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Thermal conversion of organosilicon cobalt precursors to mixed Si/Co/C/O ceramics

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Cobalt organosilicon ceramic precursors **I**, **I(D)**, **III** and **IV** were prepared by reaction of dicobalt octacarbonyl with normal and *Si*-deuterated 2,5-disilahexane, 2,4-disilapentane and 1,4-disilabutane respectively. Precursor **II** is a dimeric silicon cobalt cluster $[\mu\text{-}\{(CH_3)Si(CH_2)\}_2][Co(CO)_3]_2$. Thermal decomposition of the precursors was performed under argon. Evolution of H_2 in the early stage of the pyrolysis ($<120\,°C$) shows that an initial cross-linking of the material is induced by the remaining Si—H bonds. Between 120 and 300 °C, the thermal decomposition of the complexes results either in the elimination of the CO ligands or in their reaction with incorporation of oxygen and carbon. At higher temperature, the elimination of hydrogen and methane corresponds to the mineralisation step of the precursors. By 1000 °C, the material is formed of metal-rich nodules homogeneously dispersed in a matrix. Co_2Si is detected by X-ray analysis. Between 1000 and 1400 °C, carbothermal reduction occurs with evolution of CO. Simultaneously SiO_2, SiC and CoSi phases are formed.

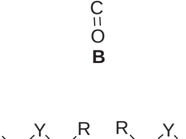
Introduction

Pyrolysis of polycarbosilanes or polysilanes has been effective in the preparation of silicon carbide.[1] Efforts have been recently concentrated on the preparation of multiphase ceramics by using such preceramic polymers as a soluble source of the elements needed for the ceramics.

Silicon containing polymers have been mixed with metal powders,[2,3] organometallics reagents[4–8] or other inorganic polymers[9,10] to produce oxide and non-oxide mixed ceramics. It was also reported that a catalytic amount of a transition metal reagent can be used to catalyze the thermal decomposition of silicon containing polymers, increasing the final ceramic yield.[11–13]

Our current interest in that field led us to investigate the potential of low molecular weight organosilicon complexes as ceramic precursors.[14–16] We thought it might be possible to prepare them by the reaction between $Co_2(CO)_8$ and (organosilyl)hydrocarbons containing $\text{-}SiH_2\text{-}$ groups. The previous literature has well established the reaction of Si—H with transition metal compounds.[17] Starting from compounds of the general formula $R\text{-}SiH_2\text{-}Y\text{-}SiH_2\text{-}R$ led us to expect a mixture of compounds with different structures like **A**, **B**, **C** and **D**.

A



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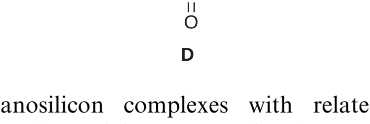


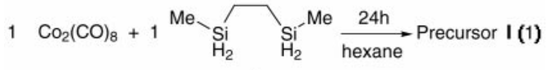
D

Transition metal–organosilicon complexes with related structures were reported to be useful precursors for the preparation of transition metal silicides by CVD technology.[18] However, for application purposes, our aim was to produce liquid or soluble polymers or oligomers. It implies a cross-linking step in order to hinder, first, the distillation of light fractions and, secondly, the splitting of the chain by thermal fragmentation reactions and formation of volatile compounds. A good knowledge of the chemistry involved in this process is necessary to design efficient ceramic precursors and to control the temperature of the cross-linking steps. We report here the results of our studies on the syntheses of these precursors and on the chemistry that occurs during their thermal transformation.

Results and Discussion

Preparation of the precursors

The preparation and the characterization of the 2,5-disilahexane/cobalt carbonyl precursor, **I**, were detailed in a previous paper [eqn. (1)].[16] From the spectroscopic analyses, compounds **2** and **3** with their *cis* and *trans* isomers are assumed to be the major constituents of precursor **I.** Compound **4** was also identified in the mixture but the presence of compound **5** was excluded since we do not observe any signal around −29 ppm corresponding to the initial $\text{-}SiH_2\text{-}CH_3$ groups.



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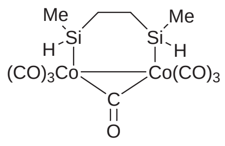

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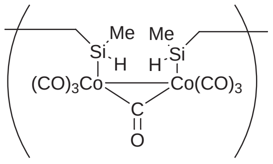

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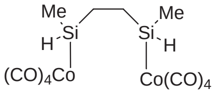

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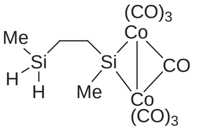

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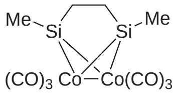
Owing to the mild reaction conditions, the silicon atoms of compounds **2** to **4** are linked to only one transition metal atom, leaving an average of one Si—H bond per silicon atom.

