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New η^2-Formamidinyl Zirconium Complexes: Synthesis, Characterization, and Catalytic Activity

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The new η^2-formamidinyl Zr complex $\overline{\mathrm{Zr(NMeCyc)_2[C(NAr)N}}\mathrm{MeCyc]_2}$ (**1**) (Ar = 2,6-dimethylphenyl, Cyc = cyclohexyl) was prepared upon double insertion of 2,6-dimethyl phenyl isocyanide in the Zr−N bond of $\mathrm{Zr(NMeCyc)_4}$. **1** was then converted into $\overline{\mathrm{Zr(OC_6F_5)_2[C(NAr)N}}\mathrm{MeCyc]_2}$ (**2**) and $\overline{\mathrm{ZrCl_2[C(NAr)N}}\mathrm{MeCyc]_2}$ (**3**) by reacting it with $\mathrm{C_6F_5OH}$ and $\mathrm{[NHMe_3]Cl}$, respectively. The crystal structure of **1** was established by X-ray analysis. All the complexes have been tested as catalysts for the polymerization of ethylene and 1-hexene in the presence of $\mathrm{[NHMe_2Ph][B(C_6F_5)_4]}$ as cocatalyst.

Introduction

Homogeneous catalysts for the olefin polymerization have known a huge development after the first Ziegler−Natta catalysts were discovered.[1] In the last 20 years group 4 element metallocenes offered to academic and industrial research simple, structurally well defined, and molecularly easily tunable models, very useful for the study of the olefin polymerization parameters controlling the activity, stereoselectivity, molecular weight, polydispersivity, and the microstructure of the polyolefins.[2] However, the increasing demand for more active and selective catalysts to provide greater control over the properties of the polymers and to achieve the possibility of introducing new monomer combinations is forcing the research toward a new generation of olefin polymerization catalysts that are an alternative to metallocene-based systems.

At present the replacement of the Cp ligand by a less electron-rich group would make the metal center more electrophilic, thus affording a potentially more active catalyst by favoring the coordination step of the Ziegler−Natta polymerization. In addition the ligand selection must satisfy steric requirements both to increase the stereoselectivity and to prevent termination reactions such as β-H elimination, which would compromise the chain growth. Nitrogen- and oxygen-based ligands to form electronically unsaturated early transition metal complexes have been reported to have more or less remarkable effects.[3]

We focused our interest on the synthesis of zirconium amides of general formula $\mathrm{ZrX_2(NRR')_2}$, to be used as starting material for the new zirconium diamido di(η^2-formamidinyl) species formed by double migratory insertion of isocyanides, CNR, into the Zr−N amide bonds.

To date, the insertion of CNR into early transition metal−amido bonds has been poorly investigated. To the best of our knowledge only one paper has appeared regarding specifically Zr−η^2-formamidinyl complexes starting from mixed silylamido−Zr compounds.[4]

Several years ago we started to study the reactivity of $\mathrm{ZrCl_2(NMe_2)_2{\cdot}2THF}$ with various isocyanides, and we isolated the products of double insertion of isocyanides, $\mathrm{ZrCl_2[C(NR)NMe_2]}$ (R = *p*-tolyl, *p*-MeO-$\mathrm{C_6H_4}$, *t*-Bu), as red-orange powders, which exhibited appreciable catalytic activity in the polymerization of ethylene by activation with $\mathrm{[NHMe_2Ph][B(C_6F_5)_4]}$ and/or MAO.[5] These results prompted us to extend our research to other analogous substrates containing differently substituted zirconium amides.

Here we report our most recent results on the synthesis of the new η^2-formamidinyl complexes $\overline{\mathrm{ZrX_2\text{-}[C(NAr)N}}\mathrm{MeCyc]_2}$ (Ar = 2,6-dimethylphenyl, Cyc =

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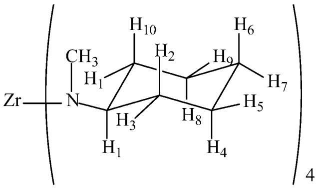


Figure 1. Numbering scheme for the protons in the Zr$(NCycMe)_4$ and related complexes containing the cyclohexyl group.

cyclohexyl, X = NMeCyc, OC_6F_5, Cl), their characterization, and the catalytic activity in the polymerization of 1-hexene and ethylene in the presence of $[NHMe_2Ph][B(C_6F_5)_4]$.

Results and Discussion

Synthetic Approaches to the Isocyanide Insertion Products. The synthetic approach to zirconium complexes containing two η^2-formamidinyl moieties (FAM) of the type $ZrX_2(FAM)_2$ could be carried out in two different ways by using either Zr diamide dichloride or Zr tetra-amide complexes as starting materials. The presence of the two η^2-formamidinyl ligands helps stabilize these complexes and their derivatives. By varying the ancillary X groups, the catalytic behavior of these electrophilic complexes can be modified as needed.

