

Hydrozirconation of first-generation allyl-functionalized dendrimers and dendrimer model compounds

Reinout Meijboom^{a,*}, John R. Moss^{a,*}, Alan T. Hutton^a, Tracy-Ann Makaluza^b,
Selwyn F. Mapolie^b, Fazlin Waggie^b, Mark R. Domingo^c

^a Department of Chemistry, University of Cape Town, South Africa

^b Department of Chemistry, University of the Western Cape, South Africa

^c Sasol Polymers, P.O. Box 2525, Randburg 2125, South Africa

Received 20 February 2004; accepted 11 March 2004

Abstract

Several allyl-functionalized dendrimers and mono-functional model compounds have been prepared. These have been hydrozirconated using $[\text{Cp}_2\text{ZrHCl}]_x$ to give zirconocene terminated dendrimers. These dendrimers have been characterized using spectroscopic techniques, particularly NMR.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Dendrimer; Schwartz's reagent; Hydrozirconation; Zirconium

1. Introduction

The rising demand for materials with improved and novel properties has shifted the emphasis in polymer research from traditional linear polymers, via cross-linked and branched polymers, to hyperbranched or dendritic polymers. This new class of highly branched three-dimensional molecules has intrigued researchers and numerous review articles have been published in recent years [1,2]. Many applications for dendrimers have been found, one of the most exciting applications being the use of dendrimers as an immobilisation phase for homogeneous catalysts [3]. From our ongoing research into dendrimers and their applications in organometallic chemistry [2,4], it has become clear that the number of synthetic routes available to attach an organometallic moiety to the branches of a dendrimer is limited. This limitation is mainly due to the requirement

to employ reactions that have a quantitative yield in order to prevent imperfections and by-products in the dendrimer build-up [5,6].

Schwartz's reagent is a well-known and convenient reagent in organic chemistry for the functionalization of alkenes [7]. In our search towards new organometallic dendrimers [2,4] we have utilized Schwartz's reagent to functionalize a series of organic dendrimers. We have also hydrozirconated some mono-functional model compounds in order to compare the reactions of these compounds with those of the dendrimers with Schwartz's reagent. The poly-zirconium species reported here are valuable reactants for the functionalization of easily-obtained poly-alkene functionalized dendrimers. For example the hydrozirconation reaction has been used to build up organogermanium dendrimers in the past [8]. Only a few other examples of zirconocene functionalized dendrimers have been reported [9] up to date.

2. Results and discussion

The allyl terminated dendrimer (entry 9, Table 1) was prepared according to Scheme 1. Allylbromide was

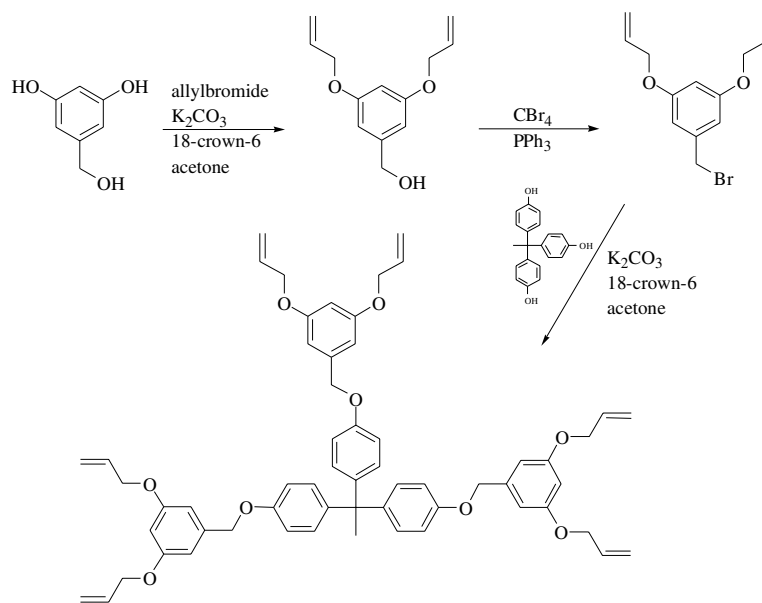
* Corresponding authors. Tel.: +27-11-4892363; fax: +27-11-4892819.

E-mail addresses: Reinout@science.uct.ac.za (R. Meijboom), jrm@science.uct.ac.za (J.R. Moss).

¹ Present address: Department of Chemistry and Biochemistry, Rand Afrikaans University, P.O. Box 524, Auckland Park 2006, South Africa.

