Articles

Gas-Phase Reactions of Bis(η^5-cyclopentadienyl)methylzirconium Cations with Ketones and Aldehydes

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The reactions of the bis(η^5-cyclopentadienyl)methylzirconium cation (**1**) with ketones and aldehydes in the gas phase have been studied by Fourier transform ion cyclotron resonance mass spectrometry. Reactions of **1** with a majority of the ketones studied resulted in consecutive addition of one and two substrate molecules and/or elimination of alkanes. Deuterium-labeled substrates and methylzirconocene were used to investigate the mechanistic details. On the basis of DFT calculations, the key products of the elimination reaction(s) were identified as η^3-enolate complexes formed via an insertion/elimination mechanism. Similar product ion structures are postulated for the reaction of **1** with aldehydes in cases where these complexes are either the only or the major reaction product. A multiple-step mechanism is proposed, which involves migratory insertion of an aldehyde molecule into the methylzirconocene cation, followed by β-H elimination, and, via a six-membered cyclic transition state, formation of the resulting enolate complex. When a β-H elimination pathway is not available for ketones, the reaction is instead proposed to proceed via direct nucleophilic attack of the metal-bound alkyl preceded by a fast migratory insertion equilibrium.

Introduction

The d^0 Group 4 metallocenes are of great interest as precursors of alkene polymerization catalysts,[1,2] which can be tuned to make polymers of very specific tacticities. The active species is generally accepted to be a coordinatively unsaturated cation such as LL′MCH$_3^+$ (M = Ti, Zr; L = η^5-cyclopentadienyl or related ligand). Single-center metal-catalyzed polymerization has evolved from an area of purely academic interest into commercially important technology.[3]

Valuable insights into reaction mechanisms, including those of polymerization reactions, can be obtained using Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS)[4−8] to study intrinsic gas-phase reactivity of transition-metal complexes. The spatial separation of reacting species under high-vacuum conditions has certain advantages, most importantly the absence of complicating factors prevailing in solution, such as association by ion pairing, interactions with solvent, and intra- and, especially, intermolecular processes leading to destruction/modification of the active species. The latter are especially relevant in catalytic studies, since active species are often present in trace amounts and are very short-lived. On the other hand, reaction mechanisms in the gas phase may be different from those observed in the condensed phase.

The low-pressure gas-phase reaction of bis(η^5-cyclopentadienyl)methylzirconium cations with alkenes results in formation of η^3-allyl complexes instead of polymerization due to insufficient thermalization of ionic intermediates in the absence of a solvent.[9] Theoretical studies of zirconocene and titanocene cations indicate that the limiting step in this reaction is a β-hydrogen elimination, with an activation barrier of ~11 kcal/mol for the zirconium complex.[10,11] Thermalization can be achieved, however, by increasing the pressure to about 10 mTorr, and the observed rate constant of propylene polymerization under these conditions was estimated to be about 6 orders of magnitude higher than that in solution.[12,13] This result is an excellent illustration of the intrinsic high reactivity of isolated cations in the absence of coordinating counterions or solvent molecules.

In addition to reactions of metallocenes with unsaturated hydrocarbons, previous gas-phase studies have involved investigation of the reactivity patterns of bis(η^5-cyclopentadienyl)-methylzirconium cations with nitriles[14] and other alkenes[15] and effects of ancillary ligands on LL′ZrCH$_3^+$ cation reactivity with

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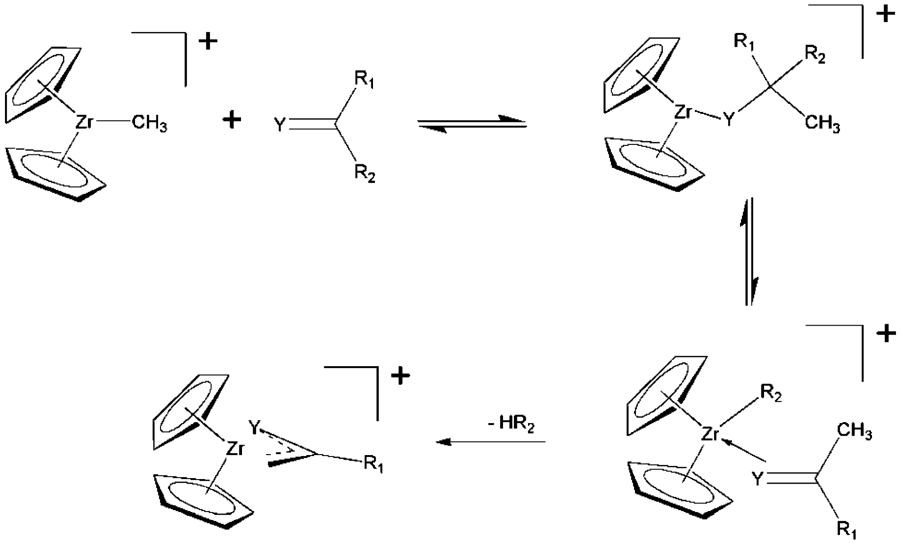
Scheme 1



dihydrogen and ethylene.[16] The intrinsic reactivity of hydroxyzirconocenes was also studied as a model for metal−hydroxide complex ion reactions with a range of compounds.[17]

Despite rapid growth in the gas-phase chemistry of organometallic complexes, especially metal ions,[18−21] and the importance of metallocene catalysis, gas-phase studies of metallocene ions are still rather scarce. The purpose of the present work was to gain a deeper understanding of the reaction mechanisms for electrophilic early-transition-metal metallocenes and to attempt a generalization of the gas-phase reactions with unsaturated compounds. The formation of an η^3-allyl complex could be described as an example of a more general scheme describing such reactions under high-vacuum, nonequilibrium conditions (Scheme 1).

In Scheme 1, for the reaction mechanism suggested in earlier studies for the reactions of methyl zirconocenes with terminal olefins,[15] $Y = CH_2$ and $R_2 = H$. In the case of 1,1-disubstituted alkenes (e.g., $R_2 = CH_3$) the elimination of methane was observed.[9] In the liquid phase, the alkene insertion products of zirconocenes are generally stable and have little tendency to eliminate the neutral species.

In the case of aldehydes and ketones, $Y = O$ and $R_2 = H$, alkyl in Scheme 1. In comparison to the case for alkenes, the carbonyls are expected to be coordinated more strongly to Zr(IV) by donation of an electron pair from oxygen (as opposed to π-bonding electrons in the alkenes) to an empty d-orbital of the metal. Therefore, initial binding of the substrate with the metal is expected to occur via the substrate's carbonyl oxygen. In the gas phase, under high-vacuum, high-energy collision conditions, the reactivity exhibited might also be described by the general Scheme 1. This would be quite different from the known chemistry in the solution phase such as, for example, silver-mediated (chloride abstraction by a catalytic amount of $AgClO_4$[22]) aldehyde addition reactions of Cp_2ZrRCl complexes, where a mechanism involving generation of alkyl-/alkenylzirconocene was proposed[22] and the resultant reaction products are alcohols formed through condensation of the aldehyde and the R ligand of zirconocene.

The present work reports a study of reactivity pathways in the gas phase of bis(η^5-cyclopentadienyl)methylzirconium (**1**), chosen as a versatile d^0 model compound, with series of simple ketones and aldehydes.

