ELSEVIER

Journal of Organometallic Chemistry 499 (1995) 199–204

Journal of Organometallic Chemistry

Synthesis of new poly(2,4-disilapentane) oligomers via dehydrocondensation reaction using Group IV metallocene catalysts ☆

Philippe Roux, Jean-Paul Pillot, Marc Birot, Jacques Dunoguès *, P. Lapouyade

Laboratoire de Chimie Organique et Organométallique, (URA 35 CNRS, Université Bordeaux I), 351 cours de la Libération, F-33405 Talence Cédex, France

Received 30 December 1994; in revised form 24 February 1995

Abstract

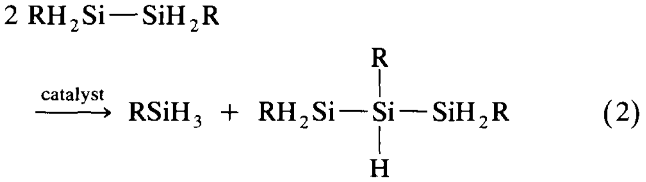
Polycondensation of 2,4-disilapentane in the presence of titanium or zirconium-based catalysts afforded original poly(2,4-disilapentane) oligomers useful as ceramic precursors.

Keywords: Silicon; Titanium; Zirconium; Metallocene crystals; Poly(2,4-disilapentane) oligomers

1. Introduction

The formation of Si–Si bond-containing oligomers from primary silanes or symmetrical tetrahydrodisilanes in the presence of dimethylmetallocene catalysts was first reported by Harrod and Samuel [1] who prepared poly(phenylsilane). Harrod et al. [2] also proposed a catalytic route to poly(methylsilane) (Eq. (1)).

The catalyst activity decreases in the following order: (Zr > Ti ≫ Hf) [1,3–8]. The proportions of cyclic to linear polysilanes depend on the reaction conditions (nature of the catalyst, silane, substituents, concentration, reaction time) [9]. Long reaction times lead to side reactions such as Si–Si bond cleavage, giving short-chain oligomers. A study of the disilane condensation clearly showed that redistribution reactions occur, yielding monosilanes (Eq. (2)) [10].



$$2\ RH_2Si{-}SiH_2R \xrightarrow{\text{catalyst}} RSiH_3 + RH_2Si{-}\overset{\displaystyle R}{\underset{\displaystyle H}{Si}}{-}SiH_2R \qquad (2)$$

More recently, a Japanese group [11] has reported similar results concerning the polymerisation of primary silanes using lanthanocenes as catalysts. Extension of the transition-metal-catalysed dehydrocoupling reaction to secondary and tertiary silanes showed a fall in their reactivity in the sequence primary > secondary ≫ tertiary. Thus, even under more severe conditions, polycondensation of phenylmethylsilane only yielded the dimer, the trimer and traces of higher oligomers. To improve this method, Corey et al. [7] reinvestigated the catalytic dehydrocondensation of phenylmethylsilane with butylmetallocenes prepared in situ. In fact, dimethylmetallocenes are difficult to synthesise and rapidly decompose upon heating or exposure to UV light [12], and in cases such as methylphenylsilane oligomers from disilanes to hexasilanes were easily prepared. Therefore, activation of the Si–H bond with Group IV metallocenes constitutes a convenient alternative to the coupling reaction of halosilanes. Hengge has reported the dehydropolymerisation of disilanes using the same scheme [13], and Corriu et al. [14] and Okumura et al. [15] have recently described the preparation of SiC precursors possessing Si–CH_2–CH_2–Si units. Suppression of chain-scission reactions and increase in the polysilane chain length have been achieved very recently by Djoumaev and Harrod [16] who used a borane as a cocatalyst.

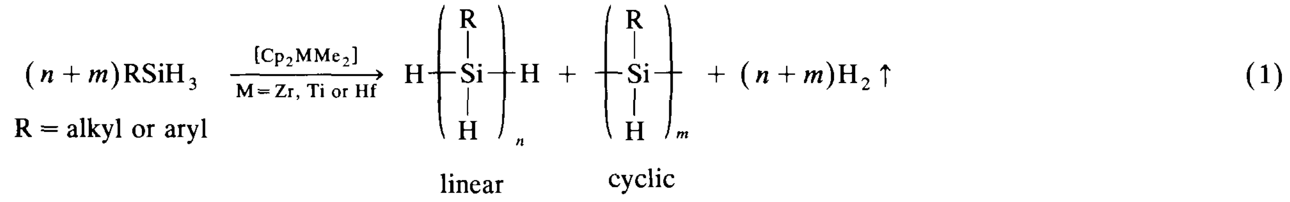
We reported earlier the synthesis of 2,4-dichloro-2,4-disilapentane $(ClMeSiH)_2CH_2$ [17] from methylene

---

☆ Dedicated to Professor Hideki Sakurai on the occasion of his retirement from Tohoku University, in recognition for his outstanding contribution to the development of organosilicon chemistry.