First we tried to react $ZrCl_2(NMe_2)_2{\cdot}2THF$ and $ZrCl_2(NEt_2)_2{\cdot}2THF$ (more stable and easier to isolate and purify than $ZrCl_2(NMe_2)_2{\cdot}2THF$) with 2 equiv of 2,6-dimethylphenyl isocyanide. However in both cases we obtained mixtures of products which could not be readily separated. Then, we reacted $Zr(NMe_2)_4$ with 2 equiv of 2,6-dimethylphenyl isocyanide: even at −90 °C, the main product was $Zr[C(NAr)NMe_2]_4$ (Ar = 2,6-dimethylphenyl) derived by the tetra-insertion of the isocyanide into the Zr−N bond, already described in the literature.[4]

Since the doubly inserted product has never been isolated from the reaction mixture, such results have shown that the double-insertion reaction is strictly governed by the reactivity of the substrates and their steric hindrance. In view of these results we increased the steric bulk of the amido ligands by incorporation of a cyclohexyl group to see if the additional steric hindrance could be used to control the extent of isocyanide insertion. The tetra-amide $Zr(NCycMe)_4$ was synthesized by reacting $ZrCl_4$ with 4 mol of LiNCycMe, prepared in situ from Li*n*-Bu and cyclohexylmethylamine, and it was characterized via elemental analysis and NMR spectroscopy. The ^1H NMR spectrum of $Zr(NCycMe)_4$ in C_6D_6 solution at 295 K (for the assignments see the proton numbering in Figure 1) displays a singlet at δ 3.05 (integrated for 12 H) assignable to the $N-CH_3$ protons and a multiplet (triplet of triplets) centered at δ 3.00 assignable to the H^1 protons of the cyclohexyl groups both coupled with the neighboring axial protons (H2, H6) ($^3J = 11.05$ Hz) and with the two neighboring equatorial protons (H3, H11) ($^3J = 3.06$ Hz).

A series of multiplets ranging from δ 1.1 and 2.0 could be assigned to the 40 residual cyclohexyl protons.

The tetra-amide $Zr(NCycMe)_4$ was then reacted with 2 mol of 2,6-dimethylphenyl isocyanide at −90 °C in *n*-hexane (Scheme 1), giving the complex $Zr(NMeCyc)_2[C(NAr)NMeCyc]_2$ (**1**) as a white powder after workup in 77% yield, according to the reaction in Scheme 1.

The IR spectrum in *n*-hexane shows an absorption at 1639 cm^{-1} characteristic of the stretching of a double C=N bond.

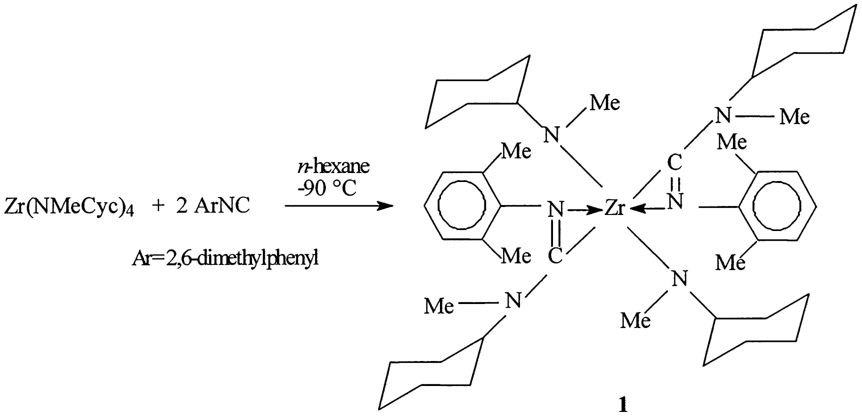
Reactivity. The presence in complex **1** of two Zr−amido groups which easily undergo substitution by protonolysis suggests that complex **1** could be used as a starting material to prepare other complexes. In fact, complex **1** was then converted into the pentafluoro phenoxide and chloride derivatives by reaction with 2 equiv of C_6F_5OH and $[NMe_3H]Cl$ in Et_2O, respectively, (Scheme 2): $Zr(OC_6F_5)_2[C(NAr)NMeCyc]$ (**2**) is a yellow oil (yield 90%), while $ZrCl_2[C(NAr)NMeCyc]$ (**3**) is a white powder (yield 83%).

The stretching frequency of the double C=N bond does not change significantly (1638 cm^{-1} for **2** and 1639 cm^{-1} for **3** in *n*-hexane).

The synthetic approach based on the double insertion of 2,6-dimethylphenylisocyanide into two Zr−N bonds of $Zr(NMeCyc)_4$ afforded the η^2-formamidinyl Zr complex **1**, which had been shown to be a versatile reagent for the preparation of **2** and **3**.

