

# X-Ray and NMR spectroscopic characterisation of cyclic titanodiphenylsiloxanes and examination of the hydrolytic stability of their Si—O—Ti bonds

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Six crystalline titanodiphenylsiloxanes have been synthesised by reaction of diphenylsilanediol (DPSD) with titanium tetraisopropoxide or its complexes with acetylacetonate (acac) as ligand. Two of them show a spirocyclic structure with the formula  $\text{TiO}_2[\text{O}_2\text{Si}_2(\text{C}_6\text{H}_5)_4]_2$  **A** and  $\text{TiO}_2[\text{O}_4\text{Si}_4(\text{C}_6\text{H}_5)_8]_2$  **B** which have already been described in the literature. Two compounds **C** and **D** were identified by X ray analysis to have the same bicyclic structure but different coordinating solvent molecules. Tetrahydrofuran acts as a non bridging ligand at the Ti atoms in  $[\text{Ti}(\text{acac})\text{O}_{1.5}]_2[\text{OSi}(\text{C}_6\text{H}_5)_2]_3 \cdot 2\text{C}_4\text{H}_8\text{O}$  **C** while dioxane acts as a bridging ligand between the Ti atoms of neighbouring molecules of  $[\text{Ti}(\text{acac})\text{O}_{1.5}]_2[\text{OSi}(\text{C}_6\text{H}_5)_2]_3 \cdot 3\text{C}_4\text{H}_8\text{O}_2$  **D**. The titanodiphenylsiloxanes **E** and **F** were identified by a cyclotetrameric structure and the formulas  $[\text{Ti}(\text{acac})_2\text{O}]_2[\text{OSi}(\text{C}_6\text{H}_5)_2]_2$  and  $[\text{Ti}(\text{acac})_2\text{O}][\text{OSi}(\text{C}_6\text{H}_5)_2]_3$ , respectively. The titanodiphenylsiloxanes **A–E** were characterised by <sup>29</sup>Si and <sup>17</sup>O NMR spectroscopy, IR and time of flight mass spectrometry measurements. The hydrolytic stabilities of the Si—O—Ti bonds in the titanodiphenylsiloxanes **A–E** have been examined mainly by means of <sup>29</sup>Si NMR spectroscopy. The results reveal a strong influence of the structure type of the titanodiphenylsiloxanes on the hydrolytic stability of their Si—O—Ti bonds apart from the hydrolytic conditions (amount of water, Si, Ti and H<sup>+</sup> concentration). The hydrolytic stability of the titanodiphenylsiloxanes **A–E** decreases in the order cyclotetramer (**E**) > spirocyclic (**A, B**) > bicyclic (**C, D**). Reasons for the different hydrolytic stability are discussed. The results on the different hydrolytic stabilities of Si—O—Ti bonds can contribute to a better understanding of the synthesis of homogeneous heterometal materials on a molecular scale *via* the sol gel process.

Oxygen bridged heterometal bonds *e.g.* Si—O—Al, Si—O—Ti or Si—O—Zr are important in terms of the structure and properties of glasses, ceramics and hybrid polymers. In addition to high temperature processes the sol gel process is an often used method for the preparation of materials with heterometal bonds, starting from mixtures of metal alkoxides or their organic derivatives.<sup>1–5</sup> Until now, there is insufficient knowledge concerning the existence and the amount of heterometal bonds and their hydrolytic stability in the course of the sol gel process.<sup>6–10</sup> The knowledge of the stability of heterometal bonds, however, is a basis for the preparation of homogeneous heterometal materials on a molecular scale. Recently, it has been shown that Si—O—Ti and Si—O—Zr bonds in sol gel systems are hydrolysed and converted to SiO<sub>2</sub> and TiO<sub>2</sub> or ZrO<sub>2</sub> rich phases which lower the homogeneity of sol gel derived materials.<sup>11–14</sup> Previous work on the hydrolytic stability of the heterometal bonds has been carried out mainly on mixtures of different metal alkoxide hydrolysates with a wide distribution of unidentified species. The objective of this work is to reveal, for well defined cyclic titanodiphenylsiloxanes, the influence of the structure on the hydrolytic stability of Si—O—Ti bonds, which is important with respect to the synthesis of materials with high homogeneity at the molecular scale *via* the sol gel process.

