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Catalytically Active *N*-Acylamidine−Zirconium Complexes: Synthesis, Structures, and Application in Ethylene Polymerization

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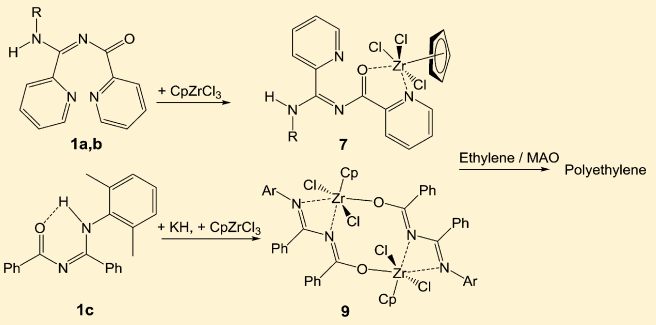
Supporting Information

ABSTRACT: Three novel *N*-acylamidines **1a−c** with varying steric bulk and substitution patterns were synthesized and thoroughly characterized by X-ray diffraction. Compounds **1a** and **1b**, which contain two additional binding sites located at two pyridine substituents, were treated with equimolar amounts of cyclopentadienylzirconium(IV) trichloride at room temperature. The X-ray data of the resulting coordination compounds **7a** and **7b** indicate the formation of five-membered metallacycles with one of the pyridine nitrogen atoms and the carbonyl oxygen atom acting as binding sites. For the complexation of ligand **1c**, a different route was chosen: **1c** was first deprotonated to yield the polymeric potassium compound **8** with a very complex substitution pattern based on O , N, and aromatic interactions with the potassium ions. Transmetalation of **8** with cyclopentadienylzirconium(IV) trichloride gave amidinate complex **9**, which is dimeric in the solid state but exists in solution in equilibrium with monomeric species. After addition of methylaluminoxane (MAO), the three novel cyclopentadienylzirconium complexes **7a**, **7b**, and **9** gave active homogeneous single-site catalysts for the polymerization of ethylene. Of these three systems, **9**/MAO turned out to be the most efficient one, showing activities 3−5 times higher than **7a**/MAO and **7b**/MAO, respectively, and producing polymers with a well-defined "monomodal" molecular weight distribution. An important feature of these materials is their broader distribution in molecular weight (PDI > 3), which is best seen in the products of reactions at 53 °C, with a "monomodal" main fraction at higher molecular weight and only small fractions of low molecular weight.



INTRODUCTION

After more than 30 years, the development of new single-site catalysts for olefin polymerization based on early transition metals continues to be one the fields of highest interest for industry and academia. In recent years, research has been centered on robust and efficient precatalysts that can be synthesized in few steps from common (not exotic) materials with the purpose of making them commercially more attractive.

Precatalysts based on bi-, tri-, and tetradentate ligands in which carbon, nitrogen, or oxygen atoms efficiently stabilize an early transition metal are worth mentioning (Scheme 1). The advantage of such ligands is the easy access and great control of the steric and electronic environment of the atoms that coordinate the metal, characteristics that are essential for having access to thermally more stable and efficient catalysts in olefin homo- and copolymerization reactions. Among others, reviews[1−4] and articles from the groups of Edelmann,[5] Sita,[6] Hagadorn,[7] Eisen,[8] Rausch,[9] Green,[10] Lappert,[11] Kretschmer and Kempe,[12] and Jin[13] describe the work in this challenging field and deserve special attention.

A second strategy to achieve greater competitiveness of the systems based on early transition metals has focused on reducing or eliminating the dependence of these systems on the use of methylaluminoxane (MAO) as an alkylating agent responsible for the formation of the active species. For example, the use of alkylated precursors and alkylation of halogenated complexes prior to the addition of MAO have been high-impact strategies for understanding the activation of the metal. However, usually their viability is reduced by the high instability of these species, which hinder the purification of the precatalyst and consequently make the synthesis more expensive. These strategies have been more successful with late transition metals, which have resulted in well-known single-component cata-

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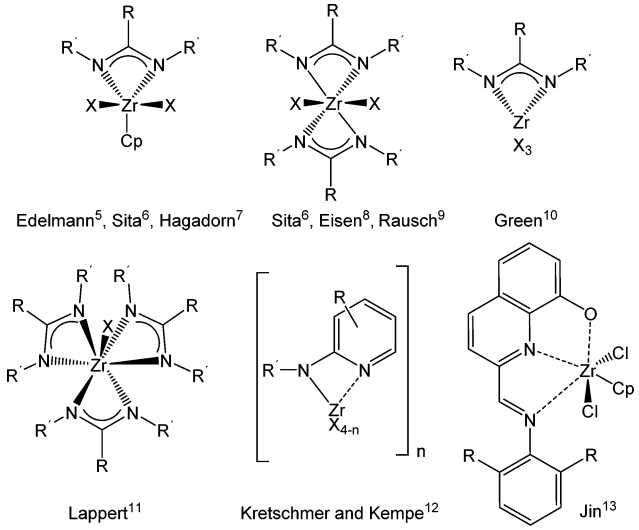
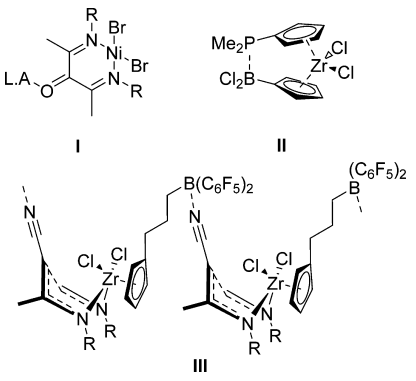
Scheme 1. Zirconium Complexes Formed by Bidentate *N,N*- and *N,N,O*-Ligands from the Literature



lysts.[14] In these studies, the incorporation of additional functionalities into the ligand with conjugated structures has a great impact as a strategy for improving the activation of the metal center. Thus, as a result of geometric or affinity limitations of the metal cation, these functionalities will remain free in the structure of the complex. In this kind of complex, binding of Lewis acids to those functionalities usually increases the metal's electrophilicity, activating it and thereby reducing its dependence on the cocatalyst (MAO). Scheme 2 shows examples of exocyclic, inter-, and intramolecular activation.

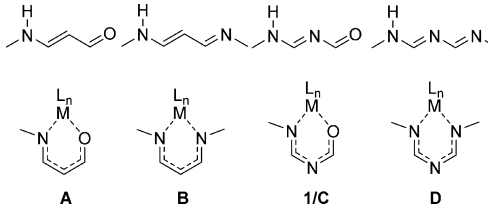
Scheme 2. Recent Examples of Remote Activation by Incorporation of Lewis Basic Functionalities into the Ligands[15] (LA = Lewis Acid)



Furthermore, on the basis of this principle, this strategy is suggested as an efficient route for phase transfer of the precatalyst to an inorganic support whose surface contains adequate Lewis acid sites to coordinate it. This will be of great importance for later applications in heterogeneous catalysis, a central step for commercial applications.[16−19]

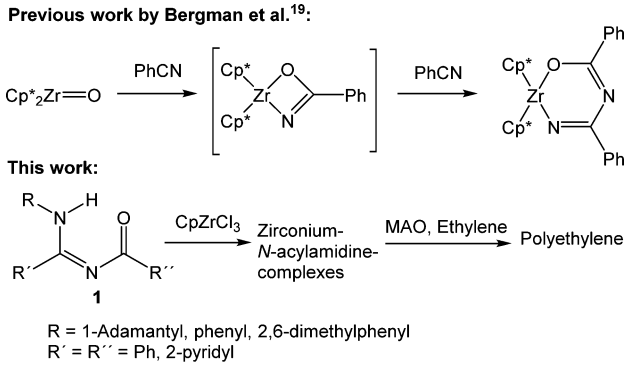
N-Acylamidines **1**/**C** (Scheme 3) are easily accessible nitrogen-rich mono, bi-, and tridentate ligands for aggregation and metal ion coordination.[20−25] They may coordinate either as neutral ligands or in deprotonated form. In comparison with *β*-imino ketones **A**[26] and *β*-diimines **B**[27] and their metal complexes, the central nitrogen atom at the 3-position influences the electronic properties at the respective binding

