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$[Me_2Al(THF)_2]^+[\{Me_2Si(NDipp)_2\}_2Zr_2Cl_5]^-$ (Dipp = 2,6-Diisopropylphenyl), an Unusual Zirconium/Aluminum Ion Pair Containing a THF-Stabilized Dimethylaluminum Cation

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The bulky chelating dianion $Me_2Si(NDipp^-)_2$ has been used to synthesize $[\{Me_2Si(NDipp)_2\}ZrCl_2(THF)_2]$ (Dipp = 2,6-diisopropylphenyl). Reaction of Al_2Me_6 and $[\{Me_2Si(NDipp)_2\}ZrCl_2(THF)_2]$ affords the unusual ionic complex $[Me_2Al(THF)_2]^+[\{Me_2Si(NDipp)_2\}_2Zr_2Cl_5]^-$.

We have recently begun an exploration of new kinetically stabilizing σ- and π-ligand systems with sufficient bulk to enable the isolation of low-coordinate, reactive metal centers and unusual group 3 containing bimetallics.[1,2] As part of this general program of research we have now turned our attention to chelating silyl diamides of the form $Me_2Si(RN^-)_2$ (R = alkyl, aryl). This class of ligand has been extensively applied in the synthesis of main-group and transition-metal complexes.[3] It is somewhat surprising, therefore, that the dianion derived from the ligand precursor, **1** (Scheme 1), bearing the bulky yet readily available 2,6-diisopropylphenyl substituent, has not been exploited previously (despite the potential of **1** having been remarked upon over a decade ago).[4]

The past few years have witnessed an increasing interest in the use of polydentate amides as suitable spectator ligands in zirconium(IV) chemistry.[5] Many of these reports are motivated by the application of these complexes as new generation “nonmetallocene” olefin polymerization catalysts.[6] The catalytic species are commonly generated in situ by activation with a large (typically 500 equiv) excess of commercially available methylalumoxane (MAO).[7] This ill-defined material can contain up to 40% unreacted trimethylaluminum and produces, via a series of alkylation and alkide abstraction reactions, a catalytically active zirconium alkyl cation.[8] It is now recognized that this active species is merely a single component in a set of complex solution equilibria that consist predominantly of dormant species.[9] The isolation and identification of defined reaction products from treatment of typical zirconium “precatalysts” with stoichiometric quantities of trialkylaluminum reagents may provide insight into the nature of these solution equilibria. For example, Stephan has recently sought to model the interaction of zirconium phosphinimide catalyst precursors with MAO by reaction with $AlMe_3$. This allowed the identification of the zirconium cluster compounds $(Cp^*Zr)_4(\mu\text{-}Cl)_5(Cl)(\mu\text{-}CH)_2$ and $(Cp^*Zr)_5(\mu\text{-}Cl)_6(\mu\text{-}CH)_3$, which were presented as possible products of catalyst decomposition pathways.[10] With similar intent, we now wish to report the application of **1** in the synthesis of the chelated diamido−zirconium dichloride **3** and the stoichiometric reaction of **3** with trimethylaluminum (Scheme 1).

Results and Discussion

The amine precursor **1** was synthesized by a method similar to that reported for $[Me_2Si(MesNH)_2]$ (Mes = 2,4,6-trimethylphenyl).[4] Compound **1** may be conveniently deprotonated with 2 equiv of ^nBuLi in hexane. Under these conditions **2** precipitates as a colorless powder, giving NMR data identical with those of an analytically pure crystalline sample obtained from concentrated hexane solution. Crystals of the dilithium derivative **2** were subjected to a single-crystal X-ray diffraction study. Compound **2** crystallizes as discrete dimeric molecules with no crystallographically imposed symmetry. There are two independent but chemically identical molecules in the asymmetric unit, one of which is illustrated in Figure 1. The dimeric units of **2** are reminiscent of those in the structure of $[Me_2Si(t\text{-}BuNLi)_2]_2$,[11] in that the primary coordination of the