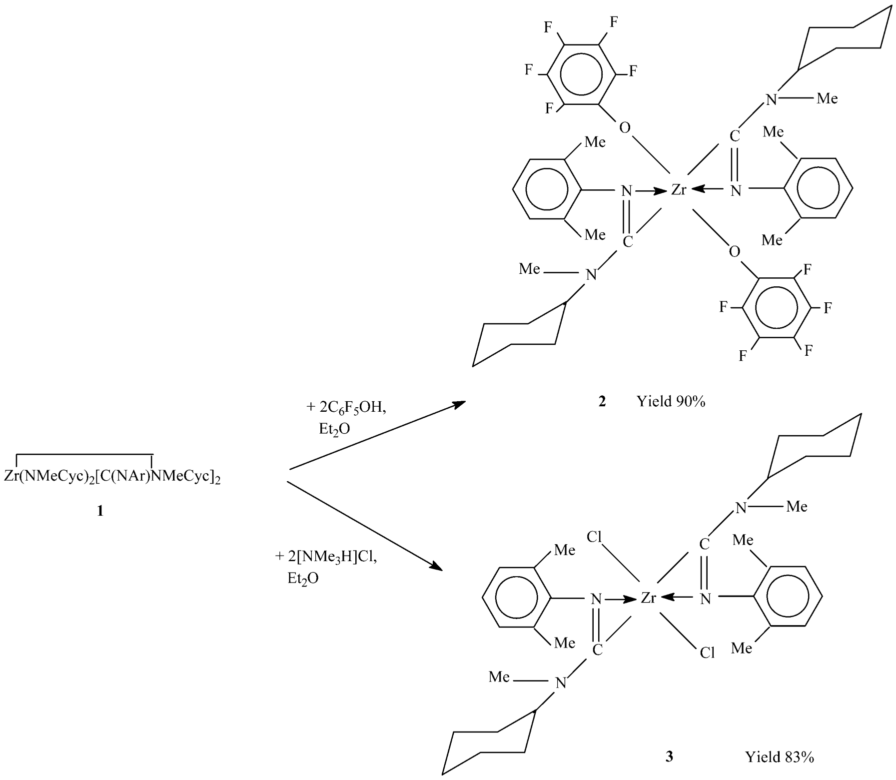
NMR Characterization. The assignments of the signals of the ^1H and ^{13}C NMR spectra of compounds **1**−**3** in C_6D_6 solution at 298 K have been carried out by means of HMQC experiments. In some cases the broadening of the signals suggests the fluxional behavior of the compounds. The presence of common ancillary ligands in the complexes **1**−**3** contributes to the assign-

Scheme 1



1

Scheme 2



ments of the ^{1}H and ^{13}C NMR spectra in addition to the HMQC experiments. The ^{1}H NMR spectrum of **1** displays in the range δ 6.89−δ 7.05 a combination of triplets and doublets assignable to the *meta*- and *para*-phenyl protons of the two $-\mathrm{C{=}N{-}C_6}\mathit{H}_3$-2,6-$(\mathrm{CH_3})_2$ group. The multiplet (triplet of triplets) centered at δ 3.85 could be assigned to the H^1 cyclohexyl protons of the two $-\mathrm{N(CH_3)C_6H_{11}}$ units (see Figure 1), and the multiplet at δ 3.60 to the H^1 cyclohexyl protons of the two $-\mathrm{N{=}C{-}N(CH_3)C_6H_{11}}$ groups. In fact the H^1 cyclohexyl protons of the $-\mathrm{N(CH_3)C_6H_{11}}$ undergo a greater deshielding than the corresponding H^1 cyclohexyl protons of the $-\mathrm{N{=}C{-}N(CH_3)C_6H_{11}}$, as they are closer to the zirconium ion. A sharp singlet at δ 3.19 was assigned to the $\mathrm{Zr{-}N(C}\mathit{H}_3\mathrm{)C_6H_{11}}$, and the strong singlet at δ 2.28 could be assigned to the methyl protons of the two $-\mathrm{C{=}N{-}C_6H_3(C}\mathit{H}_3)_2$ units and a series of broad signals ranging from δ 1.8 to 1.02 due to the remaining cyclohexyl protons. Correspondingly on the basis of the HMQC experiment the signals of the ^{13}C NMR spectrum of **1** were assigned as follows: the signals at δ 213.36 and 211.03 are due to the imino carbon atoms of the two $-\mathrm{N{=}}\boldsymbol{C}\mathrm{{-}NRR'}$ ($\mathrm{R = CH_3}$; $\mathrm{R' = C_6H_{11}}$). The series of signals at δ 151.17, 130.73, 127.48, and 122.49 were assigned to the phenyl carbon atoms of the 2,6-dimethylphenyl groups. The signal at δ 66.11 was assigned to the C1 atom of the cyclohexyl group of the $\mathrm{Zr{-}N(CH_3)C_6H_{11}}$ residue, whereas the signal at δ 61.13 is due to the C1 atom of the cyclohexyl group of the $-\mathrm{N{=}CN(CH_3)C_6H_{11}}$ molecule fragment. The signals at δ 33.44 and 31.23 are due to the methyls of the groups $-\mathrm{N{=}CN(}\mathit{C}\mathrm{H_3)C_6H_{11}}$ and $\mathrm{Zr{-}N(}\mathit{C}\mathrm{H_3)C_6H_{11}}$, respectively, and the resonance at δ 19.65 was assigned to the methyls bonded to the aromatic groups. The substitution of the methylcyclohexylamino groups in complex **1** with pentafluorophenoxy groups affords complex **2**. The ^{1}H NMR spectrum of **2** at 298 K showed a doublet centered at δ 7.14 (J = 7.6 Hz) assignable to the *meta*-phenyl protons and a triplet at δ 6.99 (J = 7.6 Hz) due to the *para*-phenyl protons. A broad signal centered at δ 2.81 was assigned to the $\mathrm{N{-}C}\mathit{H}_3$; the H^1 protons of the two cyclohexyl groups give rise to a broad signal centered at δ 2.48, while the sharp singlet at δ 2.30 is due to the methyls of the 2,6-dimethylphenyl groups. A series of unresolved broad signals in the range δ 1.70−0.80 are assigned to the remaining cyclohexyl protons. The broadness of the signals in the ^{1}H NMR spectrum of **2** could be attributable to the lesser steric hindrance of the ligands than in complex **1**, which exhibits more conformational rigidity than **2**. These signals become sharp by increasing the temperature as a consequence of the increased rotational freedom, which makes the methyl groups equivalent to one another. The HMQC experiments made possible the assignments of the signals in the ^{13}C NMR spectrum of **2** as follows: the two signals at δ 214.52 and 213.02 are due to the two $-\mathrm{N{=}}\mathit{C}\mathrm{{-}N(CH_3)C_6H_{11}}$; the four signals at δ 152.46, 129.50, 128.13, 122.03 are assigned to the carbon atoms of the disubstituted phenyl groups. A series of signals in the range δ 140.00−135.00 are assigned to the carbon atoms of the two pentafluorophenyl groups. The signal of the C1 atoms of the two cyclohexyl groups are at δ 58.49, the C atoms of the methyl groups bonded to the nitrogen are at δ 31.45, and those of the two 2,6-$(\mathrm{CH_3})_2\mathrm{C_6H_3}$ are at δ 18.85. Finally a series of signals ranging between δ 32.00 and 24.80 are assigned to the remaining cyclohexyl carbon atoms. A further confirmation of the assignments of the previous complexes **1** and **2** comes from the comparison with the ^{1}H and ^{13}C NMR spectra of the complex **3**, having only the two $-\mathrm{N{=}C{-}N(CH_3)C_6H_{11}}$ groups in common with the other complexes. The ^{1}H NMR showed a doublet centered at δ