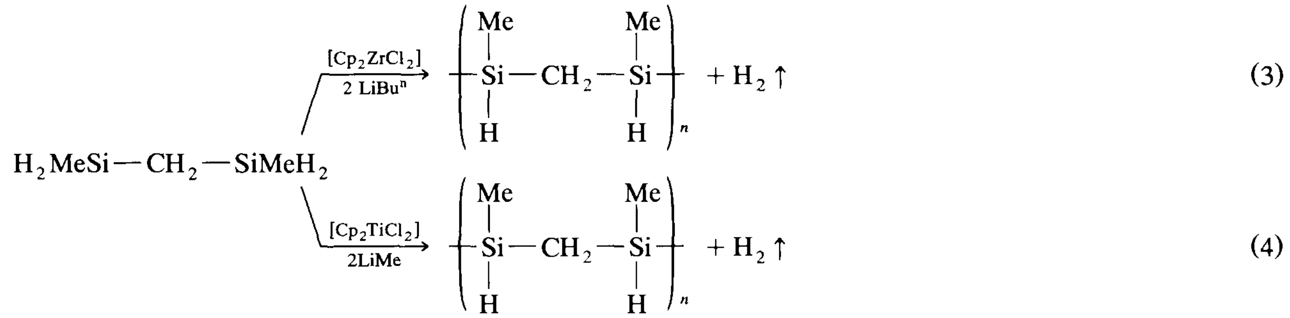
* Corresponding author.

Elsevier Science S.A.
SSDI 0022-328X(95)00305-3



$$(n+m)\mathrm{RSiH_3} \xrightarrow[\mathrm{M=Zr,\ Ti\ or\ Hf}]{[\mathrm{Cp_2MMe_2}]} \underset{\text{linear}}{\mathrm{H}\left(\overset{\overset{\textstyle \mathrm{R}}{|}}{\underset{\underset{\textstyle \mathrm{H}}{|}}{\mathrm{Si}}}\right)_n\mathrm{H}} + \underset{\text{cyclic}}{\left(\overset{\overset{\textstyle \mathrm{R}}{|}}{\underset{\underset{\textstyle \mathrm{H}}{|}}{\mathrm{Si}}}\right)_m} + (n+m)\mathrm{H_2}\uparrow \qquad (1)$$

R = alkyl or aryl



$$\mathrm{H_2MeSi{-}CH_2{-}SiMeH_2} \xrightarrow[2\ \mathrm{LiBu^n}]{[\mathrm{Cp_2ZrCl_2}]} \left(\overset{\overset{\textstyle \mathrm{Me}}{|}}{\underset{\underset{\textstyle \mathrm{H}}{|}}{\mathrm{Si}}}{-}\mathrm{CH_2}{-}\overset{\overset{\textstyle \mathrm{Me}}{|}}{\underset{\underset{\textstyle \mathrm{H}}{|}}{\mathrm{Si}}}\right)_n + \mathrm{H_2}\uparrow \qquad (3)$$

$$\mathrm{H_2MeSi{-}CH_2{-}SiMeH_2} \xrightarrow[2\mathrm{LiMe}]{[\mathrm{Cp_2TiCl_2}]} \left(\overset{\overset{\textstyle \mathrm{Me}}{|}}{\underset{\underset{\textstyle \mathrm{H}}{|}}{\mathrm{Si}}}{-}\mathrm{CH_2}{-}\overset{\overset{\textstyle \mathrm{Me}}{|}}{\underset{\underset{\textstyle \mathrm{H}}{|}}{\mathrm{Si}}}\right)_n + \mathrm{H_2}\uparrow \qquad (4)$$

$$\mathrm{RSiHCl_2} \xrightarrow[\mathrm{Zn/Mg}]{\mathrm{CH_2Cl_2/THF}} \mathrm{RHClSi{-}CH_2{-}SiClHR} \xrightarrow[\mathrm{Et_2O}]{\mathrm{LiAlH_4}} \mathrm{H_2RSi\text{-}CH_2{-}SiRH_2}$$

R = alkyl, alkenyl or phenyl

Scheme 1.

chloride (Scheme 1). This paper deals with the dehydrocoupling of the corresponding reduced derivative using metallocenes as the catalysts, to prepare polysilacarbosilane polymers possessing Si–CH_2–Si units in their main chain. These are potential silicon carbide ceramic precursors. Moreover, as the C/Si ratio in these polymers is less than in polydimethylsilane or poly(silapropylene) [18] (1.5 rather than 2), pyrolysis of these compounds should result in silicon carbide-based materials with low free carbon content [19].

