particularly on the transformation of the two-dimensional information to the three-dimensional distribution function. We express our sincere thanks to Professors Norio Nemoto and Takeji Hashimoto for their advice on the QELS experiments. This work was made possible by generous support from the Ministry of Education, Science and Culture (Grants-in-Aid for specially promoted research 59065004 and 63060003) and the Japan Society for the Promotion of Science (K.I.).

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Insertion and σ-Bond Metathesis Pathways in Gas-Phase Reactions of Bis(η^5-cyclopentadienyl)methylzirconium(1+) with Dihydrogen and Unsaturated Hydrocarbons

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Abstract: Reactions of $Cp_2ZrCH_3^+$ (**1**; Cp = cyclopentadienyl) and $Cp_2ZrCD_3^+$ (**2**) with a number of unsaturated hydrocarbon substrates and dihydrogen have been investigated. Reactions of **2** with hydrocarbon substrates and C_2D_4 with **1** support two major reaction pathways: insertion/dehydrogenation, which is accompanied by near statistical H/D scrambling, and σ-bond metathesis, which is indicated by the exclusive elimination of CD_3H in reactions of **2** with certain substrates. Reactions of **1** and **2** with ethylene and α-alkyl-substituted alkenes result in elimination of dihydrogen and formation of η^3-allyl complex cations. For reaction of **1** and **2** with α-alkyl-substituted ethylenes having *n*-alkyl substituents larger than ethyl (e.g., 1-pentene, 1-hexene) elimination of H_2 and $2H_2$ occurs, and in the current study products formed with H_2 elimination are always found in greater abundance. Reactions of **2** with α,α′-substituted alkenes (e.g., isobutene and α-methylstyrene) proceed with elimination of CD_3H exclusively, which is consistent with a σ-bond metathesis process. Reaction of **2** with isobutene also yields **1**, suggesting an insertion/β-methide shift/isobutene elimination sequence. Cation **1** is also produced in the reaction of **2** with propyne. Reaction of Cp_2ZrD^+ with ethylene shows formation of Cp_2ZrH^+, suggesting an insertion/β-hydride shift/ethylene elimination process, presumably because a η^3-allyl product cannot be formed by elimination of H_2. Reactions of **1** and **2** with cis and trans isomers of 2-butene and 2-pentene have also been investigated, and striking reactivity differences are observed for the two isomers (i.e., cis isomers react predominantly by an insertion/dehydrogenation pathway and trans isomers react almost exclusively by elimination of methane). Products consistent with both insertion/dehydrogenation and σ-bond metathesis are suggested by results of reactions of **1** and **2** with several alkynes. The reaction of **2** with H_2 proceeds with exclusive elimination of CD_3H, also indicating a σ-bond metathesis process. Rate constants for the reaction of **1** with H_2 and D_2 yield a k_H/k_D value of 2.0 ± 0.5. The reactivity of **1** with unsaturated hydrocarbons is compared to the solution reactions of the analogous solvated cation and other d^0f^n metal complexes.

Despite explosive growth in the field of organometallic chemistry of solvated complexes and gas-phase metal ions, few studies directly comparing the reactivity of organometallic compounds in the gas-phase and solution have appeared. Such gas-phase/solution comparisons have provided significant insight into the chemistry of organic compounds[1-6] in reactions such as group transfer and proton transfer. We have previously reported direct comparisons of this type for electron-transfer reactions of the metallocenes,[7a] displacement reactions involving anionic organometallic nucleophiles,[7b] and reactions of highly electrophilic d^0 complexes with dihydrogen, ethylene, and propylene.[7c] We report here further investigations of the gas-phase reactions of electrophilic zirconium(IV) complexes with unsaturated hydrocarbons. These initial gas-phase studies show many similarities to reactivity observed for lanthanide, actinide, and early-transition-metal complexes in solution, and, furthermore, new reaction pathways are observed that may eventually be found for related complexes in solution.

High reactivity and potential usefulness have led to considerable interest in the reactions of electrophilic organometallic complexes in solution.[8-13] Condensed-phase reactions of neutral and cationic d^0 and d^0f^n metal alkyls and hydrides with organic substrates have been studied extensively.[14-16] Several examples of electrophilic ethylene polymerization catalysts have been discovered, and many of these complexes undergo transformations closely related to fundamental processes proposed for Ziegler–Natta catalysts

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(initiation, propagation, and termination).[14a,15b,16b,17] The d^0 and d^0f^n metal alkyl and hydride complexes often readily insert alkenes, alkynes, and polar molecules such as carbon monoxide, ketones, and nitriles.[17b,18-21] In addition, intramolecular and intermolecular C–H activation have also been observed.[15a,b,22,23] Variation of auxiliary ligands (e.g., substitution of pentamethylcyclopentadienyl for cyclopentadienyl) can have a profound effect on the reactivity of these complexes by sterically inhibiting certain reaction pathways.[24]

The relationship of early-transition-metal alkyls and hydrides to Ziegler–Natta catalysts has prompted recent studies of homogeneous and heterogeneous systems based on d^0 and d^0f^n metal centers.[16a,17,25-28] In particular, examples of 14-electron complexes of Sc(III), Zr(IV), Ln(III), and Ac(IV) have been thoroughly investigated, and evidence suggests that metal centers isoelectronic with these complexes are active species in Ziegler–Natta polymerization (at least in homogeneous systems). The nature of the solvent profoundly affects the reactivity of coordinatively unsaturated compounds, and strongly coordinating solvents can significantly attenuate or eliminate practical catalytic activity in the Zr(IV) cation studied by Jordan and co-workers.[25] These observations suggested to us that a coordinatively unsaturated d^0 complex might exhibit a number of chemical transformations with hydrocarbon substrates in the gas phase, where solvent is not available to block open-coordination sites.

We have chosen to concentrate on the reactions of the electron-deficient, 14-electron, d^0 cation $Cp_2ZrCH_3^+$ (**1**; Cp = cyclopentadienyl) and its derivatives for several reasons. Cation **1** has a well-characterized direct analogue in condensed phase.[14,18,25] Solution chemistry and solid-state structures for solvated complexes of **1** have been reported by Jordan and co-workers following their isolation of the complex $[Cp_2Zr(CH_3)(THF)][B(C_6H_5)_4]$.[18] Several other isoelectronic (neglecting f electrons) bis(cyclopentadienyl) and bis(pentamethylcyclopentadienyl) complexes are also known, and their solution reactivities provide background information to aid in the interpretation of our gas-phase results.[15-17,21,22] The unsolvated $Cp_2ZrCH_3^+$ cation has been implicated as the active species in the polymerization of ethylene and in other reactions, in part because of the results obtained in various solvents (e.g., polymerization of ethylene by $Cp_2Zr(CH_3)(THF)^+$ is strongly inhibited in THF solvent but occurs rapidly in CH_2Cl_2).[14c,18,25] Earlier gas-phase studies indicated that the homolytic bond strength order for Zr–CH_3 and Zr–H bonds in **1** and Cp_2ZrH^+ is D(Zr–H) > D(Zr–CH_3),[7c] which is typical of metal alkyl and hydride complexes normally encountered in solution and unlike the order often found in gas-phase bare metal ion chemistry.[29] Reactions of **1** with ethylene and propylene suggested mechanistic pathways similar to those observed for analogous reactions in solution. The possibility of oxidative addition to **1** is remote since the metal center has a d^0 electronic configuration; therefore, the number of mechanistic interpretations is reduced, and the oxidative addition/reductive elimination sequences commonly proposed for reactions of bare metal ions with hydrocarbons in the gas phase are not expected. Finally, **1** can be easily produced from the volatile precursor $Cp_2Zr(CH_3)_2$.

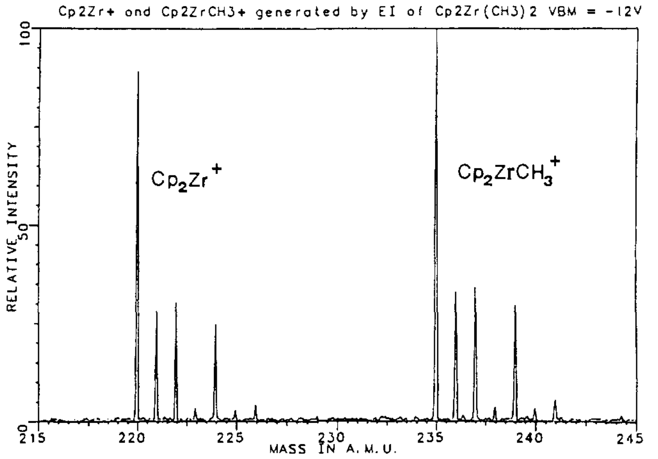

Figure 1. Electron impact ionization mass spectrum of $Cp_2Zr(CH_3)_2$ at 12 eV ($p = 5 \times 10^{-8}$ Torr). The parent ion peak is not observed under any conditions and no other fragments are observed at 12-eV ionization energy in significant abundance (>1% relative intensity).

Extensive results from gas-phase reactions of $Cp_2ZrCH_3^+$ with unsaturated hydrocarbons are given in the present work. Deuterium-labeled reactants such as $Cp_2ZrCD_3^+$ have been used to support the mechanisms proposed for observed transformations at the Zr(IV) metal center. A number of similarities to solution mechanisms and reactivities are observed in gas-phase reactions of **1** with unsaturated hydrocarbons, and additional products are formed through reaction pathways available for chemically activated[30] ions.

Results

We applied FTICR mass spectrometry[31] to study the reactions of $Cp_2ZrCH_3^+$ (**1**) with H_2, D_2, and a number of alkenes and alkynes. $Cp_2ZrCD_3^+$ (**2**) was also employed to provide further insight into the mechanisms of these reactions.

Zirconium has five principal isotopes, and contributions from isotopes of carbon and hydrogen result in the observation of seven principal isotopic species in the mass spectra of compounds containing zirconium, carbon, and hydrogen. In this section each product ion is reported as a single m/z value, which corresponds to the isotopic species having the most abundant ^{90}Zr isotope. A typical mass spectrum for $Cp_2Zr(CH_3)_2$ (ionization energy = 12 eV) is shown in Figure 1.

Empirical formulas of the form $Cp_2ZrC_xH_y^+$ are given for product ions in this section, and no structure is implied other than the Cp_2Zr unit. Any eliminated neutrals are taken as the most stable species possible with the correct molecular formula. Detailed structures of the zirconium product ions are presented in the Discussion.

Determination of Product Ion Distribution. Some reactions of **1** yield more than one product ion. In cases where the intensity of a m/z value has contributions from more than one product ion, it is necessary to quantify the contributions of the different product ions to that m/z value. Theoretical isotope ratios for each product

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ion were calculated using known isotopic abundances for the elements. In every case the intensity of at least one *m/z* value results from a single isotopic species for one of the product ions; therefore, contributions to the intensities of the overlapping product ion peaks can be determined and used to obtain the product distribution.

Product ion distributions were calculated from at least 5 to as many as 30 measurements at several different reaction thermalization times and substrate pressures. Constant product distributions measured under various conditions suggest that the reactions are studied under near thermal conditions. The resulting distributions are reported as percentages of the total product ion intensity and include 95% confidence limits.