## Experimental

### Synthesis

Generally, the crystalline titanodiphenylsiloxanes were synthesised by reaction of diphenylsilanediol (DPSD) or tetraphenylsiloxanediol with titanium tetraalkoxides or its complexes with acetylacetonate (Hacac).

**Spirocyclic titanodiphenylsiloxane**  $\text{TiO}_2[\text{O}_2\text{Si}_2(\text{C}_6\text{H}_5)_4]_2$  **A**. The crystalline compound was synthesised by reaction of tetraphenylsiloxanediol<sup>13</sup> with titanium tetraisopropoxide at

a molar ratio of 2:1 according to the procedure of Andrianov *et al.*<sup>15,16</sup> Tetraphenylsiloxanediol (1 g, 2.42 mmol) was dissolved in 3.47 ml dioxane and 0.356 ml (1.21 mmol) of  $\text{Ti}(\text{OPr}^i)_4$  were added dropwise under vigorous stirring at 25 °C. Colourless crystals were formed from the transparent solution in a yield of 30% after 1 h reaction time.

**Spirocyclic titanodiphenylsiloxane**  $\text{TiO}_2[\text{O}_4\text{Si}_4(\text{C}_6\text{H}_5)_8]_2$  **B**. The synthesis was carried out according to the literature.<sup>17</sup> DPSD (10 g, 46.2 mmol) dissolved in 21 ml diethyl ether was mixed with 7.86 ml (22.96 mmol) of titanium tetra *n* butoxide at a molar ratio of 2:1. Colorless crystals were obtained after reflux of the solution for 30 min and stirring of 2 h. The crystals were recrystallised from toluene with a yield of 28%.

**Bicyclic titanodiphenylsiloxanes**  $[\text{Ti}(\text{acac})\text{O}_{1.5}]_2[\text{OSi}(\text{C}_6\text{H}_5)_2]_3 \cdot 2\text{C}_4\text{H}_8\text{O}$  **C** and  $[\text{Ti}(\text{acac})\text{O}_{1.5}]_2[\text{OSi}(\text{C}_6\text{H}_5)_2]_3 \cdot 3\text{C}_4\text{H}_8\text{O}_2$  **D**. DPSD (4 g, 18.52 mmol) dissolved in 7.41 ml tetrahydrofuran (THF) was mixed with 4.08 ml (13.86 mmol) of titanium tetraisopropoxide and 1.43 ml (13.89 mmol) of acetylacetonate in 2 ml of THF at the molar ratio of 1:0.75. Colourless crystals of **C** were formed from the solution after 2 h reaction time with a yield of 35%. The bicyclic titanodiphenylsiloxane **D** was synthesised with a yield of 25% by the same procedure but with dioxane as solvent.

**Cyclotetrameric titanodiphenylsiloxanes**  $[\text{Ti}(\text{acac})_2\text{O}]_2[\text{OSi}(\text{C}_6\text{H}_5)_2]_2$  **E** and  $[\text{Ti}(\text{acac})_2\text{O}][\text{OSi}(\text{C}_6\text{H}_5)_2]_3$  **F**. A solution of 1.36 ml (4.62 mmol) titanium tetraisopropoxide and 0.95 ml (9.23 mmol) acetylacetonate in 1 ml dioxane was aged for 1 h and then added to a solution of 1 g of (4.62 mmol) DPSD in 5.03 ml dioxane. Yellow crystals of **E** were formed from the transparent solution after 10 min with a yield of 90%. A solution of 1.38 g titanodiphenylsiloxane **C** in 5.1 ml THF was hydrolysed with water at the molar ratio  $\text{H}_2\text{O}/\text{Ti}=20$ . Crystals of **F** (0.22 g, yield=20%) were obtained after 24 h reaction time.