Table 1
Hydrozirconation of poly-alkenes

Entry	Alkene starting material	Product	Appearance
1	$\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$	$\text{Me}_3\text{Si}(\text{CH}_2)_3(\text{Cp}_2\text{ZrCl})$	Yellow oil
2	$\text{PhCH}_2\text{CH}_2\text{CH}=\text{CH}_2$	$\text{Ph}(\text{CH}_2)_4(\text{Cp}_2\text{ZrCl})$	Yellow solid
3	$\text{PhOCH}_2\text{CH}=\text{CH}_2$	$\text{PhO}(\text{CH}_2)_3(\text{Cp}_2\text{ZrCl})$	Red oil
4	$\text{PhOCH}_2\text{C}_6\text{H}_3\text{-3,5-(OCH}_2\text{CH}=\text{CH}_2)_2$	$\text{PhOCH}_2\text{C}_6\text{H}_3\text{-3,5-[O}(\text{CH}_2)_3(\text{Cp}_2\text{ZrCl})_2$	Yellow oil
5	$\text{PhC}(\text{CH}_2\text{CH}=\text{CH}_2)_3$	$\text{PhC}[(\text{CH}_2)_3(\text{Cp}_2\text{ZrCl})]_3$	Yellow solid
6	$1,2,4,5\text{-C}_6\text{H}_2(\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)_4$	$1,2,4,5\text{-C}_6\text{H}_2[(\text{CH}_2)_3(\text{Cp}_2\text{ZrCl})]_4$	Yellow solid
7	$\text{Si}(\text{CH}_2\text{CH}=\text{CH}_2)_4$	$\text{Si}[(\text{CH}_2)_3(\text{Cp}_2\text{ZrCl})]_4$	Yellow solid
8	$1,4\text{-C}_6\text{H}_4[\text{C}(\text{CH}_2\text{CH}=\text{CH}_2)_3]_2$	$1,4\text{-C}_6\text{H}_4\{\text{C}[(\text{CH}_2)_3(\text{Cp}_2\text{ZrCl})]_3\}$	Yellow oil
9	$\text{CH}_3\text{C}[\text{C}_6\text{H}_4\text{-4-OCH}_2\text{C}_6\text{H}_3\text{-3,5-(OCH}_2\text{CH}=\text{CH}_2)_2]_3$	$\text{CH}_3\text{C}\{\text{C}_6\text{H}_4\text{-4-OCH}_2\text{C}_6\text{H}_3\text{-3,5-[O}(\text{CH}_2)_3(\text{Cp}_2\text{ZrCl})]_2\}_3$	Yellow oil
10	$\text{Si}[(\text{CH}_2)_3\text{Si}(\text{CH}_2\text{CH}=\text{CH}_2)_3]_4$	$\text{Si}\{(\text{CH}_2)_3\text{Si}[(\text{CH}_2)_3(\text{Cp}_2\text{ZrCl})]_3\}_4$	Yellow oil



Scheme 1. Synthesis of allyl-functionalized dendrimer (entry 9, Table 1).

reacted with 3,5-dihydroxybenzylalcohol to give 3,5-diallyloxybenzylalcohol in acetone in the presence of base in good yields after chromatographic purification. The alcohol functionality was subsequently converted to a bromide by using $\text{PPh}_3/\text{CBr}_4$. The resulting 3,5-diallyloxybenzyl bromide was used to react with both phenol and the dendrimer core $\text{CH}_3\text{C}(\text{C}_6\text{H}_4\text{OH})_3$. All compounds were isolated in good yields after chromatographic purification.

2.1. Hydrozirconations of mono-allyl species

The product of hydrozirconation reactions of allyl functionalized silanes (see Scheme 2) and alkanes in toluene resulted in yellow oils or solids, which were very soluble in common organic solvents. These species were highly oxygen- and moisture-sensitive, which interfered with analytical techniques such as elemental analysis and mass spectrometry. Due to the sensitive nature of the hydrozirconation products, only NMR spectro-

scopic data is provided. The products were purified by extraction into pentane, leaving the pure $\text{R}(\text{CH}_2)_3\text{-}(\text{Cp}_2\text{ZrCl})$ ($\text{R} = \text{SiMe}_3, \text{CH}_2\text{Ph}, \text{OPh}$) after evaporation of the pentane. The products are thermally stable and can be stored for a long period (several months) under an inert atmosphere at room temperature without apparent decomposition (^1H NMR spectroscopy). Hydrozirconation of allyltrimethylsilane was also performed in benzene, THF, and CH_2Cl_2 . This resulted in the same product, as was concluded from ^1H and ^{13}C NMR spectroscopy, and by chemical derivation. The products of hydrozirconation were identified as the expected hydrometallation complexes $\text{R}(\text{CH}_2)_3(\text{Cp}_2\text{ZrCl})$ ($\text{R} = \text{SiMe}_3, \text{CH}_2\text{Ph}, \text{OPh}$). The hydrozirconation reaction in THF was faster than the reaction in benzene, due to the more polar character of the solvent, as observed by consumption of the insoluble zirconocene hydride reagent. This resulted in enhanced solubility of the reactive $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ monomer because of solvent co-ordination. Reaction in CH_2Cl_2 was even faster; but a

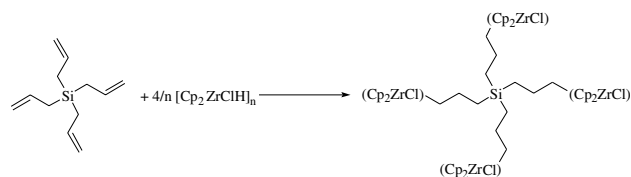


Scheme 2. Hydrozirconation of allyltrimethylsilane (entry 1, Table 1).

competitive reaction of zirconocene hydrochloride with dichloromethane to form zirconocene dichloride also occurred in this solvent (^1H NMR) [10] resulting in a lower yield.

