Ansa Complexes

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Synthesis of a Paramagnetic Polymer by Ring-Opening Polymerization of a Strained [1]Vanadoarenophane**

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During the last three decades it has been impressively demonstrated that the molecular ring-strain present in bridged [*n*]metallocenophanes can be exploited in a variety of useful ways.[1] The strained character of [*n*]metallocenophanes, and related [*n*]metalloarenophanes, is reflected by enhanced reactivity of either the bond between the carbocyclic ligands and the bridging element(s),[2] that between the bridging elements[3] or those between the metal and one of the carbocyclic ligands.[4] Both insertion and substitution chemistry have been demonstrated to afford ring-expanded or ring-opened products, respectively. In particular, the discovery of the ring-opening polymerization (ROP) of strained [*n*]ferrocenophanes in 1992 to yield high-molecular-weight polyferrocenes represented a landmark moment in both organometallic chemistry and materials science. As a consequence of this advance, the last 15 years has seen tremendous interest in the syntheses of compounds containing this structural motif and their propensity to undergo ring-opening reactions.[1,5] Whereas ROP techniques enabled the successful polymerization of [*n*]ferrocenophanes with varying bridging elements, the preparation of polymers containing transition-metal centers other than iron still remains a challenging area of research.[1,5b] In fact, their number is limited to a few examples of titanium,[2g] chromium,[6] or ruthenium-based[7] materials. To date, no controlled access to well-defined organometallic polymers containing repeat units with unpaired electrons has been reported using ROP, even though these polymers could potentially exhibit highly interesting physical properties such as intramolecular electro- and magnetocommunication.

It was shown that even dinuclear sandwich derivatives exhibit strong electronic and magnetic communication between the paramagnetic d^5-vanadium centers, which are transmitted by different silicon or carbon spacers.[8] Combining these properties with the ease of processing commonly associated with polymers may therefore lead to desirable materials. Besides the attempted thermally induced ROP of silicon-bridged [1]trovacenophanes reported by Elschenbroich and co-workers in 2004,[9] the polymerization behavior of strained [*n*]metalloarenophanes derived from the paramagnetic sandwich complexes trovacene, $[V(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)]$, and bis(benzene)vanadium, $[V(\eta^6\text{-}C_6H_6)_2]$, has not yet been investigated in detail. However, the molecular distortion of [*n*]vanadoarenophanes resembles that found in the corresponding [*n*]ferrocenophanes, and hence suggests their suitability as monomers in ROP processes. Virtually all of the paramagnetic polymers prepared to date are either coordination polymers[10] or have been obtained by polycondensation routes, whereby the isolated materials are usually either of low molecular weight, insoluble, or of poorly defined structure.[11] Consequently, the application of a chain-growth polymerization, such as ROP, appears to be much more suitable for the preparation of well-defined paramagnetic polymers. Herein we report on the synthesis and characterization of [1]bora- and [1]sila derivatives of bis(benzene)vanadium, as well as on their polymerization behavior. The ROP of the silicon-bridged species leads to a soluble organometallic polymer containing paramagnetic repeat units, whereas the [1]boravanadoarenophane undergoes a stoichiometric ring-opening reaction under similar conditions.

Stoichiometric salt-elimination reactions of dilithiated bis(benzene)vanadium, $[V(\eta^6\text{-}C_6H_5Li)_2]\cdot$tmeda (**1**), with $Cl_2BN(SiMe_3)_2$ or $Cl_2Si\textit{i}PrMe$ in nonpolar solvents at −78 °C resulted in the formation of the strained ansa complexes **2** and **3**, respectively. Both [1]vanadoarenophanes were isolated after recrystallization as deep red or orange crystalline solids in good yields (75 and 61 %, respectively; Scheme 1).[12]

The identity of **2** and **3** was unambiguously confirmed by mass spectrometry, elemental analysis, and EPR spectroscopy. Both complexes proved to be thermally very robust, which, for example, allowed the observation of the molecular ion as the most intense peak in the mass spectrum of **2**. Further evidence for the formation of ansa complexes was derived from NMR spectroscopy. Whereas the aromatic protons of the C_6H_5 moieties are not observed in the NMR spectra of **2** and **3** due to paramagnetic line broadening, controlled decompostion of C_6D_6 solutions by exposure to air

