GAS PHASE STRUCTURE AND REACTIVITY OF ZIRCONOCENE CATIONS

By

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This work is dedicated to my loving wife Karina
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GAS PHASE STRUCTURE AND REACTIVITY OF ZIRCONOCENE CATIONS

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The reactions of bis(η⁵-cyclopentadienyl)methylzirconium cation with aldehydes, ketones and imines in the gas phase have been studied by Fourier transform ion cyclotron resonance mass spectrometry. Reactions of bis(η⁵-cyclopentadienyl)methylzirconium cation with a majority of the ketones studied resulted in consecutive addition of one and two substrate molecules and/or elimination of neutral. The key ionic products of the elimination reactions were identified as η³-enolate complexes. Similar product ion structures are also postulated for the reactions with aldehydes, where these complexes are either the only or the major reaction product.

Deuterium-labeled substrates and methylzirconocene were used to investigate mechanistic details. Results indicate a multiple-step mechanism, with migratory insertion of an aldehyde molecule into the methyl zirconocene cation, followed by β-H elimination and, via a 6-membered cyclic transition state, formation of the resulting enolate complex. When a β-H elimination pathway is not available for ketones, the reaction is proposed to
proceed instead via direct nucleophilic attack of the metal-bound alkyl preceded by a fast migratory insertion equilibrium.

In reactions with the majority of imines, the reactivity toward bis(η⁵-cyclopentadienyl)methylzirconium cation is governed by the availability of a labile hydrogen. This leads to reaction products different from those which might be expected in analogy with reaction products observed for ketones and aldehydes, i.e., the azomethyne/benzylidene species instead of the enamines. Also, due to lack of lability of the aryl groups, the migratory insertion equilibrium was not possible for reactions of aryl-substituted imines. Consequently, only methane elimination was observed. However, a general reaction mechanism resembles that proposed for ketones. The proposed mechanisms account very well for all of the observed reaction features.
CHAPTER 1
CHEMISTRY OF ZIRCONOCENES AND ZIRCONOCENE CATIONS IN THE
CONDENSED PHASE

1.1 Introduction and Historical Background

Among other transition metals, Zr and its complexes, especially cyclopentadienyl
derivatives, have special significance in view of their potential to serve as catalysts or
reagents for multitudes of synthetically interesting reactions. Even though zirconium
occurs to the extent of 0.022% in the lithosphere (more abundant than carbon but less
abundant than Ti, 0.63%) and is one of the least expensive metals, its application in
organic syntheses of any kind was virtually unknown until the 1970s (apart from use as a
rather unsuccessful substitute for Ti salts in the Ziegler-Natta polymerization) [1].
However, over the last twenty years organozirconium compounds (almost exclusively
zirconocenes) have become some of the most widely used organometallics, along with
other metals such as Ni, Cr, Rh, and Fe. The explosive growth of this area is documented
in multiple reviews (a few of the most recent are given [2-15]) and the chemistry of
organozirconium and other group 4 transition metals has been extensively discussed in
some monographs [16, 17]. Most importantly, the d0 group 4 metallocenes are of great
interest as precursors of alkene polymerization catalysts [18, 19], and can be tuned to
make polymers of very specific tacticities. Single-center metal-catalyzed polymerization
has attracted ample attention and evolved from an area of purely academic interest into
commercially important technology [20]. The remainder of this chapter reviews some of
the most important aspects of the chemistry of organozirconium compounds.
1.2 Structure of Zirconocenes

The majority of known Zr compounds are derivatives of the so-called “Cp₂Zr unit” (Cp = cyclopentadienyl or related ligand) with Zr in +4 or, less often, +2 oxidation states. Zr (+3) compounds are also known, but are generally considered as unwanted by-products [21].

Figure 1.1. Structural types of Cp₂Zr(IV) compounds (adapted from ref. [23]); examples of each structural type are listed in the right column.
Structural types of Cp$_2$Zr(IV) compounds are shown in Fig. 1.1. In addition to the structures shown in Fig. 1.1, it is well known for the coordinatively unsaturated 14 and 16 electron zirconocene species to form dimers, oligomeric species, or polymeric aggregates. It is common for the “Cp$_2$Zr unit” to remain intact in the majority of chemical transformations. However, under certain conditions, for example, treatment with an excess of very strong nucleophiles such as alkyl lithium compounds, the Cp ring (or both) can be displaced [22].

Zirconocene (IV) derivatives represented by the general formula Cp$_2$ZrR$_1$R$_2$ (both R$_1$ and R$_2$ being X ligands), such as zirconocene dichloride, Cp$_2$ZrCl$_2$, the Schwartz reagent Cp$_2$ZrHCl [24, 25], Cp$_2$ZrMe$_2$, etc., are d$^0$, 16-electron compounds, with an empty valence-shell orbital, but with no filled orbitals available for interaction. This makes these complexes inherently electrophilic (Lewis acidic), but not nucleophilic. The empty 2d orbital of zirconium is able to interact with σ- and π- bonding electrons, as well as nonbonding electron pairs, and this interaction is usually a first step in the reaction of Zr derivatives. Formation of the π-complexes of transition metals is described by the Dewar-Chatt-Duncanson model [26, 27] (Figure 1.2). In this model, a σ-type donation from the C=C π orbital with concomitant π-backbonding into an empty π* orbital of the alkene results in synergistic bonding: the greater the σ-donation to the metal, the greater the π-backbonding. Also, the greater the electron density back-donated into the π* orbital of the alkene, the greater the reduction in the C=C bond order, which can ultimately lead to formation of η$^2$ alkene insertion product. This, in turn, implies that only metals with at least one filled nonbonding orbital can form such complexes. For the d$^0$ zirconocenes, only donation of electrons is possible from alkenes, so these complexes act solely as
Lewis acids, thus forming only unstable (usually transient) species. This interaction is more efficient for the cationic zirconocenes.

Figure 1.2. Dewar-Chatt-Duncanson model of alkene bonding by a metal complex (adapted from ref. [28])

1.3 Reactivity of Zirconocene Derivatives

The reactivity of various zirconocene derivatives can be generalized into several distinct types of reactions, as shown on Figure 1.3. The most important and relevant reactions are discussed below.
a) $\sigma$-Complexation and $\sigma$-dissociation

$$L_n\text{Cp}_2\text{Zr} \quad + \quad Y \quad \xrightarrow{\text{complexation}} \quad L_n\text{Cp}_2\text{Zr} \quad \xrightarrow{\text{dissociation}} \quad L_n\text{Cp}_2\text{Zr}.$$ 

b) $\pi$-Complexation and $\pi$-dissociation

$$L_n\text{Cp}_2\text{Zr} \quad + \quad \text{C} = \text{C} \quad \xrightarrow{\text{hydrozirconation}} \quad L_n\text{Cp}_2\text{Zr} \quad \xrightarrow{\text{dehydrozirconation}}.$$ 

c) Hydrozirconation and dehydrozirconation

$$L_n\text{Cp}_2\text{Zr} \quad + \quad \text{C} = \text{C} \quad \xrightarrow{\text{carbozirconation}} \quad L_n\text{Cp}_2\text{Zr} \quad \xrightarrow{\text{decarbozirconation}}.$$ 

d) Carbozirconation and decarbozirconation

$$L_n\text{Cp}_2\text{Zr} \quad + \quad \text{X} - \text{Y} \quad \xrightarrow{\text{oxidative addition}} \quad L_n\text{Cp}_2\text{Zr} \quad \xrightarrow{\text{reductive elimination}}.$$ 

e) Oxidative addition and reductive elimination

$$L_n\text{Cp}_2\text{Zr} \quad + \quad \text{X} - \text{Y} \quad \xrightarrow{\text{oxidative addition}} \quad L_n\text{Cp}_2\text{Zr} \quad \xrightarrow{\text{reductive elimination}}.$$ 

f) $\sigma$-Bond metathesis
g) Migratory insertion and migratory deinsertion

Figure 1.3. Two-electron reactions of zirconocene complexes.

1.3.1 Formation of Zirconium-Carbon Bonds

Apart from transmetallation, the most synthetically important reaction resulting in zirconium-carbon bond formation is hydrozirconation [25, 29] (Fig. 1.2c), which provides an easy and convenient way of converting alkenes and alkynes into alkyl- and vinyl- zirconium derivatives, respectively [30]. The commonly used “Cp₂Zr” precursor is the Schwartz reagent, Cp₂ZrHCl, in conjunction with an aluminium hydride, such as LiAlH₄ [24]. The formation of the insertion product occurs with good regio- and stereoselectivity (anti-Markovnikov, syn addition, with the formation of the E-alkenyl complex in reactions with alkynes) [31]. The availability of β-hydrogens in the insertion product can possibly lead to intramolecular rearrangement.

Another synthetically important means of formation of organozirconocene derivatives is oxidative addition (Fig. 1.2e). It should be noted, however, that since the Cp₂Zr(IV) complexes have d⁰ configuration, the oxidative addition process is not possible, since it requires that both empty and filled orbitals be available for interaction.
It has been shown that the actual reaction is oxidative coupling-elimination [32]. The oxidative addition reaction is valuable for converting allyl ethers into allylzirconocenes [33], as well as for conversion of alkenyl chlorides into alkenylzirconocene chlorides.

1.3.1 Cleavage of Zirconium-Carbon Bonds

The zirconocene alkyl/alkenyl insertion product can be converted by protonolysis/deuterolysis and halogenolysis into the corresponding (halogenated) alkane/alkene. Cleavage of the Zr-C bond occurs in relatively mild conditions: protonolysis requires treatment with diluted acid or even water, while halogenolysis occurs under treatment with bromine or iodine, or, when an alkene group is present, succinimides (NBS or NCS) at room temperature. The configuration of alkene is usually preserved [34]; however, some examples of concomitant skeletal rearrangement are known [25, 29]. Another path for Zr-C bond cleavage is treatment with peroxides, which leads to formation of alcohols [35].

The inherent low intrinsic nucleophilicity of alkyl/alkenyl zirconocenes renders them unable to react with a majority of common electrophilic substrates, with the only exception known to be the reaction with aldehydes [36]. On the other hand, dienezirconocenes can react with a variety of substrates, such as alkenes, alkynes, aldehydes/ketones and even nitriles [37].

1.3.2 Other Organozirconium Derivatives

An important class of compounds containing a Zr-C bond is the acylzirconocenes, which can be easily and straightforwardly obtained via treatment of alkyl/alkenyl derivatives with carbon monoxide at atmospheric pressure, resulting in a generally clean reaction of CO inserting into the Zr-C bond [34, 38]. The stability of the acylzirconocenes depends strongly on the ligand of the given derivative, with the
acylzirconocene chlorides being most stable (not losing CO even at pressures significantly lower than atmospheric). Acylzirconocenes can be further involved in a variety of other reactions shown in Figure 1.4. All of those reactions proceed via migratory insertion [34, 39] (Fig. 1.2g).

Figure 1.4. Reactions of Cp₂ZrC(O)RCl (adapted from Ref. [23]).

Another very important class of organozirconium compounds are the π-complexes, which can be considered as zirconocyclopropanes. The π-complexation (or, rather, oxidative π-complexation) can be considered as a two-electron red-ox process with the alkene being reduced by zirconium. The required Zr(II) species can be generated by a reducing agent (alkali metal amalgam) prior to reaction, or in situ [39-41]. The resultant zirconacycle, called the “Negishi reagent” is a valuable reagent, enabling synthesis of various zirconocycles and serving as a very convenient source of the “Cp₂Zr” unit. The sequence of reactions involving formation of zirconium π-complexes is called the “Negishi protocol,” and was shown to be a concerted non-dissociative process (the Cp₂Zr species is not generated at any stage [42]). Along with the more recently developed Erker-Buchwald protocol [43-47], these two protocols, often used complementarily to each other, provide synthetic routes to tri-member zirconocycles and a variety of compounds obtained from them.
1.4 Cationic Zirconocene Species

Zirconocene cations are not found as isolated species in the solution phase. The high reactivity of such species usually leads to their immediate conversion/reaction. Furthermore, if such cations are indeed produced, they always exist as an ionic pair with varying degree of coordination by a counterion. In general, it is impossible to define a discrete cation as part of a salt: in most cases, no indication of a cationic nature is found either (by the means of X-ray) in the solid state, or in solution, and the only indication of the zirconocene cation’s presence is the characteristic chemistry taking place.

Normally, the ionic species are formed from a suitable precursor with appropriate in situ activation. The most widely used methods in organic synthesis include halide abstraction from Cp₂ZrCl₂ with Ag salts, such as AgClO₄, AgAsF₆, AgSbF₆, etc. (the counterion must be non-nucleophilic) and protonation of methyl zirconocenes with acids containing the BARF (tetrakis(3,5-bis(trifluoremethyl)phenyl)borate) [48] anion. The variety of methods used for the generation of bis(η⁵-cyclopentadienyl)methylzirconium and related cations employed in polymerization catalysis is considered below in Chapter 1.4. A vast number of studies have been carried out [49].

1.4.1 Structure and Reactivity of Zirconocene Cations

The zirconocene cations generated in solution always exist in their solvated form and/or ion pairs with a counterion. Depending on the nucleophilicity of the anion, the degree of coordination can vary and the free cation is never observed. Weakly coordinating counterions such as BARF⁻ provide the only way to utilize the reactivity of the zirconocene cation, while common nucleophilic anions such as Cl⁻ can completely shut down the reactivity in most cases. Moreover, these cationic species exhibit a tendency to abstract chlorine ion from chlorinated solvents, and show even greater
tendency to abstract and bind fluoride (usually forming Cp₂ZrX₂[50]) (so counterions like BF₄⁻ cannot be used[51]). This feature is used for synthetic purposes for C-F bond activation in glycosyl fluorides [52, 53].

The observed rate for reactions involving zirconocene cationic species Cp₂ZrX(L)⁺ depends on the rate of dissociation of the coordinated ligand to give the 14-electron species. The latter complexes are the most reactive ones, since their electrophilicity is unimpeded by electron donation from the base. Of course, such species tend to coordinate solvent molecule(s), thus establishing a solvent association-dissociation equilibrium which determines the cation’s reactivity.

1.4.2 Nucleophilic Addition Reactions

The Cp₂ZrRCl complex is not electrophilic enough to react with the most substrates efficiently, i.e., cleanly and with a sufficient rate; thus, the synthetically interesting addition reactions may involve zirconocene cations as intermediates. Alkyl and alkenyl zirconocene cations can be produced from the hydrozirconation products of alkenes and alkynes by the Schwartz reagent via chloride abstraction by a catalytic amount of (most commonly) AgClO₄ [54].

In aldehyde addition reactions of Cp₂ZrRCl complexes, a mechanism involving generation of alkyl/alkenyl zirconocene was proposed [54]. The resultant reaction products are alcohols formed through condensation of the aldehyde and R ligand of zirconocene. Another application of silver-mediated addition is synthesis of homologues of unsaturated aldehydes by hydrozirconation of alkene/alkyne ethers with the Schwartz reagent and addition of aldehyde followed by acidic hydrolysis. This method allows 2 and 4 carbon homologization with very good to excellent yields [55]. Also, utilizing
addition of aldehydes by a bimetallic 3-methylsilyl-1-propenylzirconocene chloride allows synthesis of such valuable organic reagents as 1,3 dienes [56, 57].

Other reactions of practical importance are the ring opening of oxiranes producing alcohols [58] and carbometallation of alkenes and alkynes. The interesting feature of the latter is that only single addition is achieved through the metal-alkyl addition, rather than polymerization. Among possible carbometallations, carboalumination is the most common; this method is highly stereo- and regioselective and can produce various products depending on the starting alkene/alkyne and the subsequent Al-C bond cleavage method [59-61].