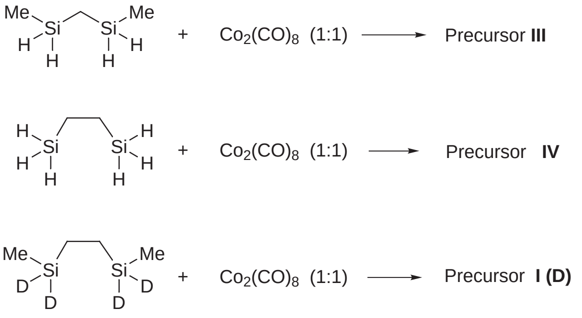
To investigate the mechanism of the thermal conversion from precursor to ceramic, model compounds were prepared. They were chosen from analogues of 2,5-disilahexane in order to find a relation between their structure and their behaviors during the pyrolysis. Precursors **III, IV** and **I(D)** were prepared following Scheme 1 by reacting 2,4-disilapentane (**6**), 1,4-disilabutane (**7**) and deuterated 2,5-disilahexane (**8**) with a stoichiometric amount of $Co_2(CO)_8$, using the experimental conditions described for the preparation of precursor **I**. Precursor **II** is a cyclic complex with no Si—H bonds, formed from 2,5-disilahexane and $Co_2(CO)_8$ under different conditions. We previously reported its synthesis and its characterization by X-ray crystal diffraction analysis.[19]



Precursor **II**

The corresponding precursors **III**, **IV** and **I(D)** were obtained as viscous oils and in high yield, assuming that all the Si and Co atoms remained in the precursors. All of these compounds were easily soluble in hexane and not air stable. No further purification was carried out and the characterization of the crude material indicates the presence of structures similar to those observed for **I**. Si—Co and remaining Si—H bonds are clearly shown by ^{29}Si NMR and ^{1}H NMR spectroscopy. The results of these analyses are consistent with the presence of analogues of structures **2**, **3** and **4** proposed for precursor **I**.

For the deuterated precursor **I(D)**, we observed the presence of some Si—H bonds. It is well demonstrated by the increase of the ν_{Si-H} absorption frequency (ν_{Si-H}=2132 cm^{-1}) when aging of the precursor at room temperature was followed by infrared spectroscopy. Such a reaction probably occurs in all the precursors but can only be detected for precursor **I(D)**. This result arises from an exchange reaction between Si—D and C—H bonds. To our knowledge, such phenomena were only observed by Ryan and Speier during the hydrosilylation of vinylic compounds catalyzed by H_2PtCl_6.[20] In this case, the reversible interconversion between π and σ complexes was proposed to explain these phenomena. Such a mechanism cannot be considered here and we proposed a mechanism based on the insertion/elimination of Co species in the Si—D and C—H bonds, as is presented in Scheme 2. This reaction can occur by an intra- or inter-molecular process, however, the intramolecular pathway is probably more accurate since the reaction is observed at low temperature and in a polymeric state.



Scheme 1

Such a reaction could also occur *via* a mechanism involving an intermediate η^2-silene (η^2-$R_2Si{=}CH_2$) complex, the formation of these ruthenium or osmium complexes was proposed to explain the H/D exchange between Me_3SiH and [$^2H_6$]benzene,[21] or the dehydrogenative coupling of trialkylsilanes.[22] However, we did not find evidence for it.

Thermal transformation

Precursor **I** was pyrolyzed under argon from 50–1400 °C and the gases were characterized by mass spectrometry. The TGA curve is given in Fig. 1 and the results are discussed by looking at the different weight losses and comparing them with the behavior of the other precursors (Fig. 2–5).

(a) Between 50 and 120 °C. In this temperature range, a quick weight loss occurs with elimination of H_2 and a small amount of CO. At the same time, infrared spectroscopy analysis of precursor **I** shows a decrease of the intensity of the absorption of the stretching vibration of Si—H (ν_{SiH}: 2120 cm^{-1}) and

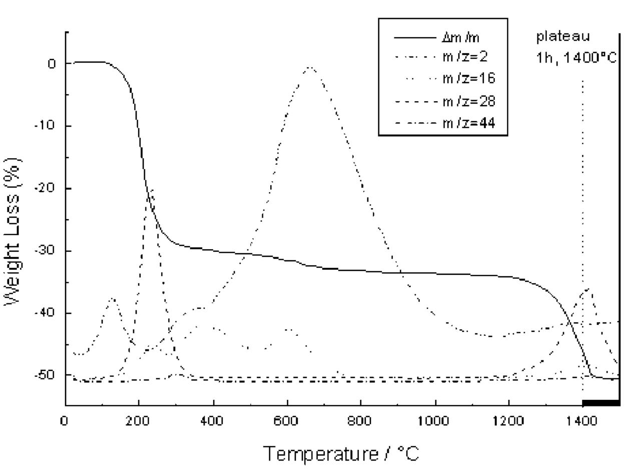


Fig. 1 TGA curve and gas analyses (ionic current for $m/z=2$, 16, 28, 44) evolved during pyrolysis of precursor **I**