Scheme 3. *N,N*- and *N,O*-Chelating Ligands and the η^5 Coordination Compounds of Their Deprotonated Forms



sites considerably. For example, *π* conjugation over all five atoms is present in both the neutral and anionic forms. In the context of this work, the investigation of the influence of the additional binding site at the central nitrogen atom is of predominat interest. Neutral 2:1 *N*-acylamidine metal complexes were reported by Ley and Werner as early as 1913.[28] The constitutions of such coordination compounds were established in 1969 as trans complexes by Oehme and Pracejus.[29] Bergman and co-workers published the synthesis of a zirconocene complex featuring a doubly deprotonated *N*-acylamidine ligand[19] (Scheme 4). A first platinum(II) complex

Scheme 4. *N*-Acylamidine Ligands in Zirconium Chemistry



of a chelating *N*-acylamidine was reported by Bokach, Kukushkin, and co-workers.[30] Our group has reported several types of metal complexes formed from primary *N*-acylamidines and copper(II) or palladium(II) salts.[20−22] 1,3,5-Triazapentadienes **D**, in which the terminal oxygen atom of *N*-acylamidines is replaced by an imino functionality, show similar coordination properties (Scheme 3).[31−33]

In this article, we report on the synthesis and structural properties of three novel zirconcene complexes and of a potassium compound with secondary *N*-acylamidines acting as ligands. The main emphasis of this study is directed toward an investigation of the use of the zirconium coordination compounds in metal-catalyzed polymerization of ethylene (Scheme 4).

RESULTS AND DISCUSSION

Syntheses and Structures of Ligands 1a−c. Three different secondary *N*-acylamidines **1a−c** were investigated with respect to their ability to form catalytically active zirconium coordination compounds for ethylene polymerization. Two of them (**1a** and **1b**) contain as additional coordination sites two 2-pyridyl subunits and vary in bulkiness at the N5 substituent. They were prepared from the corresponding ethyl imidate **2**[34] and 2-picolinic acid chloride hydrochloride **3** to give ethyl *N*-acylimidate **4**. Subsequent

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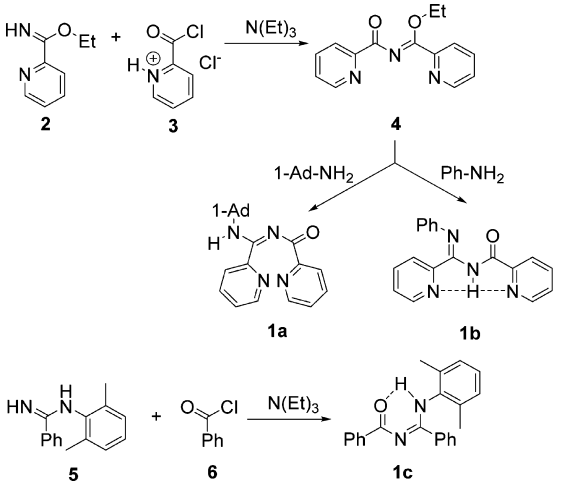
treatment with either 1-adamantylamine or aniline afforded *N*-acylamidines **1a** and **1b** in 80 and 56% yield, respectively (Scheme 5). The third *N*-acylamidine, **1c**, has no other

Scheme 5. Synthesis of Ligands 1a−c



coordination sites besides the *N*-acylamidine subunit, and it is characterized by a very bulky group at N5. It was prepared in 50% yield from amidine **5** by benzoylation using benzoyl chloride (**6**). **5** was obtained from 2,6-dimethylaniline upon deprotonation using *n*BuLi and benzonitrile.

The structures of **1a**, **1b**, and **1c** in the solid state were elucidated by X-ray crystallography. *N*-Acylamidine **1a** adopts a 4-amino-1-oxa-3-azabuta-1,3-diene tautomeric form with a W-shaped configuration having the two picolinyl subunits in endo positions and the spacious adamantylamino group in the exo position. The NH group enables the formation of linear head-to-tail-chains within the crystal lattice by weak hydrogen bonding to the carbonyl group of the next molecule (NH···O distance = 2.140 Å; O−N distance = 3.014 Å; sum of van der Waals radii = 3.14 Å) (Figure 1, top). In contrast, **1b** shows a tautomer with the proton attached to the central nitrogen atom and a twisted U-shaped configuration with the phenyl group bent significantly out of the molecular plane (Figure 1, bottom). The distances from the proton at N3 to the picolinyl nitrogen atoms amount to 2.230 and 2.400 Å, indicating intramolecular hydrogen bonding (Figure 1, bottom). In **1c**, a third structural possibility, namely, another type of U-shaped configuration with an intramolecular hydrogen bond between O1 and N5 (O−N distance = 2.62 Å; H···O distance = 1.87(2) Å) is realized (Figure 2), indicating the various structural motifs possible for *N*-acylamidines due to hydrogen bonding and configurational flexibility in the solid state, where crystal forces may also have a profound influence on the structural properties.

Zirconium Complexes 7a, 7b, and 9. Treatment of equimolar amounts of *N*-acylamidines **1a** and **1b** with cyclopentadienylzirconium(IV) trichloride in dry tetrahydrofuran under argon for 12 h at room temperature yielded the novel 1:1 coordination compounds **7a** and **7b** in 88 and 92% yield, respectively, as colorless solids. These complexes of the neutral ligands were completely characterized by spectroscopic methods as well as by X-ray diffraction analysis (Scheme 6). Attempts to synthesize the related ionic complexes by deprotonation of **1a** and **1b** with potassium hydride and subsequent treatment with cyclopentadienylzirconium(IV)

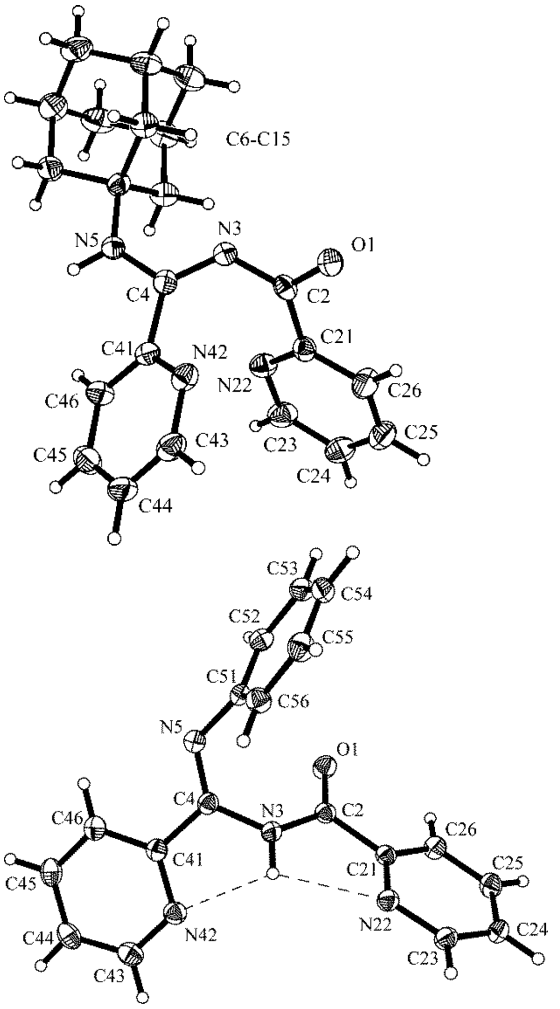


Figure 1. Molecular structures of compounds **1a** (top) and **1b** (bottom) in the solid state (X-ray diffraction, XP-plot, 30% probability level).

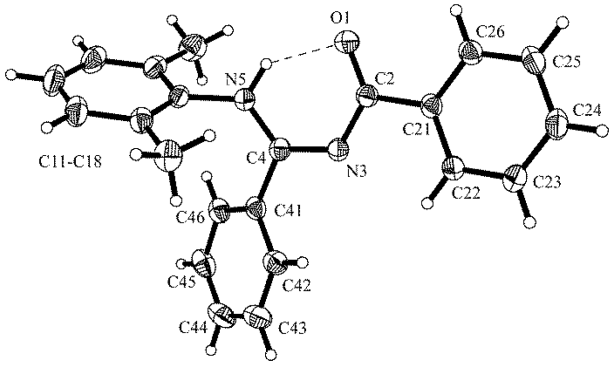


Figure 2. Molecular structure of compound **1c** in the solid state (X-ray diffraction, XP-plot, 30% probability level).

trichloride did not lead to isolable compounds (compare, however, to the reaction of **1c** described below).