Results and Discussion

All data presented here were obtained using FTICR-MS. The active species, $Cp_2ZrCH_3^+$ (**1**) and $Cp_2ZrCD_3^+$ (**2**), were formed from the volatile neutral precursors $Cp_2Zr(CH_3)_2$ and $Cp_2Zr(CD_3)_2$ by electron ionization. In addition to **1** and **2**, formation of a second major fragment ion, Cp_2Zr^+, is also observed (see the Supporting Information, Figure S1a).

Zirconium has five stable isotopes, which in superposition with $^{13}C/^{12}C$ isotopes result in a unique pattern of seven peaks in the mass spectra for all of the organozirconium compounds studied in this work, enabling unambiguous identification of the presence of Zr. For the sake of simplicity, all of the seven Zr-containing isotopic ions are reported as a single mass corresponding to the most abundant (51.45%) ^{90}Zr isotope. In cases where there is overlap of several series of peaks corresponding to different products, a detailed analysis of the contributions from individual ions has been carried out. Since the isotopic abundances of the constituent elements are known, and at least one peak containing the lightest ^{90}Zr isotope and thus of lowest m/z does not overlap with other peaks, the heights of individual series of contributing peaks can be estimated.

In previous studies under similar conditions it has been demonstrated that the cyclopentadienyls are solely spectator ligands, as Cp "switching" reactions and HD elimination for the complexes with fully deuterated ligands but non-deuterated Cp rings have not been observed.[9] Therefore, the Cp_2Zr unit was presumed to remain intact throughout all of the experiments. Where questions exist about the structures of the product ions, the formulas are reported in the form $Cp_2ZrC_xH_yO_z^+$ with the

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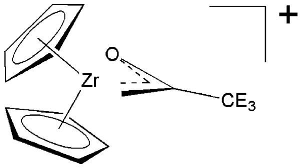

Figure 1. Postulated structure for the most stable form of the $Cp_2ZrC_3H_5O^+$ ion (E = H).

corresponding *m*/*z* ratio. Since all of the reported ions were singly charged, we use the term "empirical formula" throughout the text. Detailed structural considerations are presented later in this section.

Reactions of $Cp_2ZrCH_3^+$/$Cp_2ZrCD_3^+$ with Acetone/*d*$_6$-Acetone. The reaction of **1** (*m*/*z* 235) with acetone proceeds with formation of several products. Two principal ones, with *m*/*z* 293 and 351, correspond to consecutive addition of one and two substrate molecules (see the Supporting Information, Figure S2). Addition of the second acetone molecule becomes pronounced only after about 4 s reaction time (at a total pressure of approximately 2×10^{-7} Torr). An ion with *m*/*z* 277, corresponding to the empirical formula $Cp_2ZrC_3H_5O^+$, apparently results from elimination of methane from the ion with *m*/*z* 293. It is coordinatively unsaturated and adds an additional acetone molecule, forming an ion with *m*/*z* 335.

A variety of structures can be postulated for the observed adducts, e.g., η^1 vs η^2 complexes, etc., and, therefore, theoretical geometry optimizations are useful. Consideration of the gas-phase chemistry of bis(η^5-cyclopentadienyl)methylzirconium cations described in the literature suggests that the species with *m*/*z* 277 has a structure similar to those postulated for the gas-phase reaction of **1** with unsaturated hydrocarbons: i.e., η^3-allyl complexes.[9,14] The possibility of η^3-allyl complex formation is well documented.[13,15,23−29] Density functional theory studies also confirm the plausibility of allyl intermediate formation as a possible side reaction in homogeneous single-site olefin polymerization.[10,11]

Our DFT calculations, presented below in Computational Studies, suggest that the most stable structure is *not* an η^3-allyl complex but, rather, that of the complex shown in Figure 1, which is an η^3-enolate complex.

The high stability of this complex can be understood: the η^3-enolate complex is isoelectronic with the η^3-allyl complex, and both the allyl and enolate complexes in either resonance form participate in both σ and dative bonding of the ligand to a metal center. However, the σ-bonded oxygen resonance form of the η^3-enolate complex should be more strongly bound than the corresponding allyl structure. In comparison to the methylene group, oxygen is a weaker σ-donor, but the ability of the oxygen atom to provide additional bonding by partially transferring its available lone pair into an empty zirconium 4d orbital increases the total bond strength. In the other, carbon-bonded, resonance form of the η^3-enolate complex, dative bonding from the oxygen atom would be expected to be more efficient than π complexation of the C═C bond by a metal center. According to the Dewar−Chatt−Duncanson model[30,31] efficient π-bonding occurs when σ-type donation from the C═C π orbital is synergistic with concomitant π back-bonding into an empty π^* orbital of the alkene, which in turn implies that only metals with at least one filled nonbonding orbital can efficiently form such complexes. For the d^0 zirconocene, only donation of electrons is possible from the C═C bond, making the π complexation rather weak.

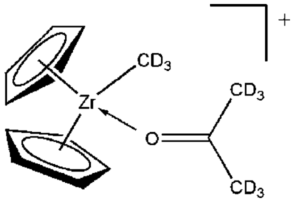

Figure 2. Postulated structure of the *m*/*z* 302 ion resulting from CH_3/CD_3 scrambling between metal and carbonyl.

In the reactions of Cp_2ZrMe^+ with *d*$_6$-acetone, simple addition products of *d*$_6$-acetone (nominal molecular mass 64 amu) to **1** are expected to have *m*/*z* 299 and *m*/*z* 363, 6 and 12 amu higher, respectively, than the products of reaction with undeuterated acetone. Both of these ions are observed. In addition, formation of a product ion with *m*/*z* 302 was seen. The gain of 3 amu can be assigned to the product in Figure 2.

This ion results, apparently, from CH_3/CD_3 scrambling between metal and carbonyl. Three ions with *m*/*z* 279, 280 (major product), and 282, corresponding to the empirical formula $Cp_2ZrC_3H_{5-n}D_nO^+$ ($n = 2, 3, 5$) (approximate peak height ratios 2:5:1), replace $Cp_2ZrC_3H_5O^+$ (*m*/*z* 277), the ion reported above in reactions of **1** with acetone (postulated to be an η^3-enolate complex).

The observed CH_3/CD_3 scrambling and lack of H/D scrambling suggest reversible transfer of the methyl group between the Zr and a coordinated acetone molecule as a unit, rather than transfer of individual H atoms. This in turn implies that in the complex with *m*/*z* 280 the CD_3 group remains intact (Figure 1; E = D).

Transfer of the deuterated methyl group introduces only a negligible secondary isotope effect; thus, the migratory insertion−deinsertion equilibrium (the first reaction in Scheme 1) remained unaffected for all of the combinations of zirconocene/acetone which were studied.

$Cp_2ZrCD_3^+$ (**2**) reacted with acetone similarly to **1** with a corresponding shift of all the peaks by 3 mass units. However, two ions, those with *m*/*z* 277 ($Cp_2ZrC_3H_5O^+$) and 280 ($Cp_2ZrC_3H_2D_3O^+$), had comparable peak heights and a small amount of an ion with *m*/*z* 279 was also formed.