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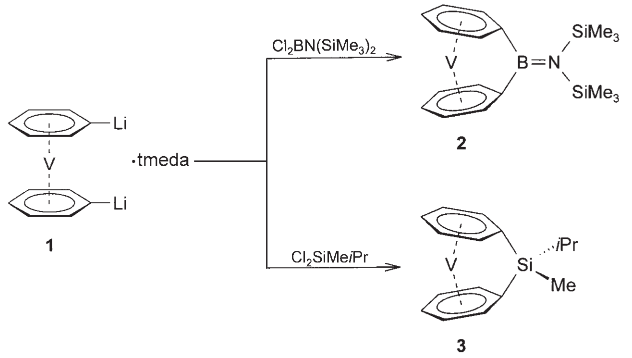


Scheme 1. Syntheses of the strained [1]vanadoarenophanes **2** and **3**.

yielded a black, vanadium-containing precipitate and a clear solution of the free ligands $Ph_2BN(SiMe_3)_2$ and Ph_2Si*i*PrMe.[13]

To authenticate the formation of a strained species, the molecular structure of **2** was determined by single-crystal structure analysis (Figure 1).[14,15] As expected, the incorporation of a small boron bridge results in a substantial deviation of the carbocyclic ligands from the ideal coplanar arrangement observed in the parent sandwich complex **1**.[16] Accordingly, the distortion imposes pronounced molecular ring strain that is manifested by the tilt angle $\alpha = 31.12(7)°$. This value is noticeably larger than those in the related [1]silavanadoarenophanes ($\alpha = 19$–$20°$)[8a,b,17] and [1]borachromoarenophanes ($\alpha = 26.6°$),[18] a fact that is attributable to the smaller covalent radius of the boron atom and the longer interannular distance in bis(benzene)vanadium. Bis(benzene)vanadium (332 pm) and ferrocene (335 pm), however, feature similar interannular distances and hence the molecular distortion of **2** is comparable to that of the corresponding [1]boraferrocenophane ($\alpha = 32.4°$).[4a] As a result of the tilted structure of **2**, the deformation angle δ of 155.6° is smaller than that in the unstrained derivatives $[V(\eta^6\text{-}C_6H_5)_2ZrCp'_2]$ ($Cp' = C_5H_4t\text{Bu}$; $\delta = 176.3°$)[19] and bis(benzene)vanadium ($\delta = 180°$).[16]

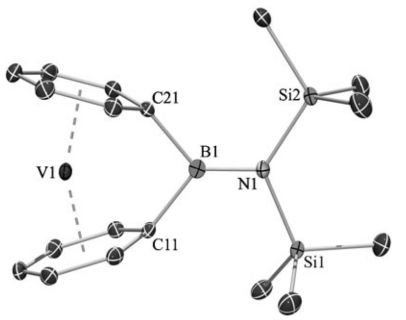


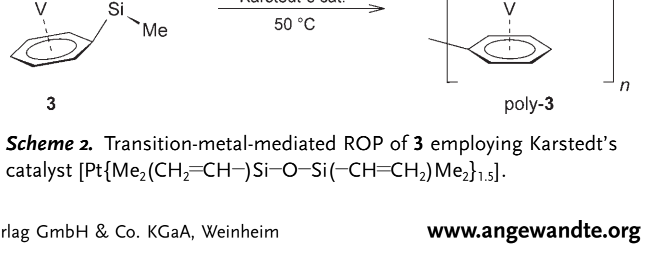
Figure 1. Molecular structure of **2** in the solid state. Selected bond lengths [Å] and angles [°]:V1-C_{Ph} 2.1373(19)–2.2563(19), C11-B1 1.6177(28), C21-B1 1.6077(28), B1-N1 1.3982(27), V1-X_{Ph1} 1.679, V1-X_{Ph2} 1.676; C11-B1-C21 98.91(15), C11-B1-N1 129.08(18), C21-B1-N1 131.98(18), X_{Ph1}-V1-X_{Ph2} 155.6, $\alpha = 31.12(7)$. (X_{Ph1} = centroid C11–C16, X_{Ph2} = centroid C21–C26.).

