Iminohydroxamato Early and Late Transition Metal Halide Complexes − New Precatalysts for Aluminoxane-Cocatalyzed Olefin Insertion Polymerization

Alexander Krajete,[a] Georg Steiner,[a] Holger Kopacka,[a] Karl-Hans Ongania,[b] Klaus Wurst,[a] Marc O. Kristen,[c] Peter Preishuber-Pflügl,[d] and Benno Bildstein*[a]

Keywords: N,O ligands / N ligands / Chelates / Transition metals / Polymerization

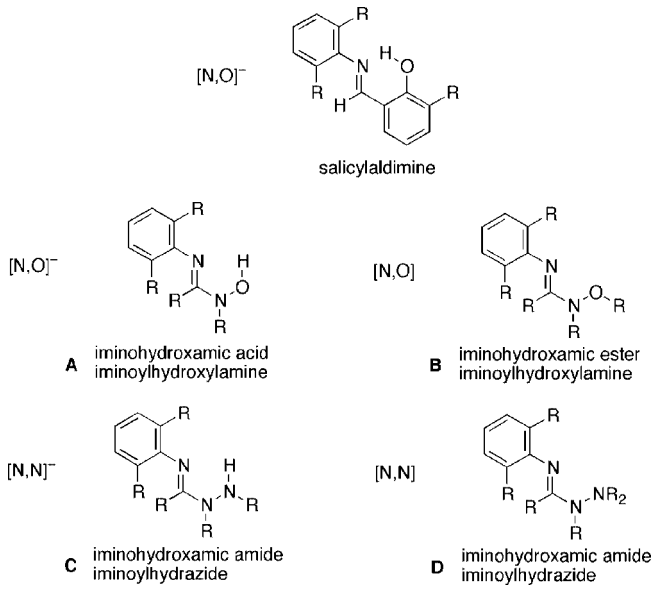
We report on new families of non-metallocene metal precatalysts for olefin polymerization with titanium, zirconium, vanadium and nickel as the active metal sites. The novel ligand design concept is based on iminohydroxamic acids and their derivatives as the principal chelating units. Various anionic and neutral [*N*,*O*] and [*N*,*N*] ligand systems are easily accessible by a modular synthetic sequence of imidoyl chlorides with substituted hydroxylamines or hydrazines, respectively. Steric protection of the metal coordination site, a necessary requirement for suppression of chain termination pathways of non-metallocene catalysts, is brought about by bulky aryl substituents on the imino nitrogen atoms. Crystal structures of some of the hydroxamato ligands reveal interesting intermolecular hydrogen-bridged structures, whereas in the solid-state structure of one titanium precatalyst a five-membered chelate was observed, in line with the design principle of these systems. Preliminary ethylene polymerization studies with methylaluminoxane-activated metal complexes (M = Ti, Zr, V, Ni) show that the most active systems are [*N*,*O*]$NiBr_2$ catalysts containing neutral *O*-alkyl iminohydroxamate ligands.

Introduction

Olefin polymerization catalysis based on transition metal complexes containing non-cyclopentadienyl ligand frameworks is an extremely active research area[1] since the recent key discoveries of very active (i) (diimine)nickel[2] catalysts, (ii) [bis(imino)pyridine]iron[3] catalysts, and (iii) (salicylaldiminato)nickel[4] and -titanium[5] catalysts. These new systems show some significant advantages in comparison with the more familiar traditional Ziegler−Natta titanium/zirconium or Phillips chromium systems, including (i) simplified ligand design, (ii) metal centers ranging from early to late transition metals, (iii) decreased oxophilicity of the late transition metal complexes, allowing polymerizations and/or copolymerizations of polar monomers or even polymerizations in water,[6] (iv) access to new branched microstructures of the polymers due to "chain-walking" of the catalytically active species,[7] and (v) living polymerization of olefins,[8] giving precise control of polymer molecular weights and giving access to block copolymers and other new materials. Due to the economic importance of polyolefinic materials in general, academic and industrial research activity in this area is very high and an ever increasing number of catalyst improvements and developments are being published and/or patented.[1]

Here we introduce a new family of ligands based on the iminohydroxamate backbone and we report on their transition metal halide complexes as new precatalysts for methylaluminoxane (MAO) activated olefin polymerizations.[9] Our design principle is based on chelating [*N*,*O*] and [*N*,*N*] ligands in accordance with (salicylaldiminato)nickel and -titanium systems reported by the groups of Grubbs[4] and Fujita[5] (Scheme 1). Such salicylaldimine ligands form six-membered metal chelates and for steric protection they usually contain bulky aromatic imine moieties (in most cases 2,6-diisopropylphenyl) and sterically shielding groups in the *ortho* position of the oxygen donor site. In contrast, in our newly designed iminohydroxamate ligands, the metal chelate is an energetically favored five-membered ring and steric protection is provided by bulky arylimino substituents. This is similar to most non-cyclopentadienyl transition metal polymerization catalysts.[1] Scheme 1 outlines the chemical relationships between the parent iminohydroxamic acids (**A**), their *O*-alkyl esters (**B**), their *N*-mono- (**C**) and *N*,*N*-disubstituted amides (**D**), showing the large structural

[a] Institute of General, Inorganic and Theoretical Chemistry; University of Innsbruck,
Innrain 52a, 6020 Innsbruck, Austria
E-mail: benno.bildstein@uibk.ac.at
[b] Institute of Organic Chemistry, University of Innsbruck,
Innrain 52a, 6020 Innsbruck, Austria
[c] Basell Polyolefin GmbH,
67056 Ludwigshafen, Germany
[d] BASF Aktiengesellschaft,
67056 Ludwigshafen, Germany



Scheme 1. Design principle of chelating [*N*,*O*] and [*N*,*N*] hydroxamate ligands

varieties possible and indicating the obvious ligand design opportunities in these [*N*,*O*] and [*N*,*N*] ligand families.

In a historical perspective, in situ generated hydroxamic acids are well known in qualitative organic analysis for their formation of magenta- or burgundy-colored Fe^{III} complexes,[10] a more or less specific color test for carboxylic acid derivatives in the presence of hydroxylamine. Simple (iminohydroxamato)metal complexes have been investigated for over 100 years,[11] mainly in spectrophotometric and pharmaceutical studies. However, no applications as olefin polymerization precatalysts have been reported up to now.

Results and Discussion

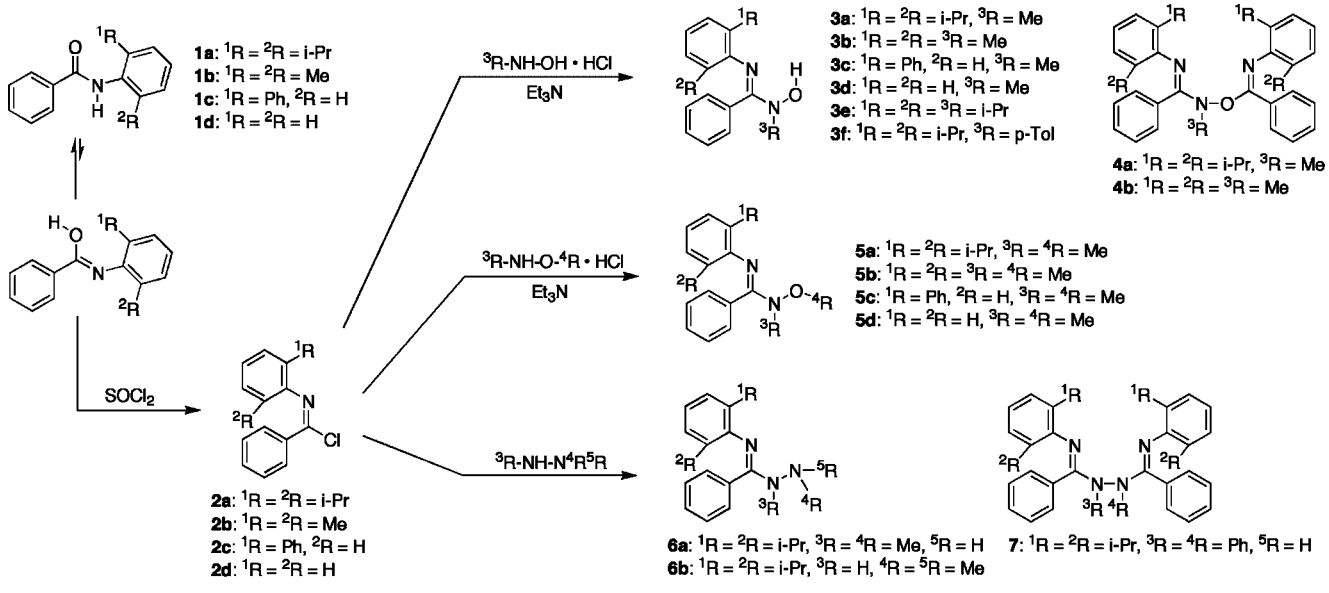
Synthesis and Characterization of Ligands

In general, ligand design is an essential part of the search for new and improved metal catalysts because steric bulk and stereoelectronic effects of the ligand architecture control the selectivity and activity of the metal complexes in their function as catalysts. From a preparative viewpoint the synthetic route should be straightforward, avoid tedious workup and separations, and should be of wide scope, thereby allowing parallel synthetic optimization.

The preparation of our new families of hydroxamate-based ligands fulfill these requirements (Scheme 2). *N*-Substituted benzamides **1a**−**1d** containing *N*-aryl groups with different substitution pattern are easily available in large quantities from the corresponding anilines and benzoyl chloride. Conversion into the corresponding imidoyl chlorides **2a**−**2d** can be brought about quantitatively by treatment with an excess of thionyl chloride employing standard published chemistry.[12] Usually these synthons were prepared in situ only, and used in the following reactions without being isolated. In one case, however, single crystals were obtained by chance (Table 2).

Figure 1 shows the molecular structure of **2a** in the solid state, clearly visible is the steric shielding of the imine functionality by the bulky *N*-(2,6-diisopropyl) group. As a result of the two *ortho*-alkyl substituents the aryl group is tilted by 80.56(10)° in relation to the imidoyl chloride plane, as anticipated and in line with our design principle of axial steric shielding brought about by bulky *N*-imino substituents (vide infra).

Iminohydroxamic acids **3a**−**3f** can be quite easily synthesized by iminoacylation of *N*-monosubstituted hydroxylamines. Similar chemistry has been reported earlier in the literature employing *N*-phenylhydroxylamine.[11b] As antici-



Scheme 2. Synthesis of iminohydroxamate ligands

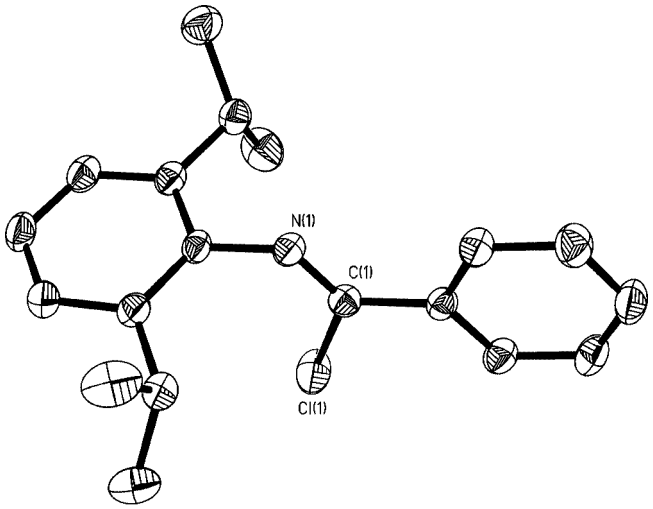


Figure 1. Molecular structure of **2a**; hydrogen atoms are omitted for clarity; selected bond lengths [pm]: Cl(1)−C(1) 178.0(2), C(1)−N(1) 124.8(2); tilt angles [°]: plane of phenyl ring versus plane Cl(1)−C(1)−N(1): 3.25(24); plane of 2,6-diisopropylphenyl ring versus Cl(1)−C(1)−N(1): 80.56(10)

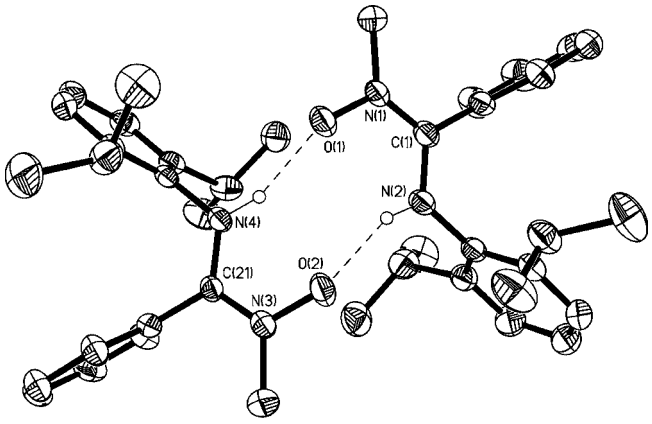


Figure 2. Molecular structure of **3a**; except for N−H−O hydrogen bonds, hydrogen atoms are omitted for clarity; selected bond lengths [pm]: C(1)−N(1) 131.2(3), N(1)−O(1) 134.5(3), C(1)−N(2) 133.8(3), C(21)−N(3) 131.1(3), N(3)−O(2) 134.6(3), C(21)−N(4) 134.4(3), N(2)−H(2N) 87(3), N(4)−H(4N) 91(3); tilt angles [°]: plane of phenyl ring of C(1) versus plane N(1)−C(1)−N(2): 83.48(15); plane of 2,6-diisopropylphenyl ring of N(2) versus plane N(1)−C(1)−N(2): 88.55(21); plane of phenyl ring of C(21) versus plane N(3)−C(21)−N(4): 75.17(15); plane of 2,6-diisopropylphenyl ring of N(4) versus plane N(3)−C(21)−N(4): 85.38(22)

pated, the more nucleophilic nitrogen atom is acylated first in these ambident substrates affording the desired ligands in isolated yields of 18−63%, followed by *O*-acylation which always occurs to a certain degree, dependent on the substitution pattern of the building blocks. Due to the much higher polarity of the mono(iminoacylated) hydroxamic acids **3a**−**3f** in comparison with the undesired *N*,*O*-bis(iminoacylated) side products, separation and purification of the hydroxamic acids can be conveniently accomplished by a simple filtration through a short silica column (see Exp. Sect.). In two cases, **4a** and **4b**, the undesired *N*,*O*-bis(iminoacylated) products were isolated and characterized spectroscopically.

