Gas-phase reactions of the bis(η^5-cyclopentadienyl)methylzirconium cation with imines

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Abstract

The reactions of the bis(η^5-cyclopentadienyl)methylzirconium cation (**1**) with four imines have been studied in the gas phase by Fourier transform ion cyclotron resonance mass spectrometry. Reactivity of the bis(η^5-cyclopentadienyl)methylzirconium cation is governed by the availability of a labile hydrogen in the corresponding imine. The products observed differ from those that might be expected in analogy with earlier work on ketones, aldehydes and alkenes (e.g., zirconocene η^3-enolate and η^3-allyl complexes): azomethyne/benzyl-idene species are found instead of enamines; however, the general reaction mechanism resembles that proposed for ketones and alkenes. An elimination reaction leading to final products was shown to be preceded by a fast migratory insertion/deinsertion equilibrium for alkyl-substituted imines. Such an equilibrium is not possible for aryl-substituted imines due to lack of lability of the aryl groups and thus only methane elimination was observed for these imines.
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1. Introduction

The significant interest in the chemistry of d^0 group 4 zirconocenes [1–14] arises mainly from their application in alkene polymerization catalysis as precursors to active species [15,16]. Single-center metal-catalyzed polymerization has attracted ample attention and evolved from an area of purely academic interest into a commercially important technology [17]. While various mass spectrometric methods have been successfully applied to studies of Ziegler–Natta catalysts [18–21], valuable insights into zirconocene reaction mechanisms, including those of polymerization reactions, can be obtained using Fourier transform ion cyclotron resonance mass spectrometry (FTICR MS).

It can be expected that the reaction mechanisms observed in ICR studies under high-vacuum conditions may differ from those in the condensed phase largely due to insufficient thermalization of ionic intermediates in the absence of a solvent bath. The first gas-phase study of reactivity of $Cp_2ZrCH_3^+$ with unsaturated hydrocarbons [22] indicated that instead of polymerization, the reaction proceeded exclusively via elimination of dihydrogen or alkene and formation of an η^3-allyl complex. Increased pressure leads to eventual thermalization and multiple insertion of the alkene can be observed and the observed rate constant of propylene polymerization at 10 mTorr was estimated to be about six orders of magnitude higher than in solution [23,24], which illustrates the intrinsic high reactivity of isolated cations in the absence of coordinating counterions or solvent molecules. Such comparison of gas-phase and condensed phase results and bridging the gap between them has many advantages. Most importantly, gas-phase studies can furnish information which can lead to much better understanding of the role of solvent, ancillary ligand

effects, clustering, inhomogeneity, etc. in corresponding solution reactions [22,25–32]. Also, the detection of elusive reaction intermediates may be possible in such gas-phase experiments.

A recent gas-phase study of the reactivity of the bis(η^5-cyclopentadienyl)methylzirconium cation involved simple ketones and aldehydes [30]. It was found that reactions with a majority of the ketones resulted in consecutive addition of one or two substrate molecules and/or elimination of alkanes. The key products of the elimination reaction(s) were identified as η^3-enolate complexes. Similar product ion structures were postulated for reaction of the bis(η^5-cyclopentadienyl)methylzirconium cation with aldehydes, where they were either the major or the only observed product. A multi-step mechanism was proposed: migratory insertion of an aldehyde molecule into the methyl zirconocene cation is followed by β-H elimination and, via a six-membered cyclic transition state, formation of the resulting enolate complex (Scheme 1 with Y=O). When a β-H elimination pathway is not available for ketones, the reaction was proposed to proceed via direct nucleophilic attack of the metal-bound alkyl.

It may be postulated that the formation of both an η^3-allyl complex for alkenes and an η^3-enolate complex for aldehydes and ketones are examples of a general process (shown in 1) which takes place under high-vacuum, non-equilibrium conditions. For the reactions of methyl zirconocenes with terminal olefins, Y=CH$_2$ [32]. For reactions with olefins such as isobutene or styrene, Y=C(R$_1$)R$_2$ (R$_1$ = H or R). In the case of 1,1 disubstituted alkenes, elimination of methane was observed [22]. In the case of aldehydes and ketones, group Y is the carbonyl oxygen. It was shown that this mechanism encompasses reactions with both aldehydes, and, with the appropriate modifications, ketones [30].