Even though the solid-state structure of **3** has not yet been determined, the molecular distortion can be estimated by EPR spectroscopy.[12] It has been established by Elschenbroich and co-workers that the tilting of the carbocyclic ligands in [*n*]metalloarenophanes results in a noticeable increase in the metal-to-ligand spin delocalization and a decrease in the hyperfine coupling constant a_{iso}.[8a,b,9,19] The isotropic EPR spectra of **2** and **3** in fluid solutions (toluene; 240 K) are very similar and feature well resolved coupling to one ^{51}V center ($I = {}^7\!/_2$). The hyperfine coupling constants (**2**: $a_{iso} = 54.5$ G; **3**: $a_{iso} = 56.9$ G) are smaller than in the unstrained sandwich complexes $[V(\eta^6\text{-}C_6H_5)_2ZrCp'_2]$ ($Cp' = C_5H_4\text{-}t\text{Bu}$; $a_{iso} = 62.3$ G)[19] and bis(benzene)vanadium ($a_{iso} = 63.8$ G),[17] and strongly resemble that of the silicon-bridged derivative $[V(\eta^6\text{-}C_6H_5)_2SiPh_2]$ ($a_{iso} = 56.3$ G; $\alpha = 19.2°$).[17] These data suggest that **3** and $[V(\eta^6\text{-}C_6H_5)_2SiPh_2]$ exhibit a comparable degree of molecular distortion, and further highlight the more tilted nature of the [1]boravanadoarenophane **2**.

To quantify the amount of ring strain present in **2** and **3**, their thermal behavior was investigated by differential scanning calorimetry (DSC).[12,20] The DSC thermograms of **2** and **3** revealed endothermic peaks at approximately 131 °C and 199 °C (onset), respectively, followed by distinct exothermic peaks (**2**: 169 °C, $\Delta H = 92\ \text{kJ mol}^{-1}$; **3**: 204 °C, $\Delta H = 18\ \text{kJ mol}^{-1}$). This sequence of events is similar to that observed during the preparation of polyferrocenylsilanes from [1]silaferrocenophanes, where the former corresponds to the melting point of the monomer and the latter arises from the ROP process.[5a,21]

It has been demonstrated that strained, cyclic carbosilanes undergo transition-metal-catalyzed ROP[22] and that this methodology can be extended to [1]silaferrocenophanes.[23] In the case of the latter, platinum catalysts were shown to follow a heterogeneous catalytic mechanism[24] and this particular system has been successfully applied to the polymerization of other metalloarenophanes.[25] It therefore seemed a logical method to employ for the polymerization of **3**, given the expected similarities between this compound and the [1]silaferrocenophanes. Heating a solution of **3** and Karstedt's catalyst (5 mol %) in toluene resulted in the original deep yellow solution becoming orange over a period of about 18 h. The resulting material was soluble in THF, and could be precipitated by addition to hexanes, but was only isolated in low yield.

The material arising from **3** (poly-**3**) (Scheme 2) exhibited an EPR signal ($g = 1.987$ G) at 110 K.[12] This spectrum contains only a single line, which was rather broad (linewidth = 70 G) and unfortunately precluded the observation of any ^{51}V hyperfine coupling, and which therefore prevents



Scheme 2. Transition-metal-mediated ROP of **3** employing Karstedt's catalyst $[Pt\{Me_2(CH_2{=}CH{-})Si{-}O{-}Si({-}CH{=}CH_2)Me_2\}_{1.5}]$.