According to the X-ray data, in spite of the distinct differences between the structures of ligands **1a** and **1b**, the two coordination compounds **7a** and **7b** show very similar structural properties, which are characterized by coordination to the oxygen atom of the acyl moiety and the nitrogen atom of the adjacent pyridine ring by the zirconium(IV) ion in its

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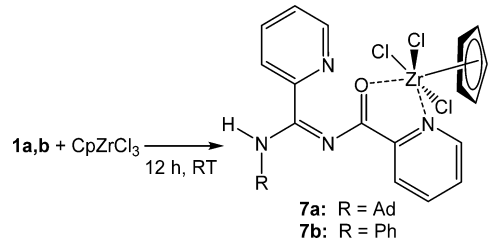
Scheme 6. Synthesis of Zirconium Complexes 7a and 7b



octahedral environment. The other coordination sites of the amidine part and of the second pyridine subunit are not involved in the bonding. The *N*-acylamidine ligand adopts a slightly twisted sickle-shaped structure (Figure 3). The

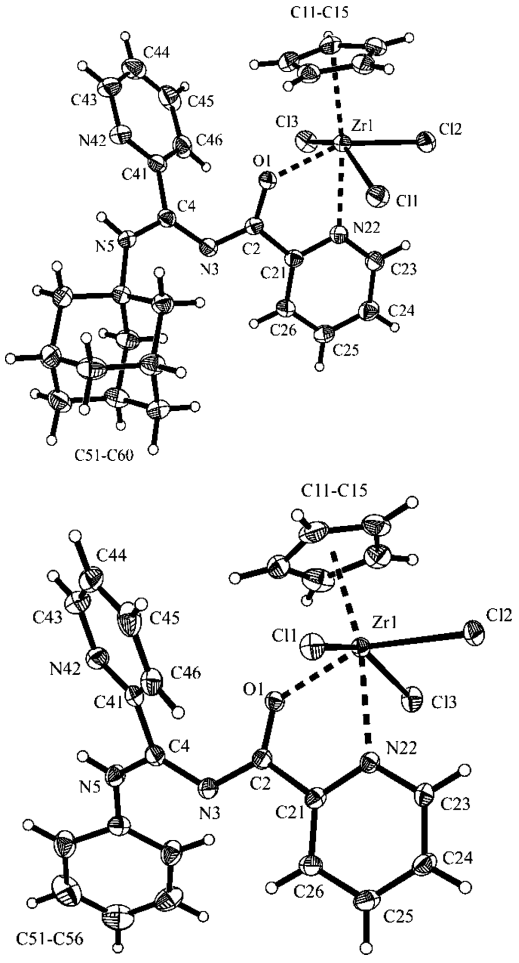
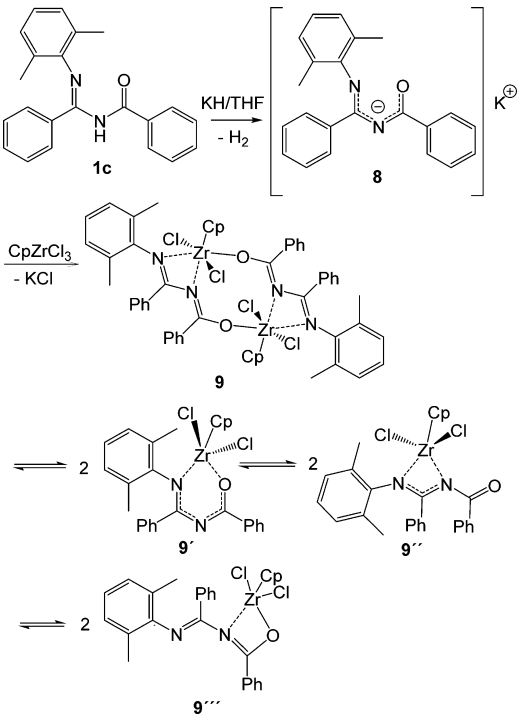


Figure 3. Molecular structures of compounds **7a** (left) and **7b** (right) in the solid state (X-ray diffraction, XP-plot, 30% probability level).

formation of the five-membered metallacycle resembles results obtained by Sengupta and co-workers (no X-ray) for picolinoyl hydrazone derivatives.[35] The preference for the η^4 structure over other coordination modes is well in line with the results of quantum-chemical density functional theory (DFT) calculations at the TPSS/def2-TZVP level of theory including the Grimme dispersion energy GD3.[36−38] Thus, the η^4 structural mode (Figure 3) is preferred by 10.7 kcal/mol (including zero-point energy (ZPE) corrections) over an η^6-*N,O* structure (see Scheme 3), by 16.9 kcal/mol over an η^3-*N,O* chelate, and by 28.1 kcal/mol over an η^3-*N,N* chelate, the latter two both involving the *N*-acylamidine submoiety but not the pyridine rings (for details, see the Supporting Information).

For the synthesis of coordination compounds of *N*-acylamidine **1c**, which in this case was used as an anionic ligand, a different synthetic route was chosen. In a first step, **1c** was deprotonated using potassium hydride in dry THF for 4 h to give **8** in a yield of 97% (Scheme 7) as a yellow solid. We

Scheme 7. Synthesis of Zirconium Complexes 9 and Suggestions for Possible Monomers 9′, 9″, and 9‴ in Solution



were able to obtain single crystals suitable for X-ray diffraction of the potassium compound **8** by slow diffusion of pentane into a dichloromethane solution at room temperature. In the solid state, compound **8** forms a complicated three-dimensional polymeric network in which the *N*-acylamidine moieties are interconnected by O and N coordination to the potassium ions and also by strong π interactions of the η^6, η^2, and η^1 coordination type to the aromatic rings of the ligands (Figure 4).

Transmetalation from potassium compound **8** using cyclopentadienylzirconium(IV) trichloride in tetrahydrofuran at room temperature for 4 h resulted in a complete restructuring of the polymeric metal−organic network, producing the 2:2 coordination compound **9** in 47% yield, which is best described as an amidinate complex. Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a trichloromethane solution of **9** (Figure 5). Compound **9** crystallizes in the asymmetric, chiral space group $P2_12_12_1$ with slightly different (monomer) subunits. The *N*-acylamidine ligands are present in an almost planar W-shaped configuration with the two hexacoordinate zirconium atoms interconnecting both ligands via both nitrogen atoms and the oxygen atom, forming four-membered Zr−N−C−N heterocycles with additional contacts to the acyl oxygen atoms. The ^{1}H NMR data obtained in CD_2Cl_2 solution from −90 to 25 °C, however, show the presence of three independent main species,

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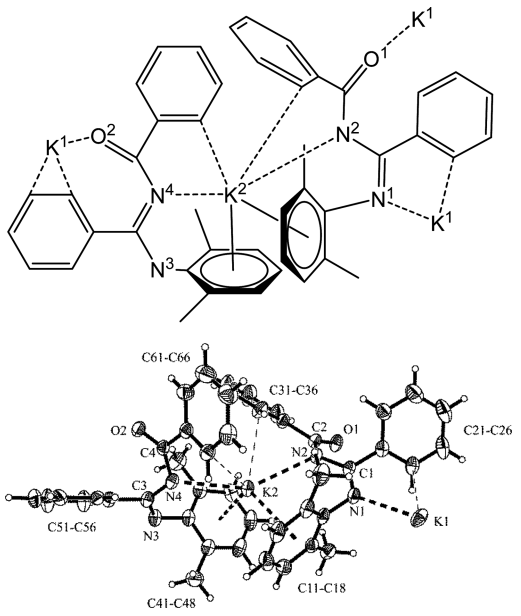

Figure 4. Schematic details (top) and X-ray structure (bottom) of the asymmetric unit of compound **8**, showing the arrangement around K2 in the solid state and indicating the various potassium interactions (X-ray diffraction, XP-plot, 30% probability level; for the environment of K1, see the Supporting Information).