2.2. Hydrozirconations of polyalkenes

The reaction of $[\text{Cp}_2\text{Zr}(\text{H})\text{Cl}]_n$ with $\text{R}(\text{CH}_2\text{-CH}=\text{CH}_2)_4$, ($\text{R} = \text{Si}, \text{C}_6\text{H}_2(\text{CH}_2)_4$) resulted in the tetrakis-insertion product $\text{R}[(\text{CH}_2)_3(\text{Cp}_2\text{ZrCl})]_4$, as was concluded from ^1H and ^{13}C NMR spectroscopy (see Table 1). During the reactions, a solvent effect was once again observed. The reaction of these compounds in THF took about 2 h to reach completion, whereas the same reaction in benzene took 48 h. This made it possible to monitor the reaction of $[\text{Cp}_2\text{Zr}(\text{H})\text{Cl}]_n$ with tetraallylsilane in benzene. Thus it was possible to identify all four possible insertion products by ^1H NMR. However, upon reaction of 1 equivalent of tetraallylsilane with 1 equivalent of $[\text{Cp}_2\text{Zr}(\text{H})\text{Cl}]_n$ in benzene, a statistical mixture of insertion products was obtained – and not just the mononuclear organometallic complex. From the ^1H NMR spectrum of the reaction mixture obtained by using a 1:1 mole ratio of starting materials, it can be concluded that the products do not undergo $\beta\text{-H}$ elimination. It can also be concluded that a fast ligand redistribution reaction, as reported for Cp_2ZrXY [11] ($\text{X}, \text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$), is not likely to occur. The tetrakisinsertion species $\text{Si}[(\text{CH}_2)_3(\text{Cp}_2\text{ZrCl})]_4$ could be isolated as a yellow, crystalline solid (see Scheme 3). However, no crystals suitable for X-ray crystallography could be obtained. This was mainly due to the increased reactive nature of the tetrakisinsertion species towards oxygen and moisture. This increased reactivity (as compared to normal alkyl-zirconocene compounds [5]) precluded the normal analytical analyses such as elemental analysis and mass spectrometry. In order to additionally confirm the existence of the polyzirconated species, some of the compounds (entry 5, 6 and 8) were reacted with H_2O to give the alkane and $[\text{Cp}_2\text{ZrCl}]_2\text{O}$, as was concluded from NMR spectroscopy. In addition entries 1, 5 and 6 were treated with I_2 . The compound $\text{Me}_3\text{Si}(\text{CH}_2)_3(\text{Cp}_2\text{ZrCl})$ (entry 1) reacted with I_2 to completely decompose. This is presumably because I_2 also cleaves the Me_3Si group in addition to the Zr-C bond. In the reaction of the other compounds with I_2 the appropriate alkyl iodide was found and analyzed. The identity of these products was confirmed by NMR spectroscopy.



Scheme 3. Hydrozirconation of tetraallylsilane (entry 7, Table 1).

3. Conclusion

The hydrozirconation of several allyl-functionalized alkanes, carbosilane and hydrocarbon dendrimers was successful as shown by NMR spectroscopy. In the process, several new dendrimers were synthesized and characterized. All hydrozirconation products gave the expected spectroscopic characteristics. In addition selected hydrozirconated polyalkenes were reacted with H_2O and I_2 to show that hydrozirconation is a feasible and successful route to functionalize dendrimers.

4. Experimental

4.1. General

Manipulations of sensitive compounds were carried out under purified nitrogen using glovebox (MBraun Unilab) or standard Schlenk line techniques under purified argon [12]. Solvents (diethyl ether, pentane, THF, toluene) were pre-dried by passage through a column containing alumina (neutral, Brockmann grade I) followed by distillation from sodium/benzophenone ketyl/tetraglyme [13] prior to use. Acetone was distilled from Drierite prior to use. CDCl_3 was dried over CaH_2 and C_6D_6 was dried over NaK and both were distilled prior to use. Allylbromide, allyltrimethylsilane, allyloxy-benzene, carbontetrabromide, 18-crown-6, 5-hydroxymethylbenzene-1,3-diol, K_2CO_3 , phenol, 4-phenyl-1-butene, triphenylphosphine, tetraallylsilane and 1,1,1-tris(4-hydroxyphenyl)ethane were purchased from Sigma Aldrich and used as received. $[\text{Cp}_2\text{ZrHCl}]_n$ [10], $\text{Si}[\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_2\text{CH}=\text{CH}_2)_3]_4$ [14], 1,3-bisallyloxy-5-bromomethyl benzene [15], (1,1-diallylbut-3-enyl)-benzene [16] and 1,4-bis-(1,1-diallylbut-3-enyl)-benzene [16] were prepared according to literature procedures. NMR spectra were recorded on either a Varian Unity-400 (^1H : 400 MHz; ^{13}C : 100.6 MHz) spectrometer, a Varian Mercury-300 (^1H : 300 MHz; ^{13}C : 75.5 MHz) spectrometer or a Varian Gemini 2000 (^1H : 200 MHz, ^{13}C : 50.3 MHz) at ambient temperature. NMR spectra were referenced relative to TMS using either the residual protonated impurities in the solvent (^1H NMR: CDCl_3 : δ 7.27; C_6D_6 : δ 7.16) or the solvent resonances (^{13}C NMR: CDCl_3 : δ 77.0; C_6D_6 : δ 128.0). Infrared spectra were recorded neat between NaCl disks on a Perkin-Elmer Paragon 1000 FTIR

spectrometer. Mass spectra were recorded on a Finnigan MAT GCQ GC/MS. Elemental analyses were performed using a Carlo Erba EA1108 elemental analyzer in the microanalytical laboratory of the University of Cape Town.