1.4.3 Cationic Zirconocene as Lewis Acid Catalysts

As in nucleophilic addition reactions, cationic zirconocene species are produced by abstraction of an anion from a neutral complex, usually zirconocene dichloride or triflate, by AgClO₄. The main application of such species is catalysis of Diels-Alder reactions of α,β-unsaturated aldehydes or ketones and common dienes [62]. Zirconocene catalysts are advantageous over the usual AlCl₃ Lewis acid catalyst because of their lower susceptibility to water and oxygen, thus eliminating the need for extensive drying of reaction solvents, and generally leading to significantly lower amounts of catalyst required (<1 mol%). Albeit efficient (up to 10⁶ reaction acceleration), the catalysts provide rather poor reaction product regio- and stereoselectivities [63]. The major drawback, however, is the tendency to catalyze polymerization reactions instead, resulting in the competing side reaction of a diene polymerization, thus limiting possible application of such catalysts to only very reactive diene/dienophile pairs. Other reactions catalyzed by cationic zirconocene species include various rearrangements/isomerization
reactions, such as, for instance, rearrangement of epoxides into corresponding aldehydes [58], which proceeds with generally good yields.

1.5 Single-Center Metal Polymerization

The main practical application of zirconocenes is undoubtedly in polymerization catalysis. The active species is generally accepted to be a coordinatively unsaturated cation such as LL’MCH₃⁺ (M=Ti, Zr; L=η⁵-cyclopentadienyl or related ligand). The extensive interest in this class of compounds was triggered not only by very high catalytic activities (comparable to those of enzymes!), but also by the ability to exert stereocontrol of the resultant polymer by modification of the “Cp” ligands, thus creating polymers with a wide array of properties unattainable by other means [64]. Single-center metal polymerization has stemmed from conventional Ziegler-Natta polymerization, which is reviewed briefly below.

1.5.1 Ziegler-Natta Polymerization

In classical heterogeneous Ziegler-Natta polymerization, the process takes place at the structural defects (dislocations and edges) of TiCl₃ crystals [65]. The proposed mechanism for such reactions postulates polymer chain growth by cis-insertion of the olefin into a Ti-C bond on the surface [66, 67]. The non-uniformity of the active sites in heterogeneous catalysts is partially responsible for the polymer’s high polydispersity.

The more advanced version of the Ziegler-Natta catalyst, developed on the basis of group 4 metalloccenes, was comprised of mixtures of Cp₂TiCl₂ and AlR₂Cl and exhibited moderate activity [68]. The proposed mechanism of its action involves olefin coordination and insertion into the Ti-C bond of electron-deficient Cp₂Ti⁺R species. The latter are formed via ligand exchange between aluminum and titanium and formation of Cp₂TiRCl, followed by coordination of the Lewis acidic aluminum to the titanium’s
chloride and polarization of the Ti$^{5+}$-Cl$^{-}$ bond. The Ti-C bond “prepared” in this way readily inserts ethylene [69]. This mechanism is similar to that postulated for heterogeneous Ziegler-Natta catalysis: in both cases the Lewis acidity of the metal center plays a key role, and cis insertion of the olefin into the M-R bond is observed. Originally the nature of the active center was not fully established; however there were early indications that Cp$_2$TiR$^+$ was an actual catalyst [70]. Unambiguous proof of this premise was obtained when the ionic species [Cp$_2$ZrMe(L)]$^+$[BPh$_4$]$^-$ was found to be a very active ethylene polymerization catalyst [71]. It was shown that this compound generates cationic metallocene species that are capable of olefin polymerization without the aluminum alkyl activators. Further studies confirmed the crucial role of metallocene cations as catalytically active species in homogeneous polymerization catalysis [72-83].

1.5.2 Metalloocene-Catalyzed Olefin Polymerization

The major drawback of homogeneous polymerization catalysts, which impeded their industrial application, was unacceptably low efficiency and an inability to polymerize alkenes other than ethylene. A breakthrough was achieved with the application of methylaluminoxane (MAO) [84, 85], which, at the present time, is used almost exclusively in catalytic olefin polymerization. Unlike in Ziegler-Natta catalysis, treatment of the metallocene/Al alkyl catalyst with miniscule, but exact, amounts of water can immensely augment the catalyst’s activity as well as providing the ability to polymerize alkenes more complex than ethylene. Various otherwise inactive systems were shown to achieve exceptional activity upon such treatment [84, 85].

The currently accepted mechanism of MAO formation assumes partial hydrolysis of the solid AlMe$_3$ resulting in formation of extended networks of (AlMeO)$_n$. Introduction of catalytic amounts of Cp$_2$MR$_2$ (Cp = cyclopentadienyl or related ligand; M
= Ti, Zr; R = Cl, Me) into an excess of MAO generates Cp₂MMe⁺ species via initial methylation of metal-halide bonds and further abstraction of a methyl anion from the Cp₂MMe₂. The MAO serves as a very low-coordinating counterion, thus forming a [Cp₂MMe⁺][MAO-Me⁻] “salt”. Very low coordination of the anion enables high activity of the catalyst.

The importance of the zirconocene cation being “free” in order to exhibit its activity, also discussed in Chapter 1.3, has led to development of various ways for preparation of weakly coordinating anions. Such systems are called ‘single site’ metallocene catalysts, implying that polymerization occurs solely at the metal center. Large anions such as [B(C₆H₄R)]⁻ and carboranes have been used as counterions, but they exhibit rather strong interactions with the cation [86]. Less than two decades ago, a very weakly coordinating perfluorinated tetraphenylborate anion was introduced as a counterion [79] which afforded exceptionally high activity of the single-site zirconocene catalyst for alkene polymerization, exceeding that of the catalysts with MAO as a counterion (co-catalyst). Various co-catalysts for metal-catalyzed olefin polymerization have been reviewed [87].
CHAPTER 2
FTICR MS: METHOD OVERVIEW

2.1. Introduction and Historical Background

Valuable insights into reaction mechanisms, including those of polymerization reactions, can be obtained using Fourier transform ion cyclotron resonance mass spectrometry (FTICR MS) [88-92] for studies of the 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 intermolecular processes leading to destruction/modification of the active species. This is especially relevant in catalytic studies, since active species are often present in trace amounts and very short-lived. On the other hand, reaction mechanisms in the gas phase may be different from those observed in the condensed phase. However, information about such processes can provide a valuable description of reactions occurring at extreme conditions and assist in explanation of possible reaction intermediates/side products which might occur in traditional chemistry in the liquid phase. The key issues that can be addressed by the gas-phase studies are: the effects of solvent and intrinsic reactivity, as well as the effects of ancillary ligands and impact of aggregation and ion-pairing on reactivity of ionic species; the thermochemical determinations of various gas-phase reaction energies; and, importantly, direct observation of key reactive intermediates, as well as identification of solution species in
general (speciation). It is possible to refine our understanding of the condensed-phase chemistry through the study of analogous gas-phase chemistry.

FTICR has become very important technique due to the method’s ability to provide mass resolution and accuracy unmatched by any other type of mass spectrometer. Another important factor is the ability to combine FTICR mass spectrometry with various ionization techniques. Rapid growth of the number of FTICR mass spectrometers installed in laboratories around the world has occurred after the discovery of electrospray ionization (ESI), which triggered extensive application of FTICR mass spectrometry in studies of biomolecules [93, 94]. Another advantage of this method is the capability of trapping and storing ions inside the spectrometer, which enables investigation of the ion chemistry.

The principles of Fourier transform mass spectrometry are based on the cyclotron resonance theory, developed in the 1930s [95]. The first attempt at employing the principle of ion cyclotron resonance in a mass spectrometer was undertaken in 1950 [96], while the first FTICR mass spectrometer was built in 1974 by Comisarow and Marshall [97] At the present time, FTICR mass spectrometry is used widely for studies and characterization of a broad range of systems. A large number of reviews have been written on this topic [92, 98-104]. The principles of the FTICR MS technique are briefly reviewed below.

### 2.2 Theory and Instrumentation

All FTICR mass spectrometers are comprised of certain components. Since the ion cyclotron motion is caused by a magnetic field, a magnet is required. The magnets can be permanent, electromagnetic or superconducting. The first of these three have very low field strengths, unacceptable in many cases for the purposes of FTICR. The best of
electromagnets are capable of producing fields in the 1-2 Tesla range, which is suitable for ions of relatively low mass-to-charge ratio. Since the performance of the FTICR MS correlates with the magnetic field strength, superconducting magnets capable of producing fields ranging from 2 to 9.4 Tesla are commonly used. The highest magnetic field used in any of the currently operational mass spectrometers is 14.5 T at the National High Magnetic Field Laboratory in Tallahassee, Florida [105].

Another main component of any FTICR mass spectrometer is the analyzer cell. All of the manipulations with ions (storage, ion/molecule reactions etc.) and ion signal detection are carried out inside it. Various cell designs have been used, with cubic and cylindrical cells being the most common ones. The cubic cell is composed of six plates: two plates are perpendicular to the magnetic field and used to confine the ions inside the cell, hence the “trapping” plates name. Normally the trapping plates of cubic cells have openings for the electrons or ions to be introduced into the cell. The other four plates are the ion excitation and detection plates. The function of those is discussed below. Other types of cells, though different in design, are comprised of plates or cylinders which perform the same functions as in the cubic cell. In the cylindrical cell, excitation and detection plates form a cylinder, with the trapping plates remaining parallel to each other (Fig 2.1), while in the open cylindrical cell trapping plates are replaced by two open cylinders at either side of the cell. The advantage of such designs is better suitability for positioning in the bore of a superconducting magnet. Various other cell designs have been developed [92].
2.2.1 Ion Cyclotron Motion

The magnetic field exerts force on a charged particle moving in it, if a component of the particle’s velocity is perpendicular to the magnetic field axis. This force is called the “Lorentz force”. For a charged particle its velocity, magnetic field and the exerted Lorentz force are mutually perpendicular. The value of the Lorentz force acting on a charged particle in the magnetic field is:

\[ F = qvB \sin \theta \]

where \( q \) is the charge on the particle, \( v \) is the velocity of the particle, \( B \) is the magnetic field strength (in Tesla) and \( \theta \) is the angle between the velocity of the charged particle and the direction of the magnetic field. In case when \( \theta = \pi/4 \) (particle moves perpendicularly to the magnetic field), this expression simplifies to

\[ F = qvB \]

The total charge on an ion is equal to:

\[ q = ze \]
where \( e \) is the charge of electron and \( z \) is the total number of electronic charges on the ion. The resultant trajectory of an ion will be circular, so it will be precessing in the plane perpendicular to the magnetic field in a fashion called “cyclotron motion”. The frequency of such motion depends on the mass-to-charge ratio of the ion and strength of the magnetic field:

\[
\omega = \frac{qB}{m}
\]

or

\[
f = \frac{qB}{2\pi m}
\]

Here \( m \) is the mass of the ion and \( \omega \) is the angular frequency, \( f \) is the cyclotron frequency. Therefore, ions of lower \( m/z \) have higher cyclotron frequencies than ions of higher \( m/z \).

As mentioned above, the FTICR analyzer cell (Fig. 2.1) consists of two excitation and two detection plates along with two trapping plates in order to confine the ions inside the cell. Potentials applied to the trapping plates are usually low (~1 volt), but they lead to the side effect of a non-zero potential at the center of the FT-ICR analyzer cell due to electrostatic fields from the trapping plates. This can offset the center of the cyclotron motion and result in the “magnetron motion” \[92, 103\] in addition to the orbiting motion. The magnetron frequency can be calculated as follows:

\[
f_m = \frac{V_{\text{trap}}\alpha}{2\pi Ba^2}
\]

Here \( f_m \) is the magnetron frequency (in Hz), \( V_{\text{trap}} \) is the potential applied to the trapping plates, \( a \) is the distance between the trapping plates and \( \alpha \) is a geometry factor of the
FTICR analyzer cell [92, 106]. Magnetron frequencies are usually of an order of magnitude of a few hundred Hz (unlike cyclotron frequencies, which are typically within the kHz to MHz range). The magnetron frequency depends upon cell dimensions, design, applied trapping potentials, and magnetic field strength. The resultant trajectory of an ion in the cell is a combination of three components: the cyclotron motion, the magnetron motion, and the oscillation between the trapping plates along the magnetic field axis. The magnetron motion [92, 106] and the overall complex ion motion [102, 107-109] are discussed in detail in the literature.

2.2.2 Acquisition of Mass Spectra

When the packets of ions in cyclotron motion repeatedly move past two detection plates, charge moves within the detection circuit to counteract the proximity of the passing ions. The voltage change between the detection plates can be measured as a function of time. The resultant data are called “transient”, “time-domain” data, or “free induction decay” (Fig 2.3a). Prior to detection, however, it is necessary to perform ion “excitation” - application of a radio frequency voltage to the two excitation plates at the frequency resonant with the cyclotron frequency of individual ions. The excitation is necessary due to two factors: when the ions are first formed in, or enter into the FTICR cell, the radii of their cyclotron orbits are too small to be detectable and the ions therefore must be excited to detectable radii (Fig 2.2). Also, prior to the excitation, initial cyclotron motion of ions is incoherent, and the effect of ions passing opposite detection plates cancels out so no transient can be observed. Application of the RF voltage drives the ions to larger orbits along with collection of ions into “ion packets”, which results in coherent motion, i.e. the cyclotron motion of an ion cloud, rather than individual ions. Such an ion
packet will induce a potential in the detection plates which alternates with the cyclotron frequency of ions with various $m/z$.

![Schematic representation of a cross section of an FT-ICR analyzer cell](image)

Figure 2.2. Schematic representation of a cross section of an FT-ICR analyzer cell, where ions are being excited by the RF potential applied to the excitation electrodes (adapted from Ref. [104]).

The magnitude of the signal induced on detection plates is proportional to the total charge and the proximity of the ions to the detection plates (orbital radius), and is independent of the magnetic field strength. Such a waveform is comprised from different cyclotron frequencies of all of the ions in the cell. The next step is, therefore, extraction of data about the different ion packets. This is achieved through application of the “Fourier transform” operation (FT)[110] where frequency information is obtained from time-domain data (Fig 2.3b).
Figure 2.3. Stages of data in the FTICR experiment.

a) Time-domain waveform.

b) Frequency domain data.

c) Resultant spectrum calibrated in terms of $m/z$.
A resultant spectrum is a function of signal magnitude from cyclotron frequencies of the ions present. As shown above, the cyclotron frequency depends on the $m/z$ ratio, so it is feasible to plot signal magnitude as a function of $m/z$ (Fig 2.3c).

An excitation waveform consisting of a linear increase or sweep through the resonant frequency range of interest at constant amplitude is known as a “chirp”. Ions of different $m/z$ values are excited to orbits of the same radius, even though their cyclotron frequencies differ. Such application of a complex frequency signal to the excitation plates, which causes the trapped ions to absorb energy at their specific resonance frequency, can also be used for selective ejection of ions from the cell. If a broad range of frequencies is applied to cover the mass range of interest with amplitude and duration adjusted to drive all ions to cyclotron orbits still contained within the cell dimensions, the optimal image current can be obtained. However, such excitation also allows ejection of all of the ions from the cell if their orbits reach the electrodes. It is possible, therefore, to construct a complex signal that misses one or more frequency windows of a predetermined width. Such an approach is called “stored waveforms inverse Fourier transform” or SWIFT [111]. Applying such a signal to the trapped ions causes ejection of all ions with exception of a selected cluster of ions with given $m/z$.

### 2.3 Ionization Methods

Formation of ions can be achieved by multiple means: ions can be formed either by removal/addition of an electron leading to ions $M^+/M^-$, by protonation/deprotonation leading to protonated/deprotonated molecules $MH^+/M-H^-$, or by addition of another small ion leading to cationized molecules such as $MNa^+$. Ions can be formed in an MS ion source from a neutral precursor, or pre-exist in a solution phase. Also, ionization can be occurring within the homogeneous high magnetic field region (internal ionization...
sources) or externally to the magnetic field. In the latter case, transfer of ions into the MS cell is required. Despite sometimes limited understanding of the exact means of ion formation [112] the use of various ionization methods enables mass spectroscopic analysis of a wide array of species from small molecules to large proteins. A brief review of some of the ionization methods is given below.

