Bis(triisopropylsilyl)-*o*-phenylenediamido Complexes of Titanium and Zirconium: Investigation of a New Ancillary Ligand

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From the dilithio reagent *o*-$C_6H_4(NLiSi^iPr_3)_2$ (**2**), the new complexes [*o*-$C_6H_4(NSi^iPr_3)_2]_2Zr$ (**3**), [*o*-$C_6H_4(NSi^iPr_3)_2]Zr(O^tBu)_2$ (**4**), [*o*-$C_6H_4(NSi^iPr_3)_2]TiCl_2$ (**5**), and [*o*-$C_6H_4(NSi^iPr_3)_2]TiMe_2$ (**6**) have been prepared. X-ray crystallographic and variable-temperature NMR studies characterize these complexes as possessing η^4-$C_6H_4(NSi^iPr_3)_2$ ligands (bonded to the metal via two carbon atoms in the phenylene group), which undergo a $\eta^4-\eta^2$ fluxional process in solution.

In recent years, the chemistry of d^0 metal complexes has emerged as a major frontier in the search for new metal-mediated transformations. Work in this area is still dominated by complexes with ancillary cyclopentadienyl ligands, a class of compounds which were first introduced by Wilkinson in the mid 1950s.[1] Especially given the notable breakthroughs that have recently been based on early-transition-metal chemistry (in coordination polymerizations,[2] hydrocarbon activations,[3] various catalytic reactions,[4] etc.), it is of interest to explore further possibilities with these metals by examining their chemical properties with varied, and even less traditional, coordination environments. Ligand design studies have in fact allowed significant advances in the use of d^0 metal complexes as catalysts for olefin polymerizations,[2] oxidations,[5] and hydrogenations.[6]

Considerable interest in d^0 metal complexes is associated with their ability to participate in σ-bond metathesis processes which activate chemical bonds.[3,7] Of particular interest to us is the activation of Si−H and Sn−H bonds, which may be incorporated into a catalytic cycle to achieve the dehydropolymerization of silanes and stannanes to σ-conjugated polymers.[8] This polymerization chemistry would find wider application if improved catalysts providing greater control over molecular weight properties for the resulting polymers could be developed. Unfortunately, there is little definitive information available to suggest which steric and electronic factors might contribute to higher activity toward σ-bond metathesis. However, our studies on catalyst design indicate that good dehydropolymerization catalysts are electrophilic metal hydride complexes that are sterically stabilized as monomers.[9] Thus, one strategy for designing new catalysts is based on use of sterically hindered ancillary ligands that will enforce coordinative unsaturation. Bulky silyl amide ligands have already gained a reputation for supporting reactive, electrophilic metal centers, and early-metal derivatives have provided new C−H bond activation processes.[10] More recently, considerable attention has focused on development of chemistry supported by multidentate silyl amide ligands.[11] In this contribution, we describe

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Table 1. Selected Bond Distances (Å) and Angles (deg) for $[C_6H_4(NSi^iPr_3)_2]_2Zr$ (3)[a]

(a) Bond Distances

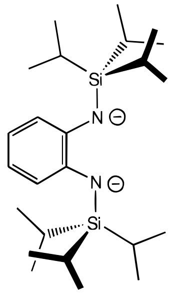
Zr(1)−N(1)	2.078(6), 2.087(6)	N(1)−Si(2)	1.759(6), 1.750(6)	Zr(1)−C(37)	2.597(7), 2.599(7)	N(1)−C(37)	1.460(9), 1.449(9)
Zr(1)−N(2)	2.081(5), 2.087(6)	N(2)−Si(4)	1.747(6), 1.757(6)	Zr(1)−C(42)	2.602(7), 2.652(7)	N(2)−C(42)	1.432(8), 1.440(9)
Zr(1)−N(3)	2.067(5), 2.061(6)	N(3)−Si(3)	1.753(6), 1.744(6)	Zr(1)−C(43)	2.603(7), 2.591(7)	N(3)−C(43)	1.419(9), 1.432(9)
Zr(1)−N(4)	2.093(6), 2.083(6)	N(4)−Si(1)	1.755(6), 1.760(6)	Zr(1)−C(48)	2.563(7), 2.578(7)	N(4)−C(48)	1.423(9), 1.433(9)

