[{(η⁵-C₅Me₄)Me₂Si(η¹-NCMe₃)}(PMe₃)ScH]₂: A Unique Example of a Single-Component α-Olefin Polymerization Catalyst[†]

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Summary: The synthesis and structure of the title compound are described. [{(η⁵-C₅Me₄)Me₂Si(η¹-NCMe₃)}Sc-(PMe₃)]₂(μ-H)₂ (3) crystallizes with a molecule of toluene per scandium in the monoclinic system, space group $C2/c$, with $a = 21.238 (3)$ Å, $b = 11.470 (2)$ Å, $c = 22.253 (3)$ Å, $\beta = 113.16 (1)°$, $V = 4984.0 (14)$ Å³, $Z = 8$ (four dimers), and $d = 1.24$ g·cm⁻³. Propene, 1-butene, and 1-pentene are cleanly, albeit slowly, polymerized with >99% "head-to-tail" coupling to produce linear, atactic polymers with $M_n = 3000$–4000 and PDI's of 1.7–2.1. Chain transfer is relatively slow and appears to occur by β-H elimination. All evidence points to a one-component catalyst system with all scandium centers functioning alike.

Despite the tremendous importance of Ziegler–Natta olefin polymerization,[2] the structures of the catalysts have remained elusive. Direct characterization is complicated by their multicomponent composition, and normally only a small percentage of the transition-metal centers are active.[3]

Well-defined early-transition-metal or lanthanide-metal complexes that undergo facile olefin insertion reactions provide models for soluble Ziegler–Natta polymerization systems, and many are active ethylene polymerization catalysts.[4] On the other hand, well-defined organometallic systems that oligomerize or polymerize α-olefins are rare, with chain lengths limited to $C_{\leq 24}$ for those few systems that effect propene oligomerization.[4b,e] We report herein a well-characterized, single-component organoscandium system that is capable of catalyzing the regiospecific polymerization of α-olefins with relatively slow chain transfer to produce chains with degrees of polymerization as high as 70.

Our research group has found that scandocene derivatives of the types (η⁵-C₅Me₅)₂Sc-R, {(η⁵-C₅Me₄)₂SiMe₂}-
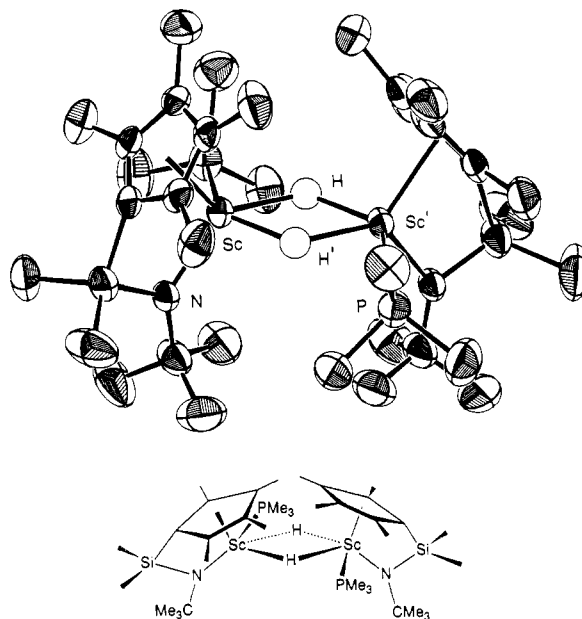
Figure 1. ORTEP drawing of [(Cp*SiNR)Sc(PMe₃)]₂(μ-H)₂ (3). Thermal ellipsoids are shown at the 50% probability level; methyl hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Sc–P, 2.996 (1); H–H′, 2.13 (4); ring centroid–Sc–N, 104.8 (3); H–Sc–H′, 65.9 (10); H–Sc–P, 68.8 (7); N–Sc–P, 95.3 (1).

Sc–R, and {(η⁵-C₅H₃CMe₃)₂SiMe₂}Sc–R undergo facile olefin insertion and β-H and β-alkyl elimination, elementary transformations pertinent to Ziegler–Natta catalysis.[5] The striking effect on the reactivity of the scandium center we observe as the steric properties of the supporting ligand system are varied prompted us to examine further variations of the ligand framework.[6] We anticipated that scandium derivatives of the type {(η⁵-C₅Me₄)Me₂Si(η¹-NCMe₃)}ScR ("(Cp*SiNR)ScR") would differ significantly from the scandocene systems, since the amido group should render the metal more Lewis acidic and even more electron deficient,[7] two properties that we felt would encourage olefin insertion.

