# The New Tridentate Ligand CpSiNSiCp and Its Zirconium Complexes: Incorporation of Two Bridged Constrained-Geometry Units into One Molecule

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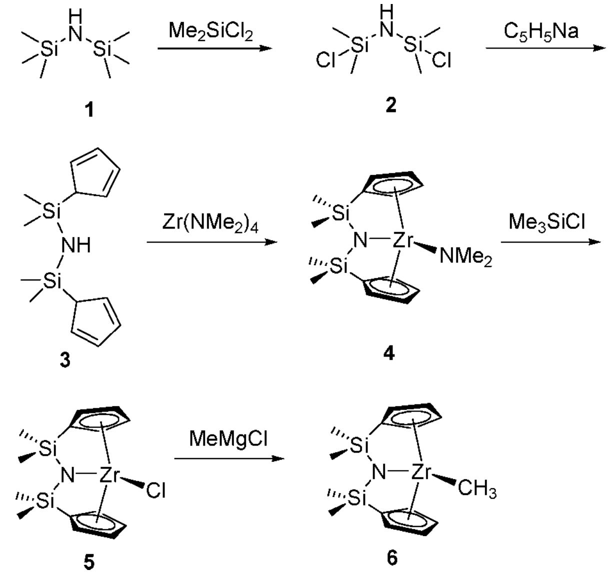
*Summary: The new tridentate ligand CpSiNSiCp and its zirconium complexes have been prepared. These zirconium complexes, containing two constrained-geometry units that are linked together via the N−Zr bond in each molecule, are active catalysts for olefin polymerization when activated with MAO or* $B(C_6F_5)_3$.

The silicon-bridged constrained-geometry catalyst (CGC) systems $Me_2Si(C_5Me_4)(t\text{-BuN})MX_2$ (M = Ti, Zr, X = Cl, alkyl), especially the titanium complexes, have attracted great interest due to their excellence in ethene/1-alkene copolymerization,[1,2] forming linear low-density polyethylene (LLDPE), which has a commercial scale of over one billion kg/year. Numerous contributions in this field have focused on the variations on the Cp ring, silicon bridge, and nitrogen center.[3] Most of the "CpSiNR" type ligands are dianionic, with or without additional neutral donors. There has been only one example that described the incorporation of two constrained-geometry units within one trianionic ligand, RNSiCpSiNR, in which the two amido groups are bridged to Cp ring via a silicon atom.[4] The group 4 metal complexes with this tridentate ligand were quite active toward olefin polymerization, even though the activated forms of these complexes were free of a metal-bonded σ-alkyl ligand that is thought to be necessary for the initiation and propagations.

We wish to disclose here the synthesis of the new tridentate ligand CpSiNSiCp and its zirconium complexes, in which the amido group is doubly connected to two Cp rings via the silicon bridges. Also described here is the use of new zirconcenes as homogeneous catalysts for the polymerization of olefins.

The synthesis of the ligand CpSiNSiCp and its zirconium complexes is quite straightforward (Scheme 1). With hexamethyldisilazane (**1**) as the starting material, 1,3-dichlorotetramethyldisilazane (**2**) was obtained in 85% yield following a literature method.[5] Subsequent treatment of **2** with 2 equiv of cyclopentadienylsodium gave **3** as a pale yellow oil in 96% yield. $^1H$ NMR spectroscopy showed that **3** existed as a mixture of isomers, due to the different arrangements of the double bonds in the two cyclopentadienyl rings. It is impossible and not necessary to separate the isomers, as they were transformed into the zirconium amide **4** as a single product in 60% yield using $Zr(NMe_2)_4$ in pentane. By conventional methods, compound **5** was obtained in 88% yield by chlorination of compound **4** with $Me_3SiCl$ in toluene; compound **6** was isolated in 73% yield by treatment of **5** with MeMgCl.