(b) Bond Angles

N(1)−Zr(1)−N(2)	86.8(2), 87.0(2)	Zr(1)−N(2)−Si(4)	136.9(3), 133.6(3)	N(1)−Zr(1)−N(4)	136.3(2), 136.0(2)	C(42)−N(2)−Si(4)	126.0(4), 126.5(5)
N(3)−Zr(1)−N(4)	85.3(2), 86.0(2)	Zr(1)−N(3)−Si(3)	137.9(3), 141.8(3)	N(2)−Zr(1)−N(4)	118.1(2), 119.1(2)	C(43)−N(3)−Si(3)	127.0(4), 124.2(4)
N(1)−Zr(1)−N(3)	120.7(2), 117.4(2)	Zr(1)−N(4)−Si(1)	144.8(3), 144.8(3)	Zr(1)−N(1)−Si(2)	146.3(3), 144.9(3)	C(48)−N(4)−Si(1)	123.5(5), 122.7(5)
N(2)−Zr(1)−N(3)	110.9(2), 113.1(2)	C(37)−N(1)−Si(2)	118.0(4), 118.4(4)				

[a] The second number is the corresponding geometrical parameter for the second independent molecule in the unit cell.

initial investigations into use of the chelating silyl amide ligand **A** in early-transition-metal chemistry.



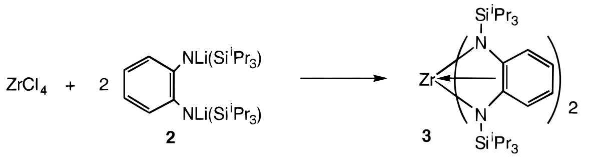
A

Results and Discussion

The dilithio salt **2** was obtained by the sequence of steps shown in eq 1. Both **1** and **2** are highly soluble in pentane but may be crystallized from that solvent at −78 °C. Compound **2** was isolated, and stored as a crystalline solid, and used as a reagent in the synthetic studies described below. Alternatively, **2** may be employed as a reagent generated *in situ* by addition of ^nBuLi to **1**.

$$o\text{-}C_6H_4(NH_2)_2 \xrightarrow[(2)\ 2^iPr_3SiCl]{(1)\ 2^nBuLi} \underset{\mathbf{1}}{o\text{-}C_6H_4(NHSi^iPr_3)_2} \xrightarrow{2^nBuLi} \underset{\mathbf{2}}{o\text{-}C_6H_4(NLiSi^iPr_3)_2} \quad (1)$$

The initial goal of this investigation was to produce the zirconium complex $[o\text{-}C_6H_4(NSi^iPr_3)_2]ZrCl_2$, which was expected to serve as a synthetic precursor to various alkyl, hydride, and silyl derivatives of the type $[o\text{-}C_6H_4(NSi^iPr_3)_2]ZrR_2$, which could be studied as catalyst precursors. For this purpose, we examined the reaction of $ZrCl_4$ with 1 equiv of **2** in refluxing benzene. This reaction produced a single new product (**3**) isolated as yellow prisms from pentane. Preliminary qualitative analysis tests indicated the absence of both chlorine and lithium in this product, and the combustion analysis was consistent with the formula $[o\text{-}C_6H_4(NSi^iPr_3)_2]_2Zr$ (34% isolated yield; eq 2). The NMR spectra were more complicated than expected and revealed only resonances assignable to the diamide ligand. Thus, the ^1H and ^{13}C NMR spectra contain four $-Si(CHMe_2)_3$ and two $-Si(CHMe_2)_3$ resonances. The ^{29}Si NMR spectrum contains two resonances, at 4.25 and 8.26 ppm. No coalescence behavior was observed on heating a benzene-d_6 solution of the compound to 100 °C (by ^1H NMR spectroscopy).



(2)

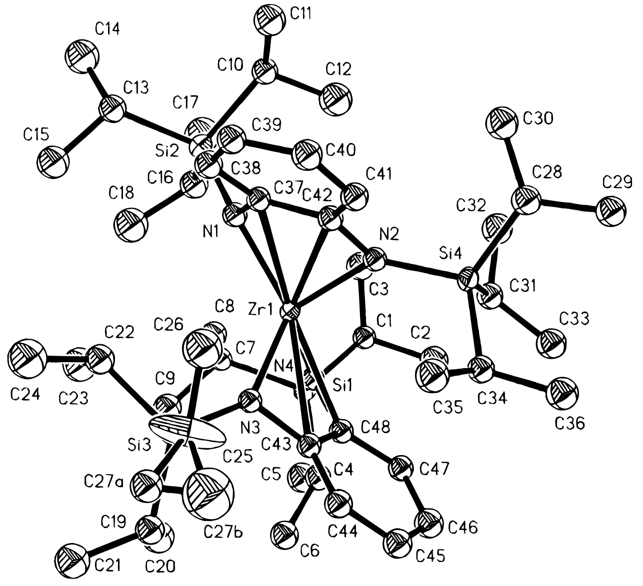


Figure 1. ORTEP view of the molecular structure of $[C_6H_4(NSi^iPr_3)_2]_2Zr$ (**3**).