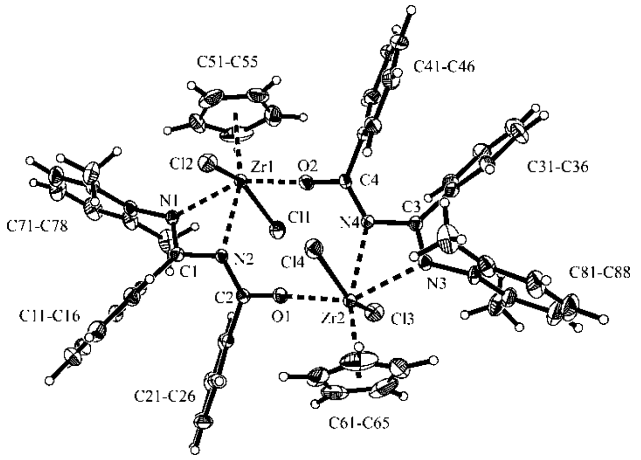

Figure 5. Molecular structure of compound **9** in the solid state (X-ray diffraction, XP-plot, 30% probability level).

possibly involving the dimer **9** and the monomeric 1:1 coordination compounds **9′**, **9″**, and **9‴**, as seen predominantly from the signals of the 2,6-dimethylphenyl groups as well as those of the cylopentadienyl subunits (Scheme 7). Also, ^{13}C NMR data support this observation (see the Supporting Information for the spectra). Because of the low solubility of **9** in toluene-d_8, however, high-temperature spectra could not be measured. At present, we have no direct evidence for the structures of the monomeric species possibly formed in solution nor of the existence of a possible equilibrium. DFT calculations at the TPSS/Def2-TZVP/GD3 level predict the lowest relative energy for species **9′** (E_{rel} = 0.0 kcal/mol, including ZPE), followed by species **9″** (0.6 kcal/mol) and then species **9‴** (2.1 kcal/mol). **9‴** resembles the nitrile adducts described by Bergman and co-workers[19] and may be understood as a 1,3-diazabutadiene−zirconium complex. Dimerization of **9′** in the gas phase is calculated to be exothermic by −42.7 kcal/mol, indicating the enormous Lewis acidity of the $ZrCl_2Cp$ unit.

A zirconium compound with an iminoquinolinol ligand, published by Jin and co-workers[13] shows *N*,*N*,*O*-binding sites comparable to our structure **9** and was used successfully in polymerization reactions of ethylene.

Reactivity toward Ethylene. A series of ethylene polymerization reactions were carried out using zirconium compounds **7a**, **7b**, and **9** under specific reaction conditions in the presence of MAO (10 wt % in toluene ("MAO 10T"), Chemtura Organometallics GmbH) as a coactivator. The gel-permeation chromatography (GPC) results are summarized in Table 1. Reactions were performed in a 100 mL autoclave reactor in toluene at an ethylene pressure of 178 psi and a [Al]/[Zr−*N*-acylamidine] ratio of 500 or 1000 (determined in our previous studies).[15d] Entry 1 corresponds to the reactivity previously reported for [(NC-nacnac)-η^5-cyclopentadienyl] zirconium dichloride/MAO and is provided for comparison.[15d] In all cases we observed the formation of high-molecular-weight polyethylene (PE) with melting points in the range of 134−140 °C, indicating that the materials are highly linear.

Entries 2−5 show the results obtained using compound **9** at reaction temperatures of 53 and 72 °C with Al/Zr ratios of 1000 and 500 (Figure 6). Comparison of entry 2 with entry 1[15d] shows that the activity of the new systems is more than twice as high as that of the reference under the same reaction conditions, but the molecular weight of the resulting polymers is lower and the polydispersity index (PDI) is broader (M_w/M_n

Table 1. Results of Selected Polymerization Experiments Using Catalysts 7a, 7b, and 9[a]

entry	compd	amount of catalyst[b]	Al/Zr ratio[c]	temp[d]	activity[e]	M_n[f]	M_w[f]	PDI	T_m[g]
1	ref 15d	6.8	1000	75	845	65	138	2.1	137
2	**9**	6.8	1000	72	1853	13	44	3.3	134
3	**9**	6.8	500	71	1235	21	74	3.4	133
4	**9**	6.0	1000	53	1600	34	154	4.6	133
5	**9**	6.0	500	53	800	25	200	8.1	138
6	**7a**	7.5	1000	72	400	5	16	3.1	136
7	**7a**	7.5	1000	53	520	20	158	7.7	134
8	**7a**	7.5	500	53	240	29	157	5.4	134
9	**7b**	6.5	1000	55	323	19	164	8.4	134
10	**7b**	6.5	500	54	258	30	260	8.6	134

[a]Polymerizations were carried out in 30 mL of toluene at an ethylene pressure of 178 psi (12.3 bar). The cocatalyst was MAO. The reaction time was 10 min. Precatalysts were dissolved in 2 mL of dichloromethane prior to the addition of toluene. [b]Zr content in μmol. [c][Al]/[Zr−*N*-acylamidine] ratio. [d]Reaction temperature in °C. [e]Activity in kg of polymer (mol of Zr)$^{-1}$ h^{-1}. [f]In units of 10^3 g/mol. [g]Melting temperature in °C.

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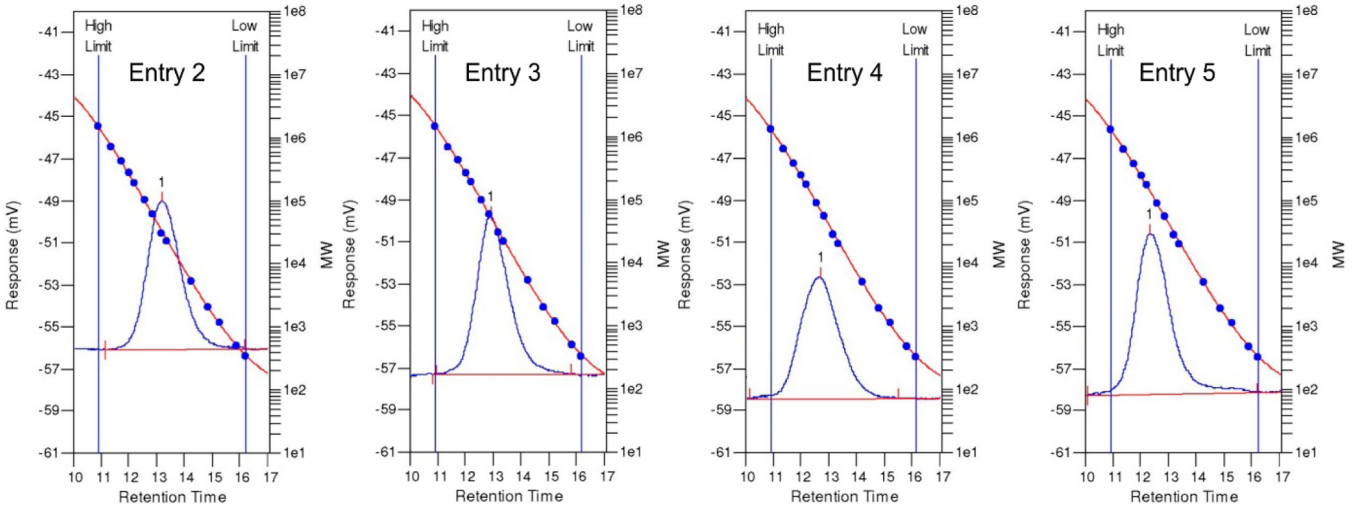
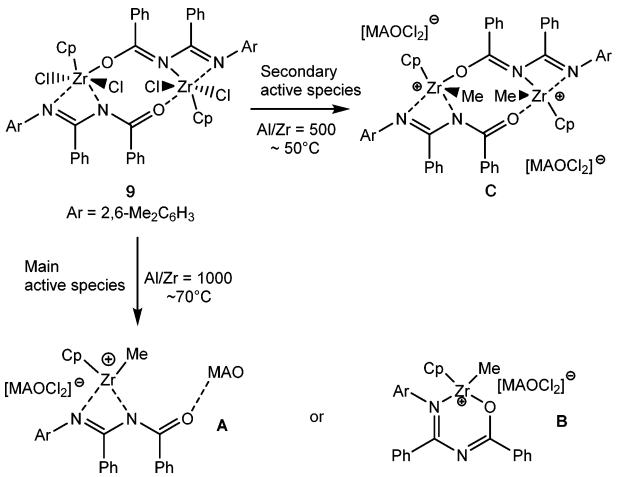


Figure 6. GPC results for entries 2–5 in Table 1.

ratio = 3.3). Reduction of the Al/Zr ratio to 500 at 70 °C leads to decreased activity and, as expected, to the polymer having a higher molecular weight without a change in the PDI (entry 3). It is important to remark that the activity is still greater than that of the reference. Entries 4 and 5 indicate that at a lower temperature (53 °C) compound **9** shows lower activity than at 70 °C (entries 2 and 3) and also results in products with broad PDIs, especially at an Al/Zr ratio of 500.