Similarly, the reaction of **2** with *d*$_6$-acetone resulted in formation of ions with *m*/*z* 302 and 366 (addition of one and two molecules of *d*$_6$-acetone, respectively) and an ion with *m*/*z* 282, corresponding to the empirical formula $Cp_2ZrC_3D_5O^+$. The latter complex is analogous to the product with *m*/*z* 277 (η^3-enolate complex), except it is fully deuterated (except for the Cp rings). Formation of the complex with *m*/*z* 282 proceeded with a deuterium kinetic isotope effect, as the apparent rate of formation of the corresponding complex (*m*/*z* 277) in the reaction of **1** and acetone was approximately twice as high. The primary isotope effect indicates C−D bond cleavage in the rate-

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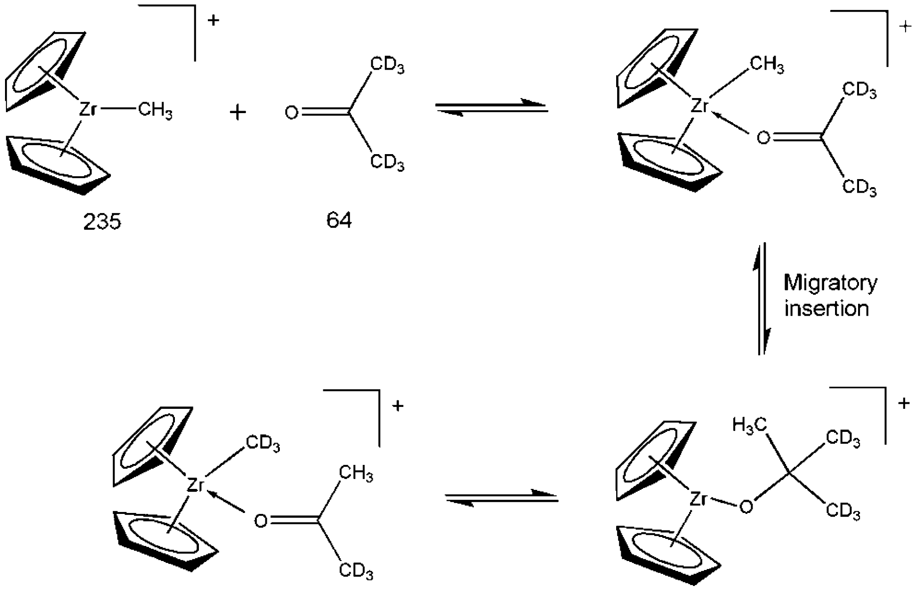
Scheme 2



determining step in the reaction sequence leading to the formation of the enolate complex, since, in this case, there are no C−H bonds available in the reacting ligands. Increasing the reaction time, as in the reaction of **1**, led to increasing addition of a second acetone molecule to the zirconocene complex.

The proposed reaction mechanism for the reaction of **1** with d_6-acetone as an example is shown in Scheme 2. The migratory insertion of a coordinated ketone molecule is reversible and leads to CH_3/CD_3 scrambling. This equilibrium is fast and proceeds via the intermediate insertion product where all three substituents at the oxygen-bound carbon are equivalent, thus leading to a statistical distribution of methyl and methyl-d_3 groups between the metal and coordinated ketone (Scheme 2).

When a ketone molecule is coordinated by the metal center, a Brønsted−Lowry acid−base reaction can take place. The metal-bound alkyl group acts as a Brønsted base, the α-proton of a ketone is slightly acidic (made significantly more acidic in the ketone molecule coordinated by a metal), and the nascent enolate is expected to be a reasonably good leaving group (Scheme 3). This reaction is assumed to be the slowest step and to proceed via the least strained six-membered cyclic transition state. If two different groups are available at the carbonyl group, two different products can be formed, which, in combination with products formed in the reaction of either the CH_3- or CD_3- nucleophile, will comprise the observed set of products (Scheme 3). The products resulting from reaction involving nucleophilic attack on a deuteron are expected to be less abundant, due to the primary isotope effect for C−D bond cleavage. The expected product abundance ratios are completely consistent with those observed in the experiment.

Reactions of $Cp_2ZrCH_3^+/Cp_2ZrCD_3^+$ with 2-Butanone, Methyl Isobutyl Ketone, and Cyclohexanone. The product distributions in reactions of **1** and **2** with ketones other than acetone are also entirely consistent with the proposed reaction mechanisms. Both **1** and **2** sequentially add two substrate molecules. The major observed products are summarized in Table S1 (Supporting Information).

In the reaction of **1** with 2-butanone, as predicted by the above reaction mechanism (Scheme 3), the complexes with *m*/*z* 277 and 291 were observed. The complex with *m*/*z* 277 is presumed to be the same reaction product for butanone, methyl isobutyl ketone, and acetone: i.e., the η^3-enolate complex. The complexes with *m*/*z* 291 and 319 were formed in comparable amounts with *m*/*z* 277, and, according to the reaction mechanism proposed above, differ from the η^3-enolate complex with *m*/*z* 277 (carrying the methyl group) only by an alkyl substituent (Et, *i*Bu) at the central carbon, or both carbons (Me, Me and Me, *i*Pr) of the enolate ligand. Thus, the ketones other than acetone, $R_1C(=O)R_2$ (R_1 = Me, R_2 = Et, *i*Bu), react with $Cp_2ZrCH_3^+/Cp_2ZrCD_3^+$ in a similar manner, but two different substituents at the carbonyl carbon enable additional possible reaction pathway(s), when either R_1 or R_2 is lost as the corresponding alkane, as shown in Scheme 4 for the reaction of **2** with 2-butanone. The expected product abundances are quite consistent with the experimental values, except for higher abundance of the complex with *m*/*z* 277 in the reactions of **1** and **2** with methyl isobutyl ketone, which was almost 3 times more abundant than would be expected from a purely statistical distribution of alkyl groups and assumed isotope effect $k_H/k_D \approx 2$. This, possibly, results from a combination of two factors: higher nucleophilicity of the isopropyl as compared to the methyl group and release of steric tension when the relatively bulky *i*Bu group is removed from the metal coordination sphere.

Cyclohexanone (nominal molecular mass 98 amu) reacts with **1**, forming only simple addition products of *m*/*z* 333 and 431, with no other complexes and just two other products: the loss of methane leads to formation of complexes with *m*/*z* 317 and 415 (minor), respectively (Table S1). The enolate product (*m*/*z* 317) is formed in the reaction of **2**. This is additional evidence for the proposed reaction mechanism, as two groups at the ketone's carbonyl are locked into the ring and unable to migrate so that CD_3 group scrambling is impossible, and the deuterated group is eliminated as methane, resulting in the same complex as for the reaction of **1** (Figure 3).

