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Synthesis of zirconocene amides and ketimides and an investigation into their ethylene polymerization activity

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Abstract

The zirconocene amide $[Cp_2Zr(Cl)N(CH_2Ph)_2]$ (**5**), and the zirconocene ketimides $[Cp_2Zr(Cl)N{=}C(Bu^t)Ph]$ (**7**), and $[Cp_2Zr(Cl)N{=}C(NMe_2)_2]$ (**9**), have been prepared by the transmetallation reactions between the appropriate lithiated organonitrogen compounds and zirconocene dichloride (**2**). In addition, their methylated derivatives $[Cp_2Zr(Me)N(CH_2Ph)_2]$ (**6**), $[Cp_2Zr(Me)N{=}C(Bu^t)Ph]$ (**8**), and $[Cp_2Zr(Me)N{=}C(NMe_2)_2]$ (**10**), have been prepared by the reaction of each of the complexes **5**, **7** and **9** with MeLi. Compounds **5** and **7** have been characterized by X-ray crystallography and the structure of the cocrystalline complex $[Cp_2Zr(Cl)N{=}C(Bu^t)Ph]_{0.4}[Cp_2Zr(Me)N{=}C(Bu^t)Ph]_{0.6}$ (**14**), has similarly been determined. All of the complexes **5**–**10** are active catalysts for the polymerization of ethylene in the presence of a MAO cocatalyst. In contrast, no polymer was produced using $B(C_6F_5)_3$ as an activator, indicating that direct alkene insertion into the Zr–N bonds does not occur.

Keywords: Zirconium; Amides; Ketimides; Catalysis; Polymerization

1. Introduction

Over the past decade there has been enormous academic and industrial interest in the design and use of Group 4 compounds for use in polyolefin catalysis [1,2]. Within this area complexes containing nitrogen-based ligands are currently receiving increasing attention [3]. Amide units may be used as alternatives to the more conventional cyclopentadienyl ligand, allowing the use of di- or tridentate ligand configurations [4–6]. Furthermore, zirconocene complexes bearing chelating diamido ligands have been prepared (Scheme 1) [7].

For our part, we recently reported the synthesis of the zirconocene ketimide complex $[Cp_2Zr(Cl)N{=}C(Bu^t)CH_3]$ (**1**), via the metathetical reaction between zirconocene dichloride (**2**), and the 1-azaallyl compound $[CH_2(Bu^t)CN(H)Li \cdot HMPA]$ (**3**) [8]. During the metathesis reaction the 1-azaallyl unit isomerizes to its ketimido variant through a 1,3 sigmatropic rearrangement (Scheme 2) [9]. Computational studies on this system suggest that the isomerization process is energetically favoured due to the formation of strong heteroallenic (Zr–N–C) bonding [10].

Complex **1** was found to polymerize ethylene in the presence of a MAO cocatalyst. Furthermore, the methylated analogue of **1**, $[Cp_2Zr(Me)N{=}C(Bu^t)CH_3]$ (**4**), was also found to be an active ethylene polymerization catalyst in the presence of either MAO or a mixed $B(C_6F_5)_3/Bu^i_3Al$ cocatalyst. Solution NMR spectroscopic studies indicated that addition of the Lewis acid $B(C_6F_5)_3$ to **4** results in methide abstraction, and formation of a $[Cp_2ZrN{=}C(Bu^t)CH_3]^+[MeB(C_6F_5)_3]^-$ ion pair. However, the resulting zirconocene ketimide cation was found to be inactive towards ethylene polymerization unless Bu^i_3Al was also present.

This paper extends our studies into the use of ketimide ligands in these systems, and for comparison details the effects of using an amide ligand as an alternative source of a Zr–N linkage. Herein, we report the synthesis and characterization of the zirconocene amides $[Cp_2Zr(Cl)N(CH_2Ph)_2]$ (**5**), and $[Cp_2Zr(Me)N$-

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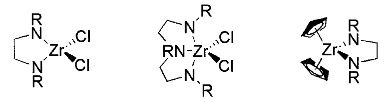
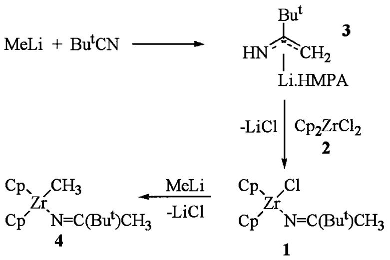


Scheme 1. Various structural arrangements of zirconium amides.



Scheme 2.