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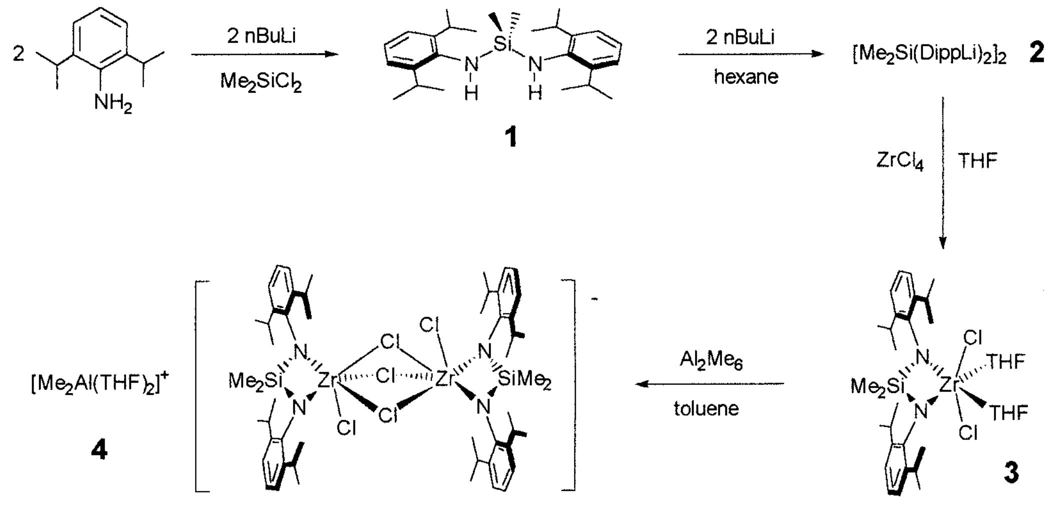
10.1021/om0201819 CCC: $22.00

Scheme 1



lithium atoms is provided by the nitrogen centers. The N_4Li_4 core is shown in Figure 2. Li(2) and Li(3) are bound by three nitrogen atoms, which gives rise to approximate trigonal-pyramidal coordination for these metals. Li(1) and Li(4) are also coordinated by two short Li−N interactions and by two close contacts to the ipso carbon atoms of the Dipp substituents. While this results in the loss of the approximate D_{2d} symmetry observed in $[Me_2Si(t\text{-}BuNLi)_2]_2$,[11] the formation of a "ladder" structure, directed by the formation of η^6-aryl to lithium interactions, like that of $[Me_2Si(MesNLi)_2]_2$, is prevented by the greater steric demands of the isopropyl groups.[4]

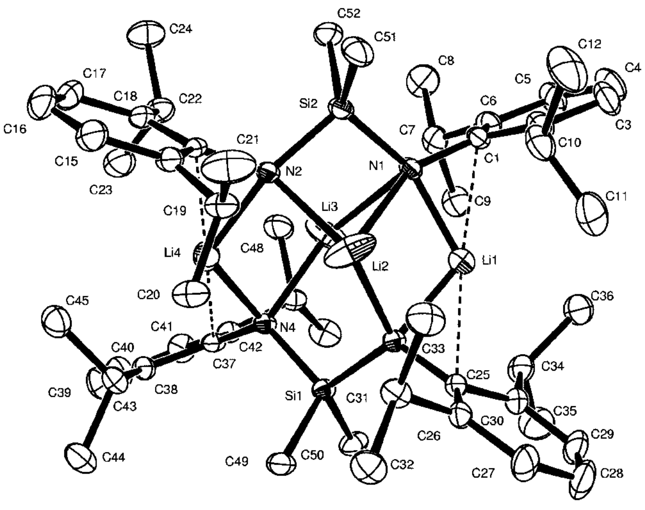


Figure 1. Molecular structure of **2** (25% probability ellipsoids). H atoms were omitted for clarity. Selected bond lengths (Å): Li(1)−N(1), 1.930(10); Li(1)−N(3), 1.959(10); Li(1)···C(1), 2.312(10); Li(1)···C(25), 2.436(11); Li(2)−N(3), 1.993(10); Li(2)−N(2), 2.111(12); Li(2)−N(1), 2.269(14); Li(3)−N(4), 2.028(10); Li(3)−N(1), 2.149(11); Li(3)−N(2), 2.222(11); Li(4)−N(4), 1.883(10); Li(4)−N(2), 1.952(10); Li(4)···C(13), 2.208(10).