**Scheme 1. Synthesis of the Tridentate Ligand CpSiNSiCp and Its Zirconium Complexes**



In solution, complexes **4**−**6** exhibit NMR spectra typical for symmetric rigid constrained metallocenes. Four sets of $^1H$ NMR signals of the diastereotopic pairs of $C_5H_4$ hydrogens were found for each of the above complexes (for example, **4**, with δ 6.57, 6.01, 5.92, 5.48). They also feature a pair of $Si-(CH_3)_2$ $^1H$ NMR signals (**4**, δ 0.46, 0.35). The upfield shift of the ipso carbon in the Cp ring is the typical behavior of constrained metallocene systems (**4**, with δ 113.5, about 15 ppm lower than that of $[(Me_3Si)_2NSiMe_2C_5H_4]_2ZrCl_2$[6]).[7] One possible explanation is that the exocyclic bond of the Cp ring is not in the plane of the

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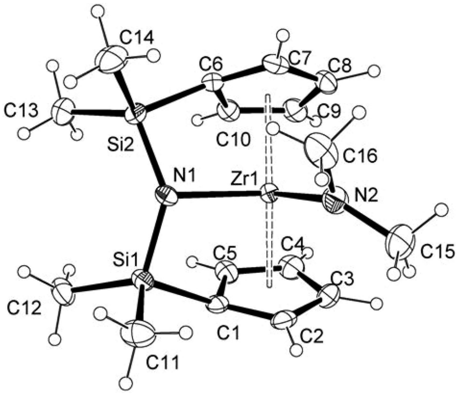

**Figure 1.** View of the molecular structure of **4**. Cp1 is formed by C1, C2, C3, C4, and C5, and Cp2 is formed by C6, C7, C8, C9, and C10. Selected bond lengths (Å) and angles (deg): C1−C2 = 1.422(6), C2−C3 = 1.410(7), C3−C4 = 1.401(7), C4−C5 = 1.391(6), C1−C5 = 1.418(6), Zr−N1 = 2.158(3), Zr−N2 = 2.075(4), Si1−C1 = 1.869(4), Si1−N1 = 1.699(3); Si1−N1−Si2 = 141.0(2), Si1−N1−Zr = 104.39(16), Si2−N1−Zr = 104.90(16), N1−Zr−N2 = 102.85(14), Cp1(centroid)−C1−Cp2(centroid) = 110.92.

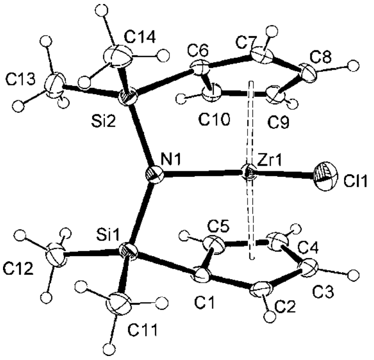

**Figure 2.** View of the molecular structure of **5**. Cp1 is formed by C1, C2, C3, C4, and C5, and Cp2 is formed by C6, C7, C8, C9, and C10. Selected bond lengths (Å) and angles (deg): Zr−C1 = 2.469(2), Zr−C(2) = 2.503(2), Zr−C3 = 2.547(2), Zr−C4 = 2.532(2), Zr−C5 = 2.460(2); Cp1(centroid)−C1−Si1 = 150.98, Cp1(centroid)−Zr−N1 = 100.06, C1−Si1−N1 = 95.14(9), Si1−N1−Zr = 105.63(8).

Cp, and the Cp ring adopts an unsymmetrical coordination mode to zirconium. The negative charge of the Cp ring is not shared equally by the five carbons but is much higher at the bridged carbon. More information was obtained by the determination of X-ray single-crystal structures of **4** and **5**.