$(CH_2Ph)_2]$ (**6**), and the zirconocene ketimides $[Cp_2Zr(Cl)N{=}C(Bu^t)Ph]$ (**7**), $[Cp_2Zr(Me)N{=}C(Bu^t)Ph]$ (**8**), $[Cp_2Zr(Cl)N{=}C(NMe_2)_2]$ (**9**), and $[Cp_2Zr(Me)N{=}C(NMe_2)_2]$ (**10**) (**9** and **10** can also be described as guanidides) and investigate their utility as catalysts for ethylene polymerization.

2. Experimental

2.1. General

All manipulations were carried out under a protective Ar atmosphere using standard Schlenk techniques [11]. Argon was purified by passage over 4 Å molecular sieves and BTS catalyst. All solvents were distilled over Na–benzophenone until blue, degassed and stored over 4 Å molecular sieves prior to use. All glassware was flame-dried under vacuum before use. MeLi was standardized by titration with diphenylacetic acid before use [12]. Zirconocene dichloride was purchased from Lancaster and used as received. Bu^i_3Al was purchased from Aldrich as a 1 M solution in $C_6H_5CH_3$ and used as received. The lithium amide and ketimide complexes were prepared by literature methods [13–15]. Deuteriated solvents for NMR studies were stored over 4 Å molecular sieves under an Ar atmosphere. Ethylene was purchased from Air Products. MAO was purchased from Witco as a 10 wt.% solution in $C_6H_5CH_3$ 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 $C_6H_3Cl_3$ 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 2400 elemental analyzer.

2.2. Syntheses

2.2.1. $[Cp_2Zr(Cl)N(CH_2Ph)_2]$ (5)

Zirconocene dichloride (1.46 g, 5 mmol) and 40 ml of $C_6H_5CH_3$ were added to a Schlenk tube and the resultant suspension was then cooled to −78 °C. Dibenzylamidolithium (1.02 g, 5 mmol) was added via a solids addition tube and the mixture was then stirred at −78 °C for 30 min, before it was allowed to warm to ambient temperature. The suspension was stirred at ambient temperature for 16 h, and then filtered through a pad of Celite to afford a clear solution. Cooling of the solution to −20 °C yielded **5** as yellow crystalline needles. Yield: 1.02 g, 47%. M.p. 178–180 °C. Anal. Calc. for $C_{24}H_{24}ClNZr$: C, 63.6; H, 5.3; N, 3.1. Found: C, 63.6; H, 5.9; N, 2.6%. FTIR (Nujol mull, cm^{-1}): 1600w, 1343sh, 1312sh, 1157w, 1087m, 1022m, 927w, 811w. Upon exposure to air the characteristic signal for the free amine at 3334 cm^{-1}, ν(N–H), was produced. ^1H-NMR (400.13 MHz, d_6-C_6H_6): δ 7.20–7.14 (10H, series of overlapping signals, *o*-, *m*-, *p-Ph*), 5.81 (10H, s, η^5-C_5H_5), 4.24 (4H, s, $PhCH_2$). ^{13}C-NMR (100.63 MHz, d_6-C_6H_6): δ 140.24 (*i-C*), 129.28–129.15 (series of overlapping signals, *o*-, *m-Ph*), 127.69 (*p-Ph*), 113.47 (η^5-C_5H_5), 60.69 ($PhCH_2$).

2.2.2. $[Cp_2Zr(Me)N(CH_2Ph)_2]$ (6)

Compound **5** (4.53 g, 10 mmol) and 30 ml of $C_6H_5CH_3$ were added to a Schlenk tube and the mixture was then cooled to −78 °C. MeLi (6.85 ml of a 1.46 M solution in ether, 10 mmol) was added to afford a yellow suspension. The mixture was then stirred at −78 °C for 30 min before it was allowed to warm to ambient temperature. The suspension was stirred at ambient temperature for 2 h, after which 20 ml of $C_6H_5CH_3$ was added as diluent. The mixture was then filtered through a pad of Celite to afford a yellow solution. All solvent was removed under reduced pressure to yield the title compound as a yellow powder. Yield: 3.32 g, 77%. M.p. 168–170 °C. Anal. Calc. for $C_{25}H_{27}NZr$: C, 69.4; H, 6.3; N, 3.2. Found: C, 68.8; H, 6.3; N, 3.9%. FTIR (Nujol mull, cm^{-1}): 1620w, 1382w, 1150m, 1064s, 941m. ^1H-NMR (d_6-C_6H_6): δ 7.35–7.01 (10H, series of overlapping signals, *o*-, *m*-, *p-Ph*), 5.71 (10H, s, η^5-C_5H_5), 4.17 (4H, s, $PhCH_2$), 0.31 (3H, s, Zr–CH_3). ^{13}C-NMR (100.63 MHz, d_6-C_6H_6): δ 142.50 (*i-Ph*), 130.05 (*o-Ph*), 128.89 (*m-Ph*), 127.39 (*p-Ph*), 110.98 (η^5-C_5H_5), 56.04 ($PhCH_2$), 14.89 (Zr–CH_3).