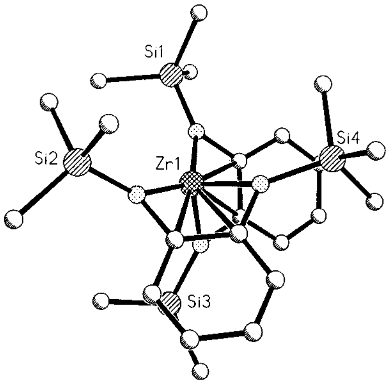


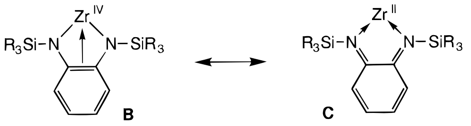
Figure 2. Alternative view of **3**, perpendicular to the molecular C_2 axis (noncrystallographic).

A view of the molecular structure of **3**, determined by X-ray crystallography, is shown in Figure 1. The unit cell contains two independent molecules with very similar geometrical parameters (Table 1). In these molecules, both diamide ligands are coordinated in a η^4 fashion via donation of electron density from the phenylene ring to the metal. Thus, the five-membered chelate rings are not planar and are folded along the N−N axis by 51° (average of four angles). As seen in Figure 2, this folding gives the molecule a rather "lopsided" appearance, with most bonds to the metal lying in one hemisphere of coordination. In solution, the two ligands on each Zr atom are related by a C_2 axis, such that there are two chemically equivalent pairs of silyl groups per molecule, giving rise to two distinct resonances for the methyne groups and four resonances for the diastereotopic methyl groups.

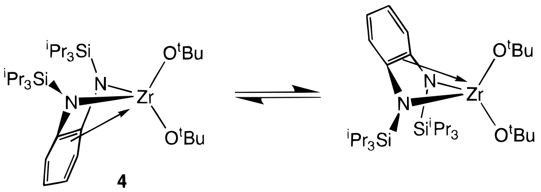
A similar coordination mode has recently been reported for the $[\eta^4\text{-}C_6H_4(NSiMe_3)_2]^{2-}$ ligand in $[o\text{-}C_6H_4(NSiMe_3)_2]W({=}NPh)Cl_2$ and $[o\text{-}C_6H_4(NSiMe_3)_2]W{=}NPh(PMe_3)(CH_2CMe_3)$.[11g] Related structures have been observed for other chelating ligands containing bridging 1,2-phenylene groups.[12] For example, Schaverien and co-workers have reported the structure of $Cr(N^tBu)_2[o\text{-}C_6H_4(CHSiMe_3)_2]$, which exhibits a fold angle for the chelate ring of 67°.[12a] In addition, Rothwell and co-workers have investigated a number of η^4-enediamido complexes obtained by the intramolecular coupling of η^2-iminoacyl ligands.[13]

The N−Zr−N angles associated with each chelate ring are fairly acute (average 86.3°), and the Zr−N bond lengths (average 2.08 Å) resemble previously reported distances in Zr(IV) silyl amide complexes.[14] The Zr−C bond distances (average 2.60 Å) reflect relatively strong donation from the aromatic ring to the metal, as seen by comparisons to Zr−C distances in other complexes which result from coordination of a π-system to Zr(IV). In $Zr(OC_6H_3\text{-}2,6\text{-}{}^tBu_2)_2[\eta^4\text{-}(Xyl)NCMe{=}CMeN(Xyl)]$ (Xyl = 2,6-$Me_2C_6H_3$), the Zr−C distances are 2.70 Å.[13a] Also, the Zr−C_β distances in $Cp_2Zr(\sigma^2,\pi\text{-diene})$ complexes range from 2.55 to 2.71 Å,[15] and the Zr−C_{ipso} distances in $Cp_2Zr(\eta^2\text{-benzyl})(L)^+$ are 2.63−2.65 Å.[16] Note that the Zr−C distances in the arene complex $(\eta^6\text{-}C_6Me_6)ZrCl_2(\mu\text{-}Cl)_3ZrCl_3$ are longer (2.72−2.77 Å).[17] Despite the observed "folding" of the ligands to accommodate arene-to-metal donation, the nitrogen atoms maintain a planar, sp^2 environment, as seen by the summation of angles at the N atoms (average 358.1°).

