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Synthesis and Structural Diversity of Group 4 Metal Complexes with Multidentate Tethered Phenoxy-Amidine and Phenoxy-Amidinate Ligands

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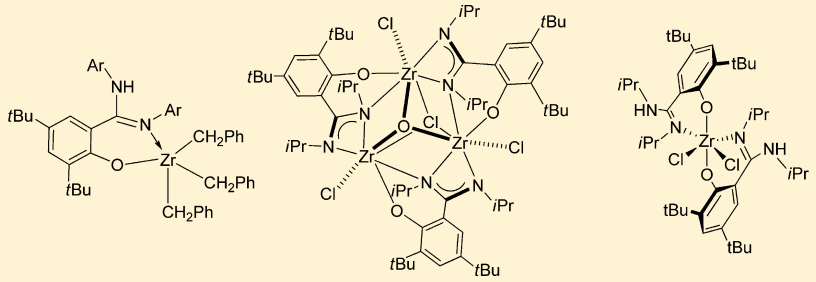
Supporting Information

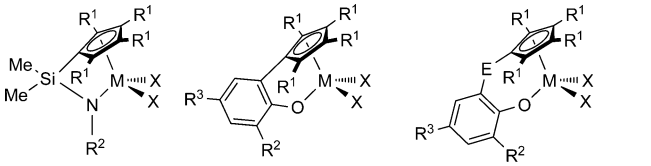


ABSTRACT: The coordination chemistry of the multidentate tethered amidine-phenol {4,6-tBu$_2$C$_6$H$_2$O(2-C(NR)═NR}H$_2$ ({LON^R}H$_2$, R = iPr, 2,6-iPr$_2$C$_6$H$_3$ (Ar)) and new guanidine-phenol {4,6-tBu$_2$C$_6$H$_2$ON(C$_6$H$_5$)(2-C(NR)═NR}H$_2$ ({LON(Ph)N^{iPr}}H$_2$) pro-ligands with group 4 metals has been studied. σ-Bond and salt metathesis reactions were explored to coordinate these (pro)ligands onto zirconium and hafnium. Alkane elimination reactions between {LON^R}H$_2$ and Zr(CH$_2$Ph)$_4$ afforded mixed-ligand monobenzyl {LO^{H}N^R}{LON^R}Zr(CH$_2$Ph) (R = iPr; **1**) and monoligand tribenzyl {LO^{H}N^{Ar}}Zr(CH$_2$Ph)$_3$ (R = Ar; **2**) complexes, respectively. Alkane and amine elimination reactions between {LON(Ph)N^{iPr}}H$_2$ and Zr(CH$_2$Ph)$_4$ or Hf(NMe$_2$)$_4$ unexpectedly resulted in cleavage of the ligand backbone and eventual isolation of {(Ph)NC$_6$H$_2$(tBu)$_2$O}Zr{(iPrN)$_2$CCH$_2$Ph}$_2$ (**3**) and {(Ph)NC$_6$H$_2$(tBu)$_2$O}Hf{(iPrN)$_2$CNMe$_2$}$_2$ (**4**), respectively. Salt metathesis reactions between {LON^R}Li$_2$ and ZrCl$_4$(THF)$_n$ (n = 0, 2), conducted in 1:1 ratios, led upon crystallization to diverse chloro complexes: [{LON^{iPr}}ZrCl]$_3$(μ_3-O)(μ_3-Cl) (**5**), [{LON^{Ar}}$_2$ZrCl(μ_2-Cl)]$_2$[{L^{H}ON^{Ar}}ZrCl(μ_2-Cl)](μ_3−OH) (**6**), and {LO^{H}N^{Ar}}ZrCl$_3$(THF) (**7**). Similar salt metathesis reactions between the monolithium salts {L^{H}ON^R}Li and ZrCl$_4$, conducted in 2:1 ratios, allowed the selective preparation of bis(phenoxy-amidine) complexes with pendant amino groups {LO^{H}N^R}$_2$ZrCl$_2$ (R = iPr, **8**; R = Ar, **9**). All complexes were authenticated by elemental analysis, X-ray crystallography, and NMR spectroscopy. Complexes **5**, **6**, **8**, and **9**, upon activation with MAO, showed poor to moderate productivities (4−172 (kg of PE) mol^{-1} h^{-1}) in the polymerization of ethylene, giving linear polymers with large polydispersities.

INTRODUCTION

Group 4 metal "constrained-geometry catalysts" (CGCs) bearing dianionic bridged cyclopentadienyl-amido ligands (**1**; Scheme 1) have received considerable attention because of their unique ability to produce polyolefin materials of high commercial interest: e.g., linear low-density polyethylene (LLDPE) and poly(ethylene-*co*-styrene) copolymers.[1] The development of new single-site CGCs for the controlled (co)polymerization of α-olefins has been the focus of extensive research over the last two decades. In this line, Marks and others showed that bridged systems of type **2** (Scheme 1) are highly performing in ethylene and propylene homopolymerizations and ethylene/norbornene copolymerization.[2] Other heteroleptic complexes incorporating linked cyclopentadienyl-phenoxide scaffolds (**3**; Scheme 1) were found to be effective catalyst precursors for the homo- and copolymerizations of ethylene and α-olefins, such as 1-hexene.[3]

Scheme 1. Examples of Group 4 Metal CGC Complexes Supported by Cp-Amido and Cp-Phenoxide Ligands[1−3]



1
R^1 = H, Me,
R^2 = i-Pr, t-Bu, 1-Ad,
X = Me, Bn, Cl

2
R^1 = H, Me,
R^2 = Me, t-Bu, Ph, 1-Ad,
R^3 = H, Me, t-Bu,
X = Bn, Cl

3
R^1 = H, Me,
R^2 = i-Pr, t-Bu, 1-Ad,
R^3 = H, Me, E = CMe$_2$, SiMe$_2$,
X = Bn, Cl

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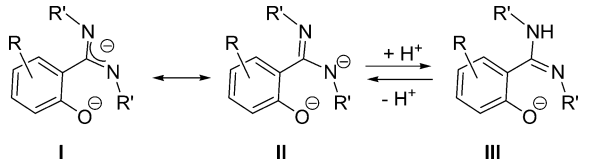
On this principle, we have recently prepared the new amidino-phenol pro-ligands {4,6-tBu$_2$C$_6$H$_2$O(2-C(NR)=NR}H$_2$ ({LON^R}H$_2$, R = iPr, cyclohexyl (Cy), 2,6-iPr$_2$C$_6$H$_3$ (Ar)) and studied their corresponding phenoxy-amidinate complexes of group 3 metals and lanthanides.[4] The coordination chemistry of this ligand system with rare-earth metals proved quite versatile: two alternative coordination modes of this dianionic ligand (**I** and **II**) and a protonated monoanionic form (**III**, Scheme 2) were evidenced.

Scheme 2. Coordination Modes of the Dianionic Phenoxy-Amidinate Ligand (I and II) and a Protonated Monoanionic Form (III) Observed in Group 3 Metal Complexes[4]



Amidinates, related aminopyridinates, and guanidinates have become ubiquitous ligands for supporting early-transition-metal centers, and many of the resulting complexes have found valuable catalytic applications.[5] For group 4 metal species, this was in particular evidenced by Kempe,[6] Sita,[7] Eisen[8] and others[9] with the effective polymerization of ethylene, α-olefins, dienes and styrene.

Accordingly, we describe herein σ-bond (alkane or amine elimination) and salt metathesis reactions of amidino-phenol {LON^R}H$_2$ and newly synthesized guanidino-phenol {LON(Ph)N$^{i\mathrm{Pr}}$}H$_2$ pro-ligands with group 4 metal precursors. Factors governing the reactivity and the coordination chemistry of these original ligand platforms onto group 4 metal centers have been investigated. Also, the performance of the prepared complexes in the polymerization of ethylene and propylene was briefly explored.

RESULTS AND DISCUSSION

Synthesis of Pro-ligands. The original amidine-phenol pro-ligands {LON$^{i\mathrm{Pr}}$}H$_2$ and {LON$^{\mathrm{Ar}}$}H$_2$ were prepared using our recently published procedure.[4] In the latter study, we have shown that coordination of such phenoxy-amidinate ligands onto group 3 metals afforded predominantly dimeric bimetallic complexes featuring "spanned" geometries, in which a single dianionic ligand was bonded to two different metal centers. This phenomenon was accounted for by the absence of a spacer between the phenoxy and amidinate moieties in the ligand skeleton. In order to decrease the constraint imposed in the ligand backbone, we have attempted a modification of the ligand system by introducing an additional heteroatom linker between the phenoxy and amidinate moieties. The corresponding new guanidine-phenol pro-ligand {LON(Ph)N$^{i\mathrm{Pr}}$}H$_2$ was synthesized by a three-step procedure, starting from 2-anilino-4,6-di-*tert*-butylphenol and *N*,*N*′-diisopropylcarbodiimide (Scheme 3). The product was isolated in good yield and characterized by NMR spectroscopy and elemental analysis.

Crystals of {LON$^{i\mathrm{Pr}}$}H$_2$ and {LON(Ph)N$^{i\mathrm{Pr}}$}H$_2$ suitable for structural determination were grown by slow evaporation of the corresponding $CHCl_3$ solutions in air, the latter compound being crystallized with an additional water molecule. The molecular structures of {LON$^{i\mathrm{Pr}}$}H$_2$ and {LON(Ph)N$^{i\mathrm{Pr}}$}H$_2$·H$_2$O are shown in Figures 1 and 2, respectively.

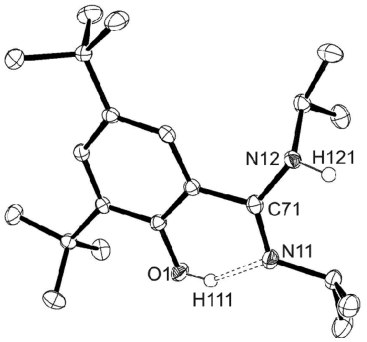
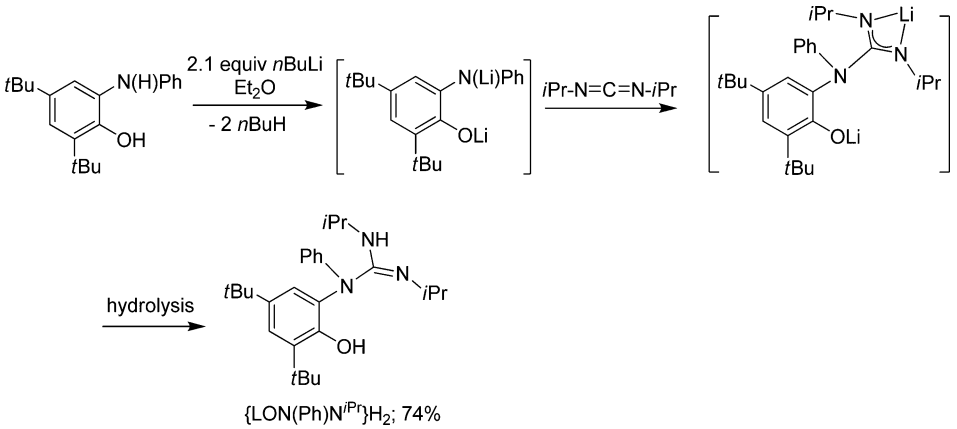


Figure 1. Molecular structure of {LON$^{i\mathrm{Pr}}$}H$_2$ (ellipsoids are drawn at the 50% probability level; H atoms, except those of the NH and OH groups, are omitted for clarity). Important bond lengths (Å): C(71)–N(11), 1.2985(19); C(71)–N(12), 1.3957(18); O(1)–H(111), 0.84(3); H(111)–N(11), 1.78(3).