2.2.3. $[Cp_2Zr(Cl)N{=}C(Bu^t)Ph]$ (7)

Zirconocene dichloride (2.92 g, 10 mmol) and 40 ml of $C_6H_5CH_3$ were added to a Schlenk tube. The lithium ketimide $[Ph(Bu^t)C{=}NLi]$ (1.67 g, 10 mmol) was added to the mixture via a solids addition tube. The resultant orange suspension was stirred at ambient temperature for 4 h, and then filtered through a pad of Celite to afford a clear orange solution. The filtrate was concentrated under reduced pressure to ca. 15 ml. Cooling of the solution to −20 °C yielded the title compound as large orange crystalline needles. Yield: 3.08 g, 74%. M.p. 150–152 °C. Anal. Calc. for $C_{21}H_{24}ClNZr$: C, 60.5; H, 5.7; N, 3.4. Found: C, 60.5; H, 6.0; N, 3.5%. FTIR (Nujol mull, cm^{-1}): 2059s, 1741w, 1598m, 1495w, 1311m, 971m, 804m, 1675s ν(C=N). Upon exposure to air the characteristic signal for the free amine at 3340 cm^{-1}, ν(N–H), was produced. ^{1}H-NMR (400.13 MHz, d_8-$C_6H_5CH_3$): δ 7.11 (2H, t, *m-Ph*), 7.05 (1H, t, *p-Ph*), 6.97 (2H, d, *o-Ph*), 5.75 (10H, s, η^5-C_5*H*$_5$), 1.15 (9H, s, NC–C(C*H*$_3$)$_3$). ^{13}C-NMR (100.63 MHz, d_8-$C_6H_5CH_3$): δ 159.78 (N=*C*), 137.46 (*i-Ph*), 128.84 (*m-Ph*), 128.17 (*p-Ph*), 127.94 (*o-Ph*), 110.66 (η^5-*C*$_5$H$_5$), 43.27 (NC–*C*(CH$_3$)$_3$), 29.09 (NC–C(*C*H$_3$)$_3$).

2.2.4. [$Cp_2Zr(Me)N{=}C(Bu^t)Ph$] (**8**)

Compound **7** (4.17 g, 10 mmol) and 40 ml of $C_6H_5CH_3$ were added to a Schlenk tube and the mixture was then cooled to −78 °C. MeLi (6.25 ml of a 1.60 M solution in ether, 10 mmol) was added and the mixture was then stirred at −78 °C for 30 min, before it was allowed to warm to ambient temperature. The resultant orange suspension was stirred at ambient temperature for 20 h, after which 10 ml of $C_6H_5CH_3$ was added as diluent. The mixture was then filtered through a pad of Celite to afford an orange solution. All the solvent was removed under reduced pressure to yield the title compound as an orange powder. Yield: 3.08 g, 81%. M.p. 123–125 °C. Anal. Calc. for $C_{22}H_{27}NZr$: C, 66.7; H, 6.8; N, 3.5. Found: C, 67.8; H, 6.1; N, 3.2%. FTIR (Nujol mull, cm^{-1}): 1680s ν(C=N). ^{1}H-NMR (400.13 MHz, d_6-C_6H_6): δ 7.12–7.09 (5H, series of overlapping signals, *o-*, *m-*, *p-Ph*), 5.67 (10H, s, η^5-C_5*H*$_5$), 1.16 (9H, s, NC–C(C*H*$_3$)$_3$), 0.14 (3H, s, Zr–C*H*$_3$). ^{13}C-NMR (100.63 MHz, d_6-C_6H_6): δ 161.14 (N=*C*), 138.51 (*i-Ph*), 127.61 (*m-Ph*), 126.56 (*p-Ph*), 124.47 (*o-Ph*), 108.70 (η^5-*C*$_5$H$_5$), 40.13 (NC–*C*(CH$_3$)$_3$), 29.69 (NC–C(*C*H$_3$)$_3$), 15.74 (Zr–*C*H$_3$).