Monomodal molecular weight distributions (MWDs) were seen for all of the polymers collected (entries 2–5), but a small shoulder corresponding to a low-molecular-weight fraction was present when the temperature was decreased to ∼50 °C. At present we assume that a second species may be produced in low concentrations. The species responsible for the predominant molecular weight fraction may involve alkylation by MAO with coordination of the oxygen by zirconium in a monomeric fashion in form of the six-membered ring **B** or the dimeric structure **C** (Scheme 8). This coordination mode could increase the steric bulk around the metal center, resulting in PE with increased molecular weight. Another possible species may involve the less crowded, monomeric four-membered ring species **A** encountering coordination at oxygen by the aluminum Lewis acid (Scheme 8), possibly leading to low-molecular-weight polymers

Scheme 8. Possible Activation Modes of Dimeric and Monomeric Complexes 9 by Addition of MAO



On the other hand, as expected, the average molecular weight decreased with increasing polymerization temperature. The accepted explanation for this widely acknowledged phenomenon is that the activation energy for chain transfer is greater than that for propagation.[39] Concerning the effect of the cocatalyst concentration (Al/Zr) on the MWD of PE obtained using catalyst **9**/MAO, it appears that the molecular weight of the polymer decreases in the presence of higher amounts of cocatalyst, possibly because the rate of the termination reaction via transfer to the cocatalyst increases with increasing cocatalyst concentration.

Entries 6–8 for **7a**/MAO polymerizations and entries 9 and 10 for **7b**/MAO polymerizations show that these combinations also offer efficient ethylene polymerization sites. A general comparison of those entries under reaction conditions similar to those for the **9**/MAO systems shows that the polymerization activities are more than 3 times lower. The **7a**/MAO systems show a strong temperature dependence. Because of the better performance found for precatalyst **7a** at 53 °C, precatalyst **7b** was studied only by changing the Al/Zr ratio at that temperature, at which **7a** and **7b** showed similar activities. In terms of the molecular weights of the resultant PE, both systems yield PE with a broad "monomodal" MWD with a shoulder toward lower molecular weight. It is assumed that the zirconium trichloride complexes (**7a** and **7b**) could probably provide multisite active species at this temperature, possibly also by dehydrochlorination, which may be responsible for the PEs with a broad distribution.

CONCLUSION

We have reported the synthesis and full characterization of three novel *N*-acylamidine ligands **1a–c** with varying steric and coordination properties. They were fully analytically and spectroscopically characterized. According to the X-ray diffraction data, these compounds adopt very different conformations in the solid state and offer the possibility for inter- (**1a**) and intramolecular (**1b** and **1c**) hydrogen bonding. Treatment of **1a** and **1b** with cyclopentadienylzirconium(IV) trichloride provided access to the novel zirconium complexes **7a** and **7b**, in which the carbonyl oxygen atom and one of the pyridine nitrogen atoms act as coordination sites. Coordination

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compound **9** was obtained from **1c** after deprotonation using potassium hydride as the base to give potassium salt **8** and subsequent treatment with cyclopentadienylzirconium(IV) trichloride. The X-ray data for **8** show interesting multiple interactions of the potassium cation with the heteroatoms as well as with the aromatic moieties. Complex **9** is best described as a dimeric amidinate−zirconium coordination compound. In solution, an equilibrium with a monomer is observed.

The compounds **7a**, **7b** and **9** are new types of active zirconium precursors that can be used to polymerize ethylene to high molecular weight in the presence of low concentrations of coactivators (Al/Zr ratios of 500 and 1000). On the basis of the results obtained with precatalyst **9** and compared with those previously obtained with the Cp-diimine complex with carbonitrile functionality,[14c] we propose that the reactivity of **9** is also a result of coordination of a Lewis acid (MAO) to a Lewis basic functionality, either a nitrogen atom of the metallocycle or the oxygen atom of the carbonyl group, leading to an η^3-*N*,*N* ligand coordination mode with the zirconium moiety. Since in this new system the position of the functionalities (N and O) to which the Lewis acid can coordinate (Scheme 8) is only two atoms away from the metal center, the effect of the reduction in the electron density at the zirconium center (by inductive effects) is greater, making the metal center more electrophilic and consequently leading to greater activity. On the other hand, although the activity seen at an Al/Zr ratio of 500 at 53 or 70 °C is lower than that at a ratio of 1000, these results are high compared with those for similar systems reported in the literature, supporting the idea that adduct formation plays an important role in these systems.

In the case of the precatalysts **7a** and **7b** activated with MAO, the activities were much lower than that of **9**. This may be associated with the presence of three free basic functional groups, which can be coordinated by MAO, reducing their effectiveness per mole of cocatalyst. Furthermore, the trihalogenated characteristic of these compounds generates multiple species, which is probably responsible for the wide molecular weight distributions of the polymers obtained.[9,10]

EXPERIMENTAL SECTION

All procedures were carried out under purified argon using standard Schlenk techniques. Compounds **7**−**9** were prepared in a glove box under dry argon. All of the solvents were purified and dried by standard methods.

Picolinoyl Chloride Hydrochloride (3). Picolinic acid (8.00 g, 65.0 mmol) was added to 80 mL (1.1 m) of thionyl chloride at 0 °C (ice cooling). At first a green suspension was formed, which turned into a clear red solution after 40 h of stirring at rt. The mixture was poured into 30 mL of pentane and stirred for 30 min, and then the solvent was separated from the violet solid by decantation. Solvent residues were removed from the crude product in vacuo. Yield: 10.35 g (58.5 mmol, 90%), violet solid. Mp: 225 °C (decomp). ^{1}H NMR (400.13 MHz, DMSO-d_6): δ 8.09−8.12 (m, 1H, *p*-C$H_{arom.}$), 8.35−8.37 (d, ^3J = 7.7 Hz, 1H, *o*-C$H_{arom.}$), 8.54−8.57 (t, ^3J = 7.7 Hz, 1H, *m*-C$H_{arom.}$), 8.88−8.89 (d, ^3J = 4.9 Hz, 1H, *m*-C$H_{arom.}$), 11.54 (br, 1H, N*H*). ^{13}C NMR (75.47 MHz, DMSO-d_6): δ 126.7 (C$_{arom.}$), 129.6 (C$_{arom.}$), 142.9 (*i*-C$_{arom.}$), 144.8, 145.2 (C$_{arom.}$), 162.1 (*C*=O).