The η^4-bonding of the diamido ligand in **2** suggests the possible contribution of two resonance forms (**B** and **C**). However, the geometrical parameters for **2** are most consistent with the σ^2,π resonance structure **B**. Thus, the N−C distances of 1.42−1.46 Å are quite consistent with single-bond distances. For diimine complexes that can be represented by structure **C**, the C−N distances are approximately 1.28 Å.[18] In addition, the Zr−N distances reflect the presence of single covalent (rather than dative) bonds.[13a]



A second attempt to obtain a complex of the type $[o\text{-}C_6H_4(NSi^iPr_3)_2]ZrX_2$ was based on reaction of **2** with the more substitutionally inert starting material $Zr(O^tBu)_4$. The reaction of **2** (generated in situ from **1** and ^nBuLi) with $Zr(O^tBu)_4$ in diethyl ether produced the desired complex (**4**) as colorless crystals from pentane. This air-sensitive compound is somewhat difficult to separate completely from the LiO^tBu byproduct, but fractional crystallizations allowed isolation of pure material in 66% yield. At room temperature the resonance for the $-O^tBu$ ligands in **4** is relatively broad, and decoalescence into two distinct peaks occurs at −10 °C. At lower temperature, the resonance for the $-Si(CHMe_2)_3$ methyl groups also decoalesces (T_c = −40 °C), into two doublets. The low-temperature spectra indicate that the diamide ligand in **4** is bonded to Zr in an η^4 fashion, as observed for **3**, and the coalescence behavior is then readily explained in terms of the fluxional process of eq 3. A variable-temperature ^1H NMR study provided a free energy of activation for this process of 12.3 ± 0.5 kcal mol^{-1}.



4

(3)

Efforts to derivatize compound **4** via substitution of the $-O^tBu$ groups have so far proven unsuccessful. For example, **4** does not react with Me_3SiCl (3 days, 70 °C), MeCOCl (7 days, room temperature), MeMgBr (12 h, room temperature), $(THF)_3LiSi(SiMe_3)_3$ (7 days, room temperature), or $(THF)_3LiSiPh_3$ (7 days, room temperature).

Reaction of diamide **2** with $TiCl_4{\cdot}2THF$ results in formation of the dark red dichloride $[o\text{-}C_6H_4(NSi^iPr_3)_2]TiCl_2$ (**5**). This complex is highly pentane-soluble and difficult to recover completely from hydrocarbon solvents via crystallization. By using hexamethyldisiloxane as the crystallization solvent, the compound was crystallized from solution at −78 °C in 33% total yield. An ORTEP diagram of this compound is shown in Figure 3, and selected distances and angles are listed in Table 2. Also in this complex, the diamide ligand coordinates its phenylene group to the metal, leading to a fold angle for the chelate ring (along the N−N vector) of 56.9°. The nitrogen atoms are in a planar environment, as shown by the summation of bond angles at N(1) (359.2°) and N(2) (358.9°). The Ti−N distances of 1.88 Å are at the low end of the known range for bond lengths of this type

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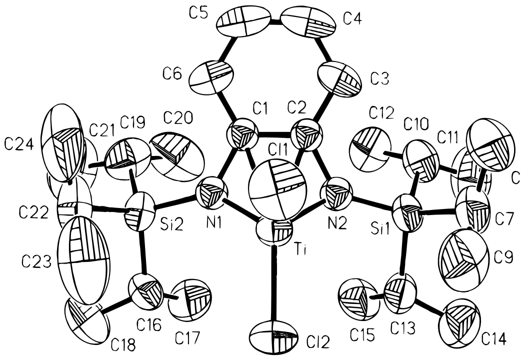


Figure 3. ORTEP view of the molecular structure of $[C_6H_4(NSi^iPr_3)_2]TiCl_2$ (**5**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[C_6H_4(NSi^iPr_3)_2]TiCl_2$ (5)

(a) Bond Distances

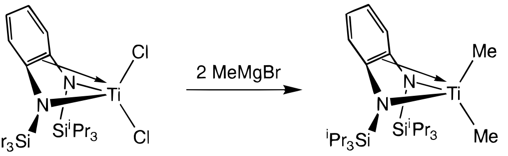
Ti−N(1)	1.878(4)	Ti−C(2)	2.353(4)
Ti−N(2)	1.883(4)	N(1)−Si(2)	1.780(4)
Ti−Cl(1)	2.251(2)	N(2)−Si(1)	1.769(4)
Ti−Cl(2)	2.217(2)	N(1)−C(1)	1.420(5)
Ti−C(1)	2.349(4)	N(2)−C(2)	1.416(5)