2.2.5. [$Cp_2Zr(Cl)N{=}C(NMe_2)_2$] (**9**)

Zirconocene dichloride (2.92 g, 10 mmol) and 50 ml of $C_6H_5CH_3$ were added to a Schlenk tube. The lithium ketimide [$(Me_2N)_2C{=}NLi$] (1.21 g, 10 mmol) was added to the mixture via a solids addition tube. The resultant suspension was stirred at ambient temperature for 6 h, and then filtered through a pad of Celite to afford a brown solution. The brown filtrate was concentrated under reduced pressure to ca. 20 ml. Cooling of the solution to −20 °C yielded the title compound as large brown crystalline blocks. Yield: 2.19 g, 59%. M.p. 154 °C. Anal. Calc. for $C_{15}H_{22}ClN_3Zr$: C, 48.6; H, 6.0; N, 11.3. Found: C, 48.3; H, 6.0; 11.1%. FTIR (Nujol mull, cm^{-1}): 1587s ν(C=N). Upon exposure to air the characteristic signal for the free amine at 3217 cm^{-1}, ν(N–H), was produced. ^{1}H-NMR (400.13 MHz, d_6-C_6H_6): δ 5.98 (10H, s, η^5-C_5*H*$_5$), 2.43 (12H, s, N–C*H*$_3$). ^{13}C-NMR (100.63 MHz, d_6-C_6H_6): δ 163.45 (N=*C*), 112.24 (η^5-*C*$_5$H$_5$), 40.62 (N–*C*H$_3$).

2.2.6. [$Cp_2Zr(Me)N{=}C(NMe_2)_2$] (**10**)

Compound **9** (3.71 g, 10 mmol) and 40 ml of $C_6H_5CH_3$ were added to a Schlenk tube and the mixture was then cooled to −78 °C. MeLi (6.25 ml of a 1.60 M solution in ether, 10 mmol) was added and the resultant suspension was then stirred at −78 °C for 30 min, before it was allowed to warm to ambient temperature. The resultant brown suspension was stirred at ambient temperature for 6 h, after which 10 ml of $C_6H_5CH_3$ was added as diluent. The mixture was then filtered through a pad of Celite to afford a brown solution. All solvent was removed under reduced pressure to yield the title compound as a brown powder. Yield: 2.19 g, 59%. M.p. 108–110 °C. Anal. Calc. for $C_{16}H_{25}N_3Zr$: C, 54.8; H, 7.2; N, 12.0. Found: C, 54.8; H, 5.8; N, 11.0%. FTIR (Nujol mull, cm^{-1}): 1608s ν(C=N). ^{1}H-NMR (400.13 MHz, d_6-C_6H_6): δ 5.76 (10H, s, η^5-C_5*H*$_5$), 2.42 (12H, s, N–C*H*$_3$), 0.20 (3H, s, Zr–C*H*$_3$). ^{13}C-NMR (100.63 MHz, d_6-C_6H_6): δ 161.96 (N=*C*), 109.49 (η^5-*C*$_5$H$_5$), 40.61 (N–*C*H$_3$), 15.77 (Zr–*C*H$_3$).

2.2.7. [$Cp_2Zr(Cl)N{=}C(Bu^t)Ph$]$_{0.4}$[$Cp_2Zr(Me)N{=}C(Bu^t)Ph$]$_{0.6}$ (**14**)

Procedure in Section 2.2.4 was followed but with the exception of 1 h stirring at ambient temperature cf 20 h. ^{1}H-NMR spectroscopy revealed the product to be a 40:60 mixture of [$Cp_2Zr(Cl)N{=}C(Bu^t)Ph$]–[$Cp_2Zr(Me)N{=}C(Bu^t)Ph$]. A single crystal from this reaction was crystallographically characterized and found to be a cocrystal of [$Cp_2Zr(Cl)N{=}C(Bu^t)Ph$] and [$Cp_2Zr(Me)N{=}C(Bu^t)Ph$] in a 40:60 ratio. ^{1}H-NMR (400.13 MHz, d_6-C_6H_6): δ 7.17–6.96 (8H, series of overlapping signals, *o-*, *m-*, *p-Ph*, **7**; *o-*, *m-*, *p-Ph*, **8**), 5.79 (6.5H, s, η^5-C_5*H*$_5$, **7**), 5.63 (10H, η^5-C_5*H*$_5$, **8**), 1.17 (6H, s, NC–C(C*H*$_3$)$_3$, **7**), 1.11 (9H, s, NC–C(C*H*$_3$)$_3$, **8**), 0.09 (3H, s, Zr–C*H*$_3$).

2.3. X-ray crystallography

Data for compounds **5**, **7** and **14** were recorded on a Rigaku AFC7S diffractometer with graphite monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71069$ Å). Absorption corrections were applied based on azimuthal scans of several reflections and data were corrected for Lp effects. All structures were refined to convergence against F^2 using the SHELXL-97 program. In **7** one Cp ring was modelled as disordered over two sites. Although the displacement parameters of several other of the Cp rings indicated considerable motion this was not modelled. Full details of refinement parameters and crystal data are given in Table 1.