Alkane and Amine Elimination Approaches. To specifically target "constrained-geometry" group 4 metal complexes containing phenoxy-amidinate and phenoxy-guanidinate ligands, we carried out alkane and amine elimination reactions between the corresponding bifunctional diprotic pro-ligands and homoleptic MR$_4$ (R = CH_2Ph, M = Zr; R = NMe_2, M = Hf) precursors. Previous investigations have shown that

Scheme 3. Synthesis of the Guanidinate-Phenol Pro-ligand {LON(Ph)N^R}H$_2$



{LON(Ph)N$^{i\mathrm{Pr}}$}H$_2$: 74%

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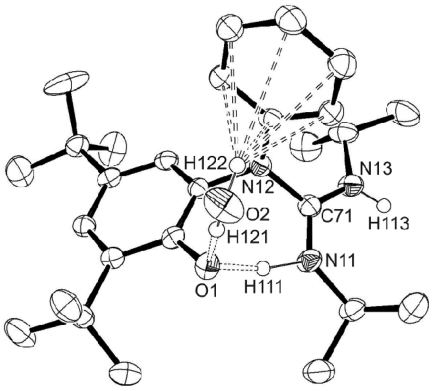


Figure 2. Molecular structure of $\{LON(Ph)N^{iPr}\}H_2.(H_2O)$ (ellipsoids are drawn at the 50% probability level; H atoms, except those of the NH and OH groups, and the H_2O molecule are omitted for clarity). Important bond lengths (Å): C(71)−N(11), 1.3012(19); C(71)−N(12), 1.3373(19); C(71)−N(12), 1.4177(19); O(1)−H(111), 1.302(2); H(111)−N(11), 1.217(2); O(2)−H(121), 1.01(2); O(2)−H(122), 0.83(2).

such approaches are efficient one-step routes toward compounds of the type L_2MR_2.[2a,3,10]

Monitoring by ^1H NMR spectroscopy of the reaction between equimolar amounts of $Zr(CH_2Ph)_4$ and $\{LON^{iPr}\}H_2$ in benzene-d_6 at room temperature showed rapid and selective formation of the monobenzyl phenoxy-amidinate phenoxy-amidine complex **1** (Scheme 4). The latter product resulted from the alkane elimination reaction of 2 equiv of bifunctional pro-ligand with 1 equiv of $Zr(CH_2Ph)_4$,[11] while 1 equiv of the zirconium precursor remained intact. Further heating of the reaction mixture at 80 °C over 6−8 h did not lead to significant changes in the mixture composition. A scaled-up reaction between $\{LON^{iPr}\}H_2$ and $Zr(CH_2Ph)_4$ (2:1) conducted in toluene gave analytically pure **1** in 95% yield as a pale yellow solid.[12] In toluene-d_8 solution at room temperature, complex **1** featured a dissymmetric structure with two nonequivalent ligands, as revealed by ^1H and ^{13}C NMR spectroscopy. Key NMR parameters for **1** include four doublets for the phenoxy hydrogens, two multiplets for the methine hydrogens, four doublets for the methyl hydrogens of the nonequivalent *i*Pr groups, two singlets for the *t*Bu groups, two doublets for the diastereotopic methylene hydrogens of the benzyl group, and one doublet for the N−H group. Complex **1** appeared to be very stable in toluene solution and did not undergo further protolytic reaction of the Zr−benzyl group by the pendant amino group of the amidine moiety, even upon heating at 100 °C overnight.[13]

The solid-state molecular structure of **1** was established by X-ray diffraction (Figure 3) and revealed the zirconium atom in a

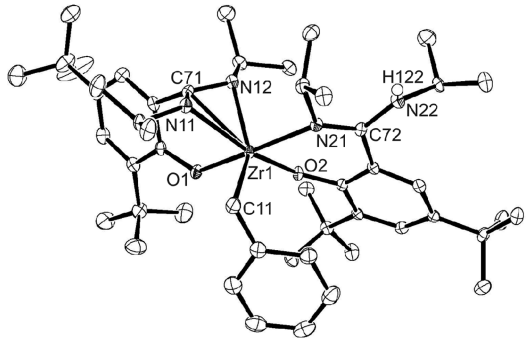
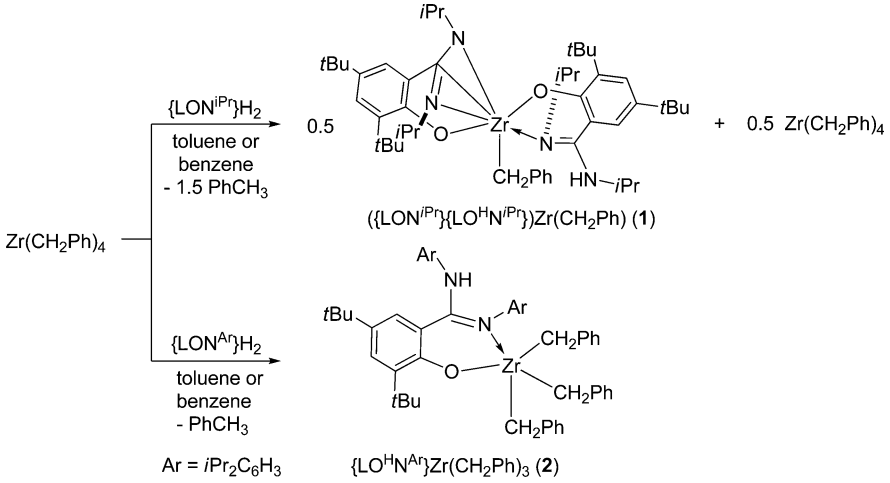


Figure 3. Molecular structure of $\{LON^{iPr}\}\{LOHN^{iPr}\}Zr(CH_2Ph)$ (**1**) (ellipsoids are drawn at the 50% probability level; H atoms, except that of the N−H group, are omitted for clarity). Important bond lengths (Å) and angles (deg): Zr(1)−O(1), 2.0516(17); Zr(1)−O(2), 2.0079(16); Zr(1)−N(11), 2.437(2); Zr(1)−N(12), 2.168(2); Zr(1)−C(71), 2.467(2); Zr(1)−N(21), 2.295(2); Zr(1)−C(11), 2.289(3); C(71)−N(11), 1.322(3); C(71)−N(12), 1.364(3); C(72)−N(21), 1.318(3); C(72)−N(22), 1.360(3); O(1)−Zr(1)−N(11), 82.67(7); O(1)−Zr(1)−N(12), 86.15(7); O(2)−Zr(1)−N(21), 79.25(7); O(1)−Zr(1)−N(21), 171.85(7); O(1)−Zr(1)−C(11), 96.67(9).

distorted-pseudo-octahedral coordination environment, provided by inequivalent dianionic phenoxy-amidinate and monoanionic phenoxy-amidine ligands and the benzyl group. Thus, the metal center is six-coordinated with the oxygen atom of the dianionic ligand and the nitrogen atom of the monoanionic ligand occupying the axial positions, while the amidinate group of the dianionic ligand, the oxygen atom of the monoanionic ligand, and the benzyl group lie in the equatorial positions. The Zr(1)−O(1) and Zr(1)−O(2) bond lengths in **1** (2.0516(17) and 2.0079(16) Å, respectively) are in the range of the values of covalent bonds reported for zirconium−salicylaldimine complexes (1.951−2.064 Å).[14] To our knowl-

Scheme 4. Formation of Complexes 1 and 2



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edge, the bonding of the amidinate fragment of the dianionic ligand to the zirconium center in **1** is unprecedented. First, unlike group 4 metal−amidinate complexes that exhibit a η^2-N,N′ binding, the coordination of the amidinate fragment in **1** is better described as allylic-like of the type η^3-N,C,N′. The Zr(1)−C(71) bond (2.467(2) Å) is significantly shorter than those observed in regular zirconium−allyl complexes (2.513−2.565 Å).[15] The amidinate fragment in **1** coordinates nonsymmetrically to the metal center, which is evidenced by the quite inequivalent Zr(1)−N(11) and Zr(1)−N(12) bonds (2.437(2) and 2.168(2) Å, respectively), the former being somewhat longer than those found in zirconium−amidinate complexes (2.123−2.333 Å).[16] Also, the Zr(1)−N(21) distance (2.295(2) Å) in **1** is somewhat shorter with respect to the usual range for Zr−N(imino) bond lengths (2.322−2.434 Å) observed in zirconium−salicylaldimine complexes.[14] The sole benzyl group in **1** is clearly η^1 bound to the metal center, as revealed by a long Zr(1)···C_{ipso} contact (2.995(2) Å) and an obtuse Zr(1)−C(11)−C_{ipso} angle (103.02(16)°).[17,18]

On the other hand, the 1:1 reaction of $Zr(CH_2Ph)_4$ with the more bulky pro-ligand $\{LON^{Ar}\}H_2$, in benzene or in toluene, afforded selectively $\{LO^HN^{Ar}\}Zr(CH_2Ph)_3$ (**2**). Attempts to obtain a bis(ligand) complex from 2:1 reactions between the pro-ligand and the metal precursor, in toluene at room temperature, systematically led to mixtures of **2** and unreacted pro-ligand.[19] Complex **2** was isolated as a pale orange solid and authenticated by IR and ^{1}H and ^{13}C NMR spectroscopy, microanalysis, and X-ray crystallography (vide infra). The ^{1}H NMR spectrum of **2** was slightly broadened at room temperature, due to fluxional dynamics possibly arising from hindered rotation of bulky diisopropylphenyl and benzyl groups and/or η^2/η^1 haptotropic rearrangements of the benzyl groups. The ^{1}H and ^{13}C NMR spectra of **2**, recorded at 80 °C in benzene-d_6, exhibited a single set of sharp resonances, consistent with a C_s-symmetric species on the NMR time scale, in which the amidine part is bound in a monodentate manner to the metal center. In contrast with the case for **1**, no signal from hydrogen of the pendant amino group was clearly detected in the ^{1}H NMR spectrum of **2**.[20] However, the presence of the NH group in **2** was evidenced from the observation of a characteristic band at 3315 cm^{-1} in the FTIR spectrum (Nujol, KBr).[4] Compound **2** is stable in the solid state and in toluene solution at room temperature. However, upon heating at 80−100 °C over several days in toluene-d_8, it slowly decomposed to a mixture of unidentified products, concomitantly releasing toluene; this suggests the possible formation of $\{LON^{Ar}\}Zr(CH_2Ph)_2$, but the latter putative species could not be unambiguously identified.

The solid-state molecular structure of **2** (crystallized as the **2**·C_6H_6 solvate) revealed a five-coordinate species, in which the zirconium center lies in a distorted-trigonal-bipyramidal environment (Figure 4). The phenoxy oxygen atom and the carbon atom of one benzyl group occupy the axial positions, while one amidine nitrogen atom and two carbon atoms of two benzyl groups occupy the equatorial plane. One benzyl group features noticeable η^2 binding with the metal center, suggesting a tendency toward 6-coordination. This is evidenced by the short Zr(1)−$C(11)_{ipso}$ distance (2.6976(15) Å) and the relatively acute Zr(1)−C(11)−$C(11)_{ipso}$ angle (89.69(10)°).[17,21] The Zr(1)−O(1) and Zr(1)−N(11) distances (2.0353(10) and 2.3490(12) Å, respectively) in **2** fall in the usual range for the corresponding bond lengths observed in zirconium complexes of salicylaldimine ligands.[14]

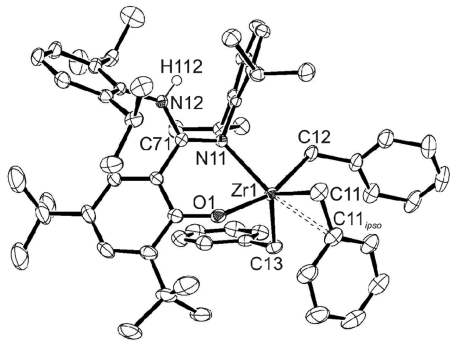
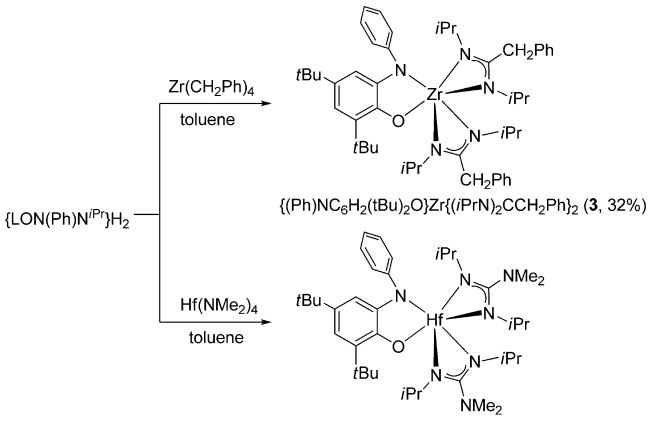


Figure 4. Molecular structure of $\{LO^HN^{Ar}\}Zr(CH_2Ph)_3$ (**2**·C_6H_6) (ellipsoids are drawn at the 50% probability level; H atoms, except those of the N−H, are omitted for clarity). Important bond lengths (Å) and angles (deg): Zr(1)−O(1), 2.0353(10); Zr(1)−N(11), 2.3490(12); Zr(1)−C(11), 2.2654(16); Zr(1)−$C(11)_{ipso}$, 2.6976(15); Zr(1)−C(12), 2.3404(16); Zr(1)−C(13), 2.2693(15); C(71)−N(11), 1.3339(14); C(71)−N(12), 1.3553(18); N(11)−Zr(1)−C(11), 121.65(5); O(1)−Zr(1)−C(13), 95.95(5); Zr(1)−C(11)−$C(11)_{ipso}$, 89.69(10); O(1)−Zr(1)−N(11), 76.74(4).