**Table 1** Crystal data of the X ray diffraction studies<sup>a</sup>

compound	C		D		E		F	
formula	C <sub>54</sub> H <sub>60</sub> O <sub>12</sub> Si <sub>3</sub> Ti <sub>2</sub>		C <sub>50</sub> H <sub>52</sub> O <sub>12</sub> Si <sub>3</sub> Ti <sub>2</sub> ·C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>		C <sub>44</sub> H <sub>48</sub> O <sub>12</sub> Si <sub>2</sub> Ti <sub>2</sub> ·C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>		C <sub>46</sub> H <sub>44</sub> O <sub>8</sub> Si <sub>3</sub> Ti	
crystal system	triclinic		monoclinic		triclinic		triclinic	
space group	P1		C2/c		P1		P1	
a/Å	13.927(3)		21.896(4)		8.96(2)		10.703(2)	
b/Å	20.158(4)		14.048(3)		11.46(2)		11.381(2)	
c/Å	20.319(4)		20.275(4)		13.38(3)		18.762(4)	
α/degrees	91.75(3)				86.0(2)		98.35(3)	
β/degrees	99.02(3)		95.94(3)		74.8(2)		90.12(3)	
γ/degrees	90.10(3)				70.7(2)		92.25(3)	
V/Å <sup>3</sup>	5631(2)		6203(2)		1251(5)		2259.4(8)	
Z	4		4		1		2	
D <sub>c</sub> /Mg m <sup>-3</sup>	1.275		1.286		1.340		1.260	
μ (MoKα)/mm <sup>-1</sup>	0.405		0.379		0.430		0.319	
diffractometer	Stoe IPDS		Stoe IPDS		Stoe AED2		Stoe IPDS	
temperature/K	293		293		293		293	
collected data	37322		24406		3271		22119	
unique reflections	13813		4711		3271		8195	
R <sub>merge</sub>	0.06		0.05				0.04	
observed reflections (I > 2σI)	10828		3682		2642		6649	
parameters	1279		327		291		523	
R <sub>1</sub>	0.072		0.066		0.0561		0.043	
wR <sub>2</sub>	0.1970		0.173		0.1506		0.125	
largest difference peak, hole/e Å <sup>-3</sup>	1.036,	0.536	0.803,	0.750	0.658,	0.259	0.274,	0.298

<sup>a</sup>The programs SHELXS and SHELXL were used to solve and refine the structures.<sup>29</sup>  $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ ,  $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)] \}^{1/2}$ .

<sup>17</sup>O labelled DPSD was used for the preparation of the <sup>17</sup>O doped tetraphenyldisiloxanediol<sup>18</sup> and <sup>17</sup>O labelled titanodi phenylsiloxanes,<sup>13</sup> as described above.

### X-Ray crystallographic analysis

Single crystals of compounds **C**, **D**, **E** and **F** were used for X ray diffraction studies with data being assembled in Table 1. Complete lists of atomic positional parameters, temperature factors, bond lengths, angles and  $F_o/F_c$  values have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich technische Information mbH, D 76344 Eggenstein Leopoldshafen (Germany) on quoting the depository numbers CSD 407304 (C), CSD 407305 (D), CSD 407306 (E) and CSD 407307 (F).†

### Hydrolysis

In a first series of experiments the titanodiphenylsiloxanes **A–D** were dissolved in tetrahydrofuran with molar Si concentration >0.5 mol l<sup>-1</sup> (0.05 mol l<sup>-1</sup> for compound **E**). A water THF solution was added at the molar ratios ( $H$ ) H<sub>2</sub>O:Ti=1 and 6 at 25 °C under vigorous stirring. The final Si concentration in the hydrolysates **A–D** amounts to 0.5 and in **E** to 0.048 mol l<sup>-1</sup>. In a second series of experiments the amount of water was related to the number of hydrolysable Si—O—Ti bonds. The molar ratio ( $K$ ) H<sub>2</sub>O:(Si—O—Ti) of 1:1 was used for the titanodiphenylsiloxanes **A–E**. The Ti concentration in the hydrolysates **A–D** was kept in the range 0.16–0.23 mol l<sup>-1</sup> and in the hydrolysate **E** at 0.048 mol l<sup>-1</sup>.

For comparison, the spirocyclic titanodisiloxane **B** was hydrolysed in a concentrated [ $c(\text{Ti})=0.16 \text{ mol l}^{-1}$ ] and dilute solution (0.023 mol l<sup>-1</sup>). The hydrolytic stability of compound **F**, a reaction product of the hydrolysis of the titanodiphenylsiloxanes **C** and **D**, was not examined in this work.

† Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/60.