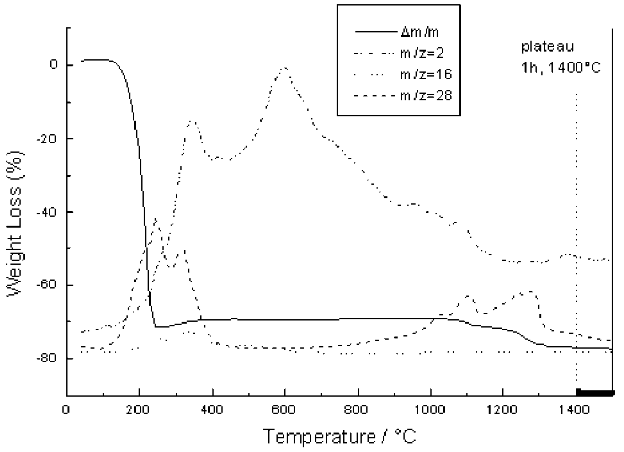
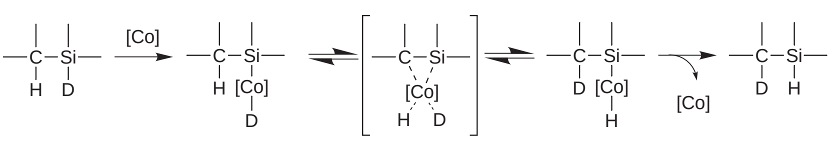


Fig. 2 TGA curve and gas analyses (ionic current for $m/z=2$, 16, 28) evolved during pyrolysis of precursor **II**



Scheme 2 Si—D/C—H exchange by cobalt insertion in Si—D and C—H bonds

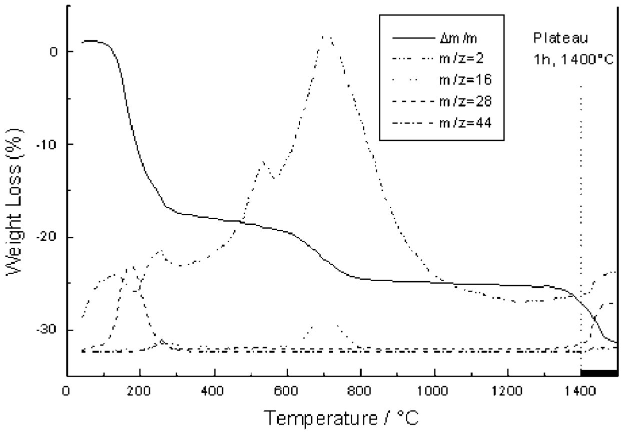


Fig. 3 TGA curve and gas analyses (ionic current for $m/z=2$, 16, 28, 44) evolved during pyrolysis of precursor **III**

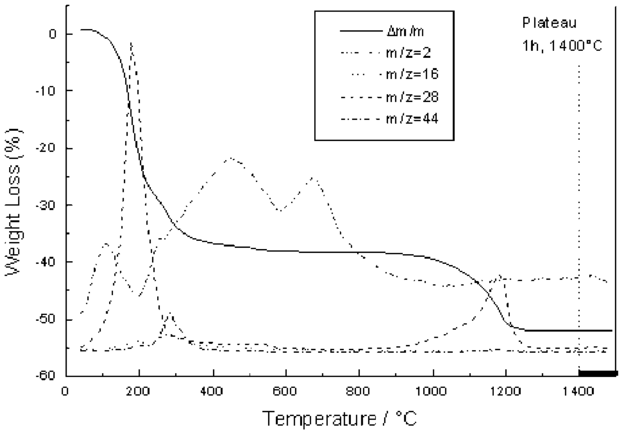


Fig. 4 TGA curve and gas analyses (ionic current for $m/z=2$, 16, 28, 44) evolved during pyrolysis of precursor **IV**