We postulated that this mechanism could also be extended to reactions with 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 of them can be isolated and stored. A majority of imines with a hydrogen on the nitrogen atom polymerize spontaneously [33] (the simplest homologue, methanimine, CH$_2$=NH, is stable in solution for several hours at $-95\,°C$, but rapidly decomposes at $-80\,°C$ [33,34]). The imines with a non-hydrogen substituent 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 (Schiff bases).

The present work reports a study of reactivity pathways of bis(η^5-cyclopentadienyl)methylzirconium (1), as a model compound for reactive d^0 organometallics, with imines in the gas phase.

2. Results and discussion

Only a few imines are commercially available, thus limiting the choice of easily accessible substrates, and the reactions of 1 with four compounds (Table 1) were investigated. All four compounds contained either aryl or bulky alkyl groups, with or without the group on the nitrogen.

2.1. Reactions of Cp$_2$ZrCH$_3^+$/Cp$_2$ZrCD$_3^+$ with 2,2,4,4-tetramethyl-3-pentanone imine

The only stable aliphatic imine studied was 2,2,4,4-tetramethyl-3-pentanone imine. The pressure of bis(η^5-cyclopentadienyl)dimethylzirconium was in the 5×10^{-8}–1×10^{-7} Torr range, and the substrate was leaked in to $\sim 1 \times 10^{-7}$ Torr pressure. The reaction time was varied in

Scheme 1.

Table 1
Imines used in this work

| Imine	Structure	Molecular weight (amu)
2,2,4,4-tetramethyl-3-pentanone imine		141.26
Benzophenone imine		181.24
N-benzylidene aniline		181.24
N-benzylidenebenzyl amine		195.26
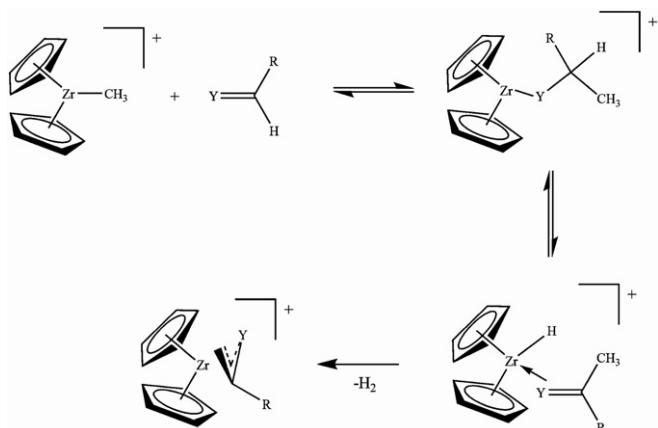
the 0–5 s range. Additional studies using selective stored waveform inverse Fourier transform (SWIFT) ejection [35] were carried out. Selective ejection of possible parent ions and analyzing resultant product distribution enabled us to determine the origin of various observed reaction products.

In the reaction of **1**, three major products were formed: m/z 376, m/z 360 (**3**) and m/z 318 (**4**). The first one is the product of addition of one imine molecule to zirconocene with no neutral elimination. The latter two result from elimination of methane and (most probably) isobutene, respectively, from the addition complex. Reaction of $Cp_2ZrCD_3^+$ (**2**) with this imine leads to products with m/z 379, m/z 360 (**3**) and m/z 321 (**5**), *i.e.* the deuterated methyl group is either lost as methane (formation of **3**) or retained and isobutane is eliminated (formation of **5**), as shown in Schemes 2a and 2b.

The course of these reactions appears to be quite similar to that of the reactions with ketones [31]. Elimination of either methane or isobutene strongly suggests, as shown in Scheme 2a, fast migratory insertion equilibrium preceding the elimination. The next step in the general reaction mechanism (Scheme 1) would be nucleophilic attack of the Zr-bound group on the α-hydrogen of a coordinated substrate. However, unlike the reactions with aldehydes and ketones, this is not the most efficient pathway in the case of imines.

