Zirconocene Ketimides: Synthesis, Structural Characterization, Ethylene Polymerization Activity, and ab Initio Computational Studies

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The metathetical reaction between the lithium 1-azaallyl compound [{HMPA·LiN(H)C-(*t*-Bu)CH$_2$}$_2$] (**1**) with zirconocene dichloride (**2**) results in the formation of the zirconocene ketimide [Cp$_2$Zr(Cl)N═C(*t*-Bu)CH$_3$] (**3**; Cp = cyclopentadienyl) and lithium chloride. After it is transferred to the transition metal, the azaallyl ligand isomerizes to a ketimido variation. An energetic preference of 11.9 kcal mol^{-1} in favor of the zirconocene ketimide over its theoretical azaallyl isomer was determined by ab initio molecular orbital calculations (at the HF/LanL2DZ level). These studies, in combination with an X-ray diffraction analysis of **3**, suggest that the preference for the ketimide isomer is due to the presence of a heteroallenic (Zr−N−C) interaction. This bonding mode is consistent with the short Zr−N bond length of 2.007(2) Å found in the crystal structure of **3**. Treatment of **3** with MeLi affords the corresponding methyl derivative [Cp$_2$Zr(Me)N═C(*t*-Bu)CH$_3$] (**4**). ^{1}H NMR spectroscopic experiments reveal that addition of the Lewis acid B(C$_6$F$_5$)$_3$ to **4** results in methide abstraction, with retention of the ketimide unit on the cationic zirconocene. Ab initio molecular orbital calculations confirmed the energetic preference for the η^1-ketimide cation [Cp$_2$ZrN═C(*t*-Bu)CH$_3$]$^+$ over either the η^1-azaallyl isomer [Cp$_2$Zr{η^1-N(H)C(*t*-Bu)CH$_2$}]$^+$ or the η^3-azaallyl isomer [Cp$_2$Zr{η^3-N(H)C(*t*-Bu)CH$_2$}]$^+$ (by 17.9 and 1.2 kcal mol^{-1}, respectively). Both **3** and **4** have been shown to be active catalysts for the polymerization of ethylene in combination with a MAO cocatalyst. In addition, **4** polymerizes ethylene in combination with a mixed B(C$_6$F$_5$)$_3$/*i*-Bu$_3$Al cocatalyst.

Introduction

Currently there is considerable interest in the use of metallocenes of group 4 elements as homogeneous catalysts for the polymerization of α-olefins.[1,2] An increased understanding of the factors controlling and stabilizing the catalyst's active site has led to the development of an array of new catalysts over the past 15 years. Indeed, this research has resulted in the ability to manufacture a wide range of polyolefinic products through the careful selection of the ligands attached to the metal center. Consequently, this has promoted a greater control of catalyst activity and selectivity and, ultimately, of the resulting polymer's properties. Moreover, the choice of the ancillary ligand set has also been shown to be an important factor in the stabilization of the active catalyst species.[3]

Multidentate nitrogen ligands such as Schiff bases,[4] porphyrins,[5] amidinates[6] (**A**), and β-diketinimates[7] (**B**) are presently receiving attention as components of zirconium catalysts for olefin polymerization. Interest in these ligand types arises from the variety of bonding modes potentially available to the metal (η^1 or η^3 terminal, chelating, or bridging). Thus, use of these

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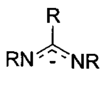

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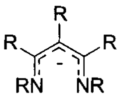

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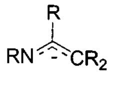


C

ligands leads to an extensive capability to alter both the stereochemistry and electronic distribution at a zirconium center.

A related fragment is the 1-azaallyl ligand (**C**), which until very recently[8] has received little attention. Fully characterized 1-azaallyl complexes are rare, and the only zirconium derivatives are those reported by Lappert.[7] These include the dinuclear and mononuclear complexes $[\{Zr(N(SiMe_3)C(t\text{-}Bu)CHR)Cl_2(\mu\text{-}Cl)\}_2]$ and $[Zr\{N(SiMe_3)C(t\text{-}Bu)CHPh\}Cl_3]$, the latter of which has been shown to be catalytically active for the polymerization of ethylene in combination with a MAO cocatalyst. To the best of our knowledge, no zirconium 1-azaallyl complexes with cyclopentadienyl (Cp) coligands bound to the metal center have been characterized.

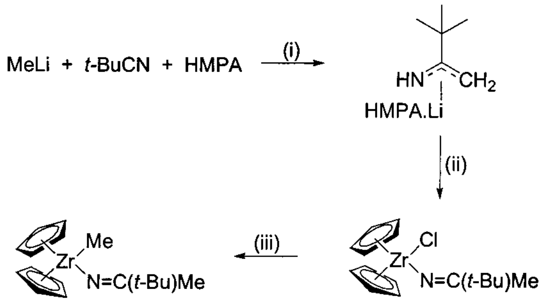
This deficiency prompted us to investigate the metathetical reaction between the lithium 1-azaallyl complex $[\{HMPA{\cdot}LiN(H)C(t\text{-}Bu)CH_2\}_2]$ (**1**) with zirconocene dichloride, Cp_2ZrCl_2 (**2**). Herein, we describe the formation of the zirconocene ketimide $[Cp_2Zr(Cl)N{=}C(t\text{-}Bu)CH_3]$ (**3**) via a proton rearrangement reaction. An ab initio molecular orbital study has been carried out to investigate the energetics of the reaction and possible driving force for the loss of the 1-azaallyl formulation in preference to the ketimide one. Additionally, the methylated derivative $[Cp_2Zr(Me)N{=}C(t\text{-}Bu)CH_3]$ (**4**) has been prepared by the reaction of **3** with MeLi. Both **3** and **4** have been tested for ethylene polymerization activity.