Ethyl *N*-Picolinoylpicolinimidate (4). To a stirred solution of picolinoyl chloride hydrochloride (**3**) (8.90 g, 1 equiv, 50 mmol) and 17 mL of TEA (2.4 equiv, 120 mmol) in 100 mL of chloroform was added ethyl 2-picolinimidate (**2**)[34] (7.55 g, 1 equiv, 50 mmol) at 0 °C. The reaction mixture was warmed to room temperature and stirred for an additional 20 h. After removal of the ammonium salt by filtration, the organic layer was washed two times with water and dried over magnesium sulfate. Then the solvent was evaporated to dryness. Multiple recrystallization from chloroform yielded colorless crystals. Yield: 3.20 g (12.5 mmol, 25%), white solid. Mp: 157 °C. IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3300 (w), 3163 (w), 3105 (w), 3088 (m), 3059 (s, CH$_{arom.}$), 3026 (m), 2976 (s, CH$_{aliph.}$), 2955 (m), 2934 (m), 2897 (m), 2864 (m), 2774 (m), 2718 (m), 2600 (w), 2448 (w), 2336 (w), 2311 (w), 1960 (w), 1944 (w), 1813 (w), 1771 (w), 1622 (s), 1603 (vs, C=N), 1661 (vs, C=N), 1589 (vs), 1572 (vs), 1493 (s), 1481 (s), 1472 (s, C=C$_{arom.}$), 1448 (vs, δ-CH$_2$), 1391 (s), 1366 (s, δ-CH$_2$), 1325 (s), 1310 (vs), 1279 (vs, COC$_{ether}$), 1223 (s), 1186 (m), 1169 (m), 1148 (vs), 1115 (s), 1061 (vs, COC$_{ether}$), 1024 (vs), 1001 (s), 988 (m), 970 (m), 922 (s), 891 (s), 881 (s), 847 (m), 829 (m), 795 (w), 779 (vs), 737 (vs), 712 (vs), 692 (vs), 671 (vs), 615 (m), 573 (m), 530 (s), 444 (m). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.50 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3), 4.56 (q, $^3J_{HH}$ = 7.1 Hz, 2H, CH_2), 7.20 (ddd, $^3J_{HH}$ = 7.5, 4.8 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, C$H_{arom.}$), 7.30 (ddd, $^3J_{HH}$ = 7.5, 4.8 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, C$H_{arom.}$), 7.69−7.76 (m, 1H, C$H_{arom.}$), 7.76−7.83 (m, 1H, C$H_{arom.}$), 7.92−7.97 (m, 1H, C$H_{arom.}$), 8.22−8.26 (m, 1H, C$H_{arom.}$), 8.27 (ddd, $^3J_{HH}$ = 4.7 Hz, $^4J_{HH}$ = 1.7, 0.9 Hz, 1H, C$H_{arom.}$), 8.50 (ddd, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.7, 0.9 Hz, 1H, C$H_{arom.}$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2 (CH$_3$), 64.3 (CH$_2$), 123.5, 123.8, 125.4, 125.6, 136.7, 137.0 (CH$_{arom.}$), 146.1 (*i*-C$_{arom.}$), 148.4, 148.9 (CN$_{arom.}$), 152.3 (*i*-C$_{arom.}$), 155.2 (*C*=N), 176.2 (*C*=O). MS (ESI): *m*/*z* 278 [M + Na]$^+$, 256 [M + H]$^+$. HRMS [M + H]$^+$: calcd, 256.1081; found, 256.1080. Formula: $C_{14}H_{13}N_3O_2$ (*M* = 255.10 g/mol). Anal. Calcd: C, 65.87; H, 5.13; N, 16.46. Found: C, 65.82; H, 4.84; N, 16.53. For details of the X-ray diffraction study, see the Supporting Information.

General Procedure for the Synthesis of Compounds 1a and 1b. A solution of 1.0 equiv of compound **4** and 1.2 equiv of amine in dry chloroform was heated under reflux for 6 h, washed three times with water, and dried over magnesium sulfate. After evaporation of the solvent, the raw product was purified by recrystallization.

***N*-((Adamant-1-ylamino)(pyridin-2-yl)methylene)-picolinamide (1a).** According to the general procedure, compound **1a** was synthesized from 1-adamantanamine (770 mg, 1.0 equiv, 5.1 mmol) and compound **4** (1.02 g, 1.0 equiv, 4.0 mmol). Recrystallization from a mixture of dichloromethane and pentane gave the pure product. Yield: 1.18 g (3.28 mmol, 80%), white solid. Mp: 144 °C. IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3346 (m, NH), 2899 (m), 2857 (w), 1630 (vs, C=O/C=N), 1607 (vs, C=O/C=N), 1582 (vs), 1568 (vs), 1526 (vs), 1435 (s), 1354 (s), 1346 (s), 1296 (s), 1279 (s), 1225 (s), 1128 (s), 1099 (s), 1070 (s), 1038 (s), 993 (s), 943 (s), 880 (s), 800 (s), 762 (s), 748 (vs), 718 (s), 675 (s), 658 (s), 619 (s), 598 (s), 567 (s), 554 (s), 546 (s), 540 (s), 530 (s). ^{1}H NMR (600 MHz, C_6D_6, 299 K): δ 1.48 (m, *J* = 39.5, 11.8 Hz, 6H, C$H_{2,adam.}$), 1.87 (s, 3H, C$H_{adam.}$), 2.27 (d, *J* = 2.4 Hz, 6H, C$H_{2,adam.}$), 6.41 (ddd, *J* = 7.5, 4.7, 1.0 Hz, 1H, *p*-C$H_{arom.}$), 6.53 (ddd, *J* = 7.5, 4.7, 1.2 Hz, 1H, *p*-C$H_{arom.}$), 6.69 (td, *J* = 7.8, 1.8 Hz, 1H, *o*-C$H_{arom.}$), 7.07 (td, *J* = 7.7, 1.8 Hz, 1H, *o*-C$H_{arom.}$), 7.43 (br s, 1H, N*H*), 7.81−7.89 (m, 1H, *m*-C$H_{arom.}$), 8.14 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H, NC$H_{arom.}$), 8.33 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H, NC$H_{arom.}$), 8.51 (dt, *J* = 7.8, 1.0 Hz, 1H, *m*-C$H_{arom.}$). ^{13}C NMR (150 MHz, C_6D_6, 299 K): δ 29.8 (3C, C$H_{adam.}$), 36.6 (6C, C$H_{2,adam.}$), 41.2 (6C, C$H_{2,adam.}$), 53.0 (*i*-C$_{adam.}$), 123.6, 124.5 (*o*-C$H_{arom.}$), 124.7, 124.9 (*p*-C$H_{arom.}$), 136.4, 136.7 (*m*-C$H_{arom.}$), 148.4, 148.8 (NC$H_{arom.}$), 150.8 (*i*-C$_{arom.}$), 154.1 (*C*=N) 154.3 (*i*-C$_{arom.}$), 172.1 (*C*=O), (the *C*=N signal could not be detected.) MS (ESI): *m*/*z* 383 [M + Na]$^+$, 361 [M + H]$^+$. HRMS [M + H]$^+$: calcd, 361.2023; found, 361.2026. Formula: $C_{22}H_{24}N_4O$ (*M* = 360.19 g/mol). Anal. Calcd: C, 73.31; H, 6.71; N, 15.54. Found: C, 72.78; H, 6.70; N, 15.46. For details of the X-ray diffraction study, see the Supporting Information.

***N*-((Pyridin-2-yl)(phenylimino)methyl)-picolinamide (1b).** According to the general procedure, ethyl *N*-picolinoylpicolinimidate (**4**) (1.62 g, 6.30 mmol) was dissolved in dichloromethane (70 mL). After addition of a solution of aniline (0.59 g, 6.30 mmol) in dichloromethane (20 mL), the reaction mixture was stirred at room temperature for 20 h. The solvent was removed, and the product was purified by column chromatography. Yield: 1.07 g (3.5 mmol, 56%), yellow crystals. R_f: 0.13 (silica gel, 2:1 pentane/ethyl acetate + 3% triethylamine). Mp: 128 °C. IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3368 (s, NH), 3082 (w), 3051 (m), 3015 (w), 2004 (w), 1977 (w), 1956 (w), 1879 (w),

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1701 (vs), 1638 (s, C═$C_{arom.}$), 1591 (s, C═O/C═N), 1566 (s, C═O/C═N), 1543 (m), 1487 (vs), 1460 (vs), 1437 (vs), 1423 (vs), 1313 (m), 1296 (s), 1269 (s), 1231 (s), 1219(s), 1177 (s), 1146 (s), 1128 (s), 1092 (s), 1072 (m), 1061 (m), 1043 (s), 997 (s), 978 (m), 945 (m), 908 (m), 841 (s), 816 (m), 799 (s), 764 (s), 744 (s), 700 (vs), 631 (m), 615 (s), 581 (m), 546 (s), 532 (s), 503 (m), 476 (m). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 7.12 (br, 3H, $CH_{arom.}$), 7.35−7.46 (m, 4H, $CH_{arom.}$), 7.77−7.87 (m, 2H, $CH_{arom.}$), 8.04−8.06 (m, 1H, $CH_{arom.}$), 8.28−8.33 (m, 1H, $CH_{arom.}$), 8.59−8.61 (m, 1H, $CH_{arom.}$), 8.66−8.69 (m, 1H, $CH_{arom.}$), 11.36 (br, 1H, N*H*). ^{13}C NMR (100.62 MHz/ $CDCl_3$): δ 120.4 (2C, $C_{arom.}$), 122.7, 122.9, 123.9, 125.0, 126.7 ($C_{arom.}$), 128.8 (2C, $C_{arom.}$), 136.9, 137.4 ($C_{arom.}$), 146.7 (*i*-$C_{arom.}$), 148.3 (2C, $C_{arom.}$), 148.9, 152.7 (*i*-$C_{arom.}$), 161.3 (C═N), (the *C*═N signal could not be detected.). MS (ESI, methanol): *m*/*z* (%) 627 (100) $[2M + Na]^+$, 325 (96) $[M + Na]^+$, 303 (38) $[M + H]^+$. Formula: $C_{18}H_{14}N_4O$ (*M* = 302.33 g/mol). Anal. Calcd: C, 71.51; H, 4.67; N, 18.53. Found: C, 71.43; H, 4.69; N, 18.45. For details of the X-ray diffraction study, see the Supporting Information.