In principle any hydroxylamine can be derivatized in this manner, including the parent unsubstituted hydroxylamine. However, the starting hydroxylamines containing one *N*-organo substituent were chosen because the *N*−H acidic site in these iminohydroxamic acids is blocked. This enables activation of the corresponding metal complexes with methylaluminoxane (vide infra) without undesired *N*-deprotonation or *N*-alumination, respectively.

Iminohydroxamic acids **3a**−**3f** are stable organic compounds and white to yellow in color. Relevant spectroscopic properties include characteristic IR stretching vibrations due to the imino groups ($\nu_{C=N}$ = 1598−1630 cm^{-1}), and diagnostic low-field ^{13}C NMR chemical shifts of the imino functionalities ($\delta_{C=N}$ = 147.7−150.5 ppm). The ν_{O-H} bands of the hydroxy groups (3600 to 3100 cm^{-1}) are very weak and broad in the IR spectra, due to line broadening and association. Also in the ^1H NMR spectra the signals of the hydroxy hydrogen atoms are usually not observed, due to exchange and overlapping with other signals (compare Exp. Sect.). For three of these iminohydroxamic acids, suitable single crystals for X-ray structural analyses were obtained (Figures 2−4).

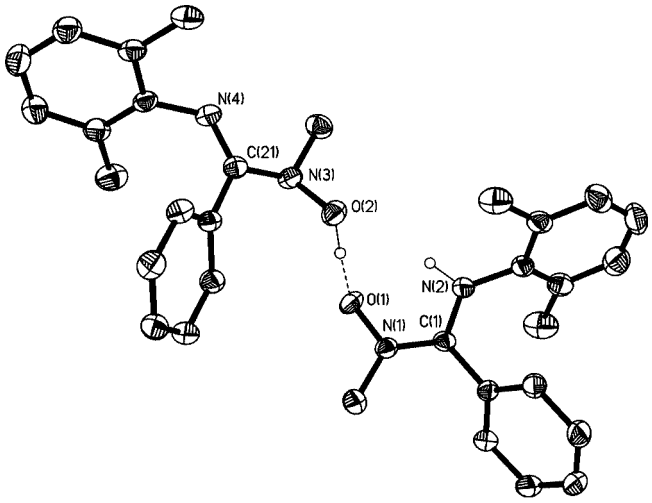


Figure 3. Molecular structure of **3b**; except for N−H and O−H hydrogen atoms, all other hydrogen atoms are omitted for clarity; selected bond lengths [pm]: C(1)−N(1) 130.6(3), N(1)−O(1) 135.1(2), C(1)−N(2) 135.7(3), C(21)−N(3) 139.0(3), N(3)−O(2) 142.2(2), C(21)−N(4) 128.1(3), N(2)−H(2N) 94(2), O(2)−H(2O) 106(3); tilt angles [°]: plane of phenyl ring of C(1) versus plane N(1)−C(1)−N(2): 62.26(13); plane of 2,6-dimethylphenyl ring of N(2) versus plane N(1)−C(1)−N(2): 70.93(16); plane of phenyl ring of C(21) versus plane N(3)−C(21)−N(4): 43.52(10); plane of 2,6-dimethylphenyl ring of N(4) versus plane N(3)−C(21)−N(4): 76.18(18)

A common feature in all three structures is the tilting of both aryl rings relative to the plane of the principal N=C−N−O unit. These tilt angles range from 43.5 to 83.5° for the *C*-phenyl ring, and from 34.0 to 88.6° for the substituted *N*-aryl moiety, respectively. Clearly the tilting in both cases is caused by steric crowding, especially in the latter case, due to the two *ortho*-alkyl groups on the *N*-aryl sub-

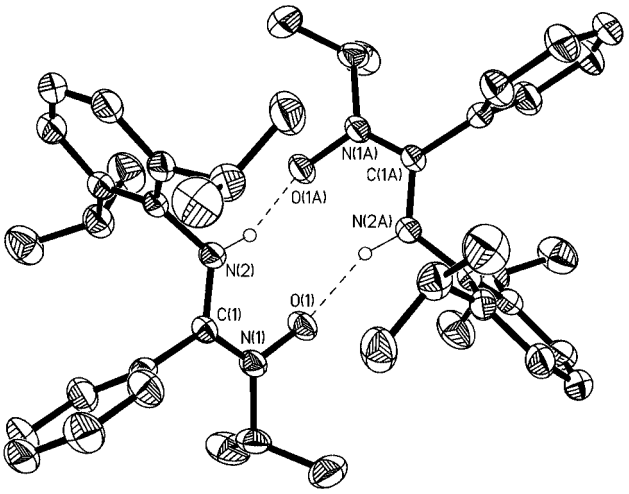


Figure 4. Molecular structure of **3e**; except for N−H−O hydrogen bonds, hydrogen atoms are omitted for clarity; selected bond lengths [pm]: C(1)−N(1) 130.5(4), N(1)−O(1) 134.0(3), C(1)−N(2) 135.9(4), N(2)−H(2N) 98(4); tilt angles [°]: plane of phenyl ring of C(1) versus plane N(1)−C(1)−N(2): 78.74(15); plane of 2,6-diisopropylphenyl ring of N(2) versus plane N(1)−C(1)−N(2): 34.02(23)

stituent. As anticipated, in all three structures, hydrogen-bridging plays a decisive role in the solid-state packing of the molecules. In all three structures two molecules are paired by one or two O−H−N hydrogen bonds. Interestingly, both possible tautomers of the iminohydoxamic acid functionality were observed, depending on the substitution pattern of the principal N=C−N−OH unit. Compounds **3a** and **3e** exist in the solid state solely in their zwitterionic iminium hydroxamate $^{+}$NH=C−N−O^{-} forms connected by two hydrogen bonds (see Figures 2 and 4), whereas in the case of compound **3b** both tautomers with only one hydrogen bond are present, the expected and "usual" neutral N=C−N−OH form and the unexpected and "exotic" zwitterionic $^{+}$NH=C−N−O^{-} form (Figure 3). It is quite clear, however, that this tautomerism is dominated by solid-state forces and in solution the position of equilibrium will be almost totally on the side of the uncharged normal iminohydroxamic acid species.

The synthesis of iminohydoxamic esters **5a**−**5d** can be very easily accomplished by iminoacylation of *N*,*O*-bis(alkylated) hydroxylamines (Scheme 2). The isolated yields of 78−94% are much higher than those of the iminohydroxamic acids discussed above, simply because there is only one nucleophilic site in the substrates. Ligands **5a**−**5d** are stable compounds which are white to yellow in color. Spectroscopically, the imine functionalities may be corroborated by their typical IR absorptions ($\nu_{C=N}$ = 1628−1636 cm^{-1}), shifted to higher wave numbers compared with the hydroxamic acids **3a**−**3f**, and by their ^{13}C NMR chemical shifts (δ = 160.8−162.8 ppm) which are also shifted to lower field in comparison with compounds **3a**−**3f**. The signals of the methyl groups of the ester functionalities were detected at δ = 3.38−3.54 ppm in the ^{1}H NMR spectra and at δ = 60.2−60.6 ppm in the ^{13}C NMR spectra; both sets of chemical shifts are in accordance with expectations at lower field in comparison with those of the *N*-alkyl substituents of **3a**−**3f** and **5a**−**5d**, respectively.

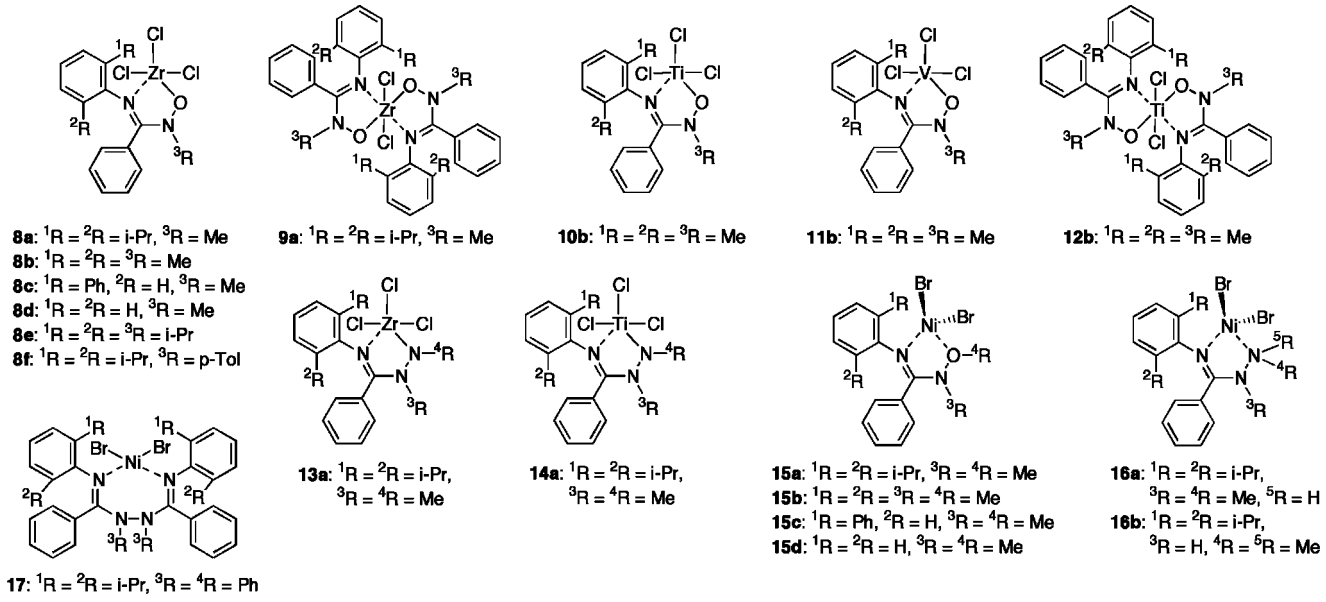
Amino derivatives of iminohydroxamic acids are accessible similarly by iminoacylation of hydrazines. In our hands, however, this chemistry was only possible for alkylated hydrazines affording ligands **6a** and **6b**, but on attempted mono(iminoacylation) of *N*,*N*′-diphenylhydrazine only the bis(derivative) **7** was obtained. This is a rather unfortunate result because diarylhydrazines can be easily synthesized from azobenzenes by reduction, and various substituted diarylhydrazines would allow a convenient stereoelectronic fine-tuning on the amino *N*-donor site of ligands of type **6**. The spectroscopic data of **6a**, **6b** and **7** are consistent with their structures with values similar to those of the other ligand families discussed above. As a minor issue, we note that the imidoyl hydrazide **6b** is the only ligand of all these compounds with an *N*−H substituent on the benzamidine moiety, in this case no protection of the *N*−H acidic moiety is present (vide infra).

Metal Complexes

[N,O] Iminohydroxamato Complexes

In principle, with tetravalent early transition metals, [*N*,*O*]MX_3 mono- and [*N*,*O*]$_2$MX_2 bis(complexes) should be accessible. Hence six differently substituted iminohydroxamic acids (**3a**−**3f**) and three different metal halides ($ZrCl_4$, $TiCl_4$, VCl_4) would afford a series of 36 different metal complexes. In this work, however, only selected examples from this rather large number of compounds were synthesized on a preparative scale (Scheme 3), based on the following criteria and objectives: (i) in order to compare the stereoelectronic influence of all six ligands **3a**−**3f**, all six zirconium mono(complexes) [*N*,*O*]$ZrCl_3$ **8a**−**8f** were synthesized, (ii) for comparing the difference between mono- and bis(complexes), one [*N*,*O*]$_2$$ZrCl_2$ complex (**9a**) was prepared, (iii) to study the effect of different metals, two additional complexes **10b** [M = Ti] and **11b** [M = V] with ligand **3b** were synthesized, and (iv) to facilitate characterization of the complexes by NMR spectroscopy we focused on the diamagnetic Zr and Ti complexes. Furthermore we note that [*N*,*O*]NiRL complexes (L = phosphane, R = alkyl or aryl) in analogy to Grubbs' (salicylaldiminato)Ni complexes[4] are also accessible, but unfortunately such compounds are very labile and, according to our preliminary results, decompose very quickly.