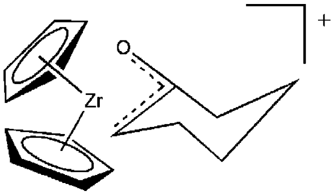
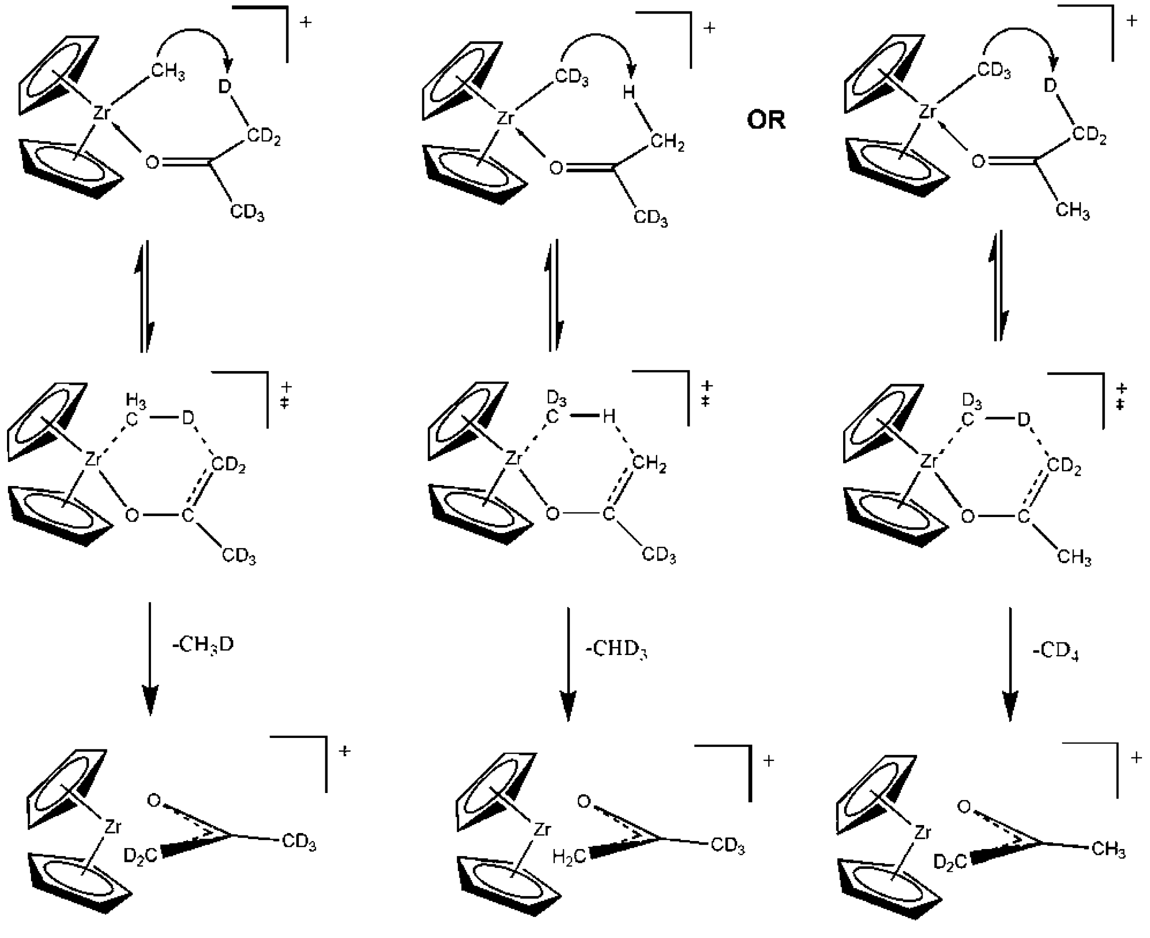


Figure 3. Structure of the postulated enolate ion (*m*/*z* 317) formed after reaction of **1** or **2** with cyclohexanone.

Scheme 3



282 280 279

Scheme 4

$$\underset{238}{Cp_2ZrCD_3^+} + \underset{72}{O{=}CH(CH_3)C_2H_5} \rightleftharpoons \underset{310}{Cp_2ZrC_5H_8D_3O^+} \rightarrow$$

$$\rightarrow [Cp_2ZrCH_3\,(O{=}C(CD_3)C_4H_{10})]^+$$

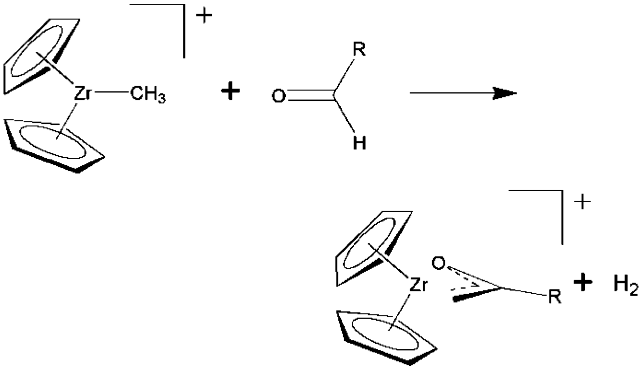
$$\rightarrow [Cp_2ZrCD_3\,(O{=}C(CH_3)C_4H_{10})]^+$$

$$\rightarrow [Cp_2ZrC_2H_5\,(O{=}C(CH_3)CD_3)]^+$$

		m/z
$[Cp_2ZrCH_3\,(O{=}C(CD_3)C_4H_{10})]^+$	$\rightarrow Cp_2ZrOC(C_2H_5){=}CD_2^+ + CH_3D$	293
	$\rightarrow Cp_2ZrOC(CD_3){=}CHCH_3^+ + CH_4$	294
$[Cp_2ZrCD_3\,(O{=}C(CH_3)C_4H_{10})]^+$	$\rightarrow Cp_2ZrOC(C_2H_5){=}CH_2^+ + CHD_3$	291
	$\rightarrow Cp_2ZrOC(CH_3){=}CHCH_3^+ + CHD_3$	291
$[Cp_2ZrC_2H_5\,(O{=}C(CH_3)CD_3)]^+$	$\rightarrow Cp_2ZrOC(CD_3){=}CH_2^+ + C_2H_6$	280
	$\rightarrow Cp_2ZrOC(CH_3){=}CD_2^+ + C_2H_5D$	279

Reactions of $Cp_2ZrCH_3^+/Cp_2ZrCD_3^+$ with Aldehydes. Reaction patterns for **1** and **2** with all of the aldehydes studied were remarkably *different* from those observed in the reactions with various ketones: often no simple substrate molecule addition products were formed at all. Instead, at short reaction times a single (or major) product, resulting from dihydrogen loss from a postulated short-lived carbonyl molecule addition product, was obtained in all of the cases (Table S2 and Figure S3, Supporting Information). It is evident that although aldehydes should also form strong adducts, the barriers to subsequent

Scheme 5



elimination reactions are lower than those for ketones, where H_2 elimination is not significant.

In the reaction of **1** with acetaldehyde, increasing the reaction time led to the addition of another substrate molecule by the single reaction product, the postulated η^3-enolate complex (*m*/*z* 277), forming an ion with *m*/*z* 321. Here a second elimination is not available and the simple adduct is formed.

The intensity distribution of the two products (*m*/*z* 279 and 280), formed in the reaction of $Cp_2ZrCD_3^+$ (**2**) with acetaldehyde, was approximately 1:3, independent of reaction time. Increasing the reaction time resulted in addition of another acetaldehyde molecule by these complexes (*m*/*z* 323/324), with the intensity distribution remaining unaffected. The same intensity ratios were observed even for the water molecule addition products (*m*/*z* 297/298). This implies that, since these ions have similar reactivity, both reaction products of **2** with acetaldehyde have similar structures, i.e., both are η^3-enolate complexes, and they differ only by the number of deuterium atoms ($Cp_2ZrC_3H_3D_2O^+$ and $Cp_2ZrC_3H_2D_3O^+$, respectively).