(2,6-Dimethylphenyl)benzimidamide (5). To a solution of 2,6-dimethylaniline (7.27 g, 1 equiv, 60 mmol) in dry THF (50 mL) was added *n*-butyllithium (60 mmol, 1 equiv, 37.5 mL of 1.6 M solution in *n*-hexane) at −78 °C. The reaction mixture was stirred for 1 h at room temperature and cooled again to −78 °C. Then benzonitrile (6.19 g, 1 equiv, 60 mmol) was added slowly. After 20 h at room temperature, the reaction was quenched with 50 mL of a 1:1 methanol/water mixture, and 50 mL of chloroform was added. The layers were separated, and the organic one was washed three times with water, dried with magnesium sulfate, and evaporated to dryness. Compound **5** was purified by crystallization from diethyl ether and pentane. Yield: 6.17 g (27.5 mmol, 46%; lit. 80%[40]), white solid. Mp: 104 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.16 (s, 9H, CH_3), 4.61 (br s, 2H, NH_2), 6.90−6.95 (m, 1H, $CH_{arom.}$), 7.08 (d, $^3J_{HH}$ = 7.5 Hz, 2H, $CH_{arom.}$), 7.41−7.52 (m, 3H, $CH_{arom.}$), 7.91 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, $CH_{arom.}$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.8 (3C, CH_3), 122.8 ($CH_{arom.}$), 126.7 (2C, $CH_{arom.}$), 128.2 (2C, $CH_{arom.}$), 128.6 (2C, $CH_{arom.}$), 128.9 (2C, *i*-*C*−CH_3), 130.5 ($CH_{arom.}$), 135.6 (*i*-*C*−C═N), 146.3 (*i*-C−N═C), 153.2 (C═N). Formula: $C_{15}H_{16}N_2$ (*M* = 224.13 g/mol).

***N*-(((2,6-Dimethylphenyl)amino)(phenyl)methylene)-benzamide (1c).** To a solution of compound **5** (2.58 g, 1 equiv, 11.52 mmol) in THF (40 mL) was added a solution of benzoyl chloride (**6**) (1.34 mL, 1 equiv, 11.52 mmol) in 15 mL of THF slowly over a period of 1 h at 0 °C. The reaction solution was stirred for 40 h. After filtration of the ammonium salt, 2.0 mL of chloroform was added, and the mixture was washed three times with water. The organic layer was dried over magnesium sulfate and evaporated to dryness. Multiple recrystallizations from a mixture of THF and pentane gave the pure product. Yield: 1.97 g (6.0 mmol, 50%), white solid. Mp: 117 °C. IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2361 (w), 2340 (w), 1593 (s, C═O/C═N), 1549 (vs, C═O/C═N), 1472 (w), 1447 (m), 1418 (m), 1412 (m), 1406 (m), 1321 (vs), 1273 (m), 1196 (s), 1169 (m), 1157 (w), 1146 (w), 1078 (w), 1061 (m), 1020 (m), 999 (w), 968 (w), 926 (w), 914 (w), 824 (m), 791 (m), 772 (s), 746 (s), 719 (s), 689 (vs), 667 (w), 611 (w), 565 (m). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.13 (s, 6H, CH_3), 6.89−6.99 (m, 2H, $CH_{arom.}$), 7.26−7.59 (m, 7H, $CH_{arom.}$), 7.88 (t, $^3J_{HH}$ = 7 Hz, 1H, $CH_{arom.}$), 8.40 (d, $^3J_{HH}$ = 7 Hz, 1H, $CH_{arom.}$), 8.63 (br s, 1H, $CH_{arom.}$), 8.97 (br s, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.30 (2C, CH_3), 122.9 (2C, $CH_{arom.}$), 126.0 (2C, $CH_{arom.}$), 127.7, 127.9, 131.5 (2C, $CH_{arom.}$), 134.3, 135.8, 136.7 (*i*-$C_{arom.}$), 137.4 (2C, $CH_{arom.}$), 148.0 (2C, $CH_{arom.}$), 148.8, 149.6 (*i*-$C_{arom.}$), 152.2 (C═N), 177.2 (C═O). MS (ESI): *m*/*z* 351 $[M + Na]^+$, 329 $[M + H]^+$. HRMS $[M + H]^+$: calcd, 329.1648; found, 329.1640. Formula: $C_{22}H_{20}N_2O$ (*M* = 328.16 g/mol). Anal. Calcd: C, 80.46; H, 6.14; N, 8.53. Found: C, 80.17; H, 6.22; N, 8.43. For details of the X-ray diffraction study, see the Supporting Information.

Potassium *N*-(((2,6-Dimethylphenyl)imino)(phenyl)methyl)-benzimidate (8). A solution of compound **1c** (203 mg, 1 equiv, 0.62 mmol) and potassium hydride (37 mg, 1.5 equiv, 0.93 mmol) was stirred in 10 mL of dry THF for 4 h. The reaction showed rapid gas evolution. The slightly cloudy mixture was filtered through Celite, and the solvent was evaporated. A light-yellow solid was collected. For purification the solid was suspended in diethyl ether, separated by decantation, and freed from the solvent by evaporation. Then the solid was washed two times with 3 mL of pentane, and a light-yellow solid was isolated with minor impurities of diethyl ether and THF. Single crystals of compound **8** suitable for X-ray diffraction analysis were grown by slow diffusion of pentane into dichloromethane at room temperature. Yield: 220 mg (0.61 mmol, 97%), yellow solid. ^{1}H NMR (600 MHz, THF-d_8, 298 K): δ 2.18 (s, 6H, CH_3), 6.53 (t, *J* = 7.4 Hz, 1H, *p*-$CH_{anil.}$), 6.77 (d, *J* = 7.4 Hz, 1H, *m*-$CH_{anil.}$), 7.11−7.19 (m, 3H, $CH_{arom.}$), 7.20−7.32 (m, 3H, $CH_{arom.}$), 7.88 (d, *J* = 5.8 Hz, 1H, *m*-$CH_{arom.}$), 8.13 (d, *J* = 4.9 Hz, 1H, *m*-$CH_{arom.}$). ^{13}C NMR (151 MHz, THF-d_8, 298 K): δ 19.3 (2C, CH_3), 120.4 (*p*-$CH_{anil.}$), 127.4 ($CH_{arom.}$), 127.6 (2C, *m*-$CH_{anil.}$), 128.0 ($CH_{arom.}$), 128.5 (2C, $CH_{arom.}$), 128.6, 128.7 ($CH_{arom.}$), 129.2 (2C, $CH_{arom.}$), 129.3 (2C, $CH_{arom.}$), 142.1 (2C, *i*-$C(CH_3)$), 143.1, 152.7 (*i*-$C_{arom.}$), 163.1 (*C*═N), 165.9 (*C*═O). Formula: $C_{22}H_{19}N_2OK$ (*M* = 366.11 g/mol). Anal. Calcd: C, 72.10; H, 5.23; N, 7.64. Found: C, 72.07; H, 5.25; N, 7.69. For details of the X-ray diffraction study, see the Supporting Information.