Results and Discussion

Syntheses. The lithium azaallyl complex **1** was prepared as described previously[9] and then reacted with **2** in a 1:1 molar ratio in toluene solution. This gave a cloudy orange suspension, which when filtered through Celite and stored at −20 °C afforded yellow crystals of **3** in a 54% yield (Scheme 1).

This azaallyl to ketimide isomerization represents a new synthetic route to zirconocene ketimides. In a previous report by Erker the zirconocene ketimide $[Cp_2Zr(Cl)N{=}CHPh]$ (**5**) was prepared via the hydrozirconation of benzonitrile by $Cp_2Zr(Cl)H$.[10] The same group later described the synthesis of the bis(alkylideneamido) complex $[Cp_2Zr(N{=}CPh_2)_2]$ (**6**), by photolysis of either Cp_2ZrPh_2 or $Cp_2Zr(CO)_2$ in the presence of benzophenone azine, $Ph_2C{=}NN{=}CPh_2$.[11] Compound **6** was originally prepared in 1971 by Lappert via the reaction of **2** with 2 mol equiv of the ketimide $LiN{=}CPh_2$,[12] although it was not structurally characterized at that time.

Scheme 1[a]



[a] HMPA = $(Me_2N)_3P{=}O$. Legend: (i) −78 °C, Et_2O, warm to 25 °C for 15 min, Et_2O removed *in vacuo* and replaced with 10 mL of toluene; (ii) −78 °C, Cp_2ZrCl_2 in 10 mL of toluene, warm to 25 °C for 30 min, −LiCl; (iii) −78 °C, MeLi in Et_2O, warm to 25 °C for 2 h, −LiCl, −20 °C, 24 h.

Treatment of **3** with an equimolar quantity of MeLi in toluene solution produced a cloudy yellow suspension which when filtered through Celite afforded a transparent, yellow solution. All the solvent was removed in vacuo, and the methyl analogue **4** was obtained as an air- and moisture-sensitive yellow powder in a 63% yield (Scheme 1).

The first indication that the new complexes **3** and **4** exist as ketimides rather than azaallylic derivatives came from their IR spectra (recorded as Nujol mulls), which reveal strong $\nu_{C=N}$ stretching frequencies at 1679 and 1689 cm^{-1}, respectively. This compares well with the value found for **5** (1678 cm^{-1}).

It is interesting to note that complex **1**, the lithium precursor to **3**, was prepared by a process involving a ketimide to azaallyl isomerization (induced by the donor solvent HMPA as shown in Scheme 1).[9] The transformation of **1** to **3** reported here thus represents the retroequivalent (i.e. an azaallyl to ketimide isomerization) of this process.

NMR Spectroscopic Studies. The ketimide character of **3** was unambiguously confirmed by ^1H and ^{13}C NMR spectroscopy (see Experimental Section). The ^1H NMR spectrum for **1** shows a characteristic splitting pattern associated with the azaallyl moiety. This is due to a long-range (^4J) coupling of the N*H* and CH*H* protons in the unsaturated NCC linkage, giving rise to splitting of one of the terminal protons with the N*H* signal into a doublet, while the other remains a singlet. This type of coupling is not seen in the ^1H NMR spectrum of **3**, since the proton formally associated with the N*H* has now moved onto the terminal carbon, resulting in a single C*H*$_3$ resonance at δ 1.46. In addition, a single resonance at δ 5.82 is observed for the Cp ring protons, representing two chemically equivalent Cp ligands.

The ^1H NMR spectrum of **4** has an appearance similar to that for **3**, with the addition of a methyl resonance at δ 0.06 corresponding to Zr−C*H*$_3$. The Cp resonance has shifted to a lower frequency by 0.15 ppm from that of **3**, and this is consistent with an enhanced shielding effect on the protons resulting from the change in electron density at the Zr center through replacing Cl by Me. Again, only one resonance is observed for the cyclopentadienyl ring protons and additionally only one

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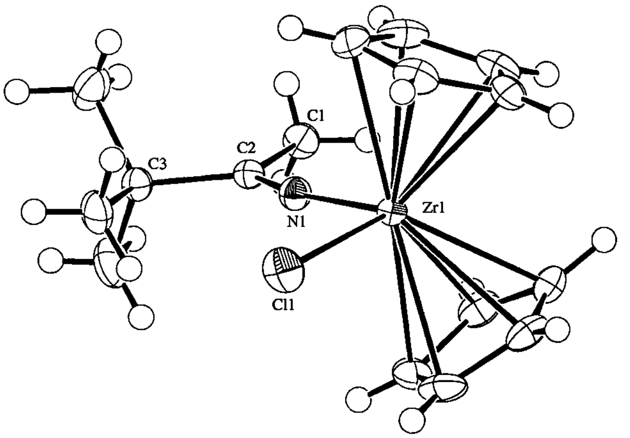

Figure 1. Molecular structure of **3** showing the atom-labeling scheme. Hydrogen atoms are omitted for clarity.

