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NEW LIGAND ENVIRONMENTS FOR SOLUBLE ZIEGLER–NATTA OLEFIN POLYMERIZATION CATALYST PRECURSORS. X-RAY STRUCTURES OF $[(\eta^5\text{-}C_5Me_4Si(Me_2)OCH_2C_4H_7NH)ZrCl_3]$ AND $[(\eta^5\text{-}C_5Me_4SiMe_3)_2Zr_2(CH_3)_2(\mu\text{-}\eta^2\text{-}C_5H_9NO)_2]$*

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Abstract—Treatment of dimethyl(tetramethylcyclopentadienyl)chloro silane with S-(-)pyrrolidine methanol provided the O-silylated ligand $(C_5Me_4H)SiMe_2OCH_2(C_4H_7NH)$, **1**, $(Cp^*SiProH_2)$ as a 90% pure, thermally unstable oil in 65% yield. Reaction of **1** with $Zr(NMe_2)_4$ resulted in attachment of **1** to the zirconium center with elimination of $HNMe_2$, yielding $(Cp^*SiPro)Zr(NMe_2)_2$, **2**, as a viscous oil in high yield (95%). Compound **2** was converted to the trichloride derivative $(Cp^*SiProH)ZrCl_3$, **3**, in 75% yield by treatment with three equivalents of $HCl \cdot HNMe_2$: compound **3** is produced as a mixture of diastereomers; the major species was characterized by X-ray crystallography, revealing a Cp*—O—N coordination mode for the Cp*SiProH ligand. (**3**: orthorhombic, space group $P2_12_12_1$, $a = 10.0009(13)$, $b = 12.7597(12)$, $c = 16.2749(15)$ Å, $V = 2076.8(4)$ Å^3, $Z = 4$, $R = 0.043$, $R_w = 0.041$.) Deprotonation of **3** (diastereomeric mixture) with $LiN(SiMe_3)_2$ produced the dichloride $(Cp^*SiPro)ZrCl_2$, **4**, in 71% yield. Alkylation of either **3** or **4** resulted in Si—O bond cleavage in the Cp*SiPro ligand and gave a dimeric complex **5** which was characterized by X-ray crystallography. (**5**: monoclinic, space group $P2_1$, $a = 9.1285(10)$, $b = 20.2197(22)$, $c = 11.0214(14)$ Å, $\beta = 90.38(7)^\circ$, $V = 2034.2(4)$ Å^3, $Z = 2$, $R = 0.040$, $R_w = 0.042$.) Limited ethylene polymerization activity was observed for **3** and **4** in the presence of MAO co-catalyst.

Development in the field of homogeneous Ziegler–Natta polymerization (Z–NP) has been rapid since Sinn and Kaminsky's landmark discovery of the highly active zirconocene dichloride/methylaluminoxane system in 1979.[1] Progress in efforts to develop catalysts tailored to produce specialty polymers has largely been a result of advances in the art of ligand design since ligand architecture plays a crucial role in determining the microstructure of the polymer assembled by a given catalyst. Thus, for example, through a combination of steric and electronic effects, the C_2 symmetric *ansa* metallocene type catalysts (**I**, Chart I) introduced by Brintzinger[2] produce isotactic polypropylene with high selectivity while Ewen's top/bottom differentiated ligand design[3] (**II**) is syndiospecific. A further permutation in ligand evolution was the

*Dedicated with respect and gratitude to Professor John E. Bercaw on the occasion of his 50th birthday.

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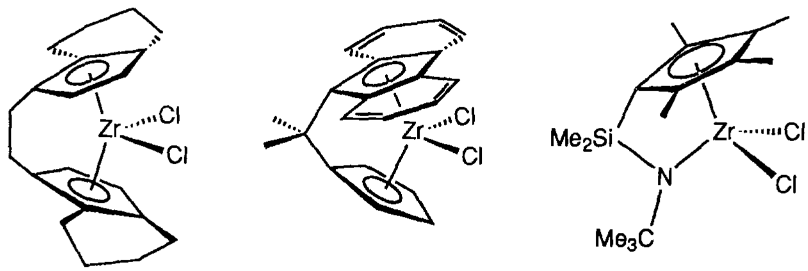


I II III

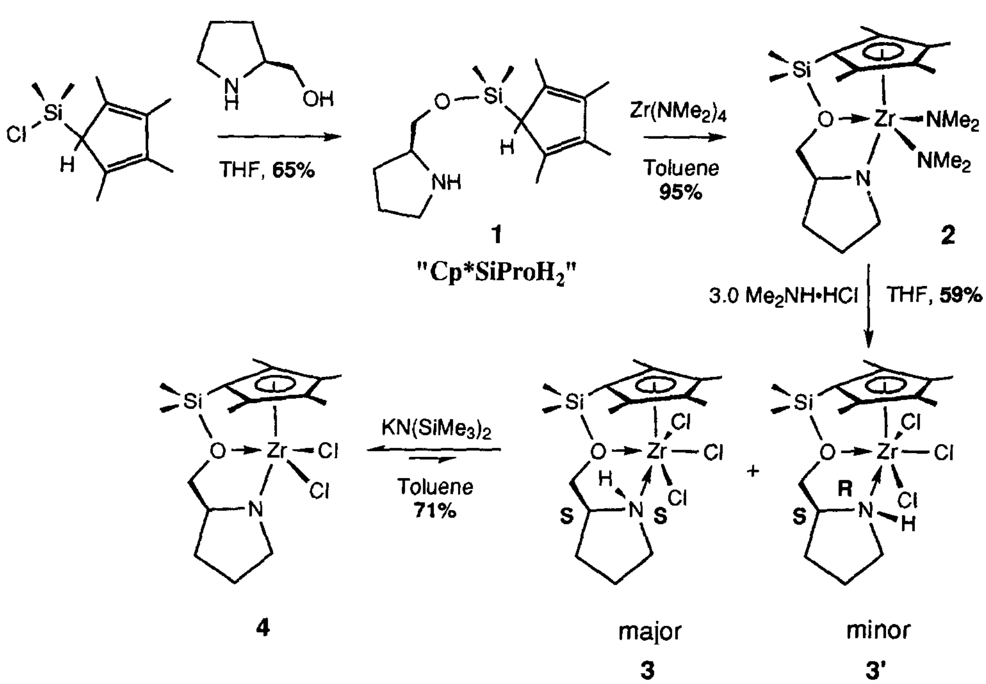
Chart I.

replacement of one of the cyclopentadienyl moieties with an amido donor[4] (**III**) to form so-called "constrained geometry" catalysts[5] capable of producing ethylene/α-olefin copolymers with remarkable properties. To date, however, production of polymers of a defined tacticity in these Cp-amido type catalysts have not been addressed. To incorporate an asymmetric element into such ligands we have attached an amido donor derived from S-(−)-proline to a cyclopentadienyl ligand. Herein we describe the ligand synthesis and its incorporation into a series of zirconium based olefin polymerization catalyst precursors.

