Organoaluminum Hydroxides Supported by β-Diketiminato Ligands: Synthesis, Structural Characterization, and Reactions

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Three β-diketiminato ligands (L^1 = HC[C(Me)N(Ar)]$_2$, Ar = 2,4,6-Me$_3$C$_6$H$_2$; L^2 = HC[C(Me)N(Ar)]$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$; L^3 = HC[C(tBu)N(Ar)]$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) were employed to prepare the organoaluminum hydroxides LAlR(OH) (R = Me, Et, Ph, OEt, OSiMe$_3$) by hydrolysis of the corresponding chlorides in the presence of a N-heterocyclic carbene as HCl scavenger. Reaction of the organoaluminum hydroxide with Cp$_2$ZrMe$_2$ in toluene afforded the heterobimetallic oxide LAlR(μ-O)ZrMeCp$_2$ under evolution of methane. All compounds were characterized by multinuclear NMR, IR, mass spectrometry, and elemental analysis. The structures of L^1AlPh(OH) (**10**), L^2AlPh(OH) (**11**), L^2AlOEt(OH) (**12**), L^2AlOSiMe$_3$(OH) (**13**), and L^2AlPh(μ-O)ZrMeCp$_2$ (**17**) were determined by single-crystal X-ray diffraction studies. The polymerization of ethylene was studied with compound **17**, which exhibits moderate catalytic activity.

Introduction

MAO-activated metallocene complexes of group 4 metals play an important role as catalysts in olefin polymerization.[1] Attempts to develop MAO-free catalyst systems began with cationic complexes stabilized by weakly coordinating anions.[2] A well-defined heterobimetallic oxide L^2AlMe(μ-O)ZrMeCp$_2$ (L^2 = HC[C(Me)N(Ar)]$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) emerged as a single-site homogeneous catalyst with noticeable activity.[3] Recent ab initio calculations demonstrate that the oxygen within the M−O−M′ unit is responsible for the necessary depletion of electron density at the metal sites.[4] These results have initiated the development of oxo-bridged heterobimetallic systems derived from organometallic hydroxides to explore potentially good catalysts.[5] Several organoaluminum hydroxides supported by a β-diketiminato ligand have been previously introduced, including L^2Al(OH)$_2$,[6] [L^2Al(OH)]$_2$(μ-O),[7] L^2Al(OH)OAlL(OCH=NtBu),[8] L^2AlMe(OH),[3] [L^2AlCl(μ-OH)]$_2$,[9] and L^2Al(OH)[C(SiMe$_3$)CH(SiMe$_3$)].[10] Among these aluminum hydroxides, however, due to uncontrolled reactivity or limited availability, only L^2AlMe(OH) so far succeeded in gaining practical application in the preparation of oxo-bridged heterometallic oxides as catalysts.[3] Very recently an ethyl-substituted aluminum hydroxide L^2AlEt(OH) and its derivative L^2AlEt(μ-O)ZrMeCp$_2$ have been prepared and characterized in our laboratory.[11] Further efforts are being made to use a ligand effect to improve the activity and thermal stability of catalysts containing the M−O−M′ moiety.[12] Herein we report the preparation of a new organoaluminum hydroxide LAlR(OH) supported by three different β-diketiminato ligands (L = L^1, L^2, L^3; Scheme 1) together with a variety of substituents on aluminum (R = Me, Et, Ph, OEt, OSiMe$_3$). Subsequently, the reactivity of the new organoaluminum hydroxides is investigated using the reaction with Cp$_2$ZrMe$_2$ to afford the corresponding heterobimetallic oxide LAlR(μ-O)ZrMeCp$_2$.

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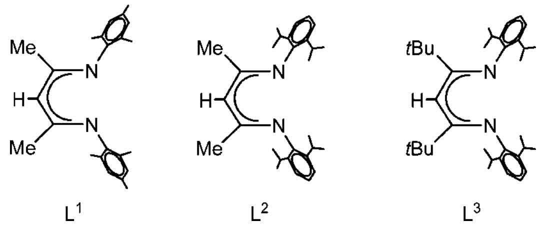
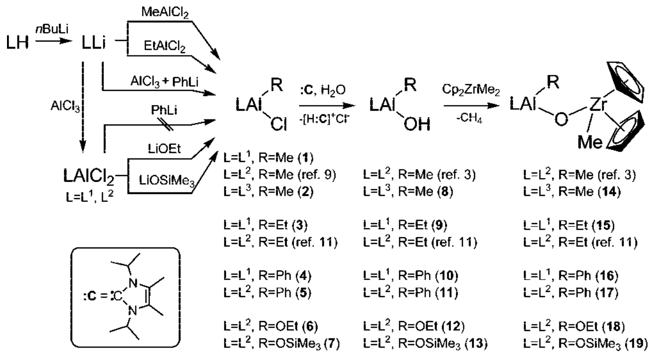
Scheme 1



Scheme 2



Results and Discussion

Synthesis of Organoaluminum Chlorides 1–7. The synthesis of the monomeric alkyl aluminum chloride LAlR(Cl) (L = L^1, R = Me, **1**; L = L^3, R = Me, **2**; L = L^1, R = Et, **3**) was readily achieved by the straightforward reaction of $RAlCl_2$ with the respective LLi in toluene (Scheme 2).

The ^{1}H NMR spectrum of L^{1}AlMe(Cl) (**1**) shows a high-field singlet (δ −0.48 ppm) corresponding to the protons of the Al-bound methyl group, which is shifted slightly downfield compared to those of L^{2}AlMe(Cl) (δ −0.64 ppm)[9] and L^{3}AlMe(Cl) (**2**) (δ −0.73 ppm). Similarly, in the ^{1}H NMR spectrum of L^{1}AlEt(Cl) (**3**), one quartet (δ 0.08 ppm) and one triplet (δ 0.89 ppm), assigned to the methylene and methyl protons of the ethyl group on Al, show downfield shifts relative to those of L^{2}AlEt(Cl) (δ −0.04, 0.80 ppm).[11] The mass spectra of the alkyl aluminum chlorides **1**−**3** exhibit the base peak as fragment [$M^+ - R$].

When a solution of $LAlCl_2$ (L = L^1, L^2) was treated with a stoichiometric amount of PhLi, however, no effective halide metathesis was observed, presumably due to the size of the phenyl group. An alternative route allowed access to the phenyl-substituted aluminum chloride LAlPh(Cl) (L = L^1, **4**; L = L^2, **5**) by adding a solution of LLi to a prereacted mixture of $AlCl_3$ and PhLi in toluene; obviously $PhAlCl_2$ has to be formed first followed by the reaction with LLi. Broad ^{13}C NMR resonances at 146.1 and 144.0 ppm for **4** and **5**, respectively, demonstrate the formation of an Al−C bond. The presence of three further ^{13}C resonances (for ortho, meta, and para CH groups) indicates that the phenyl ring rapidly rotates in solution. In the mass spectra of **4** and **5**, two strong peaks ([$M^+ - Ph$] and [$M^+ - Ph - Me$]) are present in both cases.

Treatment of L^{2}AlCl$_2$ with LiOEt and LiOSiMe$_3$ smoothly afforded L^{2}AlOEt(Cl) (**6**) and L^{2}AlOSiMe$_3$(Cl) (**7**), respectively. In the ^{1}H NMR spectrum of **6**, one quartet (δ 3.56 ppm) and one triplet (δ 0.69 ppm) characterize the ethoxyl group on Al, while for **7** the OSiMe$_3$ proton resonance is observed as a singlet (δ −0.16 ppm). In the mass spectra of both **6** and **7** the molecular ion is detected with moderate intensity.

Crystalline solids of **2**−**7** were obtained in moderate yield from toluene or hexane solutions. In contrast, L^{1}AlMe(Cl) (**1**) is prone to be oily in the presence of organic solvents and hard to crystallize, although crystalline L′AlMe(Cl) (L′ = HC[C(Me)N(Ar)]$_2$, Ar = *p*-Tol) can be isolated from toluene at −78 °C.[13]

Synthesis of Aluminum Hydroxides 8–13. Subsequent hydrolysis of aluminum chlorides **2**−**7** with 1 equiv of H_2O in the presence of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (abbreviated as **:C**) as HCl scavenger[9,14] successfully afforded organoaluminum hydroxides **8**−**13**, while the attempt to hydrolyze L^{1}AlMe(Cl) (**1**) gave only trace amounts of the target L^{1}AlMe(OH) accompanied by the free ligand L^{1}H and an insoluble precipitate.

The ^{1}H NMR spectra of **8**−**13** feature a singlet for the OH proton in the range δ 0.54–0.63 ppm, which is in agreement with previous observations for L^{2}AlMe(OH) (δ 0.53 ppm)[3] and L^{2}AlEt(OH) (δ 0.64 ppm).[11] The IR spectra of aluminum hydroxides **8** and **11**−**13** exhibit the OH stretching frequency in the range 3720–3732 cm^{-1}, consistent with those reported for L^{2}AlMe(OH) (3728 cm^{-1})[3] and L^{2}AlEt(OH) (3729 cm^{-1}).[11]

In the mass spectrum of **10**, the strongest peak corresponds to the fragment [$2M^+ - Ph - Me - 3H$], accompanied by a weak signal for the molecular ion. In the IR spectrum of **10**, the OH stretching frequency (3671 cm^{-1}) deviates substantially from the other terminal hydroxides and is more comparable to those of [(*t*Bu)$_2$Al(μ-OH)]$_3$ (3584 cm^{-1}) and [(*t*Bu)$_2$Al(μ-OH)]$_3$·2THF (3690 cm^{-1}).[15] These observations strongly suggest a dimeric composition of **10** in the solid state, in which two monomer units are associated via μ-OH groups. In solution, the ^{1}H NMR spectrum of **10** reveals the coexistence of two sets of resonances that are populated approximately in a 5:1 ratio and slowly equilibrate at room temperature. The minor species contains an OH resonance (δ 0.62 ppm), which is close to the other terminal hydroxides and was therefore assigned to the monomer, whereas the OH resonance of the major species (δ 1.79 ppm) indicates a bridging OH proton that is substantially displaced from its original position, presumably due to dimerization. A comparable variability of the μ-OH resonance has been observed in [(*t*Bu)$_2$Al(μ-OH)]$_3$ (δ 2.02 ppm) and [(*t*Bu)$_2$Al(μ-OH)]$_3$·2THF (δ 3.42 ppm).[15]

A similar effect is observed in the ^{1}H NMR spectrum of **9**; however, in this case the relative populations of the monomer (δ 0.50 ppm) and the dimer (δ 1.27 ppm) are reversed (7:1). The bridging OH group in **9** is also characterized by the OH stretch (3672 cm^{-1}) in the IR spectrum. In contrast, the mass spectrum in the gas phase shows the fragment [$M^+ - Me$] as the base peak, and no larger fragment related to the dimer is detected.