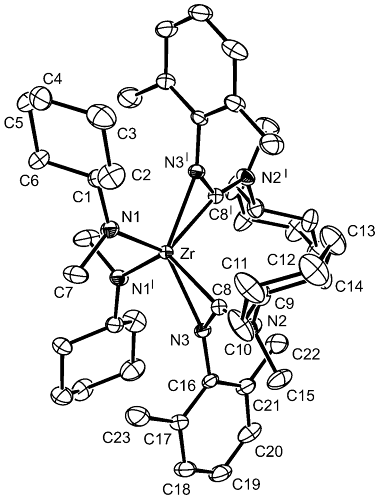


Figure 2. ORTEP view of the $Zr(NMeCyc)_2[C(NAr)N\text{-}MeCyc]_2$ (**1**) with the atom nomenclature.

7.15 (J = 7.6 Hz) due to the *meta*-phenyl protons and the triplet at δ 7.00 (J = 7.6 Hz) of the *para*-phenyl protons, a broad singlet at δ 2.82 assignable to the $-N(CH_3)C_6H_{11}$, a broad multiplet at δ 2.44 due to the H^1 protons bonded to the C1 carbon atom of the cyclohexyl groups, a singlet at δ 2.31 of the methyl groups of the $-C{=}N-C_6H_3(CH_3)_2$ units, and finally a series of broad signals ranging from δ 1.85 to 0.90 assignable to the remaining cyclohexyl protons. The signals of the ^{13}C NMR spectrum were assigned on the basis of the HMQC experiments as follows: δ 209.62, 208.44 to the two $N{=}\boldsymbol{C}-N$ quaternary carbon atoms, δ 152.31, 130.69, 127.48, 121.79 to the phenyl carbon atoms $-C_6H_3(CH_3)_2$, δ 65.67 assignable to the C1 carbon atoms of the cyclohexyl groups, δ 31.73 to the methyl group bonded to the nitrogen atom of the $N{=}C-N(CH_3)$-C_6H_{11} residue, δ 18.92 assigned to the carbon atoms of the methyl substituents in the phenyl rings $[C{=}NC_6H_3(CH_3)_2]$, and a series of signals between δ 22.8 and 26.1 assignable to the remaining cyclohexyl carbon atoms.

X-ray Crystal Structure of 1. An ORTEP view of the molecular structure of $Zr(NMeCyc)_2[C(NAr)N\text{-}MeCyc]_2$, **1**, together with the atom numbering is in Figure 2.

Selected bond distances and angles are given in Table 1. The molecular structure of **1** has C_2 symmetry. The zirconium atom lies on the 2-fold crystallographic axis, and it is coordinated to two η^2-(N=C) moieties as well as to two η^1-(NMeCyc), both symmetry related. The coordination sphere around Zr can be described as a pseudotetrahedron with each η^2-formamidinyl unit occupying a single coordination site.

The Zr−C(8) (2.259(4) Å) and Zr−N(3) (2.221(3) Å) bond distances are comparable to those found in $(Me_3CCH_2)_3Zr\{\eta^2\text{-}C[Si(SiMe_3)_3]{=}NAr\}$[6] (Zr−C(1) 2.255(4), Zr−N(1) 2.175(3)Å) despite the different hindrance of the cyclohexyl with respect to the substituted xylyl group. The C−N(Me)Cyc bond distance of 1.341(5) Å is between the double bond −C=N− [C(8)−N(3) 1.321(5) Å] and $N-C_{ar}$ (1.463(6) Å) single bond, suggesting some degree of $\pi-\pi$ bonding in the (Me)Cyc-N−C=N moiety consistent with the planarity of the C(8)−N(2)−C(9)−C(15) group and with the sum of the angles around N(2) of 360°. The same behavior has been observed in $Zr[\eta^2\text{-}C(NMe_2){=}NAr]_3\{\eta^2\text{-}C[Si(SiMe_3)_3]{=}NAr\}$,[4] where all the ligands are η^2-bonded to the central metal ion.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $Zr(NMeCyc)_2[C(NAr)NMeCyc]_2$ (1)