(b) Bond Angles

Cl(1)−Ti−Cl(2)	109.6(1)	N(2)−Ti−Cl(2)	113.8(1)
N(1)−Ti−N(2)	92.6(2)	Ti−N(1)−Si(2)	139.7(2)
N(1)−Ti−Cl(1)	113.6(1)	Ti−N(2)−Si(1)	139.2(2)
N(1)−Ti−Cl(2)	114.0(1)	Ti−N(1)−C(1)	89.8(2)
N(2)−Ti−Cl(1)	112.4(1)	Ti−N(2)−C(2)	89.8(3)

(1.90−1.99 Å),[11e,19] and the Ti−C distances of 2.35 Å are somewhat shorter than those found in the arene complexes $(\eta^6\text{-}C_6Me_6)TiCl_3^-$ (2.46−2.52 Å)[20a] and $(\eta^6\text{-}C_6Me_6)Ti(\eta^2\text{-}Cl_2AlCl_2)$ (average 2.50 Å).[20b] The related complex $Ti(OC_6H_3\text{-}2,6\text{-}{}^tBu_2)_2[\eta^4\text{-}(Xyl)NC(CH_2Ph){=}C(CH_2Ph)N^tBu]$ possesses Ti−C distances of 2.399(6) and 2.408(6) Å.[13a] The N(1)−C(1) and N(2)−C(2) single-bond distances of 1.420(5) and 1.416(5) Å, respectively, are most consistent with resonance form **B**.

The titanium dichloride **5** was alkylated with MeMgBr to give the orange dimethyl derivative **6** (eq 4).



5 **6** (4)

Chemically inequivalent Ti−Me sites in this complex are indicated by low-temperature ^1H NMR spectra, which contain two separate resonances for these groups. Their interconversion at higher temperatures ($\Delta G^\ddagger = 9.4 \pm 0.6$ kcal mol^{-1}) is apparently due to a fluxional process analogous to the one depicted in eq 3. Initial experiments with **6** show that, under relatively mild experimental conditions, it does not react with H_2, CO, or ethylene (1 atm, room temperature, 2 h).

The synthesis and characterization of complexes **3**−**6** have provided key information concerning steric and electronic properties for the $[o\text{-}C_6H_4(NSi^iPr_3)_2]^{2-}$ ligand. Efforts are currently focused on further development of the chemistry of this system, and others based on similar bidentate bis(silyl amido) ligands.

Experimental Section

All manipulations employed rigorously anaerobic and anhydrous conditions. Elemental analyses were performed by Desert Analytical Laboratories or at the University of California, Berkeley Microanalysis Facility. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 1330 infrared spectrometer or on a Mattson Galaxy Series FTIR 3000 instrument. NMR spectra were obtained with GE QE-300, Bruker AMX-300, or Varian UN-500 spectrometers. These spectra were recorded at room temperature for benzene-d_6 solutions, unless otherwise indicated. Errors in the activation parameters were determined by a conventional propagation of error analysis, based on estimated experimental error. MeMgBr and ^nBuLi were purchased from Aldrich and used as received. *o*-Phenylenediamine (Aldrich) and $ZrCl_4$ (Strem) were sublimed before use. $TiCl_4$ (Strem) was distilled before use and converted to $TiCl_4{\cdot}2THF$ according to the literature procedure.[21] $Zr(O^tBu)_4$ was also prepared according to the literature procedure.[22]

$o\text{-}C_6H_4(NHSi^iPr_3)_2$ (1). A solution of *o*-phenylenediamine (12.80 g, 0.118 mol) in tetrahydrofuran (150 mL) was cooled to 0 °C, and then ^nBuLi (0.148 L of a 1.6 M solution in hexane, 0.237 mol) was added dropwise over ca. 30 min. The stirred reaction mixture was warmed to room temperature, and stirring was continued for 12 h. The reaction mixture was then cooled to 0 °C, and $^iPr_3SiCl$ (45.7 g, 0.237 mol) was added dropwise over 30 min. The ice bath was removed, and the reaction mixture was heated at reflux for 2 h and then stirred at room temperature for an additional 12 h. Removal of the volatile material from the reaction mixture left a brown, viscous oil which was extracted with pentane (3 × 75 mL). Concentration and cooling (−78 °C) of this solution afforded 32.05 g of the product (65% yield) as light pink crystals, which melt upon warming to room temperature. Anal. Calcd for $C_{24}H_{48}N_2Si_2$: C, 68.5; H, 11.50; N, 6.66. Found: C, 68.3; H, 11.52; N, 6.66. ^1H NMR (300 MHz): δ 1.10 (d, $J = 6$ Hz, 36 H, SiCHMe_2), 1.10−1.26 (m, 6 H, SiCHMe$_2$), 3.02 (s, 2 H, NH), 6.85 (m, 2 H, C_6H_4), 7.00 (m, 2 H, C_6H_4).