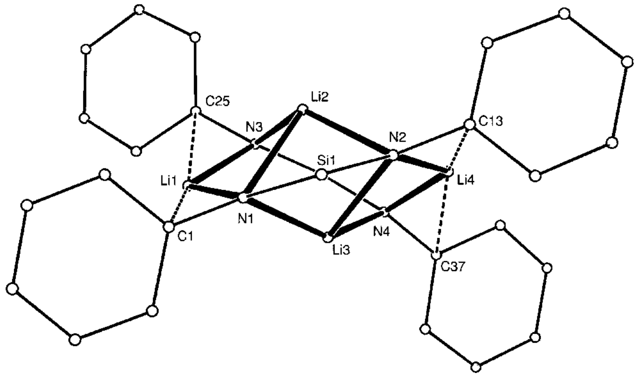


Figure 2. Ball and stick representation of the N_4Li_4 core of **2**.

The highly sterically demanding Dipp susbstituent has been employed in McConville's chelated diamidozirconium olefin polymerization catalysts.[12] Zirconium complexes supported by silyl diamides similar to **2** but bearing less sterically demanding substituents have been reported previously,[13] and N-substituted 2,6-dimethylphenyl derivatives have been studied in the context of olefin polymerization catalysis.[14] Initial attempts to synthesize base-free zirconium derivatives of **1** in wholly hydrocarbon solvents were unsuccessful. However, reaction of **2** with 1 equiv of $ZrCl_4$ in THF provided, upon crystallization from toluene, the colorless zirconium dichloride complex **3** in high (80%) yield. Like the previously reported $[\{Me_2Si(t\text{-}BuN)_2\}ZrCl_2(THF)_2]$[15] and $[CH_2(CH_2NSiMe_3)_2ZrCl_2(THF)_2]$,[16] complex **3** contains two molecules of THF per zirconium center. **3** is robust in solution, and ^1H NMR studies undertaken in C_6D_6 or d_8-toluene indicate none of the partial loss or exchange of THF reported for $[\{Me_2Si(t\text{-}BuN)_2\}ZrCl_2(THF)_2]$.[15] The methyl groups of the isopropyl substituents are diastereotopic and appear as two doublets in the ^1H NMR spectrum. We interpret this to be a consequence of restricted rotation about the N−C_{ipso} bonds.[12]

Such steric interactions were also evident in the solid-state structure of **3**, determined by an X-ray diffraction

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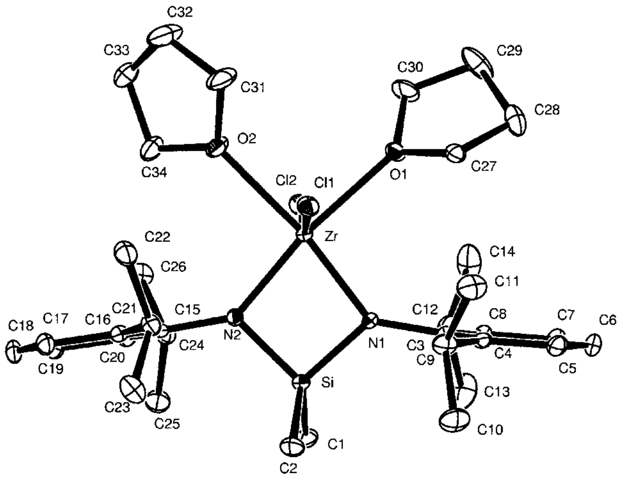


Figure 3. Molecular structure of **3** (25% probability ellipsoids). H atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr−N(1), 2.050(2); Zr−N(2), 2.051(2); Zr−Cl(1), 2.473(1); Zr−Cl(2), 2.473(1); Zr−O(1), 2.312(2); Zr−O(2), 2.326(2); N(1)−Zr−N(2), 76.83(9); N(2)−Zr−O(1), 170.98(9); N(1)−Zr−O(1), 95.21(8); N(2)−Zr−O(2), 95.37(9); N(1)−Zr−O(2), 170.58(10); O(1)−Zr−O(2), 92.93(8); N(2)−Zr−Cl(2), 96.62(7); N(1)−Zr−Cl(2), 103.35(7); O(1)−Zr−Cl(2), 80.95(6); O(2)−Zr−Cl(2), 82.60(7); N(2)−Zr−Cl(1), 102.24(7); N(1)−Zr−Cl(1), 96.72(7); O(1)−Zr−Cl(1), 82.70(6); O(2)−Zr−Cl(1), 79.60(7); Cl(2)−Zr−Cl(1), 155.10(3).