Reactions yielding products with overlapping peaks were conducted without ejection of Cp_2Zr^+. This precaution prevents any extraneous distortion of $Cp_2ZrCH_3^+$ isotope ratios that might arise due to undesired excitation during ejection of Cp_2Zr^+ and affect product ion abundances. Reactions of Cp_2Zr^+ with substrate were also investigated to ensure that the presence of Cp_2Zr^+ did not affect the interpretation or measurement of product ion intensities for reactions of **1**.

Reaction of $Cp_2ZrCH_3^+$ with H_2 and D_2. We previously reported the reaction of $Cp_2ZrCH_3^+$ with D_2 and the corresponding second-order rate constant $k_D = (3.9 \pm 0.5) \times 10^9\ M^{-1}\ s^{-1}$ [$(6.5 \pm 0.8) \times 10^{-12}\ cm^3\ s^{-1}$] (eq 1).[7c] We have measured the analogous

$$\underset{m/z\ 235}{Cp_2ZrCH_3^+} + D_2 \rightarrow \underset{m/z\ 222}{Cp_2ZrD^+} + CH_3D \qquad (1)$$

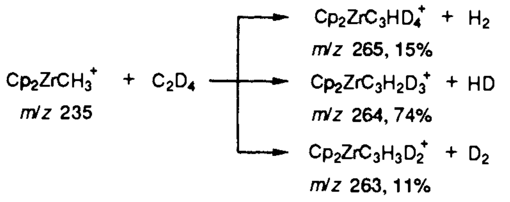
rate for reaction of **1** with H_2, which yields $k_H = (7.9 \pm 1.8) \times 10^9\ M^{-1}\ s^{-1}$ [$(1.3 \pm 0.3) \times 10^{-11}\ cm^3\ s^{-1}$]. These two rate constants give a deuterium kinetic isotope effect, $k_H/k_D \approx 2.0 \pm 0.5$.

Reactions of $Cp_2ZrCH_3^+$ with C_2H_4 and C_2D_4. The reaction of **1** with C_2H_4 proceeds with the formation of *m/z* 261 and elimination of H_2 (eq 2). Similarly, **2** reacts with C_2D_4 to produce *m/z* 266 and D_2 (eq 3).

$$\underset{m/z\ 235}{Cp_2ZrCH_3^+} + H_2C{=}CH_2 \rightarrow \underset{m/z\ 261}{Cp_2ZrC_3H_5^+} + H_2 \qquad (2)$$

$$\underset{m/z\ 238}{Cp_2ZrCD_3^+} + D_2C{=}CD_2 \rightarrow \underset{m/z\ 266}{Cp_2ZrC_3D_5^+} + D_2 \qquad (3)$$

H/D scrambling is observed for reaction of **1** with C_2D_4 and **2** with C_2H_4 (eq 4 and 5). The H_2, HD, and D_2 scrambling ratios for the reactions in eq 4 and 5 were obtained by first measuring



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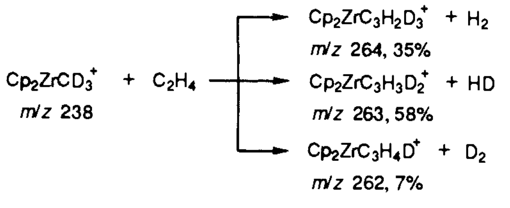


(5)

the intensities of all the isotopic species for the products of eq 2 and 3, respectively. The measured relative intensities of the isotopic species for $Cp_2ZrC_3H_5^+$ and $Cp_2ZrC_3D_5^+$ show little variation and often differ slightly from the relative intensities calculated from known isotopic abundances; therefore, the most accurate product distributions are determined by using experimentally measured intensities.

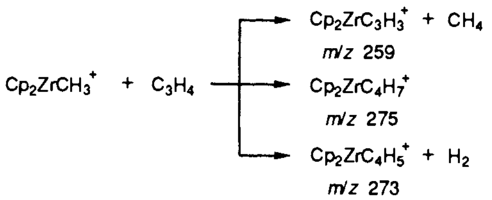
We previously reported[7c] the relative amounts of H_2, HD, and D_2 elimination for the reaction of $Cp_2ZrCH_3^+$ with C_2D_4 (eq 4). For completeness, the product distribution was determined for reaction of **2** with C_2H_4 (eq 5). The results for these two reactions indicate that significant H/D scrambling occurs prior to elimination of dihydrogen. If H_2, D_2, and HD were eliminated statistically (i.e., complete scrambling), the expected relative amounts in eq 4 would be 28.6% D_2, 57.1% HD, and 14.3% H_2 and, in eq 5, 14.3% D_2, 57.1% HD, and 28.6% H_2. The measured product distributions for the reactions indicated in eq 4 and 5 show that the amount of D_2 elimination is less than statistically predicted in both cases. The results for the reaction of Cp_2ZrD^+ and C_3H_6,[7c] 23% H_2 and 77% HD, are much closer to the statistically predicted amounts of 29% H_2 and 71% HD; however, no D_2 can be eliminated in this reaction.

Table I. Reactions of $Cp_2ZrCH_3^+$ (g) with Alkenes

substrate	neutral eliminated	product ion formula	product distribution, %
ethylene	H_2	$Cp_2ZrC_3H_5^+$	100
propylene	H_2	$Cp_2ZrC_4H_7^+$	100
1,3-butadiene	H_2	$Cp_2ZrC_4H_5^+$	100
1-butene	H_2	$Cp_2ZrC_5H_9^+$	100
1-pentene	H_2	$Cp_2ZrC_6H_{11}^+$	87 ± 5
	$2H_2$	$Cp_2ZrC_6H_9^+$	13 ± 5
1-hexene	H_2	$Cp_2ZrC_7H_{13}^+$	52 ± 7
	$2H_2$	$Cp_2ZrC_7H_{11}^+$	48 ± 7
styrene	H_2	$Cp_2ZrC_3H_4Ph^+$	100
isobutene	CH_4	$Cp_2ZrC_4H_7^+$	100
α-methylstyrene	CH_4	$Cp_2ZrC_3H_4Ph^+$	100
allene	none	$Cp_2ZrC_4H_7^+$	62 ± 4
	H_2	$Cp_2ZrC_4H_5^+$	6 ± 3
	CH_4	$Cp_2ZrC_3H_3^+$	31 ± 2
fluoroethylene	$H_2C{=}CH(CH_3)$	Cp_2ZrF^+	100
1,1,1-trifluoropropene	$H_2C{=}CH(CF_2CH_3)$	Cp_2ZrF^+	100

Reaction of $Cp_2ZrCH_3^+$ and $Cp_2ZrCD_3^+$ with Alkenes. The product distributions for reactions of **1** with a variety of α-olefins are summarized in Table I. Except for the reaction of **1** with allene producing $Cp_2Zr_4H_7^+$, all substrates react with **1** to eliminate at least one neutral molecule.

Reactions of $Cp_2ZrCD_3^+$ involving H_2 and CH_4 elimination show different H/D scrambling behavior. In all reactions resulting in H_2 elimination, H/D scrambling is observed. In contrast, for reactions where CH_4 is eliminated no scrambling of the deuterium label is detected; i.e., only elimination of CH_3D is observed. In the reaction of **1** with allene three products are concomitantly produced. Double-resonance experiments indicate that each is formed directly from **1** and allene (eq 6). Investigation of the allene reaction by using $Cp_2ZrCD_3^+$ reveals exclusive loss of CD_3H, producing $Cp_2ZrC_3H_3^+$ (*m/z* 259), and for the loss of H_2, significant H/D scrambling results in the elimination of H_2 and HD (eq 7 and 8).



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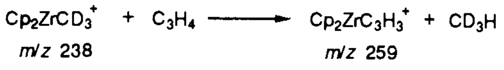

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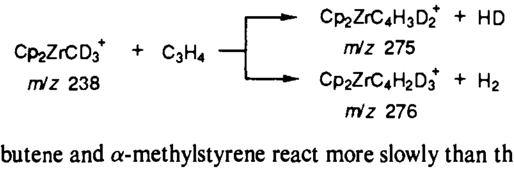


(8)

Isobutene and α-methylstyrene react more slowly than the other terminal olefins investigated. A comparison of the half-lives for the reactions of **1** with ethylene and isobutene indicates that the second-order rate constant for the ethylene reaction is approximately 4–6 times larger than the second-order rate constant for the isobutene reaction. In contrast to other alkenes studied, the neutral product for reaction of **1** with isobutene and α-methyl-

Table II. Reactions of $Cp_2ZrCH_3^+(g)$ with Internal Alkenes

substrate	neutral eliminated	product ion formula	product distribution, %
trans-2-butene	CH_4	$Cp_2ZrC_4H_7^+$	100
cis-2-butene	H_2	$Cp_2ZrC_5H_9^+$	87 ± 5
	CH_4	$Cp_2ZrC_4H_7^+$	13 ± 5
trans-2-pentene	H_2	$Cp_2ZrC_6H_{11}^+$	2 ± 2
	CH_4	$Cp_2ZrC_5H_9^+$	98 ± 2
cis-2-pentene	H_2	$Cp_2ZrC_6H_{11}^+$	85 ± 2
	$2H_2$	$Cp_2ZrC_6H_9^+$	4 ± 2
	CH_4	$Cp_2ZrC_5H_9^+$	11 ± 4
cyclohexene	H_2	$Cp_2ZrC_6H_{11}^+$	100
1,5-cyclooctadiene	H_2	$Cp_2ZrC_9H_{13}^+$	78 ± 2
	$2H_2$	$Cp_2ZrC_9H_{11}^+$	22 ± 2

Table III. Reactions of $Cp_2ZrCH_3^+(g)$ with Alkynes

substrate	neutral eliminated	product ion formula	product distribution, %
acetylene	H_2	$Cp_2ZrC_3H_3^+$	100
propyne	H_2	$Cp_2ZrC_4H_5^+$	61 ± 3
	CH_4	$Cp_2ZrC_3H_3^+$	39 ± 3
phenylethyne	none	$Cp_2ZrC_3H_4Ph^+$	37 ± 6
	H_2	$Cp2ZrC_3H_2Ph^+$	32 ± 3
	CH_4	$Cp_2ZrC_2Ph^+$	29 ± 5
	$HC{\equiv}CCH_3$	Cp_2ZrPh^+	≈2[a]
diphenylethyne	none	$Cp_2ZrC_3H_4Ph_2^+$	90 ± 4
	H_2	$Cp_2ZrC_3H_2Ph_2^+$	10 ± 4

[a] Trace amount.

styrene is methane rather than dihydrogen (eq 9 and 10). $Cp_2ZrCH_3^+$ (m/z 235) is also formed in the reaction of $Cp_2ZrCD_3^+$ with isobutene (eq 11). Only trace $Cp_2ZrCH_3^+$ and Cp_2ZrPh^+ are formed in the reaction of **2** with α-methylstyrene.