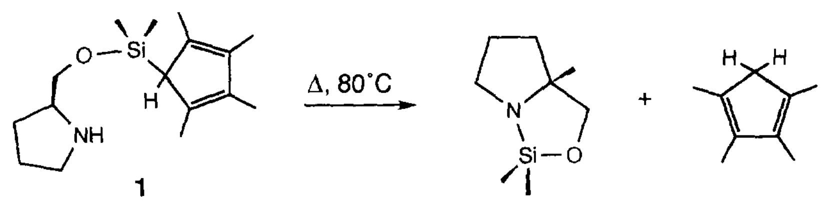
RESULTS AND DISCUSSION

The chemistry described is outlined in Scheme I. Dropwise addition of S-(−)-pyrrolidine methanol to a THF solution of dimethyl(tetramethylcyclopentadienyl)chloro silane[6] results initially in a mixture of N-silylated and desired O-silylated products. Stirring at room temperature for several hours eventually leads to mixtures in which the thermodynamically favored Cp*SiProH_2 O-silylated species is the major product. It is isolated as 90% pure oil which cannot be further purified owing to its thermal instability [eq. (1)] and sensitivity to even weak acid media, precluding chromatographic separation. Fortunately, the crude material is sufficiently pure for effective use in the next step.

Organolithium and organomagnesium reagents were found to attack the Si—O bond of the ligand and so traditional methodologies involving salt elimination reactions for attachment of related ligands to group 4 metals[5] were unavailable.



Scheme I.



(1)

However, using a strategy recently reported by Teuben *et al.*,[7] the ligand was efficiently bonded to zirconium via reaction of the diproteo ligand and tetrakis-(dimethylamido)zirconium with elimination of $HNMe_2$. The product was a highly thermally stable oil, assigned as the bis-dimethylamido derivative $(Cp^*SiPro)Zr(NMe_2)_2$, **2**, shown in Scheme I. The compound was purified by heating to 140°C under high vacuum to remove the $HNMe_2$ byproduct as well as excess $Zr(NMe_2)_4$ ($\delta = 2.98$ ppm) starting material. Unfortunately, we were not able to purify this compound completely in this manner since it decomposed before reaching sufficient temperatures for distillation or sublimation. However, samples which were >94% pure were obtained as described above and could be used to prepare chloride derivatives which were solid materials at room temperature and conveniently purified at that stage.

The presence of a chiral center in this molecule and each of the derivatives described below, renders all protons and methyl groups with the same connectivity diastereotopic. ^1H NMR spectra are therefore complex but diagnostic. Typically, two singlets for the Si—Me groups and four separate signals for the C_5Me_4 are observed along with multiplets for each of the protons associated with the prolinol moiety. Assignments were made on the basis of homonuclear decoupling experiments and, where necessary, two-dimensional NMR techniques.

Chloride derivatives were desired for use as Ziegler–Natta olefin polymerization catalyst precursors. Using Teuben's protocol for conversion of dimethyl amides to chlorides, treatment of **2** with three equivalents of dimethylamine hydrochloride yielded a mixture of two trichloride diastereomers in a 7:1 ratio (Scheme I). Attempts to generate the desired dichloride derivative **4** by limiting the amount of $Me_2NH \cdot HCl$ were unsuccessful with this reagent presumably owing to the greater basicity of the pyrrolidine amide vs NMe_2.[8] Protonation of the pyrrolidine ring nitrogen resulted in an amine functionality which remained coordinated to the zirconium thus rendering the nitrogen center chiral and making possible two diastereomeric structures. Although complex, the ^1H NMR spectrum of **3** clearly shows two sets of ligand resonances, most notably indicated by two multiplets for the N—H protons at 4.77 and 4.64 ppm for the major and minor diastereomers, respectively. We have assigned the major diastereomer the (S,S) configuration on the basis of an X-ray structural analysis (*vide infra*) and an nOe enhancement experiment. Irradiation of the N*H* resonance of the major stereoisomer resulted in enhancement of the signal for the NC*H* proton on the carbon chiral center (and vice versa). This indicated a *cisoid* relationship between these two protons as found in the (S,S) configuration. No such enhancement in the NC*H* proton was observed when the N*H* resonance of the minor diastereomer was irradiated.

Figure 1 shows the molecular structure of trichloride **3**, while Table 1 gives the molecule's bond distances and angles. The zirconium center is approximately octahedrally coordinated by the three chloride ligands and the Cp*SiProH ligand, which is bound through the C_5Me_4 ring, the oxygen and nitrogen atoms. While the potential for O coordination was recognized when the ligand was designed, the apparent strength of the interaction is perhaps surprising. To accommodate O coordination, the Si center is distorted significantly from an ideal tetrahedral geometry (Cp1—Si—O = 91.4(4)°). The Zr—O distance of 2.244(6) Å is similar to distances found in several THF ligated cationic zirconocene derivatives (Zr—O

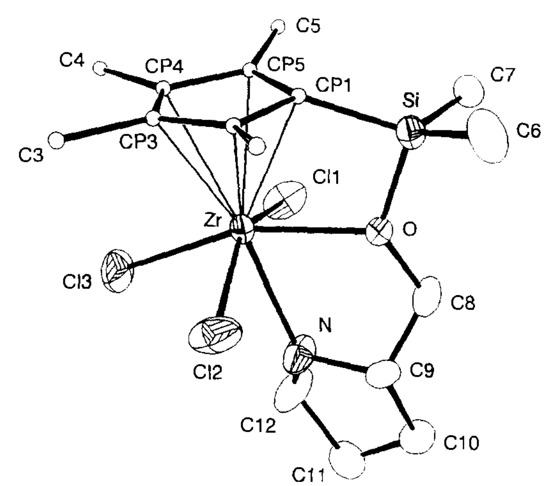


Fig. 1. Molecular structure of $(Cp^*SiProH)ZrCl_3$, **3**.