4.2. Synthesis of polyalkenes

4.2.1. Synthesis of 3,5-(H₂C=CHCH₂O)₂C₆H₃CH₂OH ((3,5-bisallyloxy-phenyl)-methanol)

A different synthesis for this compound has been reported [15]. Allylbromide (0.34 g, 2.8 mmol) was added to a mixture of 3,5-dihydroxybenzylalcohol (0.21 g, 1.47 mmol), K₂CO₃ (0.51 g, 3.70 mmol) and 18-crown-6 (0.15 g, 0.57 mmol) in acetone (20 ml). The mixture was heated under reflux for 72 h. The solids were filtered off and the volatiles removed in vacuo. The compound was dissolved in CH₂Cl₂ (30 ml) and washed with water (30 ml), dried over MgSO₄, filtered and the solvent was evaporated in vacuo to give a yellow oil. Column chromatography over silica, eluting with 10% CH₂Cl₂ in hexane followed by 50% CH₂Cl₂ in hexane and finally CH₂Cl₂ gave 0.36 g (90%) of 3,5-di(allyloxy)benzylalcohol as a yellow oil. Analytical data were in agreement with literature [15].

4.2.2. Synthesis of 3,5-(H₂C=CHCH₂O)₂C₆H₃CH₂OPh

Acetone (40 ml) was added to a mixture of 3,5-(H₂C=CHCH₂O)₂C₆H₃CH₂Br (0.33 g, 1.16 mmol), phenol (0.11 g, 1.16 mmol), K₂CO₃ (0.4 g, 2.91 mmol) and 18-crown-6 (0.62 g, 0.23 mmol) and the resulting mixture was heated under reflux for 72 h. The salts were filtered off and the volatiles removed in vacuo to give an orange oil. Column chromatography over silica, eluting with 20% CH₂Cl₂ in hexane gave a colorless oil, 0.22 g (65%) of 3,5-(H₂C=CHCH₂O)₂C₆H₃CH₂Ph. δ_{H} (200 MHz, CDCl₃): δ 7.34–7.22 (m, 2H, ArH), 7.01–6.92 (m, 3H, ArH), 6.61–6.12 (m, 2H, ArH), 6.46–6.43 (m, 1H, ArH), 6.18–5.97 (m, 2H, CH=), 5.46–5.24 (m, 4H, CH₂=), 5.0 (s, 2H, ArCH₂O), 4.53–4.51 (m, 4H, ArOCH₂); $\delta_{\text{C}\{\text{H}\}}$ (50.3 MHz, CDCl₃): δ 159.9, 158.7, 139.5, 133.1, 129.4, 121.0 (ArC), 117.7, 114.9 (C=C), 106.3 (ArCH₂), 69.8, 68.9 (CH₂).

4.2.3. Synthesis of {4-[3,5-(H₂C=CHCH₂O)₂C₆H₃-CH₂O]C₆H₄}\₃CCH₃

K₂CO₃ (0.17 g, 1.2 mmol), 18-crown-6 (0.08 g, 0.32 mmol) and 1,1,1-tris(4-hydroxyphenyl)ethane (0.1 g, 0.32 mmol) were added to a solution of 3,5-diallyloxyphenylmethylbromide (0.28 g, 0.98 mmol) in acetone (15 ml) and heated under reflux for 78 h. The suspension was filtered and the volatiles removed in vacuo. Column chromatography over silica, eluting with 20% CH₂Cl₂ in hexane, followed by 50% CH₂Cl₂ and CH₂Cl₂ gave 0.54 g (61%) of {4-[3,5-(H₂C=CHCH₂O)₂C₆H₃CH₂O]-C₆H₄}\₃CCH₃ as a yellow oil. δ_{H} (200 MHz, CDCl₃): δ

7.00 (d, 6H, ³J(H,H)=Hz, ArHcore) 6.87 (d, 6H, ³J(H,H)=Hz, ArHcore), 6.59 (d, 6H, ⁴J(H,H)=Hz, ArH), 6.42 (t, 3H, ⁴J(H,H)=Hz, ArH), 6.18–5.96 (m, 6H, 6CH=), 5.44–5.22 (m, 12H, 6CH₂=), 4.96 (s, 6H, 3ArCH₂O), 4.50 (d, 12H, ³J(H,H)=Hz, 6CH₂O); $\delta_{\text{C}\{\text{H}\}}$ (50.3 MHz, CDCl₃): δ 157.9 (ArC), 154.8 (ArCcore), 140.1 (ArCcore), 137.5 (ArC), 131.1 (CH=), 126.7 (ArCcore), 115.8 (CH₂=), 112.0 (ArCcore), 104.2 (ArC), 99.3 (ArC), 67.9 (ArCH₂O), 66.9 (CH₂O), 40 (CH₃); *m/z* (FAB): 912 (M⁺-H), 503 (C₃₀H₃₁O₇⁺), 105 (C₇H₅O⁺), 91 (C₇H₇⁺), 57 (C₃H₅O⁺). Anal. Calc. for CHO: C, 77.61; H, 6.62. Found: C, 77.52; H, 6.65%.

4.2.4. Synthesis of tetrakis-1,2,4,5-(4-butenyl)benzene

To a suspension of tetrakis-1,2,4,5-(bromomethyl)benzene (1.11 g, 2.46 mmol) in diethyl ether (20 ml) was added over 5 min a solution of allylmagnesium bromide in diethyl ether (1.0 M, 10 ml, 10 mmol). The resulting clear yellow solution was heated under reflux for 4 h and subsequently stirred at ambient temperature for 20 h. The reaction was quenched with aqueous NH₄Cl solution (1.0 M, 20 ml), the organic layer separated, dried over MgSO₄, filtered and the volatiles were removed from the filtrate in vacuo to give tetrakis-1,2,4,5-(4-butenyl)benzene as a colorless oil, 0.70 g (96%). δ_{H} (200 MHz, CDCl₃): 6.99 (s, 2H, ArH), 5.99–5.82 (m, 4H, 4CH=), 5.15–4.99 (m, 8H, 4CH₂=), 2.78–2.66 (m, 8H, CH₂CH₂Ar), 2.46–2.30 (m, 8H, 4CH₂Ar). $\delta_{\text{C}\{\text{H}\}}$ (50.3 MHz, CDCl₃): 138.4, 137.1, 130.0 (ArC), 116.8, 114.7 (C=C).