definitive confirmation of the proposed ring-opened microstructure. Small-angle X-ray scattering (SAXS) has previously been used for determination of the weight-averaged molecular weight (M_w) and the radius of gyration (R_g) of metal-containing polymers.[26] Indeed, this technique is well suited to the study of metallopolymers in solution due to the intrinsic difference in electron density between the solvent and solute.[27] This is fortunate given that determining these parameters by conventional static light scattering experiments is problematic due to the intense colors that these materials display in solution. The scattering from a solution of poly-**3** in THF has been measured over a Q range of 0.3 to 5.5 nm^{-1}. The initial decay of the intensity is in agreement with a Q^{-2} power law, which suggests that the crossover from "Guinier" to power-law occurs at a Q range that is too low to be accessed by the instrument used. Thus, we have deduced that R_g is approximately $\pi/0.3$ (≈ 10 nm) or greater. The data have been further analyzed by fitting the Debye model for monodispersed chains in a theta solvent, giving a radius of gyration of 5.8 ± 0.4 nm. However, a similar quality of fit was obtained for polydisperse chain sizes and for a self-avoiding walk rather than an ideal random walk distribution and both these models gave larger values for the radius of gyration. Thus, we conclude that the radius of gyration of poly-**3** in THF solution is 6 nm or more, which corresponds to a M_w value of 28000 $g\,mol^{-1}$ versus monodisperse polystyrene standards.[12]

It is well-established that the ROP of [1]silaferrocenophanes, in the absence of photo-excitation, is initiated by the cleavage of the strained Si$-$C$_{ipso}$ bond. Depending on the ROP technique, the bond cleavage is induced either thermally, by a low-valent transition-metal catalyst, or by nucleophilic or electrophilic reagents.[1,2a,c,24,28] Conversely, the ring-opening of [1]boraferrocenophanes is dominated by Fe$-$C$_{Cp}$ bond reactivity, which arises from a weakening of this linkage by the increase in tilt angle and a strengthening of the bridging element-C$_{ipso}$ bond, both relative to the silicon-bridged case. We, therefore, investigated which mode of reactivity would prevail with the [1]boravanadoarenophane **2**. Consistent with suggestions from mass spectrometry, **2** did not show any signs of reaction when heated at 85 °C in C_6D_6 for four days. However, under the same conditions and in the presence of catalytic amounts of $[Pt(PEt_3)_4]$, a black crystalline solid was ultimately obtained in high yield. The mass spectrum of this material exhibited a peak at m/z 460, which suggested a formulation as $\mathbf{2} + C_6D_6$. According to elemental analysis, the platinum fragment was not incorporated, and EPR spectroscopic studies indicated the presence of an unstrained compound ($a_{iso} = 63.7$ G). The composition of the product **4**, which was not immediately apparent from these data, was unambiguously elucidated by single-crystal X-ray diffraction (Figure 2).[14] The parameters for **4** are unremarkable, although they confirm the unstrained nature of the structure. In contrast to the large differences observed in the molecular structure of the strained starting material (2.1373(19)–2.2563(19) Å), the V$-$C bond lengths in **4** are found within a narrow range (2.1878(34)–2.2205(34) Å). As expected, the tilt angle $\alpha = 5.64(13)°$ is significantly smaller than in **2** ($\alpha = 31.12(7)°$), and the deformation angle $\delta = 175.0°$ is considerably wider (**2**: $\delta = 155.6°$).

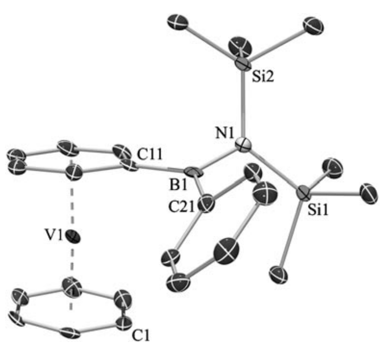


Figure 2. Molecular structure of **4** in the solid state. Selected bond lengths [Å] and angles [°]: V1-C$_{Ph}$ 2.1878(34)–2.2205(34), C11-B1 1.5491(54), C21-B1 1.5776(56), B1-N1 1.4698(49), V1-X$_{Ph1}$ 1.682, V1-X$_{Ph2}$ 1.681, C11-B1-C21 121.01(31), C11-B1-N1 119.18(34), C21-B1-N1 119.40(32), X$_{Ph1}$-V1-X$_{Ph2}$ 175.0, C12-C11-B1-N1 −160.45(32), $\alpha = 5.64(13)$. (X$_{Ph1}$ = centroid C1–C6, X$_{Ph2}$ = centroid C11–C16.)