Table 1. Interatomic distances (Å) and angles (°) for $[C_5Me_4Si(Me_2)OProH]ZrCl_3$, **3**

		Distances			
Zr—Cl1	2.503(4)	Si—O	1.701(6)	Cp2—C2	1.502(19)
Zr—Cl2	2.483(5)	Si—Cp1	1.844(11)	Cp3—Cp4	1.439(19)
Zr—Cl3	2.446(3)	Si—C6	1.874(16)	Cp3—C3	1.556(22)
Zr—O	2.244(6)	Si—C7	1.828(17)	Cp4—Cp5	1.451(25)
Zr—N	2.421(9)	O—C8	1.452(12)	Cp4—C4	1.479(23)
Zr—Cp1	2.477(8)	N—C9	1.517(16)	Cp5—C5	1.495(21)
Zr—Cp2	2.517(13)	N—C12	1.375(21)	C8—C9	1.469(18)
Zr—Cp3	2.600(16)	Cp1—Cp2	1.471(22)	C9—C10	1.527(15)
Zr—Cp4	2.594(16)	Cp1—Cp5	1.429(23)	C10—C11	1.521(19)
Zr—Cp5	2.583(14)	Cp2—Cp3	1.346(23)	C11—C12	1.523(22)
Zr—Cent	2.2470(10)				
		Angles			
Cl1—Zr—Cl2	151.69(13)	C6—Si—C7	109.8(7)	Cp4—Cp3—C3	120.4(14)
Cl1—Zr—Cl3	87.35(20)	Zr—O—Si	108.2(3)	Cp3—Cp4—Cp5	104.8(14)
Cl1—Zr—O	84.0(3)	Zr—O—C8	119.8(5)	Cp3—Cp4—C4	128.7(15)
Cl1—Zr—N	77.8(5)	Si—O—C8	129.2(6)	Cp5—Cp4—C4	125.6(13)
Cl2—Zr—Cl3	88.17(20)	Zr—N—C9	111.2(6)	Cp1—Cp5—Cp4	109.1(13)
Cl2—Zr—O	89.9(3)	Zr—N—C12	133.9(11)	Cp1—Cp5—C5	127.3(15)
Cl2—Zr—N	74.1(5)	C9—N—C12	108.7(10)	Cp4—Cp5—C5	123.3(14)
Cl3—Zr—O	157.93(19)	Si—Cp1—Cp2	123.6(12)	O—C8—C9	109.4(10)
Cl3—Zr—N	87.96(24)	Si—Cp1—Cp5	126.4(14)	N—C9—C8	107.2(10)
O—Zr—N	70.4(3)	Cp2—Cp1—Cp5	105.5(11)	N—C9—C10	106.1(9)
O—Si—Cp1	91.4(4)	Cp1—Cp2—Cp3	108.8(12)	C8—C9—C10	114.5(10)
O—Si—C6	109.2(6)	Cp1—Cp2—C2	123.1(13)	C9—C10—C11	103.8(10)
O—Si—C7	108.2(6)	Cp3—Cp2—C2	127.0(14)	C10—C11—C12	103.9(10)
Cp1—Si—C6	117.7(9)	Cp2—Cp3—Cp4	111.3(14)	N—C12—C11	107.0(14)
Cp1—Si—C7	118.1(8)	Cp2—Cp3—C3	128.3(13)		
Cl1—Zr—Cent	104.32(10)	Cl3—Zr—Cent	107.40(9)	O—Zr—Cent	94.42(16)
Cl2—Zr—Cent	103.69(11)			N—Zr—Cent	164.50(24)

= 2.20–2.23 Å) in which the THF ligand does *not* effectively π donate to the metal center. While the oxygen atom in **3** is approximately sp^2 hybridized and therefore able to π bond with the 16 electron zirconium center on symmetry grounds, constraints inherent in the chelating ligand framework and the presence of a *trans* chlorine ligand probably minimize this interaction.

The Zr—N bond distance of 2.421(9) Å is considerably longer than the Zr—O interaction, a difference which is not fully explained on the basis of the differing covalent radii of O vs N ($\Delta \approx 0.05$ Å). While several zirconium(IV) amine complexes have been prepared, to our knowledge none have been crystallographically characterized. Several examples of ligated pyridine derivatives are known,[10] however, Zr—N distances range from 2.34–2.38 Å. The sum of the angles around the nitrogen center is 353.8°, deviating significantly from an ideal pyramidalized geometry ($E = 328.5°$). Nevertheless, the center is clearly pyramidalized such that the hydrogen atom bound to N is *cis* to the hydrogen bound to C9, consistent with our assignment of the major diastereomer's solution structure.

The dichloride derivative was successfully generated by deprotonation of **3**/**3′** (mixture of diastereomers) using $LiN(SiMe_3)_2$. Use of a slight excess $LiN(SiMe_3)_2$ resulted in unwanted side reactions which also began to compete with the dehydrohalogenation process at late stages of the reaction. Mixtures of compounds composed of $\approx$80% **4**, $\approx$10% **3** and $\approx$10% of a product derived from incorporation of $N(SiMe_3)_2$ were typically produced in this reaction. Attempts to deprotonate **3** with alkyl lithium reagents were hampered by competing reactions of the dichloride with the alkylating reagent (*vide infra*). Pure samples of **4** could, however, be isolated in poor yield from the above mixture via fractional crystallization from toluene/hexanes. Attempts to grow X-ray quality crystals of **4** have thus far failed, but by analogy to the structure found for the trichloride, the Cp*Si Pro ligand probably assumes the same Cp—O—N ligating framework. We have observed this compound to be thermally unstable in solution with gradual decomposition to unknown products seen over the course of 2–3 h at 95°C.

We have also explored some simple alkylation reactions of the chlorides **3** and **4**. When a mixture of **3** and **3′** was treated with three equivalents of methyllithium (MeLi) a dimeric product, characterized as the prolinol bridged derivative **5**, was obtained in good yield (Scheme II). In this reaction, each equivalent of MeLi serves a different purpose; one deprotonates the coordinated pyrrolidine ring, another attacks the silicon center on the ligand, resulting in Si—O bond cleavage, while the last equivalent metathesizes a chloride ligand to leave a methyl group bonded to zirconium. The sequence of these three steps leading to **5** is unknown. It is likely that removal of the pyrrolidine proton occurs first but the order of the Si—O cleavage and methylation steps could be the inverse of what is depicted in Scheme II. Treatment of pure **4** with one equivalent of MeLi resulted in a mixture of products, suggesting that the two steps are competitive. When a second equivalent of alkyllithium reagent was added, **5** was produced.