4.3. Hydrozirconations

All hydrozirconations were performed using similar procedures. A representative example is given for the synthesis of Cp₂ZrCl(CH₂)₃SiMe₃.

4.3.1. Cp₂ZrCl(CH₂)₃SiMe₃

Schwartz's reagent (0.158 g, 0.61 mmol) and allyltrimethylsilane (198 mm³, 1.25 mmol) were mixed in toluene (1.6 cm³) at room temperature and stirred for 1 h. A clear yellow solution was obtained. The volatiles were removed in vacuo and the yellow oil was stripped with pentane (2 × 1.0 cm³). The product was extracted into pentane (3 × 2.0 cm³) and the volatiles were removed in vacuo to give a yellow oil Cp₂ZrCl(CH₂)₃Si(CH₃)₃ (0.23 g, 68%). δ_{H} (C₆D₆, 400 MHz): 5.78 (10H, 2C₅H₅), 1.70 (2H, m, CH₂CH₂CH₂), 1.17 (2H, m, ³J(H,H)=8 Hz, ZrCH₂), 0.62 (2H, m, ³J(H,H)=8 Hz, SiCH₂), 0.09 (9H, s, 3CH₃); $\delta_{\text{C}\{\text{H}\}}$ (C₆D₆, 50.3 MHz): 112.20 (10C, 2C₅H₅), 60.16 (1C, ZrCH₂), 28.79 (1C, CH₂CH₂CH₂), 24.18 (1C, CH₂Si), -1.04 (3C, 3 CH₃).

4.3.2. Cp₂ZrCl(CH₂)₄Ph

δ_{H} (200 MHz, CDCl₃): 7.36–7.17 (m, 5H, ArH), 6.32 (s, 10H, 2Cp), 2.64–2.57 (m, 2H, CH₂Ar), 1.67–1.55 (m,

2H, $\text{CH}_2\text{CH}_2\text{Ar}$), 1.44–1.3 (m, 2H, $\text{CH}_2\text{CH}_2\text{Zr}$), 0.98–0.95 (m, 2H, CH_2Zr); δ_{H} (400 MHz, C_6D_6): 7.20–7.16 (m, 5H, ArH), 5.72 (s, 10H, 2Cp), 2.59 (t, 2H, $^3J = \text{Hz}$ CH_2Ar), 1.57 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ar}$), 1.09 (t, 2H, $^3J = \text{Hz}$ CH_2Zr); $\delta_{\text{C}\{\text{H}\}}$ (50.3 MHz, CDCl_3): 136.4, 121.8, 121.75 (ArC), 105.5 (Cp), 47.6 (CH_2Zr), 31.0 ($\text{CH}_2\text{CH}_2\text{Zr}$), 28.8 ($\text{CH}_2\text{CH}_2\text{Ar}$), 26.8 (CH_2Ar); $\delta_{\text{C}\{\text{H}\}}$ (100 MHz, C_6D_6): 143.3, 128.6, 125.8 (ArC), 112.3 (Cp), 54.5 (CH_2Zr), 37.8, 35.7, 33.6.

4.3.3. $\text{PhO}(\text{CH}_2)_3(\text{Cp}_2\text{ZrCl})$

δ_{H} (200 MHz, CDCl_3): 7.26–7.22 (m, 2H, ArH), 6.99–6.88 (m, 3H, ArH), 6.39 (s, 10H, 2Cp), 3.93–3.91 (m, 2H, CH_2O), 1.85–1.76 (m, 2H, $\text{CH}_2\text{CH}_2\text{O}$), 1.04–1.03 (m, 2H, CH_2Zr); δ_{H} (200 MHz, C_6D_6): 7.15–7.02 (m, 5H, ArH), 5.72 (s, 10H, 2Cp), 3.68–3.65 (m, 2H, CH_2O), 2.02–1.90 (m, 2H, $\text{CH}_2\text{CH}_2\text{O}$), 1.12–0.97 (m, 2H, CH_2Zr); $\delta_{\text{C}\{\text{H}\}}$ (50.3 MHz, CDCl_3): 127.41, 127.38, 118.5 (ArC), 114.0 (Cp), 67.4 (CH_2Zr), 20.6 ($\text{CH}_2\text{CH}_2\text{O}$), 8.54 (CH_2O).

4.3.4. $3,5\text{-}[(\text{Cp}_2\text{ZrCl})(\text{CH}_2)_3\text{O}]_2\text{C}_6\text{H}_3\text{CH}_2\text{OPh}$

δ_{H} (200 MHz, CDCl_3): 7.37–7.25 (m, 3H, ArH), 6.99–6.95 (m, 3H, ArH), 6.62–6.59 (m, 2H, ArH), 6.37 (s, 20H, 4Cp), 4.99 (s, 2H, ArCH₂), 3.72–3.69 (m, 4H, 2 CH_2O), 1.9–2.09 ($\text{CH}_2\text{CH}_2\text{O}$), 1.18–0.90 (m, 4H, CH_2Zr); $\delta_{\text{C}\{\text{H}\}}$ (50.3 MHz, CDCl_3): 160.0, 129.4, 121.1 (ArC), 114.1 (Cp), 106.1 (CH_2Ar), 69.7 (CH_2Zr), 22.4 ($\text{CH}_2\text{CH}_2\text{O}$), 10.0 (CH_2O).