$$\underset{m/z\ 238}{Cp_2ZrCD_3^+} + H_2C{=}CMe_2 \rightarrow \underset{m/z\ 275}{Cp_2ZrC_4H_7^+} + CD_3H \tag{9}$$

$$\underset{m/z\ 238}{Cp_2ZrCD_3^+} + H_2C{=}C(Me)(Ph) \rightarrow \underset{m/z\ 275}{Cp_2ZrC_3H_4Ph^+} + CD_3H \tag{10}$$

$$\underset{m/z\ 238}{Cp_2ZrCD_3^+} + H_2C{=}CMe_2 \rightarrow \underset{m/z\ 235}{Cp_2ZrCH_3^+} + C_4H_5D_3 \tag{11}$$

The reactions of **1** with fluoroethylene and 1,1,1-trifluoropropene were also investigated. The single product ion in both reactions is Cp_2ZrF^+ (eq 12 and 13).

$$\mathbf{1} + H_2C{=}CHF \rightarrow \underset{m/z\ 239}{Cp_2ZrF^+} + H_2C{=}CH(CH_3) \tag{12}$$

$$\mathbf{1} + H_2C{=}CH(CF_3) \rightarrow \underset{m/z\ 239}{Cp_2ZrF} + H_2C{=}CH(CF_2CH_3) \tag{13}$$

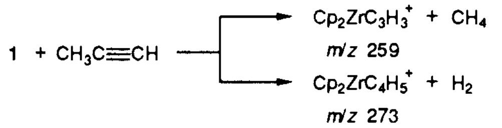
The product distributions for reaction of **1** and a number of internal olefins are listed in Table II. The rates for reactions of **1** with internal olefins including cyclohexene and 1,5-cyclooctadiene indicate that *cis*-olefins generally react more slowly than *trans*-olefins; e.g., half-lives for reaction of **1** with *cis*- and *trans*-2-pentene indicate that the second-order rate constant for reaction of the cis isomer is approximately 3 times smaller than the second-order rate constant for reaction of the trans isomer. In addition, only small amounts of CH_4 are eliminated for *cis*-olefins in contrast to nearly exclusive loss of CH_4 for the trans isomers.

Reaction of $Cp_2ZrCH_3^+$ and $Cp_2ZrCD_3^+$ with Alkynes. The reactions of **1** with several alkynes were investigated and are listed in Table III. Most of the reactions were also repeated with $Cp_2ZrCD_3^+$ as the reactant cation.

Acetylene reacts with **1** to yield $Cp_2ZrC_3H_3^+$ (m/z 259) and eliminates H_2 (eq 14). The product ion, $Cp_2ZrC_3H_3^+$, does not react detectably with acetylene substrate. The second-order rate constant for formation of $Cp_2ZrC_3H_3^+$, determined from six measurements, is $(5.6 \pm 1.9) \times 10^{10}\ M^{-1}\ s^{-1}$ [$(9.3 \pm 3.2) \times 10^{-11}\ cm^3\ s^{-1}$].

$$\mathbf{1} + HC{\equiv}CH \rightarrow \underset{m/z\ 259}{Cp_2ZrC_3H_3^+} + H_2 \tag{14}$$

The reaction of propyne is more complex than that of acetylene. Initially two products are observed, $Cp_2ZrC_3H_3^+$ (m/z 259) and $Cp_2ZrC_4H_5^+$ (m/z 273). Double-resonance experiments indicate both products are formed from **1** and propyne directly (eq 15).



(15)

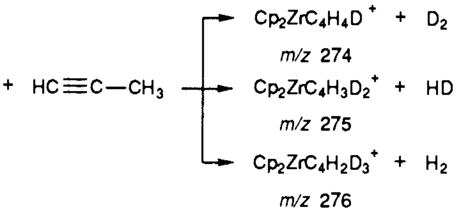
In addition, $Cp_2ZrC_3H_3^+$ (m/z 259) reacts further with propyne to produce $Cp_2ZrC_6H_7^+$ (m/z 299), and no neutral molecule is eliminated (eq 16). $Cp_2ZrC_6H_7^+$ (m/z 299) is inert to subsequent detectable reaction with propyne.

$$\underset{m/z\ 259}{Cp_2ZrC_3H_3^+} + HC{\equiv}C{-}CH_3 \rightarrow \underset{m/z\ 299}{Cp_2ZrC_6H_7^+} \tag{16}$$

Product ion $Cp_2ZrC_3H_3^+$ is produced with exclusive elimination of CD_3H in the reaction of propyne with $Cp_2ZrCD_3^+$ (eq 17). The formation of $Cp_2ZrCH_3^+$ is also observed along with the products from elimination of H_2, HD, and D_2 (eq 18 and 19).

$$\underset{m/z\ 238}{Cp_2ZrCD_3^+} + HC{\equiv}C{-}CH_3 \longrightarrow \underset{m/z\ 259}{Cp_2ZrC_3H_3^+} + CD_3H \tag{17}$$

$$\underset{m/z\ 238}{Cp_2ZrCD_3^+} + HC{\equiv}C{-}CH_3 \longrightarrow \underset{m/z\ 235}{Cp_2ZrCH_3^+} + HC{\equiv}C{-}CD_3 \tag{18}$$



(19)

The reaction of **1** with phenylacetylene is analogous to the reaction with propyne; however, two additional products are observed (eq 20 and 21).

$$\underset{m/z\ 235}{Cp_2ZrCH_3^+} + HC{\equiv}C{-}Ph \rightarrow \underset{m/z\ 337}{Cp_2ZrC_3H_4Ph^+} \tag{20}$$

$$\underset{m/z\ 235}{Cp_2ZrCH_3^+} + HC{\equiv}C{-}Ph \rightarrow \underset{m/z\ 297}{Cp_2ZrPh^+} + CH_3C{\equiv}CH \tag{21}$$

$Cp_2ZrC_3H_4Ph^+$ is inert to subsequent detectable reaction, and the small amount of Cp_2ZrPh^+ does not yield observable further reaction products.

Collision-Induced Dissociation (CID)[32] of $Cp_2ZrCH_3^+$. CID experiments on $Cp_2ZrCH_3^+$ (m/z 235) show the loss of CH_3 (eq 22). At higher fragmentation energies m/z 194 and 192 are observed. Only trace m/z 155, $CpZr^+$, is produced in the CID experiment. In addition, m/z 194, 192, and 155 are produced in the CID of m/z 220. High-energy electron impact mass spectra of cyclopentadiene, C_5H_6, show fragment ions corresponding to $C_3H_3^+$ and C_3H^+, indicating that m/z 194 and 192 may be formed by a similar fragmentation.[33]

$$\underset{m/z\ 235}{Cp_2ZrCH_3^+} \rightarrow \underset{m/z\ 220}{Cp_2Zr^+} + {}^\bullet CH_3 \tag{22}$$

CID of Product Ions. CID studies of most product ions indicate that collision-induced reactions or rearrangements such as the loss

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(32) (a) Cody, R. B.; Freiser, B. S. *Int. J. Mass. Spectrom. Ion Phys.* **1982**, *41*, 199. (b) Cooks, R. G. *Collision Spectrosc.* **1978**, 357.

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of H_2 or unsaturated hydrocarbons occur as well as more direct fragmentation processes.[34] In the present study, CID of products formed in reactions of **1** always leads to formation of the fragment Cp_2Zr^+ (m/z 220) at high CID energies. Product ions with a given m/z value may be formed from a number of different substrates. A comparison of CID spectra for ions of common m/z value often provides evidence for more than one distinct structure. For example $Cp_2ZrC_4H_7^+$ (m/z 275) is produced from propylene, allene, isobutene, *trans*-2-butene, and *cis*-2-butene (eq 23–27).

$$\mathbf{1} + C_3H_6 \rightarrow \underset{m/z\ 275}{Cp_2ZrC_4H_7^+} + H_2 \tag{23}$$

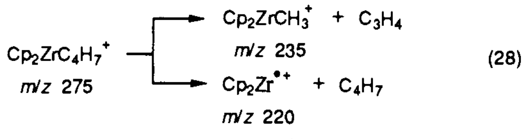
$$\mathbf{1} + C_3H_4 \rightarrow \underset{m/z\ 275}{Cp_2ZrC_4H_7^+} \tag{24}$$

$$\mathbf{1} + i\text{-}C_4H_8 \rightarrow \underset{m/z\ 275}{Cp_2ZrC_4H_7^+} + CH_4 \tag{25}$$

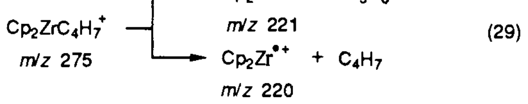
$$\mathbf{1} + trans\text{-}2\text{-}C_4H_8 \rightarrow \underset{m/z\ 275}{Cp_2ZrC_4H_7^+} + CH_4 \tag{26}$$

$$\mathbf{1} + cis\text{-}2\text{-}C_4H_8 \rightarrow \underset{m/z275}{Cp_2ZrC_4H_7^+} + CH_4 \tag{27}$$

CID of the product ions with m/z 275 in eq 23–25 produce m/z 235 and m/z 220 (eq 28) at approximately the same excitation energy and in roughly the same proportions, whereas CID of m/z 275 in eq 26 produces m/z 221 and m/z 220 (eq 29). CID of m/z 275 in eq 27 could not be obtained due to its low abundance.



(28)



(29)

Discussion

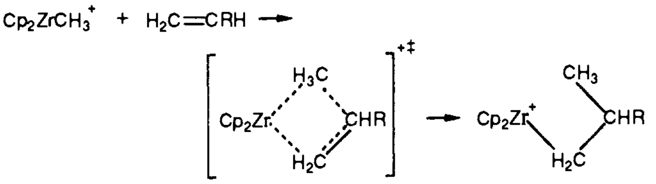
Structure of $Cp_2ZrCH_3^+$. The structure of **1** is of obvious importance when considering its reaction chemistry. The crystal structure of unligated $Cp^*_2ScCH_3$ (Cp^* = pentamethylcyclopentadienyl),[15b] which is isoelectronic with cation **1**, indicates a pseudo-trigonal-planar geometry around the metal center. It is unlikely that **1** is a methylene hydride isomer, since such a structure requires further oxidation of the d^0 zirconium center. In addition, CID of **1** initially shows the loss of CH_3 (eq 22), and no fragments corresponding to $Cp_2ZrCH_2^+$ or Cp_2ZrH^+ are observed.

In considering the reactions of **1** with hydrocarbons, it is important to characterize the extent of involvement of the Cp ligand hydrogens. Complications in the mechanistic interpretation of observed reactions and H/D scrambling would result from participation of ring hydrogens in the elimination of neutral molecules. In a prior publication we assumed the "Cp_2Zr" unit retains its integrity throughout reactions with H_2, ethylene, and propylene; no direct evidence supporting this assumption was presented.[7c]

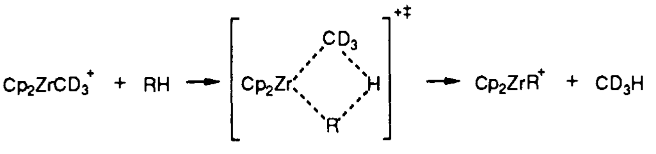
Evidence for the retention of the Cp_2Zr unit and lack of Cp ligand hydrogen involvement in observed reactions is provided by the absence of elimination of HD or H_2 for the reaction of $Cp_2ZrCD_3^+$ with C_2D_4, which yields $Cp_2ZrC_3D_5^+$ and D_2. The analogous reaction of **1** with C_2D_4 indicates significant H/D scrambling (eq 6).