$o\text{-}C_6H_4(NLiSi^iPr_3)_2$ (2). To a cooled (0 °C) solution of **1** (15.31 g, 0.0364 mol) in pentane (100 mL) was added 45.5 mL of ^nBuLi solution (1.6 M in hexane). After 10 min, the resulting transparent yellow solution was warmed to room temperature with stirring, and stirring was continued for 24 h. The solvent was then removed by vacuum transfer, the residue was dissolved in pentane (ca. 100 mL), and concentration and cooling (−78 °C) of this solution gave 12.76 g (81% yield) of colorless crystals. Anal. Calcd for $C_{24}H_{46}Li_2N_2Si_2$: C, 66.6; H, 10.72; N, 6.47. Found: C, 66.6; H, 11.05; N, 6.40. ^1H NMR (300 MHz): δ 1.16 (d, $J = 5$ Hz, 36 H, SiCHMe_2), 1.09−1.26 (m, 6 H, SiCHMe$_2$), 6.28 (m, 2 H, C_6H_4), 6.69 (m, 2 H, C_6H_4).

$[o\text{-}C_6H_4(NSi^iPr_3)_2]_2Zr$ (3). To a mixture of **2** (1.00 g, 2.31 mmol) and $ZrCl_4$ (0.54 g, 2.32 mmol) in a Schlenk flask was added 25 mL of benzene. The reaction mixture was refluxed for 12 h, the volatile material was removed under vacuum, and the residue was extracted with 100 mL of pentane. The resulting pentane solution was concentrated and cooled (−78 °C) to afford 0.74 g of yellow crystals (34% yield based on $ZrCl_4$). Anal. Calcd for $C_{48}H_{92}N_4Si_4Zr$: C, 62.1; H, 9.98; N, 6.03. Found: C, 62.5; H, 9.74; N, 5.70. ^1H NMR (500 MHz): δ 0.85 (sept, $J = 7$ Hz, 6 H, SiCHMe$_2$), 0.90 (d, $J = 7$ Hz, 18 H, SiCHMe_2), 1.07 (d, $J = 7$ Hz, 18 H, SiCHMe_2), 1.10 (d, $J = 7$ Hz, 18 H, SiCHMe_2), 1.22 (d, $J = 7$ Hz, 18 H, SiCHMe_2), 1.43 (sept, $J = 7$ Hz, 6 H, SiCHMe$_2$), 7.03−7.08, 7.36−7.40

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(m, 4 H, C$_6$*H*$_4$). ^{13}C{^{1}H} NMR (125.7 MHz): δ 14.90 (SiC*H*Me$_2$), 15.19 (SiC*H*Me$_2$), 19.03 (SiCH*Me*$_2$), 19.63 (SiCH*Me*$_2$), 19.86 (SiCH*Me*$_2$), 19.88 (SiCH*Me*$_2$), 123.6, 125.0, 126.5, 128.6, 130.6, 136.5 (C$_6$H$_4$). ^{29}Si{^{1}H} NMR (99.3 MHz): δ 4.25 (Si^{i}Pr$_3$), 8.26 (Si^{i}Pr$_3$).