Synthesis of Heterobimetallic Oxides 14–19. Further reactions were performed to study the reactivity of the OH group in the organoaluminum hydroxides. Treatment of **8**–**13**, respectively, with 1 equiv of Cp_2ZrMe_2 in toluene at 100 °C led to the formation of the corresponding LAlR(μ-O)ZrMeCp$_2$ (**14**–**19**) in modest yield, along with the elimination of methane. The IR spectra of **14**–**19** are devoid of any absorption in the reasonable range for OH groups, consistent with the absence of hydroxyl proton resonances in the ^{1}H NMR spectra. The compositions of **14**–**19** are further evidenced by mass spectra, elemental

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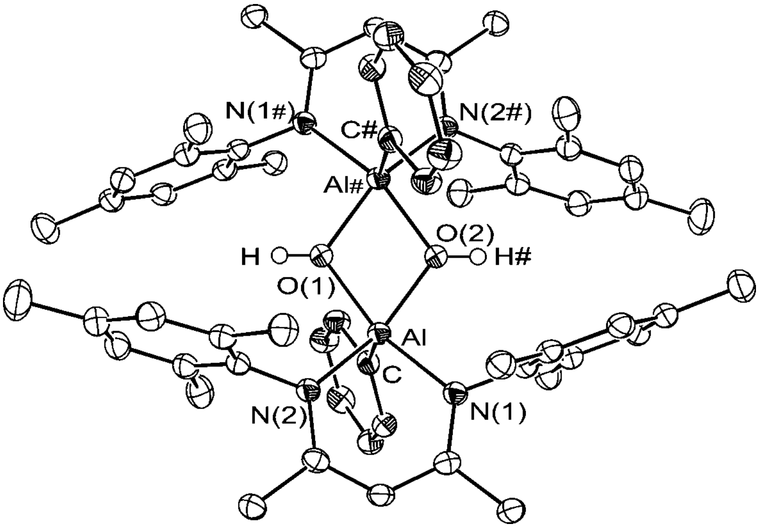

Figure 1. Molecular structure of **10**. Thermal ellipsoids are drawn at the 50% level, and all hydrogen atoms, except those of the OH groups, and one benzene solvent molecule are omitted for clarity.

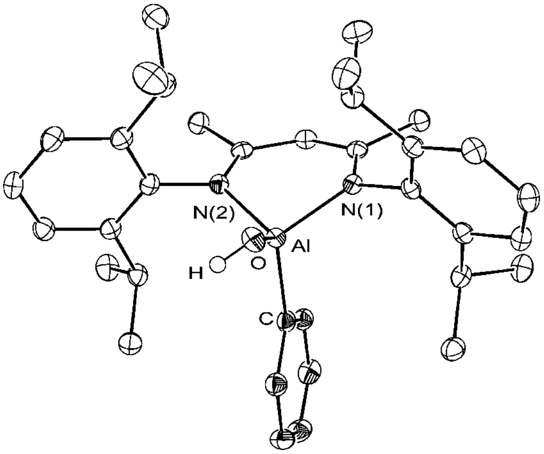

Figure 2. Molecular structure of **11**. Thermal ellipsoids are drawn at the 50% level, and all hydrogen atoms, except that of the OH group, and two THF solvent molecules are omitted for clarity.

analysis, and multinuclear NMR spectra. The ^{1}H NMR spectra of **14**−**19** exhibit one characteristic singlet (δ 5.43–5.54 ppm) attributed to two symmetry-related Cp groups, comparable to that in $L^2AlEt(\mu\text{-}O)ZrMeCp_2$ (δ 5.30 ppm).[11] Another singlet characterizes the Me group on Zr; this resonance is devoid of NOE correlations with protons of the Al-bound R group, indicating that the −O−Zr−Me linkage is stretched away from the Al atom. The compounds containing the bulky 2,6-iPr$_2$C$_6$H$_3$ substituent (**14**, **17**−**19**) possess considerable thermal stability with high melting points (376–391 °C), corresponding well to $L^2AlMe(\mu\text{-}O)ZrMeCp_2$ (385 °C, dec)[3] and $L^2AlEt(\mu\text{-}O)ZrMeCp_2$ (368–369 °C).[11] In contrast, the melting points of $L^1AlEt(\mu\text{-}O)ZrMeCp_2$ (**15**) and $L^1AlPh(\mu\text{-}O)ZrMeCp_2$ (**16**) are relatively low (145–195 °C). Furthermore, in comparison to $L^2AlMe(\mu\text{-}O)ZrMeCp_2$[3] and $L^2AlEt(\mu\text{-}O)ZrMeCp_2$,[11] compounds **14**−**19** are well soluble in benzene. These observations demonstrate accordingly that the variation of the ligand and the substituent on aluminum exhibit a profound impact on the physical and chemical properties of the M−O−M′ species.

Structural Characterization of 10–13 and 17. Molecular structures of **10–13** and **17** (Figures 1–5) were determined by single-crystal X-ray diffraction studies, with details for crystal data and structure refinement presented in Table 1 and selected bond lengths and angles provided in Table 2.

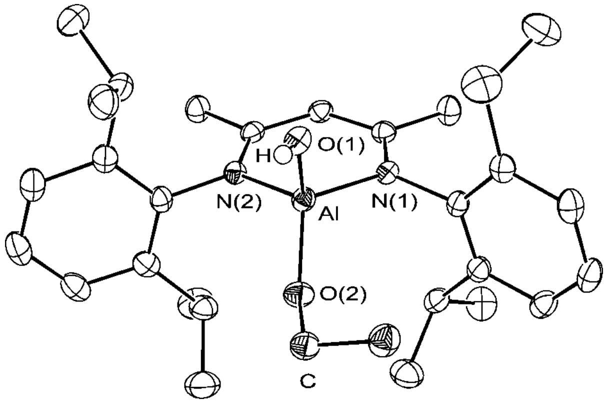

Figure 3. Molecular structure of **12**. Thermal ellipsoids are drawn at the 50% level, and all hydrogen atoms, except that of the OH group, are omitted for clarity.

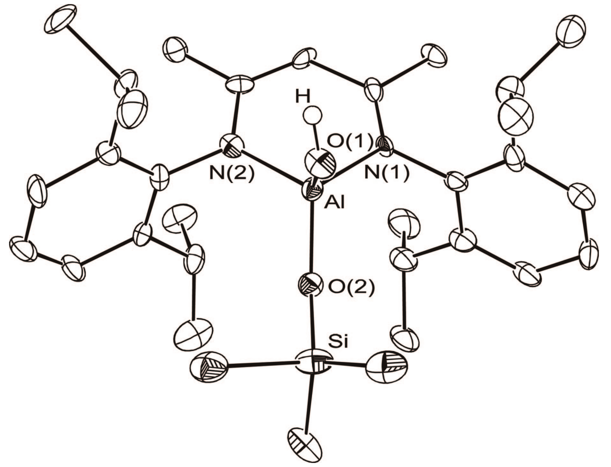

Figure 4. Molecular structure of **13**. Thermal ellipsoids are drawn at the 50% level, and all hydrogen atoms, except those of the OH group, are omitted for clarity.

$L^1AlPh(OH)$ (**10**) crystallizes as a centrosymmetric dimer (see Figure 1), which is in good agreement with the observation in the mass spectrum and the monomer–dimer equilibrium observed by NMR. The structure of **10** contains two Al atoms linked by μ-OH bridges to form a perfect planar four-membered

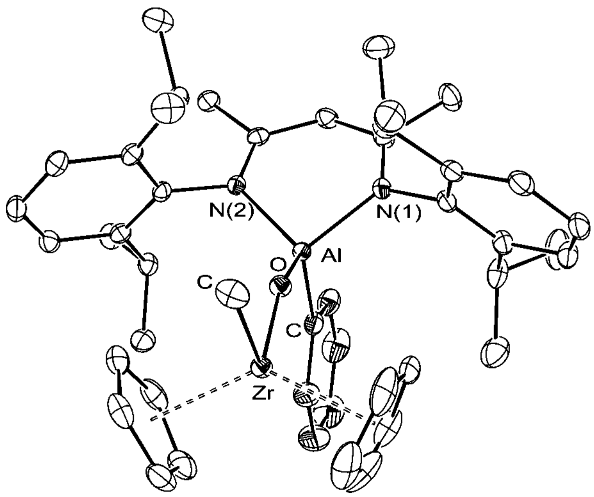

Figure 5. Molecular structure of **17**. Thermal ellipsoids are drawn at the 50% level, and all hydrogen atoms and one-half *n*-hexane solvent molecule are omitted for clarity.

Al_2O_2 ring. The same bridging mode of hydroxyl groups has been observed in $[L^2AlCl(\mu\text{-}OH)]_2$[9] and $[\{Mes_2Al(\mu\text{-}OH)\}_2]\cdot 2THF$.[16] Altogether, the Al atom is five-coordinate with a coordination sphere made up by two N atoms of the β-diketiminato ligand, two O atoms of hydroxyl groups, and a phenyl group. The bond lengths of Al–(μ-OH) (1.8825(12), 1.8583(12) Å) are comparable to those in $[L^2AlCl(\mu\text{-}OH)]_2$ (1.886(1), 1.875(1) Å),[9] but longer than those found for the four-coordinate aluminum in $[\{Mes_2Al(\mu\text{-}OH)\}_2]\cdot 2THF$ (1.822 Å)[16] and $[(t\text{Bu})_2Al(\mu\text{-}OH)]_3$ (1.846(3)–1.851(2) Å).[15] Likewise, the O–Al–O angle (72.82(6)°) is very close to that in $[L^2AlCl(\mu\text{-}OH)]_2$ (72.46(7)°),[9] but significantly narrower than those in $[\{Mes_2Al(\mu\text{-}OH)\}_2]\cdot 2THF$ (80.8°),[16] $[(t\text{Bu})_2Al(\mu\text{-}OH)]_3$ (97.9(2)–98.1(2)°),[15] and $[L^2Al(OH)]_2(\mu\text{-}O)$ (112.33(14)°).[7] The N(1)–Al–N(2) bite angle (89.98(6)°) is similar to that in $[L^2AlCl(\mu\text{-}OH)]_2$ (90.05(6)°),[9] while the angle at oxygen (107.18(6)°) lies between those in $[\{Mes_2Al(\mu\text{-}OH)\}_2]\cdot 2THF$ (98.8°)[16] and $[H_2Al(\mu\text{-}OH)]_3$ (127.8°).[17] The two phenyl groups on Al are arranged *trans* with respect to the Al_2O_2 plane, and the Al–C bond length (1.9946(18) Å) is noticeably longer than those in $AlPh_3$ (1.960, 1.956 Å)[18] and in $[Ph_2Al\cdot N{=}CPh\cdot C_6H_4Br]_2\cdot 2C_6H_6$ (1.979(13), 1.956 (13) Å).[19]