As anticipated, the synthesis of metal complexes of [*N*,*O*]H ligands **3a**−**3f** was rather simple. Deprotonation with *n*-butyllithium in THF followed by treatment with the appropriate transition metal halide afforded complexes **8a**−**11b** (Scheme 3) in isolated yields ranging from 64 to 95% (see Exp. Sect.). All the compounds are stable under dry and inert conditions. On exposure to air, however, they are quickly hydrolyzed as expected. The zirconium and titanium complexes **8a**−**10b** are diamagnetic and are yellow to orange in color, in contrast to the dark green vanadium complex **11b** which is strongly paramagnetic.

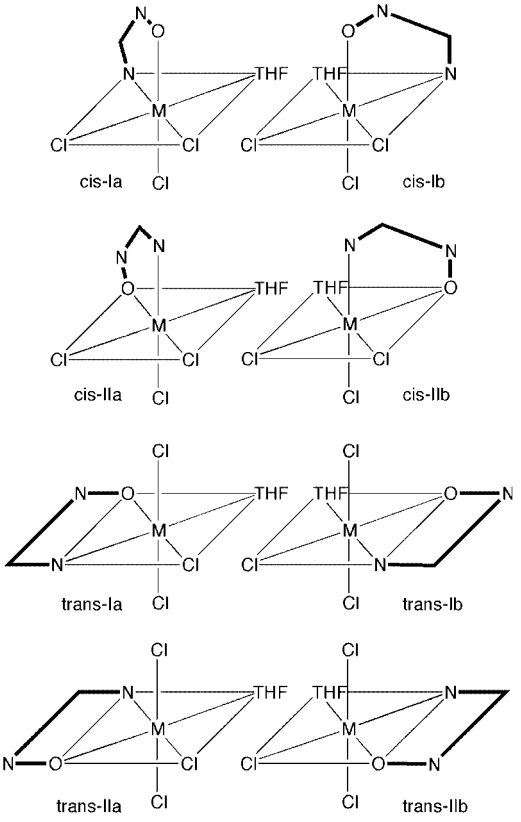


Scheme 3. Metal complexes of [*N*,*O*] and [*N*,*N*] iminohydroxamato ligands

The characterization of the diamagnetic compounds relies mainly on NMR spectroscopy. In the ^{13}C NMR spectra the coordinated imino functionalities ($\delta_{C=N}$ = 159−162 ppm) are shifted to lower field by approximately 10 ppm compared with the chemical shifts of the imine carbon signals of the free ligands ($\delta_{C=N}$ = 146−151 ppm). Other resonances were shifted as well, but to a much lesser degree. Most significantly, the ^1H and ^{13}C NMR spectra clearly show that the [*N*,*O*]$ZrCl_3$ mono(complexes) **8a**−**8f** exist predominantly as mixtures of isomers containing THF as an additional neutral ligand in an octahedral coordination environment. In principle, 4 pairs of chiral diastereoisomers are possible with these heterotopic [*N*,*O*] chelate ligands in combination with three chloride ions and one THF ligand (Scheme 4). Mono-Zr complexes containing the *N*-(2,6-diisopropylphenyl) substituent exist as one isomer (**8a**, **8e**, **8f**), whereas those with sterically less demanding *N*-aryl groups give rise to the observation of two diastereoisomers (**8b**, **8c**, **8d**) according to their NMR spectra (compare Exp. Sect.).

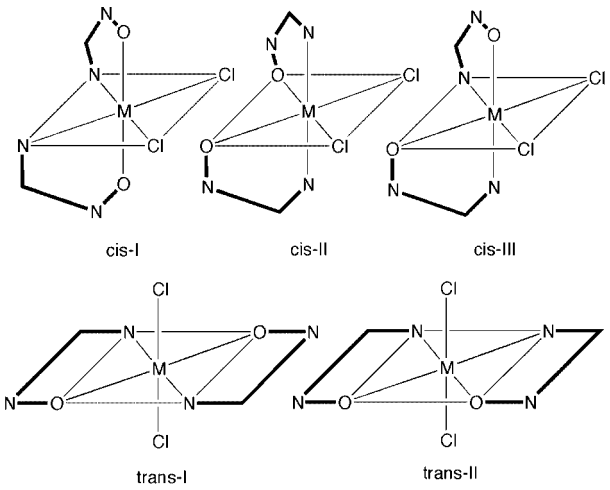
In contrast to the [*N*,*O*]$ZrCl_3$ complexes **8a**−**8f**, no coordinated THF was present in the titanium complex **10b**, most likely due to the smaller size of the lighter transition metal atom. Also, complex **9a** with two chelating [*N*,*O*] ligands had no coordinated THF, but four structural isomers of the theoretically possible 5 isomers (Scheme 5) were observed in this heterotopic and non-homoleptic complex.

In most of the zirconium compounds **8a**−**9a** (with the exception of **8a**, **8e**, **8f**) the occurrence of a mixture of isomers was clearly evident from NMR spectroscopy. On the one hand this is an expected and interesting stereochemical observation, on the other hand, however, it hampers further characterization of these complexes by X-ray crystallography. Unfortunately, under no circumstances we were able to obtain single crystals. In the case of the titanium complex



Scheme 4. Structural isomers of [*N*,*O*]$ZrCl_3$(THF) complexes

10b, however, suitable red single crystals grew after one year, together with some amorphous colorless material. Figure 5 shows the molecular structure of this crystalline material. Unexpectedly, the structure corresponds to the [*N*,*O*]$_2$-$TiCl_2$ bis complex **12b** which must have been formed from



Scheme 5. Structural isomers of $[N,O]_2ZrCl_2$ complexes

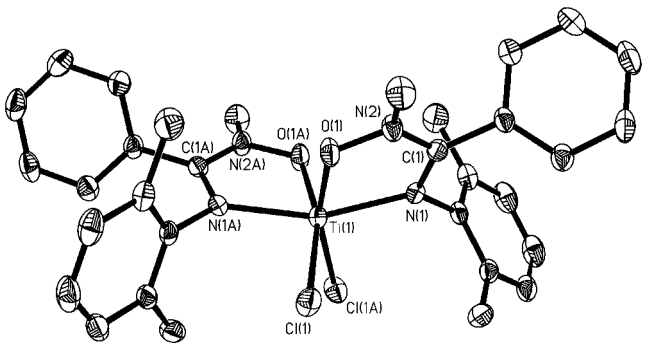


Figure 5. Molecular structure of **12b**; hydrogen atoms are omitted for clarity; selected bond lengths [pm]: Ti(1)−Cl(1) 231.97(7), Ti(1)−N(1) 210.83(18), Ti(1)−O(1) 192.44(17), C(1)−N(1) 132.9(3), C(1)−N(2) 132.4(3), N(2)−O(1) 136.1(3); selected angles [°]: Cl(1)−Ti(1)−Cl(1A) 90.22(4), O(1)−Ti(1)−O(1A) 95.10(12), N(1)−Ti(1)−O(1) 74.54(7), N(1)−Ti(1)−Cl(1) 105.26(5), O(1)−Ti(1)−Cl(1) 89.74(6), N(1)−Ti(1)−N(1A) 159.57(10), Ti(1)−N(1)−C(1) 115.12(15), N(1)−C(1)−N(2) 114.9(2), Ti(1)−O(1)−N(2) 120.79(13); tilt angle plane of phenyl group of C(1) versus plane N(1)−C(1)−N(2): 66.71(26); tilt angle of 2,6-dimethylphenyl group of N(1) versus plane N(1)−C(1)−N(2): 82.46(19)

the $[N,O]TiCl_3$ mono(complex) **10b** by ligand scrambling. Despite the obvious serendipity of this result, the molecular structure clearly demonstrates the chelating nature of the hydroxamato ligand **3b**, indicating that in all other cases such five-membered metal chelates are also present. Overall, the stereochemistry of **12b** corresponds to isomer *cis*-**II** of Scheme 5 with *cis*-oriented chloro ligands and *trans*-oriented imino donor sites of the heterotopic iminohydroxamato ligands. The coordination geometry at the central titanium atom is principally octahedral with only minor deviations from the ideal 90° (0.3−15.5°) and 180° (16.8−20.4°) angles. The bond lengths of the titanium atom to the nitrogen, oxygen, and chlorine atoms of the ligands are given in the caption of Figure 5. They are unexceptional and in the commonly observed range. In contrast to the more or less undistorted coordination geometry, the peripheral phenyl groups of the iminohydroxamato ligands are strongly tilted (66.7 and 82.5°) with respect to the hydroxamate plane, showing that steric shielding by the *N*-arylimino substituent is effective, in accordance with the general design principle of these olefin polymerization precatalysts (vide supra).

The syntheses of the imidoyl hydrazido complexes **13a** and **14a** are analogous to the preparation of the iminohydroxamato complexes discussed above (Scheme 3). Deprotonation of ligand **6a** in THF by *n*-butyllithium followed by treatment with $ZrCl_4$ or $TiCl_4$ in a 1:1 stoichiometric ratio afforded complexes **13a** and **14a**, respectively. Besides the additional *N*-methyl resonances, both compounds show NMR spectroscopic properties very similar to those of the iminohydroxamato complexes **8a**−**8f** and **10b**. Stereochemically, Zr complex **13a** exists as a mixture of two octahedral isomers containing one additional THF ligand (in analogy to the isomers in Scheme 4), whereas **14a** seems to be either five-coordinate or more likely a chloro-bridged dimer with no coordinated THF.

The synthesis of nickel(II) complexes starting from the neutral (non-acidic) iminohydroxamic esters **5a**−**5d**, imidoyl hydrazides **6a**−**6b** and **7** was very straightforward. Treatment with $NiBr_2$ in dichloromethane at room temperature overnight afforded the corresponding $[N,O]NiBr_2$ complexes **15a**−**15d** and $[N,N]NiBr_2$ complexes **16a**, **16b**, **17** in good yields (Scheme 3).

With the exception of **17**, which is a seven-membered chelate in contrast to all other complexes, all the Ni complexes are dark green or brown, air-sensitive and paramagnetic, thereby thwarting their characterization by NMR spectroscopy. In general, broad and shifted signals were observed in the ^1H NMR spectra and signal intensities in the ^{13}C NMR spectra were very low allowing, only in one case, the detection of the carbon resonances (see Exp. Sect.). The paramagnetism of these complexes clearly indicates a non-quadratic, non-planar coordination geometry and these compounds exist either as four-coordinate tetrahedrally distorted monomers or as bromo-bridged five-coordinate dimers. Clearly, crystal structures would provide the best information on the structures of these compounds, but despite many attempts with different solvents employing various crystallization procedures no suitable crystals could be obtained. On the other hand, the observed paramagnetism shows that steric shielding of the ligands is sufficient to distort the orientation of the bromo ligands from their preferred square-planar geometry, as in Grubbs'[4] and Brookhart's[2] $[N,O]$- and $[N,N]$Ni catalysts.

Polymerization Studies

The main question to be answered by this work is: "How active and selective are these newly designed catalyst families for the polymerization of olefins?" To evaluate the catalytic performance of complexes **8a**−**17** a standard polymerization procedure was applied. A steel autoclave containing a toluene solution of the precatalyst was activated with an excess of methylaluminoxane and at a temperature of 70 °C

Table 1. Polymerization of ethylene (MAO as activator, 70 °C, 40 bar)

Complex (metal)	Amount precatalyst [mg]	Polymerization time [min]	Yield polymer [g]	Viscosity of polymer [dL/g]	Activity [g mmol^{-1} h^{-1} bar^{-1}]
8a (Zr)	4.8	30	9.5	9.51	50.2
8b (Zr)	6.0	30	12.0	14.01	45.1
8c (Zr)	1.5	35	4.8	11.41	68.4
8d (Zr)	0.9	60	6.7	24.95	78.7
8e (Zr)	1.2	90	11.9	4.43	88.4
8f (Zr)	2.0	75	8.8	8.76	51.3
9a (Zr)	4.0	90	9.4	41.38	30.6
10b (Ti)	4.0	60	7.4	54.33	18.8
11b (V)	8.0	90	6.2	19.18	5.3
13a (Zr)	1.4	45	6.2	15.6	76.8
14a (Ti)	1.7	15	1.0	–	28.0
15a (Ni)	3.9	5	7.25	3.62	302.8
16a (Ni)	2.7	90	1.0	2.15	3.3
16b (Ni)	1.4	90	1.3	2.57	8.4
17 (Ni)	1.8	90	1.7	2.50	14.6

ethylene was added up to a pressure of 40 bar, the reaction was allowed to proceed for 5−90 min while maintaining a 40 bar pressure by adjusting the feed of ethylene (Table 1, for further details see Exp. Sect.).

In terms of activity, all [*N*,*O*]- and [*N*,*N*]zirconium complexes showed a moderate activity of 30.6−88.4 g polyethylene × mmol^{-1} × catalyst × h^{-1} × bar^{-1}. The bis(complex) [*N*,*O*]$_2$ZrCl$_2$ (**9a**) had the lowest activity of all Zr complexes, clearly indicating that one ligand per metal center ([*N*,*O*]ZrCl$_3$) is superior to a 2:1 ratio. Changing the metal to either titanium or vanadium resulted in a significantly reduced activity with either the [*N*,*O*] or [*N*,*N*] ligand architecture. In the case of the nickel complexes, compound **15a** truly stands out as a precatalyst with a (very) high activity of 302.8, suggesting that neutral *O*-alkyl iminohydroxamate is the best ligand framework developed in this work. However, the long-term stability of the [*N*,*O*]NiBr$_2$ complexes **15a**−**15d** in their MAO-activated form has not yet been optimized and only with **15a** under short polymerization times was a polymer obtained, indicating fast deactivation pathways. Future work towards improvements of these systems will focus on altering the *O*-alkyl substituent to create better shielding of the active metal center and to increase the stability of the activated complex.