### NMR measurements

<sup>29</sup>Si and <sup>17</sup>O NMR spectra were obtained using a liquid state spectrometer (Bruker AC 200) operating at a field of 4.7 T. <sup>29</sup>Si NMR: external reference: tetramethylsilane, internal standard: phenyltrimethylsilane, repetition time: 40 s, pulse angle: 63°, number of scans: 90–180. The dilute solutions of **B** and **E** [ $c(\text{Ti})=0.024$  and  $0.048 \text{ mol l}^{-1}$ , respectively] were recorded for 12 h. The time of hydrolysis specified results from the averaged time between the start and end of the NMR measurement. The quantitative data are obtained from the integrated signal intensities of the samples in comparison with the signal intensity of the internal phenyltrimethylsilane standard. <sup>17</sup>O NMR: the samples were enriched with <sup>17</sup>O, single pulse experiment, repetition time: 600 ms, pulse angle: 90°, reference H<sub>2</sub>O (1% <sup>17</sup>O), number of scans 4000–10000. The solid state <sup>29</sup>Si NMR spectra were recorded using a Bruker MSL 200 spectrometer at 4.7 T and the <sup>29</sup>Si{<sup>1</sup>H} inverse gated sequence. External standard: [(CH<sub>3</sub>)<sub>3</sub>Si]<sub>8</sub>Si<sub>8</sub>O<sub>20</sub> (Q<sub>8</sub>M<sub>8</sub>), MAS: 3 kHz, pulse angle 63°, repetition time: 60 s, 200–1000 scans.

### Time-of-flight (TOF) mass spectrometry and FTIR measurements

A TOF Kompact MALDI III equipped with N<sub>2</sub> laser (Shimadzu) was used for the determination of the molecular masses of the titanodiphenylsiloxanes. Conditions: positive reflectron mode, 20 kV acceleration voltage, Ag doped nicotin acid amide or nitrophenyl octyl ether as matrix and dioxane or THF as solvents.

The FTIR spectra were obtained using a Bruker IFS25 spectrometer. The KBr sample pellet was formed by mixing 200 mg KBr with 1 mg of the titanodiphenylsiloxane.

## Results and Discussion

### Structural analysis of the titanodiphenylsiloxanes

Six titanodiphenylsiloxanes (Fig. 1) were synthesised and characterised by X ray structural analysis and spectroscopic methods (NMR, molecular mass, IR). Five of them (**A–E**)

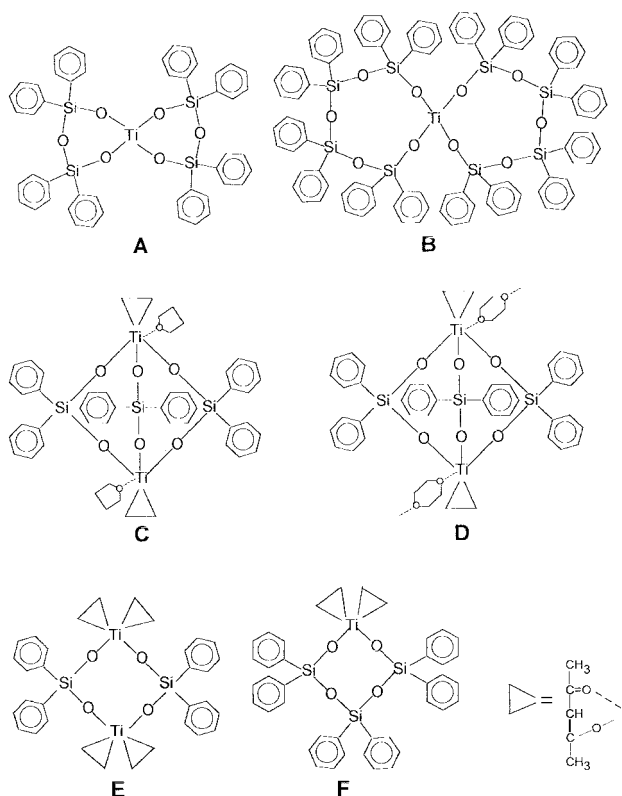


Fig. 1 Structural scheme of the titanodiphenylsiloxanes A-F

were used for the investigation of the hydrolytic stability of Si—O—Ti bonds in different structures. Titanodiphenylsiloxane A has been described by Andrianov *et al.*<sup>15,16</sup> in 1976 and was identified by its composition and its physicochemical properties as a spirocyclic compound (Fig. 1, A). The structure of the spirocyclic titanodiphenylsiloxane B was identified by means of X ray analysis.<sup>19</sup> The X ray structural analyses of the titanodiphenylsiloxanes C, D, E and F were carried out in this work. Fig. 2 shows the structures of C and E. Compounds C and D have a central eleven membered bicyclic  $Ti_2O_6Si_3$  cage as the central unit, and E and F have a simple eight membered  $Si_2O_4Ti_2$  and  $Si_3O_4Ti$  ring, respectively. The titanium atoms in all cases are hexa coordinated by oxygen atoms and the silicon atoms are in a distorted tetrahedral environment formed by oxygen atoms and two carbon atoms of the phenyl groups. In compounds C and D, one acetylacetonate group is bonded to the Ti atom in the usual