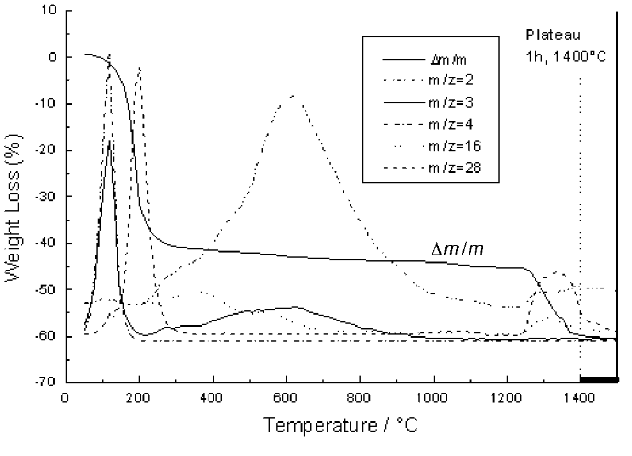


Fig. 5 TGA curve and gas analyses (ionic current for $m/z=2$, 3, 4, 16, 28) evolved during pyrolysis of precursor **I(D)**

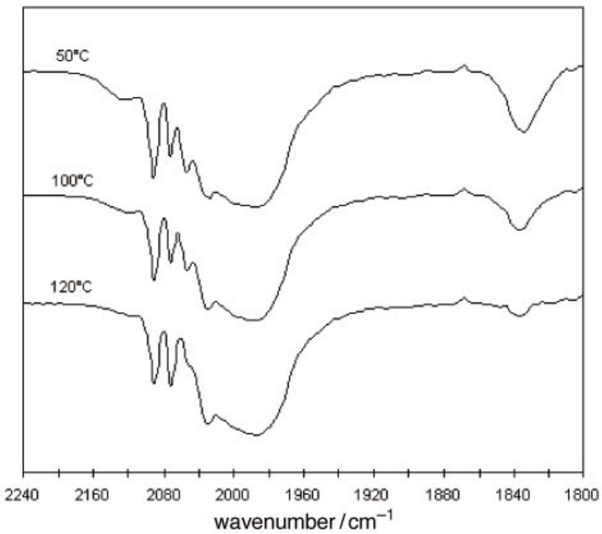
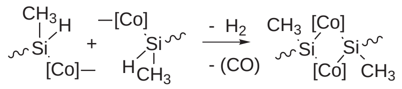


Fig. 6 Infrared analysis of precursor **I** at different pyrolysis temperatures

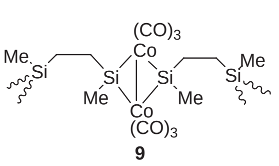
bridging CO (ν_{CO}: 1840 cm^{-1}) and increasing intensity of the absorption band $\nu_{CO}=2072$ cm^{-1} (Fig. 6). This absorption band was attributed to the $Co_2(CO)_6$ group by reference to different compounds containing this group like precursor **II**, $(CH_3)_2Si[Co_2(CO)_6]Si(CH_3)_2$ or $(CH_3)_2Ge[Co_2(CO)_6]$-$Ge(CH_3)_2$ with similar $Co_2(CO)_6$ substructure.[19,23]

Similar behavior was found for the other precursors with residual Si—H bonds like **III** and **IV**. It can be assumed that the elimination of H_2 is related to the consumption of Si—H bonds. This is clearly evidenced by the absence of hydrogen evolution during the pyrolysis of precursor **II** which does not contain any Si—H bonds. Moreover, for precursor **I(D)** with residual Si—D bonds, evolution of D_2 is observed as the major gas. Actually, HD and traces of H_2 were also detected, their intensity being increased by the aging of the precursor. It can be assumed that these gases arise from the presence of Si—H bonds formed by redistribution reactions as discussed before. The sum of these results corresponds to a loss of Si—H bonds and the formation of Si—Co bonds in $Co_2(CO)_6$ units which bridge two silicon atoms following Scheme 3.



Scheme 3

Two different processes can occur either by inter or intra molecular reactions. Starting from structure **2**, the intramolecular elimination of H_2 and CO leads to the formation of molecular species like precursor **II**. However, when the reaction proceeds between two different units, starting from compounds **2** or **3**, a structure like **9** can be formed and should result in a cross-linking of the residue.



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We did not find evidence for the formation of Si—Si bonds in the residue, and the presence of a quantitative amount of cobalt is not compatible with their presence since Si—Si bonds are known to be cleaved by cobalt derivatives.[24]

(b) Between 120 and 300 °C. In this temperature range, CO is the only gas detected. An analysis performed with a plateau at 120 °C has shown that this phenomenon starts after the first evolution of hydrogen (Fig. 7).