In contrast to **10**, the X-ray crystal structural analysis of $L^2AlPh(OH)$ (**11**) shows a monomeric composition (see Figure 2), again in agreement with the observations in the mass and NMR spectra. This is most likely due to the bulkier L^2 ligand, in which the Ar substituents cannot be packed against each other into a dimer as that of the flat mesityl substituent of L^1. Here, the four-coordinate Al atom is surrounded by two N atoms of the β-diketiminato ligand, an OH, and a phenyl group. Consequently, the Al–OH separation (1.7202(10) Å) is much shorter than those in **10** (1.8825(12), 1.8583(12) Å) and slightly shorter than those found in the alkyl-substituted terminal hydroxides $L^2AlMe(OH)$ (1.731(3) Å)[3] and $L^2AlEt(OH)$ (1.7409(17) Å),[11] but a little longer than those of the dihydroxides $L^2Al(OH)_2$ (1.695(15), 1.711(16) Å).[6] The N(1)–Al–N(2) bite angle (95.89(5)°) is much wider than that in **10** (89.98(6)°) and intermediate between those of $L^2AlMe(OH)$ (96.3(1)°)[3] and $L^2AlEt(OH)$ (95.32(8)°).[11] The phenyl group on Al is almost perpendicular to the NCCN quasi-plane, and the Al–C bond length (1.9694(15) Å) is shorter than that in **10** (1.9946(18) Å) and more comparable to those in $AlPh_3$ (1.960, 1.956 Å).[18]

$L^2AlOEt(OH)$ (**12**) crystallizes in the monoclinic space group *P*2(1)/*c* (see Figure 3). The aluminum atom is coordinate to two N atoms (from chelating β-diketiminato ligand) and two O atoms (from the OH and OEt substituents) in a distorted tetrahedral geometry. The Al–OH bond length (1.7631(13) Å) is much longer than the Al–OEt separation (1.7023(12) Å) and also longer than that in $L^2AlEt(OH)$ (1.7409(17) Å).[11] The N(1)–Al–N(2) bite angle (97.11(6)°) is wider than that in $L^2AlEt(OH)$ (95.32(8)°).[11] The O–Al–O angle (115.48(6)°) is close to that in $L^2Al(OH)_2$ (115.38(8)°).[6]

$L^2AlOSiMe_3(OH)$ (**13**) crystallizes in the monoclinic space group *P*2(1) (see Figure 4). Similarly, the aluminum site is also surrounded by two N atoms and two O atoms. Both Al–O bond lengths are nearly identical (1.7116(11), 1.7106(11) Å) and also similar to those in $L^2Al(OH)_2$ (1.695(15), 1.711(16) Å).[6] The N(1)–Al–N(2) bite angle (96.32(5)°) is close to that in **11** (95.89(5)°). The O–Al–O angle (109.80(6)°) is slightly narrower than that in $[L^2Al(OH)]_2(\mu\text{-}O)$ (112.33(14)°)[7] and $L^2Al(OH)_2$ (115.38(8)°).[6]

$L^2AlPh(\mu\text{-}O)ZrMeCp_2$ (**17**) crystallizes in the monoclinic space group *C*2/*c* (see Figure 5) and shows again a monomeric arrangement, in which the terminal OH group of **11** is replaced by a μ-oxo-linked $ZrCp_2Me$ moiety. The angle for the bent Al–O–Zr linkage is 155.73(6)°, which is a little tighter than that of $L^2AlMe(\mu\text{-}O)ZrMeCp_2$ (158.2(1)°),[3] but much wider than that of $L^2AlEt(\mu\text{-}O)ZrMeCp_2$ (144.41(6)°),[11] while correspondingly the Zr–O bond separation (1.9400(9) Å) falls between those of $L^2AlMe(\mu\text{-}O)ZrMeCp_2$ (1.929(2) Å)[3] and $L^2AlEt(\mu\text{-}O)ZrMeCp_2$ (1.9424(10) Å).[11] Similarly, the Al–O bond length (1.7171(10) Å) lies between those of its alkyl analogues (1.7285(10), 1.711(2) Å).[3,11] These observations indicate that the steric demand of R on Al offers a possibility for tuning the Al–O–Zr angle and the Al–Zr separation (Scheme 3). The Al–C bond length (1.9759(15) Å) is slightly longer relative to that in its hydroxide precursor **11** (1.9694(15) Å). The methyl group on Zr and the phenyl group on Al are arranged in a *trans* conformation to each other, similar to what is found in the ethyl analogue.[11] The X_{Cp1}–Zr–X_{Cp2} angle and the Zr–X_{Cp} distances are in the expected range.

Ethylene Polymerization Studies with Compound 17. Table 3 summarizes the polymerization results of compound **17**. All polymeric materials were isolated as white powders. Under comparable polymerization conditions, the methylalumoxane (MAO)/**17** catalyst system shows lower activity compared to that of $MAO/L^2AlR(\mu\text{-}O)MMeCp_2$ (R = Me, Et; M = Ti,[5e] Zr[3,11]). However the MAO-activated compound **17** still exhibits moderate catalytic activity for the polymerization of ethylene. It can be observed that the catalytic activity of compound $L^2AlR(\mu\text{-}O)ZrMeCp_2$ varies depending on the R group on the aluminum center. The activity is in the order Me > Et > Ph. This can be attributed to the steric and electronic factors that stabilize the cation formation.

Conclusion

New organoaluminum hydroxides LAlR(OH) (L = L^3, R = Me, **8**; L = L^1, R = Et, **9**; L = L^1, R = Ph, **10**; L = L^2, R = Ph, **11**; L = L^2, R = OEt, **12**; L = L^2, R = $OSiMe_3$, **13**) were synthesized by controlled hydrolysis of the respective chlorides. In contrast to the chlorides and depending on the steric bulk of

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Table 1. Crystal Data and Structure Refinement for Compounds 10·(benzene)$_{0.5}$, 11·(THF)$_2$, 12, 13, and 17·(*n*-hexane)$_{0.5}$

	10·(benzene)$_{0.5}$	**11**·(THF)$_2$	**12**	**13**	**17**·(*n*-hexane)$_{0.5}$
CCDC	662281	662282	662283	662284	662285
formula	$C_{32}H_{38}AlN_2O$	$C_{43}H_{63}AlN_2O_3$	$C_{31}H_{47}AlN_2O_2$	$C_{32}H_{51}AlN_2O_2Si$	$C_{49}H_{66}AlN_2OZr$
fw	493.62	682.93	506.69	550.82	817.24
T, K	100(2)	100(2)	100(2)	100(2)	100(2)
cryst syst	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2(1)/c$	$P2(1)$	$C2/c$
a, Å	11.4187(11)	9.0526(10)	16.954(2)	8.8703(10)	37.4042(15)
b, Å	11.5317(11)	12.0803(14)	10.0454(15)	19.895(2)	12.8409(5)
c, Å	12.1602(11)	18.727(2)	17.892(3)	10.2310(11)	19.3062(8)
α, deg	93.6510(10)	73.6670(10)	90	90	90
β, deg	106.2490(10)	82.3990(10)	103.031(2)	114.0800(10)	104.05
γ, deg	114.6840(10)	86.1870(10)	90	90	90
V, Å^3	1366.5(2)	1947.1(4)	2968.7(7)	1648.4(3)	8995.4(6)
Z	2	2	4	2	8
ρ_{calc}, g/cm^3	1.200	1.165	1.134	1.110	1.270
μ, mm^{-1}	0.101	0.092	0.097	0.127	0.300
cryst size, mm^3	0.1 × 0.1 × 0.05	0.4 × 0.2 × 0.2	0.25 × 0.1 × 0.05	0.15 × 0.1 × 0.05	0.4 × 0.4 × 0.2
θ range for data collection, deg	1.78 to 26.40	2.75 to 25.08	2.34 to 25.59	2.05 to 26.37	2.64 to 26.39
index ranges	$-14 \le h \le 13$	$-10 \le h \le 10$	$-20 \le h \le 20$	$-11 \le h \le 10$	$-46 \le h \le 46$
	$-14 \le k \le 14$	$-13 \le k \le 14$	$0 \le k \le 12$	$0 \le k \le 24$	$-16 \le k \le 16$
	$0 \le l \le 15$	$0 \le l \le 22$	$0 \le l \le 21$	$0 \le l \le 12$	$-24 \le l \le 24$
no. of reflns collected	25 588	36 861	5557	6706	95 350
no. of indep reflns [R_{int}]	5606 [0.0306]	6895 [0.0205]	5557 [0.0430]	6706 [0.0263]	9178 [0.0206]
no. of data/restrnts/params	5606/1/336	6895/0/444	5557/1/339	6706/16/386	9178/146/569
goodness-of-fit on F^2	1.043	1.047	1.020	1.031	1.043
R1, wR2 ($I > 2\sigma(I)$)	0.0392, 0.0948	0.0388, 0.1039	0.0379, 0.0905	0.0337, 0.0778	0.0255, 0.0672
R1, wR2 (all data)	0.0571, 0.1041	0.0427, 0.1073	0.0542, 0.0982	0.0482, 0.0856	0.0271, 0.0685
largest diff peak/hole, e Å^{-3}	0.286/−0.292	0.478/−0.410	0.317/−0.268	0.255/−0.272	0.773/−0.656

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds 10−13 and 17

	10	**11**	**12**	**13**	**17**
Al−O(1)	1.8825(12)	1.7202(10)	1.7631(13)	1.7116(11)	1.7171(10)
Al−O(2)	1.8583(12)		1.7023(12)	1.7106(11)	
Al−N(1)	1.9937(14)	1.9120(12)	1.8885(14)	1.868(4)	1.9121(12)
Al−N(2)	1.9736(14)	1.9153(12)	1.8885(14)	1.899(4)	1.9107(12)
Al−C	1.9946(18)	1.9694(15)			1.9759(15)
Zr−O					1.9400(9)
Zr−X_{Cp1}					2.258
Zr−X_{Cp2}					2.271
O(1)−Al−N(1)	149.75(6)	109.89(5)	112.51(6)	111.65(19)	113.53(5)
O(1)−Al−N(2)	89.84(6)	112.05(5)	109.03(6)	111.86(19)	114.91(5)
N(1)−Al−N(2)	89.98(6)	95.89(5)	97.11(6)	96.32(5)	95.80(5)
O(1)−Al−C	103.95(6)	117.76(6)			113.55(6)
C−Al−N(1)	105.56(7)	110.29(6)			110.21(6)
C−Al−N(2)	102.97(6)	108.78(6)			107.38(6)
Al−O−Zr					155.73(6)
X_{Cp1}−Zr−X_{Cp2}					129.23