General Considerations for Reactions of 1 with Olefins and Alkynes. The reactions of **1** with olefins and alkynes can best be described in the context of two major reaction sequences: the migratory insertion of unsaturated hydrocarbons into the zirconium–methyl bond, and the activation of C–H bonds via σ-bond metathesis (Schemes I and II, respectively). Both reaction sequences have ample precedents in the solution reactions of similar neutral and cationic, electron-deficient d^0f^n metal complexes.[15–17,25–27,35] Insertion/elimination pathways are suggested for the present study by results consistent with β-hydride shift/alkene elimination, β-methide shift/alkene elimination, and significant, virtually statistical, H/D scrambling in dihydrogen elimination reactions. Metathesis in this study is indicated by reactions of $Cp_2ZrCD_3^+$ with hydrocarbons that produce CD_3H as the sole eliminated neutral.

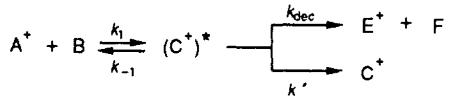
Scheme I



Scheme II



Scheme III



An attempt is made here to establish that both insertion and C–H activation processes are operative in the gas-phase reactions of $Cp_2ZrCH_3^+$ with unsaturated hydrocarbons. However, it is helpful to identify certain aspects of the low-pressure gas-phase medium that differ significantly from those of the condensed phase before arguments concerning gas-phase reactivity can be made effectively. For example, any neutral molecule formed in an ion/molecule reaction during the FTICR experiment is rapidly pumped out of the system. Thus product ions are produced only from neutral substrates admitted through inlet leak valves.

Another important difference in the two media arises from the frequencies of third-body collisions. In solution, reacting species are in contact with solvent, which acts as an energy sink by continually removing excess energy generated during a reaction. In contrast, third-body collisions occur much less frequently in the low-pressure regime of the FTICR experiment (10^{-8}–10^{-5} Torr).

Scheme III depicts a general reaction sequence with two pathways to products for an exothermic gas-phase ion/molecule reaction.[30,36,37] The following discussion is simply an abbreviated overview of the principles governing formation of products as they apply to the present system.

When reactants A^+ and B interact in a bimolecular exothermic reaction under low-pressure FTICR conditions, the energy of the reaction cannot be released to solvent and therefore resides in $(C^+)^*$ as internal energy. The excess internal energy of $(C^+)^*$ is assumed to be randomized into all vibrational modes in statistical treatments of kinetics for these processes.

Scheme III indicates two pathways are available for product formation. The activated complex $(C^+)^*$ may undergo stabili-

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(34) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 736.

(35) (a) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, C. S.; Vollmer, S. H.; Day, V. W. *Organometallics* **1982**, *1*, 170. (b) Duttera, M. R.; Fagan, P. J.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 865. (c) Manriquez, J. M.; Fagan, P. J.; Marks, T. J.; Vollmer, S. H.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1979**, *101*, 5075. (d) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2214. (e) Fendrick, C. M.; Mintz, E. A.; Schertz, L. D.; Marks, T. J.; Day, V. W. *Organometallics* **1984**, *3*, 819. (f) Marks, T. J. *Prog. Inorg. Chem.* **1978**, *24*, 51.

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zation via third-body collision or infrared photon emission to produce C^+ with an effective rate constant k'.[38] In the strong collision limit,[30] a single collision of M with $(C^+)^*$ removes the excess energy necessary for stabilization and observation of C^+, ($k' = k_c[M]$); i.e., after a third body collision, C^+ no longer has the internal energy necessary to undergo unimolecular decomposition at a significant rate. Alternatively, unimolecular decomposition produces E^+ and F or reactants A^+ and B. The only observable unimolecular process is the forward reaction yielding E^+ and F, unless labeled reactants are employed (vide infra). The elimination of F in a translationally and vibrationally excited state is likely and also provides a means for removal of excess energy from the chemically activated complex $(C^+)^*$. This type of product stabilization is not limited to the elimination of a single neutral molecule. If E^+ remains vibrationally excited after neutral elimination from $(C^+)^*$, further stabilization may occur by additional neutral loss.

Products analogous to $(C^+)^*$ are likely to form in the FTICR experiment and revert to yield the reactants if $k_{dec} \ll k_{-1}$ and the time before a third-body collision is large in comparison to the lifetime of the collision complex, $(C^+)^*$. In order to observe product formation, a stabilizing third-body collision is necessary unless energy can be removed by the elimination of a neutral product (or by infrared emission). For example, no product ion is observed in the reaction of Cp_2ZrH^+ with ethylene (eq 30). However, the reaction of Cp_2ZrD^+ and ethylene shows the formation of Cp_2ZrH^+ (eq 31). This is explained by an insertion/deinsertion/elimination process.

$$Cp_2ZrH^+ + H_2C{=}CH_2 \rightarrow \text{no products observed} \quad (30)$$

$$Cp_2ZrD^+ + H_2C{=}CH_2 \rightarrow Cp_2ZrH^+ + H_2C{=}CHD \quad (31)$$

The ethyl insertion product, $[Cp_2ZrCH_2CH_2D^+]^*$, is not observed, indicating that back-reaction to yield reactants occurs more rapidly than a stabilizing third-body collision. Even at the highest pressures presently available in our FTICR mass spectrometer, $k_c[M] = k'$ is small compared to k_{-1} for eq 30 and 31. In addition, $k_{dec} \ll k_{-1}$, which suggests any available decomposition reaction is slow compared to the back-reaction. The absence of facile dehydrogenation in the reaction of Cp_2ZrH^+ with ethylene arises because formation of an allyl complex cannot occur (vide infra).

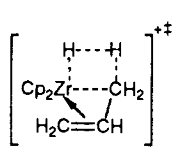
Reactions of $Cp_2ZrCH_3^+$ with H_2 and D_2. The observed kinetic isotope effect of 2.0 ± 0.5 for the reactions of **1** with H_2 and D_2 indicates a primary deuterium kinetic isotope effect. In the reaction $CH_3 + D_2/H_2 \rightarrow CH_3D/H + D/H$, $k_H/k_D \approx 4$ for the linear transition state.[39a] A nonlinear transition state leads to a lower k_H/k_D value.[39b] However, these observations for radical reactions may have limited relevance to the expected isotope effects in ion/molecule reactions, where chemical activation energy is present in the collision complex (however, for simple ion/molecule hydrogen abstraction reactions (e.g., $Ar^+ + H_2/D_2$), the observed deuterium isotope effect is rather insensitive to ion kinetic energies up to a few electronvolts[40]). In any case, the observed primary kinetic isotope effect of ~2 for H_2/D_2 reacting with **1** is consistent with a σ-bond metathesis transition state (Scheme II) for this reaction.

Thermodynamics of Insertion. We previously stated that an indication of the exothermicities of the insertion reactions is given by the enthalpies of the general reaction $^\bullet CH_3 + C_nH_m \rightarrow {}^\bullet C_{n+1}H_{m+3}$ ($\Delta H^{\circ\prime}$).[7c] The values of $\Delta H^{\circ\prime}$ for all alkene substrates investigated were found to be greater than 22 kcal mol^{-1} and less than 29 kcal mol^{-1} except for allene. The estimated exothermicity for the insertion reaction of **1** with allene is 51 kcal mol^{-1}; however, this value pertains to an η^1 product and is not corrected for the loss of allyl radical resonance stabilization that accompanies localized π-bonding in an η^1 Zr–allyl complex. Values could not be accurately estimated for reactions of **1** with alkynes because the heats of formation of the organic vinyl radicals are unknown.

The usefulness of $\Delta H^{\circ\prime}$ is limited by the assumption that the Zr–Me and Zr–R (R = alkyl) bond disruption enthalpies, D(Zr–Me) and D(Zr–R), are roughly equivalent. Recent results for methyl and alkyl bond disruption enthalpies in neutral $Cp^*_2ZrR_2$, $Cp^*_2HfR_2$,[41a] and $Cp^*_2ThR_2$[41b] complexes indicate that the difference, D(Zr–Me) – D(Zr–R), may be as high as 17 kcal mol^{-1}. However, it is not evident that such a large difference, D(Zr–Me) – D(Zr–R) = 17 kcal mol^{-1}, also pertains to the cationic complexes investigated here. Unfavorable steric interactions of alkyl groups with Cp* ligands are reduced for complexes with less bulky Cp ligands, and the unfavorable repulsive interactions of the two R groups in neutral compounds are eliminated because only one R group is present in the 14-electron cations of this study. In addition, simple electrostatic arguments concerning polarizability and charge delocalization support relatively stronger interactions for larger R groups and "Cp_2Zr^{+}". Agostic interactions involving β C–H bonds may also affect the relative bond disruption enthalpies for alkyl complexes. Furthermore, values for first, second, and third metal–methyl bond disruption enthalpies determined for Cp^*ZrMe_3 and Cp^*HfMe_3 by reaction with C_6F_5OH indicate that the metal–carbon bond strength increases from first to third by as much as 8 kcal mol^{-1}.[41a] Nevertheless, values of bond disruption enthalpies for neutral complexes suggest that D(Zr–Me) – D(Zr–R) for cationic complexes are most likely greater than 0 kcal mol^{-1}. At present we are unable to meaningfully estimate a value for D(Zr–Me) – D(Zr–R) for the cationic zirconium complexes studied; however, the arguments presented above suggest a value significantly less than 17 kcal mol^{-1}.

Reactions of $Cp_2ZrCH_3^+$ with Terminal Olefins. Two general types of terminal olefins and allene are discussed in this section. The first type has at least one hydrogen at C-2. The results are given in Table I and indicate that H_2 is eliminated as the neutral product in every reaction of **1** with substrates in this group.