In terms of polymer properties, the polyethylene samples obtained by the zirconium catalyst family were very high molecular weight (Mv = 1.5 to 10 × 10^6 g/mol, derived from viscosity measurements) polymers with viscosities ranging from 4.43 to 54.33 dl/g, dependent on the substitution pattern of the ligands. In contrast, PE samples obtained from nickel complexes **15a**−**17** were of the HDPE type with no detectable branches and molar masses (Mv) of 1.0 to 2.5 × 10^5 g/mol.

In addition, polymerization of propylene and copolymerization of ethylene with *n*-hexene was briefly investigated. In both cases, only low activities below 150 g polymer × mmol^{-1} × catalyst × h^{-1} were achieved.

Summary and Conclusions

New bidentate chelate ligands based on an iminohydroxamate backbone architecture have been developed. These new ligands contain an imino nitrogen donor site with a substituted aryl group to effect steric shielding and an anionic or neutral oxygen or nitrogen donor site, respectively. The free ligands show interesting solid-state structures in which hydrogen bonding is responsible for unusual zwitterionic tautomeric structures. New metal complexes of zirconium, titanium, vanadium, and nickel have been synthesized and evaluated for their performance as olefin polymerization catalysts. Structurally, the five-membered metal chelates exist in most cases as a number of different octahedral stereoisomers in the case of early transition metals, and as tetragonally distorted paramagnetic four- or five-coordinated compounds in the case of nickel. Polymerization studies were performed in homogeneous solution using methylaluminoxane as the cocatalyst. These showed that [*N*,*O*]NiBr$_2$ complexes containing neutral iminohydroxamate with *O*-alkyl substituents are the most active systems of these various catalyst families. Further optimization of the ligand substitution pattern is expected to improve long term stability of the catalysts and the catalytic performance for applications on a technical scale.

Experimental Section

General: Commercially available starting materials were used as obtained. Solvents were dried, deoxygenated and saturated with argon according to standard procedures in organometallic chemistry. Reactions of air-sensitive materials were performed in Schlenk glassware under argon by techniques common in inorganic/organometallic chemistry. New compounds were characterized by IR, NMR, MS, etc. using current state-of-the-art procedures, details of instrumentation have been published previously.[13]

Synthesis of Ligands

Representative Procedure for Iminohydroxamic Acids 3a−3f: A Schlenk tube was charged with *N*-(2,6-diisopropylphenyl)benzamide (**1a**, 1.9 g, 6.7 mmol) and an excess of thionyl chloride (10 mL). The mixture was heated to reflux for 1 h and the excess thionyl chloride was removed in a vacuum line, yielding a yellow oil of the corresponding imidoyl chloride **2a**. This material was dissolved in dry dichloromethane (20 mL). A second Schlenk vessel was charged with *N*-methylhydroxylamine hydrochloride (0.56 g, 6.7 mmol), dry ethanol (50 mL), and triethylamine (10 mL, 72 mmol). After the stirred mixture was cooled to −40 °C, a dropping funnel was attached to the Schlenk vessel, and a dichloromethane solution of imidoyl chloride **2a** (from above) was added dropwise over a period of 30 min. The mixture was warmed to room temperature and stirred at ambient temperature for further 60 min, resulting in a yellow suspension. Workup: the reaction mixture was hydrolyzed by addition of water (100 mL), the organic materials were extracted three times with diethyl ether, the combined organic layers were dried with Na_2SO_4 and the volatile materials were removed in a rotary evaporator yielding a semi-solid crude product consisting of *N*-(2,6-diisopropylphenyl)-*N*′-hydroxy-*N*′-methylbenzamidine (**3a**) and the apolar side product *N*-(2,6-diisopropylphenyl)-*N*′-{[2,6-diisopropylphenyl)imino]phenylmethoxy}-*N*′-methylbenzamidine (**4a**). To separate this mixture, the crude product mixture was dissolved in a small volume of dichloromethane and filtered through a short column of silica. In this manner, apolar **4a** (0.76 g, 1.3 mmol, 19.8% yield) could be removed by filtration, whereas the polar product **3a** remained immobilized on the column. Elution with ethanol and subsequent removal of ethanol in a rotary evaporator afforded 0.83 g of pure **3a** as an off-white solid in 40% yield.

All other iminohydroxamic acids **3** were prepared according to this procedure except that different benzamides and hydroxylamines were employed as starting materials. The bis(imino)-substituted hydroxylamines **4** (the apolar side product) were usually only separated and not isolated. Isolated yields of ligands **3** ranged from 18 to 63%, depending on the substitution pattern of the building blocks.

***N*-(2,6-Diisopropylphenyl)-*N*′-hydroxy-*N*′-methylbenzamidine (3a):** Starting materials: *N*-(2,6-diisopropylphenyl)benzamide (**1a**, 1.9 g, 6.7 mmol) and *N*-methylhydroxylamine hydrochloride (0.56 g, 6.7 mmol). Yield: 0.83 g (40%). IR (KBr): $\tilde{\nu}$ = 3065 (w), 2962 (m), 2869 (m), 1630 (s), 1586 (m), 1505 (m), 1470 (s), 1445 (m), 1432 (m), 1383 (m), 1324 (m), 1225 (m), 1187 (s), 1162 (m), 1105 (s), 1077 (w), 1044 (m), 971 (m), 917 (w), 807 (s), 780 (s), 758 (s), 700 (s) cm^{-1}. MS (FAB): *m*/*z* = 311 $[M + H]^+$. MS(EI, 70 eV): *m*/*z* = 310 $[M]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.96 [d, $^3J_{H,H}$ = 6.6 Hz, 6 H, $CH(CH_3)_2$], 1.09 [d, $^3J_{H,H}$ = 6.2 Hz, 6 H, $CH(CH_3)_2$], 3.18 [sept, 2 H, 2 × $CH(CH_3)_2$], 3.47 (s, 3 H, NCH_3), 6.95 (m, 2 H, C_6H_5), 7.01−7.12 (m, 3 H, C_6H_5), 7.17−7.25 (m, 3 H, C_6H_3), not observed (s, 1 H, NOH) ppm. ^{13}C NMR (75.432 MHz, $CDCl_3$): δ = 21.9, 25.4, 28.2 $[CH(CH_3)_2]$, 43.7 (NCH_3), 123.2, 127.3, 127.8, 128.2, 128.9, 130.1, 131.9, 146.2 (C_6H_5, C_6H_3), 149.1 (C=N) ppm. $C_{20}H_{26}N_2O$ (310.44): calcd. C 77.38, H 8.44, N 9.20; found C 77.42, H 8.48, N 9.16.

***N*-(2,6-Diisopropylphenyl)-*N*′-{[(2,6-diisopropylphenyl)imino]-phenylmethoxy}-*N*′-methylbenzamidine (4a):** Starting materials: *N*-(2,6-diisopropylphenyl)benzamide (**1a**, 1.9 g, 6.7 mmol) and *N*-methylhydroxylamine hydrochloride (0.56 g, 6.7 mmol). Yield: 0.76 g (19.8%). IR (KBr): $\tilde{\nu}$ = 2970 (m), 2931 (m), 2869 (m), 1683 (s), 1630 (s), 1602 (m), 1590 (m), 1578 (m), 1492 (m), 1459 (m), 1436 (m), 1407 (w), 1383 (m), 1362 (w), 1328 (m), 1287 (w), 1264 (m), 1233 (m), 1185 (w), 1108 (m), 1063 (s), 1038 (m), 1030 (m), 1013 (s), 922 (w), 803 (m), 766 (s), 726 (m) cm^{-1}. MS (FAB): *m*/*z* = 574 $[M + H]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.14−1.21 [m, 24 H, 4 × $CH(CH_3)_2$], 3.10, 3.42 [sept, 4 H, 4 × $CH(CH_3)_2$], 3.61 (s, 3 H, NCH_3), 6.46 (m, 2 H, C_6H_5), 6.91−7.90 (m, 16 H, C_6H_5, C_6H_3) ppm. ^{13}C NMR (75.432 MHz, $CDCl_3$): δ = 22.0, 23.7, 24.0, 28.9 $[CH(CH_3)_2]$, 39.7 (NCH_3), 122.9, 123.7, 127.1, 127.8, 127.9, 128.5, 128.8, 129.0, 129.3, 130.4, 131.8, 133.1, 142.1, 143.5, 146.4 (C_6H_5, C_6H_3), 154.5, 160.4 (C=N) ppm. $C_{39}H_{47}N_3O$ (573.82): calcd. C 81.63, H 8.26, N 7.32; found C 81.55, H 8.30, N 7.30.

***N*-(2,6-Dimethylphenyl)-*N*′-hydroxy-*N*′-methylbenzamidine (3b)** Starting materials: *N*-(2,6-dimethylphenyl)benzamide (**1b**, 2.30 g, 10.2 mmol) and *N*-methylhydroxylamine hydrochloride (1.30 g, 15.6 mmol). Yield: 1.63 g (63%). IR (KBr): $\tilde{\nu}$ = 1627 (s), 1590 (m), 1578 (m), 1505 (m), 1472 (m), 1445 (m), 1426 (m), 1341 (m), 1258 (m), 1237 (s), 1179 (s), 1158 (m), 1106 (m), 1092 (m), 1079 (w), 1048 (m), 1025 (m), 957 (s), 783 (s), 774 (s), 762 (s), 754 (s), 726 (s), 700 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 254 $[M]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.16 (s, 6 H, 2 × CH_3), 3.47 (s, 3 H, NCH_3), 6.82−6.92 (m, 3 H, C_6H_3), 7.08−7.27 (m, 5 H, C_6H_5), not observed (s, 1 H, NOH) ppm. ^{13}C NMR (75.432 MHz, $CDCl_3$): δ = 18.6 (CH_3), 43.6 (NCH_3), 126.6, 127.7, 128.0, 128.2, 128.5, 130.1, 135.4, 135.5 (C_6H_5, C_6H_3), 149.0 (C=N) ppm. $C_{16}H_{18}N_2O$ (254.33): calcd. C 75.56, H 7.13, N 11.01; found C 75.62, H 7.18, N 10.93.

***N*-(2,6-Dimethylphenyl)-*N*′-{[(2,6-dimethylphenyl)imino]-phenylmethoxy}-*N*′-methylbenzamidine (4b):** Starting materials: *N*-(2,6-dimethylphenyl)benzamide (**1b**, 2.30 g, 10.2 mmol) and *N*-methylhydroxylamine hydrochloride (1.30 g, 15.6 mmol). Yield: 1.1 g (23%). IR (KBr): $\tilde{\nu}$ = 2919 (w), 1688 (s), 1644 (s), 1592 (m), 1580 (w), 1493 (w), 1466 (m), 1447 (m), 1405 (w), 1326 (s), 1293 (w), 1262 (m), 1246 (m), 1229 (m), 1216 (m), 1183 (w), 1104 (w), 1079 (s), 1069 (s), 1027 (m), 1013 (m), 922 (w), 787 (m), 768 (s), 756 (m), 741 (m), 697 (s), 675 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 461 $[M]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.95, 2.20 (2 × s, 12 H, 4 × CH_3), 3.61 (s, 3 H, NCH_3), 6.25 (m, 2 H, C_6H_3), 6.67−6.96 (m, 6 H, C_6H_5 and C_6H_3), 7.05−7.22 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (75.432 MHz, $CDCl_3$): δ = 18.5, 18.8 (CH_3), 39.4 (NCH_3), 122.3, 122.9, 127.0, 127.1, 127.6, 127.8, 127.9, 128.2, 128.7, 129.4, 129.5, 130.0, 130.5, 131.7, 133.6, 135.5, 144.6, 146.1 (C_6H_5, C_6H_3), 154.7, 161.5 (C=N) ppm. $C_{31}H_{31}N_3O$ (461.60): calcd. C 80.66, H 6.77, N 9.10; found C 80.71, H 6.80, N 9.08.

***N*-(Biphenyl-2-yl)-*N*′-hydroxy-*N*′-methylbenzamidine (3c):** Starting materials: *N*-(2-biphenyl)benzamide (**1c**, 2.62 g, 9.59 mmol) and *N*-methylhydroxylamine hydrochloride (1.28 g, 15.3 mmol). Yield: 1.39 g (48%). IR (KBr): $\tilde{\nu}$ = 3257 (w), 2946 (w), 1607 (s), 1580 (m), 1509 (s), 1488 (s), 1447 (m), 1436 (s), 1422 (s), 1393 (m), 1387 (m), 1243 (s), 1196 (s), 1073 (m), 963 (s), 783 (m), 770 (s), 756 (s), 743 (s), 698 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 302 $[M]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.38 (s, 3 H, NCH_3), 6.48−6.51 (m, 1 H, C_6H_5), 6.89−7.02 (m, 4 H, C_6H_5), 7.11−7.14 (m, 1 H, C_6H_5), 7.25−7.42 (m, 8 H, C_6H_5), not observed (s, 1 H, NOH) ppm. ^{13}C NMR (75.432 MHz, $CDCl_3$): δ = 43.5 (NCH_3), 122.5, 124.0, 127.4, 127.5, 127.9, 128.7, 128.9, 129.0, 130.1, 130.7, 134.7, 135.5, 138.4 (C_6H_5, C_6H_4), 146.8 (C=N) ppm. $C_{20}H_{18}N_2O$ (302.38): calcd. C 79.44, H 6.00, N 9.26; found C 79.35, H 6.04, N 9.21.