Scheme 3

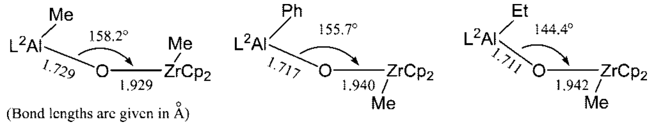

Table 3. Ethylene Polymerization for Compound 17 (22.2 μmol) in 100 mL of Toluene under 1 atm of Ethylene Pressure at 25 °C, Activity (A) = 10^5 g PE/mol cat·h

MAO/**17**	t (min)	PE (g)	A
200	30	0.12	0.11
300	30	0.26	0.23
400	30	0.72	0.65
600	30	1.12	1.01

the β-diketiminato ligand, the hydroxides tend to dimerize under formation of a planar Al_2O_2 ring. Further, the OH groups exhibit the expected reactivity toward Cp_2ZrMe_2, resulting in the formation of the oxo-bridged heterobimetallic compounds $LAlR(\mu\text{-}O)ZrMeCp_2$ (L = L^3, R = Me, **14**; L = L^1, R = Et, **15**; L = L^1, R = Ph, **16**; L = L^2, R = Ph, **17**; L = L^2, R = OEt, **18**; L = L^2, R = $OSiMe_3$, **19**) by intermolecular elimination of CH_4. Compound **17** exhibits moderate catalytic activity in ethylene polymerization. Preliminary results of $L^2AlR(\mu\text{-}O)ZrMeCp_2$ in polymerization reactions show that the activity depends on the substituents R on aluminum.

Experimental Section

General Remarks. All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. The samples for analytical measurements as well as for the reactions were manipulated in a glovebox. The solvents were purified and dried using conventional procedures and were freshly distilled under nitrogen and degassed prior to use. $MeAlCl_2$, $EtAlCl_2$, *n*BuLi, PhLi, $AlCl_3$, LiOEt, $LiOSiMe_3$, and Cp_2ZrMe_2 were purchased from Aldrich. LH,[13,20] LLi,[13,20] L^2AlCl_2,[21] and 1,3-

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diisopropyl-4,5-dimethylimidazol-2-ylidene (abbreviated as **:C**)[22] were prepared as described in the literature.

L^1AlMe(Cl) (1). To a toluene solution (40 mL) of L^1H (0.84 g, 2.5 mmol) at −78 °C was added *n*BuLi (1 mL, 2.5 M, 2.5 mmol) drop by drop. The mixture was stirred and allowed to warm to room temperature. After additional stirring for 12 h, the solution was cooled to −78 °C again and $MeAlCl_2$ (2.5 mL, 1 M, 2.5 mmol) was added. The resulting suspension was allowed to warm to room temperature and stirred for 12 h. After workup, the insoluble LiCl was removed by filtration, and the filtrate was concentrated to form an oily paste. Washing the paste with pentane (5 mL) and drying it in vacuum afforded a white solid. Yield: 0.28 g (27%); mp >100 °C (dec). ^{1}H NMR (200.13 MHz, C_6D_6): δ−0.48 (s, 3 H, Al*Me*), 1.47 (s, 6 H, C*Me*), 2.09 (s, 6 H, *p*-Ar*Me*), 2.10 (s, 6 H, *o*-Ar*Me*), 2.51 (s, 6 H, *o*-Ar*Me*), 4.94 (s, 1 H, *γ-CH*), 7.05–7.15 (m, *Ar*) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1610 (w), 1530 (w), 1299 (w), 1261 (w), 1251 (w), 1225 (w), 1200 (w), 1149 (w), 1092 (w), 1023 (w), 961 (w), 936 (w), 878 (w), 799 (w), 722 (w), 672 (w), 661 (w). EI-MS: *m/z* (%) 410.2 (4) [M$^+$], 395.2 (100) [M$^+$ − Me]. Anal. Calcd for $C_{24}H_{32}AlClN_2$ (411.0): C, 70.14; H, 7.85; N, 6.82. Found: C, 69.82; H, 8.04; N, 6.67.

L^3AlMe(Cl) (2). Preparation of **2** was accomplished like that of **1** from L^3H (0.50 g, 1 mmol), *n*BuLi (0.4 mL, 2.5 M, 1 mmol), and $MeAlCl_2$ (1 mL, 1 M, 1 mmol). Yield: 0.45 g (77%); mp 179–181 °C. ^{1}H NMR (500.13 MHz, C_6D_6): δ −0.73 (s, 3 H, Al*Me*), 1.10 (s, 18 H, C(C*H*$_3$)$_3$), 1.18 (d, *J* = 6.6 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.22 (d, *J* = 6.6 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.33 (d, *J* = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.44 (d, *J* = 6.4 Hz, 6 H, CH(C*H*$_3$)$_2$), 3.15 (sept, *J* = 6.8 Hz, 2 H, C*H*(CH$_3$)$_2$), 4.15 (sept, *J* = 6.8 Hz, 2 H, C*H*(CH$_3$)$_2$), 6.00 (s, 1 H, *γ-CH*), 7.00–7.15 (m, *Ar*) ppm. ^{13}C NMR (75.48 MHz, C_6D_6): δ 179.8 (*C*N), 146.1, 143.8, 141.5, 127.2, 125.0, 124.0 (*o*-, *o*-, *i*-, *p*-, *m*-, *m-Ar*), 101.8 (*γ-C*H), 43.32 (*β*-*C*(CH$_3$)$_3$), 32.2 (*β*-C(*C*H$_3$)$_3$), 28.7, 28.3 (*C*H(CH$_3$)$_2$), 27.8, 26.0, 24.7, 24.3 (CH(*C*H$_3$)$_2$), −11.9 (br, Al*Me*) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 3063 (w), 1623 (w), 1588 (w), 1530 (w), 1486 (m), 1401 (m), 1378 (s), 1360 (s), 1317 (m), 1306 (w), 1262 (m), 1215 (w), 1180 (w), 1098 (m), 1019 (m), 934 (w), 865 (w), 802 (m), 757 (w), 722 (w), 697 (w), 656 (w). EI-MS: *m/z* (%) 578.4 (6) [M$^+$], 563.4 (100) [M$^+$ − Me]. Anal. Calcd for $C_{36}H_{56}AlClN_2$ (579.3): C, 74.64; H, 9.74; N, 4.84. Found: C, 74.37; H, 9.74; N, 4.63.

L^1AlEt(Cl) (3). Preparation of **3** was accomplished like that of **1** from L^1H (0.84 g, 2.5 mmol), *n*BuLi (1 mL, 2.5 M, 2.5 mmol), and $EtAlCl_2$ (1.3 mL, 1.9 M, 2.5 mmol). Yield: 0.68 g (64%); mp 165–167 °C. ^{1}H NMR (300.13 MHz, C_6D_6): δ 0.08 (q, *J* = 8.2 Hz, 2 H, AlC*H*$_2$CH$_3$), 0.89 (t, *J* = 8.0 Hz, 3 H, AlCH$_2$C*H*$_3$), 1.47 (s, 6 H, C*Me*), 2.08 (s, 6 H, *p*-Ar*Me*), 2.10 (s, 6 H, *o*-Ar*Me*), 2.52 (s, 6 H, *o*-Ar*Me*), 4.95 (s, 1 H, *γ-CH*), 6.75–7.15 (m, *Ar*) ppm. ^{13}C NMR (75.48 MHz, C_6D_6): δ 170.3 (*C*N), 139.8, 135.9, 134.6, 132.8, 130.4, 129.4 (*i*-, *p*-, *o*-, *o*-, *m*-, *m-Ar*), 98.0 (*γ-C*H), 22.4 (*β-C*H$_3$), 20.8 (*p*-Ar*Me*), 19.6 (*o*-Ar*Me*), 18.6 (*o*-Ar*Me*), 8.7 (AlCH$_2$*C*H$_3$), 0.66 (Al*C*H$_2$CH$_3$) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1728 (w), 1608 (s), 1532 (s), 1299 (s), 1262 (s), 1245 (s), 1223 (s), 1198 (s), 1147 (s), 1094 (m), 1021 (s), 996 (s), 955 (m), 936 (m), 875 (s), 845 (m), 801 (m), 761 (s), 723 (m), 655 (m), 607 (s), 566 (s). EI-MS: *m/z (%)* 395.2 (100) [M$^+$ − Et]. Anal. Calcd for $C_{25}H_{34}AlClN_2$ (425.0): C, 70.65; H, 8.06; N, 6.59. Found: C, 70.26; H, 8.40; N, 6.50.

L^1AlPh(Cl) (4). A solution of PhLi (2 mL, 1.8 M, 3.6 mmol) was added at −78 °C to the suspension of $AlCl_3$ (0.48 g, 3.6 mmol) in toluene (30 mL). The mixture was allowed to warm to room temperature, and a white precipitate was observed immediately. After stirring this mixture overnight, a toluene solution (40 mL) of L^1Li (3.6 mmol) in situ was added at −78 °C. After removing the cold bath and raising the temperature to room temperature, stirring was continued for another 12 h. After filtration, the filtrate was evaporated to dryness and washed with *n*-pentane (10 mL) to afford a white solid. Yield: 0.64 g (38%); mp 133 °C. ^{1}H NMR (500.13 MHz, C_6D_6): δ 1.51 (s, 6 H, C*Me*), 1.87 (s, 6 H, *o*-Ar*Me*), 2.03 (s, 6 H, *p*-Ar*Me*), 2.45 (s, 6 H, *o*-Ar*Me*), 5.04 (s, 1 H, *γ-CH*), 6.57–7.72 (m, *Ar*) ppm. ^{13}C NMR (75.48 MHz, C_6D_6): δ 171.1 (*C*N), 146.1 (br, *i-Ph*), 139.8 (*i-Ar*), 138.0 (*o-Ph*), 135.9, 134.0, 133.2, 130.1, 129.9 (*p*-, *o*-, *o*-, *m*-, *m-Ar*), 128.5, 127.3, (*p*-, *m-Ph*), 98.4 (*γ-C*H), 22.7 (*β-C*H$_3$), 20.8 (*p*-Ar*Me*), 19.5 (*o*-Ar*Me*), 19.2 (*o*-Ar*Me*) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1610 (w), 1529 (w), 1299 (w), 1261 (w), 1246 (w), 1223 (w), 1200 (w), 1149 (w), 1090 (w), 1022 (w), 962 (w), 935 (w), 919 (w), 877 (w), 847 (w), 799 (w), 765 (w), 724 (w), 706 (w), 680 (w). EI-MS: *m/z* (%) 472.2 (10) [M$^+$], 395.2 (100) [M$^+$ − Ph], 379.1 (52) [M$^+$ − Ph − Me]. Anal. Calcd for $C_{29}H_{34}AlClN_2$ (473.0): C, 73.63; H, 7.24; N, 5.92. Found: C, 73.31; H, 7.50; N, 5.72.