In the reaction of **1** with benzaldehyde, the enolate product with *m*/*z* 339 ($Cp_2ZrC_2H_2(C_6H_5)O^+$) is presumed to be analogous to the complex with *m*/*z* 277. The reaction of **2** with benzaldehyde resulted in formation of the same set of products as in reaction of **1**, with a 2 amu shift corresponding to the two deuterium atoms in the products. In the reaction of **1** with *n*-hexanal, at reaction times of 5 s and longer, the direct addition of aldehyde molecule(s) to **1** (*m*/*z* 335 and 435) was noticeable.

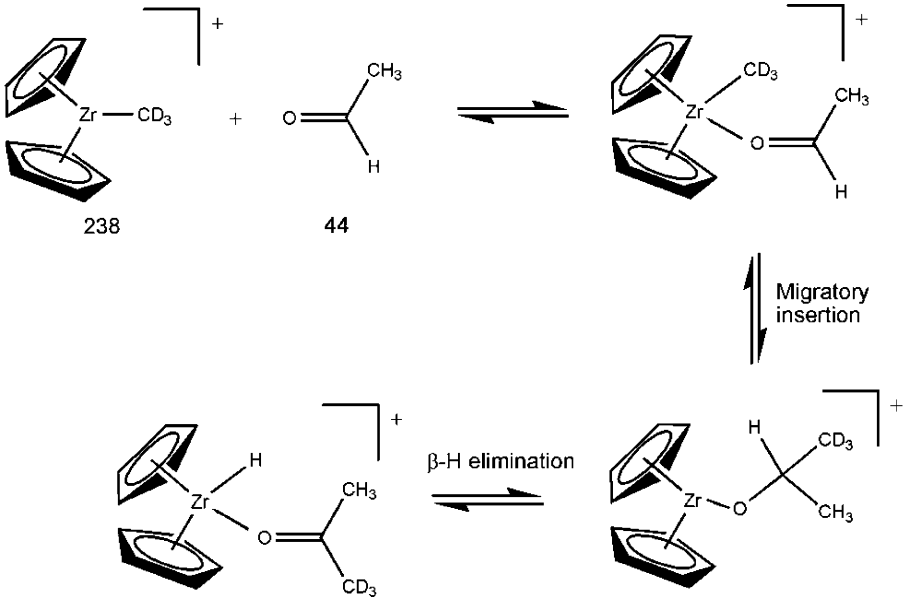
In summary, all four aldehydes reacted with **1** by the same pathway (Scheme 5; R = Me, Et, Ph, C_5H_{11}). These complexes are presumed to be the postulated η^3-enolate complexes with the corresponding R substituent and all of their isomers that are possible according to the reaction mechanism. Two products were formed in the reaction of **2** with all aldehydes (except for benzaldehyde), apparently differing only by the number of deuterium atoms in the structure.

The slowest step in the reaction mechanism, as in the case of reactions with ketones, is presumed to be a nucleophilic attack on the α-hydrogen (or deuterium) of the coordinated carbonyl. The key feature of aldehydes is the presence of a hydrogen atom at the carbonyl carbon instead of an alkyl group. This leads to the possibility of β-H elimination, provided the reaction proceeds through the same initial equilibrium as that with ketones: i.e., coordination of a substrate molecule and migratory insertion. This hydrogen further acts as a nucleophile. Since the attack on the hydrogen in the phenyl ring in the reactions of **1** and **2** with benzaldehyde will lead to the disruption of aromaticity, only deuteriums of the CD_3 bond are available for the reactions; hence, only one product is observed.

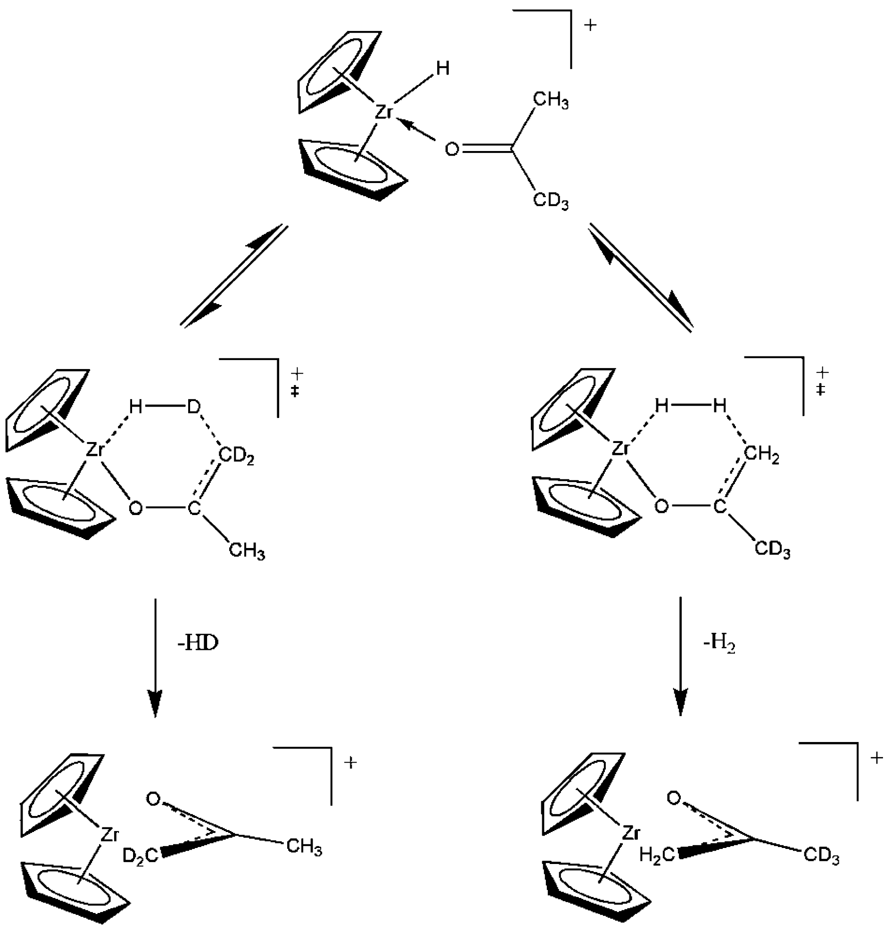
The proposed reaction mechanism, which demonstrates this for the example of reaction of **2** with acetaldehyde, is shown in Schemes 6 and 7.

The β-H elimination of Scheme 6 is known to be a very facile process.[32] In the postulated rate-limiting step, nucleophilic attack on the α-H of the coordinated ketone is by a hydride rather than a carbanion; thus, reduction of the activation barrier is significant enough to make this reaction pathway favorable (Scheme 7) over elimination of methane. The six-membered transition state preceding dihydrogen elimination is similar to that postulated for the reaction with ketones and is assumed to be the least strained. The observed kinetic isotope effect $k_D/k_H \approx 0.3$ is consistent with that typically observed for C−D vs C−H bond cleavage for relatively linear transition states.[33,34] An obvious effect of reduction in the amount of the complex carrying three deuterium atoms (i.e., the complex resulted from the nucleophilic attack on hydrogen of the R group of the aldehydes; thus, the $-CD_3$ group was retained) in the series acetaldehyde−propanal−hexanal was observed (Table S2, Supporting Information). This effect apparently results from nu-

Scheme 6



Scheme 7



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cleophilic attack on the hydrogens of different groups ($-CH_3$, $-C_2H_5$, and $-C_5H_9$). This suggests certain geometrical constraints in the reactions with bulkier radicals—the lower steric availability of the secondary hydrogen atoms and/or removal from the reactive center of more accessible primary atoms.