2. Results and discussion

2.1. Syntheses

Two series of reactions using titanium and zirconium-based catalysts have been explored (Eqs. (3) and (4)).

Reaction (3) was performed under Corey's conditions [7] whereas reaction (4) was a modification of the Harrod method [4], where the catalyst is prepared in situ. As LiMe reacts with $[\mathrm{Cp_2TiCl_2}]$ in high yield (90%), decomposition of dimethyltitanocene during its purification is avoided. The results are given in Table 1.

Small amounts of low-boiling products, probably mixtures of dimer and trimer, were distilled off under high vacuum without further characterisation. Yields of oligomers are generally good (50%–80%) whatever the method. They vary significantly with the reaction time, the nature of the transition metal and the initial quantity of the monomer (Table 1, runs 1 and 2). The oligomers obtained are viscous oils, progressively turning to gels that are insoluble in the usual organic solvents. They were stored at −20°C under dinitrogen. GPC results and TGA char yields at 950°C are given in Table 2.

Average mass molecular weights are not very high, whereas the ceramic yields increase from run **1** to **3**, suggesting that the structure is partially cross-linked.

Table 2
GPC, proton NMR integration ratios and TGA data of oligomeric polysilacarbosilanes

Run	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	$\overline{DP}_n$	r [a]		TGA residue (%)
				Calc.	Found	
1	1150	1.5	8	4	5.4	56.7
2	1600	1.5	10	4	6.32	69.6
3	1200	1.2	10	4	7.4	74.6

[a] $r = (\mathrm{Si{-}C}H_3 + \mathrm{Si{-}C}H_2\mathrm{{-}Si})/\mathrm{Si{-}}H$ (butyl groups are neglected).

Table 1
Dehydrocondensation of $(\mathrm{H_2MeSi})_2\mathrm{CH_2}$ in the presence of a zirconium or titanium derivative

Run	$(\mathrm{H_2MeSi})_2\mathrm{CH_2}$ (g)	$[\mathrm{Cp_2MCl_2}]$ M (g)	LiR R (ml)	Catalyst (mol.%)	Toluene (ml)	Time (d)	Oligomer wt. (g)	Yield [a] (%)
1	3	Zr (0.277)	Bu (1.2)	3.3	3	4	2.4	80
2	10	Zr (0.923)	Bu (4)	3.3	10	8	6.4	64
3	5	Ti (0.245)	Me (1.33)	2	5	8	2.75	50

[a] Yield = (polymer weight/monomer initial weight) × 100.

Meanwhile, the average degrees of polymerisation are slightly higher than those reported in the literature for secondary silanes [1,3–7] ($\overline{DP}_n = 8$–10). The higher reactivity of 2,4-disilapentane compared with phenylmethylsilane may be explained by its lower steric hindrance around silicon.

2.2. IR spectroscopy

IR spectra of the oligomers obtained are given in Fig. 1. They are quite similar, whatever the experimental conditions. Characteristic absorption bands are observed for ν(C–H) at 2950–2870 cm^{-1}, ν(Si–H) at 2130 and 2085 cm^{-1}, δ(Si–CH) at 1410 and 1250 cm^{-1}, ω(Si–CH_2–Si) at 1350 cm^{-1}, δ(Si–CH_2–Si) at 1040 cm^{-1}, and δ(Si–H) at 955 cm^{-1}. The narrow Si–CH_2–Si absorption band at 1040 cm^{-1} showed that almost no Si–O–Si groups are present in these oligomers. This suggests that, under our experimental conditions, contamination by oxygen does not occur significantly. However, after exposure to air at room temperature for several hours, the presence of siloxane linkages is clearly detected (shoulder at 1090 cm^{-1}). The high reactivity of these compounds towards oxygen could be due to the presence of SiH–SiH moieties, but they are still quite stable when compared to poly(methylsilane).

2.3. NMR spectroscopy

The proton NMR spectra (Fig. 2) exhibit broad signals. Besides the expected resonances centred at 0 ppm (Si–CH_2–Si), 0.3 ppm (Si–CH_3), and 4.2 ppm (Si–H), weak signals around 1 ppm (runs 1 and 2) are assigned to Si–Bu groups, resulting from hydrosilylation of coordinated butene formed during the generation of the active catalytic species [7,8]. Buchwald and Watson [20] have shown that [Cp_2ZrBu_2] and triphenylphosphine give [Cp_2Zr(butene)PPh_3] in good yield at room temperature. Similarly, the increase of r (Table 2) in the case of run **3** may be explained in part by the introduction of methyl groups during the formation of the reactive titanocene species [3–5] (Eqs. (5) and (6)).