L^2AlPh(Cl) (5). Preparation of **5** was accomplished like that of **4** using PhLi (2 mL, 1.8 M, 3.6 mmol), $AlCl_3$ (0.48 g, 3.6 mmol), and L^2Li in situ (3.6 mmol) in toluene (60 mL). Yield: 0.46 g (23%); mp 212–214 °C. ^{1}H NMR (300.13 MHz, C_6D_6): δ 0.67 (d, *J* = 6.8 Hz, 6 H, CH(C*H*$_3$) $_2$), 1.01 (d, *J* = 6.8 Hz, 6 H, CH(C*H*$_3$) $_2$), 1.16 (d, *J* = 6.8 Hz, 6 H, CH(C*H*$_3$) $_2$), 1.49 (d, *J* = 6.6 Hz, 6 H, CH(C*H*$_3$) $_2$), 1.58 (s, 6 H, C*Me*), 3.06 (sept, *J* = 6.8 Hz, 2 H, C*H*(CH$_3$) $_2$), 3.72 (sept, *J* = 6.8 Hz, 2 H, C*H*(CH$_3$)$_2$), 5.02 (s, 1 H, *γ-CH*), 6.95–7.05 (m, *Ar*), 7.05–7.20 (m, *Ar*), 6.98–7.40 (m, *Ar*) ppm. ^{13}C NMR (125.8 MHz, C_6D_6): δ 171.6 (*C*N), 144.0 (br, *i-Ph*), 145.1, 144.3, 139.7 (*o*-, *o*-, *i-Ar*), 137.9, 127.9, 127.8, (*o*-, *p*-, *m-Ph*), 127.1, 125.0, 124,5 (*p*-, *m*-, *m-Ar*), 98.9 (*γ-C*H), 28.9, 28.8 (*C*H(CH$_3$)$_2$), 25.7, 24.7, 24.5, 23.9 (CH(*C*H$_3$)$_2$), 23.5 (*β-C*H$_3$) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 3055 (m), 1584 (w), 1532 (m), 1317 (m), 1260 (m), 1197 (w), 1178 (w), 1100 (m), 1089 (m), 1056 (m), 1025 (m), 934 (w), 881 (w), 800 (m), 758 (w), 736 (w), 722 (w), 704 (w), 676 (w), 648 (w). EI-MS: *m/z (%)* 521 (4) [*M*$^+$-Cl], 478 (44) [M$^+$ − Ph], 463 (100) [M$^+$ − Ph − Me]. Anal. Calcd for $C_{35}H_{46}AlClN_2$ (557.2): C, 75.45; H, 8.32; N, 5.03. Found: C, 75.07; H, 8.48; N, 4.93.

L^2AlOEt(Cl) (6). A solution of LiOEt (5 mL, 1 M, 5 mmol) was added in excess drop by drop at −78 °C to a solution of L^2AlCl_2 (2.06 g, 4 mmol) in THF (80 mL). The mixture was allowed to warm to room temperature and stirred overnight. After workup the solvent was removed in vacuo and the crude product was extracted with Et_2O (90 mL). The solution was concentrated to 10 mL and was kept at 4 °C to afford a crystalline solid. Yield: 1.62 g (77%); mp 155–157 °C. ^{1}H NMR (500.13 MHz, C_6D_6): δ 0.69 (t, 3 H, OCH$_2$C*H*$_3$), 1.08 (d, *J* = 6.8 Hz, 6 H, CH*Me*$_2$), 1.16 (d, *J* = 6.8 Hz, 6 H, CH*Me*$_2$), 1.45 (d, *J* = 6.8 Hz, 6 H, CH*Me*$_2$), 1.49 (d, *J* = 6.6 Hz, 6 H, CH*Me*$_2$), 1.53 (s, 6 H, C*Me*), 3.37 (sept, *J* = 6.8 Hz, 2 H, C*H*Me$_2$) 3.56 (q, 2 H, *J* = 6.9 Hz, OC*H*$_2$CH$_3$), 3.57 (sept, *J* = 6.7 Hz, 2 H, C*H*Me$_2$), 4.87 (s, 1 H, *γ-CH*), 7.10–7.16 (m, *Ar*) ppm. ^{13}C NMR (125.76 MHz, C_6D_6): δ 171.3 (*C*N), 145.3, 144.6, 139.0, 127.8, 125.0, 124.3 (*o*-, *o*-, *i*-, *p*-, *m*-, *m-Ar*), 97.8 (*γ-C*H), 58.7 (O*C*H$_2$CH$_3$), 28.9, 28.2 (*C*H(CH$_3$)$_2$), 26.4, 24.9, 24.8, 24.3 (CH(*C*H$_3$)$_2$), 23.3 (*β-C*H$_3$), 20.1 (OCH$_2$*C*H$_3$) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 3057 (w), 1623 (w), 1589 (w), 1553 (m), 1533 (s), 1317 (s), 1305 (m), 1253 (m), 1169 (s), 1144 (m), 1104 (w), 1075 (w), 1056 (w), 1023 (m), 936 (w), 919 (w), 890 (w), 801 (m), 775 (w), 759 (w), 721 (w), 690 (w). EI-MS: *m/z (%)* 524.2 (40) [M$^+$], 509.2 (16) [M$^+$ − Me], 463.2 (100) [M$^+$ − OEt − Me]. Anal. Calcd for $C_{31}H_{46}AlClN_2O$ (525.1): C, 70.90; H, 8.83; N, 5.33. Found: C, 70.63; H, 8.93; N, 5.30.

L^2AlOSiMe$_3$(Cl) (7). A solution of $LiOSiMe_3$ (1 mL, 1 M, 1 mmol) was added drop by drop at −78 °C to a solution of L^2AlCl_2 (0.51 g, 1 mmol) in toluene (50 mL). The mixture was allowed to warm to room temperature and stirred overnight. After filtration the solution was removed in vacuo to afford a white solid. Yield: 0.41 g (72%); mp 240–242 °C. ^{1}H NMR (500.13 MHz, C_6D_6): δ −0.16 (s, 9 H, Si*Me*$_3$), 1.03 (d, *J* = 6.8 Hz, 6 H, CH*Me*$_2$), 1.17 (d, *J* = 6.8 Hz, 6 H, CH*Me*$_2$), 1.41 (d, *J* = 6.8 Hz, 6 H, CH*Me*$_2$), 1.50 (d, *J* = 6.6 Hz, 6 H, CH*Me*$_2$), 1.52 (s, 6 H, C*Me*), 3.30 (sept, *J* =

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7.0 Hz, 2 H, C*H*Me$_2$), 3.62 (sept, *J* = 6.6 Hz, 2 H, C*H*Me$_2$), 4.87 (s, 1 H, γ-C*H*), 7.10–7.16 (m, *Ar*) ppm. ^{13}C NMR (125.76 MHz, C$_6$D$_6$): δ 171.5 (*C*N), 145.6, 143.8, 139.0, 127.7, 125.2, 124.0 (*o*-, *o*-, *i*-, *p*-, *m*-, *m-Ar*), 97.7 (γ-*C*H), 29.0, 28.0 (*C*H(CH$_3$)$_2$), 26.8, 24.7, 24.7, 24.2 (CH(*C*H$_3$)$_2$), 23.3 (β-*C*H$_3$), 2.4 (Si(*C*H$_3$)$_3$) ppm. ^{29}Si NMR (99.36 MHz, C$_6$D$_6$): δ 4.43 ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 3585 (w), 1938 (w), 1870 (w), 1585 (w), 1528 (w), 1319 (m), 1302 (w), 1255 (w), 1179 (w), 1166 (w), 1098 (w), 1054 (m), 1020 (w), 968 (w), 934 (w), 892 (w), 854 (w), 836 (w), 799 (w), 757 (w), 660 (w). EI-MS: *m/z* (%) 568.3 (24) [M$^+$], 553.2 (100) [M$^+$ − Me]. Anal. Calcd for C$_{32}$H$_{50}$AlClN$_2$OSi (569.3): C, 67.51; H, 8.85; N, 4.92. Found: C, 67.32; H, 8.79; N, 4.77.

L^{3}AlMe(OH) (8). To a mixture of L^{3}AlMe(Cl) (**2**) (0.39 g, 0.68 mmol) and [CN(*i*Pr)C$_2$Me$_2$N(*i*Pr)] (**:C**, 0.12 g, 0.68 mmol) in toluene (40 mL) at 0 °C was added distilled H$_2$O (12 μL, 0.68 mmol). The suspension was allowed to warm to room temperature and stirred for 12 h. The insoluble solid was removed by filtration, and from the filtrate all volatiles were removed in vacuo. The resulting residue was washed with *n*-pentane (3 mL) to afford a white solid. Yield: 0.27 g (70%); mp >197 °C (dec). ^{1}H NMR (500.13 MHz, C$_6$D$_6$): δ −1.00 (s, 3 H, Al*Me*), 0.63 (s, 1 H, OH), 1.10 (s, 18 H, C(C*H*$_3$)$_3$), 1.26 (d, *J* = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.27 (d, *J* = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.36 (d, *J* = 6.4 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.37 (d, *J* = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 3.22 (sept, *J* = 6.8 Hz, 2 H, C*H*(CH$_3$)$_2$), 4.03 (sept, *J* = 6.8 Hz, 2 H, C*H*(CH$_3$)$_2$), 5.71 (s, 1 H, γ-C*H*), 7.00–7.20 (m, *Ar*) ppm. ^{13}C NMR (125.8 MHz, C$_6$D$_6$): δ 178.0 (*C*N), 145.6, 143.7, 142.3, 126.8, 124.6, 123.9 (*o*-, *o*-, *i*-, *p*-, *m*-, *m-Ar*), 99.0 (γ-*C*H), 43.0 (β-*C*(CH$_3$)$_3$), 32.5 (β-C(*C*H$_3$)$_3$), 28.7, 28.1 (*C*H(CH$_3$)$_2$), 27.4, 25.9, 24.6, 24.2 (CH(*C*H$_3$)$_2$), −13.5 (br, Al*Me*) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 3732 (w, OH), 1621 (w), 1529 (w), 1502 (w), 1401 (w), 1364 (w), 1315 (w), 1274 (w), 1262 (w), 1216 (w), 1187 (w), 1156 (w), 1138 (w), 1096 (w), 1029 (w), 1020 (w), 933 (w), 847 (w), 805 (w), 784 (w), 754 (w), 722 (w), 694 (w). EI-MS: *m/z* (%) 560.4 (4) [M$^+$], 545.4 (100) [M$^+$ − Me]. Anal. Calcd for C$_{36}$H$_{57}$AlN$_2$O (560.8): C, 77.10; H, 10.24; N, 4.99. Found: C, 76.73; H, 10.10; N, 4.95.