An additional control experiment was carried out, which proved that **2** underwent no reaction in the presence of aliphatic solvents. Thus, the reaction of **2** with $[Pt(PEt_3)_4]$ in benzene results in a stoichiometric ring-opening reaction, in which one η^6-coordinated C_6H_5 ring is cleaved from the metal center and the free coordination site is occupied by a solvent molecule. Hence, the thermodynamic driving force for this remarkable transformation is the reduction of molecular ring strain. Müller and co-workers recently reported on similar reactivity of a gallium-bridged [1]molybdoarenophane to yield the corresponding ring-opening product.[29] We are currently attempting to develop this reaction into a controlled ROP process for [1]boravanadoarenophanes.

In summary, we have shown that the highly strained [1]vanadoarenophanes **2** and **3** are susceptible to different types of ring-opening reactions. Whereas the former opens by cleavage of the V$-$C$_{arene}$ bond to yield monometallic compound **4**, the latter reacts at the Si$-$C$_{ipso}$ bond to afford a polymer. Poly-**3** represents a rare example of a well-characterized macromolecule containing spin-active metal centers in the main-chain.

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[1] a) I. Manners, *Adv. Organomet. Chem.* **1995**, *37*, 131–168; b) P. Nguyen, P. Gomez-Elipe, I. Manners, *Chem. Rev.* **1999**, *99*, 1515–1548; c) D. E. Herbert, U. F. J. Mayer, I. Manners, *Angew. Chem.* **2007**, *119*, 5152–5173; *Angew. Chem. Int. Ed.* **2007**, *46*, 5060–5081; d) V. Bellas, M. Rehahn, *Angew. Chem.* **2007**, *119*, 5174–5197; *Angew. Chem. Int. Ed.* **2007**, *46*, 5082–5104.

[2] a) J. B. Sheridan, A. J. Lough, I. Manners, *Organometallics* **1996**, *15*, 2195–2197; b) T. Mizuta, T. Yamasaki, H. Nakazawa, K. Miyoshi, *Organometallics* **1996**, *15*, 1093–1100; c) J. B. Sheridan, K. Temple, A. J. Lough, I. Manners, *J. Chem. Soc. Dalton Trans.* **1997**, 711–713; d) F. Jäkle, R. Rulkens, G. Zech, D. A. Foucher, A. J. Lough, I. Manners, *Chem. Eur. J.* **1998**, *4*, 2117–2128; e) T. Mizuta, M. Onishi, K. Miyoshi, *Organometallics* **2000**, *19*, 5005–

5009; f) T. Mizuta, M. Onishi, T. Nakazono, H. Nakazawa, K. Miyoshi, *Organometallics* **2002**, *21*, 717–726; g) M. Tamm, A. Kunst, E. Herdtweck, *Chem. Commun.* **2005**, 1729–1731.

[3] a) W. Finckh, B. Z. Tang, A. Lough, I. Manners, *Organometallics* **1992**, *11*, 2904–2911; b) M. Herberhold, U. Steffl, W. Milius, B. Wrackmeyer, *Angew. Chem.* **1997**, *109*, 1545–1546; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1508–1510; c) H. Braunschweig, M. Lutz, K. Radacki, *Angew. Chem.* **2005**, *117*, 5792–5796; *Angew. Chem. Int. Ed.* **2005**, *44*, 5647–5651; d) H. Braunschweig, M. Lutz, K. Radacki, A. Schaumlöffel, F. Seeler, C. Unkelbach, *Organometallics* **2006**, *25*, 4433–4435; e) H. Braunschweig, T. Kupfer, M. Lutz, K. Radacki, F. Seeler, R. Sigritz, *Angew. Chem.* **2006**, *118*, 8217–8220; *Angew. Chem. Int. Ed.* **2006**, *45*, 8048–8051; f) H. Braunschweig, T. Kupfer, *Organometallics* **2007**, *26*, 4634–4638.

[4] a) H. Braunschweig, R. Dirk, U. Englert, A. Berenbaum, J. C. Green, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2000**, *122*, 5765–5774; b) T. Mizuta, Y. Imamura, K. Miyoshi, *J. Am. Chem. Soc.* **2003**, *125*, 2068–2069; c) M. Tanabe, S. C. Bourke, D. E. Herbert, A. J. Lough, I. Manners, *Angew. Chem.* **2005**, *117*, 6036–6040; *Angew. Chem. Int. Ed.* **2005**, *44*, 5886–5890.