***N*′-Hydroxy-*N*′-methyl-*N*-phenylbenzamidine (3d):** Starting materials: benzanilide (**1d**, 2.12 g, 10.8 mmol) and *N*-methylhydroxylamine hydrochloride (1.28 g, 15.3 mmol). Yield: 1.03 g (42%). IR

(KBr): $\tilde{\nu}$ = 3049 (w), 2943 (w), 1615 (s), 1603 (s), 1574 (m), 1509 (s), 1482 (m), 1447 (m), 1428 (m), 1196 (s), 1160 (m), 1071 (w), 971 (s), 758 (s), 726 (s), 697 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 226 $[M]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.47 (s, 3 H, NCH_3), 6.56 (d, 2 H, C_6H_5), 6.87 (t, 1 H, C_6H_5), 7.01 (t, 2 H, C_6H_5), 7.25 (d, 2 H, C_6H_5), 7.24−7.43 (m, 3 H, C_6H_5), not observed (s, 1 H, NOH) ppm. ^{13}C NMR (75.432 MHz, $CDCl_3$): δ = 43.4 (NCH_3), 121.0, 123.3, 127.8, 128.6, 129.0, 129.1, 130.4, 138.1 (C_6H_5), 146.7 (C=N) ppm. $C_{14}H_{14}N_2O$ (254.33): calcd. C 74.31, H 6.42, N 12.38; found C 74.24, H 6.27, N 12.34.

***N*-(2,6-Diisopropylphenyl)-*N*′-hydroxy-*N*′-isopropylbenzamidine (3e):** Starting materials: *N*-(2,6-diisopropylphenyl)benzamide (**1a**, 1.47 g, 6.7 mmol) and *N*-isopropylhydroxylamine hydrochloride (0.85 g, 7.6 mmol). Yield: 0.63 g (36%). IR (KBr): $\tilde{\nu}$ = 3433 (w), 3064 (w), 3006 (w), 2968 (s), 2948 (m), 2931 (m), 2867 (m), 1683 (w), 1598 (s), 1503 (s), 1461 (s), 1436 (m), 1385 (m), 1378 (m), 1360 (s), 1343 (w), 1335 (w), 1320 (w), 1256 (w), 1173 (s), 1123 (w), 1104 (w), 1067 (s), 1040 (w), 978 (m), 930 (w), 924 (w), 822 (w), 808 (s), 781 (m), 760 (s), 702 (s) cm^{-1}. MS(EI, 70 eV): *m*/*z* = 338 $[M]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.98 [d, $^3J_{H,H}$ = 6.2 Hz, 6 H, $CH(CH_3)_2$], 1.11 [d, $^3J_{H,H}$ = 6.2 Hz, 6 H, $CH(CH_3)_2$], 1.37 [d, $^3J_{H,H}$ = 6.6 Hz, 6 H, $CH(CH_3)_2$], 3.16 [sept, 2 H, 2 × $CH(CH_3)_2$], 4.03 [sept, $^3J_{H,H}$ = 6.6 Hz, 1 H, $CH(CH_3)_2$], 6.95 (m, 2 H, C_6H_5), 7.02−7.12 (m, 3 H, C_6H_5), 7.20−7.27 (m, 3 H, C_6H_3), not observed (s, 1 H, NOH) ppm. ^{13}C NMR (75.432 MHz, $CDCl_3$): δ = 20.0, 21.9, 25.4, 28.2 [$CH(CH_3)_2$], 54.8 [$NCH(CH_3)_2$], 123.0, 127.5, 127.7, 128.3, 128.5, 129.9, 132.5, 145.9 (C_6H_5, C_6H_3), 148.1 (C=N) ppm. $C_{22}H_{30}N_2O$ (338.49): calcd. C 78.06, H 8.93, N 8.28; found C 78.00, H 8.95, N 8.24.

***N*-(2,6-Diisopropylphenyl)-*N*′-hydroxy-*N*′-(4-methylphenyl)-benzamidine (3f):** Starting materials: *N*-(2,6-diisopropylphenyl)benzamide (**1a**, 1.21 g, 4.3 mmol) and *N*-(4-methylphenyl)hydroxylamine (0.53 g, 4.3 mmol).[14] Yield: 0.30 g (18%). IR (KBr): $\tilde{\nu}$ = 2964 (s), 2927 (m), 2867 (m), 1600 (s), 1571 (s), 1507 (s), 1461 (s), 1322 (m), 1302 (w), 1285 (w), 1260 (m), 1239 (m), 1187 (w), 1106 (m), 1077 (w), 1044 (m), 818 (s), 787 (s), 776 (s), 758 (s), 697 (s) cm^{-1}. MS(FAB): *m*/*z* = 387 $[M + H]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.90 [d, $^3J_{H,H}$ = 7.0 Hz, 6 H, $CH(CH_3)_2$], 2.19 (s, 3 H, $NC_6H_4CH_3$), 3.17 [sept, $^3J_{H,H}$ = 7.0 Hz, 2 H, 2 × $CH(CH_3)_2$], 6.82−6.91 (m, 4 H, C_6H_4, C_6H_3), 6.96−7.23 (m, 8 H, C_6H_4, C_6H_3), not observed (s, 1 H, NOH) ppm. ^{13}C NMR (75.432 MHz, $CDCl_3$): δ = 14.0, 20.6, 22.0, 22.5, 25.2, 29.4, 31.5 [CH_3, 2 × $CH(CH_3)_2$], 132.1, 137.4, 141.0, 145.4 (C_6H_3, C_6H_4), 150.5 (C=N) ppm. $C_{26}H_{30}N_2O$ (386.54): calcd. C 80.79, H 7.82, N 7.25; found C 80.86, H 7.83, N 7.26.

Representative Procedure for Iminohydroxamic Esters 5a−5d and Iminohydroxamic Amides 6a, 6b: A dichloromethane solution of imidoyl chloride **2a** (*c* = 0.108 g/ml or 0.36 mmol/ml, respectively) was prepared as described above. A second Schlenk vessel was charged with *N*-methyl-*O*-methylhydroxylamine hydrochloride (0.78 g, 8.0 mmol), dry ethanol (50 mL), and triethylamine (2.2 mL, 16 mmol). After the stirred mixture was cooled to −40 °C, a dropping funnel was attached to the Schlenk vessel, and a stoichiometric amount of a dichloromethane solution of imidoyl chloride **2a** was added dropwise over a period of 30 min. The mixture was warmed to room temperature and stirred at ambient temperature for further 60 min, resulting in a yellow suspension. Workup: the reaction mixture was hydrolyzed by addition of of water (100 mL), the organic material was extracted three times with diethyl ether, the combined organic layers were dried with Na_2SO_4, the volatile materials were removed in a rotary evaporator, yielding **5a** in 93% yield as a yellow viscous oil which solidified on drying in vacuo.

All other iminohydroxamic esters **5** and amides **6** were prepared according to this procedure, only different benzamides and hydroxylamines or hydrazines were employed as starting materials, respectively. Isolated yields of ligands **5** and **6** ranged from 78 to 99%, depending on the substitution pattern of the building blocks.

***N*-(2,6-Diisopropylphenyl)-*N*′-methoxy-*N*′-methylbenzamidine (5a):** Starting materials: *N*-(2,6-diisopropylphenyl)benzamide (**1a**, 1.98 g, 7.0 mmol) and *N*-methyl-*O*-methylhydroxylamine hydrochloride (0.53 g, 4.3 mmol). Yield: 2.11 g (93%). IR (KBr): $\tilde{\nu}$ = 2962 (m), 2931 (m), 1634 (s), 1602 (m), 1590 (m), 1461 (m), 1436 (m), 1360 (w), 1324 (m), 1256 (w), 1181 (w), 1104 (m), 1057 (w), 1030 (w), 1007 (m), 778 (m), 760 (m), 722 (w), 700 (s) cm^{-1}. MS(EI, 70 eV): *m*/*z* = 324 $[M]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.91 [d, $^3J_{H,H}$ = 7.0 Hz, 6 H, $CH(CH_3)_2$], 1.06 [d, $^3J_{H,H}$ = 7.0 Hz, 6 H, $CH(CH_3)_2$], 2.89 [sept, $^3J_{H,H}$ = 7.0 Hz, 2 H, 2 × $CH(CH_3)_2$], 3.15 (s, 3 H, NCH_3), 3.49 (s, 3 H, OCH_3), 6.82−6.89 (m, 3 H, C_6H_3), 7.13 (s, 5 H, C_6H_5) ppm. ^{13}C NMR (75.432 MHz, $CDCl_3$): δ = 21.9, 23.9, 28.0 [2 × $CH(CH_3)_2$], 37.0 (NCH_3), 60.2 (OCH_3), 122.4, 122.5, 127.5, 128.1, 128.8, 137.1, 144.0 (C_6H_3, C_6H_5), 160.8 (C=N) ppm. $C_{21}H_{28}N_2O$ (324.47): calcd. C 77.74, H 8.70, N 8.63; found C 77.69, H 8.72, N 8.60.

***N*′-Methoxy-*N*′-methyl-*N*-(2,6-methylphenyl)benzamidine (5b):** Starting materials: *N*-(2,6-diisopropylphenyl)benzamide (**1a**, 2.07 g, 9.2 mmol) and *N*-methyl-*O*-methylhydroxylamine hydrochloride (0.90 g, 9.2 mmol). Yield: 2.33 g (94%). IR (KBr): $\tilde{\nu}$ = 2973 (m), 2930 (m), 1636 (s), 1591 (m), 1578 (m), 1466 (m), 1447 (m), 1325 (m), 1260 (m), 1101 (m), 1076 (m), 1051 (m), 1028 (m), 1007 (s), 783 (m), 766 (s), 727 (m), 700 (s) cm^{-1}. MS(EI, 70 eV): *m*/*z* = 268 $[M]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.02 (s, 6 H, CH_3), 3.16 (s, 3 H, NCH_3), 3.52 (s, 3 H, OCH_3), 6.64−6.79 (m, 3 H, C_6H_3), 7.16 (s, 5 H, C_6H_5) ppm. ^{13}C NMR (75.432 MHz, $CDCl_3$): δ = 18.5 (CH_3), 37.2 (NCH_3), 60.3 (OCH_3), 121.9, 127.2, 127.5, 127.55, 127.6, 129.0, 134.0, 146.7 (C_6H_3, C_6H_5), 161.7 (C=N) ppm. $C_{17}H_{20}N_2O$ (268.36): calcd. C 76.09, H 7.51, N 10.44; found C 76.16, H 7.53, N 10.41.

***N*-(Biphenyl-2-yl)-*N*′-methoxy-*N*′-methylbenzamidine (5c):** Starting materials: *N*-(biphenyl-2-yl)benzamide (**1c**, 2.08 g, 7.6 mmol) and *N*-methyl-*O*-methylhydroxylamine hydrochloride (0.74 g, 7.6 mmol). Yield: 2.18 g (91%). IR (KBr): $\tilde{\nu}$ = 1628 (m), 1593 (m), 1578 (m), 1493 (m), 1474 (m), 1447 (m), 1431 (m), 1337 (m), 1267 (m), 1103 (m), 1074 (m), 1049 (m), 1030 (m), 1009 (m), 783 (m), 762 (m), 739 (s), 698 (s), 632 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 316 $[M]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.03 (s, 3 H, NCH_3), 3.38 (s, 3 H, OCH_3), 6.68−7.27 (m, 14 H, C_6H_5, C_6H_4) ppm. ^{13}C NMR (75.432 MHz, $CDCl_3$): δ = 37.0 (NCH_3), 60.5 (OCH_3), 122.6, 122.8, 126.1, 127.3, 127.34, 127.6, 128.2, 128.5, 129.6, 129.9, 132.9, 133.2, 140.3, 147.1 (C_6H_5, C_6H_4), 161.9 (C=N) ppm. $C_{21}H_{20}N_2O$ (316.40): calcd. C 79.72, H 6.37, N 8.85; found C 79.66, H 6.39, N 8.83.

***N*′-Methoxy-*N*′-methyl-*N*-phenylbenzamidine (5d):** Starting materials: benzanilide (**1d**, 2.13 g, 10.8 mmol) and *N*-methyl-*O*-methylhydroxylamine hydrochloride (1.06 g, 10.8 mmol). Yield: 2.03 g (78%). IR (KBr): $\tilde{\nu}$ = 2932 (w), 1628 (m), 1591 (m), 1439 (m), 1335 (m), 1256 (m), 1103 (m), 1074 (m), 1028 (m), 1009 (m), 997 (m), 920 (m), 903 (m), 781 (s), 762 (s), 744 (s), 696 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 240 $[M]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.16 (s, 3 H, NCH_3), 3.54 (s, 3 H, OCH_3), 6.60 (d, 2 H, C_6H_5), 6.79 (t, 1 H, C_6H_5), 7.03 (t, 2 H, C_6H_5), 7.20−7.28 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (75.432 MHz, $CDCl_3$): δ = 37.0 (NCH_3), 60.6 (OCH_3),

121.9, 122.1, 127.7, 128.2, 128.7, 128.8, 133.1, 149.7 (C_6H_5), 162.8 (C=N) ppm. $C_{15}H_{16}N_2O$ (240.30): calcd. C 74.97, H 6.71, N 11.66; found C 74.92, H 6.73, N 11.63.