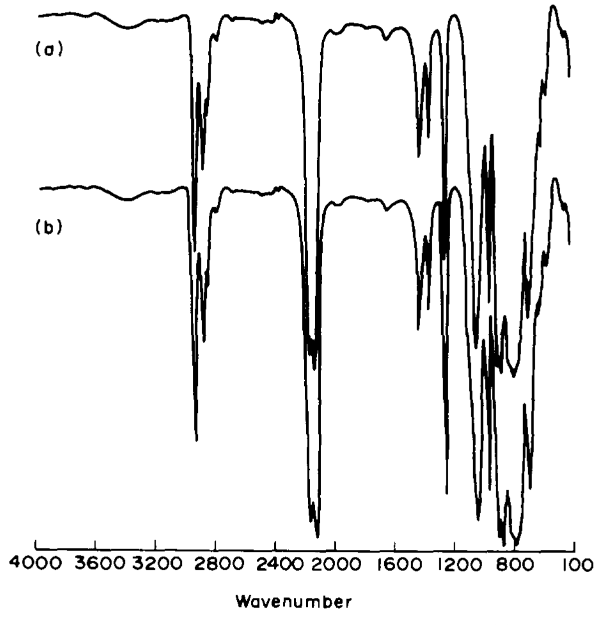


Fig. 1. IR spectra of polysilacarbosilanes from runs 1(a) and 3(b).

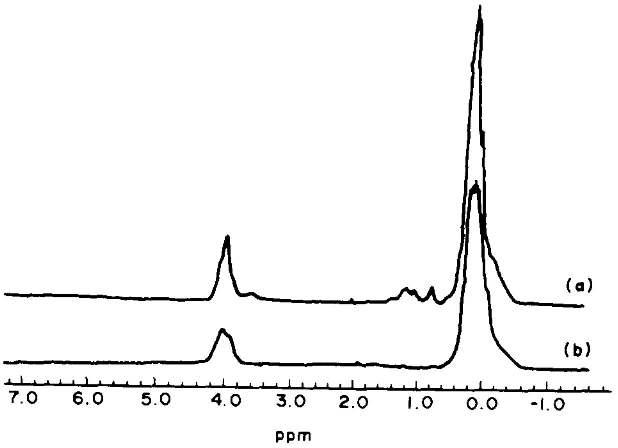
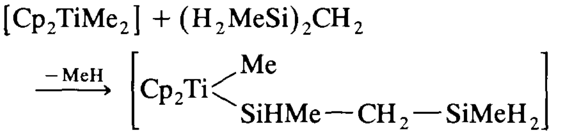
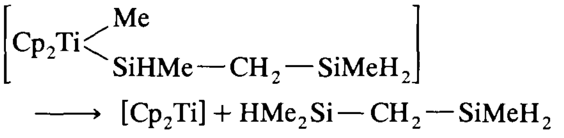


Fig. 2. Proton NMR spectra of polysilacarbosilanes from runs 1 or 2(a) and 3(b).



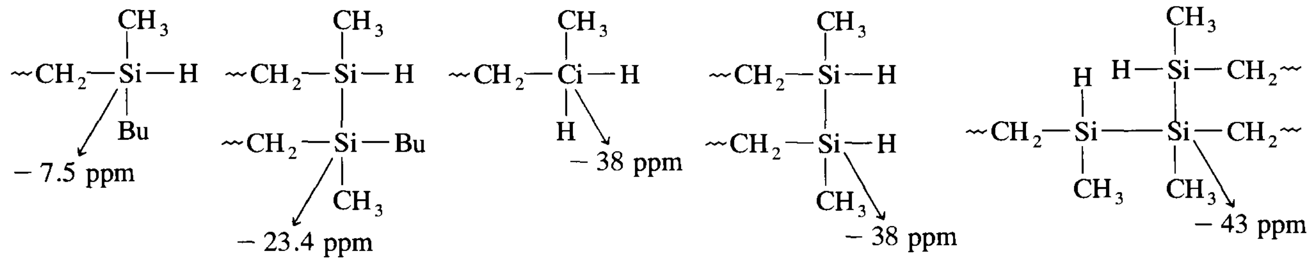
$$[\mathrm{Cp_2TiMe_2}] + (\mathrm{H_2MeSi})_2\mathrm{CH_2} \xrightarrow{-\mathrm{MeH}} \left[\mathrm{Cp_2Ti}\begin{matrix}\diagup \mathrm{Me} \\ \diagdown \mathrm{SiHMe{-}CH_2{-}SiMeH_2}\end{matrix}\right] \qquad (5)$$



$$\left[\mathrm{Cp_2Ti}\begin{matrix}\diagup \mathrm{Me} \\ \diagdown \mathrm{SiHMe{-}CH_2{-}SiMeH_2}\end{matrix}\right] \longrightarrow [\mathrm{Cp_2Ti}] + \mathrm{HMe_2Si{-}CH_2{-}SiMeH_2} \qquad (6)$$