In striking contrast with the amidine-phenol systems, the guanidine-phenol pro-ligand $\{LON(Ph)N^{iPr}\}H_2$ unexpectedly disclosed a very different reactivity trend. Reactions of equimolar amounts of $\{LON(Ph)N^{iPr}\}H_2$ and the corresponding group 4 metal precursor under regular σ-bond metathesis conditions (see the Experimental Section), followed by crystallization, gave the {anilido-phenoxy}-bis(amidinate) complex **3** and {anilido-phenoxy}-bis(guanidinate) complex **4**, in 32% and 24% isolated yields, respectively (Scheme 5). NMR

Scheme 5. Reactions between the Guanidinate-phenol Pro-ligand $\{LON(Ph)N^R\}H_2$ and $Zr(CH_2Ph)_4$ and $Hf(NMe_2)_4$



monitoring of these two reactions (toluene-d_8, −30 to +25 °C), because of the complexity of the NMR spectra, did not allow us to establish the nature of possible intermediates involved in the cleavage of the ligand backbones.

Compounds **3** and **4** were identified by microanalysis and ^{1}H and ^{13}C NMR spectroscopy and by X-ray crystallography for complex **4**. Both compounds featured a dynamic behavior in benzene-d_6 solution at room temperature, which is tentatively assigned to hindered rotation of the bulky ligand fragments. The well-resolved ^{1}H NMR spectra of **3** and **4**, recorded at 60 °C in benzene-d_6 (Figures S5 and S6, respectively; see the Supporting Information), were diagnostic of highly symmetric

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species, in which the amidinate and guanidinate ligands, respectively, exchange rapidly on the NMR time scale.

The X-ray molecular structure of **4** (Figure 5) revealed a distorted-octahedral coordination around the hafnium center,

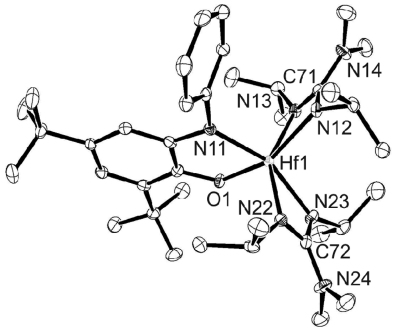


Figure 5. Molecular structure of **4** (ellipsoids are drawn at the 50% probability level; all H atoms are omitted for clarity). Important bond lengths (Å) and angles (deg): Hf(1)−O(1), 2.0063(16); Hf(1)−N(11), 2.136(2); Hf(1)−N(12), 2.111(2); Hf(1)−N(13), 2.194(2); Hf(1)−N(22), 2.2043(18); Hf(1)−N(23), 2.2325(19); C(71)−N(12), 1.378(3); C(71)−N(13), 1.378(3); C(71)−N(14), 1.378(3); C(72)−N(22), 1.335(3); C(72)−N(23), 1.340(3); C(72)−N(24), 1.386(3); O(1)−Hf(1)−N(11), 75.70(7); O(1)−Hf(1)−N(12), 154.59(7); N(12)−Hf(1)−N(22), 100.38(8).

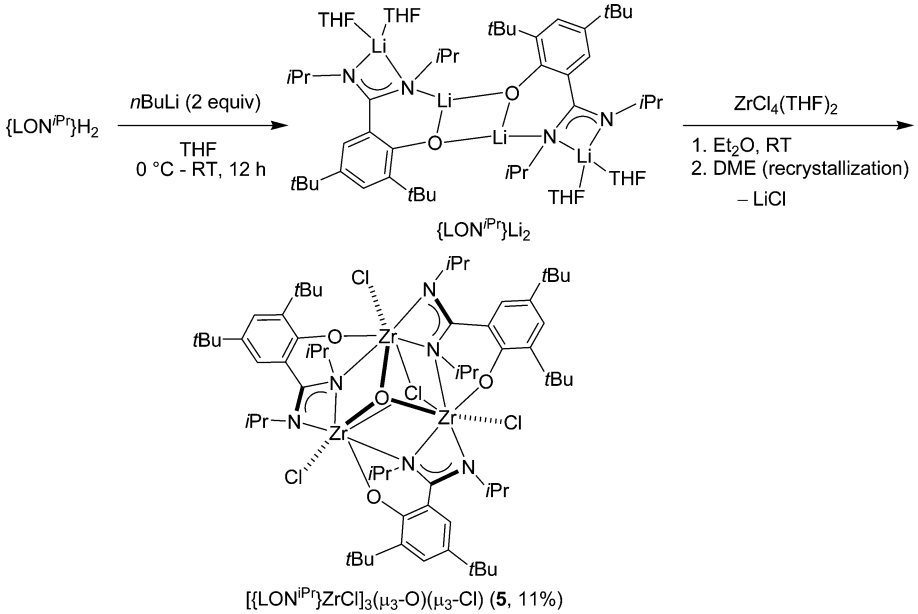
which is surrounded by four nitrogen atoms of the guanidinate ligands and one nitrogen and one oxygen atom of the chelating dianionic anilido-phenoxy ligand. The Hf−O and Hf−N bond lengths in **4** are quite close to those reported for the amido-phenoxy[22] and bis(guanidinate)[23] complexes of hafnium, respectively.

Salt Metathesis Reactions. In our previous study with these new ligand systems,[4] we have shown that double deprotonation of the amidine-phenol pro-ligands $\{LON^{iPr}\}H_2$ and $\{LON^{Ar}\}H_2$ with *n*BuLi afforded the corresponding dilithium salts $\{LON^{iPr}\}Li_2$ and $\{LON^{Ar}\}Li_2$, respectively, in high yields. The latter compounds were successfully utilized for the preparation of the corresponding chloro-yttrium products by salt metathesis.

In an attempt to obtain chloro-zirconium complexes bearing the dianionic ligand $\{LON^{iPr}\}^{2-}$, the corresponding pro-ligand was treated with 2 equiv of *n*BuLi in THF and the resulting salt was allowed to react with $ZrCl_4(THF)_2$ in Et_2O (Scheme 6). Recrystallization of the product from DME yielded small amounts of colorless crystals of $[\{LON^{iPr}\}ZrCl]_3(\mu_3\text{-}O)(\mu_3\text{-}Cl)$ (**5**). The formation of trinuclear oxo complex **5**, yet unexpected, was not completely surprising, though. Similar $Zr_3(\mu_3\text{-}O)$ clusters, supported by cyclopentadienyl, phenoxy, or alkoxy ligands, have been reported as the major products of various reactions conducted under moisture- and oxygen-free conditions: salt metathesis,[24] σ-bond metathesis,[25] and anodic oxidation of zirconium metal in anhydrous alcohols.[26] However, controlled hydrolysis reactions of Cp^*ZrCl_3 with stoichiometric amounts of water are also known to produce quite selectively diverse species incorporating $Zr_3(\mu_3\text{-}O)$ structural motifs.[27]

Complex **5** was characterized by ^1H and ^{13}C NMR and IR spectroscopy, elemental analysis, and X-ray crystallography. The ^1H and ^{13}C NMR spectra were consistent with a highly symmetric species in solution, in which all three ligands are equivalent (see the Supporting Information). The solid-state molecular structure of complex **5** is depicted in Figure 6. The central C_3-symmetric trimetallic core in **5** is reminiscent of that of $[(RO)_2Zr]_3(\mu\text{-}OR)_3(\mu_3\text{-}O)(\mu_3\text{-}Cl)$, where R = neopentyl.[24] However, in complex **5**, the Zr−μ_3-O (2.114(4)−2.125(4) Å) and Zr···Zr (3.404(4)−3.413(4) Å) distances are longer and the Zr−μ_3-Cl (2.7890(16)−2.8045(16) Å) distances are shorter than the corresponding distances in the former compound (2.082(3)−2.090(3), 3.2956(8)−3.3021(7), and 2.847(1)−2.886(1) Å, respectively). The terminal Zr−Cl bond lengths (2.4262(17)−2.4273(17) Å) in **5** are in the typical range for the corresponding bond lengths observed in zirconium complexes with $Zr_3(\mu_3\text{-}O)$ cores.[25c,26,27b] The three ligands are equivalently coordinated to the three zirconium centers, bridging them in a "spanned" manner. At the same time, the coordination of the amidinate fragments to the metal

Scheme 6. Formation of Complex 5 via Salt Metathesis



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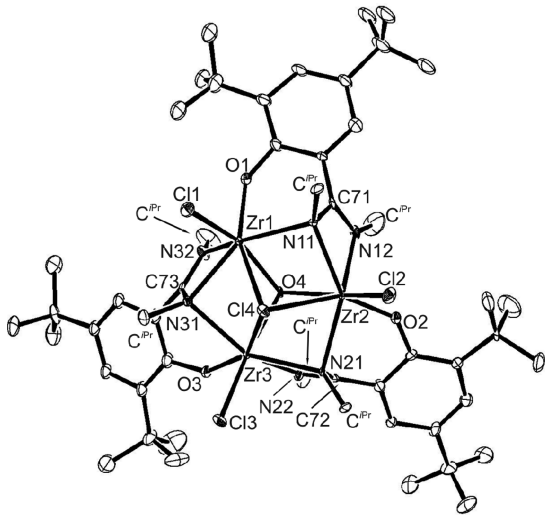


Figure 6. Molecular structure of $[\{LON^{iPr}\}ZrCl]_3(\mu_3\text{-}O)(\mu_3\text{-}Cl)$ (**5**) (ellipsoids are drawn at the 50% probability level; H atoms and *i*Pr groups are omitted for clarity). Important bond lengths (Å) and angles (deg): Zr(1)−O(1), 2.016(4); Zr(2)−O(2), 2.003(4); Zr(3)−O(3), 2.009(4); Zr(1)−O(4), 2.115(4); Zr(2)−O(4), 2.125(4); Zr(3)−O(4), 2.114(4); Zr(1)−N(11), 2.351(5); Zr(1)−N(31), 2.353(5); Zr(1)−N(32), 2.310(5); Zr(2)−N(21), 2.332(5); Zr(2)−N(11), 2.336(5); Zr(2)−N(12), 2.314(5); Zr(3)−N(31), 2.359(5); Zr(3)−N(21), 2.341(5); Zr(3)−N(22), 2.314(5); Zr(1)−Cl(1), 2.4262(17); Zr(2)−Cl(2), 2.4269(16); Zr(3)−Cl(3), 2.4273(17); Zr(1)−Cl(4), 2.8045(16); Zr(2)−Cl(4), 2.7896(16); Zr(3)−Cl(4), 2.7890(16); C(71)−N(11), 1.400(8); C(71)−N(12), 1.285(8); C(72)−N(21), 1.407(8); C(72)−N(22), 1.308(8); C(73)−N(31), 1.400(8); C(73)−N(32), 1.283(8); N(11)−Zr(1)−Cl(32), 139.41(19); O(1)−Zr(1)−Cl(4), 150.94(12); Cl(1)−Zr(1)−O(4), 152.42(11); O(1)−Zr(1)−N(11), 79.75(16).