Infrared analysis of a sample between 200 and 350 °C indicates the disappearance of all the ν_{Si-H} and the $\nu_{C\equiv O}$ frequencies (Fig. 8). All the precursors exhibit this behavior which corresponds to the thermal decomposition of the cobalt carbonyl moiety and the formation of new bonds around the cobalt atoms. For precursor **I**, the elimination of these volatile ligands accounts for almost the totality of the 30% weight loss

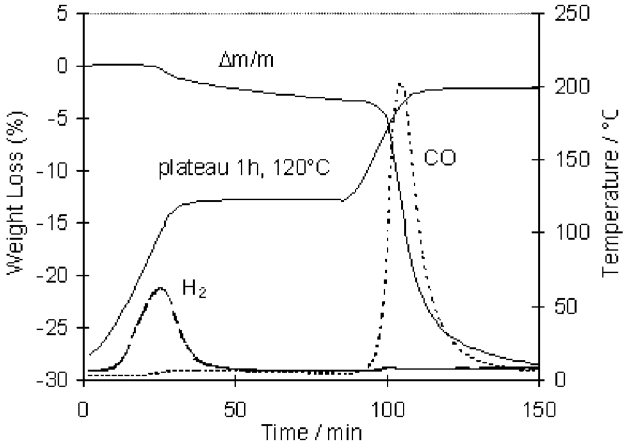


Fig. 7 TGA curve with isothermal step at 120 °C and gas analyses (ionic current for $m/z=2$ and 28) evolved during thermal treatment of precursor **I**

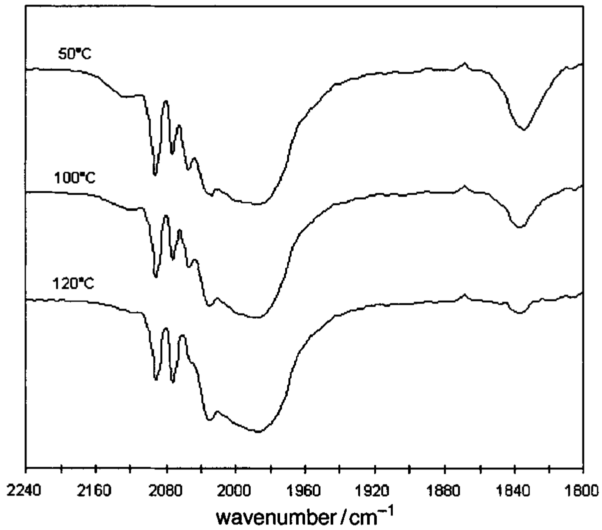


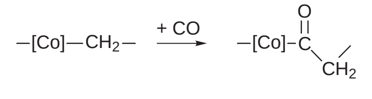
Fig. 8 Infrared analysis of precursor **I** at different pyrolysis temperatures

observed between 50 and 300 °C. This amount is much lower than the expected 50% corresponding to the elimination of all the CO ligands. It is readily apparent that reaction of CO with incorporation of oxygen and carbon in the matrix occurs and that this process is an important one at this temperature. As a confirmation, elemental analyses indicate a O/Si ratio of 1.5 corresponding to the insertion of about 3 of the initial 7–8 CO ligands (Table 1).

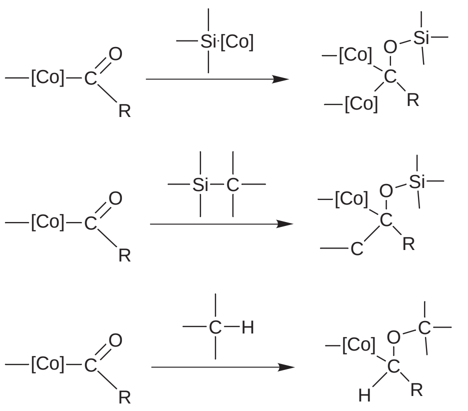
These behaviors are also observed for precursor **I(D)**. In the case of precursor **II** the important weight loss observed at this step is due to some extent to the volatilization of the material. Different processes can be proposed for the transformation of the material at this step of the pyrolysis, between 120 and 300 °C. A possible process is the reaction by insertion of Co in C—H bonds,[25] or in Si—C bonds.[26] This will result in the formation of [Co]—H and [Co]—C≡ species. The latter can react with CO, leading to the formation of [Co]—CO—C≡ complexes following Scheme 4. Such an insertion is well described in the hydroformylation process catalyzed by cobalt species.