Table 1. Key Bond Lengths (Å) and Bond Angles (deg) within 3

Zr1−Cl1	2.5155(5)	C1−C2	1.514(3)
Zr1−N	2.007(2)	C2−C3	1.542(3)
N1−C2	1.259(3)	Zr1−Cp1	2.214(3)
Zr1−Cp2	2.211(3)		
Cl1−Zr1−N1	101.21(5)	Cp1−Zr1−Cp2	130.8(1)
Zr1−N1−C2	168.2(2)	N1−C2−C3	121.1(2)
N1−C2−C1	121.1(2)	C1−C2−C3	117.8(2)

[a] Cp = ring centroid.

type of methyl resonance for the ketimide ligand is apparent. These features are consistent with a structure akin to that of **3** with the Cl ligand replaced by a Me ligand.

To investigate if the ketimide ligand would revert to the azaallyl isomer upon reaction with a methide-abstracting reagent, **4** was reacted with $B(C_6F_5)_3$ and the reaction monitored by ^1H NMR spectroscopy. The resulting ^1H NMR spectrum showed that abstraction of the methyl group had indeed taken place, as indicated by a shift in the CH_3 resonance from δ 0.06 to δ 0.38. All other signals shifted to lower frequencies, consistent with an enhanced shielding effect on the protons with the formation of the ion pair $[Cp_2ZrN{=}C(t\text{-}Bu)CH_3]^+$-$[MeB(C_6F_5)_3]^-$. Therefore, no evidence for azaallyl formation was observed.

X-ray Crystallographic Studies. An X-ray crystallographic study of **3** shows discrete molecular units, which are composed of a bent metallocene moiety to which a chloride and a ketimide ligand are attached (Figure 1; selected bond lengths and angles are provided in Table 1).

Clearly, the azaallyl moiety has been lost, as indicated by the short N1−C2 bond length of 1.259(3) Å, indicating formation of a localized N═C double bond. This is confirmed by the observation and refinement of the three methyl hydrogens. Furthermore, on comparison of the crystal structure data of **3** with those previously reported[9] for **1**, the loss of an azaallyl unit is established. The η^3-NCC anion in **1** has a long N−C contact (1.359(3) Å) and a short C−C distance (1.361(4) Å), consistent with delocalization of the electron density across the three atoms. For **3**, N1−C2 shortens (1.259(3) Å) and concomitantly C1−C2 becomes longer (1.542(3) Å) as the bond character changes to that representing a localized double and single bond, respectively.

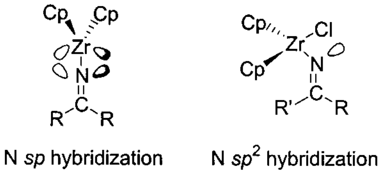

Figure 2. Comparison of the hybridization at a N center in a linear vs bent Zr ketimide formulation.

Consistent with the single Cp resonance observed in the aforementioned NMR spectrum, the crystal structure of **3** contains chemically equivalent Cp ligands. A salient feature of the structure is the short Zr1−N1 bond (length 2.007(2) Å, whereas similar Zr−N bond lengths are typically 2.16 Å[13]). This is significantly shorter than the corresponding distances in **6** (2.058(2) and 2.063(2) Å) and equivalent, within experimental error, to that in **5** (2.013(5) Å). There is also a close agreement between the ketimido N═C bond length in **3** (1.259(3) Å) and that in **5** (1.259(7) Å) and those in **6** (1.259(4) and 1.266(4) Å). Accompanying these short bonds is an almost linear Zr1−N1−C2 arrangement (168.20(2), 170.50(5), and 173.70(2)/164.10(2)° in **3**, **5**, and **6**, respectively). Taking all these features together, a Zr−N−C heteroallene-type interaction is implied, as first proposed by Erker in their analysis of the structures of **5** and **6**. The near-linearity of the Zr1−N1−C2 bond angle facilitates efficient orbital overlap and thus a π interaction between an acceptor orbital on the Zr and a filled donor orbital on the N atom (see Figure 2). In this way, the N atom becomes closer to sp-hybridized, allowing a substantial strengthening of the Zr1−N1 bond. This π bonding would be lost were the said N atom to assume sp^2 hybridization, as it would do in an azaallylic N(H)−C−C arrangement. Other dimensions in **3** (e.g. Zr1−C11 = 2.5155(5) Å) fall within normal ranges (e.g., the corresponding bond in **5** is 2.497(2) Å).[2b]