Zr−N(1)	2.064(3)	Zr−N(3)	2.221(3)
Zr−C(8)	2.259(4)	N(1)−C(1)	1.459(6)
N(1)−C(7)	1.452(7)	N(2)−C(8)	1.341(5)
N(2)−C(9)	1.464(6)	N(2)−C(15)	1.463(6)
N(3)−C(8)	1.321(5)	N(3)−C(16)	1.425(5)
N(3)−Zr−C(8)	34.3(1)	N(1)−Zr−C(8)	102.1(1)
N(1)−Zr−N(3)	120.5(1)	N(3)−Zr−N(1)[a]	89.7(2)
N(1)−Zr−N(1)[a]	100.0(2)	N(3)−Zr−N(3)[a]	134.0(2)
C(8)−Zr−C(8)[a]	108.4(2)	Zr−N(1)−C(7)	111.4(3)
Zr−N(1)−C(1)	134.1(3)	N(3)−Zr−N(1)[a]	89.7(2)
C(9)−N(2)−C(15)	118.2(4)	C(1)−N(1)−C(7)	114.5(4)
C(8)−N(2)−C(9)	117.8(4)	C(8)−N(2)−C(15)	123.9(4)
Zr−N(3)−C(8)	74.5(2)	Zr−N(3)−C(16)	152.8(3)
N(1)−C(1)−C(6)	114.0(4)	C(8)−N(3)−C(16)	132.5(3)
N(2)−C(8)−N(3)	127.6(4)	N(1)−C(1)−C(2)	113.9(4)
Zr−C(8)−N(2)	161.1(3)	Zr−C(8)−N(3)	71.3(2)
N(2)−C(9)−C(10)	111.9(4)	N(2)−C(9)−C(14)	112.8(4)
N(3)−C(16)−C(17)	120.3(3)	N(3)−C(16)−C(21)	118.6(4)

[a] At $-x$, $-y$, z.

The insertion of the monodentate amide is characterized by a short Zr−N distance (Zr−N(1) 2.064(3) Å), as found for other amido complexes such as $Zr(NMe_2)_4$[7] (electron diffraction) (Zr−N 2.07 Å) and $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr[N(R)C(Me){=}C(Me)N(R)]$ (R = *tert*-butyl and 2,6-xylyl)[8] with Zr−N bond distances ranging between 2.06 and 2.07 Å, reflecting again N π-donation to the electrophilic d^0 Zr center.

Catalytic Tests. Complexes **1**, **2**, and **3**, when treated with stoichiometric amounts of $[HNMe_2Ph]B(C_6F_5)_4$ as activator and with $Al(i\text{-}Bu)_3$ as scavenger, were found to promote the polymerization of 1-hexene and ethylene. The specific reaction conditions, the catalytic activity, and some properties of the polymers such as average molecular weights (by viscometry) and melting points are reported in Tables 2 and 3 for the polymerization of 1-hexene and ethylene, respectively.

These complexes catalyze the polymerization of 1-hexene and ethylene exhibiting low to moderate activity, respectively. The activity decreases on going from the amido to the chloride derivatives. By comparison to the zirconocene, $ZrCp_2Cl_2$, these complexes showed a lower activity but higher reproducibility of the results under the same polymerization conditions. This trend of activity, **1** > **2** > **3**, could be assigned to the electronic and steric properties of the different groups X of the complexes $ZrX_2[C(NAr)NMeCyc]_2$.

On the other hand, the physical properties of the poly(1-hexenes) and polyethylenes obtained, which have been evaluated by means of viscometry and differential scanning calorimetry (DSC), deserve a deeper insight. The poly(1-hexenes) show high molecular weights, higher than those already reported in the literature: in the temperature range −30 to +300 °C no vitreous transition is observed as well as crystallization or

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Table 2. Conditions and Results of the Polymerization of 1-Hexene[a]

run	complex (mol)	$T_{\text{init.}}$[b] (°C)	$T_{\text{fin.}}$[c] (°C)	$t_{\text{react.}}$[d] (min)	activity[e] ($\text{kg}_\text{p}/\text{mol}_\text{cat}\cdot\text{h}\cdot\text{bar}$)	% conversion of 1-hexene[f] [yield (g)]	M_{wv}[g] (g/mol)
1	**1** (5×10^{-5})	24.5	28.8	60	14	3.47 [0.70]	423 000
2	**1** (5×10^{-5})	23.0	27.7	60	15.6	3.86 [0.78]	402 000
3	**1** (5×10^{-5})	21.2	25.0	60	12.6	3.12 [0.63]	442 000
1	**2** (5×10^{-5})	22.5	26.0	60	10.0	2.48 [0.50]	578 000
2	**2** (5×10^{-5})	23.0	26.9	60	11.6	2.87 [0.58]	590 000
3	**2** (5×10^{-5})	22.0	26.1	60	9.4	2.33 [0.47]	512 000
1	**3** (5×10^{-5})	21.5	24.0	60	6.0	1.49 [0.30]	953 000
2	**3** (5×10^{-5})	23.0	25.7	60	7.6	1.88 [0.38]	915 000
3	**3** (5×10^{-5})	22.0	24.9	60	9.4	1.09 [0.22]	897 000

[a] Conditions: solvent, toluene 10 mL, $n_{\text{Al}(-\text{Bu})3}/n_{\text{cat}} = 8$, 1-hexene 30 mL. [b] $T_{\text{init.}}$ = initial temperature. [c] $T_{\text{fin.}}$ = temperature at the end of the polymerization. [d] $t_{\text{react.}}$ = reaction time. [e] kg_p = kilograms of polymer, mol_{cat} = moles of catalyst. [f] conversion = $100\cdot\text{g}_{\text{polymer}}/\text{g}_{1-\text{hexene}}$. [g] M_{wv} = average molecular weight of the polymer measured via viscometry.