A postulated reaction potential surface associated with this mechanism for the reaction of **1** with acetaldehyde is shown in Figure 4. Estimates for the different gas-phase reaction steps are obtained by summing ΔE values for breaking and forming the corresponding bonds in each step. Values of ΔE used for various Zr−X bonds have been calculated and discussed previously.[35]

Formation of ions with *m*/*z* 357 and 359 in the reactions of **1** and **2** with benzaldehyde, and similar ions for other aldehydes, is most likely due to inevitable traces of water in the instrument, leading to hydrolysis of the η^3-enolate complex according to a proposed scheme (Scheme 8).

This hydrolysis is the first directly observed gas-phase reaction of the η^3-enolate complex. The reactivity of the isoelectronic η^3-allyl complex has been studied on several occasions in solution[36] and in the gas phase.[11,37] However, no studies have been carried out so far on the gas-phase reactivity of the η^3-enolate complex, leaving this topic open for future investigation.

Liquid-phase studies[38−44] indicate potential significance of η^3-enolate complexes in polymerization catalysis. For example, in investigations of the polymerization of methylmethacrylate (MMA) with the neutral enolate $Cp_2ZrMe[OC(OMe){=}CMe_2]$ in the absence and in the presence of zirconocene cations Cp_2ZrMe^+ to bypass the rate-limited initiation of the system, it was shown that the enolate is not active in polymerization by itself alone, but as soon as the reaction system contains the cation, MMA is quantitatively converted into syndiotactic-rich PMMA with high molecular weight ($M_n > 100\,000$) and a very narrow molecular weight distribution ($M_w/M_n < 1.05$).[38]

Reactivity of the Bis(η^5-cyclopentadienyl)methylzirconium Cation. Several interrelated factors need to be considered in understanding the reactivity of this ion. Extended reaction times lead to eventual thermalization of (presumably vibrational)

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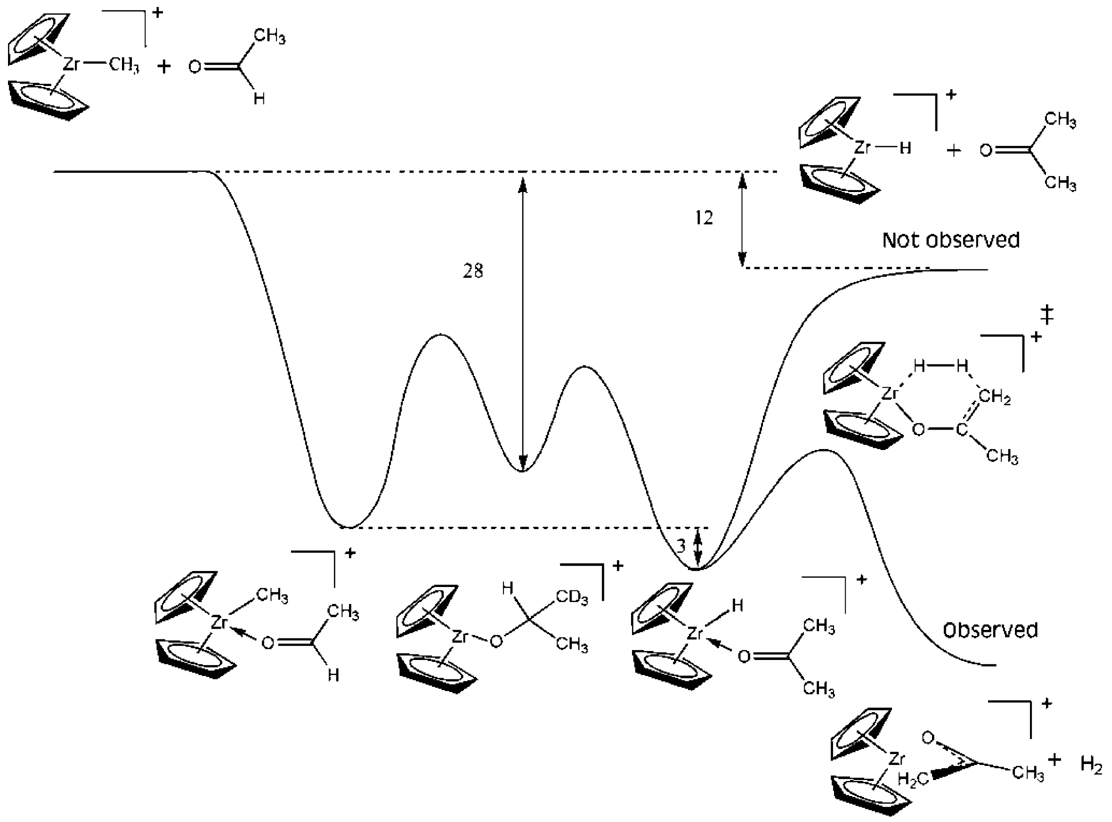
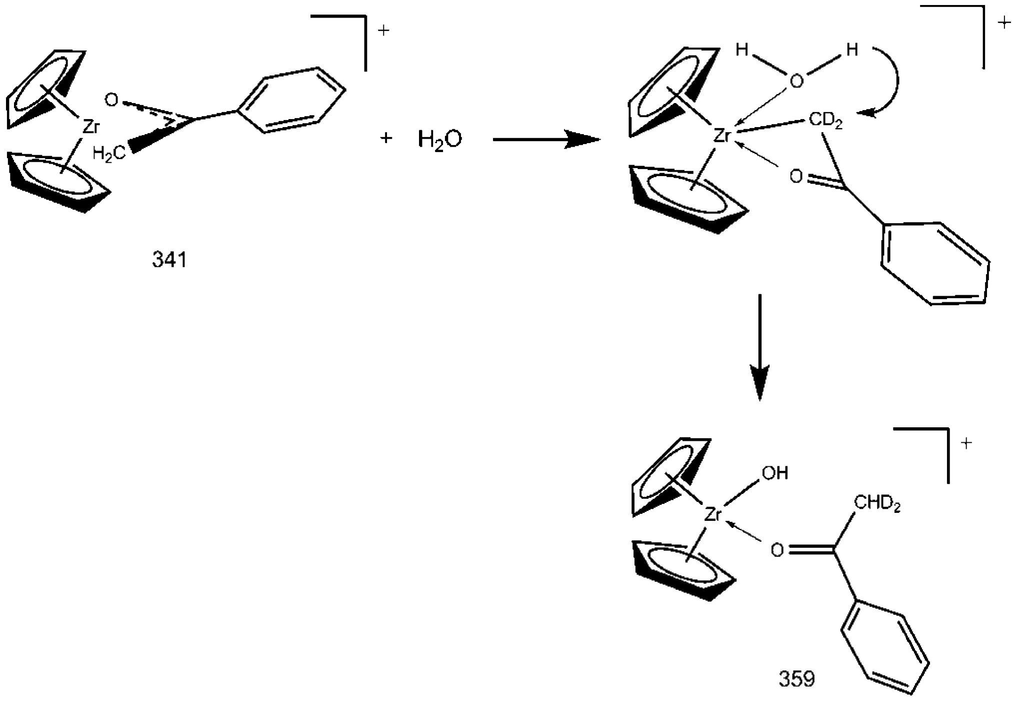