Computational Studies, *Ab initio*[14] molecular orbital calculations run at the HF/LanL2DZ[15] level of theory were used to explore the nature of the reaction between **1** and **2** (for similar calculations on other related Zr systems, see ref 16). The calculated ketimide structure $[Cp_2Zr(Cl)N{=}C(t\text{-}Bu)CH_3]$ (**I**), modeling the experimentally observed structure **3**, and its hypothetical azaallyl isomer $[Cp_2ZrCl\{\eta^1\text{-}N(H)C(t\text{-}Bu)CH_2\}]$ (**II**) were geometry-optimized with no imposed constraints. Figure 3 shows the respective geometries obtained with their relative energy values. Selected bond lengths and angles of the two compounds are given in Tables 2 and 3, respectively. A comparison of the geometry of **I** with the crystal data for **3** shows excellent agreement, with

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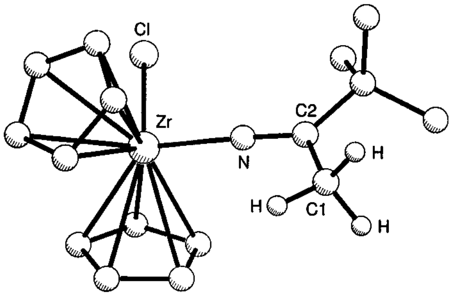
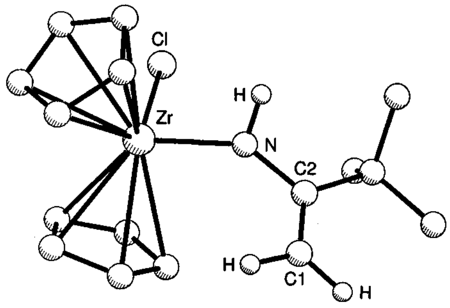
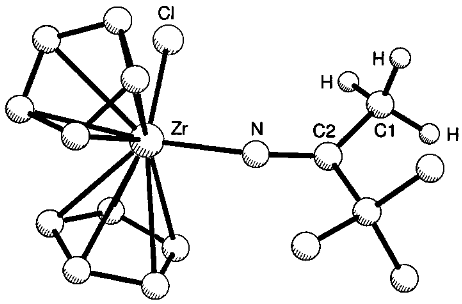


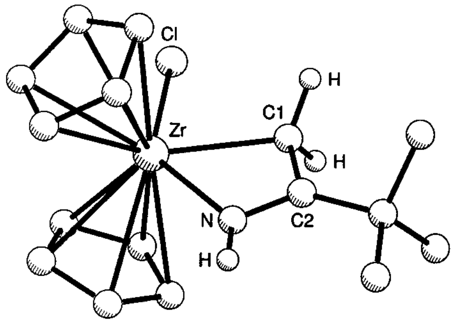
[Cp$_2$Zr(Cl)N=C(*t*-Bu)CH$_3$] **I**
0.0 kcal mol^{-1}



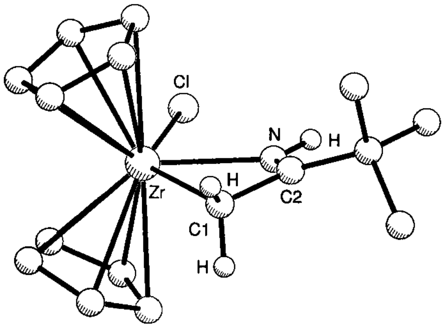
[Cp$_2$ZrCl{η^1-N(H)C(*t*-Bu)CH$_2$}] **II**
+11.9 kcal mol^{-1}



[Cp$_2$Zr(Cl)N=C(*t*-Bu)CH$_3$] **III**
+0.7 kcal mol^{-1}



[Cp$_2$ZrCl{η^3-N(H)C(*t*-Bu)CH$_2$}] **IV**
+22.9 kcal mol^{-1}



[Cp$_2$ZrCl{η^3-N(H)C(*t*-Bu)CH$_2$}] **V**
+19.0 kcal mol^{-1}

Figure 3. Energy minimum calculated structures **I**–**V** showing relative energy values.

Table 2. Key Bond Lengths (Å) within the Calculated Structures I–VIII

calcd structure	Zr–N	Zr–Cl	Zr–C1	Zr–C2	N–C2	C1–C2
I	2.002	2.591	4.195	3.624	1.265	1.526
II	2.071	2.579	3.933	3.314	1.430	1.339
III	2.001	2.591	4.125	3.258	1.265	1.526
IV	2.364	2.654	2.328	2.872	1.290	1.505
V	2.279	2.703	2.409	2.835	1.292	1.497
VI	2.039		3.811	3.251	1.447	1.335
VII	2.254		2.311	2.766	1.300	1.523
VIII	1.968		4.186	3.241	1.273	1.521

Table 3. Key Bond Angles (deg) within the Calculated Structures I–VIII

calcd structure	Cl–Zr–N	Zr–N–C2	N–C2–C1	Zr–C1–C2	Zr–N–C2–C1
I	101.23	175.72	120.16	43.61	8.84
II	97.82	141.63	120.47	53.41	−60.65
III	73.61	101.50	107.74	89.94	17.64
IV	137.29	99.41	108.17	94.60	−0.69
V	98.81	171.44	119.43	46.07	5.87
VI		136.94	119.55	55.67	−58.38
VII		98.63	110.33	89.96	−0.03
VIII		178.69	119.33	42.86	3.23

the average difference in bond lengths and angles between the two methods being <0.05 Å and <1°, respectively.