Table 3. Conditions and Results of the Polymerization of Ethylene[a]

run	complex (mol)	$t_{\text{react.}}$[b] (min)	activity[c] ($\text{kg}_\text{p}/\text{mol}_\text{cat}\cdot\text{h}\cdot\text{bar}$)	yield (g)	M_{wv}[d] (g/mol)	mp[e] (°C)
1	**1** (10^{-5})	20	58.8	0.97	n.d.	134.5
2	**1** (10^{-5})	20	66.7	1.10	n.d.	134.9
3	**1** (10^{-5})	20	54.5	0.90	n.d.	135.1
1	**2** (10^{-5})	20	45.5	0.75	n.d.	135.7
2	**2** (10^{-5})	20	49.7	0.82	n.d.	135.4
3	**2** (10^{-5})	20	41.2	0.68	n.d.	136.1
1	**3** (10^{-5})	20	22.4	0.37	n.d.	136.7
2	**3** (10^{-5})	20	33.3	0.55	n.d.	136.4
3	**3** (10^{-5})	20	26.7	0.44	n.d.	136.9
1	ZrCp_2Cl_2 (10^{-5})	20	454	7.5	13 400	126.3
2	ZrCp_2Cl_2 (10^{-5})	20	254	4.2	12 950	125.9

[a] Conditions: solvent, toluene 20 mL, $n_{\text{al}(-\text{Bu})3}/n_{\text{cat}} = 20$, pressure = 5 atm, temperature 55−60 °C. [b] $t_{\text{react.}}$ = reaction time. [c] kg_p = kilograms of polymer, mol_{cat} = moles of catalyst. [d] M_{wv} = average molecular weight of the polymer measured via viscometry; n.d.= not determined. [e] mp = melting point, determined via differential scanning calorimetry.

melting processes. However at $T > 275$ °C decomposition took place. The poly(1-hexenes) are atactic, amorphous materials with viscoelastic properties. The presence of an *n*-butyl side chain lowers the molecular cohesion (internal plasticization), suggesting a considerable flexibility even at low temperature so that vitreous transitions are expected to occur in our case at temperatures below −30 °C.

The polyethylenes (PEs) obtained using the η^2-formamidinyl complexes as catalysts were characterized by high molecular weights (magnitude order 10^6g/mol). Their insolubility in several solvents or mixtures of solvents prevented the average molecular weight determination via viscometry. On the contrary, the polyethylenes obtained using ZrCp_2Cl_2, more active catalysts, are characterized by low molecular weights, and are industrially less interesting. The PEs polymers show neat high melting points, suggesting that they are high-density polyethylenes (HDPE). The crystallinity degree X is calculated as

$$X = \frac{\Delta H_{\text{fus}}}{\Delta H_{\text{f}}t}$$

where ΔH_{fus} is the experimental enthalpy of fusion (J/g) and $\Delta H_{\text{ft}} = 276.27$ J/g reference value of the enthalpy of fusion of a sample of 100% crystalline polyethylene[9] ranges from 17% for the polymer obtained with **1** to 13% for the polymer obtained with **3**, in agreement with the fact that the crystallinity degree tends to decrease by increasing the polymerization and molecular weight.

In conclusion, the polymers produced with this new family of η^2-formamidinyl catalysts showed interesting rheological properties and high molecular weight with low dispersivity.

Experimental Section

All manipulations were performed in an oxygen- and moisture-free atmosphere in a Braun MB 200 G-II drybox. Cyclohexylmethylamine and all the solvents were purified and dried following standard procedures.[10] ZrCl_4 (Aldrich), 2,6-dimethyl phenyl isocyanide (Fluka), Li*n*-Bu (Aldrich), $\text{C}_6\text{F}_5\text{OH}$ (Aldrich), $[\text{HNMe}_2\text{Ph}]\text{B}(\text{C}_6\text{F}_5)_4$ (Montell), Al(*i*-Bu)$_3$ (TIBA) (Schering), and ethylene (SIAD, "ethylene polymerization grade") were used as received; $[\text{HNMe}_3]\text{Cl}$ (Aldrich) was purified by precipitation from saturated CHCl_3 (previously distilled on CaH_2) solutions. 1-Hexene (Aldrich) was fractionally distilled on CaH_2 and kept on molecular sieves (NaA zeolites, 8−12 mesh). Microanalyses were performed at Istituto di Chimica Inorganica e delle Superfici, CNR, Padova. The IR spectra were recorded on a Galaxy Series FT-IR 3000 Mattson in Nujol. The ^{1}H and ^{13}C NMR spectra were obtained as C_6D_6 solutions on a Bruker AMX-300 spectrometer operating at 300 and 100.61 MHz, respectively. The assignments of the proton resonances were performed by standard chemical shift. The ^{13}C resonances were attributed through 2D-heterocorrelated COSY experiments (HMQC with *bird* sequence[11] and quadrature along F1 achieved using the TPPI method[12] for the H-bonded carbon atoms). The determination of the average molecular weight of the polymer was carried out on a Hubbehold viscometer in toluene solutions at 55 °C. The analysis via differential scanning calorimetry was done with a TA DSC 2920 instrument.