However, these alkyl groups could be responsible for only a slight increase in the C/Si ratio due to the low concentration of the catalyst, the theoretical maximal value being 1.566 (vs. 1.5). In comparison, an "idealized" dehydrocondensation product would lead to a linear -(MeHSi–CH_2–SiMeH)$_n$- polymer having a calculated C–H/Si–H proton integration ratio $r = 4$. Experimental r values (Table 2) are higher than expected, showing that additional Si–H bonds were consumed. Accordingly, branched structures containing Si_2*Si*Me-CH_2- nodes should also be formed. This inference is constant with the values of the ceramic yields and the ^{29}Si NMR spectra of runs 1 and 2 (Fig. 3).

Spectrum 3(a) (SiH polarisation) exhibits three massifs centred at -7.5, -23.4 and -38 ppm which are assigned to *Si*HC_2Bu, *Si*SiC_2Bu and *Si*C_2H_2 or *Si*Si_2CH [21]. Spectrum 3(b) (Si–CH_3 polarisation) shows a new signal centred at -43 ppm assigned to *Si*Si_2C_2 nuclei (Scheme 2).



Scheme 2.

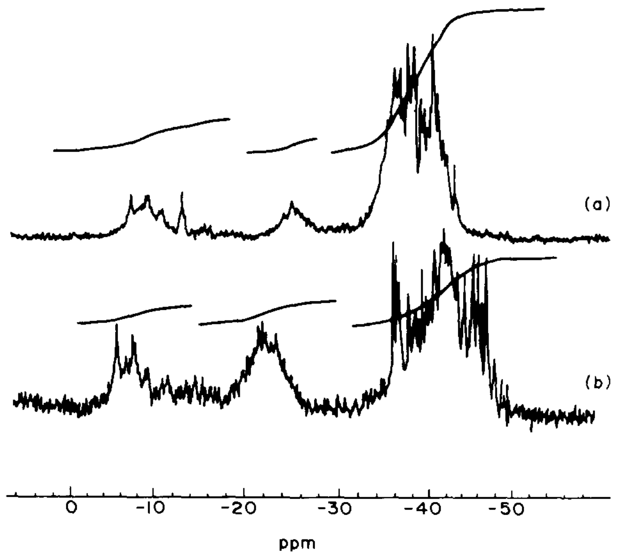
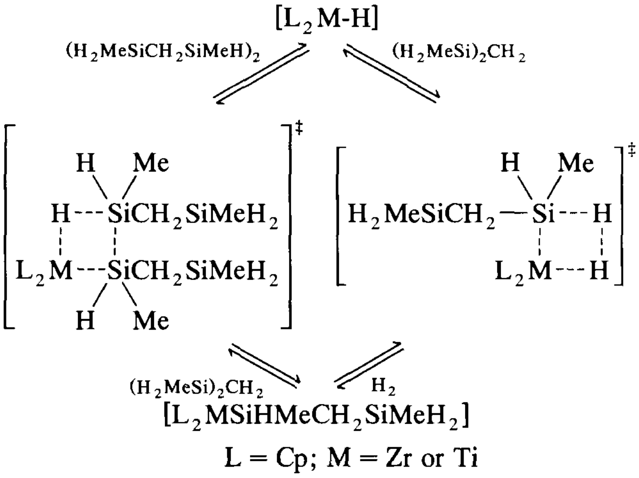


Fig. 3. ^{29}Si NMR spectra from run 1 and 2 using SiH (a) or $SiCH_3$ (b) INEPT pulse sequence.



Scheme 3.

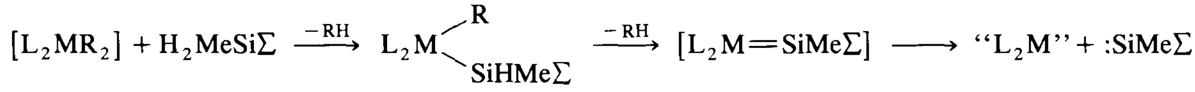
The catalytic polymerisation of 2,4-disilapentane appears to be a competition between two opposing reactions. The major dehydrocondensation reaction produces linear and branched oligomers via secondary/secondary or secondary/tertiary Si–H/Si–H coupling, but splitting of the polymer chain via Si–Si bond cleavage produces low-boiling oligomers. Our results are consistent with the two-step σ-bond metathesis mechanism via a four-centre transition state as previously proposed by Tilley and Woo [6] for other silanes (Scheme 3). Harrod suggested a different mechanism, appropriate only to primary silanes [22].