Single crystals for X-ray structure analysis were obtained from **4** and **5** from pentane and toluene/pentane, respectively, at −20 °C (Figures 1 and 2). [8] The structure of **4** will be discussed in detail to outline the general characteristics of this class of compounds. In the crystal of **4**, the zirconium atom is in a pseudotetrahedral environment surrounded by the CpSiNSiCp and amido ligands. A typical feature of **4** is the constrained nature of its framework formed by the tridentate CpSiNSiCp ligand. The connecting vectors C1−Si1 and C6−Si2 are both bent out of the Cp planes toward the metal center, as shown by the two corresponding angles (Cp1(centroid)−C1−Si1 = 152.0° and Cp2(centroid)−C6−Si2 = 151.9°). As the NMe$_2$ ligand is much more flexible than the amido group in CpSiNSiCp, the constrained -geometry feature in **4** is also well explained by the Cp(centroid)−metal−N angles: Cp1(centroid)−Zr−N1 (98.9°) is much smaller than Cp1(centroid)−Zr−N2 (106.8°). Another remarkable feature of the structure is the lateral tilting of the two Cp rings with respect to the disilylamido bridge, similar to that known for disiloxane bridged compounds.[9] This can be easily corroborated by a comparison of the distances between the respective carbons in the two Cp rings: C1−C6 (4.418 Å), C2−C7 (5.012 Å), C3−C8 (4.312 Å), C4−C9 (3.280 Å), and C5−C10 (3.349 Å). This tilting effect is caused by the repulsion between the dimethylamido group and the two Cp rings, and it is also responsible for the deviation from planarity for N1 (the sum of the three angles around N1 is 350.3°, and that for N2 is 360°). The thus lower $\pi$-bond contribution is consistent with Zr−N1 (2.158(3) Å) being longer than Zr−N2 (2.075(4) Å). In complex **5**, this strain is alleviated due to the smaller chlorine atom, as seen from the shorter bond length of Zr−N1 (2.1120(16) Å) and larger value of the sum of the corresponding angles around N1 (353.5°).

The complexes **4**−**6** gave active homogeneous catalysts for ethene polymerization when treated with excess methylalumoxane (MAO). In particular, an activity of 230 g of polymer/((mmol of Zr) h bar) was obtained with the methyl complex **6** (conditions: 27.5 $\mu$mol of **6**, 100 mL of toluene, 3 bar of ethene, Al/Zr = 613, $T_p$ = 60 °C, $t_p$ = 15 min, 4.76 g of PE). The polyethylene showed a bimodal molecular weight distribution with a polydispensity index of 49 ($M_w$ = 78 300). There could be two active species in this MAO-activated polymerization system: one is a cationic zirconium complex free of the metal-bonded $\sigma$-alkyl ligand, and the other is a cationic complex with the Zr−N bond broken by MAO that behaves similarly to those *ansa*-metallocones with a Si−N−Si bridge.[10] Compound **6** was also active for the copolymerization of ethene and 1-octene with an activity of 1600 g of copolymer/((mmol of Zr) h bar) (conditions: 27.5 $\mu$mol of **6**, 30 mL of toluene, 20 mL of MAO, 50 mL of 1-octene, 1 bar of ethene, Al/Zr = 1200, $T_p$ = 60 °C, $t_p$ = 20 min, yield 14.65 g). The copolymer is a light viscous oil with an incorporation ratio of 1-octene up to 30% on the basis of NMR analysis. The molecular weight of the product is relatively low ($M_w$ = 2600), while its distribution is narrow ($M_w/M_n$ = 1.5). The results may imply that the presence of 1-octene accelerates the chain transfer or termination. Indeed, end group analysis showed a considerable amount of unsaturated double bonds existed as the end groups due to $\beta$-H elimination and part of the chains ended with 1-octene as the last inserted monomer.