Table 1 Elemental analyses of precursor **I** at different pyrolysis temperatures

temperature/°C	Si	Co	C	O	H
20	11.4	25.8	31.4	not titrable	2.9
200	16.4	30.6	24.2	14.0	4.1
400	18.5	32.1	23.1	15.6	3.1
900	21.9	33.6	22.2	19.3	
1400	22.1	42.3	17.7	15.6	

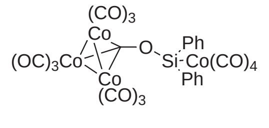


Scheme 4



Scheme 5

The occurrence of such processes might explain the insertion of CO in the precursors.[27–29] Absorption bands of carbonyl bonds $\nu_{C=O}$ were not detected by infrared analysis because these species can immediately react with C—H, Si—C or Si—Co bonds, leading to the formation of structures **10**–**12** following Scheme 5. In support of this, cluster **13** is reported to be formed by incorporation of a CO ligand in the Si—Co bond.[30] Similarly, the thermal reaction of Me_3Si—$Co(CO)_4$ was reported to result in the formation of Si—O—C—M derivatives like compounds **14** and **15**.[31–33]



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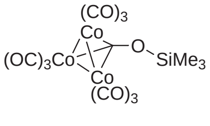

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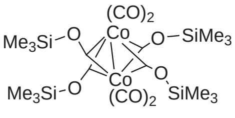

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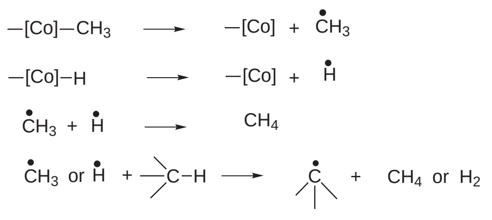
Formation of Si—O—Si bonds has also to be considered since the thermolysis of silyl–metal carbonyl complexes like $[Co(CO)_4SiR_3]$ was reported to form siloxanes $O(SiR_3)_2$ (R = H,[34] Me[35]).

Finally, it is also necessary to consider the formation and the elimination of gaseous cobalt containing species like $HCo(CO)_4$ since the elemental analyses clearly show an increase of the Si/Co ratio (Table 1).

All these processes result in the breaking of the Si—Co bonds and the migration of silicon from the metal to oxygen. Thus, it can be assumed that between 120 and 300 °C, thermal reactions result in the formation of a silicon oxycarbide matrix with Si—O—Si or Si—O—C bonds.

(c) By 350 °C. By this temperature, a new process is going on. It is characterized by a limited weight loss (3–5%) and the elimination of H_2 and CH_4. More interestingly, C_2 fragments are not observed, nor are organosilyl compounds. All the precursors have the same behavior and the elimination of



Scheme 6

methane is not related to the nature of the bridge or the presence of $SiCH_3$ groups. No Si—H bonds are present at this step of the pyrolysis and no formation of these bonds is observed by infrared analysis. Therefore, it is probably worth considering a process based on Co—H and Co—C bonds formed previously. These bonds are weaker than Si—C, C—C or even Si—Co bonds[36–39] and their thermal cleavage will lead to H• and CH_3• that may abstract hydrogen to form H_2 and CH_4 (Scheme 6). Simultaneous recombination of the radical in the residue increase its cross-linking.

Formation of methane was proposed to occur by a subsequent Fisher–Tropsch reaction of CO in the presence of H_2 and catalyzed by the finely divided metal containing residue.[18] The reduction of CO should lead to the formation of water. Neither ionic current at $m/z = 18$ (by mass spectroscopy) nor O—H vibration frequencies (by infrared spectroscopy) were observed during the pyrolysis. However, the absence of water could be due to its reaction with the residue.

(d) At 700 °C. At this temperature, a weight loss occurs with elimination of H_2 and CH_4 for all the precursors excepted for precursor **IV** for which no methane evolution is observed. The formation of CH_3• from thermal homolytic cleavage of the residual CH_3—Si bonds, followed by hydrogen abstraction can be proposed. The Si—C bond is rather stable but it can be thermally cleaved.[40] For example, elimination of methane from various ceramic precursors like $MeSiO_{1.5}$ or [-$Si(CH_3)_2CH_2CH_2$-] was reported to start respectively at 600 and 450 °C.[41,42] The formed radicals can further recombine or react with the other part of the matrix.

(e) Below 1000 °C. The material prepared from precursor **I** is formed of metal-rich nodules, homogeneously dispersed and embedded in a matrix and Co_2Si is detected by X-ray diffraction.[16] The formation of this thermodynamically stable phase is not related to the presence of an excess of cobalt, indeed the Si/Co ratio in the residue is higher than 1.5. The formation of this silicide Co_2Si was reported by pyrolysis of other preceramic polymers with $Si/Co \geqslant 1$.[11,13,14] This is different from the flow pyrolysis at 500 °C of molecular complexes like $Co(CO)_4SiH_3$ which produces the single phase CoSi.[18] In the preceramic polymer process, the formation of the phase is not controlled by the stoichiometry of the precursor. Moreover, despite the initial homogeneous dispersion of metal, silicon and carbon atoms in the precursors, a thermodynamically stable phase is formed. This implies important diffusion and migration processes in the material.

