne, 74-86-2; propyne, 74-99-7.

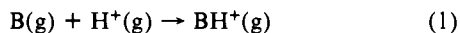
Bridging the Gap. A Continuous Scale of Gas-Phase Basicities from Methane to Water from Pulsed Electron Beam High Pressure Mass Spectrometric Equilibria Measurements

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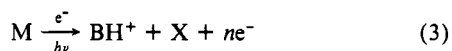
Abstract: Pulsed electron beam high pressure mass spectroscopic techniques have been used to study proton transfer equilibria involving a large number of compounds less basic than H_2O . The data obtained allow construction of a continuous scale of gas-phase proton affinities from CH_4 ($\text{PA} = 134.7 \text{ kcal mol}^{-1}$) upward. A number of new thermochemical inferences may be drawn, including a new value for the proton affinity of CO ($145.6 \text{ kcal mol}^{-1}$). Previous flowing afterflow data by Bohme et al. for compounds less basic than CH_4 may also be used to extend the continuous gas-phase basicity scale down to oxygen atom. Comparisons of data derived in the present work and proton affinities from appearance potential measurements for CO_2 , N_2 , and O have been made. An excellent correlation between gas-phase proton affinity of oxygen bases and the corresponding O_{1s} binding energies obtained from ESCA experiments is obtained. The value of using ESCA data to predict unknown proton affinities is presented.

The investigation of gas-phase basicities of molecules has been a major preoccupation of the field of gas-phase ion chemistry for over 2 decades.² The proton affinity of a molecule, B, defined as the negative of the enthalpy change for eq 1 in the gas phase, is a quantitative measure of gas-phase basicity. The earliest



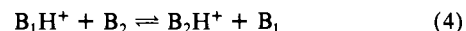
$$\text{PA}(\text{B}) = -\Delta H^\circ_1 = \Delta H_f^\circ(\text{B}) + \Delta H_f^\circ(\text{H}^+) - \Delta H_f^\circ(\text{BH}^+) \quad (2)$$

studies of proton affinities were based on a determination of ΔH°_1 with $\Delta H_f^\circ(\text{BH}^+)$ arrived at from electron impact or photoionization appearance potential measurements of BH^+ fragments from more complex molecules, eq 3.³⁻⁵ Such determinations suffered



from the difficulty of identifying exactly the threshold for appearance of BH^+ and also relied on thermochemical data for the

neutral species B, M, and X. In the late 1960's, with the advent of the techniques of flowing afterglow,⁶ high-pressure mass spectrometry,⁷ and ion cyclotron resonance⁸ for the study of ion molecule reactions at thermal energies a more direct method for the determination of relative proton affinities became available. Since only exothermic or near thermoneutral ion-molecule reactions proceed with significant rates, these techniques allowed ready observation of the exothermic direction of proton transfer, eq 4, between bases B_1 and B_2 which allowed qualitative relative



proton affinities to be established. Further advances in the above study of near-thermoneutral proton transfer reactions in both forward and reverse directions have allowed equilibrium constants, K_4 , to be determined, either from a known ratio of neutral pressures of B_1 and B_2 and observed steady-state ionic abundances of B_1H^+ and B_2H^+ or from direct determination of forward and reverse rate constants, eq 5. From the observation of many proton

$$K_4 = \frac{[\text{B}_2\text{H}^+]}{[\text{B}_1\text{H}^+]} \frac{P_{\text{B}_1}}{P_{\text{B}_2}} = \frac{k_4}{k_{-4}} \quad (5)$$

transfer equilibria involving small steps up the basicity scale, relative proton affinity⁹⁻¹² scales spanning 60-70 kcal mol⁻¹ were

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