[*o*-C$_6$H$_4$(NSi^{i}Pr$_3$)$_2$]Zr(O^{t}Bu)$_2$ (4). To a cooled (0 °C) solution of **1** (1.47 g, 3.49 mmol) in 100 mL of diethyl ether was added ^{n}BuLi (4.40 mL of a 1.60 M hexane solution, 6.99 mmol). The ice−water bath was removed, and the solution was stirred for 1 h before adding it via cannula to a solution of Zr(O^{t}Bu)$_4$ (1.34 g, 3.49 mmol) in pentane (50 mL). The solution turned light brown after the addition. After 6 h, the solvent was removed under reduced pressure, and the residue was extracted into 20 mL of pentane. Undissolved LiO^{t}Bu was allowed to settle, and the solution was filtered and concentrated. The filtration and concentration steps were repeated (typically two times) to remove as much LiO^{t}Bu as possible. Further concentration and cooling to −40 °C afforded 1.59 g (66%) of white crystals in two crops (mp 245−250 °C). Anal. Calcd for $C_{32}H_{64}N_2O_2Si_2Zr$: C, 58.6; H, 9.83; N, 4.27. Found: C, 58.1; H, 10.0; N, 4.44. IR (cm^{-1}): 2360 (w), 2341 (w), 1587 (w), 1462 (s), 1379 (s), 1360 (s), 1230 (s), 1203 (s), 1119 (s), 1018 (s), 987 (s), 984 (s), 897 (s), 883 (s), 941 (s), 771 (s). ^{1}H NMR (300 MHz, 60 °C): δ 1.09 (br s, 18 H, O^{t}Bu), 1.21 (d, *J* = 7.5 Hz, 36 H, SiCH*Me*$_2$), 1.51 (sept, *J* = 8 Hz, 6 H, SiC*H*Me$_2$), 7.11−7.15 (m, 2 H, C$_6$*H*$_4$), 7.28−7.31 (m, 2 H, C$_6$*H*$_4$). ^{13}C NMR (benzene-*d*$_6$, 125.7 MHz): δ 13.73 (SiCH*Me*$_2$), 19.06 (Si*C*HMe$_2$), 32.56 (OC*Me*$_3$), 123.4 (*C*HCHCN), 127.6 (CH*C*HCN), 132.1 (CHCH*C*N).

[*o*-C$_6$H$_4$(NSi^{i}Pr$_3$)$_2$]TiCl$_2$ (5). To a cold (0 °C) diethyl ether (100 mL) solution of **1** (10.02 g, 23.81 mmol) was added ^{n}BuLi (30.5 mL of a 1.56 M solution in hexane, 47.6 mmol), which resulted in an orange solution. The ice−water bath was removed, and the solution was stirred for 3 h. This solution was then added to a cold (0 °C) suspension of TiCl$_4$·2THF in 100 mL of diethyl ether, resulting in a dark green color which turned red as a yellow precipitate formed. After 24 h, the volatile material was removed and the resulting red-brown solid was extracted into pentane (ca. 100 mL). The pentane solution was then filtered, concentrated to 20 mL, and cooled to −78 °C. Dark red crystals (1.21 g, mp 87−90 °C) of the product were isolated. A second crop of crystals (3.06 g) was obtained by cooling a 30 mL hexamethyldisiloxane solution to −78 °C, resulting in an overall yield of 33%. Anal. Calcd for $C_{24}H_{46}N_2Si_2Cl_2Ti$: C, 53.6; H, 8.62; N, 5.21. Found: C, 53.5; H, 8.84; N, 5.10. IR (cm^{-1}): 2725 (w), 1464 (s), 1434 (m), 1377 (w), 1369 (w), 1275 (m), 1221 (m), 1205 (s), 1126 (s), 1072 (w), 1018 (m), 995 (w), 926 (s), 883 (s), 779 (s), 754 (m), 723 (s), 679 (s), 650 (s), 615 (w), 614 (w), 557 (w), 517 (m), 505 (m), 486 (m), 440 (m). ^{1}H NMR (300 MHz): δ 1.09 (d, *J* = 8 Hz, 36 H, CH*Me*$_2$), 1.60 (sept, *J* = 8 Hz, 6 H, C*H*Me$_2$), 7.26−7.37 (m, 4 H, C$_6$*H*$_4$). ^{13}C NMR (125.7 MHz): δ 13.70 (SiCH*Me*$_2$), 18.63 (Si*C*HMe$_2$), 122.9 (*C*HCHCN), 126.4 (CH*C*HCN), 130.1 (CHCH*C*N).