chelating form and tetrahydrofuran or dioxane molecules complete the coordination sphere. In the crystal structure of D, besides the dioxane molecule bonded to titanium and bridged to a neighbouring molecule, two other dioxane molecules are present in the crystal which have no bonds to Ti or Si and seem to serve as space filling molecules. The most pertinent bond lengths and angles of compounds C, D, E and F are listed in Table 2. The experimental values compare well with standard Si—O<sup>19</sup> and Ti—O<sup>20,21</sup> bond lengths. Similar —O—SiPh<sub>2</sub>—O—SiPh<sub>2</sub>—O— bridges have been recently described for aluminopolysiloxanes with geometrically analogous dimensions.<sup>22</sup>

### Spectroscopic characterisation of the titanodiphenylsiloxanes

Results of the <sup>29</sup>Si and <sup>17</sup>O NMR characterisation, molecular masses and elemental analyses of the crystalline titanodiphenylsiloxanes A-E are summarised in Table 3. Compound F, a reaction product of the hydrolysis of samples C and D, was not studied. Generally, the results of the elemental analysis of the compounds A-E and those of the determination of molecular masses by time of flight (TOF) measurements are in accordance with the crystal structures.

It is remarkable that the THF coordinated compound C shows the signal for the molecular mass of the basic structure ( $M + Na^+ = 959$ ) without the coordinating solvent in the TOF spectrum. Probably, the bonding of the solvent in the molecules is too weak for the identification of the actual molecular mass (1080) under TOF conditions. No TOF spectrum was obtained from the compound D using dioxane as solvent.

The <sup>29</sup>Si NMR spectra of THF solutions of the titanodiphenylsiloxanes A, C, D and E with always one type of chemically equivalent Si atoms show, in accordance with their structures, one signal with a chemical shift  $\delta$  in the region between 44 and 49 (Table 3). It should be noted that the <sup>29</sup>Si NMR spectra of the bicyclic compounds C and D dissolved in chloroform show no single signal near  $\delta$  47.6 but several signals in the range  $\delta$  45 to 48. This result indicates a degradation of the bicyclic structure in  $CHCl_3$ . Possibly, chloroform which is not suitable for coordination of Ti atoms, removes the coordinating dioxane or THF molecules from the titanodiphenylsiloxanes and because of this process the titanodiphenylsiloxanes lose their structural stability. The <sup>29</sup>Si hNMR spectra of the spirocyclic compound B dissolved in THF show two signals with chemical shifts  $\delta$  44.44 (—Si—O—Si—O—Ti—) and 46.06 (—Si—O—Si—O—Si—O—Ti—) and with comparable signal intensities corresponding to the two different types of Si atoms in its structure. On the basis of the results, signals of the Si atoms

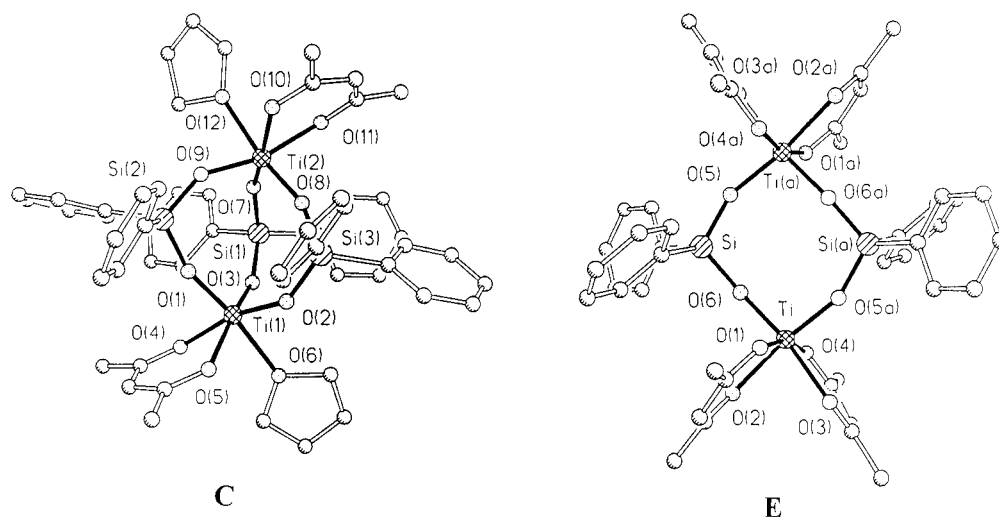


Fig. 2 Structures of the bicyclic (C) and cyclotetrameric (E) titanodiphenylsiloxanes