Zr(NMeCyc)$_4$. Li(NMeCyc) was prepared in situ by adding dropwise a solution of NHMeCyc (3.13 mL, 24 mmol) in toluene (5 mL) to a solution of Li*n*-Bu (15 mL, 1.6 M in hexane, 24 mmol) in toluene (20 mL) and stirring for 2.5 h at room temperature. To this suspension was added gradually ZrCl_4 (1.398 g, 6 mmol) in 30 min. After stirring for 18 h the solution was filtered and the filtrate was reduced to a dark yellow oil under reduced pressure. Yield: 3.20 g (98.7%). Anal. Calcd (Found) for $\text{C}_{28}\text{H}_{56}\text{N}_4\text{Zr}$: C 62.26 (62.00), H 10.47 (10.01), N 10.38 (10.11). ^{1}H NMR (C_6D_6, δ ppm, 295 K): 3.05 (s, 12H, CH_3), 3.00 (tt, 4H, $^3J = 11.07$ Hz, $^3J = 3.6$ Hz), 1.1−2.0 (m, 40H, $H_4\text{C}_2{-}\text{C}{-}\text{C}_3H_6$). ^{13}C NMR ($\text{C}_6\text{D}_6$, δ ppm, 295 K): 63.22 (N−CH$_3$), 34.22 (C2, C6), 33.18 (C1), 26.63 (C3, C5), 26.59 (C4).

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Zr(NMeCyc)$_2$[C(NAr)NMeCyc]$_2$, Ar = 2,6-dimethylphenyl, 1. To a solution of Zr(NMeCyc)$_4$ (1.080 g, 2 mmol) in *n*-hexane (30 mL) at −90 °C was gradually added 2,6-dimethylphenyl isocyanide (0.525 g, 4 mmol). The reaction was checked via IR spectroscopy. After stirring for 2.5 h the mixture was filtered and the filtrate was concentrated and put in the freezer at −31 °C to give a white precipitate, which was collected by filtration and washed with cold *n*-hexane. Yield: 1.24 g (77%). Anal. Calcd (Found) for $C_{46}H_{74}N_6Zr$: C 68.86 (69.72), H 9.29 (9.64), N 10.47 (9.95). IR (Nujol): 1639 cm^{-1} ν(C=N). ^{1}H NMR (C_6D_6, δ ppm, 295 K): 7.05−6.89 [m, 6H, C=NC$_6$*H*$_3$(Me)$_2$], 3.85 [m, 2H, ZrN(C*H*C$_5$H$_{10}$)], 3.60 [m, 2H, N=CN(C*H*C$_5$H$_{10}$)], 3.19 (s, 6H, Zr−NCyC*H*$_3$), 2.28−2.17 [m, 18H, N=CNC$_6$H$_{11}$C*H*$_3$ and C=NC$_6$H$_3$(C*H*$_3$)$_2$], 1.82−1.02 (m, 40H, cyclohexyl protons). ^{13}C NMR (C_6D_6, δ ppm, 295 K): 213.36, 211.03 (N=*C*NCycMe), 151.17, 130.73, 127.48, 122.49 (*C*$_6$H$_3$), 66.11 [Zr−N(*C*HC$_5$H$_{10}$)Me], 61.13 [N=CN(*C*HC$_5$H$_{10}$)Me], 33.44 (N=CNCyc*C*H$_3$), 31.23 (Zr−NCyc*C*H$_3$), 25.90−22.82 [N(CH*C*$_5$H$_{10}$)Me], 19.65 [C=NC$_6$H$_3$(*C*H$_3$)$_2$].

Zr(OC$_6$F$_5$)$_2$[C(NAr)NMeCyc]$_2$, Ar = 2,6-dimethylphenyl, 2. To a solution of **1** (0.401 g, 0.5 mmol) in Et$_2$O (30 mL) was added dropwise a solution of C_6F_5OH (0.184 g, 1 mmol) in Et$_2$O (10 mL): the reaction occurs instantaneously and exothermally, and the color changed to dark yellow. After 2 h the solution was dried under reduced pressure, giving a yellow oil. Yield: 0.424 g (90%). Anal. Calcd (Found) for $C_{44}H_{46}N_4F_{10}Zr$: C 55.98 (56.78), H 4.91 (5.10), N 5.94 (6.19). IR (Nujol): 1638 cm^{-1} ν(C=N). ^{1}H NMR (C_6D_6, δ ppm): 7.14 [d, 4H, J = 7.6 Hz, *meta*-C$_6$*H*$_3$(Me)$_2$], 6.99 (t, 2H, J = 7.6 Hz, *para*-C$_6$*H*$_3$-(Me)$_2$), 2.81 (bs, 6H, N=CN(C*H*$_3$)Cyc), 2.48 [bm, 2H, N=CN-(C*H*C$_5$H$_{10}$)], 2.30 (s, 12H, C=NC$_6$H$_3$(C*H*$_3$)$_2$), 1.70−0.80 (m, 20H, cyclohexyl protons). ^{13}C NMR (C_6D_6, δ ppm): 214.52, 213.02 (N=*C*NCycMe), 152.46, 129.50, 128.13, 122.03 (*C*$_6$H$_3$), 140.0−135.0 (*C*$_6$F$_5$O), 58.49 [N=CN(*C*HC$_5$H$_{10}$)Me], 31.45 (N=CN-Cyc*C*H$_3$), 32.0−24.8 [N(CH*C*$_5$H$_{10}$)Me], 18.85 [C=NC$_6$H$_3$(*C*H$_3$)$_2$].