[5] a) D. A. Foucher, B. Z. Tang, I. Manners, *J. Am. Chem. Soc.* **1992**, *114*, 6246–6248; b) I. Manners, *Chem. Commun.* **1999**, 857–865; c) M. J. MacLachlan, M. Ginzburg, N. Coombs, T. W. Coyle, N. P. Raju, J. E. Greedan, G. A. Ozin, I. Manners, *Science* **2000**, *287*, 1460–1463; d) I. Manners, *Science* **2001**, *294*, 1664–1666.

[6] a) K. C. Hultzsch, J. M. Nelson, A. J. Lough, I. Manners, *Organometallics* **1995**, *14*, 5496–5502; b) A. Berenbaum, I. Manners, *Dalton Trans.* **2004**, 2057–2058.

[7] a) J. M. Nelson, A. J. Lough, I. Manners, *Angew. Chem.* **1994**, *106*, 1019–1021; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 989–991; b) U. Vogel, A. J. Lough, I. Manners, *Angew. Chem.* **2004**, *116*, 3383–3387; *Angew. Chem. Int. Ed.* **2004**, *43*, 3321–3325.

[8] a) C. Elschenbroich, A. Bretschneider-Hurley, J. Hurley, W. Massa, S. Wocadlo, J. Pebler, E. Reijerse, *Inorg. Chem.* **1993**, *32*, 5421–5424; b) C. Elschenbroich, A. Bretschneider-Hurley, J. Hurley, A. Behrendt, W. Massa, S. Wocadlo, E. Reijerse, *Inorg. Chem.* **1995**, *34*, 743–745; c) C. Elschenbroich, J. Plackmeyer, M. Nowotny, K. Harms, J. Pebler, O. Burghaus, *Inorg. Chem.* **2005**, *44*, 955–963; d) C. Elschenbroich, O. Schiemann, O. Burghaus, K. Harms, *Chem. Commun.* **2005**, 2149–2151; e) C. Elschenbroich, J. Plackmeyer, M. Nowotny, A. Behrendt, K. Harms, J. Pebler, O. Burghaus, *Chem. Eur. J.* **2005**, *11*, 7427–7441, and references therein.

[9] C. Elschenbroich, F. Paganelli, M. Nowotny, B. Neumüller, O. Burghaus, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1599–1606.

[10] For example: a) C.-T. Chen, K. S. Suslick, *Coord. Chem. Rev.* **1993**, *128*, 293–322; b) M. Rosenblum, H. M. Nugent, K.-S. Jang, M. M. Labes, W. Cahalane, P. Klemarczyk, W. M. Reiff, *Macromolecules* **1995**, *28*, 6330–6342; c) W. Kaim, *Coord. Chem. Rev.* **2002**, *230*, 126–139; d) M. A. Kiskin, I. G. Fomina, G. G. Aleksandrov, A. A. Sidorov, V. M. Novotortsev, Y. V. Rakitin, Z. V. Dobrokhotova, V. N. Ikorskii, Y. G. Shvedenkov, I. L. Eremenko, I. I. Moiseev, *Inorg. Chem. Commun.* **2005**, *8*, 89–93; e) M. Mitsumi, H. Goto, S. Umebayashi, Y. Ozawa, M. Kobayashi, T. Yokoyama, H. Tanaka, S. Kuroda, K. Toriumi, *Angew. Chem.* **2005**, *117*, 4236–4240; *Angew. Chem. Int. Ed.* **2005**, *44*, 4164–4168.

[11] a) J. E. Sheats, C. E. Carraher, C. U. Pittman, *Metal Containing Polymer Systems*, Plenum, New York, **1985**; b) "Organometallic Polymers": C. U. Pittman, C. E. Carraher, J. R. Reynolds, *Encycl. Polym. Sci. Eng.* **1987**, *10*, 541; c) E. W. Neuse, H. Rosenberg, *J. Macromol. Sci. Rev. Macromol. Chem.* **1970**, *4*, 1–145.