The polymerization of these α-olefin substrates might be expected since $Cp_2ZrCH_3(THF)^+$ and a number of complexes similar to **1** polymerize ethylene.[12,16b,17a,b,26,42] However, we have pointed out insertion of ethylene into the Zr–CH_3 bond generates a chemically activated $[Cp_2Zr(n\text{-}Pr)^+]^*$ complex (internal chemical activation energy ≈23 kcal mol^{-1}), which has been suggested to undergo an intramolecular rearrangement resulting in the elimination of H_2 through a six-membered transition state.[7c] We have further proposed that the zirconium product ion is an η^3-allyl complex. The proposed transition state for dehydrogenation may also be drawn in analogy to the transition state for intramolecular σ-bond metathesis, **3**. A similar transition state has been proposed in the reaction of Sc^+ with n-butane[43] and Cp^*_2LnR (Ln = Nd, La) with propene and 1-hexene.[16b,c]



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A number of early-transition-metal allyl complexes are weakly active catalysts for the polymerization of certain vinyl monomers.[44] In addition, $Cp^*Nd(\eta^3\text{-allyl})$ is also effective as a catalyst for ethylene polymerization.[16b] The mechanism proposed for initiation requires conversion of the η^3-allyl complex to an η^1 isomer prior

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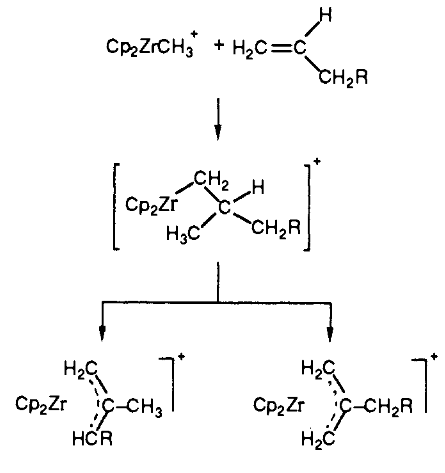
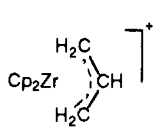
Scheme IV



to π-coordination of monomer and subsequent insertion.[44] The η^3 to η^1 isomerization is much slower than propagation and causes an induction period in the polymerization reaction. The allyl complex, $Cp_2Zr(C_4H_7)(THF)^+$, polymerizes ethylene in CH_2Cl_2, but no definitive kinetic information concerning the polymerization is available.[45]

In the gas phase, the proposed allyl complex, $Cp_2ZrC_3H_5^+$, does not react observably with ethylene. The absence of observable $Cp_2ZrC_3H_5^+$ reactivity toward ethylene is attributed to a slow conversion of the η^3-allyl to η^1 and decreased exothermicity for the insertion compared to the reactions of **1** with ethylene. A distinct inhibition of insertion is associated with structures that do not readily allow the coordination of unsaturated substrates.[17b,18,20] Isomerization is expected to be endothermic due to localization of charge on the zirconium center and localization of π-bonding in the C_3H_5 group; however, initial conversion of the η^3-allyl to η^1 may not be required for insertion to occur. Nevertheless, if ethylene insertion were to occur, the η^3-allyl species $Cp_2ZrC_3H_5^+$ would be converted to η^1 complex $Cp_2ZrC_5H_9^+$. Since the $Cp_2ZrC_5H_9^+$ product does not have an η^3-allyl structure, insertion is accompanied by loss of resonance stabilization and charge delocalization in the product. Thus, the insertion of ethylene would be less exothermic for the $Cp_2ZrC_3H_5^+$ allyl complex and increase the barrier for insertion compared to the insertion reaction of ethylene with cation **1**.

Assuming the η^3-allyl structure for the products, structure **4** can be assigned unambiguously to the allyl cation generated by reaction of **1** with ethylene, but assignment of structures for higher terminal alkenes must be based on indirect evidence. CID experiments yield some information on the structure of the product ion for propylene (eq 23). One interpretation of the CID process invokes elimination of neutral allene by β-methyl shift/allene elimination to produce cation **1** (eq 28), which is the reverse of allene insertion. If a β-methyl group were not available, collisionally induced elimination of hydrocarbon likely would proceed following β-hydride shift, yielding Cp_2ZrH^+ (as found for the σ-bond metathesis product of **1** and *trans*-2-butene, eq 29). Thus, we assign the product of the reaction of **1** with propylene as structure **5**. Reactions of **1** with terminal alkenes larger than propylene are likely to yield allyl product ions with two different structures (Scheme IV), and the CID of these product ions was complicated and could not be used to assign structures.



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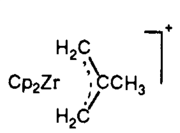
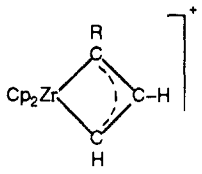


5

$Cp^*_2ScCH_3^+$ reacts with alkenes other than ethylene by elimination of methane rather than insertion, presumably because of the sterically restricting Cp* ligands.[15b] Crowding is less pronounced in cation **1** and insertion is apparently preferred. A scandium hydride complex with a less crowded ligand sphere has been shown to insert and isomerize a variety of pentadienes.[24]

The dehydrogenation of allyl ions generated from alkene substrates greater than C_4 found for reactions of **1** with 1-pentene and 1-hexene (Table I) has also been observed in the gas-phase reactions of $CoCH_3^+$ and $FeCH_3^+$.[46] Two molecules of H_2 are eliminated in some reactions of bare metal ions with alkanes.[47] The loss of two molecules of H_2 for reactions of **1** with alkenes is most likely driven by the exothermicity of the insertion and formation of charge delocalized metallocyclobutenes **6** and **7**.



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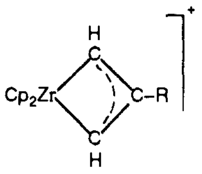
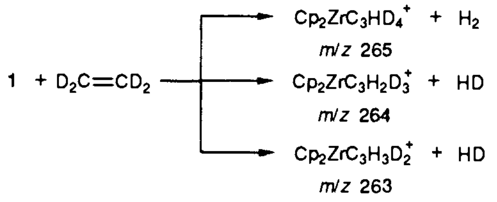


7

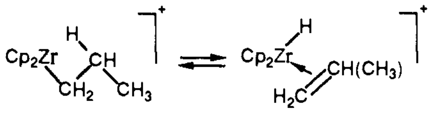
Several titanacyclobutene complexes have been isolated and characterized.[48] Clearly, our present observations cannot be explained by successive oxidative additions/H_2 eliminations, because oxidation of the d^0 zirconium center is energetically prohibitive. Oxidative addition/reductive elimination mechanisms are not expected in reactions of d^0 cations nor are they required to interpret our observations. Reasonable alternatives to oxidative addition/reductive elimination, e.g., Scheme II and transition state **3**, have been used to explain H_2 elimination reactions of **1** in the gas phase, indicating that oxidative addition/reductive elimination is not the only plausible mechanistic sequence for H_2 elimination reactions involving highly unsaturated metal ion centers such as $CoCH_3^+$ and $FeCH_3^+$.

Hydrogen/deuterium scrambling is also observed in all H_2 elimination reactions involving $Cp_2ZrCD_3^+$. Only a slight amount of H/D scrambling was previously reported in the reaction of C_2D_4 with the 6-electron species, $Cl_2TiCH_3^+$.[49] Scrambling is also observed in the reaction of the highly coordinatively unsaturated 9-electron $CoCD_3^+$ cation with ethylene.[46]

Hydrogen/Deuterium Scrambling in Insertion/Dehydrogenation Reactions. The following discussion of H/D isotope scrambling for $Cp_2ZrCH_3^+$ and C_2D_4 (eq 32) is also applicable to the scrambling process for all terminal alkenes studied. Insertion of terminal alkenes other than isobutene and α-methylstyrene yields methyl migratory insertion products with at least one β-hydrogen. The β-hydrogen is apparently rapidly and reversibly transferred before elimination of H_2 (eq 33). This reversible β-hydride abstraction in conjunction with 1,2 hydrogen shifts along the carbon framework provide a mechanism for H/D scrambling.



$$1 + D_2C{=}CD_2 \longrightarrow \begin{cases} Cp_2ZrC_3HD_4^+ + H_2 & m/z\ 265 \\ Cp_2ZrC_3H_2D_3^+ + HD & m/z\ 264 \\ Cp_2ZrC_3H_3D_2^+ + HD & m/z\ 263 \end{cases} \tag{32}$$



(33)

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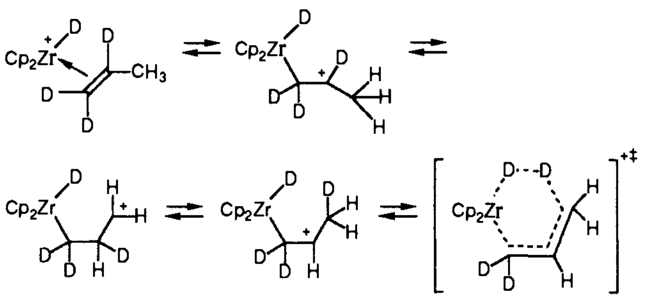
(47) (a) Byrd, G. D.; Burnier, R. C.; Freiser, S. B. *J. Am. Chem. Soc.* **1982**, *104*, 3565. (b) Byrd, G. D.; Freiser, D. S. *J. Am. Chem. Soc.* **1982**, *104*, 5944.

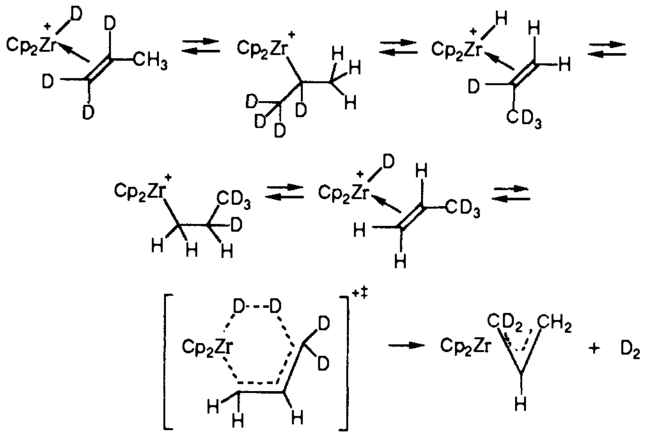
(48) (a) Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 5074. (b) Tebbe, F. N.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 6149.

(49) Uppal, J. S.; Johnson, D. E.; Staley, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 508.

Scheme V



Scheme VI

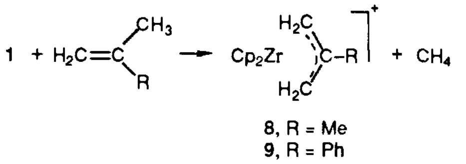


Schemes V and VI indicate two pathways for H/D scrambling and elimination of D_2. D_2 elimination was chosen as an example because it requires the greatest amount of rearrangement, and HD and H_2 elimination may be similarly described.

Scheme V requires a β-hydride shift and the formation of a carbonium ion on the carbon chain. The energy required to generate the primary carbonium ion in Scheme V should not be in excess of 16 kcal mol^{-1} (the value of the energy difference for the 1° and 2° carbonium ions generated from propane).[50] The possibility of a favorable interaction of the charge on the carbon framework with the metal center and the stabilization generally associated with charge dispersal in larger ions suggest that the energy required to generate the 1° carbonium ion intermediate is less than 16 kcal mol^{-1}. $Cp_2Zr(n\text{-}Pr)^+$ is produced from **1** and ethylene with significant chemical activation energy, and subsequent β-hydride shift reduces the excess energy of the complex. Thus formation of the 1° carbonium may not be thermodynamically viable.

Scheme VI for elimination of D_2 invokes anti-Markovnikov addition of propylene to a Zr–D bond rather than H/D scrambling along a carbonium ion. The scrambling is thereby explained by a series of facile insertion/deinsertions in the precursor complex, and this mechanism appears more plausible energetically than Scheme V. The reaction of **1** with isobutene (eq 9, 11, and 34) indicates that Markovnikov addition is strongly preferred, but the same result does not necessarily follow for the reaction of Cp_2ZrH^+ with propylene.