The ^{1}H and ^{13}C NMR data for **5** were indicative of an unsymmetrical dimeric structure in which all ligand protons and carbons are chemically inequivalent. For example, eight separate resonances were observed for ring methyl groups in both ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra. Precise assignment of the structure for **5** required crystallographic techniques; Fig. 2 shows its molecular structure and Table 2 contains metrical data for this compound.

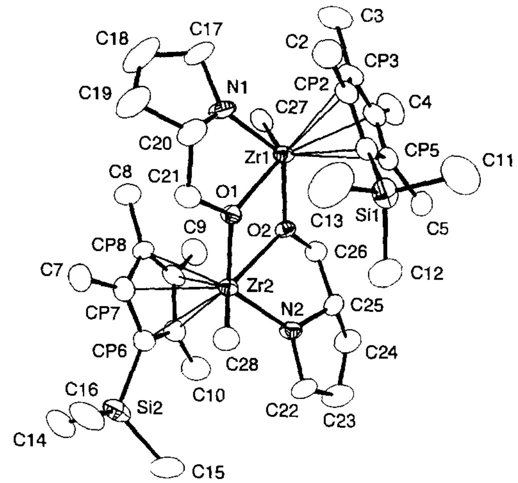
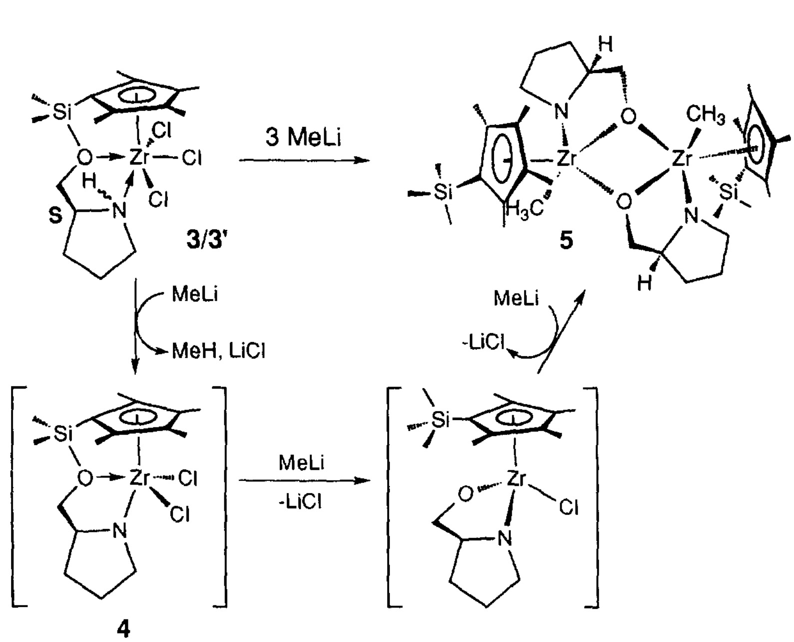


Fig. 2. Molecular structure of $[(C_5Me_4SiMe_3)Zr(CH_3)(\mu\text{-}\eta^2\text{-}C_5H_9NO)]_2$, **5**.

All distances and angles fall within reasonable values by comparison to other zirconium(IV) amides,[7,11] μ-alkoxides[12] and alkyls.[13] Cleavage of the Si—O bond leads to a chelating S-prolinol ligand which also bridges the two zirconium centers via μ-alkoxide moieties. Each zirconium atom in the dimer exhibits a "four-legged piano stool" type of coordination. While it appears at first glance that an S_2 axis exists in the molecule (provided $C_5Me_4SiMe_3$ rotation is fast in solution), careful examination of the core of the molecule (Fig. 3) shows that the Zr1—O1—Zr2—O2 centroid is not an inversion center. The S configurations at C20 and C25 cause the five-membered pyrrolidine ring



Scheme II.

Table 2. Interatomic distances (Å) and angles (°) for $[(C_5Me_4SiMe_3)Zr(CH_3)(\mu\text{-}\eta^2\text{-}C_5H_9NO)]_2$, **5**