4.3.5. $\text{PhC}[(\text{CH}_2)_3(\text{Cp}_2\text{ZrCl})]_3$

δ_{H} (200 MHz, CDCl_3): 7.22–7.10 (br m, 5H, C_6H_5), 6.09 (s, 30H, 6Cp), 1.46–1.40 (br m, 12H, 3 (CH_2)₂ CH_2Zr), 0.95 (br t, 6H, 3 CH_2Zr); $\delta_{\text{C}\{\text{H}\}}$ (50.3 MHz, CDCl_3): 145.1, (ArC), 133.41 (ArC), 115.00 (Cp), 56.81 (ZrCH₂), 43.88 ($\text{C}_6\text{H}_5\text{-C}$), 40.91 (ZrCH₂CH₂), 28.31 (ArCH₂CH₂).

4.3.6. $\text{C}_6\text{H}_4\{\text{C}[(\text{CH}_2)_3(\text{Cp}_2\text{ZrCl})]_3\}_2$

δ_{H} (200 MHz, CDCl_3): 7.23, (s, 4H, C_6H_4), 6.12 (s, 60H, 6Cp), 1.45 (br m, 24H, 6 (CH_2)₂ CH_2Zr), 0.97 (br t, 12H, 6 CH_2Zr); $\delta_{\text{C}\{\text{H}\}}$ (50.3 MHz, CDCl_3): 144.39 (ArC), 135.34 (ArC), 116.00 (Cp), 57.36 (ZrCH₂), 44.18 ($\text{C}_6\text{H}_5\text{-C}$), 41.80 (ZrCH₂CH₂), 27.61 (ZrCH₂CH₂CH₂).

4.3.7. $\text{Si}[(\text{CH}_2)_3(\text{Cp}_2\text{ZrCl})]_4$

δ_{H} (C_6D_6 , 400 MHz): 5.95 (40H, s, 8 C_5H_5), 2.00 (8H, m, 4 $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.41 (8H, m, $^3J(\text{H,H}) = 8$ Hz, ZrCH₂), 0.98 (8H, m, $^3J(\text{H,H}) = 8$ Hz, SiCH₂); $\delta_{\text{C}\{\text{H}\}}$ (C_6D_6 , 50.3 MHz): 112.20 (10C, 2 C_5H_5), 60.16 (1C, ZrCH₂), 28.79 (1C, $\text{CH}_2\text{CH}_2\text{CH}_2$), 24.18 (1C, CH_2Si).

4.3.8. $1,2,4,5\text{-C}_6\text{H}_2[(\text{CH}_2)_4(\text{CpZrCl})]_4$

δ_{H} (200 MHz, CDCl_3): 6.9 (s, 2H, ArH), 5.96 (s, 10H, 2Cp), 2.52–2.49 (m, 2H, CH_2Ar), 1.65–1.55 (m, 2H,

$\text{CH}_2\text{CH}_2\text{Ar}$), 1.46–1.41 (m, 2H, $\text{CH}_2\text{CH}_2\text{Zr}$), 1.08–0.90 (m, 2H, CH_2Zr); $\delta_{\text{C}\{\text{H}\}}$ (50.3 MHz, CDCl_3): 137.7, 130.0 (ArC), 116.0 (Cp), 56.2 (CH_2Zr), 37.5 ($\text{CH}_2\text{CH}_2\text{Zr}$), 34.3 ($\text{CH}_2\text{CH}_2\text{Ar}$).

4.3.9. $\{3,5\text{-}[(\text{Cp}_2\text{ZrCl})(\text{CH}_2)_3\text{O}]_2\text{C}_6\text{H}_3\text{CH}_2\text{OC}_6\text{H}_4\}_3\text{CCH}_3$

δ_{H} (200 MHz, CDCl_3): 7.19–6.80 (br m, ArH), 6.31 (s, 60H, 12Cp), 4.99 (s, 6H, 3ArCH₂), 3.74–3.70 (m, 12H, CH_2O), 2.08–2.01 (m, 12H, $\text{CH}_2\text{CH}_2\text{O}$), 1.28 (s, 3H, CH₃), 1.05–0.90 (m, 12H, CH_2Zr); δ_{H} (200 MHz, C_6D_6): 7.15–6.90 (br m, ArH), 5.73 (s, 60H, 12Cp), 4.98 (s, 6H, 3ArCH₂), 3.83–3.78 (m, 12H, CH_2O), 2.04–1.99 (m, 12H, $\text{CH}_2\text{CH}_2\text{O}$), 1.25 (s, 3H, CH₃), 1.01–0.90 (m, 12H, CH_2Zr).