The dimeric hydride derivative [(Cp*SiNR)Sc-(PMe₃)]₂(μ-H)₂ (3; Cp*SiNR = (η⁵-C₅Me₄)Me₂Si(η¹-NCMe₃)) is obtained in ca. 20% overall yield by the sequence shown in eq 1 and 2 (see the supplementary material for experimental details). Single crystals of 3 (as

$$\text{Li}_2\{(C_5Me_4)Me_2Si(NCMe_3)\} \xrightarrow{\text{ScCl}_3(\text{THF})_3}$$

$$(\text{Cp*SiNR})\text{ScCl} \xrightarrow{\text{LiCH(SiMe}_3)_2} (\text{Cp*SiNR})\text{ScCH(SiMe}_3)_2$$
$$\mathbf{1} \qquad\qquad\qquad\qquad\qquad\qquad \mathbf{2}$$
$$(1)$$

$$(\text{Cp*SiNR})\text{ScCH(SiMe}_3)_2 \xrightarrow[-\text{CH}_2(\text{SiMe}_3)_2]{\text{H}_2, \text{ PMe}_3}$$
$$\mathbf{2}$$

$$[(\text{Cp*SiNR})\text{Sc(PMe}_3)]_2(\mu\text{-H})_2 \quad (2)$$
$$\mathbf{3}$$
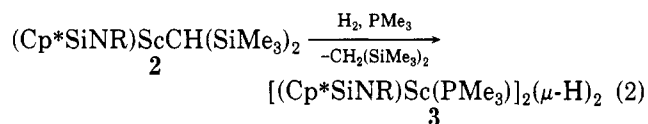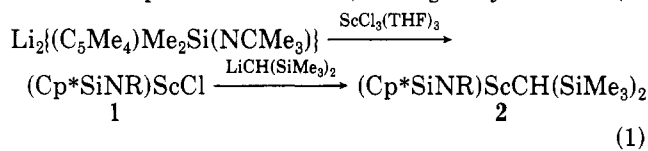
the toluene-d_8 solvate) grew in an NMR tube when a concentrated solution of 2 in toluene-d_8 was hydrogenated. An X-ray structure determination (Figure 1) revealed a double-hydrogen-bridged dimer of C_2 symmetry. The

[†] Contribution No. 7928.

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(2) For reviews on Ziegler–Natta polymerization see: (a) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *99*, 99. (b) Pino, P.; Mulhaupt, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 857. (c) Boor, J. *Ziegler-Natta Catalysts and Polymerizations*; Academic Press: New York, 1979. (d) Tait, P. J. T. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eds.; Pergamon Press: Oxford, 1989; Chapter 1.

(3) Tait, P. J. T.; Watkins, N. D. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eds.; Pergamon Press: Oxford, 1989; Chapter 2.

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(6) (a) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; Van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21. (b) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett*, in press.

(7) With use of the "neutral ligand formalism", an amido group can donate, at most, three electrons to Sc, two electrons fewer than a η⁵-cyclopentadienyl ligand.