2.3.1 Electron Ionization

The process of electron ionization (EI) involves interaction of gas phase molecules with electrons accelerated to about 10-100 eV. As a primary product, EI forms an excited odd electron ion-radical \( M^+ \). These ions are additionally destabilized by having an unpaired electron and, usually, are capable of high-energy, sometimes quite complex, reactions. Although the stability of ions may be increased by lowering the energy of the ionizing electrons, most of the time ion fragmentation is observed. In general, the presence of molecular ions in spectra is an exception rather than a rule. Some structural characteristics, such as those favoring charge localization, may have a profound effect on fragmentation and may increase the relative stability of parent ions or channel fragmentation processes. For example, for a series of normal hydrocarbons, the intramolecular vibrational and rotational super-cooling of molecules in a supersonic molecular beam (SMB) lead to a significant increase in the stability of molecular ions formed by EI [113]. With conventional EI normal hydrocarbons show only barely detectable \( M^+ \), while such ions dominated in the spectra obtained with SMB.

In a variation on the EI method, metastable atom bombardment (MAB), gas phase chemi-ionization (not chemical ionization!) can be induced by metastable atoms of noble gases. Employing one of the five of them (with excitation energy decreasing from 20 to 8
eV from helium to xenon, it is possible to control the energy transferred to the molecules being ionized.

### 2.3.2 Chemical Ionization

Chemical ionization (CI) is a gas phase process involving ion-molecule reactions with species derived from a reagent gas (or gas mixture) that is first ionized by EI at high electron energy. Typically, the even electron protonated molecule MH⁺ is formed. An efficient CI process, in the case of ion sources producing a constant beam of ions, requires relatively high pressure of the reagent gas (~1 Torr), but in instruments that trap ions for an extended time, ion sources may work at much lower pressure. Due to collisional cooling of the nascent ions by molecules of the reagent gas the CI process is relatively soft. The ionization efficiency and type of ions formed depend on the specificity of ion-molecule reactions. For example, a high electron affinity can provide very efficient ionization leading to M⁻ ions. Other types of CI ion formation include association with species derived from the reagent gas or from “true” chemical reactions [114].

### 2.3.3 Electrospray Ionization

Electrospray ionization (ESI) [115-118] is the ionization technique most frequently used in conjunction with FTICR mass spectrometry. ESI has the advantage of being a “soft” ionization technique, resulting in the vaporization and ionization of a sample, at the same time minimizing fragmentation. The latter is particularly important for labile molecules such as biological molecules, and for the study of complex mixtures where fragments must not interfere with the mass spectrum so the original constituents can be determined. ESI frequently leads to formation of multiply charged ions, particularly in the case of large biomolecules. Since mass spectrometry is based upon the
determination of $m/z$, not mass alone, it is frequently the case that a mass spectrum will contain the same molecules but in a variety of charge states, and therefore at several different $m/z$ values. As ions become more highly charged, the $m/z$ becomes lower and the spacing between the “isotopomers” becomes narrower. As a result, it becomes more difficult to resolve the signals and the resolution of the mass analyzer becomes more important. The charge state of an ion can be determined by examining the spacing between the isotopomer signals. The increasing importance of the electrospray ionization technique is promoting the growth of the FTICR mass spectrometry, due to the ultra-high resolution of FTICR mass spectrometers. For these reasons, the ESI FTICR mass spectrometry has become increasingly important for study of biological molecules in recent years.

2.3.4 Matrix Assisted Laser Desorption/Ionization

An alternative mean of ion formation is desorption of ionic species from the solid phase with desorption energy supplied by a laser. Direct laser desorption of analyte can only be effective if the $\lambda_{\text{max}}$ of the analyzed compound matches the laser output. Matrix assisted laser desorption/ionization (MALDI), on the other hand, does not pose this restriction and provides good ionization efficiency at high mass ranges [119]. In MALDI, the light energy is first absorbed by an excess (usually $>1000$) of a crystalline matrix with the absorption maximum close to the laser output. A short burst of ions formed by a single laser pulse is followed by ion analysis. In a simplified model, matrix evaporation forms excited and ionized species that in turn ionize other components. As in the case of other soft ionization methods, neutral species which are present in the plume (before its dissipation in vacuum) provide a cooling effect, thus contributing to the stability of ions
formed. Many compounds have been tested as matrices for MALDI, but only some work well. For different classes of compounds, matrices show striking differences in the ionization efficiency and the difference in their suitability for different method of ion analysis. For instance, matrices working well with MALDI TOF may not be suitable for MALDI FTICR. MALDI may show lack of reproducibility resulting from the matrix selection, matrix-to-compound ratio, form of matrix crystallization, and possible presence of impurities including those formed by a degrading matrix. MALDI and other soft ionization methods are highly selective and subject to strong suppression effects. Although this selectivity may facilitate detection of compounds with well recognized ionization characteristics, at the same time it may create an uncertainty in characterizing novel compounds as well as in evaluating purity. Suppression effects may completely prevent some or all components from producing ions and may lead to a situation in which ions observed represent only the most easily ionized components and not those that are quantitatively important. As a result, the removal of salts, organic buffers, and detergents is important in avoiding sample unrelated ions and suppression effects [120].

2.3.5 Atmospheric Pressure Chemical Ionization

Atmospheric pressure chemical ionization (APCI) is most commonly used in combination with liquid chromatography. This ionization technique involves high temperature nebulization of solutions in the presence of a corona discharge or β-emitter while solvents or solvent additives (such as, for example, ammonium acetate) play the role of a reagent gas. Ions formed at the atmospheric pressure are transferred to the high vacuum part of a mass spectrometer via several stages of pumping and mass analyzed [121].
2.3.6 Cationization

The formation of cationized ions has been recognized as a very useful in the analysis of compounds that resist protonation [122]. Even traces of alkali metals, especially the ubiquitous sodium ion, may lead to full or partial cationization, but dissolving salts or hydroxides in a matrix allows much better control of this process. Elements with well recognizable isotopic patterns, for example silver or thallium, both with two naturally occurring isotopes ($^{107}\text{Ag}$ 51.3% and $^{109}\text{Ag}$ 48.7%, $^{203}\text{Tl}$ 29.5% and $^{205}\text{Tl}$ 70.5%), produce easily discernable attachment ions [123]. Analogously, mixtures of alkali metal salts can produce well recognizable patterns. It is also possible to facilitate cationization by using special derivatives incorporating groups with a high affinity for alkali ions (such as, for example, crown ethers) [124].
CHAPTER 3
GAS-PHASE CHEMISTRY OF METAL IONS AND IONIC COMPLEXES

3.1 Gas-Phase vs. Solution Chemistry

It is quite apparent that ions studied under the conditions inside an FTICR mass spectrometer will exhibit higher reactivity than those in the solution due to a combination of two factors. The isolated charge on the ions due to the absence of counterions and solvent, coupled with high-energy collisions, result in the accumulation of significant energy that cannot be discarded into a solvent bath. Furthermore, the possible formation of excited states during high energy ionization events, such as collisions with “hot” electrons (exceeding the appearance energy (AE) by numerous electron volts) during EI, can lead to a distribution of excited states. Often the ground states species comprise less than a half of the total ion population [125-130]. Application of special techniques, like surface ionization (SI) or high-pressure ionization sources, is required to overcome this complication. The value of such gas-phase studies, therefore, is not only in the possibility of determining thermodynamic and kinetic data (which often cannot be directly applied to the processes in solution). It is also in the possibility of obtaining a precise and thorough description of the impact of factors which would be very hard to account for in the actual reaction in the solution phase due to interaction of species of interest with solvent, clustering, nonhomogeneity and so on. Examples of such factors are the effects of ligands, electronic configuration and periodic trends, as well as the detection of possible elusive reaction intermediates, etc. A brief review of some aspects of the gas phase chemistry of metal ions and simple organometallics is given below.
3.2 Gas-Phase Reactivity of Bare and Oxo-Metal Ions

Significant interest in the chemistry of metal ions in the gas phase was triggered by a discovery of their ability to perform specific activation of carbon-hydrogen and carbon-carbon bonds [131]. Both activation of unstrained carbon-carbon bonds by bare transition metals [132, 133] as well as by oxide cations, MO⁺ [134] have been discussed in number of reviews. A recent review provides an update of the chemistry of alkane activation in the gas phase with a focus on thermochemical data for various metal-carbon bond energies [135].

An alkane activation reaction is promoted when there is an empty orbital on the metal which accepts electrons from the carbon-carbon bond being cleaved. If such an orbital is filled, the repulsive interaction makes the reaction inefficient [130, 136]. Simultaneously, the electrons on the metal’s orbital with π-symmetry are back-donated into the σ* orbital of the breaking bond, thus leading to its dissociation if the reactants are capable of getting sufficiently close. For efficient activation both of the interactions described above are required.

Interest in the chemistry of metal oxo-ions stems from their potential role as reaction intermediates in various oxidation processes, in particular the oxidation of hydrocarbons. Since alkane oxidation by a transition metal oxo-cation is generally exothermic (Fig. 3.1), a catalytic cycle can potentially be devised if the metal cation can be reoxidized in situ by a suitable reagent (such as oxygen, hydrogen peroxide, nitrogen oxides, etc.).
An example of methane activation by FeO$^+$, a most widely studied species, is shown in Scheme 3.1 [134].

$$\text{FeO}^+ + \text{CH}_4 \rightarrow \left[ \text{Fe}^{\cdot}\text{CH}_3 \right]^+$$

$$\text{FeOH}^+ + \text{CH}_3^\cdot \quad 57\%$$

$$\text{FeCH}_2^+ + \text{H}_2\text{O} \quad 2\%$$

$$\text{Fe}^+ + \text{CH}_3\text{OH} \quad 41\%$$

Scheme 3.1

An example of a true gas-phase catalytic cycle for the oxidation of ethylene by nitrogen dioxide with CeO$_2^+$ as a catalyst is shown in Scheme 3.2 [137]. However, the turnover rate was limited to only 8 cycles per CeO$_2^+$ ion due to reaction of the latter with the hydrocarbon contaminants present in the NO$_2$ gas, resulting in generation of CeO$_2$H$^+$ species, which were unreactive toward ethylene.
3.3 Gas-phase Reactivity of Ligated Metal Ions

Even though studies of ligated metal ions in the gas phase are not as comprehensive as those of bare ions, there is a significant number of publications on this subject, especially for the complexes of group 8-10 metals, with the main focus on Fe and Co.

The simplest complexes, metal hydrides, can react with alkanes and alkenes in the gas phase to form either metal alkyl or allyl complexes by the loss of one or two molecules of dihydrogen (or methane) [138]. Co(allyl)$^+$ is generally more reactive than Fe(allyl)$^+$. Both complexes react rapidly with alkanes (excluding methane) by a C-H bond activation mechanism resulting in the formation of one or two dihydrogen molecules [139].

Among MCH$_3$$^+$ and LMCH$_3$$^+$ ions, FeCH$_3$$^+$ and CoCH$_3$$^+$ ions are also the most widely studied. The latter is capable of reacting with alkanes larger than ethane by an initial insertion into a C-H bond. Subsequent methane loss is followed by dehydrogenation or alkane elimination resulting in cobalt allyl complexes [140]. Both FeCH$_3$$^+$ and CoCH$_3$$^+$ react with cyclic alkanes.

\[
\text{CeO}^+ + \text{NO}_2 \xrightarrow{100\%} \text{CeO}_2^+ + \text{NO}
\]

\[
\text{CeO}_2^+ + \text{C}_2\text{H}_4 \xrightarrow{100\%} \text{CeO}^+ + \text{C}_2\text{H}_4\text{O}
\]

\[
\text{R} \quad \text{CeO}_2\text{H}^+
\]

Scheme 3.2
The reaction of MCH$_3^+$ ions with alkenes is particularly important with regard to Ziegler-Natta polymerization. The Cp$_2$ZrCH$_3^+$ complex exhibits distinct reactivity with unsaturated hydrocarbons in the gas phase. Reactions of Cp$_2$ZrCH$_3^+$ are reviewed in the following sub-chapter. FeCH$_3^+$ is unreactive with ethylene, while CoCH$_3^+$ forms an insertion product which decomposes via loss of dihydrogen to form a stable allyl complex. Such M(allyl)$^+$ complexes are also formed by FeCH$_3^+$ and CoCH$_3^+$ ions from higher alkenes as a result of methane loss and possible elimination of dihydrogen or alkene [139].

Alkene complexes Me(alkene)$^+$ of Fe$^+$[141], Co$^+$ and Ni$^+$ [142] primarily exhibit ligand displacement and condensation reactions. However, bis(allyl) complexes resulting from dehydrogenation by double allylic C-H activation could also be formed. These complexes were not observed for the bare metal ions. Also, some ligand coupling, similar to metal-assisted Diels-Alder reactions, was reported for Co(alkene)$^+$ and to a small extent for Fe(alkene)$^+$ complexes.

Studies of cyclopentadienyl complexes, in particular CpCo$^+$, in reactions with aliphatic alkanes larger than methane revealed formation of mainly dehydrogenation products along with a small amount of products resulting from C-C bond cleavages [143]. In the reaction of CpNi$^+$ with a variety of aldehydes, formation of decarbonylation products was reported [144].

It was shown that Cp$_2$Zr$^+$ is capable of abstracting a chlorine atom from chloro-substituted methanes, indicating that the dissociation energy of the Zr-Cl bond is at least 81 kcal/mol [145]. In addition, the cyclopentadienyl complexes of iron and nickel were
shown to undergo a metal-switching reaction with a number of metal ions (Ti, Rh, Nb) [146].

3.4 Reactions of the Bis($\eta^5$-cyclopentadienyl)methylzirconium Cation in the Gas Phase

The following sub-chapter reviews application of FTICR MS as a primary tool for studying species involved in the process of metallocene-catalyzed olefin polymerization. The physico-chemical properties of zirconocene ions, their intrinsic reactivity, and their reaction patterns have been studied. The effect of the solvent on reactivity can be estimated by comparison of gas-phase results with data for condensed phase single-site polymerization catalysis.

3.4.1 Reactions with Alkenes

The first study of reactivity of Cp$_2$ZrCH$_3^+$ with unsaturated hydrocarbon in the gas phase [147] indicated that no polymerization took place at all, but rather that the reaction proceeded exclusively via elimination of dihydrogen or alkene and formation of an $\eta^3$-allyl complex (Table 3.1) [147].

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Neutral eliminated</th>
<th>Product ion formula</th>
<th>Product distribution, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethylene</td>
<td>H$_2$</td>
<td>Cp$_2$ZrC$_2$H$_5^+$</td>
<td>100</td>
</tr>
<tr>
<td>propylene</td>
<td>H$_2$</td>
<td>Cp$_2$ZrC$_2$H$_5^+$</td>
<td>100</td>
</tr>
<tr>
<td>1,3-butadiene</td>
<td>H$_2$</td>
<td>Cp$_2$ZrC$_2$H$_5^+$</td>
<td>100</td>
</tr>
<tr>
<td>l-butene</td>
<td>H$_2$</td>
<td>Cp$_2$ZrC$_2$H$_5^+$</td>
<td>100</td>
</tr>
<tr>
<td>l-pentene</td>
<td>H$_2$, 2H$_2$</td>
<td>Cp$_2$ZrC$_2$H$_5^+$</td>
<td>87 ± 5, 13 ± 5</td>
</tr>
<tr>
<td>l-hexene</td>
<td>2H$_2$</td>
<td>Cp$_2$ZrC$_2$H$_5^+$</td>
<td>52 ± 7</td>
</tr>
<tr>
<td>styrene</td>
<td>H$_2$</td>
<td>Cp$_2$ZrC$_2$H$_5$Ph$^+$</td>
<td>100</td>
</tr>
<tr>
<td>isobutene</td>
<td>CH$_4$</td>
<td>Cp$_2$ZrC$_2$H$_5^+$</td>
<td>100</td>
</tr>
<tr>
<td>o-methylstyrene</td>
<td>CH$_4$</td>
<td>Cp$_2$ZrC$_2$H$_5^+$</td>
<td>100</td>
</tr>
<tr>
<td>allene</td>
<td>none</td>
<td>Cp$_2$ZrC$_2$H$_5^+$</td>
<td>62 ± 4</td>
</tr>
<tr>
<td>fluoroethylene</td>
<td>H$_2$, CH$_4$</td>
<td>Cp$_2$ZrF$^+$</td>
<td>100</td>
</tr>
<tr>
<td>1,1,1-trifluoropropene</td>
<td>H$_2$C=CH$^-$ (CF$_3$CH$_3$)</td>
<td>Cp$_2$ZrF$^+$</td>
<td>100</td>
</tr>
</tbody>
</table>
The suggested reaction mechanisms involve insertion/dehydrogenation accompanied by statistical H/D scrambling with deuterated ethylene or a σ-bond metathesis (Fig. 3.2).