***N*-(2,6-Diisopropylphenyl)-*N'*-methyl-*N'*-(methylamino)benzamidine (6a):** Starting materials: *N*-(2,6-diisopropylphenyl)benzamide (**1a**, 1.01 g, 3.6 mmol) and *N,N'*-dimethylhydrazine hydrochloride (0.55 g, 4.1 mmol). Yield: 1.10 g (94%). IR (KBr): $\tilde{\nu}$ = 3244 (w), 3062 (w), 3022 (w), 2973 (m), 2960 (m), 1609 (s), 1596 (s), 1586 (s), 1576 (s), 1492 (w), 1439 (m), 1382 (m), 1364 (s), 1329 (m), 1262 (m), 1183 (w), 1111 (m), 1069 (s), 1046 (m), 1025 (s), 924 (m), 845 (s), 824 (m), 808 (w), 799 (m), 772 (s), 760 (s), 714 (s), 700 (s) cm^{-1}. MS(EI, 70 eV): *m/z* = 323 $[M]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.94 [d, $^3J_{H,H}$ = 7.0 Hz, 6 H, $CH(CH_3)_2$], 1.06 [d, $^3J_{H,H}$ = 6.6 Hz, 6 H, $CH(CH_3)_2$], 2.64 (s, 3 H, NCH_3), 2.90 (s, 3 H, NCH_3), 2.94 [sept, 2 H, 2 × $CH(CH_3)_2$], 6.78−6.86 (m, 3 H, C_6H_3), 7.01−7.14 (m, 5 H, C_6H_5), not observed (s, 1 H, NH) ppm. ^{13}C NMR (75.432 MHz, $CDCl_3$): δ = 21.8, 24.1, 28.1 [$CH(CH_3)_2$], 36.4, 39.2 (NCH_3), 122.1, 122.2, 127.8, 128.1, 128.8, 133.1, 138.2, 144.7 (C_6H_3, C_6H_5), 157.3 (C=N) ppm. $C_{21}H_{29}N_3$ (323.48): calcd. C 77.97, H 9.04, N 12.99; found C 78.01, H 9.07, N 13.02.

***N*-(2,6-Diisopropylphenyl)-*N'*-(dimethylamino)benzamidine (6b):** Starting materials: *N*-(2,6-diisopropylphenyl)benzamide (**1a**, 1.01 g, 3.6 mmol) and *N,N*-dimethylhydrazine (0.58 mL, 0.46 g, 7.7 mmol, excess). Yield: 1.15 g (99%), brown viscous oil. MS (EI, 70 eV): *m/z* = 323 $[M]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, $CH(CH_3)_2$], 1.10 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, $CH(CH_3)_2$], 2.57 [s, 6 H, $N(CH_3)_2$], 3.13 (sept, $^3J_{H,H}$ = 6.9 Hz, 2 H, 2 × $CH(CH_3)_2$], 6.98−7.21 (m, 8 H, C_6H_3, C_6H_5), 7.95 (s, 1 H, NH) ppm. ^{13}C NMR (75.432 MHz, $CDCl_3$): δ = 21.9, 24.9, 26.3 [$CH(CH_3)_2$], 46.7 [$N(CH_3)_2$], 123.3, 126.9, 127.6, 128.5, 129.1, 132.9, 134.3, 145.2 (C_6H_3, C_6H_5), 159.7 (C=N) ppm. $C_{21}H_{29}N_3$ (323.48): calcd. C 77.97, H 9.04, N 12.99; found C 77.92, H 9.07, N 12.95.

***N*-(2,6-Diisopropylphenyl)-*N'*-{[(2,6-diisopropylphenyl)iminobenzyl]-phenylamino}benzamidine (7):** Starting materials: *N*-(2,6-diisopropylphenyl)benzamide (**1a**, 2.03 g, 7.2 mmol) and *N,N'*-diphenylhydrazine (1.40 g, 7.6 mmol). Yield: 0.42 g (16% based on limiting reagent **1a**). IR (KBr): $\tilde{\nu}$ = 2964 (m), 2929 (m), 2869 (m), 1627 (s), 1607 (s), 1589 (m), 1574 (s), 1497 (m), 1463 (m), 1443 (w), 1356 (w), 1328 (m), 1104 (w), 1057 (w), 1007 (w), 822 (w), 805 (w), 789 (w), 778 (w), 762 (w), 700 (m) cm^{-1}. MS(FAB): *m/z* = 712 $[M + H]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.00 [d, 12 H, $^3J_{H,H}$ = 6.6 Hz, 2 × $CH(CH_3)_2$], 1.25 [d, $^3J_{H,H}$ = 6.6 Hz, 12 H, 2 × $CH(CH_3)_2$], 3.13 [sept, 4 H, 4 × $CH(CH_3)_2$], 6.92 (d, 4 H, C_6H_3), 7.04 (m, 8 H, C_6H_3, C_6H_5), 7.13−7.36 (m, 14 H, C_6H_5) ppm. ^{13}C NMR (75.432 MHz, $CDCl_3$): δ = 21.7, 25.5, 28.9 [$CH(CH_3)_2$], 123.8, 124.5, 124.6, 124.9, 127.5, 128.6, 128.8, 129.1, 129.3, 129.5, 129.7, 132.6, 135.3, 137.9, 145.3 (C_6H_3, C_6H_5), 164.9 (C=N) ppm. $C_{50}H_{54}N_4$ (711.01): calcd. C 84.46, H 7.66, N 7.88; found C 84.51, H 7.66, N 7.85.

Synthesis of Metal Complexes

Representative Procedure for Iminohydroxamato and Imidoyl Hydrazido Complexes 8a−14a: A Schlenk tube was charged with **3a** (0.28 g, 0.90 mmol) and dry, deoxygenated THF (20 mL). After the mixture was cooled to −80 °C, a 2.0 M *n*-pentane solution of *n*-butyllithium (0.90 mmol, 0.45 mL) was added through a syringe. The stirred mixture changed gradually in color from orange to dark red, indicating deprotonation of **3a**. After 1 h of stirring at −80 °C, $ZrCl_4$ (0.21 g, 0.90 mmol, 1 mol-equiv. in relation to **3a**) was added under protection from air and the external cooling bath was removed. Stirring was continued overnight, resulting in a brown solution. Workup: THF and other volatile materials were removed in a vacuum line, the brown residue was dissolved in dry, deoxygenated dichloromethane giving a brown solution and a precipitate of lithium chloride. The inorganic salt was removed by filtration through a Schlenk frit, the dichloromethane was removed in a vacuum line, and the residue was triturated with dry, deoxygenated *n*-hexane (10 mL) to remove apolar impurities from the solid product. The precipitate was allowed to settle, *n*-hexane was removed by pipette followed by drying in vacuo, affording the product as an orange air-sensitive powder in 90% yield.

Trichloro[*N*-(2,6-diisopropylphenyl)-*N'*-methyl-*N'*-oxybenzamidinato]zirconium(IV) (8a): Starting materials: **3a** (0.28 g, 0.90 mmol), *n*-butyllithium (0.90 mmol, 0.21 g), $ZrCl_4$ (0.90 mmol, 1 mol-equiv. in relation to **3a**). Yield: 0.41 g (90%) as an orange, air-sensitive powder. ^1H NMR (300 MHz, CD_2Cl_2): δ = 1.04 [d, 6 H, 2 × $CH(CH_3)_2$], 1.81 (br. s, 4 H, CH_2 of coordinating THF), 3.33 [m, 5 H, NCH_3, 2 × $CH(CH_3)_2$], 3.83 (br. s, 4 H, CH_2 of coordinating THF), 6.94−7.02 (m, 3 H, C_6H_3), 7.10−7.35 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (75.432 MHz, CD_2Cl_2): δ = 24.2, 25.9, 28.1 [$CH(CH_3)_2$], 41.6 (NCH_3), 123.6, 124.2, 126.1, 128.5, 128.7, 129.1, 129.3, 129.4, 130.6, 143.9, 144.2 (C_6H_3, C_6H_5), 161.7 (C=N) ppm. $C_{20}H_{25}Cl_3N_2OZr{\cdot}THF$ = $C_{24}H_{33}Cl_3N_2O_2Zr$ (579.11): calcd. C 49.78, H 5.74, N 4.84; found C 49.67, H 5.70, N 4.77.

Trichloro[*N*-(2,6-dimethylphenyl)-*N'*-methyl-*N'*-oxybenzamidinato]zirconium(IV) (8b): Starting materials: **3b** (0.54 g, 2.12 mmol), *n*-butyllithium (2.4 mmol, 0.56 g), $ZrCl_4$ (2.4 mmol, 1.1 mol-equiv. in relation to **3b**). Yield: 0.82 g (86%) as an orange, air-sensitive powder. ^1H NMR (300 MHz, CD_2Cl_2): δ = 1.91 (br. s, 4 H, CH_2 of coordinating THF), 2.28, 2.31, 2.34, 2.39 (4 × s, 6 H, CH_3), 3.27, 3.33 (2 × s, 3 H, NCH_3), 3.85, 4.3 (2 × br. s, 4 H, CH_2 of coordinating THF), 6.83−7.37 (m, 8 H, C_6H_3, C_6H_5) ppm. ^{13}C NMR (75.432 MHz, CD_2Cl_2): δ = 18.7, 19.5, 19.7, 20.7, 20.9 (CH_3, THF), 39.5, 41.3, 41.9, 42.2 (NCH_3), 69.3 (THF), 125.5, 126.0, 127.2, 127.9, 128.0, 128.1, 128.4, 128.7, 128.9, 129.2, 130.1, 130.3, 130.4, 130.5, 130.9, 131.4, 133.1, 133.4, 133.8, 134.4, 134.7, 146.3 (C_6H_3, C_6H_5), 161.3 (C=N) ppm. $C_{16}H_{17}Cl_3N_2OZr{\cdot}THF$ = $C_{20}H_{25}Cl_3N_2O_2Zr$ (523.01): calcd. C 45.93, H 4.82, N 5.36; found C 45.87, H 4.79, N 5.31.

Trichloro[*N*-(biphenyl-2-yl)-*N'*-methyl-*N'*-oxybenzamidinato]zirconium(IV) (8c): Starting materials: **3c** (0.49 g, 1.62 mmol), *n*-butyllithium (1.7 mmol, 0.46 g), $ZrCl_4$ (2.0 mmol, 1.2 mol-equiv. in relation to **3c**). Yield: 0.71 g (88%) as an orange-brown, air-sensitive powder. ^1H NMR (300 MHz, CD_2Cl_2): δ = 1.88 (br. s, 4 H, CH_2 of coordinating THF), 2.33, 2.84, 2.97, 3.15 (4 × s, 3 H, NCH_3), 3.82, 4.56 (2 × br. s, 4 H, CH_2 of coordinating THF), 6.90−7.43 (m, 14 H, C_6H_4, C_6H_5) ppm. ^{13}C NMR (75.432 MHz, CD_2Cl_2): δ = 25.9 (THF), 41.1 (NCH_3), 69.2 (THF), 126.3, 127.2, 127.8, 127.9, 128.1, 128.5, 128.6, 128.7, 129.3, 129.4, 129.7, 130.2, 130.2, 131.2, 139.9, 144.5 (C_6H_4, C_6H_5), 160.9 (C=N) ppm. $C_{20}H_{17}Cl_3N_2OZr{\cdot}THF$ = $C_{24}H_{25}Cl_3N_2O_2Zr$ (571.05): calcd. C 50.48, H 4.41, N 4.91; found C 50.40, H 4.38, N 4.86.

Trichloro[*N'*-methyl-*N'*-oxybenzamidinato-*N*-phenyl]zirconium(IV) (8d): Starting materials: **3d** (0.34 g, 1.49 mmol), *n*-butyllithium (1.5 mmol, 0.41 g), $ZrCl_4$ (1.8 mmol, 1.2 mol-equiv. in relation to **3d**). Yield: 0.58 g (92%) as a yellow, air-sensitive powder. ^1H NMR (300 MHz, CD_2Cl_2): δ = 1.86 (br. s, 4 H, CH_2 of coordinating THF), 2.78, 3.32 (2 × s, 3 H, NCH_3), 3.84, 4.54 (2 × br. s, 4 H, CH_2 of coordinating THF), 6.92−7.35 (m, 10 H, C_6H_5) ppm. ^{13}C NMR (75.432 MHz, CD_2Cl_2): δ = 25.8 (THF), 40.0 (NCH_3), 125.2, 126.5, 128.3, 128.4, 128.6, 128.8, 129.0, 129.1, 129.2, 130.8,

146.3 (C_6H_5), 159.3 (C=N) ppm. $C_{14}H_{13}Cl_3N_2OZr\cdot THF$ = $C_{18}H_{21}Cl_3N_2O_2Zr$ (494.96): calcd. C 43.68, H 4.28, N 5.66; found C 43.57, H 4.24, N 5.61.