**Table 2** Selected bond lengths (Å) and angles (degrees) in compounds **C**, **D**, **E** and **F**. (The values for **C** were taken from both molecules present in the asymmetric unit cell)

<b>C</b>					
Ti O(Si)	1.787(3)	1.836(4)	O Si O	110.8(2)	113.5(2)
Ti O(acac)	2.048(4)	2.082(4)	O Ti O <sup>a</sup>	98.0(2)	100.7(2)
Ti O(THF)	2.205(4)	2.231(4)	Ti O Si <sup>a</sup>	141.6(2)	161.9(2)
Si O	1.616(4)	1.631(4)			
<b>D</b>					
Ti O(1)	2.049(3)		Si(2) O(3)	1.632(3)	
Ti O(2)	2.045(3)		Si(2) O(4 <sup>′</sup> )	1.617(3)	
Ti O(3)	1.796(3)		Si(1) C(6)	1.872(5)	
Ti O(4)	1.844(3)				
Ti O(5)	1.840(3)		O Ti O <sup>a</sup>	100.2(2)	101.0(2)
Ti O(6)	2.244(3)		O Si O	110.2(2)	113.2(2)
Si(1) O(5)	1.628(3)		Ti O Si <sup>a</sup>	144.3(2)	150.6(2)
<b>E</b>					
Ti O(1)	1.972(5)		O(5a) Ti O(4)	96.7(2)	
Ti O(2)	2.071(6)		O(6) Ti O(1)	95.6(2)	
Ti O(3)	2.078(6)		O(5a) Ti O(1)	95.1(2)	
Ti O(4)	1.958(5)		O(4) Ti O(1)	162.4(2)	
Ti O(5a)	1.821(5)		O(6) Ti O(2)	89.8(2)	
Ti O(6)	1.806(5)		O(5a) Ti O(2)	171.8(2)	
Si O(5)	1.620(5)		O(4) Ti O(2)	82.6(2)	
Si O(6)	1.624(5)		O(1) Ti O(2)	83.9(2)	
O(5) Si O(6)	111.6(3)		O(6) Ti O(3)	171.6(2)	
Si O(5) Ti(a)	154.9(2)		O(5a) Ti O(3)	90.0(2)	
Si O(6) Ti	156.4(2)		O(4) Ti O(3)	83.7(2)	
O(6) Ti O(5a)	98.4(2)		O(1) Ti O(3)	83.2(2)	
O(6) Ti O(4)	95.6(2)		O(2) Ti O(3)	81.8(2)	
<b>F</b>					
Ti O(1)	1.965(2)		Si(2) O(7)	1.631(2)	
Ti O(2)	2.072(2)		Si(3) O(5)	1.622(2)	
Ti O(3)	1.968(2)		Si(3) O(8)	1.630(2)	
Ti O(4)	2.054(2)		O(5) Ti O(6)	97.83(8)	
Ti O(5)	1.829(2)		O Si O	109.08(9)	111.40(9)
Ti O(6)	1.807(2)		Si(3) O(5) Ti	142.7(1)	
Si(1) O(7)	1.631(2)		Si(2) O(6) Ti	170.3(1)	
Si(1) O(8)	1.621(2)		Si(2) O(7) Si(1)	139.5(1)	
Si(2) O(6)	1.619(2)		Si(1) O(8) Si(3)	155.9(1)	

<sup>a</sup>Within the cage.**Table 3** Analytical results for the titanodiphenylsiloxanes **A E**