Table 1
Crystallographic parameters for **5**, **7** and **14**

Compound	**5**	**7**	**14**
Chemical formula	$C_{24}H_{24}ClNZr$	$C_{21}H_{24}ClNZr$	$C_{21.56}H_{25.69}NCl_{0.44}Zr$
Formula weight	453.11	417.08	405.60
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	16.013(3)	7.962(5)	8.005(1)
b (Å)	8.093(2)	11.412(4)	11.420(2)
c (Å)	16.317(3)	21.040(6)	21.068(8)
β (°)	100.12(2)	92.02(4)	92.204(6)
V (Å^3)	2081.7(8)	1911(1)	1924.5(4)
Z	4	4	4
D_{calc} (g cm^{-3})	1.446	1.450	1.400
μ (mm^{-1})	0.665	0.717	0.634
Crystal size (mm)	0.40 × 0.25 × 0.15	0.45 × 0.25 × 0.20	0.70 × 0.48 × 0.28
Reflections collected	4959	4710	6511
Independent reflections	4791	4396	6125
R_{int}	0.0502	0.0614	0.0254
R	0.0396	0.0651	0.0280
wR_2	0.1020	0.1869	0.0755

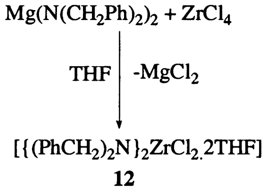
2.4. Polymerization of ethylene

Polymerization experiments were carried out on a Buchi miniclave rig, consisting of three 200 ml glass reactors (max $P = 10$ atm at 200 °C) each fitted with magnetically coupled stirrers. The ethylene feed was controlled by a Bronkhorst Hi Tec mass flow controller/pressure controller (max flow rate 500 ml min^{-1}) 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 $C_6H_5CH_3$ to give concentrations of 3.42×10^{-2} M for **2**, 8.84×10^{-3} M for **5**, 9.26×10^{-3} M for **6**, 1.92×10^{-2} for **7**, 2.02×10^{-2} for **8**, 2.16×10^{-2} for **9**, 2.29×10^{-2} for **10**, 1.50 M for MAO, 9.78×10^{-3} M for $B(C_6F_5)_3$ and 0.01 M for Bu^i_3Al. 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 glove-box and the total reaction volume made up to 50 ml with $C_6H_5CH_3$. The reactor was sealed, removed from the glove-box and attached to the Buchi miniclave rig. After 1 h the polymerization was vented to the atmosphere and quenched with MeOH. The mixture was poured into an acidified solution of MeOH and stirred. The polyethylene produced was filtered off, washed with MeOH and dried to constant weight under reduced pressure.

3. Results and discussion

3.1. Syntheses

Complexes **5**, **7** and **9** were prepared in a similar manner via the transmetallation reaction of **2** with one molar equivalent of the appropriate lithiated amide or ketimide. Regarding the synthesis of metal amide **5**, this was prepared by the equimolar reaction of lithium dibenzylamide, $[(PhCH_2)_2NLi]$ (**11**), with **2**. Attempts to perform a second amination using two molar equivalents of **11** proved unsuccessful, with only **5** isolated as product. However, we have recently reported that two dibenzylamido units may be transferred onto a zirconium center using the less sterically hindered $ZrCl_4$ as a reagent, to yield the bis-solvated complex $[\{(CH_2Ph)_2N\}_2ZrCl_2\cdot 2THF]$ (**12**) [16]. This reaction was completed using the magnesium bisamide $[Mg(N(CH_2Ph)_2)_2]$ (**13**), as the amide transfer reagent, Eq. (1) [17].



$$Mg(N(CH_2Ph)_2)_2 + ZrCl_4 \xrightarrow[\text{THF}]{-MgCl_2} \underset{\mathbf{12}}{[\{(PhCH_2)_2N\}_2ZrCl_2.2THF]} \qquad (1)$$

However, reaction of **13** with **2** again only resulted in the preparation of the monosubstituted product **5**, regardless of the stoichiometry of the amide used. In comparison, Otero reported that the equimolar reaction of **2** with the lithium amide $[LiN(H)C_6H_4$-*o*-SMe$]$ consistently resulted in the formation of a mixture of the mono- and disubstituted zirconocenes $[Cp_2Zr(Cl)N(H)C_6H_4$-*o*-SMe$]$ and $[Cp_2Zr\{N(H)C_6H_4$-*o*-SMe$\}_2]$, respectively [18]. In this instance the reduced steric encumbrance of the primary amide unit clearly influences the outcome of the reaction. Nevertheless, the chloride of **5** was readily replaced by the small and highly nucleophilic methyl unit, on reaction with one molar equivalent of MeLi, to form **6**.