In **I** the methyl group of the ketimide ligand is oriented anti with respect to the chloride attached to the metal center, as is observed in the crystal structure of **3**. Rotating the ligand to place the methyl syn with respect to the chloride, as in model **III**, resulted in a destabilization of 0.7 kcal mol^{-1}. In this regard it is pertinent to note that the hydrozirconation reactions performed by Erker[10] are stereospecific, giving syn stereochemistry; i.e. for **5** the Cl and H atoms are positioned syn to the linear Zr–N1–C1 moiety.

As indicated in Figure 3, the ketimide model **I** is 11.9 kcal mol^{-1} more stable than its azaallylic isomer **II**. This

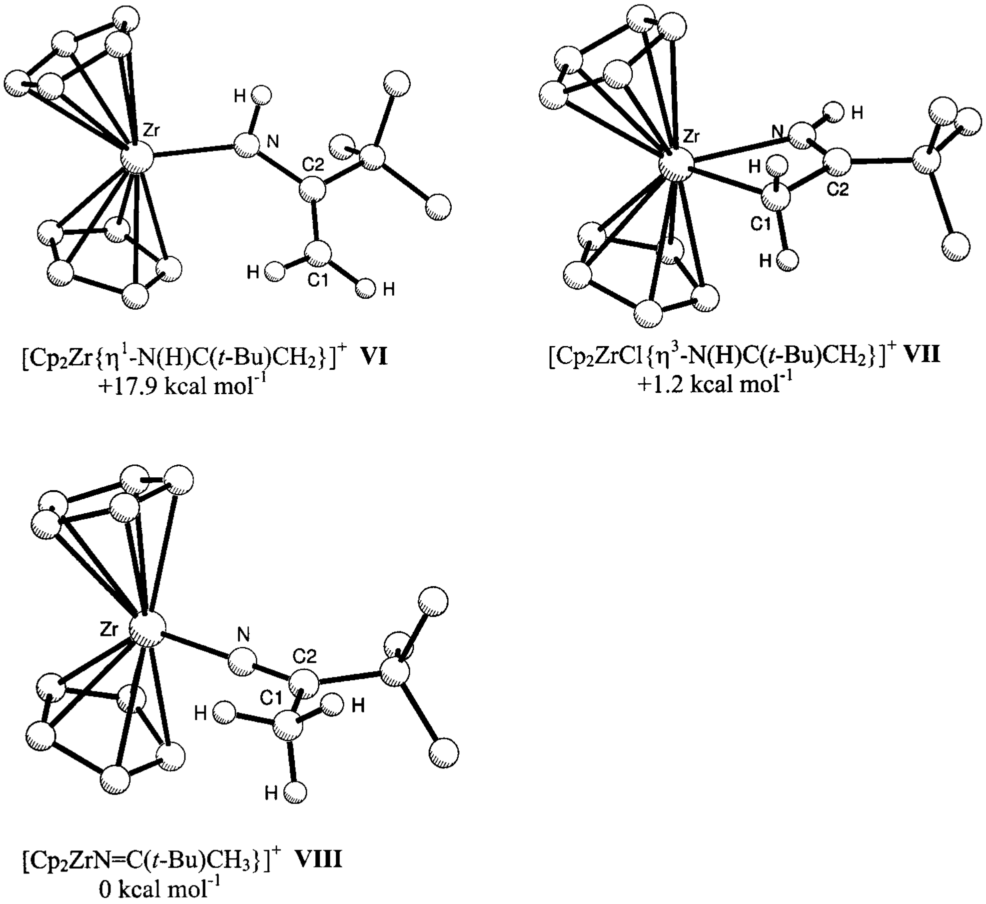


Figure 4. Energy minimum calculated structures **VI**–**VIII** showing relative energy values.

represents a reversal in the order of stability and a significantly greater energy differential, when compared to that previously calculated[9] for the lithium counterparts: calculations performed at the HF/6-31G* level of theory predicted that the lithium η^3-azaallyl model [LiN(H)C(*t*-Bu)CH$_2$] is 3.9 kcal mol^{-1} more stable than its ketimide isomer [LiN=C(*t*-Bu)CH$_3$], although the margin of difference reduces to only 0.08 kcal mol^{-1} when each is solvated by one HMPA molecule. In the Zr case, a major contributory factor in the pronounced preference for **I** over **II** relates to the strength of the Zr–N bond in **I**, which is 0.069 Å shorter than its counterpart in **II**. This high bond strength is facilitated by the near linearity (175.72°) of the Zr–N–C2 linkage, which sets up a stabilizing π interaction (between a donor orbital on the iminic N atom and an acceptor orbital on the Zr atom) in addition to a Zr–N σ bond, as discussed in the previous section. In the Li case, with no suitable vacant orbitals of low enough energy available, it can be assumed that no equivalent π orbital overlap can operate and that the relative stability of the ketimido isomer is diminished accordingly.[17] As a consequence of the substantial bending of the Zr–N–C2 linkage (38.37° removed from perfect linearity), the π contribution to the Zr–N bonding in **II** is significantly reduced.