![Diagram showing reaction mechanisms](image)

a) Insertion/dehydrogenation reaction mechanism

\[
\text{Cp}_2\text{ZrCD}_3^+ + \text{H}_2\text{C} = \text{C}R \rightarrow \text{Cp}_2\text{ZrCD}_3^+ + \text{CD}_3\text{H}
\]

b) σ-bond metathesis reaction mechanism

Figure 3.2. Reactions of Cp₂ZrCH₃⁺ with alkenes (adapted from Ref. [147]).

The observed reaction pathways were rationalized by the insufficient thermalization of “hot” ions produced during the electron ionization event (Fig. 3.3) [147-151]. The observed loss of a neutral molecule (H₂, CH₄) in the gas-phase reactions can be suppressed. Three ways can be suggested so the reaction pathway observed in the liquid phase would be approached: first, increasing the pressure by, for example, pulsing an inert gas, to quench excess internal energy by collisions; second, by coordination of a weakly bound molecule (for example, a solvent) by the coordinatively unsaturated
metallocene cation. The loss of a solvent molecule will result in excess energy being taken away as translational energy of a departing moiety; or third, by increasing the size and complexity of coordinated ligands, creating an “energy sink” where the excess energy can be efficiently redistributed among a multitude of available vibrational states, thus decreasing the probability of allyl complex formation.

Figure 3.3. Comparison of qualitative potential energy surfaces for the reaction of \(\text{Cp}_2\text{ZrCH}_3^+\) with ethylene in solution and the gas phase (adapted from Ref. [147]).
The first approach was implemented by Plattner et al. [152]. Stable solutions of the tetrakis(pentafluorophenyl)borate salt of the methylzirconocene cation, Cp₂ZrCH₃⁺, in a mixture of acetonitrile and CH₂Cl₂ were electrosprayed with a "high" pressure, 10 mTorr, of thermalization gas (Ar). This led to insertion of up to four molecules of alkene before deactivation. The observed rate constant of propylene polymerization under these conditions was estimated to be about 6 orders of magnitude higher than that in solution [152, 153], which is an excellent illustration of intrinsic high reactivity of an isolated cation in the absence of a coordinating counterion or coordination by solvent molecules. The loss of hydrogen was more difficult to suppress –reaction with ethylene still led to allyl complex formation.

Besides reactions of metallocenes with unsaturated hydrocarbons, previous gas-phase studies have involved investigation of the reactivity patterns of bis(η⁵-cyclopentadienyl)methylzirconium cations with nitriles [154] and effects of ancillary ligands on LL’ZrCH₃⁺ cation reactivity with dihydrogen and ethylene [150] and other alkenes [151]. Also, the intrinsic reactivity of hydroxyzirconocenes was studied as a model for metal-hydroxide complex ion reactions with a range of compounds [155].

Our experimental data (Figure 3.4) indicate the ability of C-H bond activation by the Cp₂ZrCH₃⁺ complex in cyclic alkanes with consecutive formation of a complex with cyclic allyl structure. In the reaction with cyclopentane, a complex with m/z 287 was observed. The experimental procedure and appearance of mass spectra of zirconocene complexes are discussed in detail in Chapter 4. The ion with m/z 287 was presumably formed via loss of dihydrogen and methane (Scheme 3.3). The proposed structure of the complex is shown on Figure 3.5.
Figure 3.4. Mass spectrum for the reaction of Cp₂ZrCH₃⁺ with cyclopentane.

\[
\text{Cp}_2\text{ZrCH}_3^+ + C_5H_{10} \rightarrow \text{Cp}_2\text{ZrC}_5\text{H}_7^+ + \text{CH}_4 + \text{H}_2
\]

Scheme 3.3

Formation of such a complex assumes initial activation of a C-H bond by a metal center.

Figure 3.5. Proposed structure of the complex with m/z 287.

3.4.2 Allyl Complex Formation: Mechanistic Differences of Reaction Patterns in the Gas and Liquid Phases

One of the main drawbacks of metallocene catalysts is a gradual decrease in the rate of monomer uptake with time, which occurs on the timescale of several hours, or, in some cases, even minutes [156, 157]. The exact nature of this phenomenon is still debatable; to a certain degree, the deactivation results from factors such as presence of impurities and high-temperature decomposition. Recently, it has been postulated that a
possible cause may be accumulation of a less active or inactive zirconium-allyl complex [72, 151, 152, 158-162]. The formation of this complex was observed or inferred on several occasions in both (as discussed above) gas-phase experiments [148, 154] and in the solution phase [72, 151, 152, 158-161, 163-165]. Formation of H₂ gas during the polymerization reactions catalyzed by zirconocenes is a possible indication of the allyl complex formation [166].

Various theoretical studies of the bis(η⁵-cyclopentadienyl)methylzirconium cation reactivity toward dihydrogen and alkenes [167-171] or even alkanes [172, 173] have been reported. However, the subsequent transformation of the allyl complex after its formation in the reaction mixture is not completely clear. Initially, it was presumed that this complex is catalytically inactive [72]. As shown by Ziegler and co-workers [174, 175], the allyl complex can be reactivated by alkene molecule insertion; their theoretical studies of zirconocene and titanocene cations indicate that the limiting step in the reaction of the allyl complex formation reaction is a β-hydrogen elimination and that it has an activation barrier of ~ 11 kcal/mol for the zirconium and ~ 13 kcal/mol for the titanium complex. The liquid-phase studies by Britzinger and co-workers of the Cp₂ZrMe(methallyl) complex [162] showed that its perfluorotriphenylborane adduct, the contact ion pair [Cp₂Zr(methallyl)]⁺[MeB(C₆F₅)₃]⁻, reacts with propene with rates substantially lower than those of cationic Zr-alkyl species. The propene molecule inserts between Zr and one of the allylic termini. Their DFT calculations have indicated that insertion of propene directly into an η³-coordinated Zr-allyl unit occurs with lower activation energy than insertion into an η¹-bound Zr-allyl species and that the lowest-
energy pathway for the reactivation of a cationic zirconocene allyl species is its reconversion to the corresponding Zr-alkyl species by H$_2$.

Nevertheless, experimental proof of the allyl complex reactivation has yet to be demonstrated. It is expected that formation of the transition state for alkene insertion by the allyl complex and its consecutive transformation into a vinyl-terminated product can be controlled by various means. It also appears to be necessary to test the *intrinsic* reactivity of the Cp$_2$Zr(allyl)$^+$ complex by studying its reactivity under the gas phase low-pressure conditions of an FTICR MS spectrometer, thus eliminating various perplexing factors such as effects of impurities, electric permeability of the solvent, ligands exchange, etc.
4.1 Rationale

Despite rapid growth in the gas-phase chemistry of organometallic complexes and, especially, metal ions [134, 135, 176, 177], and the major importance of metallocene catalysis, gas-phase studies of metallocenes are still rather scarce. The purpose of the work reported in this chapter was to gain a deeper understanding of this chemistry, with a focus on reaction mechanisms of the gas-phase chemistry of metallocenes, and to attempt to draw general conclusions about these processes. For example, based on the work reported in Chapter 3, it may be postulated that the formation of an $\eta^3$-allyl complex is an instance of a general process which takes place under high-vacuum, non-equilibrium conditions.

Scheme 4.1 shows for the reaction mechanism suggested in earlier studies [151] for the reactions of methyl zirconocenes with terminal olefins, $Y = CH_2$. For reactions with olefins such as isobutene or styrene, this scheme can be applied for the $Y=C(R_1)R_2$ substrate ($R_1 = H$ or $R$). In the case of 1,1 disubstituted alkenes, elimination of methane was observed [147]. At the same time, in the liquid phase, the $\eta^2$ alkene insertion products of zirconocenes are generally stable and have no tendency to eliminate a neutral molecule.
In the case of aldehydes and ketones, the group Y is the carbonyl oxygen. Compared to alkenes, the carbonyls are expected to be coordinated more strongly to Zr(IV) by donation of an electron lone pair from oxygen (as opposed to $\pi$-bonding electrons in the alkenes) to an empty d-orbital of the metal. Therefore, initial bonding 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
observed might possibly also be described by the general Scheme 4.1. This would be quite different from the known chemistry in the solution phase, as discussed in the last chapter. For example, for silver-mediated (i.e. chloride abstraction from Schwarz reagent by a catalytic amount of AgClO₄ [54]) aldehyde addition reactions of Cp₂ZrRCl complexes, a mechanism involving generation of alkyl/alkenyl zirconocene was proposed [54]. The resultant reaction products are alcohols formed through condensation of the aldehyde and R ligand of zirconocene.

The chemistry of zirconocene carbonyl, acyl and related species presents interest due to, for example, the potential of complexes like \([L_nM\{CHClCH₂C(=O)R\}^+]\) to carry out insertion polymerization/copolymerization of vinyl chloride, thus enabling better control of PVC polymer structure and properties than is possible by conventional radical methods [178].

The work presented in this chapter represents a study of the reactivity pathways of bis(η⁵-cyclopentadienyl)methylzirconium (1), chosen as a model compound, with a series of simple ketones and aldehydes in the gas phase.

### 4.2 Experimental Procedures

Ion-molecule reactions were studied using Fourier transform ion cyclotron resonance mass spectrometry. The primary mass spectrometer used in the experiments was based on a 2.0 Tesla magnet with an internal electron ionization (EI) ion generation source (Fig. 4.1).

A common experiment sequence was used:

1) Quench: application of +/- 9.5 V to trapping plates in order to eliminate any ions present prior to the experiment.
2) Electron beam: irradiation of the neutral substrates with the flux of electrons produced by the filament of the EI (Electron Ionization) source (Fig. 4.2). The number of electrons was controlled by the filament current, typically in the range of 1-2 A. The electron energy distribution, controlled by the voltages on the repeller plate and the grid, was varied from 15 to 50 eV in order to produce an optimal number of ions.

3) Ion ejection (optional): if necessary, the ejection of ions with selected m/z from the MS cell by applying SWIFT waveform [179] could be carried out.
4) Reaction delay: time delay varying from 0 to 10 s allowing unejected ions to react with the neutral(s) present in the cell.

5) Excitation: excitation of the reaction product ions.

6) Detection: detection of the image current with subsequent Fourier transform of the transient to obtain the mass spectrum.

The above sequence of events (scan) was repeated for each experiment 20 to 40 or more times in order to achieve a higher signal to noise ratio by a signal averaging.

Table 4.1. Isotopes of zirconium.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Natural Abundance, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{90}\text{Zr}$</td>
<td>51.45</td>
</tr>
<tr>
<td>$^{91}\text{Zr}$</td>
<td>11.22</td>
</tr>
<tr>
<td>$^{92}\text{Zr}$</td>
<td>17.15</td>
</tr>
<tr>
<td>$^{93}\text{Zr}$</td>
<td>Radioactive</td>
</tr>
<tr>
<td>$^{94}\text{Zr}$</td>
<td>17.38</td>
</tr>
<tr>
<td>$^{95}\text{Zr}$</td>
<td>Radioactive</td>
</tr>
<tr>
<td>$^{96}\text{Zr}$</td>
<td>2.80</td>
</tr>
</tbody>
</table>

Zirconium has five stable isotopes (Table 4.1), which in superposition with $^{13}\text{C}/^{12}\text{C}$ isotopes result in a unique pattern of seven peaks in mass spectra for all of the organozirconium compounds studied in this work, enabling unambiguous identification of the presence of Zr. Electron ionization of $\text{Cp}_2\text{Zr(CH}_3)_2$ resulted in the formation of two ions: $\text{Cp}_2\text{ZrCH}_3^+$ and $\text{Cp}_2\text{Zr}^+$. The typically obtained mass spectra of $\text{Cp}_2\text{Zr(CH}_3)_2$ are shown in Fig. 4.3.
Figure 4.3. EI mass spectrum of Cp₂Zr(CH₃)₂: Cp₂ZrCH₃⁺ (m/z 235-242), Cp₂Zr⁺ (m/z 220-227) and Cp₂ZrOH⁺ (m/z 237-244)

Since the Cp₂Zr⁺ ion and its reaction products complicate the spectrum, in order to distinguish products from these two possible parents, additional studies using selective SWIFT ejection were implemented when necessary. An example of a SWIFT experiment is shown in Figure 3.4. When one possible parent ion Cp₂ZrMe⁺ (m/z 235-242) is ejected,
the reaction products’ peaks (m/z 277-284) disappear. On the other hand, when another possible parent Cp₂Zr⁺ (m/z 220-227) is ejected, no change is observed. This indicates that the product is formed from the Cp₂ZrMe⁺ ion. An incomplete removal of either complex by SWIFT, especially of the Cp₂ZrMe⁺ ion, stems from a partial re-formation during a reaction delay event via collisions of neutral Cp₂Zr(CH₃)₂, which is present in the cell at all times, with Cp₂Zr⁺ ions.

![Graph](image)

- **a)** No ions ejected
- **b)** Cp₂Zr⁺ (m/z 220-227) is ejected
c) Cp₂ZrMe⁺ (m/z 235-242) is ejected

Figure 4.4. Example of a SWIFT experiment.

The typical background pressure on the 2.0 T instrument was ~ 2·10⁻⁹ Torr; pressure of zirconocene was ~ 10⁻⁷ Torr, decreasing throughout experiment at the rate of approximately 10⁻⁸ Torr/hour due to the 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 common reaction times of ~ 0, 0.5, 1, 2, 5 s and longer were carried out for each reaction.

The formation of binuclear metal ions Cp₄Zr₂(CH₃)ₙ⁺ (n = 0 - 3) in reactions of both parent ions with the neutral complicated the spectrum, especially at longer reaction times (Fig. 4.5), which impeded the ability to study reactions with rate coefficients below ~ 10⁹ 1/M·s.

Figure 4.5. Binuclear complexes Cp₄Zr₂(CH₃)ₙ⁺ (n = 0 - 3)
The presence of water also decreased the amount of the ion of interest as it reacted very rapidly to form a hydroxyl complex (m/z 237-244) (see Fig. 4.3):

$$\text{Cp}_2\text{ZrCH}_3^+ + \text{H}_2\text{O} \rightarrow \text{Cp}_2\text{ZrOH}^+ + \text{CH}_4$$

Therefore, precautions had to be taken to minimize the extent of hydrolysis. At prolonged reaction times the \(\text{Cp}_2\text{ZrOH}^+\) ion and its reaction products dominated the spectrum. In some cases hydrolysis interfered with the identification of reaction products even at typical reaction times of 1-5 seconds.