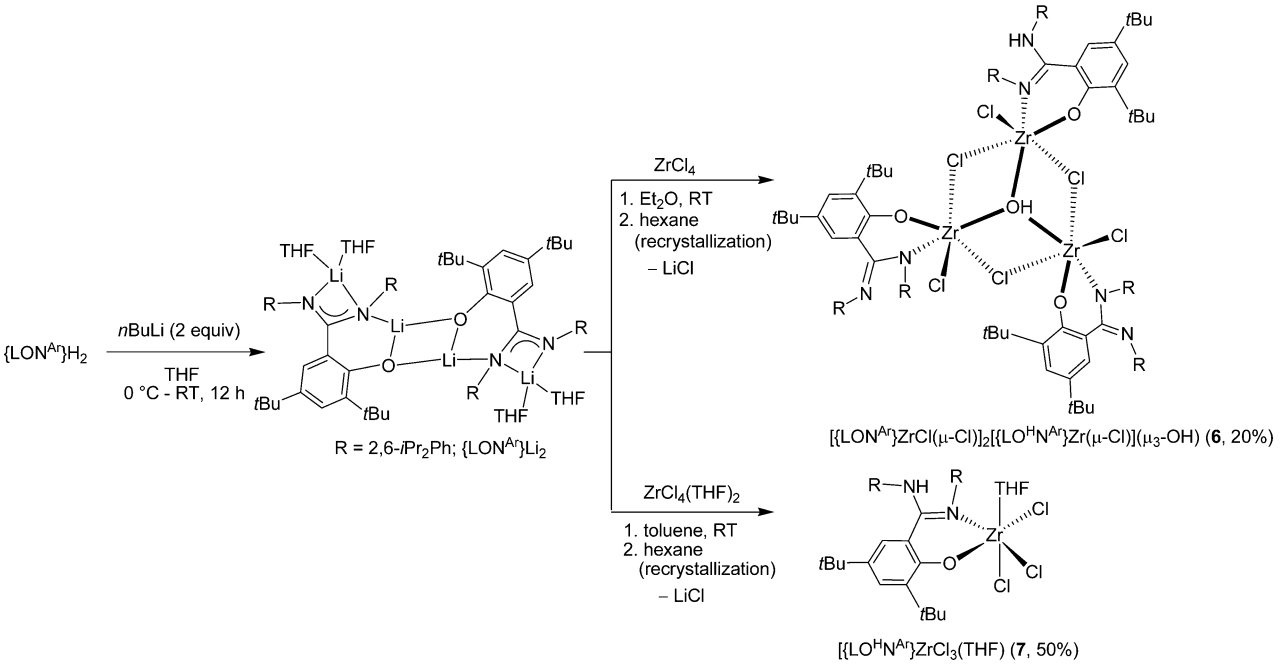
centers is not that typical: each moiety chelates a Zr center nonsymmetrically, as indicated by inequivalent Zr−N(amidinate) bonds (2.353(5), 2.336(5), and 2.341(5) Å vs 2.310(5), 2.314(5), and 2.314(5) Å, respectively); in addition, one of the two nitrogen atoms of each amidinate moiety binds a neighboring Zr center (2.351(5), 2.332(5), and 2.359(5) Å, respectively). These Zr−N distances are on the longer side of values reported in zirconium amidinates (2.123−2.333 Å).[16]

As summarized in Scheme 7, reactions of the in situ generated $\{LON^{Ar}\}Li_2$ salt with $ZrCl_4$, conducted under similar conditions in Et_2O, led, after recrystallization of the crude product from hexane, to the isolation of yellow crystals of $[\{LON^{Ar}\}ZrCl(\mu_2\text{-}Cl)]_2[\{L^{H}ON^{Ar}\}ZrCl(\mu_2\text{-}Cl)](\mu_3\text{-}OH)$ (**6**). Complex **6** was authenticated on the basis of ^1H and ^{13}C NMR and IR spectroscopy, elemental analysis, and an X-ray diffraction study.

In contrast to **5**, the FTIR spectrum of **6** (Nujol mulls in KBr plates) displayed two distinct bands at 3323 and 3308 cm^{-1} assigned to ν(O−H) and ν(N−H) vibrations. This suggests that, in complex **6**, at least one of three ligands is monoanionic and bears a pendant N(H)Ar moiety, but also an O−H group is present in the structure (vide infra). Surprisinglt, however, both the ^1H and ^{13}C NMR spectra of **6** in CD_2Cl_2 at room temperature were diagnostic of a highly symmetric species in solution, in which all three ligands are equivalent on the NMR time scale (see Figures S8 and S9, respectively, in the Supporting Information). No signals from the N−H or O−H protons could be detected in the ^1H NMR spectrum of **6**, possibly due to exchange on the NMR time scale between ligand moieties and extreme broadening.

As revealed by the X-ray diffraction study, complex **6** is a cluster that contains a triangular core of three Zr atoms nearly symmetrically capped by a μ_3-O(H) group (Figure 7). The Zr−μ_3-O(H) bond lengths in **6** (2.115(6)−2.130(6) Å) are very similar to those in **5** with the oxo Zr−μ_3-O core (2.114(4)−2.125(4) Å). Comparison of the given distances in **6** with the appropriate ones in $[Cp^*ZrCl]_3(\mu\text{-}O)_3(\mu_3\text{-}OH)(\mu_2\text{-}OH)_3$, which has two types of the in-core groups (Zr−μ_3-O, 2.092(4)−2.196(4) Å; Zr−μ_3-OH, 2.198(4)−2.336(4) Å),[27b] did not allow us to unambiguously identify the exact nature of

Scheme 7. Formation of Complexes 6 and 7 via Salt Metathesis



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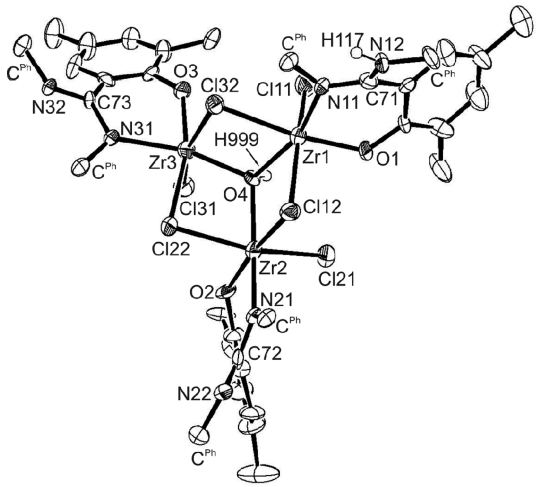

Figure 7. Molecular structure of $[\{LON^{Ar}\}ZrCl(\mu_2\text{-}Cl)]_2[\{L^{H}ON^{Ar}\}ZrCl(\mu_2\text{-}Cl)](\mu_3\text{-}OH)$ (**6**) (ellipsoids are drawn at the 50% probability level; H atoms, except those of the N−H and O−H groups, iPr$_2$C$_6$H$_2$, and tBu groups are omitted for clarity). Important bond lengths (Å) and angles (deg): Zr(1)−O(1), 1.974(6); Zr(2)−O(2), 1.980(6); Zr(3)−O(3), 1.977(6); Zr(1)−O(4), 2.119(5); Zr(2)−O(4), 2.130(6); Zr(3)−O(4), 2.115(6); Zr(1)−N(11), 2.291(7); Zr(2)−N(21), 2.245(7); Zr(3)−N(21), 2.241(7); Zr(1)−Cl(11), 2.394(3); Zr(1)−Cl(12), 2.577(2); Zr(2)−Cl(21), 2.389(3); Zr(2)−Cl(22), 2.586(2); Zr(3)−Cl(31), 2.389(3); Zr(3)−Cl(32), 2.584(2); C(71)−N(11), 1.316(10); C(71)−N(12), 1.362(11); C(72)−N(21), 1.400(11); C(72)−N(22), 1.339(12); C(73)−N(31), 1.384(14); C(73)−N(32), 1.339(11); Cl(11)−Zr(1)−Cl(12), 164.60(18); O(1)−Zr(1)−Cl(32), 163.42(9); O(1)−Zr(1)−N(12), 81.50(20); Cl(12)−Zr(1)−O(4), 76.60(16).

the central group. Also, the three Zr atoms in **6** are symmetrically bridged by three μ_2-Cl groups, with Zr−Cl bond distances (2.577(2)−2.586(2) Å) expectedly longer than the terminal ones (2.389(3)−2.394(3) Å). However, some structural data suggest that the three ligands in **6** are not of the same nature. Despite the fact that the Zr−O bonds of the three phenoxide groups are nearly equivalent (1.974(6), 1.980(6), and 1.977(6) Å), the Zr−N bonds in the amidinate moieties do substantially differ: the Zr(1)−N(11) bond (2.291(7) Å) is somewhat longer as compared with Zr(2)−N(21) and Zr(3)−N(21) (2.245(7) and 2.241(7) Å, respectively) and is, as observed in **1**, approaching the usual range of the Zr−N(imino) bond lengths (2.322−2.434 Å) in zirconium salicylaldimine complexes.[14] Also, the C(71)−N(11) bond (1.316(10) Å) in **6** is shorter than that in two other ligands (C(72)−N(21), 1.400(11) Å; C(73)−N(31), 1.384(14) Å), which is in agreement with its double-bond character. These geometric data indicate that the ligand bound to the Zr(1) center is monoanionic, while those coordinated to Zr(2) and Zr(3) are dianionic. Consistent with this trend, the overall neutrality of the molecule is ensured by the anionic OH group in the central trigonal core.

In a separate experiment targeted on the synthesis of a chloro zirconium complex supported by the $\{LON^{Ar}\}^{2-}$ ligand, the dilithium salt $\{LON^{Ar}\}Li_2$ was treated with $ZrCl_4(THF)_2$ (Scheme 7). The product isolated in 50% yield as white crystals after recrystallization from hexanes was authenticated as $\{LO^{H}N^{Ar}\}ZrCl_3(THF)$ (**7**), on the basis of ^{1}H and ^{13}C NMR and IR spectroscopy, elemental analysis, and an X-ray diffraction study. The ^{1}H and ^{13}C NMR spectra of **7** in benzene-d_6 at 60 °C showed a single set of resonances, consistent with an average C_s-symmetric structure of this species on the NMR time scale. Similarly to complex **2**, no clear signal from the proton of the pendant N(H)Ar group was observed in the ^{1}H NMR spectra of **7**. The actual presence of the amino group in the structure of **7** was evidenced from the observation of a characteristic band at 3313 cm^{-1} in the FTIR spectrum (Nujol, KBr).[4]

Complex **7** is structurally similar to zirconium salicylaldiminate complexes $\{LON\}ZrCl_3(THF)$,[28] with the Zr center lying in a distorted-octahedral coordination environment (Figure 8).

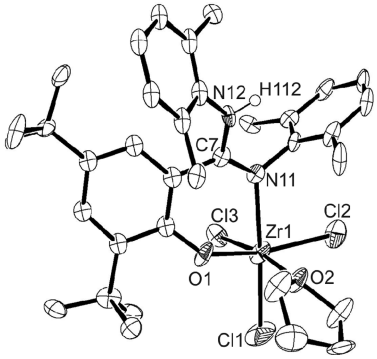

Figure 8. Molecular structure of $\{LO^{H}N^{Ar}\}ZrCl_3(THF)$ (**7**) (ellipsoids are drawn at the 50% probability level; H atoms, except that of the N−H group, and iPr groups are omitted for clarity). Important bond lengths (Å) and angles (deg): Zr(1)−O(1), 1.963(6); Zr(1)−O(2), 2.288(6); Zr(1)−N(11), 2.364(7); Zr(1)−Cl(1), 2.452(3); Zr(1)−Cl(2), 2.434(2); Zr(1)−Cl(3), 2.411(3); C(71)−N(11), 1.332(10); C(71)−N(12), 1.336(10); N(11)−Zr(1)−Cl(1), 175.38(18); O(1)−Zr(1)−Cl(2), 161.0(2); O(1)−Zr(1)−N(11), 78.8(3).

The zirconium−ligand distances in **7** (Zr−O, 1.963(6) Å; Zr−N, 2.364(7) Å; Zr−Cl, 2.452(3), 2.434(2), and 2.411(3) Å) are comparable with those in the latter compounds (1.951−1.956, 2.371−2.393, and 2.397−2.442 Å, respectively).[28]

The remarkable propensity of the phenoxy-*amidinate* ligands implemented in this study to systematically afford species with phenoxy-*imine* coordinating moieties and pendant N(H)R arms prompted us to target the synthesis of new species. Given the great success in olefin polymerization catalysis of group 4 metal systems incorporating two chelating phenoxy-imino ligands (often referred to as Fujita's FI catalysts),[29] we set out to purposely prepare zirconium complexes with two monoanionic phenoxy-amidine ligands $\{L^{H}ON^{R}\}$.

As summarized in Scheme 8, the target complexes were conveniently obtained by salt metathesis reactions using the corresponding monolithium salts $\{L^{H}ON^{R}\}Li$ and $ZrCl_4$ in a 2:1 stoichiometry. Regular workup and recrystallization of the products from benzene or hexanes allowed the recovery of $\{LO^{H}N^{iPr}\}_2ZrCl_2$ (**8**, isolated as **8**·3.5C$_6$H$_6$) and $\{LO^{H}N^{Ar}\}_2ZrCl_2$ (**9**), respectively.