For the coordinated 2,2,4,4-tetramethyl-3-pentanone imine, the most acidic hydrogen is expected to be that of the N–H bond. A pK_a value for primary alkyl C–H bonds is ∼ 56 [36], while it is much lower for imines: for example, for the N–H bond of benzophenone imine pK_a ∼ 31 [37]. Also, due to coordination of the imine by the metal center, donation of a nitrogen atom's lone pair results in an induced δ^+ charge which promotes the imine hydrogen's acidity. Therefore, nucleophilic attack in this case is expected to target exclusively the nitrogen-bound hydrogen of the imine (Scheme 2b).

Such attack leads to final product(s) different from those suggested by the general reaction mechanism shown in
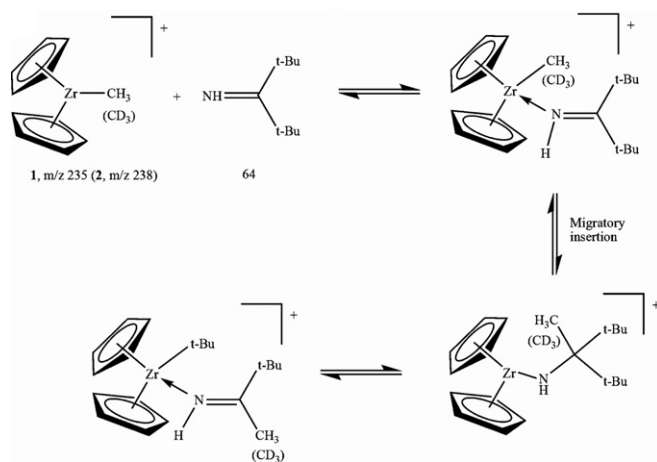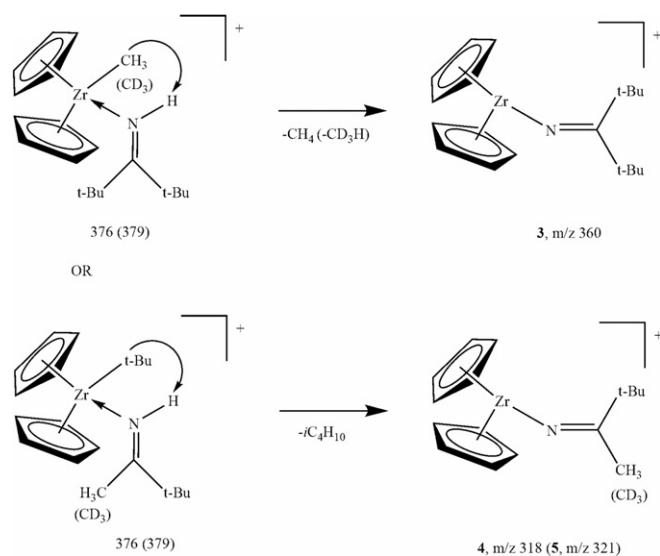

Scheme 2b.

Scheme 1, as the zirconocene η^3-enamine complex (**6**) (analogous to the η^3-enolate and η^3-allyl complexes in the case of aldehydes/ketones and alkenes, respectively) can no longer be formed. The proposed resultant azomethine structures have been postulated in earlier gas-phase studies of reactions of bis(η^5-cyclopentadienyl)methylzirconium cations with nitriles (as opposed to nitriles coordinated by the methyl zirconocene cation) [38], as well as in liquid phase studies of cationic Zr and Ti complexes [39–41].
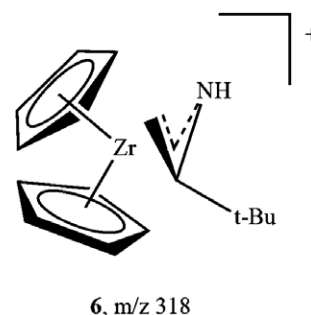
6, m/z 318

The η^3-enamine complex (**6**) can be formed via a facile hydrogen shift from the methyl carbon to the nitrogen. The calculated absolute electronic energies (as described in Section 3.2 below) of the azomethine and the enamine complexes are nearly equal (calculated difference is ∼2 kcal/mol). This suggests that these structures may potentially interconvert into each other and that both complexes may contribute to the observed peak with m/z 318.