However, Hengge and Weinberger have recently proposed a mechanism involving silylene insertion into Si–H or Si–Si bonds [23] (Scheme 4). The active catalyst would be a d^0 metal complex "L_2M" instead of a d^0 metal hydride complex "L_2M-H".

3. Experimental details

3.1. Characterisations

IR spectra in the range 4000–400 cm^{-1} were recorded on a Nicolet 20 SXC FTIR spectrometer (neat film between KBr plates). Proton NMR spectra (250 MHz) were recorded on a Bruker AC 250 spectrometer, while ^{29}Si NMR spectra (39.73 MHz) were recorded on a Bruker AC 200 spectrometer using the INEPT pulse sequence [24] (solvent C_6D_6, δ ppm from TMS). The purity of the monomer was determined by gas chromatography (GC) with an OV 101 column (5% on Chromosorb P, 1.5 m, 1/8″, helium carrier flow 30 ml min^{-1}). Gel permeation chromatography (GPC) analyses were performed with four TSK columns (porosity $40–10^7$ Å) calibrated with polystyrene standards, and a



$$[L_2MR_2] + H_2MeSi\Sigma \xrightarrow{-RH} L_2M\begin{matrix} \diagup R \\ \diagdown SiHMe\Sigma \end{matrix} \xrightarrow{-RH} [L_2M{=}SiMe\Sigma] \longrightarrow \text{“}L_2M\text{”} + :SiMe\Sigma$$

$$H_2MeSiCH_2SiMeH\text{-}H + :SiMe\Sigma \longrightarrow H_2MeSiCH_2SiMeHSiMe\Sigma H$$

$$H_2MeSiCH_2SiMeH\text{-}SiMe\Sigma H + :SiMe\Sigma \longrightarrow H_2MeSiCH_2SiMeHSiMe\Sigma SiMe\Sigma H$$

$M = Zr$ or Ti; $R = H$, Me, or Bu; $\Sigma = CH_2Si{\equiv}$; $L = Cp$

Scheme 4.

IOTA refractometer. THF was used as the eluent at 1 ml min^{-1}. Average molecular weights were calculated with a Varian DS 650 data station. Thermogravimetric analyses from 40 to 950°C were obtained with a Perkin Elmer TGS-2 thermobalance equipped with a model 3600 data station (argon N56 flow rate 40 ml min^{-1}; heating rate 5°C min^{-1}; sample mass 10–20 mg). Mass spectra were obtained from a AG-F VG Micromass spectrometer (EI 70 eV).

3.2. Solvents and reagents

Dibutyl ether Solvants Documentation Synthèses (SDS), pentane (SDS), and THF (SDS) were distilled twice under argon over Na/benzophenone, then over $LiAlH_4$. Dichloromethane was dried over alumina before distillation. Toluene (SDS) was distilled over sodium then $LiAlH_4$. Solvents were stored in the dark under argon over molecular sieves (4 Å). Chlorosilanes were generous gifts from the Rhône–Poulenc Company. They were distilled over magnesium turnings and then stored under argon over magnesium powder. $LiAlH_4$, $[Cp_2TiCl_2]$ and $[Cp_2ZrCl_2]$ (Aldrich) were used as received.

Manipulations, filtrations, and reactions were carried out with an argon line or in a dry box. Glassware was carefully dried and purged with argon before use.