The solid-state structures of **8** and **9** (Figures 9 and 10, respectively) both revealed zirconium atoms in distorted-octahedral coordination environments with global C_2-symmetric environments around the metal centers. The relative arrangement of ligands in the recovered crystals of **8** is trans-O,O/cis-N,N, whereas it is cis-O,O/trans-N,N in **9**. These molecules exhibit geometrical parameters essentially similar to those of dichlorozirconium salicylaldiminate complexes.[14] For example, the Zr−O bond lengths in **8** and **9** (2.012(4), 2.007(4) Å and 2.0186(17), 2.0115(18) Å, respectively) are in

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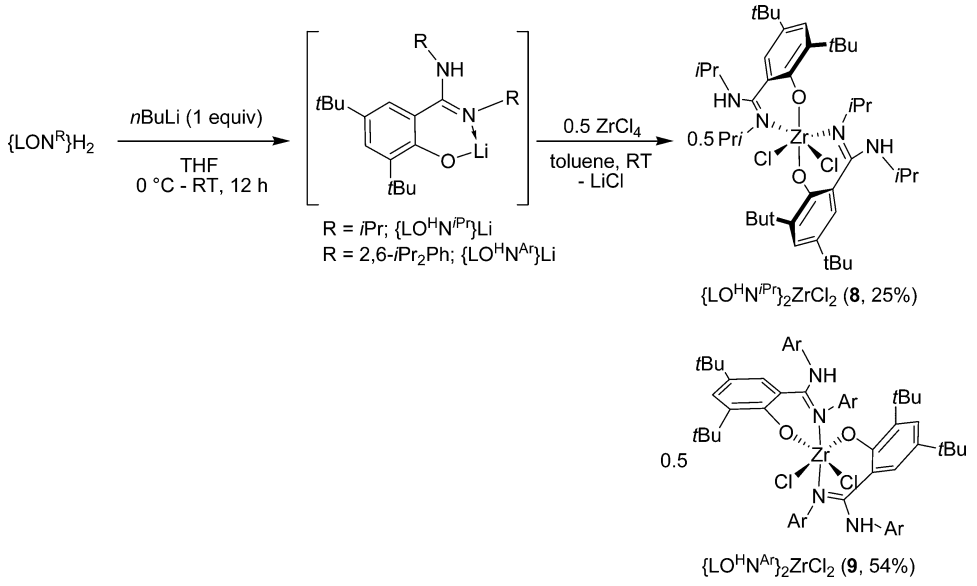
Scheme 8. Synthesis of Complexes 8 and 9



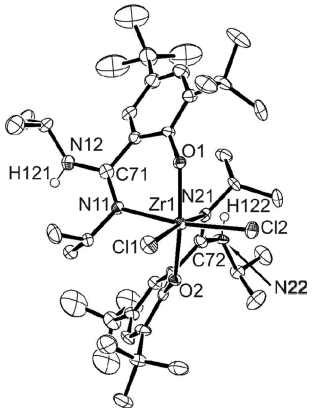


Figure 9. Molecular structure of $\{LO^HN^{iPr}\}_2ZrCl_2$ (**8**) (ellipsoids are drawn at the 50% probability level; H atoms, except those of the N−H groups, are omitted for clarity). Important bond lengths (Å) and angles (deg): Zr(1)−O(1), 2.012(4); Zr(2)−O(2), 2.007(4); Zr(1)−N(11), 2.304(5); Zr(1)−N(21), 2.319(5); Zr(1)−Cl(1), 2.4464(16); Zr(1)−Cl(2), 2.4541(16); C(71)−N(11), 1.322(8); C(71)−N(12), 1.359(8); C(72)−N(21), 1.342(7); C(72)−N(22), 1.354(8); Cl(11)−Zr(1)−Cl(12), 94.42(6); O(1)−Zr(1)−O(2), 166.17(16); N(11)−Zr(1)−N(21), 88.49(16).

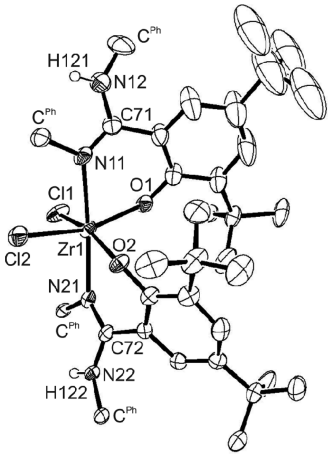


Figure 10. Molecular structure of $\{LO^HN^{Ar}\}_2ZrCl_2$ (**9**) (ellipsoids are drawn at the 50% probability level; H atoms, except those of the N−H groups, and $iPr_2C_6H_2$ moieties are omitted for clarity). Important bond lengths (Å) and angles (deg): Zr(1)−O(1), 2.0186(17); Zr(2)−O(2), 2.0115(18); Zr(1)−N(11), 2.355(2); Zr(1)−N(21), 2.370(2); Zr(1)−Cl(1), 2.4360(7); Zr(1)−Cl(2), 2.4550(7); C(71)−N(11), 1.333(3); C(71)−N(12), 1.348(3); C(72)−N(21), 1.320(7); C(72)−N(22), 1.347(4); Cl(11)−Zr(1)−Cl(12), 97.65(3); O(1)−Zr(1)−O(2), 90.92(7); N(11)−Zr(1)−N(21), 175.45(7).

the range of the values of covalent bonds previously reported for zirconium analogues (1.951−2.064 Å). Similarly, the Zr−N bond distances in **8** and **9** (2.304(5), 2.319(5) Å and 2.355(2), 2.370(2) Å, respectively) show little variation and are comparable with those found in bis(salicylaldiminato)-zirconium complexes (2.322−2.434 Å).[14]

The ^1H and ^{13}C NMR spectra of **8** in toluene-d_8 at room temperature contain two sets of resonances in a ca. 45:55 ratio that indicate the coexistence of two species in solution, each of average C_2 symmetry on the NMR time scale (see Figure S11 in the Supporting Information). Key resonances for the first species include two doublets from phenoxy hydrogens, two multiplets from methine hydrogens, four doublets from methyls of the nonequivalent *i*Pr groups, two singlets from *t*Bu groups, and a doublet from N−H groups. The second species is presented by a similar series of broadened signals, which do not become sharper in the range of 213−298 K. The ^{13}C NMR data, recorded at 253 K in toluene-d_8, confirmed these features. When the temperature is raised above 343 K in toluene-d_8, these two series of ^1H NMR signals collapse into one series of broadened resonances, consistent with a single averaged symmetric species. It is thus reasonable to assume that the two species, observed in solution at room temperature, correspond to O,O/N,N positional isomers of **8**, one of which crystallized preferentially (vide supra).

At the same time, all ^1H and ^{13}C NMR data for complex **9** in toluene-d_8 showed the presence of a single highly symmetric species on the NMR time scale (see Figures S13 and S14 in the Supporting Information), suggesting that the solid-state structure observed for **9** is retained in solution.

As noted above for complexes **1**, **2**, **6**, and **7**, the presence of N−H groups in **8** and **9** was corroborated by the observation of

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Table 1. Results of Ethylene Polymerizations Mediated by Complexes 2 and 5−9[a]

entry	precat.	amt of precat. (μmol)	activator (amt (equiv))	T_{polym} (°C)	P (bar)	m_{polym} (g)	productivity[b] (kg mol^{-1} h^{-1})	T_m (°C)[c]	$10^3 M_w$[d]	M_w/M_n[d]
1	**2**	10	$[Ph_3C][B(C_6F_5)_4]$ (2)/Al(iBu)$_3$ (50)	50	5	traces	0			
2	**5**	7	MAO (1000)	50	1	0.831	40	136.7	insoluble[e]	
3	**6**	7	MAO (1000)	50	1	0.086	4	130.2	115	26.9[f]
4	**7**	7	MAO (1000)	50	5	traces	0			
5	**8**	10	MAO (1000)	60	5	1.710	172	129.9	470	305[f]
6	**9**	10	MAO (1000)	60	5	0.120	12	136.9	580	3.46[f]

[a]Polymerization conditions: 300 mL high pressure glass reactor; solvent toluene, 150 mL; time 30 min. [b]Apparent productivity calculated over the whole polymerization time. [c]Determined by DSC (first heating). [d]In g mol^{-1}, determined by GPC in 1,2,4-trichlorobenzene at 150 °C. [e]PE could not be solubilized in 1,2,4-trichlorobenzene at 160 °C. [f]Multimodal distribution.

characteristic bands at 3448 and 3315 cm^{-1}, respectively, in their FTIR spectra (Nujol, KBr).[4]

Preliminary Olefin Polymerization Tests. The catalytic potential of complexes **2** and **5**−**9**, in combination with MAO or $[Ph_3C][B(C_6F_5)_4]$/Al(iBu)$_3$ (2:50) as the activating system[10c,30] (applied for benzyl complex **2**), was briefly evaluated in the homogeneous polymerization of ethylene (toluene solution, 1−5 bar constant pressure, 50−60 °C).[31] The results are summarized in Table 1.

Trialkyl and trichloro complexes **2** and **7**, respectively, both bearing one and the same type of coordinated ligand, were found to be inactive in the polymerization of ethylene under the conditions used (entries 1 and 4). These results are consistent with those previously obtained with the related {LON}$ZrCl_3$(THF)/MAO system, where LON is a bulky diisopropylphenylimino-phenoxide ligand, which also proved ineffective.[28] Complexes **5** and **6**, incorporating $Zr_3(\mu_3$-O) cores, upon activation with MAO were poorly active toward ethylene (entries 2 and 3, respectively). In the series of bis(phenoxy-amidine) zirconium dichlorides, the most effective ethylene polymerization precatalyst appeared to be the complex bearing the less bulky ligand **8** (entry 5). However, the productivity of the latter compound (172 kg mol^{-1} h^{-1}), activated with MAO, was inferior by 2−3 orders of magnitude than those reported for bis(salicylaldiminato) catalysts of group 4 metals.[14] Hypothetically, this may be accounted for by the additional NH functionality in the current systems, which may react with excess MAO and induce uncontrolled decomposition pathways.

Another general feature of these polymerizations concerns the nature of the polymers obtained. The GPC data obtained for the PE samples showed multimodal traces, resulting in very large abnormal polydispersity values. This can be directly related to the existence of multiple catalytically active species during the course of polymerization reactions. Again, the acidic pending amino groups present in precatalysts **2** and **7**−**9** can potentially be involved in further protolytic reactions with Me−Al bonds of MAO itself or Me_3Al (typical component of commercial MAO), giving rise to various polymetallic/aggregated species exhibiting different reactivities. The melting temperatures of the polyethylene polymers in the range 129−137 °C are indicative of essentially linear long-chain microstructures.[10b,32]

CONCLUSIONS

The preparation of discrete group 4 metal complexes based on multidentate phenoxy-amidinate $\{LON^R\}^{2-}$ and phenoxy-amidine $\{L^HON^R\}^-$ ligand platforms has been studied. Also, the new guanidine-phenolate pro-ligand $\{LON(Ph)N^{iPr}\}H_2$ has been synthesized and used for complexation with group 4 metals. The preparation of dibenzyl Zr(IV) complexes based on the aforementioned ligands proved to be arduous and resulted instead in the formation of structurally diverse compounds. Salt metathesis reactions between $ZrCl_4(THF)_n$ (n = 0, 2) and $\{LON^R\}Li_2$ salts unexpectedly afforded $Zr_3(\mu_3$-O) oxo clusters with different distributions of monoanionic and dianionic ligands. On the other hand, treatment of $ZrCl_4$ with monolithium salts $\{L^HON^R\}$Li provided a facile synthesis of octahedral bis(phenoxy-amidine) complexes $\{L^HON^R\}ZrCl_2$ bearing pendant amino groups. The latter may be used as suitable precursors for synthesis of multinuclear heterometallic compounds. Further investigations on the reactivity of these species and this promising coordination chemistry are underway in our laboratories.

EXPERIMENTAL SECTION

General Conditions. All manipulations requiring an anhydrous atmosphere were performed under a purified argon atmosphere using standard Schlenk techniques or in a glovebox. Anhydrous $ZrCl_4$ and $ZrCl_4(THF)_2$ precursors (99.99%) were purchased from Strem Chemicals and used as received. 2-Anilino-4,6-di-*tert*-butylphenol[33] and the metal precursors $Zr(CH_2Ph)_4$ and $Hf(NMe_2)_4$[34] were prepared by the corresponding literature procedures. $[Ph_3C][B(C_6F_5)_4]$ (Boulder), Al(iBu)$_3$ (Aldrich), and MAO (30 wt % solution in toluene, Albermale; contains ca. 10 wt % of free $AlMe_3$) were used as received. Other starting materials were purchased from Acros, Strem, and Aldrich and used as received. Solvents were freshly distilled from Na/benzophenone (THF, toluene, Et_2O, DME) or Na/K amalgam (pentane, hexanes) under argon and degassed thoroughly by freeze−pump−thaw cycles prior to use. Deuterated solvents were freshly distilled from Na/K amalgam (THF-d_8, benzene-d_6, toluene-d_8) or CaH_2 (CD_2Cl_2) under argon and degassed prior to use.

Instruments and Measurements. NMR spectra were recorded on Bruker AC 200, Bruker AC 300, Bruker Avance DRX 400, and Bruker AC 500 spectrometers in Teflon-valved NMR tubes. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm vs $SiMe_4$ and were determined by reference to the residual solvent resonances. Assignment of signals was carried out via multinuclear 1D (^{1}H, ^{13}C{^{1}H}) and 2D (^{1}H−^{13}C HMBC and HMQC) NMR experiments. Coupling constants are reported in Hz.