(f) Above 1000 °C. Above 1000 °C a carboreduction process occurs with formation of CO. This corresponds to the decomposition of the silicon oxycarbide matrix formed by the 'incorporation' of the CO ligand at 300 °C. We found that the temperature of this carboreduction steps depends on the precursor: 1250 °C for **I**, 1350 °C for **III** and 1000 °C for **IV**, but at this time, there is no clear relation with their structure.

For precursor **I**, the formulations of the ceramics are based on the elemental analyses with respect to the initial composition of the precursor and the weight loss during the pyrolysis. The levels of oxygen and carbon decrease due to the elimination of CO, but a large amount of these elements is still present after carboreduction, even in the presence of an excess of carbon. Moreover, we observed the formation of a fibrous white solid characterized as whiskers of SiO_2. It thus appears that the formation of CO is rather limited compared to the formation of SiO_2. The structure of the SiO_2 deposit and its presence mainly at the surface of the residue argue for a decomposition of gaseous SiO following eqn. (2).

$$3\ SiO(g) + CO(g) \rightleftharpoons 2\ SiO_2(g) + SiC(s) \qquad (2)$$

The occurrence of this reaction can also explain the formation of SiC which is characterized by X-ray analysis. However, a part of the SiO is probably eliminated during the carboreduction since the Si/Co ratio decreased. This gas is stable above 1000 °C but decomposes at low temperature and is not detected by mass spectrometry. The reaction leading to the formation of SiO and CO is not clear at this time. Reactions like eqn. (3), (4) and (5) are known to occur during the carboreduction of silicon oxide but cannot be directly used for the oxycarbide material reported here.[43,44]

$$SiO_2(s) + C(g) \rightleftharpoons SiO(g) + CO(g) \qquad (3)$$

$$SiO_2(s) + CO(g) \rightleftharpoons SiO(g) + CO_2(g) \qquad (4)$$

$$2\ SiO_2(s) + + SiC(s) \rightleftharpoons 3\ SiO(g) + CO(g) \qquad (5)$$

Other characterization of the material indicates that phase transformations have occurred during the carboreduction step. Cobalt silicide is still present but X-ray analysis indicates the absence of the initial Co_2Si phase while a new phase, CoSi, is detected. It can be assumed that this transformation arises from the reaction of the Co_2Si phase with SiC which was formed following eqn. (3). For example, a catalytic amount of cobalt is known to promote the crystallization of SiC,[12,15] but cobalt is also known to react quantitatively with SiC from 900 °C to give carbon and a mixture of silicides.[45,46] Thus, one possible process would correspond to the formation of SiC from SiO and CO followed by its reaction with Co_2Si leading to CoSi and graphite and corresponding to eqn. (6) and (7). This is also supported by the presence of a large amount of carbon in the residue.

$$3\ SiO(g) + CO(g) \rightleftharpoons 2\ SiO_2(g) + SiC(s) \qquad (6)$$

$$SiC(s) + Co_2Si(s) \rightleftharpoons C(s) + 2\ CoSi(s) \qquad (7)$$

Conclusion

We have found that ceramic precursors of mixed SiC/ cobalt silicides can be prepared from dicobalt octacarbonyl and organosilicon compounds with SiH_2 groups. The reaction can be limited to the reaction of one Si—H bond which permits the preparation of an oily product. The presence of a remaining Si—H bond is crucial since it allows the thermal cross-linking of the material. We have also found that an important number of the CO ligands are incorporated in the matrix leading to an oxide matrix in the materials.

Experimental section

All the reactions were carried out under an atmosphere of dry nitrogen. Solvents were dried using standard techniques. Infrared spectra were recorded on a Perkin Elmer 1600 series FTIR spectrometer. NMR spectra were obtained with a Bruker Advance DPX 200 (^1H, ^{13}C) or a Bruker WP 200 SY (^{29}Si), solvent $CDCl_3$ or C_6D_6, TMS as an internal standard. Pyrolyses were performed with an Eurotherm or Carbolite furnace. The heating rate was 5 °C min^{-1}. Thermogravimetric analyses were performed on a Netzsch STA 409 Thermobalance under an argon atmosphere. The heating rate was 5 °C min^{-1}. The gases were analyzed by a Balzers quadrupolar mass spectrometer. Elemental analyses were performed at the Service Central d'Analyses du CNRS at Vernaison, France. X-Ray diffraction measurements were obtained using Cu-Kα radiation, on a Phillips diffractometer. SEM was performed on a Leica S 360 Cambridge at 20 kV and TEM was performed on a JEOL 1200 EX2 at 100 kV. Elemental analyses (%) for the precursors are given Table 1.