In order for the enamine structure to be formed from the azomethine complex **3**, a methyl group transfer is necessary. This is far less likely than the hydrogen transfer, so formation of the enamine structure in this case is not expected. The alternative isomeric complexes **7** and **8** (coordinated nitriles) may also partially contribute to the

Scheme 2a.

observed peaks. However, earlier studies have postulated that such complexes are not in equilibrium with the azomethine species, but that interconversion between them is possible under CID conditions [38].


7, m/z 318   8, m/z 360
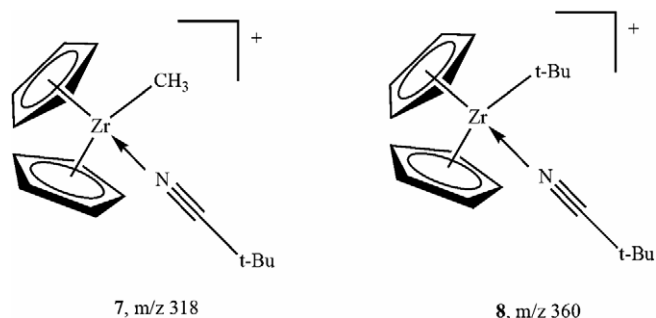
## 2.2. Reactions of $Cp_2ZrCH_3^+$/$Cp_2ZrCD_3^+$ with aryl substituted imines

The 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. In the reactions of benzophenone imine with the $Cp_2ZrCH_3^+$ (*m/z* 235) or $Cp_2ZrCD_3^+$ (*m/z* 238) parent ions, only an ion with *m/z* 400 (**9**) was produced. Most probably, this ion resulted from elimination of methane/d3-methane from adducts with *m/z* 416/ *m/z* 419 which were either not observed or seen only in very low abundance (Scheme 3).

A similar pattern was found for the reactions of **1** and **2** with *N*-benzylidene aniline: the only product seen in reactions of $Cp_2ZrCH_3^+$ (*m/z* 235)/$Cp_2ZrCD_3^+$ (*m/z* 238) with this imine had *m/z* 400 (**10**). It is most likely that this ion also was formed by methane elimination from the complex with *m/z* 416 (observed in very low abundance), *i.e.* the elimination reaction proceeds almost to completion. *N*-benzylidenebenzyl amine exhibited an almost complete absence of reactivity with the methyl zirconocene cation as well as absence of coordination by the metal center.

Unlike in 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 ani-
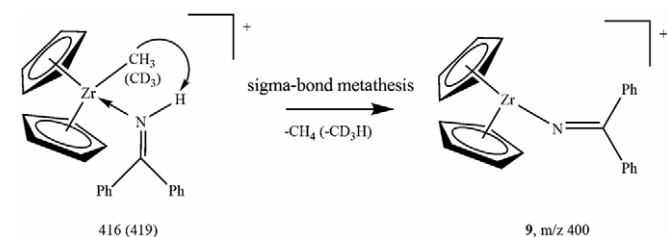
Scheme 3.
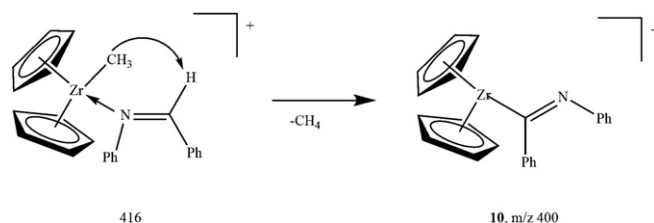
line, therefore, will be directed toward this hydrogen. Therefore, a different reaction product is expected to be formed (Scheme 4).