Complexes **7** and **9** were prepared by reaction of the respective lithium ketimides with **2**, and subsequently transformed into their methylated derivatives **8** and **10** upon reaction with MeLi. Interestingly, conversion of **7** to **8** was only partially completed after a period of 1 h, when a cocrystalline material, **14**, was formed. The ratio of the two components **7** and **8** was confirmed to be 40:60 by both ^{1}H-NMR spectroscopic studies and X-ray analysis of the crystalline sample produced. Allowing the reaction to proceed for 20 h resulted in complete conversion to the methylated complex **8**.

3.2. X-ray crystallographic studies

Previously, we used X-ray crystallography as a key tool in determining the mode of bonding within the Zr–N–C unit for compound **3** [8]. Hence, compounds **5**, **7** and **14** were characterized by X-ray crystallography for a similar purpose. As can be seen from Figs. 1–3, the compounds have similar gross structural features. Discussion of the detailed geometric parameters within **14** will be restricted due to the sample being a cocrystalline mixture, we note however that it is isostructural and isomorphous with **7**.

Table 2 lists the important bond lengths and angles associated with **5**, **7** and **14**. In all of the structures the cyclopentadienyl rings are η^5-bound to the metal, with Zr–Cp(centroid) distances in the narrow range 2.216–2.249 Å, which compares well with those of other $Cp_2Zr(IV)$ complexes [19]. Next, regarding the local bonding environment around the anionic nitrogen centers, it can be seen that the Zr–N bond distance in **5** (2.068(3)), is similar to those found in the related dibenzylamide **12** (2.038(3) and 2.049(2) Å) but is somewhat shorter than those found in other Zr(IV) amides [16]. More specifically, the Cambridge Structural Database indicates that the mean Zr–N bond distance in complexes of the type Cp_2ZrNR_2 is ca. 2.16 Å [20]. Furthermore, in both **5** and **12** the anionic nitrogens are essentially planar; with the sum of the angles surrounding N being 359.7° for **5**, and 359.9 and 360.0° for **12**. However, the individual angles at each N are highly distorted from the ideal trigonal planar arrangement of 120° and range between 109.5(3) and 135.3(2)° for **5** and between 112.5(3) and 124.4(2)° for **12**. Adopting the planar geometry may accentuate overlap of the lone pair on the nitrogen atom with an acceptor orbital on the zirconium center [21]. Overall, this result in a relatively strong metal–anion interaction, which rationalizes the short Zr–N distances, found in **5** and **12**.

The Zr–N bond in the ketimide **7** is significantly shorter than for the amide **5** (2.006(4) versus 2.068(3) Å) as would be expected due to the extra stabilization inferred by the heteroallenic bonding [10]. In both **7** and **14** the Bu^t groups of the ketimide ligands are orientated *syn* with respect to the chloride attached to the metal center. The remaining geometric parameters found in **7**, such as the almost linear Zr1–N1–C7 angle of 174.6(4)° and the N1–C7 bond distance of 1.268(6) Å, are similar to those found in **3** and are in accord with zirconium to ketimide bonding [8].

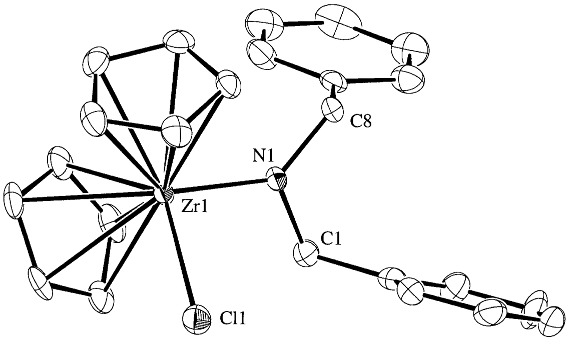


Fig. 1. ORTEP view of **5** with hydrogen atoms omitted for clarity, showing 50% thermal ellipsoids.

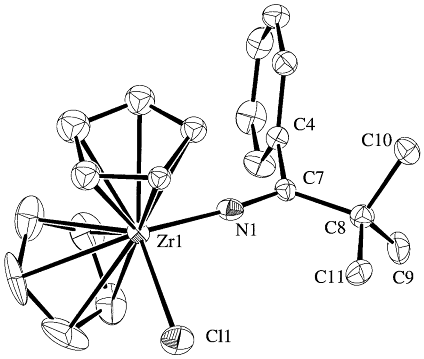


Fig. 2. ORTEP view of **7** with disordered Cp ring components and hydrogen atoms omitted for clarity. Drawn with 50% thermal ellipsoids.