Distances					
Zr1—O1	2.217(6)	Si1—C12	1.909(13)	Cp4—C4	1.519(14)
Zr1—O2	2.150(6)	Si1—C13	1.840(14)	Cp5—C5	1.507(15)
Zr1—N1	2.075(8)	Si2—Cp6	1.882(9)	Cp6—Cp7	1.434(14)
Zr1—Cp1	2.464(10)	Si2—C14	1.866(14)	Cp6—Cp10	1.459(14)
Zr1—Cp2	2.526(11)	Si2—C15	1.843(13)	Cp7—Cp8	1.426(15)
Zr1—Cp3	2.597(10)	Si2—C16	1.868(13)	Cp7—C7	1.502(15)
Zr1—Cp4	2.634(10)	O1—C21	1.448(11)	Cp8—Cp9	1.386(16)
Zr1—Cp5	2.611(10)	O2—C26	1.414(11)	Cp8—C8	1.506(13)
Zr1—C27	2.265(10)	N1—C17	1.485(13)	Cp9—Cp10	1.441(13)
Zr2—O1	2.126(6)	N1—C20	1.464(13)	Cp9—C9	1.531(14)
Zr2—O2	2.222(6)	N2—C22	1.474(12)	Cp10—C10	1.451(16)
Zr2—N2	2.051(8)	N2—C25	1.445(12)	C17—C18	1.490(22)
Zr2—Cp6	2.560(10)	Cp1—Cp2	1.416(14)	C18—C19	1.445(20)
Zr2—Cp7	2.603(11)	Cp1—Cp5	1.444(14)	C19—C20	1.517(17)
Zr2—Cp8	2.604(10)	Cp2—Cp3	1.392(15)	C20—C21	1.538(15)
Zr2—Cp9	2.533(11)	Cp2—C2	1.546(15)	C22—C23	1.519(16)
Zr2—Cp10	2.571(11)	Cp3—Cp4	1.376(16)	C23—C24	1.519(16)
Zr2—C28	2.279(9)	Cp3—C3	1.537(14)	C24—C25	1.520(13)
Si1—Cp1	1.876(9)	Cp4—Cp5	1.406(14)	C25—C26	1.511(13)
Si1—C11	1.842(16)	Zr1—Dcent1	2.2712(3)	Zr2—Dcent2	2.2698(12)
Angles					
O1—Zr1—O2	66.98(21)	Zr2—O1—C21	124.0(6)	Cp7—Cp6—Cp10	108.0(8)
O1—Zr1—N1	73.5(3)	Zr1—O2—Zr2	111.98(24)	Cp6—Cp7—Cp8	108.1(9)
O1—Zr1—C27	122.5(3)	Zr1—O2—C26	135.7(6)	Cp6—Cp7—C7	127.6(10)
O2—Zr1—N1	132.9(3)	Zr2—O2—C26	112.0(5)	Cp8—Cp7—C7	123.5(9)
O2—Zr1—C27	89.4(3)	Zr1—N1—C17	133.2(7)	Cp7—Cp8—Cp9	108.0(8)
N1—Zr1—C27	91.0(4)	Zr1—N1—C20	119.9(6)	Cp7—Cp8—C8	125.7(10)
Cp1—Zr1—C27	134.1(3)	C17—N1—C20	106.7(8)	Cp9—Cp8—C8	126.0(9)
O1—Zr2—O2	67.29(21)	Zr2—N2—C22	133.1(6)	Cp8—Cp9—Cp10	110.9(8)
O1—Zr2—N2	126.4(3)	Zr2—N2—C25	122.6(5)	Cp8—Cp9—C9	125.3(9)
O1—Zr2—C28	87.1(3)	C22—N2—C25	104.3(7)	Cp10—Cp9—C9	123.0(10)
O2—Zr2—N2	73.52(25)	Si1—Cp1—Cp2	127.8(8)	Cp6—Cp10—Cp9	104.9(9)
O2—Zr2—C28	130.3(3)	Si1—Cp1—Cp5	124.3(7)	Cp6—Cp10—C10	128.5(9)
N2—Zr2—C28	91.7(3)	Cp2—Cp1—Cp5	104.8(8)	Cp9—Cp10—C10	126.5(9)
Cp1—Si1—C11	110.0(5)	Cp1—Cp2—Cp3	109.1(9)	N1—C17—C18	102.8(10)
Cp1—Si1—C12	111.9(5)	Cp1—Cp2—C2	125.0(9)	C17—C18—C19	112.3(11)
Cp1—Si1—C13	112.4(6)	Cp3—Cp2—C2	125.6(10)	C18—C19—C20	103.5(11)
C11—Si1—C12	106.9(7)	Cp2—Cp3—Cp4	109.3(9)	N1—C20—C19	107.6(9)
C11—Si1—C13	109.7(8)	Cp2—Cp3—C3	123.9(11)	N1—C20—C21	109.3(7)
C12—Si1—C13	105.7(7)	Cp4—Cp3—C3	126.7(10)	C19—C20—C21	113.4(10)
Cp6—Si2—C14	105.5(5)	Cp3—Cp4—Cp5	107.8(9)	O1—C21—C20	109.9(8)
Cp6—Si2—C15	114.6(5)	Cp3—Cp4—C4	126.3(9)	N2—C22—C23	107.2(8)
Cp6—Si2—C16	113.7(5)	Cp5—Cp4—C4	125.1(10)	C22—C23—C24	105.2(8)
C14—Si2—C15	109.5(6)	Cp1—Cp5—Cp4	108.4(9)	C23—C24—C25	103.4(8)
C14—Si2—C16	107.7(6)	Cp1—Cp5—C5	126.0(9)	N2—C25—C24	105.5(8)
C15—Si2—C16	105.6(6)	Cp4—Cp5—C5	125.2(9)	N2—C25—C26	106.9(7)
Zr1—O1—Zr2	113.09(24)	Si2—Cp6—Cp7	124.8(8)	C24—C25—C26	116.6(8)
Zr1—O1—C21	118.6(5)	Si2—Cp6—Cp10	124.8(7)	O2—C26—C25	109.0(7)
Dcent1—Zr1—O1	132.76(18)	Dcent1—Zr1—C27	104.6(3)	Dcent2—Zr2—N2	116.31(24)
Dcent1—Zr1—O2	114.75(18)	Dcent2—Zr2—O1	113.99(19)	Dcent2—Zr2—C28	110.8(3)
Dcent1—Zr1—N1	110.7(3)	Dcent2—Zr2—O2	118.33(17)		

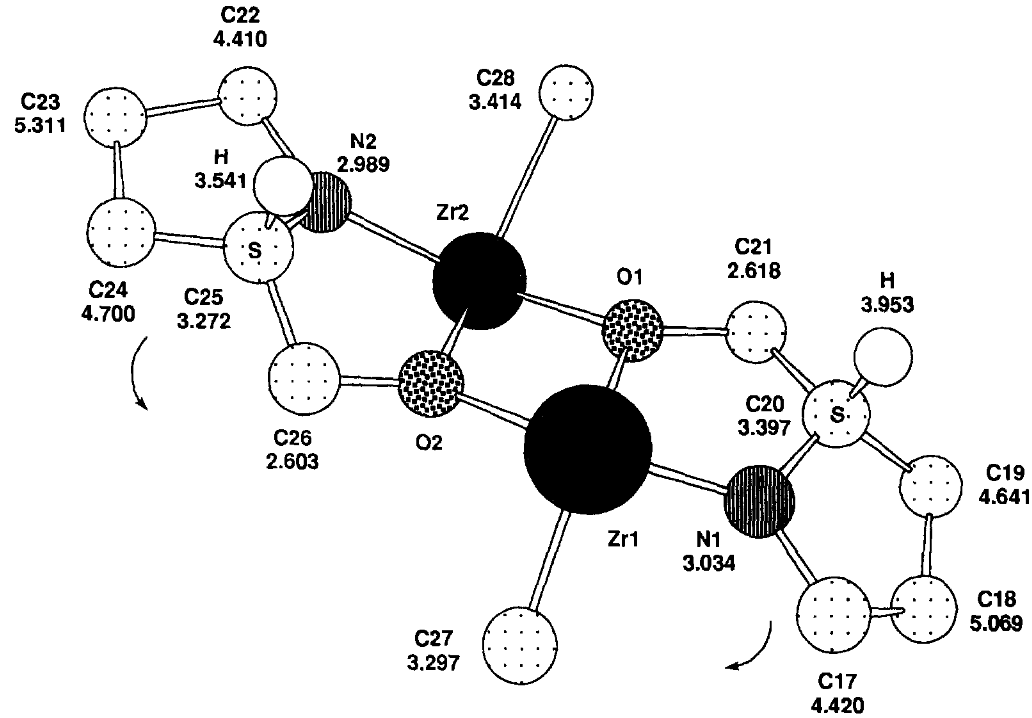


Fig. 3. Molecular core of **5**. Distances shown (Å) indicate the atom's position with respect to the Zr1—O1—Zr2—O2 ring centroid.

to pucker in the same direction and since the legs of the piano stool point in *opposite* directions, the two halves of the molecule are chemically inequivalent.