Elemental analyses (C, H, N) were performed using a Flash EA1112 CHNS Thermo Electron apparatus and are the average of two independent determinations. IR spectra were recorded as Nujol mulls on a Bruker-Vertex 70 spectrophotometer.

{(iPrN)$_2$CN(Ph)C$_6$H$_2$(tBu)$_2$O}H$_2$ ({LON(Ph)N^{iPr}}H$_2$). To a solution of 2-anilino-4,6-di-*tert*-butylphenol (2.01 g, 6.76 mmol) in diethyl ether (30 mL) was added *n*-butyllithium (5.70 mL of a 2.50 M solution in hexane, 14.25 mmol) at 0 °C. The reaction mixture was stirred for 0.5 h at room temperature, and a solution of *N*,*N*′-diisopropylcarbodiimide (1.16 mL, 7.45 mmol) in diethyl ether (10

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mL) was added dropwise. The reaction mixture was stirred under reflux overnight and then cooled to room temperature. The white precipitate that formed was separated by filtration under argon. Water (50 mL) and Et_2O (50 mL) were added stepwise. The organic layer was separated and dried over $NaSO_4$, and volatiles were removed in vacuo. The residue was dried in vacuo to give $\{LON(Ph)N^{iPr}\}H_2$ as a pale pink solid (2.13 g, 5.03 mmol, 74%). ^1H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 7.28 (d, J = 2.5, 1H, C_6H_2), 7.18 (m, 2H, Ph), 7.07 (d, J = 2.5, 1H, C_6H_2), 6.84 (m, 1H, Ph), 6.73 (br m, 2H, Ph), 3.66 (br m, 2H, $CH(CH_3)$), 1.44 (s, 9H, $C(CH_3)$), 1.34 (s, 9H, $C(CH_3)$), 1.18 (d, J = 6.5, 12H, $CH(CH_3)$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 25 °C): δ 152.4 (CN_3), 146.4 (O-C_6H_2), 140.5, 130.1, 129.4, 128.9, 126.7, 125.8, 119.6, 115.2, 114.4, 45.3 ($CH(CH_3)_2$), 35.3 ($C_6H_2C(CH_3)_3$), 34.24 ($C_6H_2C(CH_3)_3$), 31.7 ($C_6H_2C(CH_3)_3$), 29.8 ($C_6H_2C(CH_3)_3$), 23.8 ($CH(CH_3)_2$). Anal. Calcd for $C_{27}H_{41}N_3O$: C, 76.55; H, 9.76; N, 9.92. Found: C, 77.04; H, 10.15; N, 10.01.

Reaction between $\{LON^{iPr}\}H_2$ and $Zr(CH_2Ph)_4$ (2:1 Ratio). Synthesis of $\{(iPrN)_2(H)CC_6H_2(tBu)_2O\}\{(iPrN)_2CC_6H_2(tBu)_2O\}Zr(CH_2Ph)$ ($\{LO^HN^{iPr}\}\{LON^{iPr}\}Zr(CH_2Ph)$, 1). *Protocol A.* In the glovebox, a Teflon-valved NMR tube was charged with $\{LON^{iPr}\}H_2$ (0.0358 g, 0.1077 mmol) and $Zr(CH_2Ph)_4$ (0.0245 g, 0.0538 mmol). To this mixture, C_6D_6 (ca. 0.6 mL) was vacuum-transferred in and the tube was shaken for 2 h at room temperature. ^1H NMR indicated that **1** formed quantitatively.

Protocol B. A Schlenk flask was charged with $\{LON^{iPr}\}H_2$ (0.319 g, 0.0959 mmol) and $Zr(CH_2Ph)_4$ (0.219 g, 0.0481 mmol), and toluene (ca. 5 mL) was vacuum-transferred in. The reaction mixture was stirred overnight at room temperature, filtered, evaporated, and dried in vacuo to give **1** as a pale yellow microcrystalline material (0.385 g, 0.0457 mmol, 95%). ^1H NMR (C_6D_6, 500 MHz, 25 °C): δ 7.67 (d, J = 2.0, 1H, C_6H_2), 7.63 (d, J = 2.0, 1H, C_6H_2), 7.56 (d, J = 2.0, 1H, C_6H_2), 7.45 (d, J = 2.0, 1H, C_6H_2), 7.11 (d, J = 7.3, 2H, CH_2Ph), 7.01 (t, J = 7.3, 2H, CH_2Ph), 6.76 (t, J = 7.3, 1H, CH_2Ph), 5.41 (sept, J = 7.2, 1H, $CH(CH_3)$), 4.49 (d, J = 9.8, 1H, NH), 4.08 (sept, J = 6.2, 1H, $CH(CH_3)$), 3.86 (m, 1H, $CH(CH_3)$), 3.32 (sept, J = 6.2, 1H, $CH(CH_3)$), 3.03 (d, J = 10.7, 1H, CHHPh), 2.80 (d, J = 10.7, 1H, CHHPh), 1.84 (s, 9H, $C(CH_3)$), 1.63 (s, 9H, $C(CH_3)$), 1.61 (d, J = 7.2, 3H, $CH(CH_3)$), 1.55 (s, 9H, $C(CH_3)$), 1.52 (s, 9H, $C(CH_3)$), 1.49 (m, 6H, $CH(CH_3)$), 1.35 (d, J = 7.2, 3H, $CH(CH_3)$), 1.30 (m, 6H, $CH(CH_3)$), 1.09 (d, J = 6.4, 3H, $CH(CH_3)$), 0.69 (d, J = 6.4, 3H, $CH(CH_3)$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz, 25 °C): δ 171.4 (CN_2), 167.6 (CN_2), 159.0 (O-C_6H_2), 158.2 (O-C_6H_2), 146.3 (*ipso*-CH_2Ph), 139.3 (three signals of the C_6H_2tBu moieties from both ligands), 136.9 (C_6H_2-*t*Bu), 128.1 (C_6H_2 and CH_2Ph), 127.3 (C_6H_2 and CH_2Ph), 124.5 (C_6H_2), 122.3 (C_6H_2), 120.8 (C_6H_2 and CH_2Ph), 119.8 (C_6H_2), 58.6 (CH_2Ph), 51.3 ($CH(CH_3)_2$), 50.1 ($CH(CH_3)_2$), 49.1 ($CH(CH_3)_2$), 47.7 ($CH(CH_3)_2$), 35.5 ($C_6H_2C(CH_3)_3$), 35.4 ($C_6H_2C(CH_3)_3$), 34.3 ($C_6H_2C(CH_3)_3$), 34.2 ($C_6H_2C(CH_3)_3$), 31.8 (two signals overlapped from $C_6H_2C(CH_3)_3$ groups), 30.3 ($C_6H_2C(CH_3)_3$), 30.2 ($C_6H_2C(CH_3)_3$), 27.7 ($CH(CH_3)_2$), 26.5 ($CH(CH_3)_2$), 25.0 ($CH(CH_3)_2$), 24.2 ($CH(CH_3)_2$), 24.1 ($CH(CH_3)_2$), 23.2 ($CH(CH_3)_2$), 21.5 ($CH(CH_3)_2$), 19.3 ($CH(CH_3)_2$). IR (Nujol, KBr; ν (cm^{-1})): 3444 w, 2361 m, 1604 m, 1576 s, 1302 m, 1290 m, 1256 m, 1240 s, 1201 m, 1170 m, 1113 m, 941 w, 835 m, 795 w, 729 s, 694 w, 598 w, 548 m. Anal. Calcd for $C_{49}H_{76}N_4O_2Zr$: C, 69.70; H, 9.07; N, 6.64. Found: C, 70.12; H, 9.33; N, 6.81.

Reaction between $\{LON^{Ar}\}H_2$ and $Zr(CH_2Ph)_4$ (1:1 Ratio). Synthesis of $\{(iPr_2C_6H_3N)_2(H)CC_6H_2(tBu)_2O\}Zr(CH_2Ph)_3$ ($\{LO^HN^{Ar}\}Zr(CH_2Ph)_3$, 2). *Protocol A.* Following a protocol similar to that described above for **1** (protocol A), complex **2** formed quantitatively from $\{LON^{Ar}\}H_2$ (0.0364 g, 0.0639 mmol) and $Zr(CH_2Ph)_4$ (0.0292 g, 0.0639 mmol).

Protocol B. A protocol similar to that described above for **1** (protocol B) was used, starting from $\{LON^{Ar}\}H_2$ (0.191 g, 0.3357 mmol) and $Zr(CH_2Ph)_4$ (0.153 g, 0.3357 mmol). Workup afforded **2** as a pale yellow microcrystalline material (0.291 g, 0.3124 mmol, 93%). ^1H NMR (C_6D_6, 300 MHz, 80 °C): δ 7.60 (br m, 1H, C_6H_2), 7.40–7.16 (m, 11H, arom), 7.15–6.80 (m, 11H, arom), 6.76 (br m, 1H, C_6H_2), 2.96 (sept, J = 10.9, 4H, $CH(CH_3)$), 2.48 (br s, 6H, CH_2Ph), 1.64 (s, 9H, $C(CH_3)$), 1.32 (d, J = 10.9, 6H, $CH(CH_3)$), 1.16 (d, J = 10.9, 6H, $CH(CH_3)$), 1.07 (s, 9H, $C(CH_3)$), 0.86 (m, 12H, $CHC(CH_3)$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz, 80 °C): δ 169.5 (CN_2), 159.9 (O-C_6H_2), 143.5, 138.9, 138.7, 133.5, 128.5, 128.3, 125.8, 125.6, 124.5, 124.4, 122.0, 121.9, 118.7, 74.7 (CH_2Ph), 36.4 ($C_6H_2C(CH_3)_3$), 33.8 ($C_6H_2C(CH_3)_3$), 30.9 ($C_6H_2C(CH_3)_3$), 30.8 ($C_6H_2C(CH_3)_3$), 26.2 ($CH(CH_3)_2$), 24.8 ($CH(CH_3)_2$), 24.3 ($CH(CH_3)_2$), 22.05 ($CH(CH_3)_2$). IR (Nujol, KBr; ν (cm^{-1})): 3315 w, 2361 m, 1604 w, 1591 m, 1541s, 1262 m, 1202 m, 980 w, 885 w, 839 w, 791 m, 745 m, 727 m, 698 m, 550 m. Anal. Calcd for $C_{60}H_{75}N_2OZr$: C, 77.37; H, 8.12; N, 3.01. Found: C, 77.56; H, 8.44; N, 3.13.

Reaction between $\{LON(Ph)N^{iPr}\}H_2$ and $Zr(CH_2Ph)_4$ (1:1 Ratio). Synthesis of $\{(Ph)NC_6H_2(tBu)_2O\}Zr\{(iPrN)_2CCH_2Ph\}_2$ (3). A Schlenk flask was charged with $\{LON(Ph)N^{iPr}\}H_2$ (0.204 g, 0.4816 mmol) and $Zr(CH_2Ph)_4$ (0.219 g, 0.4816 mmol), and toluene (ca. 5 mL) was vacuum-transferred in. The reaction mixture was stirred overnight at room temperature. Then, volatiles were evaporated in vacuo and hexanes (ca. 10 mL) was vacuum-transferred under reduced pressure. The mixture was filtered, and the solvent was removed from the filtrate to give **3** as a deep yellow solid (0.126 g, 0.1541 mmol, 32%). ^1H NMR (C_6D_6, 500 MHz, 60 °C): δ 7.56 (d, J = 7.3, 2H, Ph), 7.45 (t, J = 7.3, 2H, Ph), 7.25–7.15 (m, 11H, Ph and CH_2Ph), 7.05 (d, J = 2.2, 1H, C_6H_2), 6.70 (d, J = 2.2, 1H, C_6H_2), 3.70 (s, 4H, CH_2Ph), 3.69 (m, 4H, $CH(CH_3)$), 1.87 (s, 9H, $C(CH_3)$), 1.41 (s, 9H, $C(CH_3)$), 1.28 (d, J = 6.2, 12H, $CH(CH_3)$), 1.20 (d, J = 6.2, 12H, $CH(CH_3)$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz, 60 °C): δ 175.8 (CN_2), 151.3 (O-C_6H_2), 151.2 (NC_6H_2), 150.0 (*ipso*, N-*Ph*), 141.2, 137.6, 135.6, 132.4, 129.0, 128.8, 126.6, 126.5, 123.1, 112.8, 107.7, 48.5 (CH_2Ph), 34.6 ($C_6H_2C(CH_3)_3$), 34.5 ($C_6H_2C(CH_3)_3$), 31.9 ($C_6H_2C(CH_3)_3$), 31.8 ($CH(CH_3)_2$), 30.2 ($C_6H_2C(CH_3)_3$), 25.5 ($CH(CH_3)_2$), 25.1 ($CH(CH_3)_2$). Anal. Calcd for $C_{48}H_{67}N_5OZr$: C, 70.20; H, 8.22; N, 8.53. Found: C, 71.00; H, 8.34; N, 8.93.