Insertion and Metathesis for α,α-Disubstituted Olefins. The second category of terminal olefins is represented by isobutene and α-methylstyrene. Both substrates react with **1** to eliminate methane and apparently form η^3-allyl complexes (**8**, R = CH_3; **9**, R = Ph) (eq 34). The assignment of allyl structures for isobutene and α-methylstyrene reaction products is based on CID spectra that indicate these ions are identical with the products formed in the reaction of **1** with propylene and styrene, respectively.

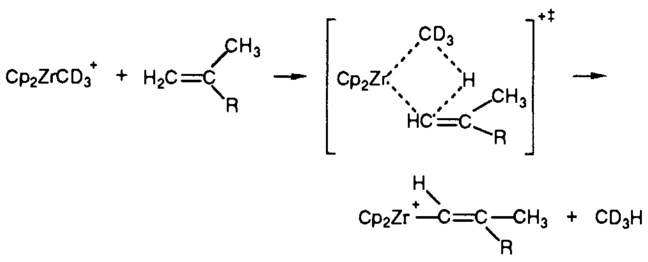


(34)

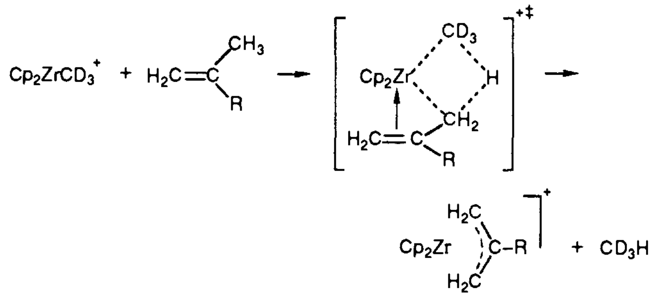
8, R = Me
9, R = Ph

Qualitatively, reaction 34 occurs more slowly than reactions of other terminal alkenes. Both substrates react with $Cp_2ZrCD_3^+$ to eliminate CD_3H exclusively. An analogous reactivity is seen in solution for $Cp^*{}_2ScCH_3$ in reactions with several alkanes, alkenes, and alkynes.[15b] This σ-bond metathesis process (Scheme II) normally occurs rather than insertion because of the steric interaction of the reacting substrate with the ligand environment. The ligand-imposed steric requirements for insertion of alkenes other than ethylene prevent the facile, proper orientation of the C=C double bond necessary for migratory insertion in $Cp_2^*ScCH_3$ chemistry.

Scheme VII



Scheme VIII



In the reaction of $Cp_2ZrCH_3^+$ with isobutene and α-methylstyrene, both vinylic and allylic C–H activation are possible as depicted in Schemes VII and VIII. Vinylic C–H activation of isobutene and α-methylstyrene implies the formation of a zirconium vinyl species, which rearranges by a 1,3 hydride shift to generate **8** and **9**. Generally, 1,3 hydride shifts are only probable when the origin and terminus of the shifting hydride are in close proximity.[51] However, examples of isomerization of vinyl to allyl complexes are known,[52] and the driving force for the formation of the allyl products is likely to be significant. Note that only vinylic C–H activation can occur in the reaction of **1** with allene, and it is competitive with insertion for that substrate.

Allylic C–H activation would yield the η^3-allyl cation directly. The reactivity of $CoCH_3^+$ and $FeCH_3^+$ indicates that C–H activation occurs at the allylic position because of the ca. 20 kcal mol^{-1} lower C–H bond energy.[46] The mechanism proposed for reactions of $CoCH_3^+$ and $FeCH_3^+$ involves initial insertion of the metal ion into the allylic C–H bond followed by the reductive elimination of methane. Oxidative addition is not invoked in the reactions of d^0 metal complexes since further oxidation of the metal center is recognized as energetically unreasonable.[15b] The present results suggest that oxidative addition mechanisms are not the only possible pathways for elimination of neutral molecules in analogous bare metal ion reactions.

$Cp_2ZrCH_3^+$ is produced in the reaction of $Cp_2ZrCD_3^+$ with isobutene and provides evidence for migratory insertion in a Markovnikov fashion. Evidently, insertion produces a zirconium–neopentyl species, **10**, in which all three methyl groups are equivalent. Thus the reverse reaction, β-alkyl shift followed by

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(50) Lossing, F. P.; Semeluck, G. P. *Can. J. Chem.* **1970**, *48*, 955.

(51) Lowry, T. H.; Richardson, K. S. *Mechanisms and Theory in Organic Chemistry*; Harper and Row Publishers: New York, 1987; 483.

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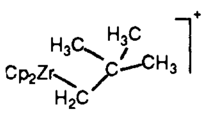

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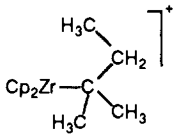
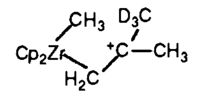


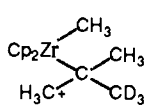
11

isobutene elimination, results in the formation of **1**. β-alkyl shift has been observed in solution for d^0 and d^0f^n metal complexes in reactions with unsaturated hydrocarbons.[17c,24] H_2 is not eliminated because no β-hydrogens are available to initiate the rearrangements necessary for H_2 loss (Schemes V and VI). Anti-Markovnikov addition of isobutene evidently is not significant, as that would produce ion **11**, which has eight β-hydrogens and would be expected to undergo facile H_2 elimination (vide infra).

Apparent insertion/deinsertion of isobutene without H/D scrambling is further evidence for the necessity of the β-hydride shift sequence in scrambling rearrangements. One might expect scrambling through intermediates analogous to those presented in Scheme V (i.e., **12** and **13**). However, 1,2 hydride shifts would not accomplish the interchange of hydrogen and deuterium.



12



13

The evidence given above supports the operation of two pathways for reactions of **1** with α,α′-olefins: insertion/deinsertion (not seen for unlabeled reactants) and σ-bond metathesis (CH_4 elimination). The σ-bond metathesis pathway is also available for α-olefins, but the dehydrogenation pathways are far more facile for these substrates. Work in progress using selectively deuterated isobutene will clarify the mechanistic pathways that operate in this chemistry.

Reaction of Allene with $Cp_2ZrCH_3^+$ and $Cp_2ZrCD_3^+$. The reaction of **1** with allene yields three products. Two of the products are proposed to result from an insertion process and the third from σ-bond metathesis (eq 6). CID spectra of the $Cp_2ZrC_4H_7^+$ ions produced from allene are identical with those for products observed in the reaction of propylene and isobutene; therefore, insertion of allene evidently forms the methylallyl cation, **8**, directly. A small portion of product **8** is dehydrogenated to produce $Cp_2ZrC_4H_5^+$, the structure of which is most likely a charge delocalized metallocyclobutene analogous to that given previously for **7** (R = Me).

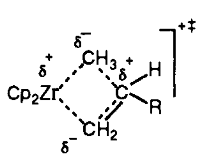
The product of σ-bond metathesis, $Cp_2ZrC_3H_3^+$, is also proposed to be a metallocyclobutene with structure **7** (R = H). The propargyl structure is proposed for $Cp_2ZrC_3H_3^+$ formed in the reaction of **1** with propyne, since the isomer of $Cp_2ZrC_3H_3^+$ produced reacts further to insert propyne (vide infra). CID of $Cp_2ZrC_3H_3^+$ yields uninformative spectra similar to those obtained for the product of the same mass generated in the reaction of **1** with acetylene. None of the ions react further with allene, implying that they are not σ-complexes.

Reactions of $Cp_2ZrCH_3^+$ with Internal Olefins. Cis and trans isomers of 2-butene and 2-pentene as well as cyclohexene and 1,5-cyclooctadiene have been investigated (Table II). The trans isomers react almost exclusively by σ-bond metathesis, resulting in the elimination of CH_4. This conclusion is supported by reactions of $Cp_2ZrCD_3^+$, which show no H/D scrambling and only CD_3H elimination. Cis isomers yield products from both insertion/elimination and σ-bond metathesis. The major product for *cis*-2-butene and *cis*-2-pentene results from the insertion sequence. No σ-bond metathesis is observed for either of the two cycloalkenes studied.

The influence of the isomeric cis and trans structures for internal alkenes leads to striking differences in reactivity. The trans isomers are ~1 kcal mol^{-1} more stable than the cis isomers. Thus, insertion of cis substrates is more exothermic than insertion of trans substrates. Since either isomer yields identical insertion products, the reactivity difference must arise from the initial orientation of the alkene as it interacts with the zirconium center and the slight difference in exothermicity of the insertion. Trans isomers are generally bound more weakly than their cis counterparts in π-complexes with transition metals,[53] and this may explain the lack of insertion for the *trans*-alkenes. This explanation hinges on the assertion that coordination of the alkene as a π-complex seems necessary for insertion to occur. In the present scenario there is obviously a vacant coordination site in cation **1**. However, it is not obvious by using molecular models that cis coordination is significantly less sterically hindered than trans coordination. Thus the mechanistic feature responsible for the large difference in reactivity observed for cis and trans isomers presently defies adequate description.

The cycloalkenes offer additional information because these substrates only show products from insertion/H_2 elimination reactions. One might expect similar products for reactions of *cis*-2-butene and cyclohexene. The controlling factor in this case is apparently the stability of the resulting products from σ-bond metathesis. The product of the reaction of *cis*-2-butene and **1** is proposed to generate an allyl complex, because subsequent reaction with *cis*-2-butene is not observed. Allylic and vinylic C–H activation are possible in reactions of **1** and **2** with internal olefins. For cyclohexene the formation of an η^3-allyl complex produced from σ-bond metathesis is probably precluded by an unfavorable steric interaction of the C_6 ring with the Cp ligands. The η^3-allyl species generated by insertion and elimination of H_2 is not as sterically unfavorable as the η^3-allyl formed from the metathesis reaction. Alternatively, the C–H activation reaction of **1** with cyclohexene may occur more slowly than the reaction with *cis*-2-butene because of increased steric hinderance at the allylic positions of cyclohexene.

Reaction of $Cp_2ZrCH_3^+$ with Fluorinated Alkenes. The absence of products clearly attributable to insertion for reactions of **1** with fluorinated substrates may be explained by polarization considerations in a four-membered four-electron transition state, **19** (R = F, CF_3). The barrier for methyl migration is significantly increased due to destabilization of the transition state caused by the electron-withdrawing inductive effect of the fluoro or trifluoromethyl substituents. However, insertion and β-F shift/alkene elimination to produce only Cp_2ZrF^+ cannot be eliminated as a possible pathway for either substrate.



19, R = F, CF_3

Reactions of $Cp_2ZrCH_3^+$ with Alkynes. Reactions of **1** with four alkynes were investigated, and products proposed to result from both σ-bond metathesis and insertion are observed. Acetylene reacts readily with **1** to produce $Cp_2ZrC_3H_3^+$ (**6**, R = H) and eliminate H_2. Reaction of **2** with acetylene occurs with H/D scrambling (i.e., HD and D_2 are eliminated); however, the elimination of H_2 is not observed in significant amount. Since no further insertion occurs, the structure of $Cp_2ZrC_3H_3^+$ is most likely a charge delocalized metallocyclobutene analogous to **6** (R = H). No products from σ-bond metathesis are observed in the reaction of **1** with acetylene.