Trichloro[*N*-(2,6-diisopropylphenyl)-*N*′-isopropyl-*N*′-oxybenzamidinato]zirconium(IV) (8e): Starting materials: **3e** (0.28 g, 0.83 mmol), *n*-butyllithium (0.82 mmol, 0.22 g), $ZrCl_4$ (0.90 mmol, 1.2 mol-equiv. in relation to **3e**). Yield: 0.28 g (64%) as a colorless, air-sensitive powder. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.00−1.45 [m, 15 H, 2 × $CH(CH_3)_2$, $NCH(CH_3)_2$], 1.61 [d, $^3J_{H,H}$ = 6.6 Hz, 3 H, $NCH(CH_3)_2$], 1.83, 2.10 (br. s, 4 H, CH_2 of coordinating THF), 3.28−4.02 [3 overlapping sept, 3 H, $NCH(CH_3)_2$], 3.76, 4.70 (br. s, 4 H, CH_2 of coordinating THF), 6.92−7.46 (m, 8 H, C_6H_3, C_6H_5) ppm. ^{13}C NMR (75.432 MHz, CD_2Cl_2): δ = 20.0, 20.1, 22.0, 23.8, 24.3, 25.9, 26.1, 16.3, 28.2, 29.0, 29.2 [$CH(CH_3)_2$], 55.1 [$NCH(CH_3)_2$], 123.5, 123.6, 123.8, 124.1, 126.1, 126.3, 127.9, 128.5, 128.6, 128.8, 129.0, 129.2, 129.6, 129.7, 130.5, 131.9, 143.8, 144.5, 146.9, 147.4, 155.0 (C_6H_3, C_6H_5), 162.0 (C=N) ppm. $C_{22}H_{29}Cl_3N_2OZr\cdot THF$ = $C_{26}H_{37}Cl_3N_2O_2Zr$ (607.17): calcd. C 51.43, H 6.14, N 4.61; found C 51.38, H 6.10, 4.56.

Trichloro[*N*-(2,6-diisopropylphenyl)-*N*′-4-methylphenyl-*N*′-oxybenzamidinato]zirconium(IV) (8f): Starting materials: **3f** (0.22 g, 0.56 mmol), *n*-butyllithium (0.60 mmol, 0.13 g), $ZrCl_4$ (0.56 mmol, 1.0 mol-equiv. in relation to **3f**). Yield: 0.29 g (90%) as a tan, air-sensitive powder. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.05−1.35 [m, 12 H, 2 × $CH(CH_3)_2$], 1.82, 1.97 (br. s, 4 H, CH_2 of coordinating THF), 2.27 (s, 3 H, CH_3), 3.20, 3.40 [2 × sept, 2 H, $CH(CH_3)_2$], 3.77, 4.48 (br. s, 4 H, CH_2 of coordinating THF), 6.77−7.67 (m, 12 H, C_6H_3, C_6H_4, C_6H_5) ppm. $C_{26}H_{29}Cl_3N_2OZr\cdot THF$ = $C_{30}H_{37}Cl_3N_2O_2Zr$ (655.21): calcd. C 54.99, H 5.69, N 4.28; found C 55.06, H 5.73, N 4.25.

Dichlorobis[*N*-(2,6-diisopropylphenyl)-*N*′-methyl-*N*′-oxybenzamidinato]zirconium(IV) (9a): Starting materials: **3a** (0.65 g, 2.08 mmol), *n*-butyllithium (2.04 mmol, 0.21 g), $ZrCl_4$ (0.90 mmol, 0.5 mol-equiv. in relation to **3a**). Yield: 0.54 g (77%) as a tan, air-sensitive powder. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 0.23, 0.34. 0.29. 1.04 [4 × d, $^3J_{H,H}$ = 6.6 Hz, 24 H, 4 × $CH(CH_3)_2$], 2.89 [sept, 2 H, 2 × $CH(CH_3)_2$], 3.18 [sept, 2 H, 2 × $CH(CH_3)_2$], 3.40, 3.54, 3.60, 3.97 (4 × s, 6 H, NCH_3), 6.80−7.29 (m, 16 H, C_6H_3, C_6H_5) ppm. ^{13}C NMR (75.432 MHz, CD_2Cl_2): δ = 24.5, 25.1, 25.9, 26.2, 27.9, 28.1 [$CH(CH_3)_2$], 43.6 (NCH_3), 123.5, 124.2, 124.8, 125.8, 127.7, 127.9, 128.3, 128.3, 128.7, 129.0, 129.4, 130.0, 130.3, 143.3, 143.5, 145.5 (C_6H_3, C_6H_5), 159.8 (C=N) ppm. $C_{40}H_{50}Cl_2N_2O_2Zr$ (752.98): calcd. C 63.81, H 6.69, N 3.72; found C 63.95, H 6.72, N 3.70.

Trichloro[*N*-(2,6-dimethylphenyl)-*N*′-methyl-*N*′-oxybenzamidinato]-titanium(IV) (10b): Starting materials: **3b** (0.44 g, 1.73 mmol), *n*-butyllithium (1.9 mmol, 0.68 g), $TiCl_4$ (2.0 mmol, 1.2 mol-equiv. in relation to **3b**). Yield: 0.67 g (95%) as an orange, air-sensitive powder. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.13, 2.34 (2 × s, 6 H, CH_3), 3.40, 3.49, 3.63 (3 × s, 3 H, NCH_3), 6.85 (m, 3 H, C_6H_3), 7.12−7.41 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (75.432 MHz, CD_2Cl_2): δ = 19.6, 20.4 (CH_3), 30.0, 39.2, 41.5 (NCH_3), 125.8, 126.0, 128.1, 128.5, 128.7, 129.0, 129.3, 131.0, 131.7, 133.2, 133.5, 145.4, 149.9 (C_6H_3, C_6H_5), 160.3 (C=N) ppm. $C_{16}H_{17}Cl_3N_2OTi$ (407.56): calcd. C 47.15, H 4.20, N 6.87; found C 47.07, H 4.16, N 6.82.

Trichloro[*N*-(2,6-dimethylphenyl)-*N*′-methyl-*N*′-oxybenzamidinato]-vanadium(IV) (11b): Starting materials: **3b** (0.40 g, 1.56 mmol), *n*-butyllithium (1.7 mmol, 0.2 mL), VCl_4 (1.9 mmol, 1.2 mol-equiv. in relation to **3b**). Yield: 0.67 g (95%) as a dark green, air-sensitive powder. Due to strong paramagnetism no informative NMR spectra were obtained. $C_{16}H_{17}Cl_3N_2OV$ (410.62): calcd. C 46.80, H 4.17, N 6.82; found C 45.72, H 4.25, N 6.70.

Trichloro[*N*-(2,6-diisopropylphenyl)-*N*′-methylamino-*N*′-methylbenzamidinato]zirconium(IV) (13a): Starting materials: **6a** (0.52 g, 1.61 mmol), *n*-butyllithium (1.6 mmol, 0.49 g), $ZrCl_4$ (2.1 mmol, 1.3 mol-equiv. in relation to **6a**). Yield: 0.71 g (85%) as a yellow, air-sensitive powder. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 0.93−1.24 [4 × d, 12 H, 2 × $CH(CH_3)_2$], 1.82 (br. s, 4 H, CH_2 of coordinating THF), 2.94, 3.07, 3.18, 3.29 [4 × s, sept, 5 H, NCH_3, 2 × $CH(CH_3)_2$], 3.39, 3.48, 3.57, 3.89 (4 × s, 3 H, NCH_3), 3.84, 4.56 (2 × br. s, 4 H, CH_2 of coordinating THF), 6.90−7.60 (m, 8 H, C_6H_3, C_6H_5) ppm. ^{13}C NMR (75.432 MHz, CD_2Cl_2): δ = 21.8, 22.6, 24.2, 25.3, 25.9, 27.0, 28.2, 29.2 [$CH(CH_3)_2$], 34.9, 38.8, 40.4 (NCH_3), 123.0, 124.0, 124.3, 128.3, 128.6, 128.9, 129.5, 129.7, 129.8, 133.0, 143.8, 144.0, 146.1 (C_6H_3, C_6H_5), not observed: (C=N) ppm. $C_{21}H_{28}Cl_3N_3Zr\cdot THF$ = $C_{25}H_{36}Cl_3N_3Zr$ (576.16): calcd. C 52.12, H 6.30, N 7.29; found C 52.06, H 6.26, N 7.21.

Trichloro[*N*-(2,6-diisopropylphenyl)-*N*′-methylamino-*N*′-methylbenzamidinato]titanium(IV) (14a): Starting materials: **6a** (0.40 g, 1.24 mmol), *n*-butyllithium (1.24 mmol, 0.49 g), $TiCl_4$ (1.5 mmol, 1.2 mol-equiv. in relation to **6a**). Yield: 0.56 g (95%) as a green, air-sensitive powder. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.05 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, $CH(CH_3)_2$], 2.93 [sept, $^3J_{H,H}$ = 6.9 Hz, 2 H, $CH(CH_3)_2$], 3.38 (s, 3 H, NCH_3), 4.38 (s, 3 H, NCH_3), 6.99−7.36 (m, 8 H, C_6H_3, C_6H_5) ppm. ^{13}C NMR (75.432 MHz, CD_2Cl_2): δ = 23.9, 25.3, 28.6 [$CH(CH_3)_2$], 38.0, 45.2 (NCH_3), 123.8, 128.0, 128.7, 128.9, 129.0, 131.4, 141.2, 150.9 (C_6H_3, C_6H_5), 160.0 (C=N) ppm. $C_{21}H_{28}Cl_3N_3Ti$ (476.71): calcd. C 52.91, H 5.92, N 8.81; found C 53.03, H 5.88, N 8.75.

Representative Procedure for Iminohydroxylamino and Hydrazido Complexes 15a−17: A Schlenk tube was charged with **5a** (0.97 g, 3.0 mmol), dibromo(dimethoxethane)nickel(II) (1.25 g, 3.1 mmol) and dry, deoxygenated dichloromethane (20 mL). The mixture was stirred overnight, resulting in a dark green solution/suspension. Workup: dry dichloromethane (60 mL) was added, the solution was filtered through a Schlenk frit, the green solution was concentrated in a vacuum line, and the residue was dried in vacuo affording a green air-sensitive powder in 94% yield.

Dibromo[*N*-(2,6-diisopropylphenyl)-*N*′-methoxy-*N*′-methylbenzamidinato]nickel(II) (15a): Starting materials: **5a** (0.97 g, 3.0 mmol), $NiBr_2\cdot$DME (1.25 g, 3.1 mmol). Yield: 1.53 g (94%) as a green, paramagnetic, air-sensitive powder. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.10−1.49 [br. m, 12 H, $CH(CH_3)_2$], 2.97−3.56 [br. m, 8 H, $CH(CH_3)_2$, NCH_3, OCH_3], 6.80−8.30 (br. m, 8 H, C_6H_3, C_6H_5) ppm. ^{13}C NMR (75.432 MHz, CD_2Cl_2): due to paramagnetism, only very weak signals were observed. $C_{21}H_{28}Br_2N_2NiO$ (542.96): calcd. C 46.45, H 5.20, N 5.16; found C 46.52, H 5.25, N 5.07.

Dibromo[*N*-(2,6-dimethylphenyl)-*N*′-methoxy-*N*′-methylbenzamidinato]nickel(II) (15b): Starting materials: **5b** (0.79 g, 2.94 mmol), $NiBr_2\cdot$DME (1.17 g, 2.94 mmol). Yield: 1.08 g (66%) as a green, paramagnetic, air-sensitive powder. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.75 [br. s, 12 H, $CH(CH_3)_2$], 3.99 [br. m, 8 H, $CH(CH_3)_2$, NCH_3, OCH_3], 6.80−7.70 (br. m, 8 H, C_6H_3, C_6H_5) ppm. ^{13}C NMR (75.432 MHz, CD_2Cl_2): due to paramagnetism, no informative signals were observed. $C_{17}H_{20}Br_2N_2NiO$ (486.86): calcd. C 41.94, H 4.14, N 5.75; found C 42.02, H 4.16, N 5.70.

Dibromo[*N*-(biphenyl-2-yl)-*N*′-methoxy-*N*′-methylbenzamidinato]-nickel(II) (15c): Starting materials: **5c** (0.87 g, 2.75 mmol), $NiBr_2\cdot$DME (1.10 g, 2.75 mmol). Yield: 1.43 g (97%) as a green,

paramagnetic, air-sensitive powder. ^{1}H NMR (300 MHz, CD_2Cl_2): only one very broad signal from δ = −4 to +24 ppm centered at δ = 12.0 ppm was observed. ^{13}C NMR (75.432 MHz, CD_2Cl_2): due to paramagnetism, no informative signals were observed. $C_{21}H_{20}Br_2N_2NiO$ (534.90): calcd. C 47.15, H 3.77, N 5.24; found C 47.04, H 3.81, N 5.18.

Dibromo[*N*′-methoxy-*N*′-methyl-*N*-phenylbenzamidinato]nickel(II) (15d): Starting materials: **5d** (0.62 g, 2.58 mmol), $NiBr_2$·DME (1.03 g, 2.58 mmol). Yield: 0.70 g (59%) as a green, paramagnetic, air-sensitive powder. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 0.07, 0.87, 1.27, 4.33 (4 × br. s, 6 H, NCH_3, OCH_3), 6.84−9.96 (br. m, 10 H, C_6H_5) ppm. ^{13}C NMR (75.432 MHz, CD_2Cl_2): due to paramagnetism, no informative signals were observed. $C_{15}H_{16}Br_2N_2NiO$ (458.80): calcd. C 39.27, H 3.52, N 6.11; found C 39.19, H 3.56, N 6.06.