Preferential elimination of methane and formation the aryl substituted imines likely results from higher efficiency of the β-H elimination compared to β-Ph elimination due to the low lability of the aryl groups, which is well known in organic chemistry [42,43]. Some steric hindrance arising from the bulky N–Ph group screening the β-Ph group and inhibiting formation of the transition state π-complex may also play a role. Furthermore, such low lability of the phenyl group would also make any rearrangement leading to isomerization of the product structures in Schemes 3 and 4 into one another improbable.

3. Conclusions

The reactivity of bis(η^5-cyclopentadienyl)methylzirconium cations with imines is governed by the availability of a labile hydrogen in the respective imine. This leads to reaction products different from those expected based on the general mechanism shown in Scheme 1, *i.e.*, zirconocene azomethyne/benzylidene species are formed instead of η^3-enamines. However, in general the reaction mechanism resembles that proposed for aldehydes/ketones and alkenes. Due to lack of lability of the aryl groups, the migratory insertion equilibrium is apparently not possible in reactions of aryl-substituted imines, and consequently only methane elimination was observed. The proposed mechanisms account very well for the observed reaction features.

3.1. Experimental

Ion–molecule reactions were studied by Fourier transform ion cyclotron resonance mass spectrometry. The primary mass spectrometer used in the experiments was based on a 2.0 T magnet with an internal electron ionization (EI) source [44]. Electron ionization of $Cp_2Zr(CH_3)_2$ results in the formation of $Cp_2ZrCH_3^+$ and Cp_2Zr^+. Since the Cp_2Zr^+ ion and its reaction products complicate the spectrum, in order to distinguish products from these two possible parent ions, additional studies using selective stored waveform inverse Fourier transform (SWIFT) ejection [35] were implemented.

The background pressure on the 2.0 T instrument was $\sim 2 \times 10^{-9}$ Torr; pressure of zirconocene was $\sim 10^{-7}$ Torr,

416   10, m/z 400

Scheme 4.

decreasing throughout the experiment at a rate of approximately 10^{-8} Torr/h 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 reaction times of ~ 0, 0.5, 1, 2, 5 s and longer were carried out for each reaction.

It was found that under the EI conditions used in these experiments, the benzophenone imine tended to decompose, with biphenyl (molecular weight 154 amu) being the most abundant product of decomposition. The mass spectra obtained for reactions of **1** and **2** with the benzophenone imine are quite complex, partially due to reactions of positively charged benzophenone imine fragments with the neutral $Cp_2Zr(CH_3)_2$ (or $Cp_2Zr(CD_3)_2$).

The formation of binuclear metal ions $Cp_4Zr_2(CH_3)_n^+$ ($n = 0–3$) in reactions of both parent ions with their respective precursor neutrals complicated the spectra, especially at longer reaction times. This impeded the ability to study reactions with rate coefficients below $\sim 10^9$ 1/M s. The presence of water also decreased the amount of the ion of interest, as it reacted very rapidly to form a hydroxyl complex:

$$Cp_2ZrCH_3^+ + H_2O \rightarrow Cp_2ZrOH^+ + CH_4$$
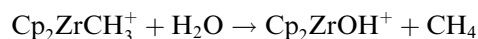
$Cp_2Zr(CH_3)_2$ and all of the imines used in these studies were purchased from commercial sources and purified by repeated freeze–pump–thaw cycles for liquid substrates; $Cp_2Zr(CD_3)_2$ was synthesized from commercially purchased precursors in accordance with a preparation procedure described in the literature [45].

3.2. Computational

Density functional theory (DFT) calculations were carried out for the zirconocene complexes to establish most stable structures. To reduce optimization time, the proposed molecular structures were created using HYPERCHEM™ software and then were geometry optimized using the semi-empirical Zerner's modified version of INDO for transition metals (*i.e.* ZINDO/1 in HYPERCHEM™). These structures served as the initial input configurations for geometry optimization in GAUSSIAN98 [46] using the Modified Perdew–Wang one parameter exchange and correlation functional (MPW1PW91) [47] hybrid DFT method with a 6-311+G(d,p) basis set.

Acknowledgement

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