Looking at the bonding mode of the azaallyl unit in **I** (Figure 2), it is evident that it is η^1-bound to the zirconium center. In contrast, the azaallyl ligand in **1** is bound η^3 to the metal. Additional calculations were therefore performed in order to investigate the energies of structures with a η^3-azaallyl ligand bound to the zirconium center, i.e. [Cp$_2$ZrCl{η^3-N(H)C(*t*-Bu)CH$_2$}], as modeled by **IV** and **V**. Two isomers may exist, as the CH$_2$ group can either be syn (**IV**) or anti (**V**) to the chloride ligand. Figure 3 shows the geometry-optimized structures and the relative energies for **IV** and **V** (selected dimensions are given in Tables 2 and 3). Both **IV** and **V** proved to be less stable (by 11.0 and 7.1 kcal mol^{-1}, respectively) than the η^1-azaallyl system in **II**. This destabilization can mainly be attributed to an increase in steric crowding on moving from a η^1 to a η^3 ligand coordination.

Relevant to the performance of systems of this type as olefin polymerization catalysts, two calculations were performed to investigate the energetics of the cationic (triligated) azaallyl species [Cp$_2$Zr{η^1-N(H)C(*t*-Bu)CH$_2$}]$^+$ (**VI**) and [Cp$_2$Zr{η^3-N(H)C(*t*-Bu)CH$_2$}]$^+$ (**VII**) (Figure 4; selected dimensions are given in Tables 2 and 3). As expected, **VII** is the more stable isomer by 16.7 kcal mol^{-1}, since the metal center can gain the electronic benefit of the chelating N/C bound ligand without the steric constraints imposed by a tetracoordinate geometry, as was the case in **IV** and **V**.

A calculation was carried out in order to determine the relative energy of the cationic ketimide species [Cp$_2$ZrN=C(*t*-Bu)CH$_3$]$^+$ (**VIII**). This allows for an estimation of the degree to which the energetic preference for the ketimide **I** is due to steric factors. The results from the

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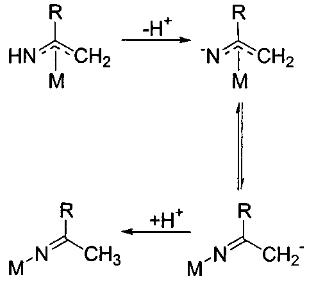
[17] Transfer of a 1-azaallyl unit to an aluminum center has been shown to occur with both retention of this conformation and also isomerization to the ketimide: Bourget, L.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1999**, 2645.

Scheme 2. Possible Mechanism of the Azaallyl to Ketimide Isomerization (Where M is a Generic Term for Any Metal)



calculations indicate that the ketimide form **VIII** is still more stable (albeit by a relatively small margin of 1.2 kcal mol^{-1}) than the η^3-azaallylic isomer **VII**. One can conclude that the σ/π-bonded Zr−N interaction is electronically preferred to a chelating N/C−Zr interaction when steric factors are minimized. The strong heteroallene-type bonding in **VIII** is reflected in an extremely short Zr−N bond length of 1.968 Å (0.286 Å shorter than that in **VII**) and a Zr−N−C2 bond angle of 178.69°. It is pleasing to note that these calculations are consistent with the ^{1}H NMR spectroscopic experiments, which demonstrated that the ketimide linkage of **4** remains intact upon methide abstraction with the Lewis acid $B(C_6F_5)_3$.

Finally, the mechanism of the azaallyl to ketimide rearrangement reaction was investigated. A concerted process where the proton is directly transferred from the NH to the CH_2 unit appears unlikely, since the energy barrier for this transformation has been predicted by calculation to be prohibitively high (67.7 kcal mol^{-1} for the lithiated ligand).[9] Another possibility is a process involving proton elimination from the azaallylic NH followed by addition of the proton to the carbanionic CH_2 (Scheme 2). This mechanism is supported by calculations on the model anion $[H_2ZrNC(H)CH_2]^-$ (**IX**), and they indicate that the ketimide anion is stable, whereas no minima could be obtained for its azaallylic isomer (which rearranges on optimization to the ketimido structure). As before, this is due to the aforementioned stability of the Zr−N=C linkage. This anion, **IX**, has its charge localized on the carbanionic CH_2 (the Mulliken charges have been calculated to be +0.17 and −0.61 on the carbons N−C(H) and CH_2, respectively), and this will undoubtedly facilitate the formation of a new C−H bond in the proton rearrangement reaction. In contrast, each of the lithium variants $[LiN{=}C(H)CH_2]^-$ (**X**) and $[Li\{\eta^3{-}NC(H)CH_2\}]^-$ (**XI**) gave a different geometry-optimized minimum, with the azaallylic isomer being more stable by 8.6 kcal mol^{-1}. In this instance the electrostatic bonding nature of lithium determines the relative stability of the isomers.

Polymerization Studies. The ketimide complexes **3** and **4** were tested for ethylene polymerization activity with a methylaluminoxane (MAO) cocatalyst (Al:Z = 1000:1). Additionally, **4** was tested for ethylene polymerization activity with a $B(C_6F_5)_3$ activator, both with and without the addition of *i*-Bu_3Al. Complex **2** was used as a standard catalyst for comparison. The polymerization results are summarized in Table 4.