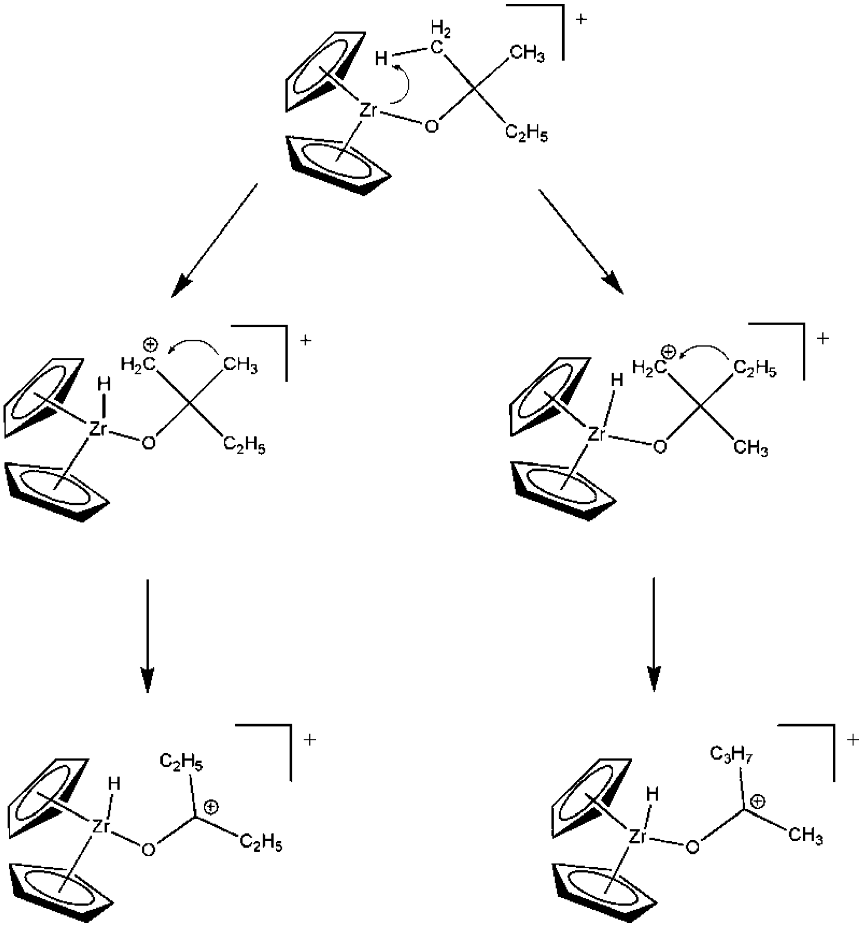
Figure 4. Qualitative potential surface for the reaction of **1** with acetaldehyde in the gas phase. Gas-phase estimates of energetic effects are based on data from ref 35. The centrifugal barriers for these ion/molecule reactions are not shown.

Scheme 8



excitation in the reactant ions through collisions. Because the Zr metal center has a d^0 configuration, there are no low-lying electronic states which might be initially excited. At short reaction times, due to an insignificant number of molecular collisions under the high-vacuum conditions found in the FTICR cell, reaction products are formed under nonequilibrium conditions. Having a d^0 configuration, the Zr metal center cannot be involved in further oxidation; therefore, the possible reaction pathways will not feature oxidative addition. Traces of background water invariably lead to hydrolysis products which must be accounted for, especially in experiments with deuterium-labeled compounds. The hydrolysis reaction leads to substitution of the species of interest, **1** or **2**, by the Cp_2ZrOH^+ cation, thus decreasing total ion abundances of these cations and their reaction products. However, the significantly lower reactivity of the hydroxyl complex[17] compared to that of **1** and **2** reduces

Scheme 9



possible competition for the substrate and does not hinder reaction product identification for times less than 5 s at the pressures used in these studies.

The unsaturated nature of the bis(η^5-cyclopentadienyl)-methylzirconium cation results in a propensity to coordinate at least two carbonyl molecules in order to increase its electron count from 14 to a closed-shell 18 electrons. The extent of the insertion reaction equilibrium depends on various factors, such as the nature of the substituents at the metal center. For the reaction of olefin insertion into an M−X bond, K_{eq} varies by several orders of magnitude. The reaction of carbonyl insertion, compared to the reaction with alkenes, can be expected to be shifted in the direction of the substrate coordinated by the dative bond rather than the $M-O-CR_1R_2R_3$ insertion product, due to the higher stability of the carbonyl adduct. This assumption is supported by the experiments reported here—no addition of a third molecule of carbonyl was observed in any reaction of the carbonyls investigated.

In the reactions of $Cp_2ZrCH_3^+/Cp_2ZrCD_3^+$ with 2-butanone and methyl isobutyl ketone, several minor fragmentation products which do not conform with the reaction mechanisms discussed above were observed. The amounts of such products normally increased at longer reaction times. The reactions of **2** with 2-butanone and methyl isobutyl ketone produced fragmentation patterns that were remarkably similar to those of reaction of **1**, which strongly suggests common loss of the zirconocene methyl group (and probable elimination of a neutral alkene), possibly in a multiple-step process. The observed fragmentation product peaks most likely result from ions with different isomeric structures with the same *m*/*z* values. The ease of fragmentation was more pronounced for the more branched methyl isobutyl ketone. Scheme 9 shows possible initial steps in the fragmentation pathways for the reaction of **1** with 2-butanone. The formation of carbocations via C−H bond scission enables further rearrangements[45] and at some point can be followed by elimination of neutral(s), leading to the variety of fragmentation products.

In the reactions of $Cp_2ZrCH_3^+/Cp_2ZrCD_3^+$ with aldehydes, similar ligand fragmentation was observed only for the reactions with *n*-hexanal.

Computational Studies. In order to establish the structure of the unsaturated complex $[Cp_2Zr(C_3H_5O)]^+$ (*m*/*z* 277), we have carried out theoretical studies of possible isomers of this ion, optimizing geometries and determining ground-state energies. The computational procedures are described in the Experimental Section. The results are summarized in Tables 1 and S3. The optimized structures are shown in Figure 5.

From the procedure described in the Experimental Section, six stable configurations for the unknown structure of $Cp_2ZrC_3H_5O^+$ (*m*/*z* 277) were considered. The labeling is in decreasing order of stability: i.e., conformation A has the lowest total energy, while conformation F is calculated to have the highest total energy. This order of stability should coincide with the most stable species in the experiment, and thus structure A is predicted to be the major contributor to the peak at *m*/*z* 277. In Figure 5, it can be seen that when the oxygen atom on the C_3H_5O ligand is in a carbonyl group, and points toward zirconocene, the entire complex is stabilized more than when the oxygen is in a hydroxyl group. Table 1 indicates that the

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Table 1. Distances between Various Atoms for the Structures Shown in Figure 5[a]

	atom−atom dist (Å)					
	A	B	C	D	E	F
Zr−C_α	2.56	2.19	2.60	2.76	2.84	3.27
Zr−C_β	2.48	3.63	2.44	2.30	2.50	2.29
Zr−C_γ	3.83	4.31	2.42	3.99	2.31	2.57
Zr−O	2.14	2.21	3.54	2.29	3.78	3.85
O−C_α	1.30	1.24	1.33	1.44	1.34	1.21
C_α−C_β	1.40	1.48	1.41	1.48	1.45	1.47
C_α−C_γ	1.49		1.41	1.33		
C_β−C_γ		1.52			1.37	1.50

[a] Greek letter designations on carbons correspond to the labeling in Figure 5. Data were obtained using the MPW1PW91 DFT method, with an sdd(97)/6-311+G(d,p) mixed basis.