\(\text{Cp}_2\text{Zr(CH}_3)_2\) and all of the aldehydes, ketones, and imines used in these studies were purchased from commercial sources. The liquids were purified by repeated freeze-pump-thaw cycles. \(\text{Cp}_2\text{Zr(CD}_3)_2\) was synthesized from commercially purchased precursors in accordance with a preparation procedure described in the literature [180] via the following reaction:

$$\text{Cp}_2\text{ZrCl}_2 + 2\text{CD}_3\text{MgI} \rightarrow \text{Cp}_2\text{Zr(CD}_3)_2 + 2\text{MgICl}$$

A Schlenk line was used at all times due to the extreme air and moisture sensitivity of both the reactants and the product. The reaction was carried out in diethyl ether solvent at room temperature under a flow of dry nitrogen in thoroughly desiccated glassware. The reaction product’s precipitate was dissolved in ether/pentane mixture for the final product extraction followed by a recrystallization from benzene at -20 °C. The mass spectra of the \(\text{Cp}_2\text{Zr(CD}_3)_2\) obtained from this procedure are shown in Fig. 4.6. As expected, the \(\text{Cp}_2\text{ZrCH}_3^+\) (m/z 235) complex is replaced with the \(\text{Cp}_2\text{ZrCD}_3^+\) (m/z 238) complex, while the hydrolysis product, \(\text{Cp}_2\text{ZrOH}^+\) (m/z 237), is unaltered.
Figure 4.6. EI mass spectrum of Cp₂Zr(CD₃)₂ (* Noise peaks).

*Ab initio* (Hartree-Fock) as well as Density Functional Theory (DFT) calculations were carried out by Cesar S. Contreras for the zirconocene complexes to establish the most stable structures.
4.3 Reaction with Ketones

For the sake of simplicity, all of the seven Zr-containing isotopic ions are further reported as a single mass corresponding to the most abundant (51.45%) $^{90}$Zr isotope. In cases where there is an 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 peaks can be estimated.

In previous studies under similar conditions it has been demonstrated that the cyclopentadienyls are solely spectator ligands – as no Cp “switching” reactions and HD elimination for the complexes with fully deuterated ligands but non-deuterated Cp rings have been observed [147]. Therefore, the Cp$_2$Zr unit was presumed to remain intact throughout all of the experiments. Where questions exist about the structures of the product ions, their formulae are reported in the form Cp$_2$ZrC$_x$H$_y$O$_z^+$ with the corresponding m/z ratio. Since all of the reported ions were singly charged the term “empirical formula” is used throughout the text. Detailed structural considerations are presented later in this chapter.

4.3.1 Reactions of Cp$_2$ZrCH$_3^+$/Cp$_2$ZrCD$_3^+$ with Acetone/d6-Acetone

The reaction of 1 (m/z 235) with acetone (nominal molecular weight 58 amu) proceeds with formation of several products (Fig. 4.7). Two principal ones with m/z 293 and 351 correspond to the consecutive addition of one and two substrate molecules, as shown in Scheme 4.2. Addition of the second acetone molecule becomes pronounced only after 4 seconds of reaction time (at a total pressure of approximately 2·10$^{-7}$ torr). A variety of structures can be postulated for the observed adducts, e.g. $\eta^1$ vs. $\eta^2$ complexes,
etc., (only one of the likely structures is shown), and, therefore, theoretical geometry optimizations and/or spectroscopic data are needed for more definitive “proof” of structure.

Figure 4.7. Mass spectra of ions formed in the reaction of Cp₂ZrMe⁺ with acetone.

An ion with m/z 277 (Fig.4.7; the peak with m/z 278 corresponds to the product depicted in Scheme 4.2), corresponding to the empirical formula Cp₂ZrC₃H₅O⁺, apparently resulting from elimination of methane from the ion with m/z 293, is formed to a lesser extent than the latter, and its peak height decreases at longer reaction times. It is coordinatively unsaturated and adds an additional acetone molecule, forming an ion with m/z 335 (Scheme 4.3, Figure 4.8).
Scheme 4.2

Scheme 4.3
Figure 4.8. Mass spectra of ions formed in the reaction of Cp₂ZrMe⁺ with acetone

The hydrolysis product of 1 (m/z 235), bis(cyclopentadienyl)zirconium hydroxyl cation Cp₂ZrOH⁺ (m/z 237, Fig. 4.3), formed by reaction with trace amounts of water present in the mass spectrometer, reacts with acetone to give an addition product with m/z 295, which becomes predominant at very long reaction times (5 seconds or more). This indicates a slower reaction rate and, for these species reacting with acetone, is consistent with the demonstrated intrinsic lower reactivity of the hydroxide derivative compared to the methylzirconium cation itself [155]. The formation of binuclear metal ions Cp₄Zr₂(CH₃)ₙ⁺ (n = 0 - 3) and their derivatives complicated the spectrum, especially at longer reaction times and had to be taken into account as well.

Reaction of 1 with acetone proceeds differently for different stages of thermalization of the reaction mixture. The consecutive addition of two acetone molecules by the Cp₂ZrCH₃⁺ ion results in a coordinatively saturated 18 electron complex. The loss of methane and the subsequent generation of the complex with m/z 277 results from the reaction of 1 ions with sufficient internal energy (Scheme 4.4):
Consideration of the gas-phase chemistry of bis(\(\eta^5\)-cyclopentadienyl) methylzirconium cations described in the literature suggests that the species with m/z 277 have structures similar to those postulated for the gas-phase reaction of 1 with unsaturated hydrocarbons, i.e. \(\eta^3\)-allyl complexes [147, 154]. The possibility of \(\eta^3\)-allyl complex formation is well documented [72, 151, 152, 158-161, 163, 164]. Density functional theory studies also confirm the plausibility of allyl intermediate formation as a possible side reaction in homogeneous single-site olefin polymerization [174, 175]. However, there is no direct evidence supporting \(\eta^3\)-allyl structures postulated for the reaction of 1 with acetone. Also, it is difficult to suggest tenable reaction mechanisms which would lead to the formation of such complex(es).

Our DFT calculations, carried out by Cesar S. Contreras, suggest that the most stable structure is not an \(\eta^3\)-allyl complex, but rather that of the complex shown in Fig. 4.9, which is an \(\eta^3\)-enolate complex. The higher stability of this complex can be understood: the \(\eta^3\)-enolate complex is isoelectronic with the \(\eta^3\)-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, thus contributing to high stability of the complex. The ability of the oxygen atom in the \(\eta^3\)-enolate complex (even though it is weaker σ-donor compared to the methylene group) in the oxygen σ-bonded resonance form to provide additional bonding by partially transferring its available lone pair into empty Zr 2d orbital results in increased total bond strength. In another resonance form, dative bonding from the oxygen atom is substantially more efficient than π-complexation of the
C=C bond by a metal center. According to the Dewar-Chatt-Duncanson model discussed above [26, 27], an efficient \( \pi \)-bonding occurs when a \( \sigma \)-type donation from the C=C \( \pi \) orbital is synergistic with concomitant \( \pi \)-backbonding into an empty \( \pi^* \) 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 \( \pi \)-complexation rather inefficient.

Figure 4.9. The a) \( \eta^3 \)-enolate and b) \( \eta^3 \)-allyl complexes.

In the reactions of \( \text{Cp}_2\text{ZrMe}^+ \) with d6-acetone, normal addition products of d6-acetone (nominal molecular weight 64 amu) to 1 are expected to have m/z 299 and m/z 363, 6 and 12 mass units, respectively, higher than for the products seen with the nondeuterated substrate. Both of these ions were observed, and their intensities obeyed the same trend as in case of nondeuterated acetone: only one molecule was coordinated initially and the product with two acetone molecules became the major peak after few
seconds reaction time. In addition, formation of a product ion with m/z 302 was observed, which became predominant after 5 s. The 3 mass unit gain can be assigned to the following product (Scheme 4.5):

![Scheme 4.5](image)

This ion results, apparently, from CH$_3$/CD$_3$ scrambling between the metal center and carbonyl substrate.

Three ions with m/z 279, m/z 280 (major product), and m/z 282, corresponding to the empirical formula Cp$_2$ZrC$_3$H$_{5-n}$D$_n$O$^+$, $n = 2, 3$ and 5 (approximate peak height ratios ~ 2.5:1), replace Cp$_2$ZrC$_3$H$_5$O$^+$ (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 (Scheme 4.6):

![Scheme 4.6](image)
The transfer of the deuterated methyl group introduces only a negligible secondary isotope effect, so the migratory insertion-deinsertion equilibrium remains unaffected for all of the studied combinations of zirconocene/acetone: in the approximation of a $\Delta E$ arising only from a change in zero-point energy of the stretching vibration of the Zr-C bond the predicted isotope effect is:

$$k_{\text{CD}_3}/k_{\text{CH}_3} = e^{-\lambda},$$

where

$$\lambda = \frac{h c \nu}{2 k T} \left(1 - \sqrt{\frac{\mu_{\text{CH}_3}}{\mu_{\text{CD}_3}}}ight).$$

Assuming $\nu$ (Zr-C) $\approx$ 500 cm$^{-1}$, the calculated value for $\lambda$ is $\approx 1 \cdot 10^{-3}$, thus $k_{\text{CD}_3}/k_{\text{CH}_3} \approx 1$.

Cp$_2$ZrCD$_3^+$, (2), reacted with acetone similarly to 1, with a corresponding shift of all the peaks by 3 mass units. However, two ions (m/z 277 and m/z 280, corresponding to the empirical formulae Cp$_2$ZrC$_3$H$_5$O$^+$ and Cp$_2$ZrC$_3$H$_2$D$_3$O$^+$) with comparable peak heights, and a small amount of an ion with m/z 279 were 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$_2$ZrC$_3$D$_5$O$^+$ (Scheme 4.7).

$$\text{Cp}_2\text{ZrCD}_3^+ + \text{O} = \text{C(CD}_3)_2 \rightarrow \text{Cp}_2\text{ZrC}_4\text{D}_9\text{O}^+ \rightarrow \text{Cp}_2\text{ZrC}_3\text{D}_5\text{O}^+ + \text{CD}_4$$

m/z 238       m/z 64       m/z 302       m/z 282

Scheme 4.7

This complex is analogous to the product with m/z 277 ($\eta^3$-enolate complex), but 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-
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. All other observed reactivity trends were similar to those described above for the reactions of 1: increasing reaction time led to increasing addition of a second acetone molecule to the zirconocene complex, disappearance of the m/z 282 complex along with concomitant hydration and hydrolysis reactions due to inevitable traces of water, prevalent at very long reaction times (5 seconds and above).

The proposed reaction mechanism for the reaction of 1 with d6-acetone as an example is shown in Schemes 4.8 a) and b). The second step, the migratory insertion of a coordinated ketone molecule, is reversible and leads to CH₃/CD₃ 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-d₃ groups between the metal and coordinated ketone (Scheme 4.8a).

When a ketone molecule is coordinated by the metal center, the Brønsted-Lowry acid-base reaction can take place. The metal-bound alkyl group is a good Brønsted base, the α-proton of a ketone is slightly acidic (and significantly more acidic in the ketone molecule coordinated by a metal) and the nascent enolate is expected to be a reasonably good leaving group. The combination of these factors enables nucleophilic attack of the alkyl on the α-proton of a ketone. This reaction is assumed to be the slowest step and to proceed via the least strained 6-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 CH₃- or CD₃- nucleophile,
will comprise the observed set of products (Scheme 4.8b). The products resulting from reaction involving nucleophilic attack on a deuteron are expected to be less abundant due to the primary isotope effect resulting from C-D bond cleavage.

Scheme 4.8a

The expected product abundance ratios are completely consistent with those observed in the experiment.
4.3.2. The Reactions of Cp₂ZrCH₃⁺/Cp₂ZrCD₃⁺ 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 mechanism. Both 1 and 2 sequentially add two substrate molecules (Scheme 4.9 illustrates the case for methyl isobutyl ketones as a substrate, examples of spectra are shown in Fig. 4.10).
a) 1 second reaction time

b) 5 seconds reaction time

Figure 4.10. Mass spectra of ions formed in the reaction of Cp₂ZrMe⁺ with methyl isobutyl ketone.
The major products observed are summarized in Table 4.2

Table 4.2. Major reaction products observed in the reactions of 1 and 2 with 2-butanone, and methyl isobutyl ketone at various reaction times (1 to 5 seconds).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Observed Reaction Products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Observed Reactant Products</strong></td>
</tr>
<tr>
<td></td>
<td><strong>m/z</strong></td>
</tr>
<tr>
<td>1 (m/z 235) + 2-butane (nominal molecular weight 72 amu)</td>
<td>307</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction</td>
<td>Observed Reaction Products</td>
</tr>
<tr>
<td>----------</td>
<td>---------------------------</td>
</tr>
<tr>
<td></td>
<td>m/z</td>
</tr>
<tr>
<td>2 (m/z 238) + 2-butanone (nominal molecular weight 72 amu)</td>
<td>310</td>
</tr>
<tr>
<td></td>
<td>382</td>
</tr>
<tr>
<td></td>
<td>279</td>
</tr>
<tr>
<td></td>
<td>280</td>
</tr>
<tr>
<td></td>
<td>291</td>
</tr>
<tr>
<td></td>
<td>293</td>
</tr>
<tr>
<td></td>
<td>294</td>
</tr>
<tr>
<td>1 (m/z 235) + methyl isobutyl ketone (nominal molecular weight 100 amu)</td>
<td>335</td>
</tr>
<tr>
<td></td>
<td>435</td>
</tr>
<tr>
<td></td>
<td>277</td>
</tr>
<tr>
<td></td>
<td>319</td>
</tr>
<tr>
<td></td>
<td>377</td>
</tr>
<tr>
<td>2 (m/z 238) + methyl isobutyl ketone (nominal molecular weight 100 amu)</td>
<td>338</td>
</tr>
<tr>
<td></td>
<td>438</td>
</tr>
<tr>
<td></td>
<td>279</td>
</tr>
<tr>
<td></td>
<td>280</td>
</tr>
</tbody>
</table>
Table 4.2 Continued

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Observed Reaction Products</th>
<th>Neutral eliminated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m/z</td>
<td>Suggested Empirical Formula</td>
</tr>
<tr>
<td>2 (m/z 238) + methyl isobutyl ketone (nominal molecular weight 100 amu)</td>
<td>319</td>
<td>Cp₂ZrC₆H₁₁O⁺</td>
</tr>
<tr>
<td></td>
<td>321</td>
<td>Cp₂ZrC₆H₉D₂O⁺</td>
</tr>
<tr>
<td></td>
<td>322</td>
<td>Cp₂ZrC₆H₈D₃O⁺</td>
</tr>
<tr>
<td>1 (m/z 235) + cyclohexanone (nominal molecular weight 98 amu)</td>
<td>333</td>
<td>[Cp₂ZrCH₃ · O=C(CH₂)₅]⁺</td>
</tr>
<tr>
<td></td>
<td>431</td>
<td>[Cp₂ZrCH₃ · 2O=C(CH₂)₅]⁺</td>
</tr>
<tr>
<td></td>
<td>317</td>
<td>Cp₂ZrC₆H₉O⁺</td>
</tr>
<tr>
<td>2 (m/z 235) + cyclohexanone (nominal molecular weight 98 amu)</td>
<td>336</td>
<td>[Cp₂ZrCD₃ · O=C(CH₂)₅]⁺</td>
</tr>
<tr>
<td></td>
<td>434</td>
<td>[Cp₂ZrCD₃ · 2O=C(CH₂)₅]⁺</td>
</tr>
<tr>
<td></td>
<td>317</td>
<td>Cp₂ZrC₆H₉O⁺</td>
</tr>
</tbody>
</table>

In the reaction of 1 with 2-butanone, a complex with m/z 277, (most likely resulting from the loss of ethane from the single adduct ion with m/z 307), was produced to a lesser extent than in the reactions with acetone. An ion with m/z 291 (most likely produced by methane loss from the m/z 307 ion) was nearly as abundant as the m/z 277 ion. The intensities of both peaks appeared to change with time in a similar fashion. Substantial fragmentation of the coordinated ligands resulted in multiple product peaks, increasing with reaction time. Scheme 4.10 shows as an example possible origination of the ion with m/z 293 in the reaction of 1 with 2-butanone:
The reaction of 1 with methyl isobutyl ketone also produced a m/z 277 complex (presumably resulting from C\textsubscript{4}H\textsubscript{10} loss by the m/z 335 ion), which was the major reaction product for reaction times less than one second. The complex with m/z 277 was nearly three times more abundant than the complex with m/z 319 (presumably resulting from the loss of methane by the m/z 335 ion). For both ketones, variations of peak heights with reaction time followed the same trends as for complexes with m/z 277, 291 and 319.