4.4. Reactions of polyalkylzirconium species

4.4.1. Reaction of $\text{PhC}[(\text{CH}_2)_3(\text{Cp}_2\text{ZrCl})]_3$ with H_2O

To a suspension of $[\text{Cp}_2\text{Zr}(\text{H})\text{Cl}]_n$ (0.1 g, 0.39 mmol) in toluene (5 ml) was added a solution of $\text{C}_6\text{H}_5\text{-C}(\text{CH}_2\text{CH}=\text{CH}_2)_3$ (0.028 g, 0.13 mmol) in toluene (5 ml). The solution was stirred overnight at room temperature giving a clear yellow solution. The reaction mixture was filtered and the solvent removed in vacuo. A yellow solid was obtained which was dissolved in diethyl ether (5 ml). H_2O (1 ml) was added and the mixture stirred for 30 min. The solution decolorized and a white precipitate formed. The white solid was filtered off. The organic layer was separated from the aqueous layer, dried over MgSO_4 , filtered and the volatiles evaporated in vacuo to give $\text{C}_6\text{H}_5\text{C}(\text{CH}_2\text{CH}_2\text{CH}_3)_3$ (0.020 g, 67%) as a colorless oil δ_{H} (200 MHz, CDCl_3): 7.00 (br d, 2H, C_6H_5), 7.19 (br t, 1H, C_6H_5), 7.55 (br t, 2H, C_6H_5), 1.53 (t, 6H, $\text{C}(\text{CH}_2\text{CH}_2)_3$), 1.30 (m, 6H, 3 $\text{CH}_2\text{CH}_2\text{CH}_3$), 0.83 (t, 9H, 3CH₃); $\delta_{\text{C}\{\text{H}\}}$ (50.3 MHz, CDCl_3): 160.71, 128.43, 125.78 (ArC), 42.81 (PhC), 40.25 ($\text{C}(\text{CH}_2)_3$), 20.06 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 14.92 (CH₃).

4.4.2. $1,2,4,5\text{-C}_6\text{H}_2[(\text{CH}_2)_3\text{CH}_3]_4$

Reaction performed in a similar way to the above. δ_{H} (200 MHz, CDCl_3): 6.90 (s, 2H, C_6H_2), 2.54 (t, 8H, 4 $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.41 (m, 16H, 4 $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.94 (t, 12H, 4CH₃); $\delta_{\text{C}\{\text{H}\}}$ (50.3 MHz, CDCl_3): 137.64, 129.85 (ArC), 33.64 (ArCH₂), 32.05 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 22.92 (CH_2CH_3), 14.02 (CH₃).

4.4.3. $1,4\text{-C}_6\text{H}_4\{\text{C}[(\text{CH}_2)_2\text{CH}_3]_3\}_2$

Reaction performed in a similar way to the above. δ_{H} (200 MHz, CDCl_3): 7.10 (br s, 4H, C_6H_4), 1.53 (br t, 12H, 2 $\text{C}(\text{CH}_2)_3$), 1.27 (m, 12H, 6 $\text{CH}_2\text{CH}_2\text{CH}_3$), 0.83 (t, 18H, 6CH₃); $\delta_{\text{C}\{\text{H}\}}$ (50.3 MHz, CDCl_3): 144.45, 125.78 (ArC), 42.81 (Ph-C), 40.28 ($\text{C}(\text{CH}_2)_3$), 20.12 (CH_2CH_3), 14.92 (CH₃).

4.4.4. Reaction of $\text{PhC}[(\text{CH}_2)_3(\text{Cp}_2\text{ZrCl})]_3$ with I_2

The zirconium alkyl was prepared as described previously. To the toluene solution of the compound was added solid I_2 (0.1 g, 0.39 mmol). The mixture was stirred overnight at room temperature. The resultant precipitate was filtered off and the filtrate washed with a 1 M solution of sodium thiosulphate (3×20 ml). The organic layer was dried over MgSO_4 , filtered and the solvent removed in vacuo leaving a pale yellow solid. δ_{H} (200 MHz, CDCl_3): 7.23 (m, 2H), 7.15 (m, 1H), 7.10 (m, 2H, Ar), 2.97 (br t, 6H, $3\text{CH}_2\text{I}$), 1.66 (br t, 6H, $\text{C}(\text{CH}_2)_3$), 1.49 (br t, 6H, $3\text{CH}_2\text{-CH}_2\text{CH}_2$); $\delta_{\text{C}\{\text{H}\}}$ (50.3 MHz, CDCl_3): 128.21, 128.21, 125.55, 122.95 (ArC), 40.99 (Ph-C), 38.89 (Ph-C(CH_2) $_3$), 30.45 ($\text{CH}_2\text{CH}_2\text{I}$), 6.05 (CH_2I).

4.4.5. $1,2,4,5\text{-C}_6\text{H}_2[(\text{CH}_2)_3\text{I}]_4$

Reaction performed in a similar way to the above. δ_{H} (200 MHz, CDCl_3): 6.76 (s, 2H, Ar), 3.12 (br t, 8H, CH_2I), 2.46 (br t, 8H, 4PhCH_2), 1.74 (br m, 16H, $4\text{CH}_2\text{CH}_2\text{CH}_2$); $\delta_{\text{C}\{\text{H}\}}$ (50.3 MHz, CDCl_3): 134.34, 125.55 (ArC), 32.90 (Ph CH_2CH_2), 32.80 ($\text{CH}_2\text{CH}_2\text{I}$), 32.40 (Ph CH_2), 6.70 (CH_2I).

Acknowledgements

We would like to thank Sasol Polymers, the University of Cape Town, the University of the Western Cape, THRIP and the NRF for financial support.