The catalytic activity of the MAO-activated ketimides **3** and **4** was found to be slightly lower than that of the parent dichloride **2**, at both 1 and 5 atm ethylene pressure. This is probably a consequence of the stronger metal−anion bonding in **3** and **4** compared to that in **2** (Zr−N versus Zr−Cl), hindering the formation of a catalytically active cation. In this context it should be noted that highly active ethylene polymerization catalysts have recently been prepared using the related phosphinimide ligands ($R_3P{=}N^-$) as steric equivalents to Cp.[18]

Polymerization using $\mathbf{4}/B(C_6F_5)_3$ was not observed at either low or high ethylene pressures (1 and 5 atm, respectively), unless combined with the alkylaluminum *i*-Bu_3Al. Since the ^{1}H NMR spectroscopic studies of the $\mathbf{4}/B(C_6F_5)_3$ system indicate methide abstraction, it appears that insertion of ethylene into the Zr−N bond does not occur. However, in combination with either a MAO or a *i*-$Bu_3Al/B(C_6F_5)_3$ mixture, **4** becomes an active catalyst, presumably via replacement of the ketimide by an alkyl group.

Experimental Section

All manipulations were carried out under a protective argon atmosphere using standard Schlenk techniques.[19] Argon was purified by passage over 4 Å molecular sieves and BTS catalyst. All solvents were distilled over sodium/benzophenone until blue, degassed, and stored over 4 Å molecular sieves prior to use. All glassware was flame-dried under vacuum before use. Trimethylacetonitrile and hexamethylphosphoramide (HMPA) were distilled and stored over 4 Å molecular sieves prior to use. MeLi was standardized by titration with diphenylacetic acid[20] before use. Zirconocene dichloride was purchased from Lancaster and used as received. *i*-Bu_3Al was purchased from Aldrich as a 1 M solution in toluene and used as received. The lithium azaallyl complex **1**[9] was prepared by literature methods. Deuterated solvents for NMR studies were stored over 4 Å molecular sieves under an argon atmosphere. Ethylene was purchased from Air Products. MAO was purchased from Witco as a 10 wt % solution in toluene and used as received. $B(C_6F_5)_3$ was purchased from Boulder Scientific and used without further purification. The molecular weight of polyethylene was determined by gel permeation chromatography (GPC) using a Waters 150CV GPC system with trichlorobenzene diluent. The NMR spectra were recorded on a Bruker AMX 400 spectrometer at 25 °C. The IR spectra were recorded on a Mattson Galaxy Series FTIR 3000 spectrometer, and elemental analyses were carried out on a Perkin-Elmer 240 elemental analyzer.

Synthesis of $[Cp_2Zr(Cl)N{=}C(t\text{-}Bu)CH_3]$ (3). Compound **2** (2.92 g, 10 mmol) was suspended in 10 mL of toluene in a Schlenk tube and cooled to −78 °C in a dry ice/acetone bath. Compound **1** was dissolved in 10 mL of toluene and added to the suspension of **2** via cannula tubing. The mixture was stirred at −78 °C for 30 min and warmed to 25 °C to afford a cloudy orange mixture. This was stirred for a further 2 h at ambient temperature and filtered through Celite. The resulting orange solution was reduced in volume to ca. 12 mL, and on standing at −20 °C overnight, small crystalline needles of **3** were deposited. Yield: 54% (nonoptimized, first crystalline batch). Mp: 162−164 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 5.82 (s, 10H, *H* Cp), 1.46 (s, 3H, CH_3), 1.00 (s, 9H, $C(CH_3)_3$).

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[18] (a) Stephan, D. W.; Stewart, J. C.; Guérin, F.; Spence, R. E. v. H.; Xu, W.; Harrison, D. G. *Organometallics* **1999**, *18*, 1116. (b) Stephan, D. W.; Guérin, F.; Spence, R. E. v. H.; Koch, L.; Gao, X.; Brown, S. J.; Swaby, J. W.; Wang, Q.; Xu, W.; Zoricak, P.; Harrison, D. G. *Organometallics* **1999**, *18*, 2046.

[19] Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*; Wiley: New York, 1986.

[20] Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.

Table 4. Polymerization of Ethylene Catalyzed by 2−4[a]

catalyst	MAO/Zr[b]	$B(C_6F_5)_3$/Zr[b]	^{i}Bu$_3$Al/Zr[b]	$P_{ethylene}$[c]	yield[d]	activity[e]	M_w	M_w/M_n
2	1000			1	8.23	4.06	71 000	2.29
3	1000			1	2.22	1.09	688 000	2.74
4	1000			1	0.81	0.40	664 000	2.60
2	1000			5	10.80	5.33	49 000	5.16
4	1000			5	4.73	2.33	560 000	2.01
4		1		1	0	0		
4		1		5	0	0		
4		1	1	1	6.62	3.27	448 000	2.64
4		1	10	1	5.83	3.08	458 000	2.37

[a] Conditions: Zr, 20 μmol; toluene, 50 mL; T, 20 °C; $t = 1$ h. [b] Amount in mol equiv. [c] In atm. [d] In g. [e] In 10^5 g mol^{-1} h^{-1} atm^{-1}.