Zirconium(IV) Coordination Compounds 7a, 7b, and 9. *(N-((Adamant-1-ylamino)(pyridin-2-yl)methylene)picolinamide)-(cyclopentadienyl)zirconium(IV) Trichloride (**7a**).* A solution of compound **1a** (155 mg, 1 equiv, 0.513 mmol) in THF (5 mL) was added to $CpZrCl_3$ (129 mg, 0.95 equiv, 0.491 mmol) dissolved in THF (5 mL). The reaction mixture was stirred for 12 h, and the resulting mixture was filtered, washed three times with 5 mL of ether, and dried under vacuum. Single crystals of compound **1a** suitable for X-ray crystal structure analysis were grown by diffusion of cyclopentane into dichloromethane at room temperature. Yield: 250 mg (0.44 mmol, 88%), colorless powder. ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ 1.75 (m, 6H, $CH_{2,adam.}$), 2.21 (br s, 3H, $CH_{adam.}$), 2.29 (t, *J* = 12.9 Hz, 6H, $CH_{2,adam.}$), 6.31 (s, 5H, CH_{Cp}), 7.67 (ddd, *J* = 7.3, 4.7, 1.4 Hz, 1H, $CH_{arom.}$), 7.72 (ddd, *J* = 7.6, 5.4, 1.4 Hz, 1H, $CH_{arom.}$), 8.00 (m, 2H, $CH_{arom.}$), 8.09 (td, *J* = 7.7, 1.6 Hz, 1H, $CH_{arom.}$), 8.30 (ddd, *J* = 7.8, 1.3, 0.8 Hz, 1H, $CH_{arom.}$), 9.70 (ddd, *J* = 5.4, 1.6, 0.8 Hz, 1H, $CH_{arom.}$), (the N*H* signal could not be detected). ^{13}C NMR (151 MHz, C_6D_6, 298 K): δ 29.3 (3C, CH_{adam}), 35.6 (3C, $CH_{2,adam.}$), 40.5 (3C, $CH_{2,adam.}$), 57.4 (*i*-$C_{adam.}$), 118.4 (5C, C_{Cp}), 125.8, 125.9, 128.2, 128.4 ($CH_{arom.}$), 136.8 (*i*-$C_{arom.}$), 139.1, 138.4 ($CH_{arom.}$), 143.0 (*i*-$C_{arom.}$), 149.3 ($NCH_{arom.}$), 149.4 ($NCH_{arom.}$), 166.1 (C═N), 167.6 (*C*═O). Formula: $C_{27}H_{29}Cl_3N_4OZr$ (*M* = 620.05 g/mol). Anal. Calcd: C, 52.04; H, 4.69; N, 8.99. Found: C, 51.91; H, 4.78; N, 8.78. For details of the X-ray diffraction study, see the Supporting Information.

*(N-((Phenylamino)(pyridin-2-yl)methylene)picolinamide)-(cyclopentadienyl)zirconium(IV) Trichloride (**7b**).* Compound **7b** was synthesized according to the procedure for compound **7a** from compound **1b** (100 mg, 1 equiv, 0.332 mmol) and $CpZrCl_3$ (86 mg, 0.98 equiv, 0.327 mmol). Single crystals of compound **7b** suitable for X-ray crystal structure analysis were grown by diffusion of cyclopentane into dichloromethane at room temperature. Yield: 172 mg (0.31 mmol, 92%), colorless powder. ^{1}H NMR (600 MHz, THF-d_8, 298 K): δ 6.24 (br s, 4H, CH_{Cp}), 7.39 (t, *J* = 7.4 Hz, 1H, $CH_{arom.}$), 7.48−7.50 (m, 2H, $CH_{arom.}$), 7.73−7.78 (m, 5H, $CH_{arom.}$), 8.05 (td, *J* = 7.7, 1.6 Hz, 1H, $CH_{arom.}$), 8.08−8.12 (m, 2H, $CH_{arom.}$), 8.20 (d, *J* = 7.8 Hz, 1H, $CH_{arom.}$), 8.89−8.90 (m, 1H, $CH_{arom.}$), 9.76 (d, *J* = 4.6 Hz, 1H, $CH_{arom.}$), (the N*H* signal could not be detected). ^{13}C NMR (151 MHz, THF-d_8, 298 K): δ 118.7 (5C, C_{Cp}), 124.9 (2C, $CH_{arom.}$), 127.1, 128.0, 129.1 (2C, $CH_{arom.}$), 129.3, 130.2 (2C, $CH_{arom.}$), 136.9 (*i*-$C_{arom.}$), 139.3, 139.8 ($CH_{arom.}$), 145.9, 150.5 (*i*-$C_{arom.}$), 150.6, 150.9 ($NCH_{arom.}$), 167.4 (*C*═N), 171.4 (*C*═O). Formula: $C_{23}H_{19}Cl_3N_4OZr$ (*M* = 561.97 g/mol). Anal. Calcd: C, 48.89; H, 3.39; N, 9.92. Found: C, 49.28; H, 3.27; N, 9.91. For details of the X-ray diffraction study, see the Supporting Information.

*(((((2,6-Dimethylphenyl)imino)(phenyl)methyl)imino)(phenyl)-methoxy)(cyclopentadienyl)zirconium(IV) Dichloride (**9**).* A solution of potassium salt **8** (150 mg, 1 equiv, 0.37 mmol) in THF (5 mL) was added to a mixture of $CpZrCl_3$ (100 mg, 1 equiv, 0.38 mmol) in THF (20 mL), and the resulting mixture was stirred at room temperature for 4 h. The resulting yellow solution was filtered over Celite. The

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solvent was evaporated, and the solid was washed with diethyl ether. Single crystals of compound **9** suitable for X-ray diffraction analysis were grown by slow diffusion of pentane into a trichloromethane solution at room temperature. Yield: 215 mg (0.18 mmol, 47%), yellow solid. ^{1}H NMR (500 MHz, CD_2Cl_2, 223 K): δ 1.82 (s, 3H, CH_3), 1.91 (s, 3H, CH_3), 2.19 (s, 12H, CH_3), 2.45 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 5.91 (s, 5H, CH_{Cp}), 6.14 (s, 5H, CH_{Cp}), 6.27 (s, 10H, CH_{Cp}), 6.74−6.86 (m, 12H, $CH_{arom.}$), 6.95−7.02 (m, 13H, CH_{arom}), 7.07−7.21 (m, 14H, CH_{arom}), 7.27−7.33 (m, 7H, CH_{arom}), 7.52 (t, $^{3}J_{HH}$ = 9.2 Hz, 2H, $CH_{arom.}$), 7.82 (t, $^{3}J_{HH}$ = 7.8 Hz, 2H, $CH_{arom.}$), 7.89 (t, $^{3}J_{HH}$ = 9.2 Hz, 1H, $CH_{arom.}$), 8.72−8.76 (m, 1H, $CH_{arom.}$) (unambiguous assignment was difficult because of overlap of resonances and the complicated splitting patterns). ^{13}C NMR (125.7 MHz, CD_2Cl_2, 223 K): δ 19.3 (CH_3), 19.4 (CH_3), 19.6 (4C, CH_3), 20.7 (CH_3), 21.5 (CH_3), 118.3 (5C, CH_{Cp}), 119.0 (10C, CH_{Cp}), 119.1 (5C, CH_{Cp}), 125.3 (3C, CH_{arom}), 126.6, 126.7, 127.2, 127.5 (CH_{arom}), 127.7 (2C, CH_{arom}), 127.8, 128.0, 128.1, 128.4, 128.5, 128.6, 128.8 (CH_{arom}), 129.0 (2C, CH_{arom}), 129.1, 129.5, 129.8, 129.9 (CH_{arom}), 130.1 (2C, CH_{arom}), 130.5 (2C, CH_{arom}), 130.6, 131.1 (CH_{arom}), 130.5 (2C, CH_{arom}), 131.3 (i-C_{arom}), 131.5 (i-C_{arom}), 131.8 (2C, i-C_{arom}), 132.1 (i-C_{arom}), 132.3 (2C, i-C_{arom}), 132.9 (i-C_{arom}), 133.5 (2C, CH_{arom}), 134.9, 135.0 (3C, CH_{arom}), 135.1, 135.9 (CH_{arom}), 136.6 (i-C_{phen}), 137.0 (3C, i-$C_{phen.}$), 142.9 (4C, i-C−CH_3), 142.3 (2C, i-C−CH_3), 142.7 (2C, i-C−CH_3), 170.5 (C═N), 174.8 (C−O), 176.2 (2C, C═N), 180.0 (2C, C−O), 180.9 (C═N), 185.2 (C−O). Formula: $C_{54}H_{48}N_4O_2Zr_2Cl_4{\cdot}CHCl_3$ (M = 1221.98 g/mol). Anal. Calcd: C, 53.77; H, 4.02; N, 4.56. Found: C, 53.46; H, 3.98; N, 4.57. For details of the X-ray diffraction study, see the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00240.

Crystallographic data for **1a** (CIF)
Crystallographic data for **1b** (CIF)
Crystallographic data for **1c** (CIF)
Crystallographic data for **7a** (CIF)
Crystallographic data for **7b** (CIF)
Crystallographic data for **8** (CIF)
Crystallographic data for **9** (CIF)
Crystallographic data for **4** (CIF)
NMR spectra, detailed X-ray data, GPC diagrams, and quantum-chemical results (PDF)

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Notes

The authors declare no competing financial interest.

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