References

- [1] (a) Several reviews on dendrimers: H.-B. Meikelburger, W. Jaworek, F. Vögtle, *Angew. Chem. Int. Ed. Engl.* 31 (1992) 1571; (b) D.A. Tomalia, H.D. Durst, *Top. Curr. Chem.* 165 (1993) 193; (c) J. Issberner, R. Moors, F. Vögtle, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 2413; (d) I. Cuadrado, M. Morán, J. Losada, C.M. Casado, C. Pascual, B. Alonso, F. Lobete, *Adv. Dendritic Macromol.* 3 (1996) 61; (e) D. Gudat, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 1951; (f) H. Frey, C. Lach, K. Lorenz, *Adv. Mater.* 10 (1998) 279; (g) R.J. Puddephatt, *J. Chem. Soc., Chem. Commun.* (1998) 1055; (h) J.-P. Majoral, A.-M. Caminade, *Chem. Rev.* 99 (1999) 845; (i) D.K. Smith, F. Diederich, *Chem. Eur. J.* 4 (1998) 1353; (j) M. Fischer, F. Vögtle, *Angew. Chem. Int. Ed. Engl.* 38 (1999) 884; (k) H. Frey, C. Schlenk, *Top. Curr. Chem.* 210 (2000) 69; (l) E. Lukevics, P. Arsenyan, O. Pudova, *Main Group Met. Chem.* 25 (3) (2002) 135.
- [2] (a) M.A. Hearshaw, J.R. Moss, *Chem. Commun.* (1999) 1; (b) M.A. Hearshaw, A.T. Hutton, J.R. Moss, K.J. Naidoo, *Adv. Dendritic Macromol.* 4 (1999) 1.
- [3] (a) J.W.J. Knapen, A.W. van der Made, J.C. de Wilde, P.W.N.M. van Leeuwen, P. Wijkens, D.M. Grove, G. Van Koten, *Nature* 372 (1994) 659; (b) G.E. Oosterom, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, *Angew. Chem. Int. Ed. Engl.* 40 (2001) 1828.
- [4] (a) Y.-H. Liao, J.R. Moss, *J. Chem. Soc., Chem. Commun.* (1993) 1774; (b) Y.-H. Liao, J.R. Moss, *Organometallics* 14 (1995) 2130; (c) Y.-H. Liao, J.R. Moss, *Organometallics* 15 (1996) 4307; (d) I.J. Mavunkal, J.R. Moss, J. Bacsa, *J. Organomet. Chem.* 593 (2000) 361; (e) R. Meijboom, A.T. Hutton, J.R. Moss, *Organometallics* 22 (2003) 1811; (f) R. Meijboom, M.J. Overett, J.R. Moss, *J. Organomet. Chem.* 689 (2004) 987; (g) S. Harder, R. Meijboom, J.R. Moss, *J. Organomet. Chem.*, in press; (h) I.J. Mavunkal, M.A. Hearshaw, J.R. Moss, J. Bacsa, *Inorg. Chim. Acta, J. Organomet. Chem.* 689 (2004) 1095.
- [5] The composition of dendrimers formed in a reaction of the arms with a less than 100% yield can be calculated from the yield of the specific reaction using the following formula: $P = \left(\frac{N!}{n!m!}\right) Y^n (1-Y)^m$; where P = mole fraction of product; $N = n + m$ = total number of reactive groups; n = number of reacted groups; m = number of unreacted groups and Y = reaction yield. For example a reaction with a yield of 95% on a dendrimer with 4 arms gives a mole fraction of $P = (4!/4!0!)(0.95)^4(0.05)^0 = 0.815$ of pure product. The other 18.5% are impure dendrimers with one or more branches unreacted.
- [6] R. Meijboom, Ph.D Thesis, University of Cape Town, 2001.
- [7] (a) See for example: P.C. Wailes, H. Weigold, *J. Organomet. Chem.* 24 (1970) 405; (b) J.W. Hart, J. Schwartz, *J. Am. Chem. Soc.* 96 (1974) 8115; (c) J. Schwartz, J.A. Labinger, *Angew. Chem. Int. Ed. Engl.* 15 (1976) 33, and references therein; (d) T.N. Sorrell, *Tetrahedron Lett.* (1978) 4983; (e) D.E. Laycock, H. Alper, *J. Org. Chem.* 46 (1981) 289; (f) J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987; (g) T. Gibson, *Organometallics* 6 (1987) 918; (h) D.R. Swanson, T. Nguyen, Y. Noda, E.-I. Negishi, *J. Org. Chem.* 56 (1991) 2590.
- [8] V. Huc, P. Boussagnet, P. Mazerolles, *J. Organomet. Chem.* 512 (1996) 253.
- [9] (a) V. Cadierno, A. Igau, B. Donndieu, A.-M. Caminade, J.-P. Majoral, *Organometallics* 18 (1999) 1580; (b) R. Andrés, E. de Jesus, F.J. de la Mata, J.C. Flores, R. Gómez, *Eur. J. Inorg. Chem.* (2002) 2281; (c) S. Arevalo, E. de Jesus, F.J. de la Mata, J.C. Flores, R. Gómez, M.P. Gómez-Sal, P. Ortega, S. Vigo, *Organometallics* 22 (2003) 5109.
- [10] S.L. Buchwald, S.J. LaMaire, R.B. Nielsen, B.T. Watson, S.M. King, *Tetrahedron Lett.* 28 (1987) 3895.
- [11] R.F. Jordan, *J. Organomet. Chem.* 294 (1985) 321.
- [12] D.F. Shriver, M.A. Drezdson, *The Manipulation of Air-sensitive Compounds*, Wiley-Interscience, New York, 1986, p. 80.
- [13] D.D. Perrin, W.L.F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed., Pergamon Press, Oxford, 1988.
- [14] A.W. van der Made, P.W.N.M. van Leeuwen, *J. Chem. Soc., Chem. Commun.* (1992) 1400.
- [15] Y. Yamakawa, M. Ueda, R. Nagahata, K. Takeuchi, M. Asai, *J. Chem. Soc., Perkin 1* 24 (1998) 4135.
- [16] D. Catheline, D. Astruc, *J. Organomet. Chem.* 272 (1984) 417.