L^{1}AlEt(OH) (9). Preparation of **9** was accomplished like that of **8** from L^{1}AlEt(Cl) (**3**) (0.42 g, 1 mmol), [CN(*i*Pr)C$_2$Me$_2$N(*i*Pr)] (**:C**, 0.18 g, 1 mmol), and distilled H$_2$O (18 μL, 1 mmol). Yield: 0.18 g (44%); mp 158–159 °C. ^{1}H NMR (500.13 MHz, C$_6$D$_6$) for the primary conformation: δ −0.05 (q, *J* = 8.0 Hz, 2 H, AlC*H*$_2$CH$_3$), 0.54 (s, 1H, O*H*), 0.78 (t, *J* = 8.0 Hz, 3 H, AlCH$_2$C*H*$_3$), 1.51 (s, 6 H, C*Me*), 2.11 (s, 6 H, *p*-Ar*Me*), 2.16 (s, 6 H, *o*-Ar*Me*), 2.51 (s, 6 H, *o*-Ar*Me*), 4.91 (s, 1 H, γ-C*H*), 6.78–7.15 (m, *Ar*) ppm; for the second conformation: δ 0.23 (q, *J* = 8.0 Hz, 2 H, AlC*H*$_2$CH$_3$), 1.27 (s, 1H, O*H*), 1.35 (s, 6 H, C*Me*), 1.55 (t, *J* = 8.0 Hz, 3 H, AlCH$_2$C*H*$_3$), 2.04 (s, 6 H, *o*-Ar*Me*), 2.16 (s, 6 H, *o*-Ar*Me*), 2.28 (s, 6 H, *p*-Ar*Me*), 4.91 (s, 1 H, γ-C*H*), 6.78–7.15 (m, *Ar*) ppm. ^{13}C NMR (75.48 MHz, C$_6$D$_6$, primary conformation): δ 169.1 (*C*N), 140.9, 135.4, 134.7, 132.9, 130.0, 129.3 (*i*-, *p*-, *o*-, *o*-, *m*-, *m-Ar*), 96.6 (γ-*C*H), 22.3 (β-*C*H$_3$), 20.9 (*p*-Ar*Me*), 19.1 (*o*-Ar*Me*), 18.4 (*o*-Ar*Me*), 9.3 (AlCH$_2$*C*H$_3$), −0.78 (br, Al*C*H$_2$CH$_3$) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 3672 (s, OH), 1766 (w), 1738 (w), 1609 (w), 1534 (s), 1287 (m), 1262 (m), 1244 (m), 1221 (m), 1198 (m), 1145 (m), 1094 (m), 1021 (s), 991 (m), 919 (s), 859 (s), 800 (m), 765 (m), 723 (m). EI-MS: *m/z* (%) 406.3 (>1) [M$^+$], 389.3 (>1) [M$^+$ − OH], 377.2 (100) [M$^+$ − Et]. Anal. Calcd for C$_{25}$H$_{35}$AlN$_2$O (406.5): C, 73.86; H, 8.68; N, 6.89. Found: C, 73.49; H, 8.41; N, 6.62.

L^{1}AlPh(OH) (10). Preparation of **10** was accomplished like that of **9** from L^{1}AlPh(Cl) (**4**) (0.95 g, 2 mmol), [CN(*i*Pr)C$_2$Me$_2$N(*i*Pr)] (**:C**, 0.36 g, 2 mmol), and distilled H$_2$O (36 μL, 2 mmol). Yield: 0.44 g (48%); mp 203–205 °C. ^{1}H NMR (500.13 MHz, C$_6$D$_6$) for the primary conformation: δ 1.39 (s, 6 H, C*Me*), 1.52 (s, 6 H, *o*-Ar*Me*), 1.79 (s, 1H, O*H*), 2.16 (s, 6 H, *p*-Ar*Me*), 2.25 (s, 6 H, *o*-Ar*Me*), 5.14 (s, 1 H, γ-C*H*), 6.50–8.04 (m, *Ar*) ppm; for the second conformation: δ 0.62 (s, 1H, O*H*), 1.54 (s, 6 H, C*Me*), 1.92 (s, 6 H, *o*-Ar*Me*), 2.07 (s, 6 H, *p*-Ar*Me*), 2.49 (s, 6 H, *o*-Ar*Me*), 4.99 (s, 1 H, γ-C*H*), 6.50–8.04 (m, *Ar*) ppm. ^{13}C NMR (75.48 MHz, C$_6$D$_6$, primary conformation): δ 169.1 (*C*N), 145.7–125.6 (*Ph*, *Ar*), 99.8 (γ-*C*H), 23.9 (β-*C*H$_3$), 22.6 (*o*-Ar*Me*), 21.4 (*p*-Ar*Me*), 20.9 (*o*-Ar*Me*) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 3671 (w, OH), 3055 (w), 1610 (w), 1538 (w), 1510 (w), 1290 (w), 1261 (w), 1243 (w), 1220 (w), 1199 (w), 1146 (w), 1085 (w), 1019 (w), 919 (w), 859 (w), 800 (w), 728 (w), 705 (w), 669 (w). EI-MS: *m/z* (%), 813.4 (100) [2M$^+$ − Ph − Me − 3H], 753.4 (56) [2M$^+$ − 2Ph − H], 454.2 (4) [M$^+$], 437.2 (14) [M$^+$ − OH], 377.2 (66) [M$^+$ − Ph]. Anal. Calcd for C$_{29}$H$_{35}$AlN$_2$O (454.6): C, 76.62; H, 7.76; N, 6.16. Found: C, 76.24; H, 7.71; N, 5.88. X-ray quality crystals of **10**·(benzene)$_{0.5}$ were grown from the solution of benzene.

L^{2}AlPh(OH) (11). Preparation of **11** was accomplished like that of **9** from L^{2}AlPh(Cl) (**5**) (1.11 g, 2 mmol), [CN(*i*Pr)C$_2$Me$_2$N(*i*Pr)] (**:C**, 0.36 g, 2 mmol), and distilled H$_2$O (36 μL, 2 mmol). Yield: 0.49 g (45%); mp 192 °C. ^{1}H NMR (500.13 MHz, C$_6$D$_6$): δ 0.63 (s, 1 H, O*H*), 0.68 (t, *J* = 6.8, 6 H, CH(C*H*$_3$)$_2$), 1.05 (d, *J* = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.20 (d, *J* = 7.0 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.40 (d, *J* = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.61 (s, 6 H, C*Me*), 3.09 (sept, *J* = 6.8 Hz, 2 H, C*H*(CH$_3$)$_2$), 3.76 (sept, *J* = 6.8 Hz, 2 H, C*H*(CH$_3$)$_2$), 4.98 (s, 1 H, γ-C*H*), 7.00–7.19 (m, *Ar*) ppm. ^{13}C NMR (125.8 MHz, C$_6$D$_6$): δ 170.3 (*C*N), 146.8 (br, *i-Ph*), 145.1, 144.3, 140.7 (*o*-, *o*-, *i-Ar*), 138.0, 127.7 (*o*-, *p-Ph*), 127.4 (*p-Ar*), 126.9 (*m-Ph*), 124.7, 124,4 (*m*-, *m-Ar*), 97.7 (γ-*C*H), 28.8, 28.4 (*C*H(CH$_3$)$_2$), 25.5, 24.7, 24.6, 23.8 (CH(*C*H$_3$)$_2$), 23.3 (β-*C*H$_3$) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 3720 (w, OH), 3053 (w), 1623 (w), 1584 (w), 1533 (w), 1317 (w), 1257 (w), 1197 (w), 1179 (w), 1101 (w), 1085 (w), 1056 (w), 1025 (w), 935 (w), 880 (w), 800 (w), 785 (w), 759 (w), 734 (w), 708 (w), 674 (w). EI-MS: *m/z* (%) 537.4 (28) [M$^+$ − H], 521.4 (100) [M$^+$ − Me − 2H]. Anal. Calcd for C$_{35}$H$_{47}$AlN$_2$O (538.7): C, 78.03; H, 8.79; N, 5.20. Found: C, 77.91; H, 8.85; N, 5.20. X-ray quality crystals of **11**·(THF)$_2$ were grown from the solution of THF.

L^{2}AlOEt(OH) (12). Preparation of **12** was accomplished like that of **8** from L^{2}AlOEt(Cl) (**6**) (1.05 g, 2 mmol), [CN(*i*Pr)C$_2$Me$_2$N(*i*Pr)] (**:C**, 0.36 g, 2 mmol), and distilled H$_2$O (36 μL, 2 mmol). Yield: 0.22 g (22%); mp 146–148 °C. ^{1}H NMR (500.13 MHz, C$_6$D$_6$): δ 0.59 (s, 1 H, O*H*), 0.67 (t, 3 H, OCH$_2$C*H*$_3$), 1.14 (d, *J* = 6.8 Hz, 6 H, CH*Me*$_2$), 1.17 (d, *J* = 6.6 Hz, 6 H, CH*Me*$_2$), 1.36 (d, *J* = 6.6 Hz, 6 H, CH*Me*$_2$), 1.48 (d, *J* = 6.8 Hz, 6 H, CH*Me*$_2$), 1.57 (s, 6 H, C*Me*), 3.38 (sept, *J* = 6.8 Hz, 2 H, C*H*Me$_2$) 3.46 (q, 2 H, *J* = 6.8 Hz, OC*H*$_2$CH$_3$), 3.54 (sept, *J* = 6.8 Hz, 2 H, C*H*Me$_2$), 4.90 (s, 1 H, γ-C*H*), 7.10–7.16 (m, *Ar*) ppm. ^{13}C NMR (125.76 MHz, C$_6$D$_6$): δ 170.3 (*C*N), 144.9, 144.6, 140.0, 127.3, 124.4, 124.2 (*o*-, *o*-, *i*-, *p*-, *m*-, *m-Ar*), 96.6 (γ-*C*H), 58.4 (O*C*H$_2$CH$_3$), 28.8, 28.0 (*C*H(CH$_3$)$_2$), 25.8, 24.8, 24.7, 24.5 (CH(*C*H$_3$)$_2$), 23.1 (β-*C*H$_3$), 20.6 (OCH$_2$*C*H$_3$)) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 3733 (w, OH), 3176 (w), 1584 (w), 1552 (w), 1533 (m), 1319 (m), 1252 (w), 1197 (w), 1169 (w), 1144 (w), 1103 (w), 1073 (w), 1056 (w), 1022 (w), 936 (w), 913 (w), 890 (w), 801 (w), 776 (w), 765 (w), 759 (w), 722 (w), 675 (w). EI-MS: *m/z* (%) 506.3 (64) [M$^+$], 445.3 (100) [M$^+$ − Et − 2Me − 2H]. Anal. Calcd for C$_{31}$H$_{47}$AlN$_2$O$_2$ (506.7): C, 73.48; H, 9.35; N, 5.53. Found: C, 73.13; H, 9.58; N, 5.39.