study (Figure 3). This revealed distorted-octahedral coordination at zirconium and confirmed the overall C_2 symmetry inferred from the multinuclear NMR studies. The nitrogen atoms of the chelating diamide and the cis oxygen atoms of the THF ligands define a plane around Zr (the rms deviation of the N1N2O1O2ZrSi plane is 0.0831 Å). Despite the small bite of the diamido chelate (N(1)−Zr−N(2) = 76.84(2)°), the Cl(1)−Zr−Cl(2) angle is somewhat bent from linearity (155.09(3)°) by the steric compression caused by the large Dipp substituents.

Complex **4** was obtained as large colorless crystals in ca. 60% isolated yield after reaction of **3** with 1 equiv of Al_2Me_6 in toluene and crystallization from the same solvent. **4** was shown by X-ray diffraction analysis to be the ionic complex $[Me_2Al(THF)_2]^+[\{Me_2Si(NDipp)_2\}_2Zr_2Cl_5]^-$ (Figure 4). The solid-state structure of **4** comprises a bis-THF-solvated dimethylaluminum cation and a dinuclear zirconium anion in which the coordination sphere of each six-coordinate zirconium center is provided by chelation of a single diamido ligand, three bridging chlorides, and a single terminal chloride.

Compound **4** may have formed as the result of a series of reaction steps initiated by partial methylation of zirconium to form Me_2AlCl. Subsequent fast chloride abstraction by the remaining **3** from Me_2AlCl and stabilization of the resultant alumocenium cation by coordination of THF would then result in the formation of **4**. We have not yet been successful in the isolation of other products from this reaction. However, examination of the brown glassy solid remaining after evaporation of volatiles from the mother liquor of **4** by ^1H NMR in C_6D_6 indicated a complex mixture containing the intact diamido ligand and coordinated THF, along with multiple methylaluminum or methylzirconium environments. The isolated yield of **4** is consistent with an overall reaction stoichiometry similar to that tentatively proposed by eq 1, in which Al_2Me_6 acts both as a methylating reagent and as a Lewis acid capable of abstracting residual THF from the coordination sphere of **3**.

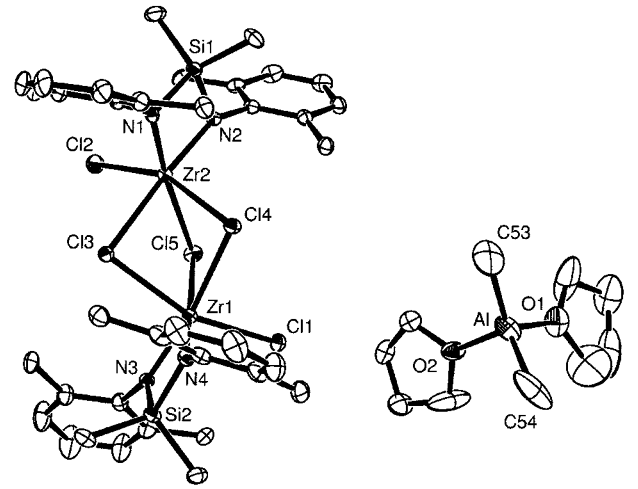
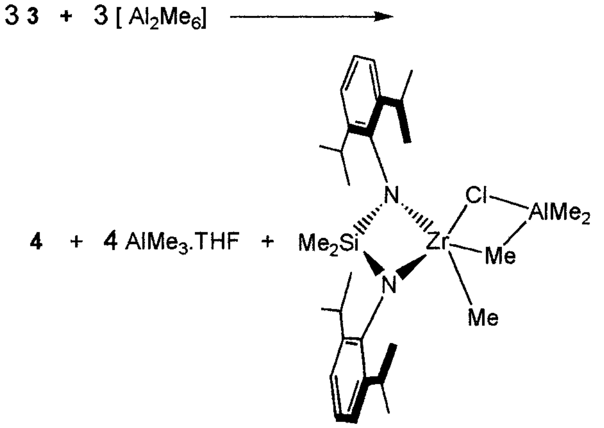