^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): δ 184.03 (N=*C*), 110.92 (*C* Cp), 37.43 (*C*(CH$_3$)$_3$), 28.76 (C(*C*H$_3$)$_3$), 24.58 (*C*H$_3$). Anal. Found (calcd): C, 54.4 (54.1); H, 6.8 (6.2); N, 3.6 (3.9). IR: C=N, 1679 cm^{-1}.

Synthesis of [Cp$_2$Zr(Me)N=C(*t*-Bu)CH$_3$] (4). MeLi (6.25 mL, 10 mmol of a 1.6 M solution in Et$_2$O) was added dropwise to a Schlenk tube containing a solution of **3** (3.55 g, 10 mmol) in 10 mL of toluene which was cooled to −78 °C. The mixture was stirred at this temperature for 30 min before warming to 25 °C and stirred for a further 4 h. The resultant yellow suspension was filtered through Celite, and all the solvent was removed in vacuo to give **4** as a yellow powder. Yield: 63%. Mp: 87 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 5.67 (s, 10H, *H* Cp), 1.63 (s, 3H, C*CH$_3$*), 0.95 (s, 9H, C(C*H*$_3$)$_3$), 0.06 (s, 3H, Zr−C*H*$_3$). ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): δ 181.27 (N=*C*), 111.60 (*C* Cp), 42.48 (*C*(CH$_3$)$_3$), 28.53 (C(*C*H$_3$)$_3$), 25.53 (C*C*H$_3$), 13.68 (Zr−*C*H$_3$). Anal. Found (calcd): C, 57.4 (61.1); H, 6.2 (7.5); N, 3.9 (4.2). IR: C=N, 1689 cm^{-1}.

X-ray Crystallography. Data for **3** were recorded on a Rigaku AFC7S diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 69$ Å). Absorption corrections were applied on the basis of azimuthal scans of several reflections, and data were corrected for Lorenz and polarization effects. The structure was solved by Patterson methods and refined on F values to convergence. Non-hydrogen atoms were given anisotropic displacement parameters, and H atoms were refined isotropically.

Crystallographic Data for 3: $C_{16}H_{22}ClNZr$, $M_r = 355.03$, orthorhombic, $P2_12_12_1$, $a = 11.812(3)$ Å, $b = 18.296(4)$ Å, $c = 7.486(1)$ Å, $V = 1617.9(5)$ Å^3, $D_c(Z = 4) = 1.46$ g cm^{-3}, $\mu = 0.831$ mm^{-1}, $F(000) = 728$, $T = 123$ K, crystal dimensions 0.45 × 0.20 × 0.15 mm, $\theta_{max} = 27.5°$, 4328 reflections measured, 3737 unique reflections, $R_{int} = 0.020$, R1 = 0.024, wR2 = 0.032 (based on 3147 observed reflections with $I > 2\sigma(I)$ and 260 refined parameters), GOF = 1.14, maximum/minimum electron density 0.17/−0.20 e Å^{-3}, $T_{max}/T_{min} = 0.688/0.599$.

Computational Details. The Gaussian 94 program, revision E.2, run on a Silicon Graphics Origin 200 workstation, was used for the calculations.[14] Geometry optimization was carried out at the HF/LanL2DZ level of theory. No constraints were used in any of the optimizations. Absolute energy values for the calculated molecules are as follows (hartrees): **I,** −733.852 95; **II**, −733.833 93; **III**, −733.851 85; **IV**, −733.816 50; **V**, −733.822 62; **VI**, −718.853 20; **VII**, −718.879 76; **VIII**, −718.881 80; **IX**, 179.668 15; **X**, 139.235 39; **XI**, 139.249 10.

Polymerization of Ethylene. Polymerization experiments were carried out on a Buchi miniclave rig, consisting of three 200 mL glass reactors (maximum $P = 10$ atm @ 200 °C) each fitted with magnetically coupled stirrers. The ethylene feed was controlled by a Bronkhorst Hi Tec mass flow controller/pressure controller (maximum flow rate 500 mL/min) to maintain constant pressure. The ethylene flow rate, vessel pressure, and temperature was logged on a PC using OpTo 22 software. Standard solutions of each catalyst and cocatalyst were made up in toluene to give concentrations of 3.42×10^{-2} M for **2**, 1.13×10^{-2} M for **3**, 1.20×10^{-2} M for **4,** 1.5 M for MAO, 9.78×10^{-3} M for $B(C_6F_5)_3$, and 0.01 M for *i*-Bu$_3$Al. All polymerization reactions were based on 20 μmol of Zr. A typical polymerization was as follows. The required aliquots of catalyst and cocatalyst were transferred via syringe into the glass reactor in a glovebox, and the total reaction volume was made up to 50 mL with toluene. The reactor was sealed, removed from the glovebox, and attached to the Buchi miniclave rig. After 1 h the polymerization was vented to the atmosphere and quenched with methanol. The mixture was poured into an acidified solution of methanol and stirred. The product polyethylene was filtered off, washed with methanol, and dried to constant weight under reduced pressure.

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Supporting Information Available: Listings giving crystallographic data for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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