[*o*-C$_6$H$_4$(NSi^{i}Pr$_3$)$_2$]TiMe$_2$ (6). The Grignard MeMgBr (1.32 mL of a 3.60 M diethyl ether solution, 4.75 mmol) was added slowly to a cold (0 °C) toluene solution (40 mL) of **3** (1.278 g, 2.38 mmol). The ice−water bath was removed and the solution was stirred for 6 h. The volatile material was removed and the resulting orange solid was extracted into pentane (3 × 15 mL), concentrated to 10 mL, and cooled to −78 °C. Orange crystals (mp 76.5−84.5 °C dec) were isolated in 31% yield (0.365 g). Anal. Calcd for $C_{26}H_{52}N_2Si_2Ti$: C, 62.9; H, 10.55; N, 5.64. Found: C, 61.9; H, 10.49; N, 5.29. IR (cm^{-1}): 3367 (w), 2341 (w), 2360 (w), 1599 (w), 1577 (w), 1377 (s), 1302 (s), 1244 (w), 1014 (w), 997 (w), 916 (s), 883 (s), 754 (m), 741 (m), 667 (s), 636 (m), 576 (w), 505 (w), 459 (w), 428 (w). ^{1}H NMR (300 MHz): δ 0.98 (s, 6 H, TiMe), 1.18 (d, *J* = 8 Hz, 36 H, SiCH*Me*$_2$), 1.55 (sept, *J* = 8 Hz, 6 H, SiC*H*Me$_2$), 7.24−7.62 (m, 4 H, C$_6$*H*$_4$). ^{13}C NMR (125.7 MHz): δ 14.00 (SiCH*Me*$_2$), 19.00 (Si*C*HMe$_2$), 56.86 (TiMe$_2$), 125.0 (*C*HCHCN), 126.2 (CH*C*HCN), 128.0 (CHCH*C*N).

Table 3. Summary of Crystallographic Data

compd	[C$_6$H$_4$(NSi^{i}Pr$_3$)$_2$]$_2$Zr (**3**)	[C$_6$H$_4$(NSi^{i}Pr$_3$)$_2$]TiCl$_2$ (**5**)
empirical formula	$C_{96}H_{184}N_8Si_8Zr_2 \cdot C_6H_6$	$C_{24}H_{46}Cl_2N_2Si_2Ti$
fw	1935.8	537.62
cryst size (mm^3)	0.8 × 0.8 × 0.5	0.2 × 0.3 × 0.4
color/shape	yellow tablet	red prism
space group	*Pbca*	P2$_1$/*c*
a (Å)	25.241(9)	16.801(3)
b (Å)	21.082(5)	11.945(2)
c (Å)	41.20(2)	15.540(3)
α (deg)	90	90
β (deg)	90	95.15(3)
γ (deg)	90	90
V (Å^3)	21 921(12)	3106(3)
Z	8	4
T (K)	149	296
diffractometer	Siemens R3m/V	Siemens R3m/V
radiation, λ (Å)	Mo Kα, 0.710 73	Mo Kα, 0.710 73
2θ range (deg)	3.0−45	3.0−45
data collected: *h*; *k*; *l*	0−27; 0−22; 0−44	±18; −12 to 0; 0 to 16
no. of rflns	16,000	4221
no. of unique rflns	14,330	4055
R_{int}	0.015	0.012
no. of obsd rflns	$F > 4.0\sigma(F)$, 10,336	$F > 4.0\sigma(F)$, 2411
abs corr	semiempirical	N/A
structure soln	direct methods	direct methods[a]
GOF	1.89	1.26
R	6.74	4.94
R_w	8.81	5.93
max resid density (e/Å^3)	0.84	0.29

[a] Siemens SHELXTL PLUS (PC Version).

X-ray Structural Determinations. The structures of **3** and **5** were determined at the University of California at San Diego by Peter Gantzel. Data collection, solution, and refinement procedures and parameters are summarized in Table 3.

A yellow crystal of **3** in a glass capillary was centered with 15 randomly selected reflections with 11° ≤ 2θ ≤ 27°, and the unit cell dimensions were determined. The structure was solved by direct methods. In one of the independent molecules per unit cell, an isopropyl group has a disorder associated with the carbon positions. This disorder was successfully modeled with two sets of carbon positions (C26B−C25B−C27B; C26B−C25C−C27C). With the fixed C26B position and a fixed isotropic thermal parameter of 0.05, occupancy refinement gave 39% and 61%, respectively. All hydrogens were inserted at expected positions, and the benzene of solvation was refined as an idealized rigid body.

A dark red crystal of **5** was mounted in a glass capillary in the glovebox; the capillary was flame-sealed and transferred to the diffractometer. Centering on 14 randomly selected reflections with 10° ≤ 2θ ≤ 24° provided the unit cell dimensions. Almost all atoms were revealed in the direct methods Fourier map, and the refinement was straightforward. Hydrogens were placed at expected positions, and an idealized, rigid-body aromatic ring was employed.

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Supporting Information Available: Summaries of crystallographic data and tables of bond distances, angles, anisotropic thermal parameters, and atomic coordinates for **3** and **5** (21 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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