A large portion (90%) of the products in the reaction of **1** with diphenylacetylene do not result from elimination of a neutral molecule. Insertion followed by 1,3 hydride shift is proposed to yield the allyl complex **14**. Elimination of H_2 also takes place, probably producing a metallocycle similar to **14**. The absence of further reaction of **14** is consistent with formation of a η^3-allyl product.

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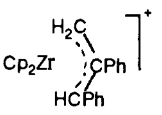
(53) Collman, J. P.; Hegedus, L. S. *Principles and Application of Organotransition Metal Chemistry*; University of Science Books: Mill Valley, CA; 1980.

(54) Christ, C. S.; Eyler, J. R.; Richardson, D. E. Manuscript submitted for publication.

(55) Samuel, E.; Rausch, M. D. *J. Am. Chem. Soc.* **1973**, *95*, 6263.



14

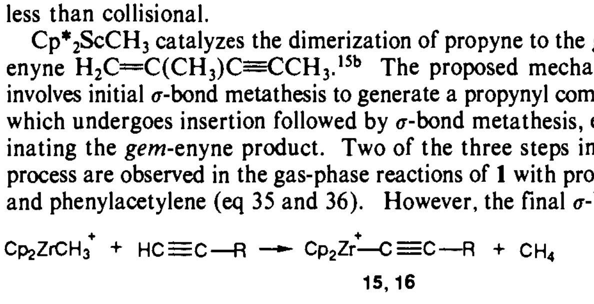
Propyne and phenylacetylene yield products from both σ-bond metathesis and insertion. The metathesis route gives products that continue to react with substrate, implying that they are σ-complexes rather than delocalized allyls or metallocycles as formed through insertion processes in reactions of **1** with acetylene and diphenylacetylene and described above. Metathesis product structures are given as **15** and **16** for propyne and phenylacetylene.

$Cp_2Zr{-}C{\equiv}C{-}CH_3^+$ **15** $\qquad$ $Cp_2Zr{-}C{\equiv}C{-}Ph^+$ **16**

A second insertion yields products $Cp_2ZrC_6H_7^+$ and $Cp_2ZrC_4HPh_2^+$, which are inert to further insertion, indicating that these species are not simple σ-complexes. However, in solution alkenyls insert more slowly than alkyls or alkynyls in similar systems, and subsequent insertion in the gas-phase chemistry may be unobservable if the rate coefficient is 3–4 orders of magnitude less than collisional.

$Cp^*{}_2ScCH_3$ catalyzes the dimerization of propyne to the *gem*-enyne $H_2C{=}C(CH_3)C{\equiv}CCH_3$.[15b] The proposed mechanism involves initial σ-bond metathesis to generate a propynyl complex, which undergoes insertion followed by σ-bond metathesis, eliminating the *gem*-enyne product. Two of the three steps in this process are observed in the gas-phase reactions of **1** with propyne and phenylacetylene (eq 35 and 36). However, the final σ-bond metathesis reaction, eliminating $H_2C{=}C(CH_3)C{\equiv}CCH_3$ does not occur detectably (eq 37). This inertness may simply be due to a significantly lower rate for the elimination process and can be explained by the interaction of the alkyne portion of the insertion product and the zirconium center. In solution this interaction can be removed by coordination of solvent, which would make the final σ-bond metathesis event kinetically more favorable.

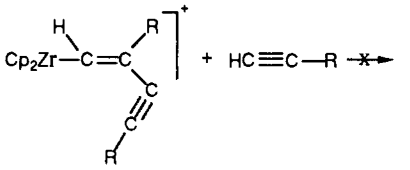
$$Cp_2ZrCH_3^+ + HC{\equiv}C{-}R \longrightarrow \underset{\textbf{15, 16}}{Cp_2\overset{+}{Zr}{-}C{\equiv}C{-}R} + CH_4 \qquad (35)$$



(36)

15, 16

17, (R = CH_3)
18, (R = Ph)



17, 18

$$H_2C{=}C(CH_3)C{=}CCH_3 + \underset{\textbf{15, 16}}{Cp_2\overset{+}{Zr}{-}C{\equiv}C{-}R} \qquad (37)$$

Several structures are possible for $Cp_2ZrC_6H_7^+$ and $Cp_2ZrC_4HPh_2^+$. CID experiments show loss of a single propyne and phenylacetylene unit, respectively. Structures **17** and **18** are consistent with the observed results and the reaction of $Cp^*{}_2ScCH_3$ with propyne. The similarity in the reactions of propyne and phenylacetylene indicates that this reactivity may be common to a variety of α-alkynes.

Conclusions

Reaction of **1** and **2** with alkenes and alkynes via methyl migratory insertion is supported by several experimental observations. Reactions of **2** with isobutene and propyne yield **1**, which is explained by an insertion/deinsertion process in which the proposed insertion product decomposes by β-methyl elimination. In addition, β-hydride elimination is proposed to explain the formation of Cp_2ZrH^+ in the reaction of Cp_2ZrD^+ with ethylene.

Insertion of terminal alkenes other than isobutene and α-methylstyrene yields products with β-hydrogens. Since insertion is exothermic by ca. −26 ± 3 kcal mol^{-1}, decomposition of the apparent insertion products is not unexpected in these gas-phase reactions. β-Hydride shift provides the initial step for the H_2 elimination and H/D scrambling in reactions with labeled reactants. Reaction of **1** with isobutene via Markovnikov addition does not yield an alkyl product with a β-hydrogen. Therefore, elimination of H_2 is not expected and not observed, strongly suggesting Markovnikov addition dominates in this chemistry (note, however, that the observed H/D scrambling may be explained by invoking anti-Markovnikov insertion, Scheme VI). The product from insertion is observed in the reaction of **1** with allene, which is the only alkene reaction in this study that occurs without elimination of a neutral.[56] CID spectra of this product are identical with that of the product generated in the reaction of **1** and propylene, and this observation is also consistent with Markovnikov addition.

The results of the gas-phase reaction of **1** with ethylene may be related to the solution polymerization and termination reactions as illustrated in Figure 2. These qualitative potential surfaces yield insight into the differences in the solution and gas-phase results. In the condensed phase, repetitive insertion of ethylene into the zirconium–alkyl bond produces polyethylene. At long chain lengths, the $\Delta H°$ for each successive insertion is approximately −23 kcal mol^{-1}. The major chain termination step is β-hydride elimination. In the gas phase, polymerization does not occur, but we contend insertion of ethylene into the zirconium–methyl bond yields a propyl species with excess vibrational energy (the actual chemical activation energy will depend on D(Zr–Me) − D(Zr–propyl). The activated propyl complex may undergo a number of reversible intramolecular transformations before irreversible elimination of dihydrogen.

Figure 2 shows that the barrier for dehydrogenation of $Cp_2Zr(n\text{-}Pr)^+$ is lower than the barrier for β-hydride shift/alkene elimination in the gas phase. Indeed, the β-hydride shift/dehydrogenation products are estimated to be as much as ~20 kcal mol^{-1} more stable than the β-hydride shift/alkene elimination products,[54] which are approximately ergoneutral with respect to the separated reactants (the process is ergoneutral if [D(Zr–H) − D(Zr–Me)] = 8 kcal mol^{-1}). Furthermore, for the reaction of Cp_2ZrD^+ with ethylene we observe β-hydride shift/alkene elimination since formation of an allyl species cannot occur, and in the reaction of $Cp_2ZrCD_3^+$ with isobutene we observe β-methide shift/alkene elimination because β-hydride shift cannot occur. In contrast, in solution the barrier for β-hydride shift/alkene elimination is evidently lower than the barrier for elimination of H_2. Both barriers will depend on the solvation of the transition states and the solvation energies of the various cationic zirconium species.

Additionally, cation **1** is specifically solvated in coordinating solvents such as acetonitrile and is isolated as a bis(acetonitrile) adduct.[14c] The bis(acetonitrile) complex readily loses one solvent molecule to afford the mononitrile adduct, and the THF solvate of **1** is isolated as a mono THF adduct. The isolation of these complexes indicates that at least one solvent molecule is strongly coordinated to the cationic zirconium center in complexes such as **1**, and, in general, the second solvent molecule is less strongly coordinated than the first. Moreover, FTICR studies of the reaction of **1** with nitriles (including acetonitrile) indicate that a single nitrile can be coordinated to the metal center, but facile addition of a second nitrile requires insertion of the first. Addition of solvent may change the relative energies of various gas-phase zirconium complex cations, and, in some cases, the energies of the complexes may actually be inverted. For example, β-hydride shift/alkene elimination yields Cp_2ZrH^+, which in solution is expected to be specifically solvated by two solvent molecules,

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[56] Such an observation is not unique in the gas-phase chemistry of **1** with hydrocarbons. Many nitriles react with **1** to produce adducts in which one or more nitriles add *without* elimination of a neutral.[54]