As in the reaction with 2-butanone, apparent ligand fragmentation was also observed. The loss of a zirconocene methyl group (and probable elimination of a neutral alkene), possibly in a multiple-step process, was commonly observed (Scheme 4.11).

The coordinatively unsaturated complex with m/z 293 reacted further by addition of a methyl isobutyl ketone molecule, resulting in a product with m/z 399. The reactions of 2 with 2-butanone and methyl isobutyl ketone produced fragmentation patterns that were remarkably similar to those produced in reaction of 1. A series of peaks with same
m/z were observed, due to the common loss of the deuterated/nondeuterated methyl group of the metallocene along with the fragmentation.

\[
\begin{align*}
\text{Cp}_2\text{ZrCD}_3^+ + \text{O=C(CH}_3\text{)C}_2\text{H}_5 & \quad \text{m/z 238} \quad \text{m/z 72} \\
\text{Cp}_2\text{ZrC}_5\text{H}_8\text{D}_3\text{O}^+ & \quad \text{m/z 310} \\
\end{align*}
\]

Scheme 4.12

The complex with m/z 277 is presumed to be the same reaction product for both of these ketones and acetone, i.e. the \(\eta^3\)-enolate complex. The complexes with m/z 291 and m/z 319 were formed in comparable amounts with m/z 277, and, according to the reaction mechanism proposed above, differ from the \(\eta^3\)-enolate complex with m/z 277.
(carrying the methyl group) only by substitution of the corresponding alkyl (Et, iBu,) at the central carbon, or both carbons (Me, Me and Me, iPr) of the enolate ligand. Thus, the ketones other than acetone, R₁-C(=O)-R₂ (R₁ = Me, R₂ = Et, iBu) react with \( \text{Cp₂ZrCH}_3^+/\text{Cp₂ZrCD}_3^+ \) in a similar manner, but two different substituents at the carbonyl carbon enable additional possible reaction pathway(s), with the loss of one of the alkyls as the corresponding alkane, as shown in Scheme 4.12 for the reaction of 2 with 2-butaneone.

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 three times more abundant than would be expected from a purely statistical distribution of alkyl groups and an assumed isotope effect \( k_H/k_D \sim 2 \). 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 iBu group is removed from the metal coordination sphere.

Scheme 4.13
Scheme 4.14

Cyclohexanone (nominal molecular weight 98 amu) reacted with 1 forming simple addition products of m/z 333 and 431 only, with no other complexes and just two products: the loss of methane leads to formation of complexes with m/z 317 and 415 respectively. The same enolate product (m/z 317) is formed in the reaction of 2 with cyclohexanone. 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 CD₃
group scrambling is impossible, and the deuterated group is eliminated as methane
resulting in the same complex as for the reaction of 1 (Scheme 4.13).

The fragmentation reactions which do not conform to the stoichiometry of the
expected products of reactions fitting the pattern of Scheme 4.8 for the reactions of both 1
and 2 with all of the ketones studied result in minor amounts of products and were
pronounced only for the more branched methyl isobutyl ketone and very long reaction
times. The observed fragmentation product peaks most likely result from ions with
different isomeric structures with the same m/z. One of the possible pathways is
shown in Scheme 4.14 for the reaction of 1 with 2-butanone. The formation of a
carbocation via C-H bond scission enables further rearrangements[182] and at some point
is followed by elimination of neutral(s) leading to the variety of fragmentation products.

4.3.3 Reactions with Other Ketones

In the reactions of Cp₂ZrCH₃⁺ with 1,4-benzoquinone and 1,4-naphthoquinone, no
interesting reactivity was observed (except for very small amounts of the complex with
m/z 277 formed in reaction with 1,4-benzoquinone). However, both substrates exhibited
an unusual tendency to coordinate readily with the binuclear metal complexes (Fig. 4.11)

In the reaction of Cp₂ZrCH₃⁺ with diethyl carbonate, the peaks corresponding to
the complex with m/z 471 (addition of two substrate molecules) overlap with the region
of the binuclear metal ions Cp₄Zr₂(CH₃)ₙ⁺ (n = 0-3), which severely impairs quantitative
analysis. The observed peaks are summarized in the Table 4.3
Figure 4.11. Ions produced in the reaction of Cp₂ZrMe⁺ with benzoquinone: products of coordination of quinone molecule by the binuclear complexes Cp₄Zr₂(CH₃)n⁺ (n = 0 - 3)

Table 4.3 Major reaction products observed in the reactions of 1 and 2 with diethyl carbonate at various reaction times (1 to 5 seconds).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>m/z</th>
<th>Empirical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 + diethyl carbonate</td>
<td>353</td>
<td>[Cp₂ZrCH₃ · O=C(OC₂H₅)₂]⁺</td>
</tr>
<tr>
<td>(nominal molecular weight</td>
<td>471</td>
<td>[Cp₂ZrCH₃ · 2O=C(OC₂H₅)₂]⁺</td>
</tr>
<tr>
<td>118 amu)</td>
<td>277</td>
<td>Cp₂ZrC₃H₅O⁺</td>
</tr>
<tr>
<td>2 + diethyl carbonate</td>
<td>356</td>
<td>[Cp₂ZrCD₃ · O=C(OC₂H₅)₂]⁺</td>
</tr>
<tr>
<td>(nominal molecular weight</td>
<td>474</td>
<td>[Cp₂ZrCD₃ · 2O=C(OC₂H₅)₂]⁺</td>
</tr>
<tr>
<td>118 amu)</td>
<td>279/280</td>
<td>[Cp₂ZrC₃H₃D₂O⁺ / Cp₂ZrC₃H₂D₃O⁺]⁺</td>
</tr>
</tbody>
</table>

The complex with m/z 277 was formed in smaller amounts than in the reaction with acetone. This complex was still abundant enough for the addition product (m/z 395) to be observed. Several ligand fragmentation products, always accompanied by the loss of a methyl (or methyl-d3 in the reactions of 2) group were observed; a few of the possible resulting structures of some of the observed ions are shown in Scheme 4.15:
In the case of the reaction of \( \text{2} \) with diethyl carbonate, instead of the unsaturated complex with \( m/z \) 277, two series of peaks, \( m/z \) 279 and 280, with relative intensities 1:3 were observed. This intensity ratio was independent of time. The total intensity obeyed the same trends observed before: a maximum intensity is reached at 2 seconds of reaction time with gradual disappearance at longer reaction times.

### 4.4 Reaction with Aldehydes

Reaction patterns for \( \text{1} \) and \( \text{2} \) with all of the studied aldehydes 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 4.4).

In reaction of \( \text{1} \) with acetaldehyde (Fig. 4.12), increasing the reaction time led to the addition of another substrate molecule by the single reaction product, the postulated \( \eta^3 \)-enolate complex (\( m/z \) 277), forming an ion with an \( m/z \) 321. The combined abundance of the ions with \( m/z \) 277 and 321 decreased significantly at longer reaction times due to water contamination of the acetaldehyde sample, and formation of the hydration product of the ion with \( m/z \) 277 (\( m/z \) 295). The \( \text{bis}(\eta^5 \text{-cyclopentadienyl}) \text{zirconium hydroxide} \) cation, \( \text{Cp}_2\text{ZrOH}^+ \) was also formed in significant amounts, resulting in an eventual
intensity shift into peaks belonging to the hydroxyl cation coordinating one substrate molecule (m/z 281), Scheme 4.16.

Table 4.4. Major reaction products observed in the reactions of 1 and 2 with acetaldehyde, benzaldehyde, propanal and n-hexanal at various reaction times (1 to 5 seconds).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Observed Reaction Products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m/z</td>
</tr>
<tr>
<td>1 (m/z 235) + acetaldehyde (nominal molecular weight 44 amu)</td>
<td>277</td>
</tr>
<tr>
<td></td>
<td>321</td>
</tr>
<tr>
<td>2 (m/z 238) + acetaldehyde (nominal molecular weight 72 amu)</td>
<td>279/280 (ion abundance ratio ~1/3)</td>
</tr>
<tr>
<td></td>
<td>323/324 (ion abundance ratio ~1/3)</td>
</tr>
<tr>
<td>1 (m/z 235) + benzaldehyde (nominal molecular weight 106 amu)</td>
<td>339</td>
</tr>
<tr>
<td>2 (m/z 238) + benzaldehyde (nominal molecular weight 106 amu)</td>
<td>341</td>
</tr>
<tr>
<td>Reaction</td>
<td>Observed Reaction Products</td>
</tr>
<tr>
<td>----------</td>
<td>---------------------------</td>
</tr>
<tr>
<td><strong>1</strong> (m/z 235) + propanal (nominal molecular weight 58 amu)</td>
<td></td>
</tr>
<tr>
<td>291</td>
<td>[Cp₂ZrC₄H₇O]⁺</td>
</tr>
<tr>
<td>293</td>
<td>[Cp₂ZrCH₃ · C₂H₅CHO]⁺</td>
</tr>
<tr>
<td>349</td>
<td>[Cp₂ZrC₄H₇O · C₂H₅CHO]⁺</td>
</tr>
<tr>
<td><strong>2</strong> (m/z 238) + propanal (nominal molecular weight 58 amu)</td>
<td></td>
</tr>
<tr>
<td>293/294 (ion abundance ratio ~1/1)</td>
<td>[Cp₂ZrC₄H₅D₂O]/[Cp₂ZrC₄H₄D₃O]⁺</td>
</tr>
<tr>
<td>295</td>
<td>[Cp₂ZrCD₃ · C₂H₅CHO]⁺</td>
</tr>
<tr>
<td>351/352 (ion abundance ratio ~1/1)</td>
<td>[Cp₂ZrC₄H₅D₂O · C₂H₅CHO]/[Cp₂ZrC₄H₄D₃O · C₂H₅CHO]⁺</td>
</tr>
<tr>
<td><strong>1</strong> (m/z 235) + n-hexanal (nominal molecular weight 100 amu)</td>
<td></td>
</tr>
<tr>
<td>333</td>
<td>[Cp₂ZrC₇H₁₃O]⁺</td>
</tr>
<tr>
<td>335</td>
<td>[Cp₂ZrCH₃ · C₅H₁₁CHO]⁺</td>
</tr>
<tr>
<td>433</td>
<td>[Cp₂ZrC₇H₁₁O · C₅H₁₁CHO]⁺</td>
</tr>
<tr>
<td><strong>2</strong> (m/z 238) + n-hexanal (nominal molecular weight 100 amu)</td>
<td></td>
</tr>
<tr>
<td>335/336 (ion abundance ratio ~3/2)</td>
<td>[Cp₂ZrC₇H₁₁D₂O]/[Cp₂ZrC₇H₁₀D₃O]⁺</td>
</tr>
<tr>
<td>338</td>
<td>[Cp₂ZrCD₃ · C₅H₁₁CHO]⁺</td>
</tr>
<tr>
<td>435/436 (ion abundance ratio ~3/2)</td>
<td>[Cp₂ZrC₇H₁₁D₂O · C₅H₁₁CHO]/[Cp₂ZrC₇H₁₀D₃O · C₅H₁₁CHO]⁺</td>
</tr>
</tbody>
</table>
Figure 4.12. Mass spectra of ions formed in the reaction of \( \text{Cp}_2\text{ZrMe}^+ \) with acetaldehyde, 1 second reaction delay.

Scheme 4.16

The intensity distribution of the two products (m/z 279 and 280) formed in reaction of \( \text{Cp}_2\text{ZrCD}_3^+ \) with acetaldehyde, was approximately 1:3, nearly independent of reaction time (Fig. 4.13). Increasing the reaction time resulted in addition of another acetaldehyde molecule by these complexes (m/z 323/324), with the intensity distribution remaining unaffected. Interestingly, the same intensity ratios were observed for the water molecule addition products, (m/z 297/298). This implies that, since these ions have similar reactivity, both reaction products of \( \text{2} \) with acetaldehyde have similar structures,
i.e. both are $\eta^3$-enolate complexes, and they differ only by the number of deuterium atoms ($\text{Cp}_2\text{ZrC}_3\text{H}_3\text{D}_2\text{O}^+$ and $\text{Cp}_2\text{ZrC}_3\text{H}_2\text{D}_3\text{O}^+$ respectively).

Figure 4.13. Mass spectra of ions with m/z 279 and 280 formed in the reaction of $\text{Cp}_2\text{ZrCD}_3^+$ with acetaldehyde, at a) 1 second and b) 5 seconds reaction delays.

In the reaction pattern of 1 with benzaldehyde (Fig.4.14), the complex with m/z 339 ($\text{Cp}_2\text{ZrC}_2\text{H}_2(\text{C}_6\text{H}_5)\text{O}^+$) is coordinatively unsaturated, analogous to the complex with m/z 277.

Figure 4.14. Ions produced in the reaction of $\text{Cp}_2\text{ZrMe}^+$ with benzaldehyde at 1 second reaction delay.
The reaction of 2 with benzaldehyde resulted in formation of the same set of products as in reaction of 1, with a two mass unit shift corresponding to the two deuterium atoms in the products, including the hydration product (m/z 359, \( \text{Cp}_2\text{ZrC}_2\text{H}_2\text{D}_2\text{(C}_6\text{H}_5\text{)}\text{O}_2^+ \)). The product of benzaldehyde molecule addition to \( \text{Cp}_2\text{ZrOH}^+ \) ion (m/z 343) dominated in the spectrum at long reaction times (>5 s.). In the reaction of 1 with propanal, a few minor products were observed at longer reaction times (unlike in reaction with acetaldehyde), but the peak with m/z 291 was always the major peak in the mass spectrum. In the reaction of 1 with \( n \)-hexanal, at reaction times 5 seconds and longer, the direct addition of aldehyde molecule(s) to 1 (m/z 335 and 435) was noticeable. Increasing the reaction time led to extensive ligand fragmentation resulting in a multitude of peaks corresponding to the loss of dihydrogen or a variety of alkenes by various ions. Analogous to the reaction patterns with other aldehydes, the ion with m/z 333 also coordinated a water molecule, forming a hydration product with m/z 351, which was predominant at reaction times of 5 seconds and longer. The reaction of 2 with \( n \)-hexanal showed the same trend of extensive ligand fragmentation at increasing reaction times as in reaction of 1 with \( n \)-hexanal.

In summary, all three aldehydes reacted with 1 in the same fashion (Scheme 4.17):

\[
\text{Cp}_2\text{ZrCH}_3^+ + \text{RCHO} \rightarrow \text{Cp}_2\text{ZrC}_2\text{H}_2\text{RO}^+ + \text{H}_2
\]

Scheme 4.17

where \( \text{R} = \text{Me, Et, Ph, C}_5\text{H}_{11} \). These complexes are presumed to be the postulated \( \eta^3 \)-enolate complexes with the corresponding \( \text{R} \)-substituent, and all of their isomers which 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 \( \alpha \)-hydrogen (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 \( \beta \)-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 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 Scheme 4.18. The \( \beta \)-H elimination is known to be a very facile process [183]. Thus, when in the rate limiting step of nucleophilic attack on an \( \alpha \)-H of the coordinated ketone an alkyl is replaced by hydrogen, a better nucleophile, while the leaving group remains the same, the reduction of the activation barrier is significant enough to make this reaction pathway favorable over any other available for a given system. The 6-member 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 [184, 185]. The noticeable effect of reduction in the amount of the complex carrying 3 deuterium atoms in the series acetaldehyde – propanal – hexanal (resulting
from the attack on hydrogen of -CH₃, -C₂H₅ and -C₅H₉ groups correspondingly) suggests certain geometrical constrains 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 ones.