Reaction between $\{LON(Ph)N^{iPr}\}H_2$ and $Hf(NMe_2)_4$ (1:1 Ratio). Synthesis of $\{(Ph)NC_6H_2(tBu)_2O\}Hf\{(iPrN)_2CNMe_2\}_2$ (4). A Schlenk flask was charged with $\{LON(Ph)N^{iPr}\}H_2$ (0.430 g, 1.2120 mmol) and $Hf(NMe_2)_4$ (0.513 g, 1.2120 mmol), and toluene (10 mL) was vacuum-transferred in. The reaction mixture was stirred overnight at room temperature. Then the volatiles were evaporated in vacuo and hexanes (ca. 15 mL) was vacuum-transferred under reduced pressure. The mixture was filtered, and the solution was removed from the filtrate. The resulting solid was recrystallized from hexanes (ca. 3 mL) at room temperature to give **4** as off-white crystals (0.236 g, 0.2909 mmol, 24%). ^1H NMR (C_6D_6, 500 MHz, 60 °C): δ 7.56 (d, J = 7.6, 2H, Ph), 7.33 (t, J = 7.6, 2H, Ph), 7.01 (t, J = 7.6, 1H, Ph), 6.93 (br d, J = 1.8, 1H, C_6H_2), 6.44 (br d, J = 1.8, 1H, C_6H_2), 3.75 (br m, 2H, $CH(CH_3)$), 3.51 (sept, J = 6.5, 2H, $CH(CH_3)$), 2.45 (br s, 6H, NCH_3), 1.78 (s, 9H, $C(CH_3)$), 1.31 (s, 9H, $C(CH_3)$), 0.92 (d, J = 6.5, 12H, $CH(CH_3)$). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 60 °C): δ 170.0 (CN_3), 152.4 (O-C_6H_2), 151.5 (NC_6H_2), 150.8 (*ipso*, N-*Ph*), 140.1, 132.7, 128.0, 122.4, 111.6, 107.7, 48.0 ($CH(CH_3)_2$), 46.1 ($CH(CH_3)_2$), 39.2 (NCH_3), 34.5 ($C_6H_2C(CH_3)_3$), 34.4 ($C_6H_2C(CH_3)_3$), 31.9 ($C_6H_2C(CH_3)_3$), 30.1 ($C_6H_2C(CH_3)_3$), 25.1 ($CH(CH_3)_2$). Anal. Calcd for $C_{38}H_{65}HfN_7O$: C, 56.04; H, 8.04; N, 12.04. Found: C, 56.98; H, 8.55; N, 12.54.

$[\{(iPrN)_2CC_6H_2(tBu)_2O\}ZrCl]_3(\mu_3\text{-}O)(\mu_3\text{-}Cl)$ ($[\{LON^{iPr}\}ZrCl]_3(\mu_3\text{-}O)(\mu_3\text{-}Cl)$, 5). A Schlenk flask was charged with $\{LON^{iPr}\}Li_2$ (generated in situ from $\{LON^{iPr}\}H_2$ (1.670 g, 5.02 mmol) and *n*-butyllithium (3.90 mL of a 2.6 M solution in toluene, 10.14 mmol) in THF (25 mL) and evaporated to dryness) and $ZrCl_4(THF)_2$ (1.900 g, 5.04 mmol), and Et_2O (ca. 40 mL) was vacuum-transferred under reduced pressure. The resulting reaction mixture was stirred at room temperature overnight. Then, the volatiles were evaporated in vacuo, and toluene (ca. 40 mL) was vacuum-transferred under reduced pressure. The mixture was filtered, and the solvent was removed from the filtrate. The residue was dissolved in DME (ca. 20 mL) and the resulting solution was kept at room temperature. A first crop of a white microcrystalline solid, poorly soluble in DME, toluene, and CH_2Cl_2 solvents, was thus recovered and discarded. The mother liquor, left after the first crystallization in DME, was concentrated and kept at room temperature to afford colorless crystals of **5** (0.250 g, 0.1757

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mmol, 11%). ^{1}H NMR (CD_2Cl_2, 500 MHz, 25 °C): δ 7.60 (d, J = 2.5, 3H, C_6H_2), 7.24 (d, J = 2.5, 3H, C_6H_2), 4.02 (sept, J = 7.0, 3H, $CH(CH_3)$), 3.65 (sept, J = 7.0, 3H, $CH(CH_3)$), 3.53 (s, 6H, CH_2O, DME), 3.37 (s, 9H, OCH_3, DME), 1.79 (d, J = 7.0, 9H, $CH(CH_3)$), 1.61 (s, 27H, $C(CH_3)$), 1.41 (d, J = 7.0, 9H, $CH(CH_3)$), 1.36 (s, 27H, $C(CH_3)$), 1.26 (m, 18H, $CH(CH_3)$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz, 25 °C): δ 187.2 (CN_2), 157.2 (O-C_6H_2), 141.2, 137.1, 128.2, 123.7, 120.9, 71.8 (CH_2O, DME), 58.6 (OCH_3, DME), 35.5 ($C_6H_2C(CH_3)_3$), 34.2 ($C_6H_2C(CH_3)_3$), 31.5 ($C_6H_2C(CH_3)_3$), 31.1 ($C_6H_2C(CH_3)_3$), 24.7 ($CH(CH_3)_2$), 24.2 ($CH(CH_3)_2$), 24.0 ($CH(CH_3)_2$), 23.6 ($CH(CH_3)_2$). IR (Nujol, KBr; ν (cm^{-1})): 1575 s, 1363 m, 1276 s, 1254 s, 1110 s, 922 m, 845 s, 762 m, 735 m, 546 m, 466 s, 451 s. Anal. Calcd for $C_{63}H_{102}Cl_4N_6O_4Zr_3$: C, 53.17; H, 7.22; N, 5.91. Found: C, 53.83; H, 7.69; N, 6.33.

[{(*i*Pr$_2$C$_6$H$_3$N)$_2$CC$_6$H$_2$(*t*Bu)$_2$O}ZrCl(μ_2-Cl)]$_2$[{(*i*Pr$_2$C$_6$H$_3$N)-(*i*Pr$_2$C$_6$H$_3$NH)CC$_6$H$_2$(*t*Bu)$_2$O}ZrCl(μ_2-Cl)](μ_3-OH) ([{LON^{Ar}}ZrCl(μ_2-Cl)]$_2$[{L^{H}ON^{Ar}}ZrCl(μ_2-Cl)](μ_3-OH), 6). To a solution of {LON^{Ar}}Li$_2$ (generated in situ from {LON^{Ar}}H$_2$ (0.979 g, 1.72 mmol) and *n*-butyllithium (1.38 mL of a 2.5 M solution in hexane, 3.45 mmol) in THF (20 mL) and evaporated to dryness) was added $ZrCl_4$ (0.401 g, 1.72 mmol), and Et_2O (20 mL) was vacuum-transferred in under reduced pressure. The resulting reaction mixture was stirred at room temperature overnight. Then the volatiles were evaporated in vacuo, and hexanes (ca. 50 mL) was vacuum-transferred in under reduced pressure. The mixture was filtered, and the solvent was removed from the filtrate. The residue was dissolved in a new portion of hexanes (ca. 10 mL), and the resulting solution was kept at room temperature to give yellow crystals of **6** (0.253 g, 0.3458 mmol, 20%). ^{1}H NMR (CD_2Cl_2, 500 MHz, 25 °C): δ 7.47 (d, J = 2.4, 3H, C_6H_2), 7.43 (d, J = 7.9, 6H, C_6H_3), 7.27 (t, J = 7.9, 6H, C_6H_3), 7.12 (d, J = 7.9, 6H, C_6H_3), 6.62 (d, J = 2.5, 3H, C_6H_2), 3.46 (br m, 6H, $CH(CH_3)_2$), 2.75 (br m, 6H, $CH(CH_3)_2$), 1.54 (d, J = 6.4, 18H, $CH(CH_3)_2$), 1.37 (s, 27H, $C(CH_3)_3$), 1.20 (d, J = 6.4, 18H, $CH(CH_3)_2$), 0.90 (s, 27H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz, 25 °C): δ 164.9 (CN_2), 156.6 (O-C_6H_2), 143.2, 141.2, 138.6, 132.8, 129.4, 129.2, 128.4, 126.1, 124.8, 124.6, 117.5, 35.2 ($C_6H_2C(CH_3)_3$), 33.9 ($C_6H_2C(CH_3)_3$), 30.6 ($C_6H_2C(CH_3)_3$), 30.0 ($C_6H_2C(CH_3)_3$), 28.8 ($C_6H_2CH(CH_3)_2$) (only one signal of this type was observed), 24.3 ($C_6H_2CH(CH_3)_2$), 21.6 ($C_6H_2CH(CH_3)_2$). IR (Nujol, KBr) ν (cm^{-1}): 3323 w, 3308 w, 2361 m, 1603 m, 1539 s, 1364 m, 1315 w, 1256 m, 1201 w, 1180 w, 1128 w, 1095 w, 1056 w, 970 w, 933 w, 887 w, 873 w, 856 w, 791 w, 771 w, 751 w, 733 w, 677 w, 634 w, 552 w. Anal. Calcd for $C_{117}H_{164}Cl_6N_6O_4Zr_3$: C, 63.73; H, 7.50; N, 3.81. Found: C, 64.12; H, 8.28; N, 4.05.

{(*i*Pr$_2$C$_6$H$_3$N)$_2$(H)CC$_6$H$_2$(*t*Bu)$_2$O}ZrCl$_3$(THF) ({LO^{H}N^{Ar}}ZrCl$_3$(THF), 7). To a solution of {LON^{Ar}}Li$_2$ (generated in situ from {LON^{Ar}}H$_2$ (0.962 g, 1.69 mmol) and *n*-butyllithium (1.35 mL of a 2.5 M solution in hexane, 3.38 mmol) in THF (20 mL) and evaporated to dryness) was added $ZrCl_4(THF)_2$ (0.638 g, 1.6913 mmol), and toluene (ca. 20 mL) was vacuum-transferred in under reduced pressure. The reaction mixture was stirred overnight and filtered, and the solvent was evaporated. The residue was recrystallized from hexanes (ca. 5 mL) at room temperature to afford **7** as a white crystalline solid (0.708 g, 0.8457 mmol, 50%). ^{1}H NMR (C_6D_6, 500 MHz, 60 °C): δ 7.61 (d, J = 2.4, 1H, C_6H_2), 7.38 (d, J = 7.5, 2H, C_6H_3), 7.32 (m, 1H, C_6H_3), 7.05 (m, 1H, C_6H_3), 7.00 (d, J = 7.5, 2H, C_6H_3), 6.96 (d, J = 2.5, 1H, C_6H_2), 4.50 (br m, 4H, α-THF), 4.14 (br m, 2H, $CH(CH_3)_2$), 3.15 (sept, J = 6.8 2H, $CH(CH_3)_2$), 1.77 (br s, 9H, $C(CH_3)_3$), 1.76 (br d, 6H, $CH(CH_3)_2$), 1.41 (br m, 4H, β-THF), 1.28 (d, J = 6.4, 6H, $CH(CH_3)_2$), 1.00 (s, 9H, $C(CH_3)_3$, 0.95 (br m, 6H, $CH(CH_3)_2$), 0.91 (br m, 6H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz, 60 °C): δ 168.2 (CN_2), 158.6 (O-C_6H_2), 144.9, 143.3, 142.4, 140.6, 137.8, 134.5, 128.2, 127.2, 125.7, 124.5, 119.7, 75.1 (α-CH_2 THF), 35.3 ($C_6H_2C(CH_3)_3$), 33.8 ($C_6H_2C(CH_3)_3$), 30.9 ($C_6H_2C(CH_3)_3$), 30.2 ($C_6H_2C(CH_3)_3$), 28.9 ($C_6H_2CH(CH_3)_2$), 28.3 ($C_6H_2CH(CH_3)_2$), 26.6 ($C_6H_2CH(CH_3)_2$), 25.9 ($C_6H_2CH(CH_3)_2$), 25.2 (β-CH_2 THF), 24.9 ($C_6H_2CH(CH_3)_2$), 24.4 ($C_6H_2CH(CH_3)_2$), 21.7 ($C_6H_2CH(CH_3)_2$). IR (Nujol, KBr; ν (cm^{-1})): 3313 w, 1539 s, 1364 m, 1264 m, 854 m, 791 w, 729 w, 559 w. Anal. Calcd for $C_{43}H_{63}Cl_3N_2O_2Zr$: C, 61.66; H, 7.58; N, 3.34. Found: C, 62.03; H, 7.98; N, 3.65.