The susceptibility of the ligand to Si—O bond cleavage under these conditions is obviously an undesirable feature of this particular ligand. However, preliminary experiments suggest that when activated with MAO, **3** and **4** polymerize ethylene albeit with low activities. The Si—O functionality is probably responsible for the poor activity and thermal instability of this generation of Cp*SiPro type catalysts. We are currently developing a ligand without this structural feature.

EXPERIMENTAL

All operations were performed under a purified argon atmosphere in a Braun MB-150 Inert Atmosphere glove box or on high vacuum lines using standard techniques.[14] Solvents were purified as follows: toluene was distilled from sodium benzophenone ketyl and stored over "titanocene";[15] tetrahydrofuran (THF) was predried with activated (10^{-4} Torr, 200°C, 3 h) 3 Å molecular sieves, distilled from and stored over sodium benzophenone ketyl; hexanes were distilled from lithium aluminum hydride (Aldrich) and stored over "titanocene"; dichloromethane was distilled from CaH_2; d_6-benzene was dried sequentially over activated 3 Å sieves and "titanocene" and stored in the glove box; other NMR solvents were dried analogously to the perprotio solvents ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Unity 400 MHz spectrometer. Assignments were confirmed by decoupling, APT, DEPT or COSY experiments. IR spectra were recorded on a Nicolet 20 DXC spectrometer. Elemental analyses were performed by Oneida Research Services, Inc., One Halsey Road, Whitesboro, NY 13492. Materials were purchased from Aldrich Chemical Company and used as received. $Zr(NMe_2)_4$,[16] $C_5Me_4H_2$[17] and C_5Me_4HLi were synthesized according to published procedures.

Synthesis of compound Cp*SiProH$_2$, **1**

C_5Me_4HLi (3.03 g, 23.6 mmol) was suspended in 40 cm^3 of THF. Against a strong argon counterflow, Me_2SiCl_2 (3.3 cm^3, 26.9 mmol) was added at −78°C. The mixture was allowed to warm to room temperature and stirred for 4 h. THF and excess Me_2SiCl_2 were removed *in vacuo*, and the residue was redissolved in 20 cm^3 of THF. To the solution was added dropwise a solution of (S)-(+)-2-pyrrolidine–methanol (2.40 g, 23.7 mmol) in 30 cm^3 of THF. The mixture was stirred overnight and *t*-$C_4H_9NH_2$ (3.5 cm^3, 33.3 mmol) was then added.

After stirring for a further 1 h, THF was removed *in vacuo* and the residues were extracted with 50 cm^3 of hexanes. The mixture was thoroughly stirred and filtered, and hexanes and other volatile material were removed *in vacuo* to give **1** as a pale yellow oil (4.41 g, 66.5%). IR (neat, KBr, cm^{-1}): 3330 (w, ν N—H), 1091 (s, ν Si—O). ^{1}H NMR (C_6D_6, ppm): 3.46 (d, 2H, ^3J = 5.8 Hz, CH_2-O), 3.13 (pent, 1H, ^3J = 5.8 Hz, N-C*H*), 2.97 (br s, 1H, N*H*), 2.85 (m, 1H, 1H of N-CH_2), 2.69 (m, 1H, 1H of N-CH_2), 2.33 (s, 1H, Si-CH of C_5Me_4H), 2.02 (s, 6H, C_5Me_4H), 1.83 (s, 6H, C_5Me_4H), 1.65 (m, 1H, 1H of N-CH-CH_2), 1.56 (m, 2H, N-CH_2CH_2), 1.34 (m, 1H, 1H of N-CH-CH_2), 0.00 (s, 6H, SiMe_2).

Thermal decomposition of **1**

Ninety percent pure samples of **1** as obtained above were heated to 80°C in a small round bottomed flask under vacuum. A liquid product identified as $C_5Me_4H_2$ by ^{1}H NMR analysis was trapped in a separate bulb at −78°C. The residue was identified as O, N-dimethylsilylated prolinol. ^{1}H NMR data (C_6D_6, ppm): 3.65 (m, 1H, NC*H*); 3.35 (dd, 1H, 1H of OCH_2), 3.22 (dd, 1H, 1H of OCH_2), 3.14 (m, 1H, 1H of NCH_2), 2.93 (m, 1H, 1H of NCH_2), 1.66 (m, 1H, 1H of NCH_2CH_2), 1.47 (m, 1H, 1H of NCHCH_2), 1.45 (m, 1H, 1H of NCH_2CH_2), 1.05 (m, 1H, 1H of NCHCH_2), 0.49, 0.22 (s, 6H, Si*Me*).

Synthesis of (Cp*SiPro)Zr(NMe_2)$_2$, **2**

Compound **1** (7.00 g, 90% pure, 22.5 mmol) in 25 cm^3 of toluene was added to a solution of Zr(NMe_2)$_4$ (6.02 g, 22.5 mmol) in 30 cm^3 of toluene at room temperature. The reaction mixture was stirred at 40°C for 5 h and toluene was removed *in vacuo*. The residue was stirred at 85°C under reduced pressure for further 5 h, dissolved in 50 cm^3 of hexanes and filtered to remove the insoluble impurities. The solvent was then removed and the residue was heated under reduced pressure to 140°C for 2 h to remove the lower boiling-point impurities; 9.70 g of **2** (21.2 mmol, 94.2%) was obtained as a pale brown oil. ^{1}H NMR (C_6D_6, ppm): 3.79 (dd, 1H, ^2J = 5.4 Hz, ^3J = 1.6 Hz, 1H of CH_2-O), 3.74 (dd, 1H, ^2J = 5.4 Hz, ^3J = 4.6 Hz, 1H of CH_2-O), 3.50 (m, 1H, N-C*H*), 3.10 (m, 1H, 1H of N-CH_2), 2.96 (m, 1H, 1H of N-CH_2), 3.03 (s, 6H, one NMe_2), 2.90 (s, 6H, one NMe_2), 2.27 (s, 3H, C_5Me_4), 2.18 (s, 3H, C_5Me_4), 1.99 (s, 3H, C_5Me_4), 1.96 (s, 3H, C_5Me_4), 1.59 (m, 1H, 1H of N-CH-CH_2), 1.52 (m, 1H, 1H of N-CH_2CH_2), 1.43 (m, 1H, 1H of N-CH_2CH_2), 1.02 (m, 1H, 1H of N-CH-CH_2), 0.48 (s, 3H, SiMe_2), 0.34 (s, 3H, SiMe_2). ^{13}C NMR (C_6D_6, ppm): 129.5, 128.8, 128.6, 128.5, (*C*Me of C_5Me_4), 127.4 (Si-*C* of C_5Me_4), 75.5 (CH_2-O), 62.7 (N-*C*H), 48.0 (N-CH_2), 44.3, 43.3 (NMe_2), 29.1, 26.8 (NCH_2CH_2), 14.0, 12.6, 10.9, 10.8 (C_5Me_4), 1.5, 1.3 (SiMe_2).