Figure 4. Molecular structure of **4** (25% probability ellipsoids). Isopropyl Me groups were omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr(1)−N(4), 2.014(5); Zr(1)−N(3), 2.029(4); Zr(1)−Cl(1), 2.457(2); Zr(1)−Cl(3), 2.611(2); Zr(1)−Cl(4), 2.655(2); Zr(1)−Cl(5), 2.694(2); Al−O(1), 1.822(7); Al−O(2), 1.849(5); Al−C(54), 1.924(11); Al−C(53), 1.931(11); O(1)−Al−O(2), 97.0(3); O(1)−Al−C(54), 104.4(6); O(2)−Al−C(54), 107.4(4); O(1)−Al−C(53), 109.2(5); O(2)−Al−C(53), 107.3(4); C(54)−Al−C(53), 127.4(7).



(1)

Although, to the best of our knowledge, the isolation of an ion pair of this general structure is unprecedented, complex equilibria that include similar alkylation reactions have long been acknowledged as a characteristic of both homogeneous and heterogeneous Ziegler−Natta chemistry.[17] Variable-temperature ^1H and ^{13}C NMR studies in d_8-toluene suggested that such equilibria may be established upon redissolving a pure sample of **4** (see the Supporting Information). The ^1H and ^{13}C NMR spectra at 348 K revealed the presence of three species that exist in an approximate 6:3:1 ratio. These were identified by selective decoupling of the observed isopropyl methine protons at 3.83 (major), 3.24, and 2.72 ppm (minor) from the respective ligand methyl resonances at 1.24, 1.13, and 1.05 ppm in the ^1H NMR. Spin saturation transfer experiments at this temperature,

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however (using 2 s of irradiation on the peak of interest), showed no sign of exchange between any of the solution components. Although this behavior may also be a result of decomposition at the elevated temperature of the experiment, it is not currently possible to assign the identity of any of these species to a structure corresponding to compound **4**. The observation of both bound and free THF (in a 2:1 ratio by integration) indicates that the integrity of the $[Me_2Al(THF)_2]^+$ cation is also not maintained in solution at 348 K. When a sample of **4** is cooled, complex reversible changes occur. At 248 K at least six separate sets of signals (that broaden with further cooling to 198 K) may be assigned to ligand isopropyl groups. The upfield signals (>ca. −0.5 ppm) arising from the aluminum-bonded methyl groups of **4** behave in a similarly complex manner. It is, however, not possible to distinguish between Al−Me and Zr−Me signals.

It is possible to regard compound **4** as an intermediate in an alkylation sequence reminiscent of those proposed for systems relevant to practical homogeneous olefin polymerization. There has been recent interest in the application of low-coordinate organoaluminum cations as catalysts for olefin polymerization in their own right,[18] and organoaluminum cations of the form $[R_2Al(donor)_2]^+$ have also been shown to act as activators in polymerization catalysis.[19] Studies of other model systems have shown that alumoxanes themselves can display Lewis base character.[20] The formation of cationic organoaluminum species effectively "immobilized" upon the Al−O−Al framework of MAO, and the possible mechanistic implications of their existence, cannot therefore be discounted. Studies are continuing, to discover the reactivity of **3** with other tri- and diorganoaluminum reagents and to clarify the behavior of **4** in solution.

Experimental Section

General Considerations. All reactions were conducted under an atmosphere of dry argon and manipulated either on a double-manifold vacuum line or in a dintrogen-filled drybox operating at less than 1 ppm of O_2. Solvents were purified by distillation from an appropriate drying agent (toluene and THF from potassium, diethyl ether from Na/benzophenone, and hexane from Na/K alloy). NMR spectra were recorded on a Bruker AMX 500 instrument at 300.13 (^1H), 125.8 (^{13}C), 99.4 (^{29}Si), and 116 MHz (^7Li) from samples in C_6D_6, chemical shifts are given relative to $SiMe_4$ and aqueous LiCl, and intensities of the quaternary and ^{29}Si signals were enhanced by INEPT polarization transfer. Mass spectra were obtained on a Fisons Instruments VG Autospec spectrometer at 70 eV.