Scheme I
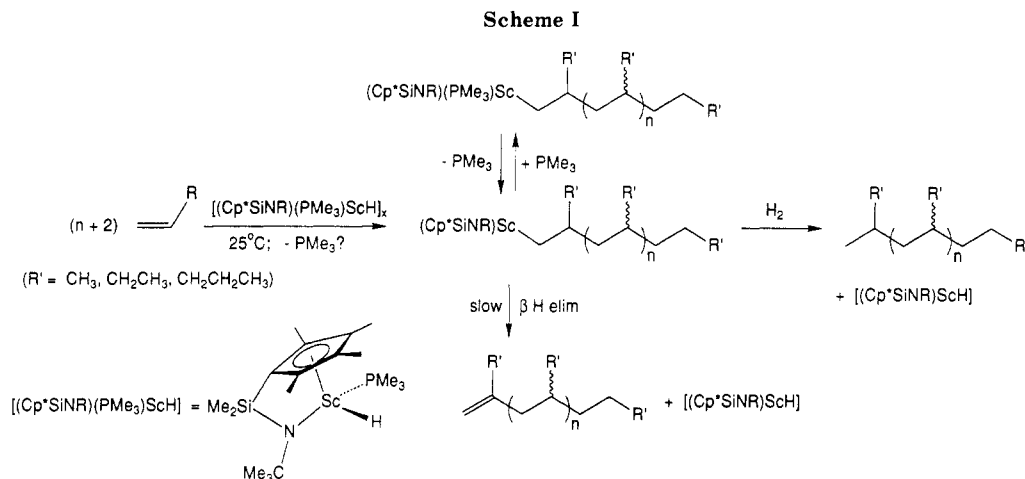
Sc–P bond length of almost 3 Å is a notable feature of the structure, and variable-temperature ^{31}P NMR studies establish that PMe$_3$ dissociation is rapid. The low solubility of 3 has prevented determination of its solution molecular weight; however, a monomer/dimer equilibrium in solution is indicated by the presence of two peaks (ca. 4:1 ratio) in the ^{31}P spectrum of 3 measured at –66 °C.[8] The variable-temperature ^{1}H NMR study was less informative, revealing only a single detectable species over the range –80 to +25 °C.

[(Cp*SiNR)Sc(PMe$_3$)]$_2$(μ-H)$_2$ (3) cleanly catalyzes the polymerization (or, perhaps more accurately, oligomerization) of propene, 1-butene, and 1-pentene, albeit rather slowly. For example, polymerization of 1-butene ca. 40% v/v in toluene at 25 °C with ca. 0.1 mol % of 3 affords after a few days polybutene with a number average molecular weight of 4000 ($X_n \approx 71$) and a polydispersity index (PDI) of 1.7 (GPC vs polystyrene). For neat 1-pentene with ca. 0.1 mol % of 3, polymerization rates of up to 52 turnovers/(Sc/h) at 25 °C are found, and after 19 h polypentene with M_n = 3000 ($X_n \approx 43$) and PDI = 2.1 is obtained. Due to its high volatility, and hence relatively low solubility at 25 °C, propene polymerization at pressures <5 atm is rather sluggish and impractical. The 1-butene and 1-pentene polymers are colorless, sticky oils, and weak vinylic resonances are observed in their ^{1}H NMR spectra, the intensity of which is consistent with β-H elimination being the principal chain transfer pathway.

Preliminary results indicate that 3 reacts with 2-methyl-1-pentene very slowly (1 day) to form the primary insertion product (Cp*SiNR)(PMe$_3$)Sc–CH$_2$CH(CH$_3$)-CH$_2$CH$_2$CH$_3$, which polymerizes propene but does not react further with excess 2-methyl-1-pentene. These results indicate the following: (1) Chain transfer by β-H elimination is only slowly reversed and does not compete effectively with the much faster addition of [(Cp*SiNR)-Sc–H] to propene. (2) Branching caused by the combination of polymer chain ends does not occur, so that only *linear* polypropene is formed.

Low-molecular-weight, saturated propene oligomers were obtained by termination with H$_2$ (4 atm) and examined by capillary GC/MS. The following observations support the conclusion that these α-olefin polymerizations involve >99% "head-to-tail" coupling to produce largely atactic polymers (Scheme I): (1) Of the four possible C$_9$ re-
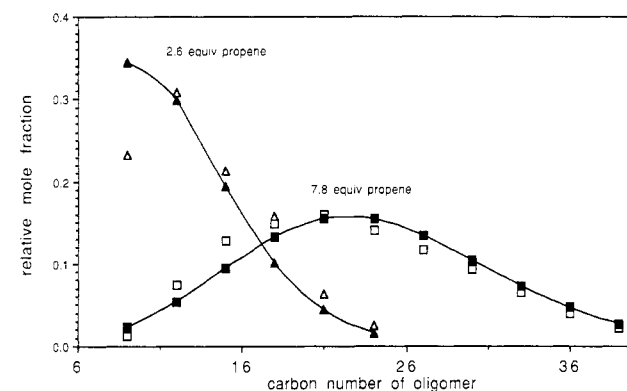

Figure 2. Experimentally (open symbols) vs calculated (solid symbols) (Poisson) oligomer distributions for the reactions of 3 with 2.6 equiv of propene (triangles) and with 7.8 equiv of propene (squares).