Synthesis of (Cp*SiProH)ZrCl_3, **3**

(Cp*SiPro)Zr(NMe_2)$_2$, **2**, (9.70 g, 21.2 mmol) was dissolved in 60 cm^3 of THF. To the solution was added anhydrous $Me_2NH \cdot HCl$ (5.19 g, 63.6 mmol) at −78°C. The mixture was allowed to warm to room temperature and stirred until the solid $Me_2NH \cdot HCl$ disappeared. The volatiles were removed *in vacuo* and the residue was washed with hexanes (50 cm^3) to give the crude product as an off-white solid. The pure product (6.0 g, 59.4%) was obtained by fractional recrystallizations from THF/hexanes. The ^{1}H NMR shows that **3** was formed as a mixture of two diastereomers in a 7:1 ratio. Found for $C_{16}H_{28}Cl_3NOSiZr$: C, 40.48; H, 5.91; N, 2.81. Calc.: C, 40.37; H, 5.93; N, 2.94. ^{1}H NMR (C_6D_6, ppm) of major diastereomer: 4.77 (br quart, 1H, ^3J=4.0 Hz, N*H*), 3.70 (m, 1H, 1H of N-CH_2), 3.54 (m, 1H, N-C*H*), 3.06 (dd, 1H, ^2J = 4.6 Hz, ^3J = 5.8 Hz, 1H of CH_2-O), 2.89 (m, 1H, 1H of N-CH_2), 2.82 (dd, 1H, ^2J = 4.6 Hz, ^3J = 2.6 Hz, 1H of CH_2-O), 2.48 (s, 3H, C_5Me_4), 2.42 (s, 3H, C_5Me_4), 2.28 (s, 3H, C_5Me_4), 2.17 (s, 3H, C_5Me_4), 1.32 (m, 1H, 1H of N-CH_2CH_2), 0.97 (m, 1H, 1H of N-CH-CH_2), 0.73 (m, 1H, 1H of N-CH_2CH_2), 0.44 (m, 1H, 1H of N-CH-CH_2), 0.28 (s, 3H, SiMe_2), 0.18 (s, 3H, SiMe_2). ^{1}H NMR (C_6D_6, ppm) for minor diastereomer: 4.64 (br dt, 1H, $^3J_1$ = 6.1 Hz, $^3J_2$ = 2.9 Hz, N*H*), 3.40 (m, 1H, 1H of N-CH_2), 3.28 (m, 1H, N-C*H*), 3.20 (m, 1H, 1H of N-CH_2), 3.00 (dd, 1H, ^2J = 4.5 Hz, ^3J = 2.2 Hz, 1H of CH_2-O), 2.90 (dd, 1H, ^2J = 4.5 Hz, ^3J = 5.7 Hz, 1H of CH_2-O), 2.46 (s, 3H, C_5Me_4), 2.43 (s, 3H, C_5Me_4), 2.24 (s, 3H, C_5Me_4), 2.21 (s, 3H, C_5Me_4), 1.22 (m, 1H, 1H of N-CH_2CH_2), 1.09 (m, 1H, 1H of N-CH-CH_2), 1.02 (m, 1H, 1H of N-CH_2CH_2), 0.45 (m, 1H, 1H of N-CH-CH_2), 0.34 (s, 3H, SiMe_2), 0.16 (s, 3H, SiMe_2). ^{13}C NMR (C_6D_6, ppm) for major diastereomer: 138.8, 136.2, 131.8, 131.6 (*C*Me of C_5Me_4), 103.0 (Si-*C* of C_5Me_4), 69.4 (CH_2-O), 58.4 (N-*C*H), 49.4 (N-CH_2), 27.2, 25.8 (NCH_2CH_2), 17.7, 17.0, 12.4, 12.0 (C_5Me_4), 1.4, −0.6 (SiMe_2). ^{13}C NMR (C_6D_6, ppm) for minor diastereomer: 138.3, 135.7, 132.03, 131.99 (*C*Me of C_5Me_4), 103.9 (Si-*C* of C_5Me_4), 66.6 (CH_2-O), 61.6 (N-*C*H), 47.4 (N-CH_2), 25.7, 24.9 (NCH_2CH_2), 17.5, 17.1, 12.3, 12.1 (C_5Me_4), 1.0, −0.3 (SiMe_2).

Synthesis of (Cp*SiPro)ZrCl_2, **4**

LiN($SiMe_3$)$_2$ (0.176 g, 1.05 mmol) in 15 cm^3 of toluene was dropwise added to a solution of **3** (0.500

g, 1.05 mmol) in 35 cm^3 of toluene. The mixture was stirred for 10 min, filtered and the solvent removed *in vacuo*. The residue was washed with hexanes (10 cm^3), filtered and dried under vacuum to give **4** (0.330 g, 71.5%) as a yellow powder. An analytically pure sample was obtained by recrystallization from 1 : 5 toluene/hexanes. Found for $C_{16}H_{27}Cl_2NOSiZr$: C, 43.53; H, 6.26; N, 3.16; Calc.: C, 43.72; H, 6.19; N, 3.19. ^1H NMR (C_6D_6, ppm): 4.22 (td, 1H, $^2J = 5.9$ Hz, $^3J = 3.0$ Hz, 1H of N-CH_2), 3.59 (m, 1H, N-C*H*), 3.52 (td, 1H, $^2J = 5.9$ Hz, $^3J = 3.6$ Hz, 1H of N-CH_2), 3.47 (dd, 1H, $^2J = 5.0$ Hz, $^3J = 2.5$ Hz, 1H of CH_2-O), 3.30 (dd, 1H, $^2J = 5.0$ Hz, $^3J = 5.2$ Hz, 1H of CH_2-O), 2.23 (s, 3H, C_5Me_4), 2.11 (s, 3H, C_5Me_4), 2.06 (s, 3H, C_5Me_4), 1.99 (s, 3H, C_5Me_4), 1.49 (m, 1H, 1H of N-CH_2CH_2), 1.32 (m, 1H, 1H of N-CH_2CH_2), 1.19 (m, 1H, 1H of N-CH-CH_2), 0.68 (m, 1H, 1H of N-CH-CH_2), 0.38 (s, 3H, SiMe_2), 0.22 (s, 3H, SiMe_2). ^{13}C NMR (C_6D_6, ppm): 132.7, 131.3, 130.0, 125.1 (*C*Me of C_5Me_4), 111.6 (Si-*C* of C_5Me_4), 70.8 (CH_2-O), 69.2 (N-CH), 55.1 (N-CH_2), 28.6, 27.3 (NCH_2CH_2), 14.9, 12.9, 12.5, 11.3 (C_5Me_4), 1.3, 1.0 (SiMe_2).