Dibromo[*N*-(2,6-diisopropylphenyl)-*N*′-methylamino-*N*′-methylbenzamidinato]nickel(II) (16a): Starting materials: **6a** (0.44 g, 1.36 mmol), $NiBr_2$·DME (0.56 g, 1.4 mmol). Yield: 0.70 g (95%) as a brown, paramagnetic, air-sensitive powder. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = −0.16, 1.76, 5.16, 5.41 [4 × br. s, 20 H, $CH(CH_3)_2$, NCH_3, OCH_3], 15.38, 19.63, 22.57 (3 × br. s, 8 H, C_6H_3,C_6H_5) ppm. ^{13}C NMR (75.432 MHz, CD_2Cl_2): due to paramagnetism, no informative signals were observed. $C_{21}H_{29}Br_2N_3Ni$ (541.98): calcd. C 46.54, H 5.39, N 7.75; found C 46.40, H 5.44, N 7.67.

Dibromo[*N*-(2,6-diisopropylphenyl)-*N*′-(dimethylamino)benzamidinato]nickel(II) (16b): Starting materials: **6b** (0.52 g, 1.6 mmol), $NiBr_2$·DME (0.70 g, 1.8 mmol). Yield: 0.66 g (76%) as a brown, slightly paramagnetic, air-sensitive powder. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 0.89, 0.95, 1.08, 2.04, 2.40, 3.47, 5.99 [6 × br. s, 21 H, $CH(CH_3)_2$, NCH_3, NH], 7.11, 7.14, 7.39, 7.82, 8.19, 8.48, 8.57, 8.96 (8 × br. s, 8 H, C_6H_3, C_6H_5) ppm. ^{13}C NMR (75.432 MHz, CD_2Cl_2): δ = 13.1, 21.8, 22.2, 24.7, 29.8, 30.7 [$CH(CH_3)_2$], 50.8 (NCH_3), 124.0, 126.0, 127.7, 129.7, 131.2, 131.7, 135.5, 140.0, 143.8 (C_6H_3, C_6H_5), not observed: (C=N) ppm. $C_{21}H_{29}Br_2N_3Ni$ (541.98): calcd. C 46.54, H 5.39, N 7.75; found C 46.58, H 5.32, N 7.70.

Dibromo[*N*-2,6-diisopropylphenyl-*N*′-({[(2,6-diisopropylphenyl)-imino]benzyl}phenylamino)benzamidino]nickel(II) (17): Starting materials: **7** (0.26 g, 0.37 mmol), $NiBr_2$·DME (0.17 g, 0.40 mmol). Yield: 0.30 g (88%) as a pale green, air-stable powder. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.07 [d, $^3J_{H,H}$ = 6.9 Hz, 12 H, $CH(CH_3)_2$], 1.31 [d, $^3J_{H,H}$ = 6.6 Hz, 12 H, $CH(CH_3)_2$], 3.14 [sept, 4 H, $CH(CH_3)_2$], 6.97 (d, 4 H, C_6H_3), 7.09 (d, 8 H, C_6H_5), 7.18−7.39 (m, 14 H, C_6H_3, C_6H_5) ppm. ^{13}C NMR (75.432 MHz, CD_2Cl_2): δ = 21.8, 26.7, 29.5 [$CH(CH_3)_2$], 124.2, 125.1, 125.3, 125.4, 127.5, 127.9, 128.1, 129.1, 129.2, 129.7, 129.8, 130.2, 133.1, 135.5, 138.4, 145.9 (C_6H_3, C_6H_5), 165.5 (C=N) ppm.

Table 2. Crystallographic data for **2a**, **3a**, **3b**, **3e**, **12b**

Compound	**2a**	**3a**	**3b**	**3e**	**12b**
Empirical formula	$C_{19}H_{22}ClN$	$C_{20}H_{26}N_2O \times 0.75H_2O \times 0.5EtOH$	$C_{16}H_{18}N_2O$	$C_{22}H_{30}N_2O \times 0.5H_2O$	$C_{32}H_{34}Cl_4N_4O_2Ti \times CH_2Cl_2$
Formula mass	299.83	346.97	254.32	347.49	710.36
Crystal system	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	*Pbcn* (No. 60)	*C*2/*c* (No. 15)
a [pm]	849.30(4)	1385.87(5)	999.74(8)	1610.5(1)	1705.81(4)
b [pm]	2683.84(9)	1688.70(7)	1096.61(8)	1661.4(2)	1542.57(3)
c [pm]	807.69(4)	1813.58(5)	1404.0(1)	1579.4(1)	1580.06(3)
α [°]	90	90	67.673(4)	90	90
β [°]	113.381(2)	93.683(2)	87.115(4)	90	122.569(2)
γ [°]	90	90	87.317(4)	90	90
Z	4	8	4	8	4
V [nm^3]	1.68986(13)	4.2356(3)	1.42140(18)	4.2260(6)	3.50384(13)
$\rho_{calcd.}$ [Mg·m^{-3}]	1.178	1.088	1.188	1.092	1.347
T [K]	233(2)	223(2)	223(2)	223(2)	233(2)
μ [mm^{-1}]	0.220	0.070	0.075	0.068	0.584
F(000)	640	1508	544	1512	1472
Color, habit	colorless prism	colorless prism	colorless prism	colorless prism	red prism
Crystal size [mm]	0.4 × 0.35 × 0.3	0.4 × 0.3 × 0.2	0.39 × 0.13 × 0.12	0.3 × 0.15 × 0.08	0.2 × 0.12 × 0.08
θ range for data collection [°]	2.61−23.50	1.90−21.00	2.01−22.00	1.76° to 19.94	1.94−24.00
Index ranges	$-9 \le h \le 0$ $-29 \le k \le 30$ $-8 \le l \le 9$	$0 \le h \le 13$ $-16 \le k \le 17$ $-18 \le l \le 18$	$0 \le h \le 10$ $-11 \le k \le 11$ $-14 \le l \le 14$	$0 \le h \le 15$ $-15 \le k \le 15$ $-15 \le l \le 15$	$-13 \le h \le 19$ $-12 \le k \le 15$ $-15 \le l \le 15$
Reflections collected	5162	17026	6271	12806	9665
Independent reflections	2316 (R_{int} = 0.0251)	4516 (R_{int} = 0.0434)	3468 (R_{int} = 0.0304)	1950 (R_{int} = 0.1025)	2759 (R_{int} = 0.0322)
Reflections with $I > 2\sigma(I)$	1970	3531	2501	1380	2299
Absorption correction	none	none	none	none	none
Refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
Data/restraints/parameters	2316/0/192	4516/0/506	3468/0/358	1950/0/246	2759/0/221
Goodness-of-fit on F^2	1.044	1.047	1.045	1.033	1.037
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0410 wR_2 = 0.0995	R_1 = 0.0489 wR_2 = 0.1226	R_1 = 0.0467 wR_2 = 0.1211	R_1 = 0.0501 wR_2 = 0.1175	R_1 = 0.0397 wR_2 = 0.0990
R indices (all data)	R_1 = 0.0513 wR_2 = 0.1050	R_1 = 0.0674 wR_2 = 0.1304	R_1 = 0.0728 wR_2 = 0.1323	R_1 = 0.0814 wR_2 = 0.1313	R_1 = 0.0516 wR_2 = 0.1050
Extinction coefficient	0.015(3)	0.0074(8)	0.017(3)	0.0060(10)	
Largest diff. peak/hole [e nm^{-3}]	166/−261	202/−144	343/−160	292/−132	335/−335

$C_{50}H_{54}Br_2N_4Ni$ (929.50): calcd. C 64.61, H 5.86, N 6.03; found C 64.72, H 5.90, N 5.98.

Crystallography: Single-crystal X-ray measurements and structure determinations of **2a**−**3a**, **3b**, **3e**, **12b** (Table 2). The data collection was performed with a Nonius−Kappa CCD instrument equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and a nominal crystal to area detector distance of 36 mm. Intensities were integrated using DENZO and scaled with SCALEPACK.[15] Several scans in φ and ω directions were made to increase the number of redundant reflections, which were averaged in the refinement cycles. This procedure replaces an empirical absorption correction. The structures were solved with direct methods (SHELXS 86) and refined against F^2 (SHELX 97).[16] Hydrogen atoms at carbon atoms were added geometrically and refined using a riding model. Hydrogen atoms at nitrogen and oxygen atoms of compounds **3a**, **3b**, **3e** were located and refined isotropically. All non-hydrogen atoms were refined with anisotropic displacement parameters. CCDC-213598 (for **2a**), -213599 (**3a**), -213600 (**3b**), -213601 (**3e**) and -213602 (**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Polymerizations: All polymerization studies and polymer characterizations were performed at Basell/BASF AG in Ludwigshafen, Germany. Ethylene polymerization: a dry 1000-mL steel autoclave was charged under strict exclusion of air with toluene (400 mL) and a small amount (1−6 mg, compare Table 1) of precatalyst **8a**−**17**. A 30% toluene solution of methylaluminoxane (MAO) was added (2 mL) and the temperature of the autoclave was kept constant at 70 °C. Ethylene gas was added up to a pressure of 40 bar and the reaction was allowed to proceed for 5−75 minutes, depending on the activity of the catalyst. After the polymerization time given in Table 1, the reaction was terminated by releasing the pressure in the autoclave. The solid polymer was isolated by filtration, washed with methanol, and dried in vacuo. Propylene polymerization: conditions were similar as those in ethylene polymerizations, but propylene was used as monomer. Ethylene/*n*-hexene copolymerizations: conditions were similar as in ethylene homopolymerizations, but in addition to the other reagents *n*-hexene (12.5 mL) was employed.

[1] Recent reviews: [1a] V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.* **2003**, *103*, 283. [1b] S. Mecking, *Angew. Chem.* **2001**, *113*, 550; *Angew. Chem. Int. Ed.* **2001**, *40*, 534−540. [1c] S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169. [1d] S. Mecking, *Coord. Chem. Rev.* **2000**, *203*, 325. [1e] G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem.* **1999**, *111*, 448.

[2] L. K. Johnson, C. M. Killian, M. Brookhart, *J. Am. Chem. Soc.* **1995**, *117*, 6414.

[3] [3a] B. L. Small, M. Brookhart, A. M. A. Bennett, *J. Am. Chem. Soc.* **1998**, *120*, 4049. [3b] G. J. P. Britovsek, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. J. McTavish, G. A. Solan, A. J. P. White, D. J. Williams, *Chem. Commun.* **1998**, 849.

[4] [4a] T. R. Younkin, E. F. Connor, J. I. Henderson, S. K. Friedrich, R. H. Grubbs, D. A. Bansleben, *Science* **2000**, *287*, 460. [4b] E. B. Coughlin, S. D. Ittel, J. Feldman, L. Wang, A. M. A. Bennett, E. Hauptmann, L. K. Johnson, A. Parthasarathy, R. D. Simpson, WO9830609, **1998**.

[5] [5a] S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, H. Tanaka, T. Fujita, *Chem. Lett.* **1999**, 1263. [5b] H. Makio, N. Kashiwa, T. Fujita, *Adv. Synth. Catal.* **2002**, *344*, 477.

[6] [6a] A. Held, F. M. Bauers, S. Mecking, *Chem. Commun.* **2000**, 301. [6b] A. Tomov, J. P. Broyer, R. Spitz, *Macromol. Symp.* **2000**, *150*, 53. [6c] S. Mecking, A. Held, F. M. Bauers, *Angew. Chem.* **2002**, *114*, 564.

[7] Z. Guan, *Chem. Eur. J.* **2002**, *8*, 3087.

[8] G. W. Coates, P. D. Hustad, S. Reinartz, *Angew. Chem. Int. Ed.* **2002**, *41*, 2237.

[9] [9a] B. Bildstein, A. Krajete, M. O. Kristen (BASF AG), DE 10206116, **2002**. [9b] B. Bildstein, A. Krajete, M. O. Kristen (BASF AG), DE 10206113, **2002**.

[10] A. Vogel, *Vogel's Textbook of Practical Organic Chemistry, Including Qualitative Organic Analysis*, Longman Inc., New York, **1978**, p. 1075.

[11] [11a] H. Ley, P. Krafft, *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 697; and references cited therein. [11b] L. H. Briggs, R. C. Cambie, I. C. Dean, P. S. Rutledge, *Aust. J. Chem.* **1976**, *29*, 357.

[12] R. T. Boere, V. Klassen, G. Wolmershäuser, *J. Chem. Soc., Dalton Trans.* **1998**, 4147.

[13] B. Bildstein, M. Malaun, H. Kopacka, K. Wurst, M. Mitterböck, K.-H. Ongania, G. Opromolla, P. Zanello, *Organometallics* **1999**, *18*, 4325.

[14] S. Blechert, *Liebigs Ann. Chem.* **1985**, 673.

[15] Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307.

[16] G. M. Sheldrick, *Program package SHELXTL V.5.1*, Bruker Analytical X-ray Instruments, Inc., Madison, USA, **1997**.

Received June 26, 2003
Early View Article
Published Online March 9, 2004