$Me_2Si(DippNH)_2$ (1; Dipp = 2,6-*i*-$Pr_2C_6H_3$). A solution of ^{n}BuLi (18.1 mL of a 2.5 M solution in hexane) was added to a stirred solution of freshly distilled H_2NDipp (8.0 g, 45.2 mmol) in diethyl ether (150 mL) at −78 °C. The pale yellow solution was warmed to room temperature before being recooled to −78 °C. Dropwise addition of a solution of Me_2SiCl_2 (2.92 g, 22.6 mmol) in diethyl ether (20 mL) produced a hazy solution that was warmed to room temperature. This was filtered to remove precipitated LiCl before evaporation of volatiles to yield **1** in stoichiometric yield as a colorless viscous oil which crystallized on standing. Anal. Calcd for $C_{26}H_{42}N_2Si$: C, 76.01; H, 10.33; N, 6.82. Found: C, 76.28; H, 10.50; N, 6.70. ^1H NMR: δ 0.21 (s, 6H, $SiMe_2$), 1.17 (d, 24H, $CH(CH_3)_2$), 2.63 (s, 2H, NH), 3.51 (sept, 4H, $CH(CH_3)_2$), 7.09 (d, 4H, H_{meta}), 7.15 (s, 2H, H_{para}). $^{13}C\{^1H\}$ NMR: δ 0.0 ($SiMe_2$), 23.8 ($CH(CH_3)_2$), 28.6 ($CH(CH_3)_2$), 123.5 (C_{meta}), 124.5 (Ar−^{i}Pr), 138.7 (C_{ipso}), 144.5 (C_{para}). ^{29}Si NMR: δ −8.3.

$[Me_2Si(DippNLi)_2]_2$ (2). A solution of ^{n}BuLi (4.9 mL of a 2.5 M solution in hexane) was added dropwise to a stirred solution of **1** (2.50 g, 6.10 mmol) in hexane (40 mL) at room temperature, producing an exothermic reaction and a colorless precipitate. Filtration and washing with hexane (25 mL) yielded **2** as a colorless pyrophoric powder (2.11 g, 82%). Crystals suitable for a single-crystal X-ray diffraction analysis were isolated upon concentration of the combined hexane washings. Anal. Calcd for $C_{52}H_{80}Li_4N_4Si_2$: C, 73.88; H, 9.56; N, 6.64. Found: C, 73.81; H, 9.54; N, 6.64. ^1H NMR: δ 0.01 (s, 6H, $SiMe_2$), 1.26 (d, 24H, $CH(CH_3)_2$), 3.71 (sept, 4H, $CH(CH_3)_2$), 6.88 (t, 2H, H_{para}), 7.01 (d, 4H, H_{meta}). $^{13}C\{^1H\}$ NMR: δ 4.0 ($SiMe_2$), 24.6 ($CH(CH_3)_2$), 27.4 ($CH(CH_3)_2$), 121.0 (Ar−^{i}Pr), 125.2 (C_{meta}), 144.1 (C_{para}), 147.7 (C_{ipso}). ^7Li NMR: δ 1.97. ^{29}Si NMR: δ −15.9.

$[Me_2Si(DippN)_2ZrCl_2(THF)_2]$ (3). A solution of **2** (0.98 g, 2.32 mmol) in THF (20 mL) was added dropwise to a solution of $ZrCl_4$ (0.54 g, 2.32 mmol) in THF (25 mL) at −78 °C. The pale yellow reaction mixture was warmed to room temperature and stirred for a further 2 h, after which the solvent was removed under vacuum. The product was extracted with toluene (30 mL) and filtered to remove LiCl. Concentration to ca. 15 mL and crystallization at room temperature gave **3** as colorless blocklike crystals suitable for an X-ray diffraction analysis (1.31 g, 79.4%). Anal. Calcd for $C_{34}H_{50}Cl_2N_2O_2SiZr$: C, 57.55; H, 7.05; N, 3.95. Found: C, 57.58; H, 6.92; N, 3.86. ^1H NMR: δ 0.45 (s, 6H, $SiMe_2$), 1.07 (m, 8H, THF), 1.39 and 1.48 (d, 24H, $CH(CH_3)_2$), 3.77 (m, 8H, THF), 4.37 (sept, 4H, $CH(CH_3)_2$), 7.08 (t, 2H, H_{para}), 7.19 (d, 4H, H_{meta}). $^{13}C\{^1H\}$ NMR: δ 2.9 ($SiMe_2$), 24.9 (THF), 25.7 ($CH(CH_3)_2$), 27.1 ($CH(CH_3)_2$), 27.4 ($CH(CH_3)_2$), 72.6 (THF) 123.9 (Ar−^{i}Pr), 124.5 (C_{meta}), 143.8 (C_{para}), 145.0 (C_{ipso}). ^{29}Si NMR: δ −33.7. MS: *m/z* 644 (25, M^+ − THF).