{(*i*PrN)$_2$(H)CC$_6$H$_2$(*t*Bu)$_2$O}$_2$ZrCl$_2$ ({LO^{H}N^{iPr}}$_2$ZrCl$_2$, 8). To a solution of {LON^{iPr}}H$_2$ (1.070 g, 3.22 mmol) in THF (20 mL) was added *n*-butyllithium (1.24 mL of a 2.6 M solution in toluene, 3.22 mmol) at room temperature with stirring. After 12 h, anhydrous $ZrCl_4$ (0.380 g, 1.63 mmol) was added, and toluene (ca. 30 mL) was vacuum-transferred in under reduced pressure. The resulting reaction mixture was stirred at room temperature overnight. The mixture was filtered, and the solvent was removed from the filtrate. The residue was recrystallized from benzene (ca. 5 mL) to give a colorless crystalline solid, namely **8**·3.5C_6H_6 (0.448 g, 0.408 mmol, 25%). ^{1}H NMR (toluene-d_8, 500 MHz, 25 °C): δ 7.59 (br d, 4H, C_6H_2), 7.17 (s, 6H, C_6H_6), 7.13 (d, J = 1.9, 2H, C_6H_2), 4.53 (sept, J = 6.9, 2H, $CH(CH_3)_2$), 4.47 (d, J = 9.4, 2H, NH), 3.57 (m, 2H, $CH(CH_3)_2$), 1.75 (s, 18H, $C(CH_3)_3$), 1.53 (d, J = 6.5, 6H, $CH(CH_3)_2$), 1.18 (s, 18H, $C(CH_3)_3$), 0.97 (d, J = 6.5, 6H, $CH(CH_3)_2$), 0.57 (d, J = 6.5, 6H, $CH(CH_3)_2$), 0.39 (d, J = 6.5, 6H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (toluene-d_8, 125 MHz, 25 °C): δ 165.3 (CN_2), 158.2 (O-C_6H_2), 139.3, 138.9, 128.2 (C_6H_6), 127.5, 124.5, 119.8, 49.8 ($CH(CH_3)_2$), 48.2 ($CH(CH_3)_2$), 35.5 ($C_6H_2CH(CH_3)_2$), 33.9 ($C_6H_2CH(CH_3)_2$), 31.4 ($C_6H_2C(CH_3)_3$), 30.2 ($C_6H_2C(CH_3)_3$), 23.5 ($CH(CH_3)_2$), 23.1 ($CH(CH_3)_2$), 21.8 ($CH(CH_3)_2$), 19.4 ($CH(CH_3)_2$). IR (Nujol, KBr; ν (cm^{-1})): 3448 w, 2360 w, 1601 m, 1558 s, 1362 m, 1311 m, 1292 w, 1257 s, 1232 w, 1166 m, 1114 s, 1033 w, 916 w, 844 s, 734 m, 682 m, 617 m, 544 s, 472 m. Anal. Calcd for $C_{126}H_{182}Cl_4N_8O_4Zr_2$: C, 68.88; H, 8.35; N, 5.10. Found: C, 69.22; H, 8.99; N, 5.54.

{(*i*Pr$_2$C$_6$H$_3$N)$_2$CC$_6$H$_2$(*t*Bu)$_2$O}$_2$ZrCl$_{2s}$ ({LO^{H}N^{Ar}}$_2$ZrCl$_2$, 9). To a solution of {LON^{Ar}}H$_2$ (1.029 g, 1.809 mmol) in THF (20 mL) was added *n*-butyllithium (0.70 mL of a 2.6 M solution in toluene, 1.820 mmol) at room temperature with stirring. After 12 h, anhydrous $ZrCl_4$ (0.211 g, 0.906 mmol) was added, and toluene (ca. 30 mL) was vacuum-transferred in under reduced pressure. The resulting reaction mixture was stirred at room temperature overnight. The mixture was filtered, and the solvent was removed from the filtrate. The residue was recrystallized from hexanes (ca. 20 mL) to give a colorless crystalline solid of **9** (0.617 g, 0.475 mmol, 54%). ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ 7.41 (dd, J = 1.9, 7.0, 2H, C_6H_3), 7.27 (d, J = 2.4, 2H, C_6H_2), 7.23 (br s, 2H, C_6H_3), 7.17 (br m, 2H, C_6H_3), 6.94−6.85 (m, 4H, C_6H_3), 6.77 (dd, J = 1.9, 7.0, 2H, C_6H_3), 6.67 (d, J = 2.4, 2H, C_6H_2), 4.19 (sept, J = 6.5, 2H, $CH(CH_3)_2$), 4.14 (sept, J = 6.5, 2H, $CH(CH_3)_2$), 3.03 (sept, J = 6.5, 2H, $CH(CH_3)_2$), 2.96 (sept, J = 6.5, 2H, $CH(CH_3)_2$), 1.67 (m, 8H, $CH(CH_3)_2$ and NH), 1.58 (d, J = 6.5, 3H, $CH(CH_3)_2$), 1.40 (d, J = 6.5, 3H, $CH(CH_3)_2$), 1.31 (s, 18H, $C(CH_3)_3$), 1.21 (d, J = 6.5, 3H, $CH(CH_3)_2$), 1.07 (d, J = 6.5, 3H, $CH(CH_3)_2$), 0.98 (d, J = 6.5, 3H, $CH(CH_3)_2$), 0.92 (s, 18H, $C(CH_3)_3$), 0.51 (d, J = 6.5, 3H, $CH(CH_3)_2$), 0.35 (d, J = 6.5, 3H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz, 25 °C): δ 165.7 (CN_2), 159.1 (O-C_6H_2), 144.4, 144.3, 144.1, 143.9, 142.2, 138.7, 137.4, 134.4, 127.3, 127.2, 127.0, 125.9, 125.6, 125.3, 125.1, 112.9, 119.1, 35.0 ($C_6H_2CH(CH_3)_2$), 33.6 ($C_6H_2CH(CH_3)_2$), 30.9 ($C_6H_2C(CH_3)_3$), 29.9 ($C_6H_2C(CH_3)_3$), 28.8 ($C_6H_2CH(CH_3)_2$), 28.6 ($C_6H_2CH(CH_3)_2$), 28.4 ($C_6H_2CH(CH_3)_2$), 28.2 ($C_6H_2CH(CH_3)_2$), 26.9 ($CH(CH_3)_2$), 26.2 ($CH(CH_3)_2$), 25.8 ($CH(CH_3)_2$), 25.4 ($CH(CH_3)_2$), 23.7 ($CH(CH_3)_2$), 23.6 ($CH(CH_3)_2$), 22.8 ($CH(CH_3)_2$), 21.2 ($CH(CH_3)_2$). IR (Nujol, KBr; ν (cm^{-1})): 3315 w, 2376 w, 1541 s, 1363 m, 1259 m, 1096 w, 1055 w, 855 w, 852 w, 790 w, 773 w, 750 w, 729 w, 542 w. Anal. Calcd for $C_{78}H_{110}Cl_2N_4O_2Zr$: C, 72.18; H, 8.54; N, 4.32. Found: C, 72.87; H, 8.72; N, 4.94.

Typical Procedure for Ethylene Polymerization. A 300 mL high-pressure glass reactor was charged with 150 mL of freshly distilled toluene under argon flash. Mechanical stirring (Pelton turbine, 1000 rpm) was started, and the reactor was then purged with ethylene and loaded with a solution of MAO or TIBAL at atmospheric pressure and kept at the desired temperature by circulating thermostated water in the double wall. A solution of $[Ph_3C][B(C_6F_5)_4]$ (when used) in 2 mL of toluene was injected in by syringe, followed by injection of a solution of the precatalyst in 2 mL of toluene. The gas pressure in the reactor was maintained immediately and kept constant with a back regulator throughout the experiment. The ethylene consumption was monitored via an Aalborg flowmeter. After a given time period, the reactor was depressurized and the reaction was quenched by adding ca.

5 mL of a 10% solution of HCl in methanol. The polymer was further precipitated by adding 500 mL of methanol, washed, and dried in vacuo overnight at room temperature.

Crystal Structure Determination of $\{LON^{iPr}\}H_2$, $\{LON(Ph)N^{iPr}\}H_2\cdot H_2O$, $\{LO^HN^{iPr}\}\{LON^{iPr}\}Zr(CH_2Ph)$ (1), $\{LO^HN^{Ar}\}Zr(CH_2Ph)_3$ (2), $\{(Ph)NC_6H_2(tBu)_2O\}Hf\{(iPrN)_2CNMe_2\}_2$ (4), $[\{LON^{iPr}\}ZrCl]_3(\mu_3\text{-}O)(\mu_3\text{-}Cl)$ (5), $[\{LON^{Ar}\}_2ZrCl(\mu_2\text{-}Cl)]_2[\{L^HON^{Ar}\}ZrCl(\mu_2\text{-}Cl)](\mu_3\text{-}OH)$ (6), $\{LO^HN^{Ar}\}ZrCl_3(THF)$ (7), $\{LO^HN^{iPr}\}_2ZrCl_2\cdot(C_6H_6)_{3.5}$ (8), and $\{LO^HN^{Ar}\}_2ZrCl_2$ (9). Diffraction data were collected at 100(2) or 150(2) K using a Bruker APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). A combination of ω and ϕ scans was carried out to obtain a unique data set. The crystal structures were solved by direct methods, and the remaining atoms were located from difference Fourier synthesis followed by full-matrix least-squares refinement based on F^2 (programs SIR97 and SHELXL-97).[35] For the structures of complexes **5**, **6**, and **9**, the contributions of the disordered solvents to the calculated structure factors were estimated following the BYPASS algorithm,[36] implemented as the SQUEEZE option in PLATON.[37] New data sets, free of solvent contribution, were then used in the final refinements. Many hydrogen atoms could be located from the Fourier difference analysis. Other hydrogen atoms were placed at calculated positions and forced to ride on the attached atom. The hydrogen atom positions were calculated but not refined. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystal data and details of data collection and structure refinement for the different compounds are given in Tables S1 and S2 (see the Supporting Information). Detailed crystallographic data (excluding structure factors) are available in the Supporting Information, as CIF files.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving crystallographic data for $\{LON^{iPr}\}H_2$, $\{LON(Ph)N^{iPr}\}H_2\cdot H_2O$, $\{LO^HN^{iPr}\}\{LON^{iPr}\}Zr(CH_2Ph)$ (**1**), $\{LO^HN^{Ar}\}Zr(CH_2Ph)_3$ (**2**), $\{(Ph)NC_6H_2(tBu)_2O\}Hf\{(iPrN)_2CNMe_2\}_2$ (**4**), $[\{LON^{iPr}\}ZrCl]_3(\mu_3\text{-}O)(\mu_3\text{-}Cl)$ (**5**), $[\{LON^{Ar}\}_2ZrCl(\mu_2\text{-}Cl)]_2[\{L^HON^{Ar}\}ZrCl(\mu_2\text{-}Cl)](\mu_3\text{-}OH)$ (**6**), $\{LO^HN^{Ar}\}ZrCl_3(THF)$ (**7**), $\{LO^HN^{iPr}\}_2ZrCl_2\cdot 3.5C_6H_6$ (**8**), and $\{LO^HN^{Ar}\}_2ZrCl_2$ (**9**), tables giving crystal and structure refinement data (Tables S1 and S2), and figures giving representative ^1H and ^{13}C NMR spectra for some complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(11) No intermediate could be detected, suggesting that coordination of the second ligand proceeds more quickly than the first one.

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(19) The analogous reactions between pro-ligand $\{LON^{Ar}\}H_2$ and $Ti(CH_2Ph)_4$, carried out at either a 1:1 or 2:1 ratio, yielded in both cases mixtures of unidentified products, as monitored by NMR spectroscopy in C_6D_6.

(20) Because of the strong fluxional dynamics, regular 2D NMR experiments (HMQC, HMBC, and COSY), even recorded at different temperatures, did not allow localizing the proton signal of the NH group in the ^{1}H NMR spectra.

(21) Due to the large number of aromatic carbons in this complex and the fluxional dynamic behavior in solution, the ^{13}C NMR resonances for the C_{ipso} atoms of benzylic groups could not be unambiguously assigned and could not be therefore used to probe the coordination mode of benzyl groups in solution.

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