A postulated reaction potential surface associated with this mechanism, for the reaction of I with acetaldehyde, is shown in Fig. 4.15a.

a) Gas-phase
Figure 4.15. Qualitative potential surface for the reaction of 1 with acetaldehyde/generic aldehyde in the gas phase and in solution. The lettering corresponds to that in Scheme 4.21. Gas-phase estimates of energetic effects are based on data from Ref. [173].

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 $\eta^3$-enolate complex according to the following proposed scheme (Scheme 4.19). This hydrolysis is the first directly observed gas-phase reaction of the $\eta^3$-enolate complex. The reactivity of the isoelectronic $\eta^3$-allyl complex has been studied on several occasions in the solution [162] and in the gas phase [175, 186]. However, no studies have been carried out so far on the gas-phase reactivity of the $\eta^3$-enolate complex, leaving this topic open for future investigation.
The liquid-phase studies [187-193] indicate potential significance of such species in polymerization catalysis: for example, in the investigation of the polymerization of the methylmethacrylate (MMA) with the neutral enolate \( \text{Cp}_2\text{ZrMe}[\text{OC(OMe)=CMe}_2] \) in the absence and in the presence of zirconocene cations \( \text{Cp}_2\text{ZrMe}^+ \) to bypass the rate-limited initiation of the system, it was shown that by itself the enolate is not active in polymerization, but as soon as the reaction system contains the cation, MMA is quantitatively converted into syndiotactic-rich PMMA with high molecular weight (\( M_n > 100,000 \text{ g/mol} \)) and very narrow molecular weight distribution (\( M_w/M_n < 1.05 \)) [187].
Scheme 4.18b

The gas-phase studies presented in this work augment our understanding of related processes taking place in the condensed phase. Individual reactions stages can be more easily discerned. The reaction mechanism postulated in the original study of the
silver-mediated addition of alkenyl- and alkylzirconocene chloride to aldehyde [54] is shown in Scheme 4.20.

Scheme 4.19

The precursor alkyl/alkenyl zirconocene chloride complex is activated via chloride abstraction by AgClO₄ and resultant cation reacts with the aldehyde molecule. The process leading from complex (IIIA) to complex (IVA) and regeneration of the active species (IIA) (transfer of the R’ group) can be either inter- or intramolecular in nature. Since only the structures of final products (RR’COH alcohols, formed after treatment of the reaction mixture with NaHCO₃ aqueous solution) were established, the detailed reaction mechanism is not completely clear.
The reaction mechanism which is consistent with the gas-phase studies data presented earlier in this chapter is shown in Scheme 4.21. According to the reaction mechanism postulated for the gas-phase reactions of 1 with aldehydes (Scheme 4.18), the coordinated aldehyde molecule undergoes migratory insertion followed by $\beta$-H elimination. This suggests formation of a side product (VI). Regeneration of the active species (IIB) occurs via chloride abstraction by cationic complex (IVB) from neutral precursor (I). Even though this process is endothermic (cation IVB is more stable than IIB), the equilibrium can be shifted toward species (V) and (IIB), as the concentration of (V) is much lower than that of (I) at all times. Hydrogen elimination and formation of $\eta^3$-enolate complex do not take place in the liquid phase due to efficient energy dissipation in the presence of solvent bath (Figure 4.15b).
Scheme 4.21

As can be seen, the gas-phase studies can provide some comprehensive insight into the reaction mechanism by direct monitoring of possible reaction intermediates and eliminating perplexing factors associated with the solution chemistry.

4.5 Comments on Suggested Reaction Mechanisms

Several inter-related factors need to be considered in understanding the reactivity of the bis($\eta^5$-cyclopentadienyl)methylzirconium cation. Having a $d^0$ configuration, the Zr metal center cannot be involved in further oxidation; therefore the number of possible reaction pathways is reduced. 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 Cp₂ZrOH⁺ cation, thus decreasing total ion abundances of these cations and their reaction products. However, the significantly lower reactivity of the hydroxyl complex [155] compared to 1 and 2 reduces possible competition for the substrate and does not hinder reaction product identification for times less than 5 seconds at the pressures used in these studies.

Extended reaction times lead to eventual thermalization of reactant ions through collisions. Ignoring long range interactions, at short reaction times, the number of molecular collisions under the high-vacuum conditions found in the FTICR cell is insignificant: since 

$$z = \frac{c_{rel} p}{kT},$$

where 

$$c_{rel} = \sqrt{\frac{8kT}{\pi\mu}}$$

and 

$$\mu = \frac{m_a m_b}{m_a + m_b},$$

when assuming collisional cross-section for zirconocene cation and carbonyl molecule \( \sigma = \pi d^2 \),

\( d = \frac{1}{2} (d_a + d_b) \) being approximately 1 nm², for typical masses of Cp₂ZrL⁺ ~ 235 amu and higher and of carbonyl ~ 70 amu, \( \mu \sim 9 \times 10^{-26} \) kg, and \( c_{rel} = 337 \) m/s; thus, for \( T = 295 \) K and \( p = 1 \times 10^{-7} \) torr (1.33 x 10⁻⁵ Pa), \( z \approx 1.1 \). However, this number is actually significantly higher (approximately an order of magnitude or more) for charged species due to a long-range interaction of the positive charge of the cation with electron cloud of the neutral. The ion-induced dipole (“Langevin”) potential and the ion-neutral collision rate constant can be calculated. The simplest case of the Langevin theory considers spiraling elastic collisions for a point-charge induced dipole force, with the attraction potential, 

$$V(r) = -\frac{\alpha e^2}{2r^4}.$$ 

Here, \( \alpha \) is the average polarizability of the neutral molecule and \( r \) is ion-molecule internuclear separation. The ion mobility, associated with this potential can be converted into the momentum transfer collision rate constant:
\[ K(\alpha) = 9.97 \times 10^{-10} \sqrt{\frac{\alpha M_r}{m}}. \]

Here \( M_r \) is the reduced mass of the system and \( m \) is the ion mass in amu [194]. Better agreement with the experimental values, especially in the case of anisotropic nonpolar molecules can be achieved if the average polarizability of the neutral is replaced by the maximum component of the diagonalized polarizability tensor \( \alpha' \) (this component is the same for spherical molecules and 5-20% larger for most anisotropic molecules [195]. This substitution gives a modified expression for the rate constant: 

\[ K(\alpha) = 9.97 \times 10^{-10} \sqrt{\frac{\alpha' M_r}{m}}. \]

The collision rate constant estimated for an ion of 100 amu colliding with a nitrogen molecule, \( k \sim 6.611 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \) [92]. By multiplying this number by the concentration of neutral, the number of collisions per second per ion can be obtained.

The limited number of collisions will lead to non-equilibrium conditions, which will result in kinetically controlled reaction products. At long reaction times, when equilibrium conditions are more closely approached, the observed products will result from thermodynamically controlled reactions. Here, the term “kinetically controlled reaction products” does not refer to irreversible reaction(s), but rather to those resulting from processes far from equilibrium.

Caution must be used when comparing the gas-phase reactivity of metallocenes to the known chemistry of their condensed-phase analogs. Very few zirconocene complexes are known in the liquid phase without triphenylphosphine or similar stabilizing ligands and such complexes react with some substrates in an unusual manner. The reactivity of direct liquid-phase analogs of the system of interest, i.e. the bis(\( \eta^5 \)-cyclopentadienyl)methylzirconium cation, as discussed above, is greatly affected by the...
nature of the counterion. These catalytic systems were quite thoroughly studied with respect to their function in alkene polymerization reactions, but the reactivity of such systems with various substrates has not been studied systematically. Thus, perhaps the best approach for examining the gas-phase reactivity of $\text{Cp}_2\text{ZrMe}^+$ cations with carbonyls would be to compare the reactivity of this complex with alkenes in both the gaseous and liquid phases.

The reaction of olefin insertion into an $\text{M-X}$ bond ($X = \text{H, R}$) proceeds via equilibrium of the alkene coordination complex and the alkene insertion product, which is exothermic by 25 kcal/mol. Both complexes are expected to be more stable for the coordination and insertion of the carbonyl group. Even though there is no $\pi$-backbonding possible for the $d^0 \text{Zr}^{4+}$ metal center, the lone electron pair of the carbonyl oxygen is more accessible than $\pi$ electrons of the alkene, making it a stronger Lewis base. Insertion of the carbonyl into the $\text{M-X}$ bond results in formation of the metal-oxygen $\sigma$ bond, which is typically significantly stronger than an $\text{M-C}$ $\sigma$ bond. This compensates for the disruption of the $\text{C}=\text{C}$ $\pi$ bond, which is usually stronger than that of $\text{C}=\text{O}$ by ~ 30 kcal/mol. Even though oxygen is a weaker $\sigma$-donor than the methylene group, it provides additional bonding by partially transferring its available lone pair into the empty Zr $d^2$-orbital, thus increasing total bond strength. Theoretical calculations of ground state energies clearly indicate higher stability of the enolate complex compared to other possible isomers (Fig. 4.16, Table 4.5)
Figure 4.16. The most stable theoretically calculated structures for the Cp₂ZrC₃H₅O⁺ cation. Canonical structures shown were calculated with the MPW1PW91/6-311+G(d,p) functional/basis set. The calculated absolute electronic energies of structures from a) through f) are listed in Table 4.5.

The unsaturated nature of the bis(η⁵-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, and for the reaction of olefin insertion into an M-X bond, \( K_{eq} \) varies by several orders of magnitude. On the other hand, 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-CR₁R₂R₃ 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, i.e. the C=O group acts as an L-ligand, rather than an X-ligand in the insertion product, thus limiting the number of coordinated entities to two.

Table 4.5. The absolute electronic energy (kcal/mol) of the most stable structure is given, and the relative energy difference is given for the remaining structures (in kcal/mol). Lettering corresponds to the structures pictured in Figure 4.16, a) through f).

<table>
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<tr>
<th>Method</th>
<th>Basis Sets</th>
<th>$E_a$</th>
<th>$\Delta E_b$</th>
<th>$\Delta E_c$</th>
<th>$\Delta E_d$</th>
<th>$\Delta E_e$</th>
<th>$\Delta E_f$</th>
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<td>22.0</td>
<td>13.4</td>
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5.1 Synthesis and Reactivity of Imines

The general reaction mechanism suggested in chapter 4 for the reactions of the methyl zirconocenes with R₁R₂C=X compounds was shown to encompass both the reactions with alkenes and aldehydes, and, with the appropriate modifications, ketones. A further advance toward generality would suggest extension of this mechanism to reactions with the next logical class of compounds containing C=N bonds, i.e. imines. However, the chemistry of imines is significantly different from that of both alkenes and carbonyls. These compounds are usually observed as transitional species and very few imines can be isolated and stored. Therefore, before consideration of the reactivity of imines with organometallic species, traditional liquid phase chemistry of this class of compounds needs to be considered and discussed.

Nucleophilic addition of ammonia/amines to aldehydes or ketones is the primary means of imine synthesis; however, only a few of these reactions are synthetically useful. For example, the addition of ammonia to aldehydes or ketones leads to two initial products, hemiaminals ("aldehyde ammonias") and imines:

\[ R_1R_2C=O + NH_3 \rightarrow R_1R_2C(NH_2)OH + R_1R_2C=NH \]

Both of these compounds are unstable. A majority of imines with a hydrogen on the nitrogen atom polymerize spontaneously[196] (the simplest homologue, methanimine CH₂=NH is stable in solution for several hours at -95°C, but rapidly decomposes at -80°C
The final reaction products are the result of various condensation reactions of combinations of hemiaminals and imines, and/or of imine with ammonia or carbonyl compounds. The most important example of such products is hexamethylenetetramine, prepared from ammonia and formaldehyde. Aromatic aldehydes give hydrobenzamides ArCH(N=CHAr).

The addition of primary, secondary and tertiary amines to aldehydes and ketones results in various of products [198], but only the reaction of primary amines gives imines:

\[ R_1R_2C=O + R_3NH_2 \rightarrow R_1R_2C=NR_3 \]

The imines with a group at the nitrogen atom are, in general, more stable and sometimes can be isolated. However, some imines, especially those with a simple R group, tend to rapidly decompose or polymerize, unless there is at least one aryl group on the nitrogen and/or the carbon. Such compounds are called Schiff bases. The formation of the Schiff bases occurs via initial formation of hemiaminals followed by loss of water.

5.2 Gas-phase Reactions of the Bis(η⁵-Cyclopentadienyl)methylzirconium Cation with Imines

Given the instability of the imines, only a few are available commercially, thus limiting our choice of substrates. The reactions with four compounds were investigated: 2,2,4,4-tetramethyl-3-pentanone imine, benzophenone imine, N-benzylidene aniline and N-benzylidenebenzyl amine (Table 5.1). All four compounds contain either aryl, or bulky alkyl groups, with or without the group on the nitrogen.
Table 5.1. Imines used in this work.

<table>
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<th>Structure</th>
<th>Molecular weight (amu)</th>
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<tr>
<td>Benzophenone imine</td>
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<tr>
<td>N-benzylidene aniline</td>
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<td>181.24</td>
</tr>
<tr>
<td>N-benzylidenebenzyl amine</td>
<td><img src="image" alt="Structure" /></td>
<td>195.26</td>
</tr>
</tbody>
</table>

5.2.1 Reactions of Cp₂ZrCH₃⁺/Cp₂ZrCD₃⁺ with 2,2,4,4-Tetramethyl-3-Pentanone Imine

2,2,4,4-tetramethyl-3-pentanone imine is the only stable aliphatic imine. The experimental setup and conditions were similar to those described in the previous chapter for the reaction with ketones and aldehydes: the pressure of bis(η⁵-cyclopentadienyl)dimethylzirconium was in the 5*10⁻⁸ – 1*10⁻⁷ Torr range, and the substrate was leaked in to ~ 1*10⁻⁷ Torr pressure. The reaction time was varied in the 0 – 5 second range and SWIFT ejection was selectively applied to different possible parent ions in order to determine the origin of various reaction products.
Scheme 5.1a

In the reaction of 1, three major products were formed: m/z 376, m/z 360 and m/z 318. The first one is the product of addition of one imine molecule to zirconocene with no neutral eliminated. The latter two result from elimination of methane (m/z 360) and (most probably) isobutane (m/z 318). At the same time, reaction of 2 leads to the products with m/z 379, m/z 360 and m/z 321, i.e. the deuterated methyl group is either
lost as methane (formation of m/z 360) or retained and isobutene is eliminated (formation of m/z 321).

Scheme 5.1b

The course of these reactions appears to be quite similar to that of the reactions with ketones (Scheme 4.8). Elimination of either methane or isobutene strongly suggests, as shown in Scheme 4.8a, fast migratory insertion equilibrium preceding the elimination (Scheme 5.1a). The next step in the reaction mechanism (Scheme 4.8) is nucleophilic attack of the Zr-bound group on the \( \alpha \)-hydrogen of a coordinated substrate. This, however, is not the most efficient pathway in the case of imines.

For coordinated 2,2,4,4-tetramethyl-3-pentanone imine, the least strongly bound hydrogen is expected to be that of the N-H bond. Even though the N-H bond is normally
6 kcal/mol weaker than the C-H bond, due to coordination of the imine by the metal center, donation of a nitrogen atom’s lone pair results in an induced $\delta^+$ charge which depletes N-H bond’s electron density and reduces the bond order. Therefore, nucleophilic attack in this case is expected to target the nitrogen-bound hydrogen of imine (Scheme 5.1b).