3.3. Synthesis of 2,4-dichloro-2,4-disilapentane

A 2 l Sovirel® reactor was equipped with a thermometric well, a pressure-equalising funnel, a mechanical stirrer, and a reflux condenser (at −20°C) fitted with a $CaCl_2$ column. Magnesium turnings (48.64 g, 2 mol), zinc powder (20 g, 3 mol), CH_2Cl_2 (85 g, 1 mol) and methyldichlorosilane (575 g, mol) were introduced, and the mixture was stirred at room temperature for 2 h before THF (750 ml) was added dropwise for 18 h. The reaction mixture rapidly darkened (due to the formation of Grignard reagent) while the temperature was maintained below 30°C and changed from black to grey while $MgCl_2$ precipitated. Once the addition was complete, the mixture was kept stirred for 36 h. The residual $MeHSiCl_2$ and THF were distilled off under high vacuum, then dry pentane (1 l) was added to the grey residue and the mixture was stirred under argon for 36 h. The solution was filtered under argon and the solid washed with pentane (3 × 150 ml). The liquid fractions were evaporated, yielding colourless, liquid chromatographically pure 2,4-dichloro-2,4-disilapentane (58.3 g, 0.337 mol, 33.7%, b.p.$_{6\ \mathrm{Torr}}$ = 42°C). The ^1H NMR spectra indicated a 1 : 1 mixture of two diastereoisomers: two doublets centred at 0.24 and 0.25 ppm (CH_3–Si) ($^3J_{SiH}$ = 3.1 Hz); two multiplets at 4.84 and 4.85 ppm (SiH protons); the CH_2 protons exhibited two overlapping signals: (a) 0.14 ppm (triplet, $^3J_{SiH}$ = 3.4 Hz); (b) 0.10–0.19 ppm (ABX_2 spectrum, J_{AB} = 15 Hz, $J_{AX} \approx J_{BX} = {}^3J_{SiH} \approx$ 3.3 Hz). Mass spectrum: 171 ($C_3H_9Cl_2Si_2^{+}$), 157 ($C_2H_7Cl_2Si_2^{+}$), 137 ($C_3H_{10}ClSi_2^{+}$).

3.4. Preparation of 2,4-disilapentane

$LiAlH_4$ (5.48 g, 0.433 mol) and Bu_2O (150 mL) were introduced into a 500 ml three-necked round-bottomed flask equipped with a magnetic stirrer, a pressure equalizing funnel, an argon inlet, a reflux condenser (at 0°C) connected to a $CaCl_2$ column. The vessel was cooled at 0°C and $(ClMeHSi)_2CH_2$ (25 g, 0.144 mol) was added during a few minutes. Then the mixture was heated at 40°C for 48 h. Low-boiling products were trapped with liquid nitrogen under high vacuum, and the residue was fractionated yielding chromatographically pure $(H_2MeSi)_2CH_2$ (10.35 g, 69%, b.p. = 71°C). ^1H NMR: Si–CH_3, 0.05 (triplet, $^3J_{SiH}$ = 4.1 Hz); Si–CH_2, −0.32 (quintuplet, $^3J_{SiH}$ = 4.2 Hz); Si–H, 3.95. Mass spectrum: 103 ($C_3H_{11}Si_2^{+}$), 89 ($C_2H_9Si_2^{+}$), 87 ($C_2H_7Si_2^{+}$), 73, 59, 43.

3.5. Dehydrocondensation of 2,4-disilapentane

A 50 ml Schlenk tube was fitted with an argon inlet and a reflux condenser at 0°C connected to a $CaCl_2$ drying column. $[Cp_2MCl_2]$ (M = Zr or Ti) was first weighted in a dry box then dissolved in toluene and introduced into a Schlenk tube through a septum. The vessel was cooled to −40°C before adding two equivalents of LiR (R = Bu^n or Me) 1.6 M in hexane. The complex slowly dissolved under magnetic stirring giving a yellowish orange solution of $[Cp_2Zr(Bu^n)_2]$, or a reddish orange solution of $[Cp_2TiMe_2]$. Then 2,4-disilapentane was added with a syringe and the mixture was heated to 90°C for a few h. The solution became brownish and finally light yellow $[Cp_2Zr(Bu^n)_2]$ or dark green $[Cp_2TiMe_2]$. The mixture was then cooled to room temperature under argon. Dry hexane was added and the solution was filtered through Celite to remove the metal complex. Low-boiling products were distilled off at 150°C under 0.1 Torr for several h, yielding a yellow, viscous oil (see Table 1).

4. Conclusion

We suggest a synthesis of new oligomeric precursors of silicon carbide-based ceramics other than the classical coupling reaction of halogenosilanes in the presence of alkaline metals. For example, using 2,4-disilapentane and Ti or Zr derivatives as the catalysts, poly(silacarbosilane)s were prepared in good yield via dehydrocondensation and hydrogen evolution. The pyrolysis yields were satisfactory and the chemical compositions of the ceramics obtained were close to those of the precursors.

The observations confirm the nature of the precursor influences strongly the composition and the properties of the resulting material. Moreover, this approach allowed us to prepare materials with a low oxygen content ($\ll 1\%$).

The use of $[Cp_2TiCl_2]/2LiMe$ as a catalyst is particularly attractive since its nature (Me rather than Bu^n) as well as its molar concentration (2% rather than 3.3% in the case of $[Cp_2ZrCl_2]/2LiBu$) theoretically entails a smaller increase of the carbon content in the polymer. However, the C/Si ratio of ca 1.5 found in both the precursor and the ceramic, implies that the remaining catalyst facilitates C–H/Si–H dehydrocoupling (Eq. 7) avoiding the release of methane, as observed by Seyferth et al. [25] in the case of poly(methylsilane) or poly(vinylsilane).

$$\equiv Si-CH_3 + H-Si\equiv \longrightarrow \equiv Si-CH_2-Si\equiv \qquad (7)$$

Acknowledgements

The authors are indebted to the Rhône–Poulenc Company (grant to P.R.), Le Conseil Régional d'Aquitaine, and Direction des Recherches et Etudes Techniques (DRET) for their financial support.