ZrCl$_2$[C(NAr)NMeCyc]$_2$, Ar = 2,6-dimethylphenyl, 3. To a solution of **1** (0.401 g, 0.5 mmol) in Et$_2$O (30 mL) was added gradually [Me$_3$NH]Cl (0.096 g, 1 mmol); the color changed slowly to light yellow. After 12 h the solution was dried under reduced pressure, dissolved in *n*-hexane, and filtered. The filtrate was cooled at −31 °C, giving a white precipitate. Yield: 0.270 g (83%). Anal. Calcd (Found) for $C_{32}H_{46}N_4ClZr$: C 59.23 (58.11), H 7.15 (7.41), N 8.63 (8.87). IR (Nujol): 1638 cm^{-1} ν(C=N). ^{1}H NMR (C_6D_6, δ ppm, 295 K): 7.15 [d, 4H, J = 7.6 Hz, C=NC$_6$*H*$_3$(Me)$_2$], 7.00 [t, 2H, J = 7.6 Hz, C=NC$_6$*H*$_3$-(Me)$_2$], 2.82 [bs, 6H, N=CN(C*H*$_3$)Cyc], 2.44 [bm, 2H, N=CN-(C*H*C$_5$H$_{10}$)], 2.31 (s, 12H, C=NC$_6$H$_3$(C*H*$_3$)$_2$), 1.80−0.90 (m, 20H, cyclohexyl protons). ^{13}C NMR (C_6D_6, δ ppm, 295 K): 209.62, 208.44 (N=*C*NCycMe), 152.31, 130.69, 127.48, 121.79 (*C*$_6$H$_3$), 65.67 [N=CN(*C*HC$_5$H$_{10}$)Me], 31.73 (N=CNCyc*C*H$_3$), 26.1−22.8 [N=CN(CH*C*$_5$H$_{10}$)Me], 18.92 [C=NC$_6$H$_3$(*C*H$_3$)$_2$].

Polymerization of 1-Hexene. In a three-neck round-bottom flask were introduced 1-hexene (30 mL), TIBA (0.1 mL), and toluene (5 mL). In another flask a solution of the complex (5 × 10^{-3} M, 1 mL) and of the cocatalyst (1.25 × 10^{-3} M, 4 mL) in toluene were mixed together before being transferred to the flask containing the olefin and the scavenger. The reaction was carried out at room temperature for 1 h.

Purification of Poly(1-hexene). After adding MeOH (1 or 2 mL) at the end of the reaction, the reaction solution was evaporated under reduced pressure and the polymer was dried at 60−70 °C under vacuum. The polymer (0.5 g) was dissolved in toluene (50−60 mL), and the solution washed three times with a solution of MeOH−HCl, 1:1 (3 × 50 mL). The addition of a MeOH−acetone solution, 1:1 (50 mL), and shaking vigorously caused the coagulation of the polymer, which was separated and dried at 90 °C for 3 h under vacuum.

Polymerization of Ethylene. A stainless steel autoclave was charged with toluene (20 mL) and TIBA (0.05 mL). In another flask a solution of the complex (5 × 10^{-3} M, 1 mL) and of the cocatalyst (1.25 × 10^{-3} M, 4 mL) in toluene were mixed together before being transferred to the autoclave. The autoclave was then heated at 55−60 °C and pressurized with ethylene (p = 5 atm) for 20 min. At the end MeOH (2 mL) was added.

Table 4. Crystallographic Data for Zr(NMeCyc)$_2$[C(NAr)NMeCyc]$_2$ (1)

formula	$C_{46}H_{74}N_6Zr$
fw	802.35
cryst syst	orthorhombic
space group	$P2_12_12$
a (Å)	12.399(3)
b (Å)	19.467(3)
c (Å)	9.607(3)
V (Å$^{3)}$	2318.9(8)
Z	2
D_c (g cm^{-3})	1.149
μ (mm^{-1})	0.272
F(000)	864
cryst dimens (mm)	0.48 × 42 × 0.38
T, K	293(2)
θ_{max} (deg)	26
no. of reflns measd	4790
no. of reflns obsd [$I \geq 2\sigma(I)$]	4346
R (on F)^a	0.045
R_w (on F^2)^a	0.131
goodness-of-fit on F^2	1.231
largest diff peak/hole (e Å^{-3})	0.662/−0.755

^{a} $R = \sum|F_o| - |F_c|/\sum|F_o|$, $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Purification of Poly(ethylene). After venting the autoclave, the polymer was filtered and washed several times with a solution of MeOH−HCl, 1:1, and then with water and acetone and dried at 90 °C under vacuum.

X-ray Measurements and Structure Determination. Crystals of **1** suitable for X-ray analysis were grown upon cooling *n*-pentane solutions. Crystal data were collected using a Philips PW1100 diffractometer, with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) following the standard procedures. All intensity data were corrected for Lorentz−polarization effects and absorption.[13] The refined lattice parameters and other pertinent crystallographic information are given in Table 4. The structure was solved by direct methods using SIR-92.[14] All non-hydrogen atoms were located in the subsequent Fourier maps. The structure was refined by full-matrix least-squares methods using anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms were introduced at calculated positions in their described geometries and during refinement were allowed to ride on the attached carbon atoms with fixed isotropic thermal parameters (1.2U_{eq} of the parent carbon atom). The Flack parameters[15] have been refined for the structure. The calculations were performed with the SHELXL-97 program,[16] implemented in the WinGX package.[17] The program for the ORTEP drawing was taken from ref 18.

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Supporting Information Available: Crystallographic data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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