$[Me_2Al(THF)_2][\{Me_2Si(NDipp)_2\}_2Zr_2Cl_5]$ (4). A solution of **3** (0.85 g, 1.20 mmol) in toluene (30 mL) was treated at room temperature with Al_2Me_6 (2.0 M in hexane, 0.60 mL) and the resulting gray solution stirred for 2 h. Concentration to incipient crystallization (ca. 15 mL) followed by warming and slow cooling to room temperature produced **4**·$3C_7H_8$ as large colorless crystals (0.45 g, 45%). A further crop of analytically pure crystalline material (0.15 g, 15%) was obtained upon cooling the residual mother liquor to −30 °C. Anal. Calcd for $C_{83}H_{126}N_4AlCl_5O_2Si_2Zr_2$: C, 60.19; H, 7.61; N, 3.38. Found: C, 59.94; H, 7.52; N, 3.28.

Crystallographic Measurements. Crystal data for **2**: $C_{52}H_{80}Li_4N_4Si_2$, M_r = 845.14, triclinic, space group $P\bar{1}$ (No. 2), a = 13.1790(8) Å, b = 20.5792(9) Å, c = 20.6279(13) Å, α = 86.418(4)°, β = 86.917°, γ = 75.749(4)°, U = 5407.5(5) Å^3, T = 250(2) K, Z = 4, D_c = 1.04 g cm^{-3}, 26 135 reflections, 12 999 unique reflections (R_{int} = 0.057), 9173 reflections with $I > 2\sigma(I)$; R1, wR2 = 0.072, 0.191 ($I > 2\sigma(I)$) and 0.107, 0.214 (all data). Crystal data for **3**: $C_{34}H_{50}N_2O_2Cl_2SiZr$, M_r = 708.97, monoclinic, space group $P2_1/c$ (No. 14), a = 10.4851(3) Å, b = 18.5447(7) Å, c = 19.1721(5) Å, β = 95.139(2)°, U = 3712(2) Å^3, T = 173(2) K, Z = 4, D_c = 1.27 g cm^{-3}, 16 064 reflections, 6532 unique reflections (R_{int} = 0.053), 4945 reflections with $I > 2\sigma(I)$; R1, wR2 = 0.041, 0.105 ($I > 2\sigma(I)$) and 0.064, 0.116 (all data). Crystal data for **4**·3(toluene): $C_{83}H_{126}AlN_4O_2Cl_5Si_2Zr_2$, M_r = 1654.73, triclinic, space group $P\bar{1}$ (No. 2), a = 16.2531(9) Å, b = 17.1893(9) Å, c = 18.3172(10) Å, α = 79.160(3)°, β = 67.470(2)°, γ = 69.910(3)°, U = 4429.9(4) Å^3, T

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$= 173(2)$ K, $Z = 2$, $D_c = 1.24$ g cm^{-3}, 30 797 reflections, 15 489 unique reflections ($R_{int} = 0.059$), 11 103 reflections with $I > 2\sigma(I)$; R1, wR2 = 0.072, 0.153 ($I > 2\sigma(I)$) and 0.107, 0.168 (all data). Data were collected on a KappaCCD diffractometer (μ(Mo Kα) = 0.710 73 Å). The structures were solved by direct methods (SHELXS-97)[21] and refined by full-matrix least squares (SHELXL-97)[22] with non-H atoms anisotropic and H atoms included in the riding mode. In **2** an absorption correction was not applied, and in **3** and **4** the data were corrected for absorption effects using MULTISCAN.

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Supporting Information Available: Figures giving ^{1}H and ^{13}C NMR spectra of **4** at 248 and 348 K and tables giving details of crystal data and structure refinement, atom coordinates, equivalent isotropic displacement factors, bond lengths and angles, and hydrogen coordinates for **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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