gioisomers, only the completely head-to-tail product, 2,4-dimethylheptane, is formed (>99%, GC). (2) The maximum theoretical number of separable stereoisomers are observed (in roughly comparable amounts), two for the tetramer, 2,4,6-trimethylnonane, and four for the pentamer, 2,4,6,8-tetramethylundecane. (3) Preliminary ^{1}H and ^{13}C NMR data for polypropylene (obtained after prolonged reaction time) fit best with published spectra of atactic polypropylene.[9]

The following experiments address the ever-present concerns that only a minor component of the mixture is responsible for the α-olefin polymerization process or that more than one active catalyst is operating: (1) Monitoring the polymerization by ^{1}H NMR spectroscopy reveals that on addition of propene the signals due to 3 completely disappear as a complex spectrum develops; addition of H$_2$ regenerates the spectrum for 3. (2) The molecular weight distributions of the oligomers obtained at relatively low propene conversion (where chain transfer effectively does not occur) correspond well with a Poisson function based on (monomer consumed)/scandium (Figure 2), indicating that a majority of the scandium centers are active.[10]

(8) Variable-temperature ^{31}P NMR spectra of ca. 0.05 M solution of 3 in toluene-d_8 were measured on a JEOL FX90Q instrument (^{31}P, 36.3 MHz). Two peaks (δ –43.7 and –55.6 vs H$_3$PO$_4$) appear in a ca. 4:1 ratio at –66 °C and coalesce at ca. –30 °C. At 20 °C, a single resonance for 3 is observed at δ –54.1.

(9) Bovey, F. A.; Jelinski, L. W. *Chain Structure and Conformation of Macromolecules*; Academic Press: New York, 1982; Chapter 3.

(10) The Poisson function, $N_n/N = [1/(n-1)!]\nu^{n-1} e^{-\nu}$, is a statistical model that applies to an ideal "living" polymerization in which there is no chain transfer or chain termination and all active centers are growing at the same rate. In Figure 2 the experimentally determined oligomer distributions are compared with statistical distributions for which ν = (monomer consumed)/scandium. For a discussion of the Poisson model for polymer size distribution see: Flory, P. J. *J. Am. Chem. Soc.* **1940**, *62*, 1561. For a discussion of living polymers see: Szwarc, M. *Living Polymers and Mechanisms of Anionic Polymerization*; Advances in Polymer Science; Springer-Verlag: West Berlin, 1983; Vol. 49.

We are currently examining the kinetics of the polymerization and are preparing various alkyl derivatives of this scandium system in order to elucidate the nature of the active catalyst.

Supplementary Material Available: Experimental details describing the syntheses of $Li_2\{(\eta^5\text{-}C_5Me_4)Me_2Si(\eta^1\text{-}NCMe_3)\}$, $\{(\eta^5\text{-}C_5Me_4)Me_2Si(\eta^1\text{-}NCMe_3)\}ScCl$, $\{(\eta^5\text{-}C_5Me_4)Me_2Si(\eta^1\text{-}NCMe_3)\}ScCH(SiMe_3)_2$, and details of the structure determination, including listings of final atomic coordinates, thermal parameters, and bond distances and angles (15 pages); a listing of structure factors (10 pages). Ordering information is given on any current masthead page.
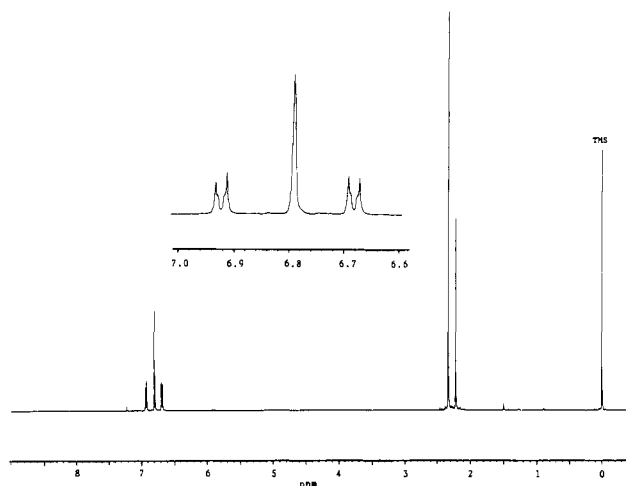

Figure 1. ^1H NMR spectrum of 1,1-dimesitylgermole (**1b**) in $CDCl_3$ (500 MHz).