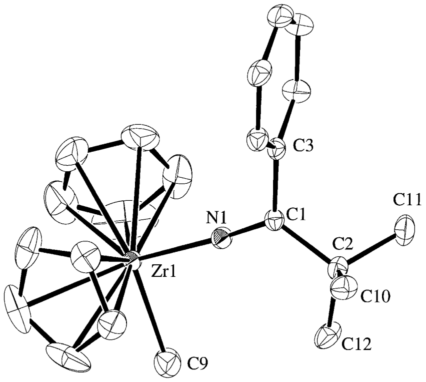


Fig. 3. ORTEP view of the methylated component of **14** with hydrogen atoms omitted for clarity, showing 50% thermal ellipsoids.

3.3. Polymerization studies

With complexes **5**–**10** in hand, we then wished to study their ability to catalyze polyethylene production. These studies were carried out using a MAO, $B(C_6F_5)_3$, or a mixed $Bu^i_3Al/B(C_6F_5)_3$ cocatalyst and the results of the polymerizations are given in Table 3.

All of the complexes were able to polymerize ethylene in the presence of a MAO cocatalyst. However, all of the Zr–N containing compounds are less active than Cp_2ZrCl_2 (with the singular exception of **6** at 5 atm pressure of ethylene). This is consistent with our previous study and suggests that the Zr–N linkages in

Table 2
Selected bond lengths (Å) and angles (°) for compounds **5**, **7** and **14**

Compound **5**		Compound **7**		Compound **14**	
Bond lengths					
Zr1–N1	2.068(3)	Zr1–N1	2.006(4)	Zr1–N1	2.0200(12)
Zr1–Cl1	2.493(1)	Zr1–Cl1	2.491(2)	Zr1–Cl1	2.500(5)
Zr1–Cp1	2.224	Zr1–Cp1	2.216	Zr1–C9	2.327(13)
Zr1–Cp2	2.249	N1–C7	1.268(6)	Zr1–Cp1	2.220
N1–C1	1.478(4)	C7–C8	1.529(6)	Zr1–Cp2	2.220
N1–C8	1.465(4)	C7–C4	1.509(6)	N1–C1	1.262(2)
C8–C9	1.521(5)	C8–C9	1.544(7)	C1–C3	1.508(2)
C1–C2	1.513(5)	C8–C10	1.541(6)	C1–C2	1.541(2)
		C8–C11	1.529(6)	C2–C10	1.537(2)
				C2–C11	1.538(2)
				C2–C12	1.529(2)
Bond angles					
Cl1–Zr1–N1	98.15(8)	Cl1–Zr1–N1	100.20(12)	Cl1–Zr1–N1	99.85(13)
Cp1–Zr1–Cp2	126.5	Cp1–Zr1–Cp2	132.2	C9–Zr1–N1	98.6(4)
Cp1–Zr1–Cl1	107.3	Cp1–Zr1–Cl1	106.1	Cp1–Zr1–Cp2	130.5
Cp2–Zr1–Cl1	104.7	Cp1–Zr1–N1	106.0	Cp1–Zr1–C9	108.9
Cp1–Zr1–N1	105.6	N1–C7–C4	119.4(4)	Cp2–Zr1–C9	103.2
Cp2–Zr1–N1	110.9	N1–C7–C8	122.2(4)	Cp1–Zr1–Cl1	103.3
Zr1–N1–C8	135.3(2)	C4–C7–C8	118.3(4)	Cp2–Zr1–Cl1	108.1
Zr1–N1–C1	114.9(2)	Zr1–N1–C7	174.6(4)	Cp1–Zr1–N1	107.5
C1–N1–C8	109.5(3)			Cp2–Zr1–N1	103.8
				N1–C1–C3	119.71(12)
				N1–C1–C2	122.31(13)
				C2–C1–C3	117.97(11)
				Zr1–N1–C1	174.42(11)

5–**10** are generally more difficult to cleave than the Zr–Cl bonds in **2** [8]. It is however interesting to note that the amides **5** and **6** show significantly greater activity than the ketimides **7**–**10**, which again indicates the presence of stronger Zr–N bonding in the latter set of compounds.