Synthesis of $[(C_5Me_4SiMe_3)Zr(CH_3)(\mu\text{-}\eta^2\text{-}C_5H_9NO)]_2$, **5**

$(Cp^*SiProH)ZrCl_3$, **3**, (0.520 g, 1.09 mmol) was dissolved in 35 cm^3 of toluene. To the solution was added 2.35 cm^3 of 1.4 M solution of MeLi (3.29 mmol) at -78°C. The mixture was allowed to warm to room temperature and stirred overnight. Solvents were removed under reduced pressure and the residue was extracted with 20 cm^3 of hexanes. The extract was reduced in volume to ~ 3 cm^3 and cooled to -20°C, giving a yellow crystalline solid of **5** (0.217 g, 49.7%). Found for $C_{36}H_{66}N_2O_2Si_2Zr_2$: C, 54.34; H, 8.54; N, 3.41; Calc.: C, 54.22; H, 8.34; N, 3.51. ^1H NMR (C_6D_6, ppm): 4.17 (dd, 1H, $^2J = 4.8$ Hz, $^3J = 2.4$ Hz, 1H of CH_2-O), 4.09 (dd, 1H, $^2J = 4.0$ Hz, $^3J = 2.7$ Hz, 1H of CH_2-O), 4.05 (m, 1H, N-C*H*), 3.79 (m, 1H, N-C*H*), 3.77 (dd, 1H, $^2J = 4.0$ Hz, $^3J = 4.2$ Hz, 1H of CH_2-O), 3.58 (m, 1H, 1H of N-CH_2), 3.52 (dd, 1H, $^2J = 4.8$ Hz, $^3J = 5.0$ Hz, 1H of CH_2-O), 3.43 (m, 1H, 1H of N-CH_2), 3.14 (m, 1H, 1H of N-CH_2), 3.02 (m, 1H, 1H of N-CH_2), 2.18 (s, 3H, C_5Me_4), 2.15 (s, 3H, C_5Me_4), 2.13 (s, 3H, C_5Me_4), 2.11 (s, 3H, C_5Me_4), 2.02 (s, 3H, C_5Me_4), 1.97 (s, 3H, C_5Me_4), 1.96 (s, 3H, C_5Me_4), 1.92 (s, 3H, C_5Me_4), 1.72 (m, 1H, 1H of N-CH_2CH_2), 1.64 (m, 1H, 1H of N-CH_2CH_2), 1.60 (m, 1H, 1H of N-CHCH_2), 1.58 (m, 1H, 1H of N-CHCH_2), 1.56 (m, 1H, 1H of N-CH_2CH_2), 1.52 (m, 1H, 1H of N-CH_2CH_2), 1.32 (m, 1H, 1H of N-CHCH_2), 0.87 (m, 1H, 1H of N-CHCH_2), 0.44 (s, 9H, SiMe_3), 0.41 (s, 9H, SiMe_3), 0.33 (s, 3H, Zr-*Me*), 0.27 (s, 3H, Zr-*Me*). ^{13}C NMR (C_6D_6, ppm): 130.0, 128.6, 127.4, 127.3, 125.3, 125.0, 124.4, 124.3 (*C*Me of C_5Me_4), 114.5, 112.1 (Si-*C* of C_5Me_4), 75.9, 74.6 (CH_2-O), 72.0, 65.4 (N-*C*H), 53.7, 51.6 (N-CH_2), 37.5, 34.2 (Zr-*Me*), 30.8, 29.3, 28.20, 28.17 (NCH_2CH2), 15.0, 14.9, 14.2, 14.1, 11.9, 11.7, 11.4 (C_5Me_4), 2.8, 2.4 (SiMe_3).

X-Ray crystallography

Single crystals suitable for X-ray crystallography were mounted in thin-walled glass capillaries and optically centered in the X-ray beam of an Enraf–Nonius CAD-4 diffractometer. Unit cell dimensions were determined via least squares refinement of the setting angles of 24 high angle reflections and intensity data were collected using the ω–2θ scan mode. Data were corrected for Lorentz, polarization and absorption effects but not for extinction. Pertinent data collection and structure refinement parameters are presented in Table 3. All structures were solved using direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. Methyl and methylene hydrogen atoms were located via inspection of difference Fourier maps and fixed, temperature factors being based upon the carbon atom to which they are bonded. A weighting scheme based upon counting statistics was used with the weight modifier k in kF_0^2 being determined via evaluation of variation in the standard reflections that were collected during

Table 3. Summary of data collection and structure refinement details for **3** and **5**

	3	**5**
Formula	$C_{16}H_{28}ZrCl_3SiON$	$C_{36}H_{66}Zr_2Si_2O_2N_2$
f_w	476.06	797.53
Crystal syst.	orthorhombic	monoclinic
a (Å)	10.0009(13)	9.1285(10)
b (Å)	12.7597(12)	20.2197(22)
c (Å)	16.2749(15)	11.0214(14)
α (°)		
β (°)		90.38(7)
γ (°)		
V (Å^3)	2076.8(4)	2034.2(4)
Space group	$P2_12_12_1$	$P2_1$
Z	4	2
$F(000)$	976	840
d_{calc} (mg m^{-3})	1.52	1.30
μ (mm^{-1})	0.97	0.59
R	0.043	0.040
R_w	0.041	0.042
GOF	2.36	2.53

the course of data collection. Neutral atom scattering factors were taken from *International Tables for X-ray Crystallography*.[18] Values of R and R_w are given by $R = (F_0 - F_c)/EF_0$ and $R_w = \{E[w(F_0 - F_0)]^2/E(wF_0^2)\}^{1/2}$. All crystallographic calculations were conducted with the PC version of the NRCVAX program package[19] locally implemented on an IBM compatible 80486 computer.

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