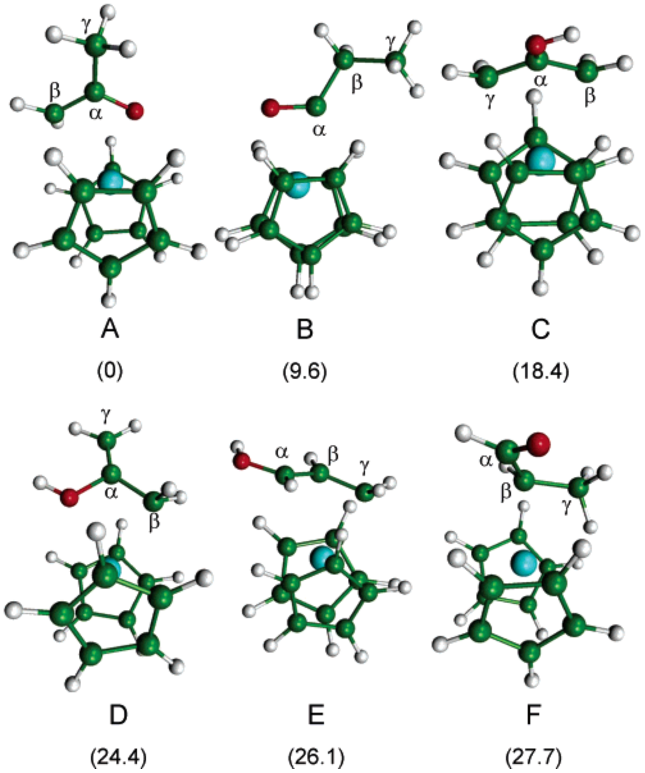

Figure 5. The most stable calculated structures for the $[Cp_2Zr(C_3H_5O)]^+$ cation. The structures shown were calculated with the MPW1PW91/sdd(97), 6-311+G(d,p) functional/mixed basis set. Numbers in parentheses are the calculated electronic energies (kcal/mol) of structures B−F relative to that of structure A.

zirconocene η^3-enolate complex has the greatest number of atoms in bonding proximity to the zirconium, one of which is the oxygen atom.

Conclusions

The reactions and proposed reaction mechanisms reported here illustrate the reactivity of bis(η^5-cyclopentadienyl)methylzirconium cations toward aldehydes and ketones under gas-phase, low-pressure conditions in the FTICR analyzer cell. In reactions with ketones, addition of up to two molecules of the various carbonyls (resulting in formation of 18e complexes for Cp_2ZrMe^+) was observed, along with formation of a postulated η^3-enolate complex whenever possible. In the reactions with aldehydes, due to the possibility of β-H elimination, the Zr-bound hydrogen acts as a nucleophile and the reaction sequence leading to the formation of the proposed η^3-enolate complex is very efficient; in all of the cases this complex was the only or major product observed. Even though the reaction with ketones proceeds by a similar mechanism, since β-H elimination is not possible the metal-bound alkyl group acts as nucleophile instead, which results in a major decrease in the amount of η^3-enolate complex(es) and multiple competing reaction pathways leading to several enolate products, as well as products of ligand fragmentation, especially pronounced in reactions with long and branched substrates. The proposed mechanisms account very well for all observed reaction features.

Experimental Section

Ion−molecule reactions were studied by Fourier transform ion cyclotron resonance mass spectrometry. The primary mass spectrometer used in the experiments was based on a 2.0 T magnet with an internal electron ionization (EI) ion generation source.[46]

Electron ionization of $Cp_2Zr(CH_3)_2$ results in the formation of $Cp_2ZrCH_3^+$ and Cp_2Zr^+. Since the Cp_2Zr^+ ion and its reaction products complicate the spectrum, in order to distinguish products from these two possible parent ions, additional studies using selective stored waveform inverse Fourier transform (SWIFT) ejection[47] were implemented.

The typical background pressure on the 2.0 T instrument was $\sim 2 \times 10^{-9}$ Torr; the pressure of zirconocene was $\sim 10^{-7}$ Torr, decreasing throughout the experiment at the rate of approximately 10^{-8} Torr/h due to sample evaporation. A set of experiments at different substrate pressures of 0.5×10^{-7}, 1×10^{-7}, 2×10^{-7}, and 4×10^{-7} Torr and reaction times of ∼0, 0.5, 1, 2, 5 s and longer were carried out for each reaction.

The formation of binuclear metal ions $Cp_4Zr_2(CH_3)_n^+$ ($n = 0-3$) or $Cp_4Zr_2(CD_3)_n^+$ ($n = 0-3$) in reactions of both parent ions with the neutral species complicated the spectrum, especially at longer reaction times. This impeded the ability to study reactions with rate coefficients below $\sim 10^9$ L/(M s). The presence of water also decreased the amount of the ion of interest, as it reacted very rapidly to form a hydroxyl complex (Figure S1b):

$$Cp_2ZrCH_3^+ + H_2O \rightarrow Cp_2ZrOH^+ + CH_4$$

Therefore, precautions had to be taken to minimize the extent of hydrolysis. At prolonged reaction times the Cp_2ZrOH^+ ion and its reaction products dominated the spectrum, and in some cases hydrolysis interfered with the identification of reaction products at very long reaction times. This is consistent with the demonstrated intrinsic lower reactivity of the hydroxide derivative compared to that of the methylzirconium cation itself.[17]

$Cp_2Zr(CH_3)_2$ and all of the aldehydes and ketones used in these studies were purchased from commercial sources and purified by repeated freeze−pump−thaw cycles; $Cp_2Zr(CD_3)_2$ was synthesized from commercially purchased precursors, in accordance with a preparation procedure described in the literature.[48]

Ab initio (Hartree−Fock) as well as density functional theory (DFT) calculations were carried out for the zirconocene complexes to establish the most stable structures. The following procedure was employed. To reduce optimization time, the proposed molecular structures were created in the Hyperchem software or by specifying a *z* matrix of the structure and were then geometrically optimized using the semiempirical Zerner's modified version of INDO for transition metals (i.e., ZINDO/1 in Hyperchem). These structures served as the initial input configurations for geometry optimization in Gaussian03[49] where the Hartree−Fock SCF method was used.

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The optimized structures that converged to different minima were then reoptimized using two hybrid DFT methods: Becke's three-parameter exchange combined with the Perdew−Wang 1991 correlation functional (B3LYP[50]) and the modified Perdew−Wang one-parameter exchange and correlation functional (MPW1PW91[51]). Final structures were calculated with contracted Gaussian basis sets[52,53] with polar and diffuse functions of the size (5s,1p)/[3s,1p] for H and (12s,6p,1d)/[5s,4p,1d] for C and O. Small- to medium-sized effective core potentials (sdd(97))[54] were used for zirconium, to reduce computational cost.

Supporting Information Available: Representative mass spectra of gas-phase reactant and product ions (Figures S1−S3), tables giving reaction products seen for **1** and **2** reacting with various ketones and aldehydes (Tables S1 and S2), and a table of calculated relative energies for various stable structures of the *m*/*z* 277 ion (Table S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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