Scheme I

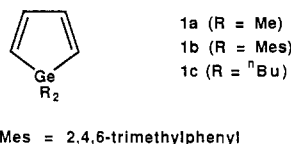# Carbon-Unsubstituted Germoles: Palladium-Catalyzed Reactions of Germylenes with Acetylene

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Summary: Dimesityl- and dibutylgermylenes react with acetylene in the presence of a catalytic amount of palladium complexes to yield the corresponding C-unsubstituted germoles **1b** and **1c**, which are characterized by their spectral data and by their reactions with maleic anhydride and diiron nonacarbonyl.

Although group 14 metalloles have proven to be quite interesting and important synthetic intermediates for various ring systems,[1,2] many of these studies have been carried out with metalloles possessing at least two substituents on the ring carbons. Regarding C-unsubstituted germoles, only 1,1-dimethylgermole (**1a**) has been isolated

1a (R = Me)
1b (R = Mes)
1c (R = ^nBu)

Mes = 2,4,6-trimethylphenyl

by the catalytic vacuum-flow dehydration of 1,1-dimethyl-1-germacyclopent-4-en-3-ol[3a] or by the thermolysis of the corresponding *N*-phenylcarbamate.[3b,c] We report
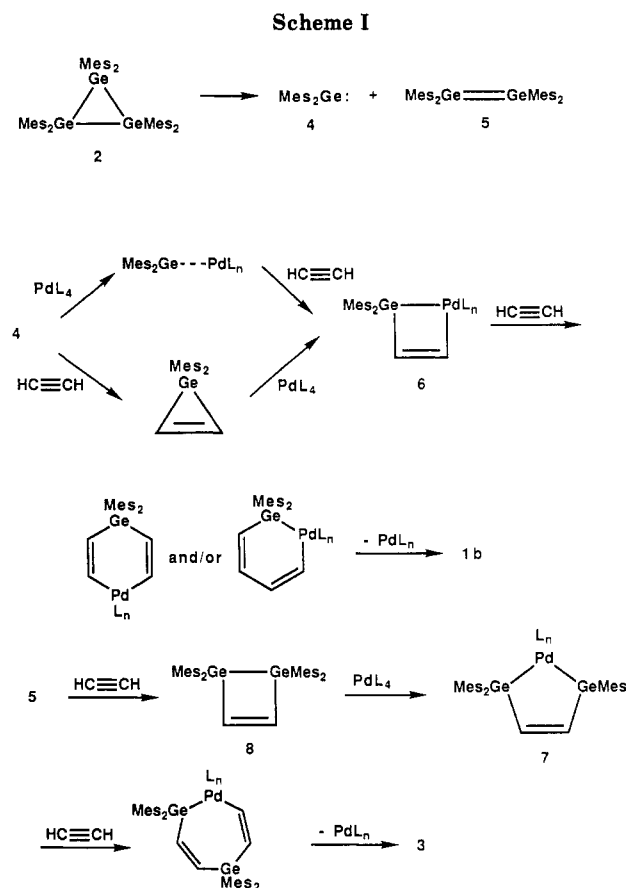
here a novel synthesis of C-unsubstituted germoles **1b** and **1c** by the palladium-catalyzed reactions of germylenes with acetyloene.[4]

When acetylene was bubbled into a toluene solution of hexamesitylcyclotrigermane (**2**)[5] in the presence of

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(4) A similar synthetic method from a disilane or siliranes gives C-substituted siloles; see: (a) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1975**, *86*, C27. (b) Ishikawa, M.; Sugisawa, H.; Harata, O.; Kumada, M. *J. Organomet. Chem.* **1981**, *217*, 43. (c) Seyferth, D.; Duncan, D. P.; Vick, S. C. *J. Organomet. Chem.* **1977**, *125*, C5. (d) Seyferth, D.; Shannon, M. L.; Vick, S. C.; Lim, T. F. O. *Organometallics* **1985**, *4*, 57 and references cited therein. (e) Ishikawa, M.; Ohshita, J.; Ito, Y.; Iyoda, J. *J. Am. Chem. Soc.* **1986**, *108*, 7417. (f) Ohshita, J.; Isomura, Y.; Ishikawa, M. *Organometallics* **1989**, *8*, 2050.

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