Such attack leads to final product(s) different from those suggested by Schemes 4.1 and 4.8, as the enamine (analogously with the enolate) complex can no longer be formed. The resultant azomethine structures have been postulated in earlier gas-phase studies of reactions of bis(η⁵-cyclopentadienyl)methylzirconium cations with nitriles (as opposed to nitriles coordinated by the methyl zirconocene cation) [154], as well as in liquid phase studies of cationic Zr and Ti complexes [81, 199, 200]. The enamine complex can be formed via facile H shift from the methyl carbon to the nitrogen (Scheme 5.2). The calculated absolute electronic energies (as described in previous section; used functional/basis set: MPW1PW91/6-311+G(d,p)) of both structures are almost equal (in kcal/mol): for the azomethine complex, Scheme 5.2 (left), $E_{\text{tot}} = -380330.7$; for the enamine complex, Scheme 5.2 (right), $E_{\text{tot}} = -380333.0$. This suggests that these structures are in equilibrium with each other and both complexes contribute to the observed peak with m/z 318. In order for the enamine structure to be formed from the azomethine complex with m/z 360, the methyl group transfer needs to take place. This is far less likely than the hydrogen transfer, so the formation of the enamine structure in this case cannot be expected.
It is possible that the alternative isomeric complexes shown in Scheme 5.3 (coordinated nitriles) also partially account for the observed peaks. It has been discussed that such complexes are not in equilibrium with azomethine species, but interconversion between them is possible under CID conditions [154]. The nitrile coordination product, however, is the most plausible complex in reactions of the concomitant parent ion, Cp₂Zr⁺ (m/z 220) as shown in Scheme 5.4.

5.2.2 Reactions of Cp₂ZrCH₃⁺/Cp₂ZrCD₃⁺ with Aryl Substituted Imines

The interesting chemistry exhibited in the reactions of 1 and 2 with 2,2,4,4-tetramethyl-3-pentanone imine was not observed for the other imines studied.
Scheme 5.4

It was found that under EI conditions used in these experiments, the benzophenone imine has an apparent tendency to decompose, with the biphenyl (molecular weight 154 amu) being the most abundant product of decomposition (Figure 5.1).

Figure 5.1. EI mass spectrum of benzophenone imine (molecular weight 181 amu).

The resultant spectra of reactions of 1 and 2 with the benzophenone imine appear to be quite complex, partially due to benzophenone imine fragments which retained
positive charge forming complexes with the neutral Cp₂Zr(CH₃)₂ (or Cp₂Zr(CD₃)₂).

However, only the ion with m/z 400 was produced from the parent ions Cp₂ZrCH₃⁺ (m/z 235)/Cp₂ZrCD₃⁺ (m/z 238) and, most probably, resulted from elimination of methane by the complex with m/z 416 (not observed or observed to a very small extent) (Scheme 5.5).

![Scheme 5.5](image)

An identical pattern is observed in reactions of 1 and 2 with N-benzylidene aniline: the only product originating from Cp₂ZrCH₃⁺ (m/z 235)/Cp₂ZrCD₃⁺ (m/z 238) had m/z 400, most probably also resulting from the methane elimination by the complex with m/z 416 (observed in very low abundance), i.e. the elimination reaction proceeds almost to completion. Unlike the case of the benzophenone imine, there is no hydrogen atom bound to nitrogen in the N-benzylidene aniline. Thus the carbon-bound hydrogen of the imine group is the only labile electrophilic hydrogen available. Nucleophilic attack in the reaction with N-benzylidene aniline, therefore, will be directed toward this hydrogen, and, due to the lack of lability of the phenyl group, lead to a different reaction product (Scheme 5.6).
N-benzylidenebenzyl amine exhibits an almost complete absence of reactivity with the methyl zirconocene cation as well as absence of coordination by the metal center.

It is apparent that the very low lability of the aryl groups precludes the migratory insertion equilibrium, which locks imine groups at the nitrogen. Consequently, only methane elimination can be observed. Furthermore, this also makes improbable any rearrangement leading to isomerization of the product structures in the Schemes 5.5 and 5.6 into one another. In summary, it is clear that the reactivity of imines with bis(η⁵-cyclopentadienyl)methylzirconium cations is governed by the availability of a labile hydrogen in the respective imine. This leads to reaction products different from expected (Scheme 4.1), i.e. the azomethyne/benzylidene species instead of the enamines. However, the reaction mechanism in general resembles that proposed for ketones (Scheme 4.8).
CHAPTER 6
CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

The reactions and proposed reaction mechanisms reported here illustrate the reactivity of bis(η⁵-cyclopentadienyl)methylzirconium cations toward ketones, aldehydes and imines under gas-phase, low-pressure conditions in the FTICR analyzer cell. These reactions exhibit distinct patterns for all of the compounds studied. In reactions with ketones, addition of up to two molecules of the various carbonyls (resulting in formation of 18e⁻ complexes for Cp₂ZrMe³) was observed, along with formation of the postulated η³-enolate complex whenever possible. In the reactions with aldehydes, due to the possibility of β-H elimination, the Zr-bound hydrogen acts as nucleophile, and the reaction sequence leading to the formation of the proposed η³-enolate complex is very efficient, so in all 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 η³-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. In reactions with the majority of imines, the reactivity toward bis(η⁵-cyclopentadienyl)methylzirconium cation is governed by the availability of a labile hydrogen. This leads to reaction products different from those which might be expected in analogy with reaction products observed for ketones and aldehydes, i.e.
azomethyne/benzylidene species instead of the enamines. Also, due to lack of lability of the aryl groups, the migratory insertion equilibrium was not possible for reactions of aryl-substituted imines. Consequently, only methane elimination was observed. However, a general reaction mechanism resembles that proposed for ketones. The proposed mechanisms account very well for all the observed reaction features.

6.2 Future Work

Our data, presented earlier in Chapter 4, indicate formation of an $\eta^3$-enolate complex isoelectronic to an allyl in reactions of $\text{Cp}_2\text{ZrMe}^+$ with aldehydes and ketones. Neither the structure nor the reactivity of the $\eta^3$-enolate complex has ever been studied in the gas phase. Even though the DFT calculations indicate that the $\eta^3$-enolate structure is the most stable among likely structures, it is still necessary to demonstrate unambiguously that such structures are, indeed, formed. Furthermore, the majority of the observed gas-phase species reported in the literature are postulated based on observed reactivity trends, data from MS/MS studies or other indirect means. There is very little definitive, spectroscopic evidence of structure for gas-phase ionic species. For example, even though the allyl complex was one of the most commonly postulated structures formed in reactions of various metal complexes with a wide array of organic substrates, there is no spectroscopic evidence confirming that conjecture.

6.2.1 IRMPD Spectroscopy

Infrared multiple photon dissociation (IRMPD) spectroscopy provides a very convenient way of obtaining infrared absorption spectra of gas phase ions. One of the currently operational facilities is built around a continuously tunable Free Electron Laser (FEL) which is located at the FOM Institute "Rijnhuizen" in Nieuwegein, the Netherlands.
The principles of operation and experimental setup are discussed in details in reference [202].

The possibility of confirming postulated ionic structures by obtaining infrared spectra of the ions in question at the new FELIX-FTICR facility is quite exciting. The current ionization capabilities for the FTICR mass spectrometer located at FELIX [203] include electron ionization (EI), multiphoton ionization (MPI), matrix assisted laser desorption ionization (MALDI) and electrospray ionization (ESI) with an octopole ion guide and a pumping station for external ion sources. An example of a spectrum obtained at the facility for the complex of chromium and diethyl ether is shown in Figure 6.1. On the spectrum, the inset shows mass spectra taken with the FEL off and on the resonance near 1010 cm\(^{-1}\). Observed dissociation channels at m/z=126 and m/z=52 correspond to detachment of one and two ether ligands, respectively. Zooming in on the m/z = 126
channel reveals the pattern due to the naturally occurring Cr isotopes, showing the level of detail typically obtainable with FT-ICR mass spectrometry.

Significant success has been achieved in the application of IRMPD spectroscopy [205] for the studies of ions in the gas phase by using the FELIX free electron laser interfaced to a FTICR spectrometer. For example, in the recent investigation of gas-phase Cr⁺ complexes for both the monomer complex [Cr(aniline)]⁺ and the dimer complex [Cr(aniline)₂]⁺, the spectra showed features indicating binding of the metal ion to the aromatic π cloud, as opposed to the N atom, thus resolving an ambiguity in computational predictions of the preferred binding site [204]. As was discussed in Chapter 3, the Cp₂ZrC₃H₅⁺ ion which has been seen during the studies of the reactions of bis(η⁵-cyclopentadienyl)methylzirconium(I⁺) with dihydrogen, ethylene, and propylene [147], was postulated to contain an allyl moiety. Even though this has been strongly suggested by earlier work [154, 166], there is no experimental (spectroscopic) evidence. Comparison of experimentally observed vibrational frequencies to those known for the allyl species and/or predicted by theoretical calculations for the Zr complex ion should give definitive proof to the postulated structure. For example, when an allyl group is π-bonded to a metal, three bands of medium to strong intensity are seen in the 1375 - 1510 cm⁻¹ region, and three more, corresponding to metal-ligand stretching vibrations, are seen in the 280 - 570 cm⁻¹ region [206]. These are substantially shifted (and increased in number) from the carbon-carbon double and triple bond stretching frequencies of 1550 - 1610 cm⁻¹ and 2000 - 2070 cm⁻¹, respectively, and metal-ligand frequencies closer to 500 cm⁻¹ which should be seen for sigma metal-allyl bonds [206].
Figure 6.2. Theoretical IR absorption spectra for the key structures discussed in the present work.

A similar approach could be used for postulated product ions seen in other studies as well. Since the ions of interest, such as zirconocene \( \eta^3 \)-allyl or \( \eta^3 \)-enolate can be (and
were) formed by EI, they should be amenable to study at the FELIX-FTICR facility. A probable complication is the strong coordination of the ligands by a metal center. The binding energy of the $\eta^3$-allyl ligand in the $\text{Cp}_2\text{Zr}(\eta^3$-allyl)$^+$ moiety is estimated to be 22 kcal/mol above that of the corresponding alkene in the cation $\text{Cp}_2\text{Zr}(\eta^2$-alkene)$^+$ [162], thus requiring at least $\sim$ 55-60 kcal/mol or greater to be provided in order for the dissociation of the $\eta^3$-allyl ligand to occur. This is close to the upper limit for bond energy for bonds successfully dissociated at the FELIX facility. In cases like that, instead of monitoring the lowest energy dissociation pathway, the lowest energy reaction pathway with a suitable reagent could be followed. For example, a possible choice of such a reagent for the zirconocene $\eta^3$-allyl complex could be $\text{H}_2$, which is known to react in the gas phase with the zirconocene $\eta^3$-allyl forming a single reaction product (zirconocene alkyl) with an activation barrier of $\sim$ 11 kcal/mol, well within the reach of the laser power at the FELIX facility. The calculated spectra for the most important species involved in the work presented in this thesis are shown on Figure 6.2.

Our preliminary data indicate that such spectra can possibly be obtained experimentally. As can be seen in Figure 6.3, the most prominent feature for zirconocene spectra, in-phase rocking motion of Cp ring hydrogen atoms at $\sim$ 12.5 µm is reproduced for the Zr(III) complex. The quality and reproducibility of the spectra can be dramatically enhanced if the spectra acquisition were carried out in the dissociation (monitoring of fragments’ intensities) rather than in the depletion (monitoring of parent ion’s disappearance) mode.
6.2.2 Other gas-phase studies of organometallic compounds

As was mentioned above, several liquid-phase studies indicate that zirconocene enolate complexes have potential importance as polymerization catalysts [187-193]. This calls for more thorough investigation of such complexes both in liquid and gas phases. By applying the FTICR MS approach, with all the advantages discussed above, it is possible to enrich our understanding of the reactivity of the $\eta^3$-enolate complex, which has never been studied in the gas phase. Varying structural complexity of the aldehydes reacting with the bis($\eta^5$-cyclopentadienyl)methylzirconium cation enabled us, as described above, to control the substituent at the central carbon of the enolate ligand. It is
feasible to carry out series of experiments on the reactivity of the $\eta^3$-enolate complex toward alkenes and other molecules, such as water, alcohols, dihydrogen, etc. This will provide valuable insight into the reactivity of such complexes and will extend our knowledge of gas-phase metallocene chemistry. The exciting possibility of imitating of the liquid-phase reactions of methylmethacrylate polymerization in the low-pressure environment of FTICR mass spectrometer should help clarify the reaction mechanism.

However, the potential of FTICR MS studies could also be applied to solve other unanswered questions. It is possible in general to investigate the effect of weakly bound ligands (such as solvent molecules) on the metallocene catalysts LL$^*$MCH$_3^+$ (L, L$^*$ = Cp or related ligands; M = Ti, Zr) reactivity. An electrospray ionization (ESI) ion source could be used. The suitable precursor (such as, for example, [Cp$_2$ZrMe]$^+[[C_6H_{5}N(CH_3)_2B(C_6F_5)_4]]$ [79] in the solvent of interest can be introduced directly, or the oxidation of the corresponding neutral in ESI source in order to produce Cp$_2$ZrMeSn$^+$ (n = 1, 2) cation can be carried out. The choice of solvents is somewhat limited by their suitability for electrospray, as well as, of course, the possibility of reaction with the metallocene. Study of the reactivity of metallocene species with alkenes, apart from the aspects discussed above, will also help to discern the effect of 16-electron or closed 18-electron shells vs. the 14-electron shell of coordinatively unsaturated Cp$_2$MMe$^+$. These experiments would somewhat mimic the effect of the solvent shell in solution-phase catalysis. Therefore, it can be anticipated that the reaction may lead to inserting of a second alkene molecule rather than formation of the allyl complex. The presence of the solvent molecules in the ICR cell may help to resolvate the metallocene complex cation. The probability of this process is negligible at typical ICR
cell operating pressures, but can increase to a noticeable value at elevated pressures available in ion traps. If the metallocene cation has already undergone alkene insertion, resolvating will lead to a consecutive insertion, ultimately resulting in oligomerization. Experimental proof of this hypothesis is a very interesting challenge. In order to discern the factors most affecting the extent of allyl complex formation vs. dimerization/oligomerization it is essential to investigate a range of metallocenes with a variety of solvent ligands. It is also possible to use different precursors LL*M(CH₃)₂ for EI or [LL*MCH₃]⁺X⁻ (L, L* = Cp or related ligand; X⁻ = [C₅H₅N(CH₃)₂B(C₆F₅)₄]⁻ [207-224] or other suitable counterion; M = Ti, Zr) for ESI.

Further advances toward the understanding liquid-phase processes could potentially be obtained from on-line ESI-FTICR MS studies of actual reaction mixtures and real-time monitoring of cationic species. Change in concentrations of (potential) active species as well as monitoring of growing polymer chains would provide important clues and mechanistic details about catalyzed homogeneous polymerization processes.

Coupling of ESI-FTICR MS studies of actual reaction mixtures (not necessarily of polymerization reactions) with IRMPD spectroscopy both at FELIX and, potentially, with simpler CO₂ laser based systems would create an immense opportunity for studying structure and functions of various elusive species which bear a charge. Due to the unique sensitivity of the FTICR MS technique it may be possible to detect and identify transient species which cannot be characterized by other means. This will tremendously enhance our understanding of various catalytic processes, as well as the intricacies of reaction mechanisms.
LIST OF REFERENCES


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BIOGRAPHICAL SKETCH

I was born in 1977 in Molodechno, Belorussia - former USSR, now the independent republic of Belarus. My family moved to Russia in 1988. In 1994, I graduated from my high school and was accepted into the Chemistry Department of the Moscow State University in Moscow, Russia. I graduated in August 1999 with B.S. in Chemistry with the Honor of Excellence Diploma. Part of my diploma project research was carried out in the School of Chemistry of the University of Nottingham, in Nottingham, United Kingdom. In the fall of 2001 I started my PhD program at the Chemistry Department of the University of Florida.