Synthesis of 2,5-disilahexane **1** was detailed previously[19] as well as the synthesis and characterization of precursors **I** and **II**. 2,4-Disilapentane **6** was synthesized following the literature.[47]

Preparation of 1,4-disilabutane 7

To 25 ml of hexane containing 0.2 ml of Speier's catalyst (2.5×10^{-4} mol Pt^{IV}) were added 1.65 g (0.01 mol) of vinyltrichlorosilane and 1.40 g (0.01 mol) of trichlorosilane. The mixture was stirred with gentle heating until an exothermic reaction commenced. Then 14.5 g (0.09 mol) of methylvinyldichlorosilane in 10 ml of hexane and 12.2 g (0.09 mol) of methyldichlorosilane in 90 ml of hexane were added slowly and stirred simultaneously in order to maintain reflux. The mixture was then cooled to room temperature and the solvent removed *in vacuo* (10 mmHg) at 25 °C. 1,1,4,4-Tetrachloro-1,4-disilabutane was purified by distillation. Yield 20.75 g (70%), bp 76 °C (1 mmHg). A solution of 15 g (0.05 mol) of 1,1,4,4-tetrachloro-1,4-disilabutane in 10 ml of diglyme was added slowly to a solution of 5.7 g (0.15 mol) of $LiAlH_4$ in 90 ml of diglyme cooled to 0 °C. The mixture was stirred for 4 h at room temperature. Distillation of the crude mixture at room temperature under 25 mmHg afforded the 1,4-disilabutane by trapping at -78 °C. Yield 3.7 g (80%). ^{1}H NMR ($CDCl_3$, δ) 3.58 (6H, t); 0.39 (4H, m). ^{13}C NMR ($CDCl_3$, δ) 1.00. ^{29}Si NMR ($CDCl_3$, δ) -55.0. IR (hexane, ν/cm^{-1}) Si—H 2155.

Preparation of 2,2,5,5-tetradeutero-2,5-disilahexane 8

2,2,5,5-Tetrachloro-2,5-disilahexane was prepared following the procedure described previously.[19] A solution of 6.4 g (0.025 mol) of 2,2,5,5-tetrachloro-1,4-disilahexane in 10 ml of diglyme was added slowly to a solution of 2.0 g (0.05 mol) of $LiAlD_4$ in 30 ml of diglyme cooled to 0 °C. The mixture was stirred for 6 h at room temperature. Distillation of the crude mixture at room temperature under 25 mmHg afforded the 1,4-disilabutane by trapping in liquid N_2. Yield 2.95 g (95%). ^{1}H NMR ($CDCl_3$, δ) 0.64 (4H, m); 0.09 (6H,t). ^{13}C NMR ($CDCl_3$, δ) 5.43; -8.85. ^{29}Si NMR ($CDCl_3$, δ) -20.21. IR (hexane, ν/cm^{-1}) Si—H 1558.

Preparation of precursor III

Under inert atmosphere, compound **6** (260 mg, 2.5 mmol) and $Co_2(CO)_8$ (855 mg, 2.5 mmol) were added to 20 ml of hexane. After 24 h of stirring at room temperature, the solvent was removed *in vacuo* and 0.99 g of precursor **III** was recovered. ^{1}H NMR (C_6D_6, δ) 4.32 (Si—H, m); 0.10; 0.88; -0.15. ^{29}Si NMR (C_6D_6, δ) -53.7; 39.0. IR (hexane, ν/cm^{-1}) 2116; 2092; 2062; 2052; 2030; 2002; 1997; 1970; 1840.

Preparation of precursor IV

Under inert atmosphere, compound **7** (225 mg, 2.5 mmol) and $Co_2(CO)_8$ (855 mg, 2.5 mmol) were added to 20 ml of hexane. After 24 h of stirring at room temperature, the solvent was removed *in vacuo* and 0.95 g of precursor **IV** was recovered. ^{1}H NMR (C_6D_6, δ) 4.58 (Si—H, m); 0.4 (broad). ^{29}Si NMR (C_6D_6, δ) -53.7; 39.0. IR (hexane, ν/cm^{-1}) 2116; 2097; 2080; 2070; 2051; 2041; 2029; 2003; 1978; 1838.

Preparation of precursor I(D)

Under inert atmosphere, compound **8** (305 mg, 2.5 mmol) and $Co_2(CO)_8$ (855 mg, 2.5 mmol) were added to 20 ml of hexane. After 24 h of stirring at room temperature, the solvent was removed under vacuum and 1.0 g of precursor **V** was recovered. ^{1}H NMR (C_6D_6, δ) 5.0 (Si—H, very weak); 1.13; 0.82. ^{29}Si NMR (C_6D_6, δ) 55.3; 42.7; 25.3. IR (hexane, ν/cm^{-1}) 2116 (very weak); 2095; 2070; 2047; 2031; 2006; 1997; 1969; 1842.

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