L^{2}AlOSiMe$_3$(OH) (13). Preparation of **13** was accomplished like that of **8** from L^{2}AlOSiMe$_3$(Cl) (**7**) (1.14 g, 2 mmol), [CN(*i*Pr)C$_2$Me$_2$N(*i*Pr)] (**:C**, 0.36 g, 2 mmol), and distilled H$_2$O (36 μL, 2 mmol). Yield: 0.49 g (44%); mp 192 °C. ^{1}H NMR (500.13 MHz, C$_6$D$_6$): δ −0.24 (s, 9 H, Si*Me*$_3$), 0.58 (s, O*H*), 1.09 (d, *J* = 6.8 Hz, 6 H, CH*Me*$_2$), 1.17 (d, *J* = 6.8 Hz, 6 H, CH*Me*$_2$), 1.36 (d, *J* = 6.8 Hz, 6 H, CH*Me*$_2$), 1.42 (d, *J* = 6.6 Hz, 6 H, CH*Me*$_2$), 1.55 (s, 6 H, C*Me*), 3.28 (sept, *J* = 6.8 Hz, 2 H, C*H*Me$_2$), 3.56 (sept, *J* = 6.8 Hz, 2 H, C*H*Me$_2$), 4.88 (s, 1 H, γ-C*H*), 7.11–7.16 (m, *Ar*) ppm. ^{13}C NMR (125.76 MHz, C$_6$D$_6$): δ 170.4 (*C*N), 144.9, 143.9, 139.9, 127.3, 124.6, 124.0 (*o*-, *o*-, *i*-, *p*-, *m*-, *m-Ar*), 96.7 (γ-*C*H), 28.7, 27.8 (*C*H(CH$_3$)$_2$), 25.9, 24.6, 24.5, 24.4 (CH(*C*H$_3$)$_2$), 23.1 (β-*C*H$_3$), 2.6 (Si(*C*H$_3$)$_3$) ppm. ^{29}Si NMR (99.36 MHz, C$_6$D$_6$): δ 2.02 ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 3730 (m, OH), 3062 (m), 1938 (w), 1870 (w), 1804 (w), 1700 (w), 1624 (w), 1584 (w), 1549 (m), 1528 (s), 1319 (s), 1252 (s), 1202 (w), 1180 (m), 1108 (m), 1100 (m), 1018 (s), 936 (m), 890 (w), 862 (m), 834 (s), 799 (s), 757 (s), 723 (m), 682 (w), 657 (w), 638 (w), 573 (m). EI-MS: *m/z* (%) 550.4 (68) [M^+], 535.3 (100) [$M^+ - Me$]. Anal. Calcd for $C_{32}H_{51}AlN_2O_2Si$ (550.8): C, 69.78; H, 9.33; N, 5.09. Found: C, 69.44; H, 9.17; N, 4.93.

$L^3AlMe(\mu\text{-}O)ZrMeCp_2$ (14). Toluene (40 mL) was added to the mixture of $L^3AlMe(OH)$ (**8**) (0.56 g, 1 mmol) and Cp_2ZrMe_2 (0.26 g, 1 mmol). The resulting solution was stirred for 2 h at room temperature and then continuously for 24 h at 100 °C. After filtration, the solution was kept at room temperature overnight to isolate colorless crystals. Yield: 0.33 g (41%); mp >390 °C (dec). ^{1}H NMR (500.13 MHz, C_6D_3): δ −0.21 (s, 3 H, Al*Me*), −0.04 (s, 3 H, Zr*Me*), 1.05 (s, 18 H, $C(CH_3)_3$), 1.26 (d, $J = 7.0$ Hz, 6 H, $CH(CH_3)_2$), 1.30 (d, $J = 6.8$ Hz, 6 H, $CH(CH_3)_2$), 1.49 (d, $J = 7.0$ Hz, 6 H, $CH(CH_3)_2$), 1.53 (d, $J = 7.4$ Hz, 6 H, $CH(CH_3)_2$), 3.37 (sept, $J = 6.8$ Hz, 2 H, $CH(CH_3)_2$), 3.59 (sept, $J = 6.4$ Hz, 2 H, $CH(CH_3)_2$), 5.43 (s, 10 H, C_5H_5), 5.74 (s, 1 H, γ-C*H*), 7.08–7.15 (m, Ar) ppm. ^{13}C NMR (125.8 MHz, C_6D_6): δ 178.8 (*C*N), 145.6, 143.5, 143.2, 127.1, 124.6, 124.4 (*o-*, *o-*, *i-*, *p-*, *m-*, *m-Ar*), 110.7 (C_5H_5), 99.6 (γ-*C*H), 43.4 (β-$C(CH_3)_3$), 32.5 (β-$C(CH_3)_3$), 28.9, 28.4 ($CH(CH_3)_2$), 28.1, 25.9, 24.9, 24.0 ($CH(CH_3)_2$), 18.5 (Zr*Me*), −10.2 (br, Al*Me*) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 3322 (w), 1647 (w), 1620 (w), 1581 (w), 1530 (w), 1402 (w), 1315 (m), 1274 (w), 1263 (w), 1216 (w), 1191 (w), 1157 (w), 1137 (w), 1097 (w), 1058 (w), 1019 (w), 967 (w), 934 (w), 919 (w), 863 (w), 847 (w), 794 (m), 753 (w), 742 (m), 723 (w), 693 (w). EI-MS: *m/z* (%) 779.4 (100) [$M^+ - Me$]. Anal. Calcd for $C_{47}H_{69}AlN_2OZr$ (796.3): C, 70.89; H, 8.73; N, 3.52. Found: C, 70.64; H, 8.55; N, 3.50.

$L^1AlEt(\mu\text{-}O)ZrMeCp_2$ (15). Preparation of **15** was accomplished like that of **14** from $L^1AlEt(OH)$ (**9**) (0.41 g, 1 mmol) and Cp_2ZrMe_2 (0.26 g, 1 mmol). Yield: 0.21 g (34%); mp 193–195 °C. ^{1}H NMR (500.13 MHz, C_6D_3): δ 0.19 (q, $J = 8.0$ Hz, 2 H, $AlCH_2CH_3$), 0.29 (s, 3 H, Zr*Me*), 1.35 (t, $J = 7.8$ Hz, 3 H, $AlCH_2CH_3$), 1.41 (s, 6 H, C*Me*), 2.11 (s, 6 H, *p*-Ar*Me*), 2.26 (s, 6 H, *o*-Ar*Me*), 2.27 (s, 6 H, *o*-Ar*Me*), 4.78 (s, 1 H, γ-C*H*), 5.46 (s, 10 H, C_5H_5), 6.80–7.15 (m, Ar) ppm. ^{13}C NMR (125.8 MHz, C_6D_6): δ 169.2 (*C*N), 141.2, 135.8, 134.7, 133.1, 130.1, 129.7 (*i-*, *p-*, *o-*, *o-*, *m-*, *m-Ar*), 110.3 (C_5H_5), 96.9 (γ-*C*H), 22.4 (β-CH_3), 20.8 (*p*-Ar*Me*), 19.5 (*o*-Ar*Me*), 18.4 (*o*-Ar*Me*), 19.5 (Zr*Me*), 9.9 ($AlCH_2CH_3$), 3.2 (br, $AlCH_2CH_3$) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1624 (w), 1609 (w), 1538 (m), 1391 (m), 1296 (w), 1261 (w), 1249 (w), 1228 (w), 1202 (w), 1149 (w), 1095 (w), 1021 (w), 958 (w), 935 (w), 874 (w), 859 (m), 799 (m), 761 (w), 740 (w), 723 (w), 653 (w), 593 (w). EI-MS: *m/z* (%) 625.2 (64) [$M^+ - Me$], 611.2 (100) [$M^+ - Et$]. Anal. Calcd for $C_{36}H_{47}AlN_2OZr$ (642.0): C, 67.35; H, 7.38; N, 4.36. Found: C, 67.24; H, 7.28; N, 4.32.

$L^1AlPh(\mu\text{-}O)ZrMeCp_2$ (16). Preparation of **16** was accomplished like that of **14** from $L^1AlPh(OH)$ (**10**) (0.22 g, 0.5 mmol) and Cp_2ZrMe_2 (0.14 g, 0.5 mmol). Yield: 0.23 g (67%); mp 145–147 °C. ^{1}H NMR (500.13 MHz, C_6D_6): δ 0.31 (s, 3 H, Zr*Me*), 1.45 (s, 6 H, C*Me*), 1.78 (s, 6 H, *o*-Ar*Me*), 2.07 (s, 6 H, *p*-Ar*Me*), 2.26 (s, 6 H, *o*-Ar*Me*), 4.92 (s, 1 H, γ-C*H*), 5.48 (s, 10 H, C_5H_5), 6.62–7.94 (m, *Ar*) ppm. ^{13}C NMR (125.76 MHz, C_6D_6): δ 169.9 (*C*N), 151.4 (br, *i-Ph*), 140.9 (*i-Ar*), 138.1 (*o-Ph*), 135.9, 134.4, 133.7, 130.0, 129.9 (*p-*, *o-*, *o-*, *m-*, *m-Ar*), 128.9, 127.4, (*p-*, *m-Ph*), 110.5 (C_5H_5), 97.3 (γ-*C*H), 22.5 (β-CH_3), 20.8 (*p*-Ar*Me*), 19.4 (*o*-Ar*Me*), 19.2 (*o*-Ar*Me*), 18.2 (Zr*Me*) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1625 (w), 1553 (w), 1528 (w), 1297 (w), 1261 (w), 1249 (w), 1225 (w), 1201 (w), 1149 (w), 1085 (w), 1019 (w), 961 (w), 890 (m), 796 (m), 746 (w), 726 (w), 704 (w), 674 (w), 570 (w), 529 (w), 508 (w), 484 (w), 449 (w). EI-MS: *m/z* (%) 688.3 (2) [M^+], 673.2 (100) [$M^+ - Me$]. Anal. Calcd for $C_{40}H_{47}AlN_2OZr$ (690.0): C, 69.63; H, 6.87; N, 4.06. Found: C, 69.55; H, 6.70; N, 3.89.