[12] The experimental section including the syntheses, full characterization, and spectroscopic data of all compounds, as well as representative EPR spectra of **3**, the EPR spectrum of poly-**3** and a complete list of EPR parameters can be found in the Supporting Information. In addition, theoretical and experimental details of the SAXS experiments are included along with a calibration curve constructed for polystyrene standards.

[13] NMR data for $Ph_2BN(SiMe_3)_2$: ^{1}H NMR (200 MHz, C_6D_6): $\delta =$ 0.15 (s, 18 H, $SiMe_3$), 7.20–7.30 (m, 6 H, C_6H_5), 7.50–7.60 ppm (m, 4 H, C_6H_5); ^{11}B NMR (64 MHz, C_6D_6): $\delta = 56.6$ ppm. NMR data for $Ph_2Si\mathit{i}PrMe$: ^{1}H NMR (200 MHz, C_6D_6): $\delta = 0.45$ (s, 3 H, CH_3), 1.13 (d, 6 H, $^3J_{H,H} = 6.0$ Hz, $CH\mathit{Me}_2$), 1.26–1.41 (m, 1 H, $C\mathit{H}Me_2$), 7.18–7.23 (m, 6 H, C_6H_5), 7.50–7.55 ppm (m, 4 H, C_6H_5).

[14] Experimental details of all X-ray crystal structure determinations are deposited with the Supporting Information. CCDC-670757 (**2**) and CCDC-670756 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[15] Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with two independent molecules in the asymmetric unit, the structural parameters of which differed only marginally. Hence, for simplicity reasons only one of the molecules is discussed.

[16] E. O. Fischer, H. P. Fritz, J. Manchot, E. Priebe, R. Schneider, *Chem. Ber.* **1963**, *96*, 1418–1423.

[17] C. Elschenbroich, J. Hurley, B. Metz, W. Massa, G. Baum, *Organometallics* **1990**, *9*, 889–897.

[18] H. Braunschweig, M. Homberger, C. Hu, X. Zheng, E. Gullo, G. Clentsmith, M. Lutz, *Organometallics* **2004**, *23*, 1968–1970.

[19] C. Elschenbroich, E. Schmidt, B. Metz, K. Harms, *Organometallics* **1995**, *14*, 4043–4045.

[20] The absence of mass loss in the TGA thermogram of the "monomer", over the temperature range corresponding to the exotherm in the DSC experiment, is generally taken to be consistent with a ROP process. The small quantities of sample required in combination with the air-sensitivity of the monomer, however, precluded performing this experiment in the case of compounds **2** and **3**.

[21] A more detailed discussion of the DSC parameters and figures of the corresponding DSC thermograms of **2** and **3** are given in the Supporting Information.

[22] See for example: H.-J. Wu, L. V. Interrante, *Macromolecules* **1992**, *25*, 1840.

[23] a) Y. Ni, R. Rulkens, J. K. Pudelski, I. Manners, *Macromol. Rapid Commun.* **1995**, *16*, 637; b) N. P. Reddy, H. Yamashita, M. Tanaka, *J. Chem. Soc. Chem. Commun.* **1995**, 2263.

[24] K. Temple, F. Jäkle, J. B. Sheridan, I. Manners, *J. Am. Chem. Soc.* **2001**, *123*, 1355.

[25] A. Bartole-Scott, H. Braunschweig, T. Kupfer, M. Lutz, I. Manners, T.-. L. Nguyen, K. Radacki, F. Seeler, *Chem. Eur. J.* **2006**, *12*, 1266.

[26] S. Kelch, M. Rehahn, *Macromolecules* **1997**, *30*, 6185.

[27] *Small Angle X-Ray Scattering* (Eds.: O. Glatter, O. Kratky), Academic Press, London, **1982**, pp. 3–13.

[28] a) Y. Ni, R. Rulkens, I. Manners, *J. Am. Chem. Soc.* **1996**, *118*, 4102–4114; b) T. Baumgartner, F. Jäkle, R. Rulkens, G. Zech, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2002**, *124*, 10062–10070.

[29] C. L. Lund, J. A. Schachner, J. W. Quail, J. Müller, *J. Am. Chem. Soc.* **2007**, *129*, 9313–9320.