Table 3
Polymerization of ethylene catalyzed by **2** and **5**–**10** [a]

Catalyst	MAO/Zr molar equivalent	$B(C_6F_5)_3$/Zr molar equivalent	Bu^i_3Al/Zr molar equivalent	$P_{ethylene}$ [b]	Yield (g)	Activity [c]	M_w	M_w/M_n
2	1000	–	–	1	8.23	4.06	71 000	2.3
2	1000	–	–	5	10.80	5.33	49 000	5.2
5	1000	–	–	1	6.71	3.31	671 000	2.7
6	1000	–	–	1	2.65	1.31	659 000	2.3
6	1000	–	–	5	16.99	8.50	321 000	5.1
6	–	1	–	1	0	0	–	–
6	–	1	–	5	0	0	–	–
6	–	1	1	1	0	0	–	–
6	–	1	1	5	0	0	–	–
7	1000	–	–	1	0.64	0.32	390 000	2.3
8	1000	–	–	1	0.76	0.37	387 000	2.4
8	1000	–	–	5	4.87	2.40	488 000	2.4
8	–	1	–	5	0	0	–	–
8	–	1	1	5	0	0	–	–
9	1000	–	–	1	0.57	0.28	462 000	2.3
10	1000	–	–	1	0.49	0.24	454 000	2.3
10	1000	–	–	5	2.21	1.09	517 000	2.3
10	–	1	1	5	0.19	0.09	472 000	2.2

[a] Zr, 20 μmol, toluene = 50 ml, $T = 20$ °C, $t = 1$ h.
[b] atm.
[c] $\times 10^5$ g mol^{-1} h^{-1} atm^{-1}.

Replacing MAO with a $B(C_6F_5)_3$, or a mixed $Bu^i_3Al/B(C_6F_5)_3$ cocatalyst generally resulted in no polymer being produced, with only compound **10** showing any activity at all. These results are in stark contrast with the similar experiments carried out using the ketimide **4**, which showed significant activity using a mixed $Bu^i_3Al/B(C_6F_5)_3$ cocatalyst system (3.27×10^5 g mol^{-1} h^{-1} atm^{-1}). Monitoring the reaction of the methylated compounds **6**, **8** and **10** with the activator $B(C_6F_5)_3$ by ^{1}H-NMR spectroscopy indicated that the methyl group of each complex was indeed abstracted. This was evidenced by the significant downfield shifts in the respective CH_3 resonances (from δ 0.31 to 0.84 for **6**, 0.09 to 0.99 for **8** and 0.23 to 0.63 for **10**) upon addition of the activator to the compounds in d_6-benzene solutions.

Recently, the ability of monocyclopentadienyl–ketimide titanium(IV) complexes, for example $[CpTi(Me)_2N{=}C(Bu^t)Bu^t]$, to polymerize ethylene in combination with a $B(C_6F_5)_3$ cocatalyst has been investigated by Piers and coworkers [22]. These studies have established that the ketimide moiety remains intact upon reaction with the boron activator. Indeed, the stability of such linkages has led to them being proposed as alternative ancillary ligands to Cp. Additionally, Stephan has prepared the related phosphinimide complexes $[CpTi(N{=}PR_3)X_2]$, where R = Cy, Pr^i or Bu^t and X = Cl or Me, which utilize phosphinimide ligands $[N{=}PR_3]$ as steric mimics to Cp [23]. In combination with a MAO, $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ cocatalyst, some of these complexes were found to be active catalysts for the polymerization of ethylene.

Considering the results from these previous studies it is unsurprising that the ketimide complexes **6**, **8** and **10** are inactive for the polymerization of ethylene in combination with a $B(C_6F_5)_3$ cocatalyst. It also appears in all of the systems studied that direct insertion of ethylene into a Zr–N bond does not occur [24]. Therefore, activation of the amide and ketimide complexes by MAO is presumably made possible through replacement of the organonitrogen anion by an alkyl group from the cocatalyst. The anomalous activity of **4**, and also the very limited activity exhibited by **10**, using a mixed $Bu^i_3Al/B(C_6F_5)_3$ cocatalyst system may be caused by replacement of the ketimide unit by a Bu^i anion on the zirconium center. In these instances the possibility of the aluminium cocatalyst incorporating chelating ligands may drive the reaction. For **4** this would involve isomerization of the ketimide to 1-azaallyl ligand upon transfer to the aluminium, which has precedence in the literature [25]. For **10** this would simply be chelation of the ligand through a dimethylamido sidearm [26].

In summary, we have prepared and characterized a series of new nitrogen containing zirconocenes which display strong Zr–N bonding. These compounds are active catalysts for ethylene polymerization but only after replacement of the amide or ketimide component by an alkyl group from a cocatalyst.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 183178–183180 for compound **5**, **7** and **14**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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