$L^2AlPh(\mu\text{-}O)ZrMeCp_2$ (17). Preparation of **17** was accomplished like that of **14** from $L^2AlPh(OH)$ (**11**) (0.54 g, 1 mmol) and Cp_2ZrMe_2 (0.26 g, 1 mmol). Yield: 0.49 g (63%); mp 390–391 °C. ^{1}H NMR (300.13 MHz, C_6D_3): δ 0.30 (s, 3 H, Zr*Me*), 0.64 (d, $J = 6.6$ Hz, 6 H, $CH(CH_3)_2$), 0.98 (d, $J = 6.8$ Hz, 6 H, $CH(CH_3)_2$), 1.07 (d, $J = 6.8$ Hz, 6 H, $CH(CH_3)_2$), 1.53 (s, 6 H, C*Me*),1.56 (d, $J = 6.8$ Hz, 6 H, $CH(CH_3)_2$), 3.03 (sept, $J = 6.7$ Hz, 2 H, $CH(CH_3)_2$), 3.33 (sept, $J = 6.8$ Hz, 2 H, $CH(CH_3)_2$), 4.88 (s, 1 H, γ-C*H*), 5.47 (s, 10 H, C_5H_5), 7.00–7.34 (m, Ar) ppm. ^{13}C NMR (125.8 MHz, C_6D_6): δ 171.3 (*C*N), 138.2 (br, *i-Ph*), 145.0, 143.9, 141.3 (*o-*, *o-*, *i-Ar*), 138.2, 128.5 (*o-*, *p-Ph*), 127.5 (*p-Ar*), 125.6 (*m-Ph*), 125.2, 124,2 (*m-*, *m-Ar*), 110.7 (C_5H_5), 97.8 (γ-*C*H), 29.2, 28.2 ($CH(CH_3)_2$), 25.0, 24.6, 24.3 ($CH(CH_3)_2$), 23.7 (β-CH_3), 19.5 (Zr*Me*) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1875 (w), 1809 (w), 1704 (w), 1581 (w), 1543 (m), 1522 (s), 1317 (s), 1257 (s), 1196 (m), 1176 (m), 1126 (m), 1096 (m), 1080 (m), 1058 (m), 1044 (m), 1018 (s), 971 (w), 952 (w), 934 (m), 875 (s), 863 (s), 798 (s), 759 (s), 726 (s), 705 (m), 670 (m), 639 (m). EI-MS: *m/z* (%) 772.3 (4) [M^+], 757.4 (100) [$M^+ - Me$]. Anal. Calcd for $C_{46}H_{59}AlN_2OZr$ (774.2): C, 71.36; H, 7.68; N, 3.62. Found: C, 71.68; H, 7.45; N, 3.52. X-ray quality crystals of **17**·(*n*-hexane)$_{0.5}$ were grown from the solution of *n*-hexane.

$L^2AlOEt(\mu\text{-}O)ZrMeCp_2$ (18). Preparation of **18** was accomplished like that of **14** from $L^2AlOEt(OH)$ (**12**) (0.51 g, 1 mmol) and Cp_2ZrMe_2 (0.26 g, 1 mmol). Yield: 0.55 g (74%); mp 377–378 °C. ^{1}H NMR (500.13 MHz, C_6D_6): δ 0.04 (s, 3 H, Zr*Me*), 1.03 (d, $J = 6.8$ Hz, 6 H, CH*Me*$_2$), 1.24 (d, $J = 6.8$ Hz, 6 H, CH*Me*$_2$), 1.40 (t, 3 H, OCH_2CH_3), 1.45 (d, $J = 6.8$ Hz, 6 H, CH*Me*$_2$), 1.51 (s, 6 H, C*Me*), 1.58 (d, $J = 6.6$ Hz, 6 H, CH*Me*$_2$), 3.10 (sept, $J = 6.8$ Hz, 2 H, C*H*Me$_2$), 3.52 (sept, $J = 6.8$ Hz, 2 H, C*H*Me$_2$), 3.97 (q, 2 H, $J = 6.8$ Hz, OCH_2CH_3), 4.82 (s, 1 H, γ-C*H*), 5.50 (s, 10 H, C_5H_5), 7.00–7.21 (m, *Ar*) ppm. ^{13}C NMR (125.76 MHz, C_6D_6): δ 170.4 (*C*N), 144.8, 143.7, 141.4, 127.5, 124.8, 124.4 (*o-*, *o-*, *i-*, *p-*, *m-*, *m-Ar*), 110.5 (C_5H_5), 97.3 (γ-*C*H), 58.5 (OCH_2CH_3)), 28.8, 27.7 ($CH(CH_3)_2$), 25.7, 24.8, 24.8, 24.5 ($CH(CH_3)_2$), 23.4 (β-CH_3), 21.0 (OCH_2CH_3)), 18.8 (Zr*Me*) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1938 (w), 1872 (w), 1806 (w), 1591 (w), 1531 (m), 1318 (m), 1258 (m), 1177 (m), 1129 (w), 1100 (w), 1079 (w), 1018 (m), 936 (w), 876 (m), 853 (m), 794 (s), 761 (m), 723 (w), 666 (w), 638(w). EI-MS: *m/z* (%) 725.3 (100) [$M^+ - Me$]. Anal. Calcd for $C_{42}H_{59}AlN_2O_2Zr$ (742.1): C, 67.97; H, 8.01; N, 3.77. Found: C, 67.88; H, 7.94; N, 3.73.

$L^2AlOSiMe_3(\mu\text{-}O)ZrMeCp_2$ (19). Preparation of **19** was accomplished like that of **14** from $L^2AlOSiMe_3(OH)$ (**13**) (0.55 g, 1 mmol) and Cp_2ZrMe_2 (0.26 g, 1 mmol). Yield: 0.51 g (65%); mp 376–377 °C. ^{1}H NMR (500.13 MHz, C_6D_6): δ −0.20 (s, 3 H, Zr*Me*), 0.31 (s, 9 H, Si*Me*$_3$), 1.04 (d, $J = 6.8$ Hz, 6 H, CH*Me*$_2$), 1.27 (d, $J = 6.8$ Hz, 6 H, CH*Me*$_2$), 1.44 (d, $J = 6.8$ Hz, 6 H, CH*Me*$_2$), 1.50 (s, 6 H, C*Me*), 1.52 (d, $J = 6.8$ Hz, 6 H, CH*Me*$_2$), 3.11 (sept, $J = 6.8$ Hz, 2 H, C*H*Me$_2$), 3.53 (sept, $J = 6.8$ Hz, 2 H, C*H*Me$_2$), 4.95 (s, 1 H, γ-C*H*), 5.54 (s, 10 H, C_5H_5), 7.01–7.23 (m, *Ar*) ppm. ^{13}C NMR (125.76 MHz, C_6D_6): δ 171.3 (*C*N), 144.9, 143.2, 141.6, 127.3, 125.1, 124.5 (*o-*, *o-*, *i-*, *p-*, *m-*, *m-Ar*), 99.1 (γ-*C*H), 28.7, 27.5 ($CH(CH_3)_2$), 26.4, 25.2, 24.8, 24.6 ($CH(CH_3)_2$), 23.7 (β-CH_3), 17.5 (Zr*Me*), 3.5 ($Si(CH_3)_3$) ppm. ^{29}Si NMR (99.36 MHz, C_6D_6): δ −4.21 ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1587 (w), 1552 (w), 1525 (m), 1320 (m), 1252 (m), 1179 (m), 1160 (w), 1110 (w), 1052 (s), 1019 (m), 936 (m), 913 (s), 843 (m), 832 (m), 797 (s), 776 (m), 758 (m), 744 (m), 726 (m), 693 (w), 678 (w), 649 (w), 597 (w), 556 (m). EI-MS: *m/z* (%) 769.3 (100) [$M^+ - Me$]. Anal. Calcd for $C_{43}H_{63}AlN_2O_2SiZr$ (786.3): C, 65.69; H, 8.08; N, 3.56. Found: C, 65.44; H, 7.87; N, 3.50.

X-ray Structure Determination of 10–13 and 17. The data for all five compounds were collected from shock-cooled crystals at 100(2) K.[23] The data for **11** were collected on a Bruker SMART-APEX II diffractometer with a D8 goniometer, and the other structures were measured on a Bruker TXS-Mo rotating anode with

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[23] (a) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615–619. (b) Stalke, D. *Chem. Soc. Rev.* **1998**, *27*, 171–178.

APEX II detector on a D8 goniometer. Both diffractometers were equipped with a low-temperature device. The Bruker SMART-APEX II diffractometer used graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å. The Bruker TXS-Mo rotating anode used INCOATEC Helios mirror optics as radiation monochromator. The data of **10**−**13** and **17** were integrated with SAINT,[24] and an empirical absorption (SADABS) was applied.[25] The structures were solved by direct methods (SHELXS-97)[26] and refined by full-matrix least-squares methods against F^2 (SHELXL-97).[27] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. The positions of the hydrogen atoms in the OH groups were found with a difference Fourier analysis of the remaining electron density. The oxygen−hydrogen bond lengths were restrained to 0.84 Å, and the U_{iso} were constrained to 1.2 times the U_{eq} of the oxygen atoms. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. The CCDC numbers are listed in Table 1. Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Polymerization of Ethylene. The polymerization reactions were carried out on a high-vacuum line (10^{-5} Torr) in an autoclave (Buchi). In a typical experiment, 100 mL of dry toluene (from Na/K) was vacuum-transferred into the polymerization flask and saturated with 1.0 atm of rigorously purified ethylene. The catalyst (22.2 μmol) was taken in the Schlenk flask and appropriate MAO (1.6 M in toluene, Witco GmbH) was added. The mixture was stirred for 20 min to activate the catalyst. The catalyst solution was then quickly injected into the rapidly stirred flask using a gastight syringe. After a measured time interval, the polymerization was quenched by the addition of methanol (5 mL) and the reaction mixture was then poured into methanol (800 mL). The polymer was allowed to fully precipitate overnight and then collected by filtration, washed with fresh methanol, and dried.

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Supporting Information Available: Crystallographic data for **10**−**13** and **17** as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700969G

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