Another interesting feature of complex **6** is its catalytic behavior toward methyl methacrylate (MMA) polymerization. While **6** was not active when it was reacted with 1 equiv or an excess of B(C$_6$F$_5$)$_3$, it polymerized MMA in the presence of 0.5 equiv of B(C$_6$F$_5$)$_3$, producing PMMA with a syndiotacticity of 73% (conditions: 55 $\mu$mol of **6**, 27.5 $\mu$mol of B(C$_6$F$_5$)$_3$, 5 mL of CH$_2$Cl$_2$, 2 mL of MMA, $T_p$ = 23 °C, $t_p$ = 60 min, 70 mg of PMMA, $M_w$ = 9.9 × 10$^4$, $M_w/M_n$ = 1.13). The result can be explained by assuming that **6** formed a cationic complex

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(8) Crystal data for **4**: $C_{16}H_{26}N_2Si_2Zr$, $M_r$ = 393.79, monoclinic, space group $P2_1/c$, $a$ = 8.7632(6) Å, $b$ = 27.233(2) Å, $c$ = 8.4558(6) Å, α = 90°, $\beta$ = 110.744(2)°, $\gamma$ = 90°, $V$ = 1887.1(2) Å$^3$, $Z$ = 4, $\rho$(calcd) = 1.386 g/cm$^{-3}$, R1 ($I > 2\sigma(I)$) = 0.0473, wR2 (all data) = 0.1094, GOF = 1.047. Crystal data for **5**: $C_{14}H_{20}ClNSi_2Zr$, $M_r$ = 385.16, space group $I4_1/a$, $a$ = 31.3250(8) Å, $b$ = 31.3250(8) Å, $c$= 7.0407(3) Å, α = 90°, $\beta$ = 90°, $\gamma$ = 90°, $V$ = 6908.7(4) Å$^3$, $\rho$(calcd) = 1.481 g/cm$^{-3}$, $Z$ = 16, R1 ($I > 2\sigma(I)$) = 0.0298, wR2(all data) = 0.0727, GOF = 1.116.

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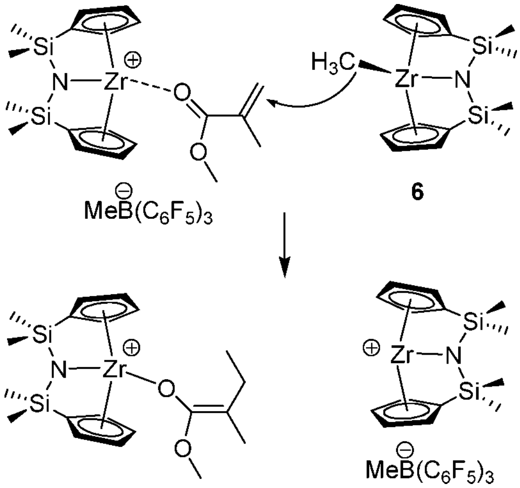
**Scheme 2. Proposed Pathway for the Polymerization of MMA using Complex 6**



with $B(C_6F_5)_3$ free of metal-bonded σ-alkyl ligand, and the remaining neutral complex **6** may act as the source of M−R to initiate the polymerization by a group transfer process through a bimolecular mechanism (Scheme 2).[11] There are a few proposed pathways for the polymer chain growth in analogous complexes,[12] including alkyl transfer from an R−[B]$^-$ or R−[Al]$^-$ counteranion to the activated ethylene and activation of the precatalyst by lithium cation for the cobalt(I) system.

In summary, the first examples of zirconocenes with the tridentate ligand CpSiNSiCp are readily available by means of a straightforward synthetic route. X-ray diffraction studies of these complexes showed that they were sterically constrained. Under activation by MAO or $B(C_6F_5)_3$, the methyl complex **6** demonstrates moderate activity as a homogeneous catalyst for olefin polymerization. The applications of the new tridentate CpSiNSiCp metal catalysts are still under exploration.

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**Supporting Information Available:** CIF files giving crystallographic data for **4** and **5** and text and figures giving details of the preparation of the ligand and its zirconium complex and GPC and NMR analysis of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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