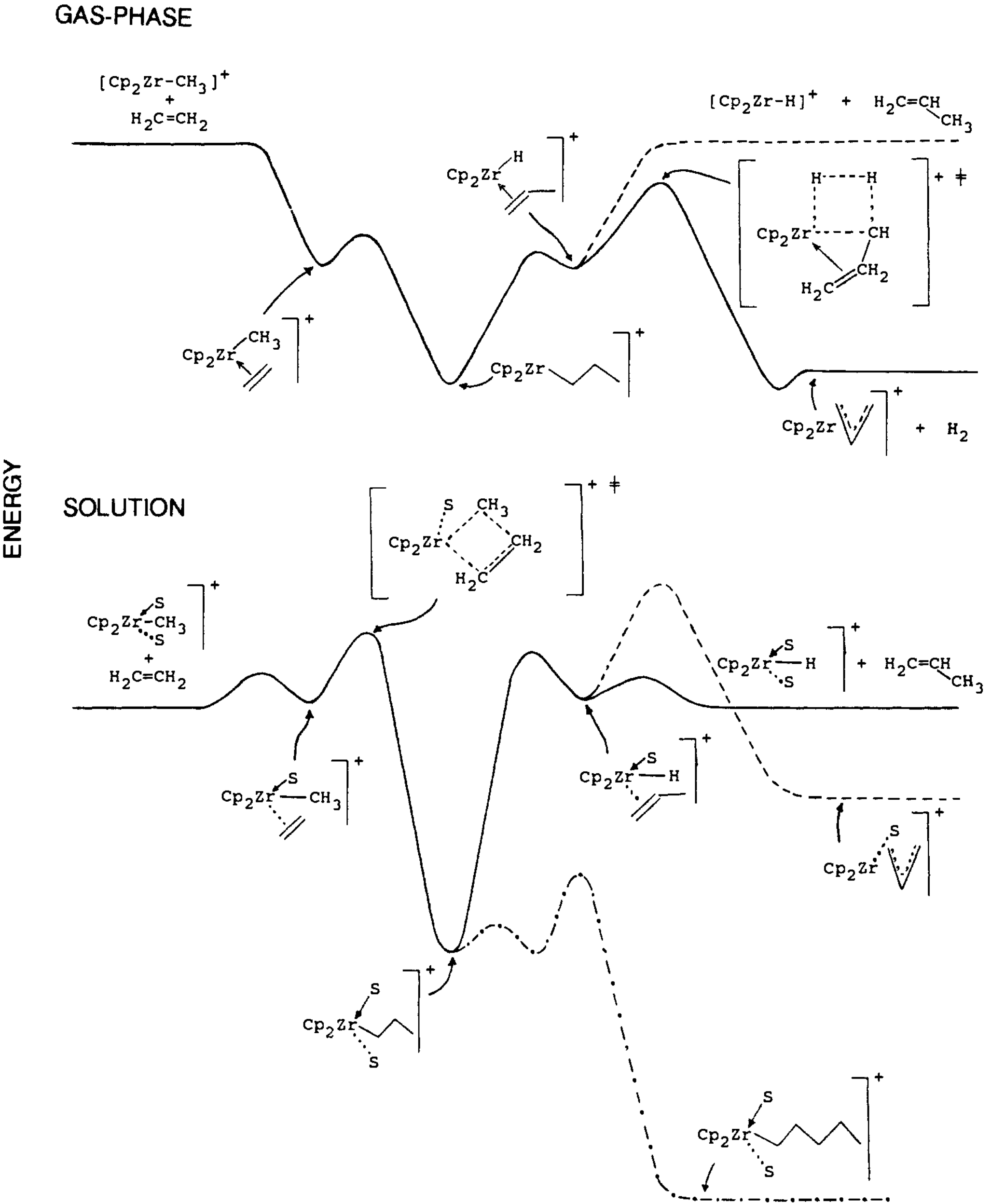

Figure 2. Comparison of qualitative potential energy surfaces for the reaction of $Cp_2ZrCH_3^+$ with ethylene in solution and the gas phase. The solid curves indicate potential surfaces for the observed reactions. The dashed portions (---) of the curves indicate higher energy pathways, which are not observed. The dot-dash curve (-•-) indicates the potential surface for the reaction of ethylene with $Cp_2Zr(n\text{-}Pr)^+$ in solution (propagation). The strong interaction of solvent with the zirconium center is depicted as a solid line, and the weak solvent interaction is shown as a dotted line.

whereas the dehydrogenation pathway (observed in the gas phase) yields $Cp_2Zr(\eta^3\text{-allyl})^+$, which is expected to coordinate only one solvent molecule.[45] The net effect of specific solvation may reverse the relative energies of Cp_2ZrH^+ and $Cp_2Zr(\eta^3\text{-allyl})^+$, as shown in Figure 2, and explain the lack of dehydrogenation in the polymerization of ethylene by solvated **1**. In view of the obvious role of solvation in the determination of the potential surfaces discussed above, variation of solvent from weakly interacting (e.g., cyclohexane, toluene) to more basic (e.g., THF, CH_2Cl_2) can profoundly affect the energetics of chain-propagating and chain-terminating steps. Weakly Lewis basic solvents will tend to make the condensed-phase potential surface more comparable to the gas-phase surface, and we would therefore expect increased probability for dehydrogenation in the chemistry of d^0f^n metal alkyls in such solvents (at least for cationic complexes).

At present, the role of the dehydrogenation pathway in the solution polymerization of ethylene has not been addressed. Since $(MeCp)_2ZrC_3H_5^+$ polymerizes ethylene,[45] a dehydrogenation reaction pathway analogous to eq 2 is not expected to cause chain termination; however, dehydrogenation and subsequent insertion would result in internal unsaturation in the polymer formed. We are unaware of the extent of internal unsaturation in polyethylene produced in solution reactions of d^0f^n metal complexes, but clearly dehydrogenation is an exothermic process in the gas-phase reactions of **1** with a number of unsaturated substrates and may be thermally accessible in solution polymerizations.

The strongest evidence for σ-bond metathesis is the exclusive elimination of CD_3H for methane elimination reactions of **2** with certain alkene and alkyne substrates in the current system. The absence of scrambling for methane elimination reactions and the exclusive elimination of CH_3D in the reaction of **1** with D_2 are consistent with a four-membered transition state proposed for σ-bond metathesis reactions in solution.

In addition, kinetic studies in the condensed phase indicate σ-bond metathesis of alkynes at a d^0 center is more facile than that for alkenes.[15b] This kinetic trend is apparently upheld for reactions of **1** with terminal alkenes and alkynes in the gas phase. Since in the absence of major steric effects the rate for insertion of alkenes and alkynes at **1** in the gas phase is near collisional (at least within 1 order of magnitude), the kinetic trend for σ-bond metathesis is indicated by an increase in the yield of products derived from σ-bond metathesis compared to insertion for alkynes.

Thus, insertion predominates for most alkene substrates, whereas σ-bond metathesis is competitive with insertion for several alkynes studied here.

The mechanistic interpretation of the reactions of **1** is simplified because of the absence of accessible higher zirconium oxidation states. Thus, oxidative addition and reductive elimination, often invoked to explain the reactions of bare metal ions,[29,46] are highly improbable mechanistic sequences in the reactions of **1**. This suggests that mechanisms other than oxidative addition/reductive elimination may also be applied to the analogous reactions of bare metal ions in the gas phase.

We have demonstrated that processes observed in the solution reactions of d^{0}f^n organometallic complexes are evidently observed for the Cp$_2$ZrCH$_3^+$ in the gas phase. The gas-phase investigation of cation **1** provides a unique opportunity to characterize the σ-bond metathesis and insertion reaction sequences in the absence of solvent, especially because the results can be compared to the same processes for analogous complexes in solution. The present results also suggest that information pertaining to the possible synthesis of a variety of new organometallic complexes and possible side reactions may be obtained through these types of gas-phase studies.

Experimental Section

Results for ion/molecule reactions were obtained by using Fourier transform ion cyclotron resonance mass spectrometry. Two different mass spectrometers were employed for reaction studies. Data used in determination of rate coefficients were acquired with a Nicolet FTMS 1000 (3.0 T). Product distributions were determined mainly on the second system, which is constructed around a 2.0-T magnet. The second system is very similar to the FTMS 1000; the main difference is a larger vacuum chamber and increased pumping capability. A check of product distributions for the same reactions determined in the two systems shows good agreement within experimental error.

Electron impact (EI) (11–12 eV) on Cp$_2$Zr(CH$_3$)$_2$ ($p \approx 10^{-8}$–10^{-7} Torr) yields predominantly Cp$_2$ZrCH$_3^+$ and Cp$_2$Zr$^+$. Cp$_2$Zr$^+$ and any ionized substrate are ejected from the ICR cell isolating Cp$_2$ZrCH$_3^+$ for reaction studies. Substrates are generally present at pressures ca. 10^{-7}–10^{-6} Torr. Argon or krypton are used as buffer gases at pressures in the 10^{-6}–10^{-5} Torr range. A thermalization time precedes the acquisition of data and permits Cp$_2$ZrCH$_3^+$ multiple collisions with buffer gas to ensure reactions are studied under thermal conditions.

The formation of binuclear zirconium ions Cp$_4$Zr$_2$(CH$_3$)$_n^+$ (n = 0–2) limits the study of ion/molecule reactions to those with rate coefficients above $\sim 10^9$ M^{-1} s^{-1} (10^{-12} cm^3 s^{-1}). However, reactions with slightly smaller rate coefficients may be investigated if pressures of Cp$_2$Zr(CH$_3$)$_2$ are reduced to the low 10^{-8} Torr range.

Water reacts with **1** rapidly, even when present as a slight impurity in a substrate (eq 38). Therefore, drying of substrates is imperative.

$$\mathrm{Cp_2ZrCH_3^+ + H_2O \rightarrow Cp_2ZrOH^+ + CH_4} \qquad (38)$$

The method used for determination of rate coefficients was described previously[7a] and yields values estimated to be within ±30% of the absolute rate constants. Product distributions and rate constants are reported in the text with 95% confidence limits.

Cp$_2$Zr(CH$_3$)$_2$ and Cp$_2$Zr(CD$_3$)$_2$ were synthesized according to a literature preparation[55] and analyzed by NMR and mass spectrometry. Deuteromethyllithium was synthesized in dry diethyl ether from CD$_3$I purchased from Aldrich. Mass spectrometric analysis of Cp$_2$Zr(CD$_3$)$_2$ indicated >99% deuteration.

Collision-induced dissociation experiments are performed by imparting kinetic energy to a given ion (by radio frequency excitation) in the presence of an inert gas at pressures in the range 5×10^{-6} to 1×10^{-5} Torr. Upon collision with the neutral, the fragmentation of the parent ion to produce a daughter ion spectrum may be used to provide structural information about the parent ion. The kinetic energy of the parent ion prior to collision can be controlled by varying the radio frequency power applied, and the dependence of the endothermic fragmentation pathways on ion translational energy can be probed.

Double-resonance experiments provide means for determining the origin of a product ion (i.e., identifies the ion from which a product ion arises following an ion/molecule reaction). By use of the ion ejection capabilities of the FTICR, various ions in a complex mass spectrum can be removed from the trap to isolate a single type of ion. The reactions of this ion with added neutrals can then be followed independently. Alternatively, in a more traditional double-resonance experiment, a suspected precursor ion is continuously ejected from the trap during the reaction time. A reduced yield of a given product ion indicates the contribution of the ejected ion to the observed product ion mass spectrum.

Liquid substrates were purchased from Aldrich in high purity and used after drying over CaH$_2$. C$_2$D$_4$ and D$_2$ were purchased from Cambridge Isotope Labs and used as received. All other gases were purchased from commercial sources in high purity and used without further purification.

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Selectivity as a Function of Anionic Base Properties in the Gas-Phase Reactions of Dimethyl Sulfite

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Abstract: The thermally equilibrated gas-phase reactions of dimethyl sulfite (CH$_3$OSO$_2$CH$_3$), in a helium bath gas at 300 K, with a variety of anions ranging from amide, phenide, and allyl anions to nitromethide and hydrosulfide, have been quantitatively examined using the flowing afterglow technique. A master reaction scheme, composed of four competitive reaction pathways, is presented to account for the experimental observations. Of primary importance in selectivity is the structure of the anionic nucleophile and then its basicity. Strongly basic, localized, heteroatomic nucleophiles yield larger amounts of elimination products compared to localized carbon bases of comparable basicity. While most anions yield methyl substitution products, localized bases are much more nucleophilic at carbon than delocalized carbon bases. For nucleophilic attack at sulfur the opposite trend is found, delocalized carbon bases being most nucleophilic at this site. Only the weakly basic cyclopentadienide and nitromethide anions were found to react with dimethyl sulfite solely by termolecular adduct formation. Anomalies in the observations for acetaldehyde enolate, cyanomethide, and anilide anions are suggestive of reaction via the heteroatomic sites of these nucleophiles. The new level of chemical understanding developed from the overall reaction scheme defined will help design future gas-phase experiments to probe specific reaction mechanisms.

The chemistry of organic sulfites is well over 100 years old; this functionality has been the subject of numerous studies. Organic sulfites have intriguing reactivity and structural features in addition to practical applications as insecticides and plant growth regulators

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