References

[1] J.F. Harrod and E. Samuel, *J. Am. Chem. Soc., 106* (1984) 1859.

[2] (a) J.F. Harrod, Y. Mu and B. Côté, *Polym. Prepr., 31* (1990) 226; (b) Z.-F. Zhang, F. Babonneau, R.M. Laine, Y. Mu, J.F. Harrod and J.A. Rahn, *J. Am. Ceram. Soc., 74* (1991) 670.

[3] C.T. Aitken, J.F. Harrod and E. Samuel, *Can. J. Chem., 64* (1986) 1677.

[4] C.T. Aitken, J.F. Harrod and E. Samuel, *J. Am. Chem. Soc., 108* (1986) 4059.

[5] J.F. Harrod and S.S. Yun, *Organometallics, 6* (1987) 1381.

[6] (a) H.G. Woo and T. Don Tilley, *J. Am. Chem. Soc., 111* (1989) 8043; (b) H.G. Woo and T. Don Tilley, *J. Am. Chem. Soc., 112* (1990) 2843; (c) H.G. Woo and T. Don Tilley in D.R. Uhlmann and D.R. Ulrich (eds.), *Ultrastructure Processing of Advanced Materials*, Wiley, New York, 1992, p. 651.

[7] J.Y. Corey, X.-H. Zhu, T.C. Bedard and L.D. Lange, *Organometallics, 10* (1991) 924.

[8] J.Y. Corey and X.-H. Zhu, *Organometallics, 11* (1992) 672.

[9] J.F. Harrod, in R.M. Laine (ed.), *Inorganic and Organometallic Polymers with Special Properties*, NATO ASI Ser., Ser. E, American Chemical Society, Washington DC, 1992, vol. 206, p. 87.

[10] T. Don Tilley and H.G. Woo, *J. Am. Chem. Soc., 111* (1989) 3757.

[11] T. Sakakura, H.J. Lautenschlager, M. Nakajima and M. Tanaka, *Chem. Lett.*, (1991) 913.

[12] G.J. Erskine, D.A. Wilson and J.D. McCowan, *J. Organomet. Chem., 114* (1976) 119.

[13] (a) E. Hengge, M. Weinberger and C. Jammegg, *J. Organomet. Chem., 410* (1991) C1; (b) E. Hengge and M. Weinberger, *J. Organomet. Chem., 433* (1992) 21.

[14] R.J.P. Corriu, J. Moreau, M. Enders and S. Huille, *Chem. Mater., 6* (1994) 15.

[15] Y. Nomura, R. Sato and Y. Okumura, Japanese Patent 06,145,360, 1994.

[16] V.K. Djoumaev and J.F. Harrod, *Organometallics, 13* (1994) 1548.

[17] J.-P. Pillot, C. Biran, E. Bacque, P. Lapouyade and J. Dunoguès, French Patent 8,607,814, 1986.

[18] E. Bacqué, J.-P. Pillot, M. Birot and J. Dunoguès, *Macromolecules*, 21 (1988) 34.

[19] A. Tazi Hémida, J.-P. Pillot, M. Birot, J. Dunoguès and R. Pailler, *J. Chem. Soc., Chem. Commun.*, (1994) 2337.

[20] S.L. Buchwald and B.T. Watson, *J. Am. Chem. Soc., 109* (1987) 2544.

[21] H. Marsmann, in P. Diehl, E. Fluck and R. Kosfeld (eds.), *NMR Basic Principles and Progress*, Springer, Berlin, 1981, p. 65.

[22] J.-F. Harrod, in M. Zeldin, K.J. Wynne and H.R. Allcock (eds.), *Inorganic and Organometallic Polymers*, ACS Symp. Ser., American Chemical Society, Washington, DC, 1988, vol. 360, p. 89.

[23] E. Hengge and M. Weinberger, *J. Organomet. Chem., 443* (1993) 167.

[24] T.A. Blinka, B.J. Hemer and R. West, *Adv. Organometal. Chem., 23* (1984) 193.

[25] D. Seyferth, G.E. Koppetsch, T.G. Wood, H.J. Tracy, J.L. Robison, P. Czubarow, M. Tasi and H.G. Woo, *Polym. Prepr., 34* (1993) 223.