	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>	<b>E</b>
composition (mass%) <sup>d</sup>					
C	66.1 (62.9)	69.2 (68.4)	60.0 (59.4)	58.0 (57.9)	57.2 (57.5)
H	4.6 (4.9)	4.8 (4.9)	5.6 (5.6)	5.7 (5.8)	5.6 (5.7)
Si	12.8 (12.9)	13.5 (13.7)	7.8 (8.4)	7.0 (7.6)	5.6 (5.8)
Ti	5.5 (6.3)	2.9 (2.8)	8.9 (9.3)	8.0 (8.5)	9.5 (9.7)
molecular mass (TOF) <sup>d</sup>	873 (873)	1666 (1666)	1080 (936) <sup>a</sup>	no spectrum	920 (920)
<sup>29</sup> Si NMR (in THF), δ	45.53	44.44, 46.06	47.63	47.62	48.78
<sup>29</sup> Si NMR (solid state), δ	42.9, (sh) 43.3, 44.2, 45.2,	42.7, 43.0, 44.1, 44.5, 44.8, 45.5, 49.4	47.2, 47.5, 47.8, 48.1, 48.5	44.7, 46.0,	49.0
<sup>17</sup> O NMR, δ	64, 284, 662 (<15%) <sup>b</sup>	74 95, 293 <sup>c</sup>	319 <sup>b</sup>		353, 575 (<10%) <sup>c</sup>
IR (region 900 1000 cm <sup>-1</sup> )	931s, 993w	916s, 993w	932s	930s	933s, 985s

<sup>a</sup>Corresponds to removal of solvent. <sup>b</sup>In THF. <sup>c</sup>In CHCl<sub>3</sub>. <sup>d</sup>Theoretical values; values in parentheses are those found experimentally.

in  $-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Ti}-$  building units [ $\text{D}^2(1\text{Ti})$ ] of structures **A** and **B** show a low field shift and those in  $-\text{Ti}-\text{O}-\text{Si}-\text{O}-\text{Ti}$  units [ $\text{D}^2(2\text{Ti})$ ] of structures **C**, **D** and **E** a high field shift compared with  $\text{D}^2(2\text{Si})$  units ( $\delta$  47.04) of the octaphenyltetrasiloxanediol in THF.<sup>13</sup>

The solid state <sup>29</sup>Si NMR MAS spectra of the titanodiphenyl siloxane **E** show a narrow single signal at  $\delta$  49.0. The single signal corresponds to the one symmetrically independent Si atom as follows from the X ray analysis. The bicyclic compound **D** shows two signals at  $\delta$  44.7 and 46.0 in a 1:2 intensity ratio. This spectrum is in line with the crystal structure which shows two identical Si atoms in positions 1 and 2 and a different one in position 3. Two symmetrically independent molecules are present in the unit cell of the second bicyclic

compound **C** with THF as coordinating ligand. Six different Si atoms are to be found in the structure and lead to five signals in the solid state <sup>29</sup>Si NMR spectrum. One of the signals ( $\delta$  47.2) shows significantly higher intensity compared to the other signals which can be caused by an overlapping of two signals of similarly symmetric Si atoms. The assignment of the NMR signals of the spirocyclic compound **B** to the Si atoms in the structure is given in the literature.<sup>23</sup> Generally, a good agreement can be stated between the results of the X ray analysis and those of the solid state <sup>29</sup>Si NMR.

The <sup>17</sup>O NMR spectra of the <sup>17</sup>O labelled titanodiphenylsiloxanes **A**, **B**, **C** and **E** in THF or CHCl<sub>3</sub> solution show a signal of high intensity in the region between  $\delta$  284 and 353 which is attributed to the oxygen atoms in Si-O-Ti bridges according

to the literature.<sup>11,24</sup> An additional broad signal in the  $^{17}\text{O}$  NMR spectra of the samples **A** and **B** in the region  $\delta$  50–95 is caused by the oxygen atom in Si–O–Si bonds. The spectra of the compounds **A** and **E** show an additional signal with low intensity (<15%) at  $\delta$  662 (**A**) and  $\delta$  573 (**E**). The first signal derives from Ti–O–Ti bonds from small impurities of the samples, the second one is caused by the external  $(\text{CD}_3)_2\text{CO}$  lock.

The FTIR spectra of the titanodiphenylsiloxanes **A–E** all show absorptions in the region 900–1000  $\text{cm}^{-1}$  (Table 3). The bands around 930  $\text{cm}^{-1}$  are attributed to stretching vibrations of Si–O–Ti bonds according to the literature.<sup>16,25,26</sup>

### Hydrolysis of the titanodiphenylsiloxanes

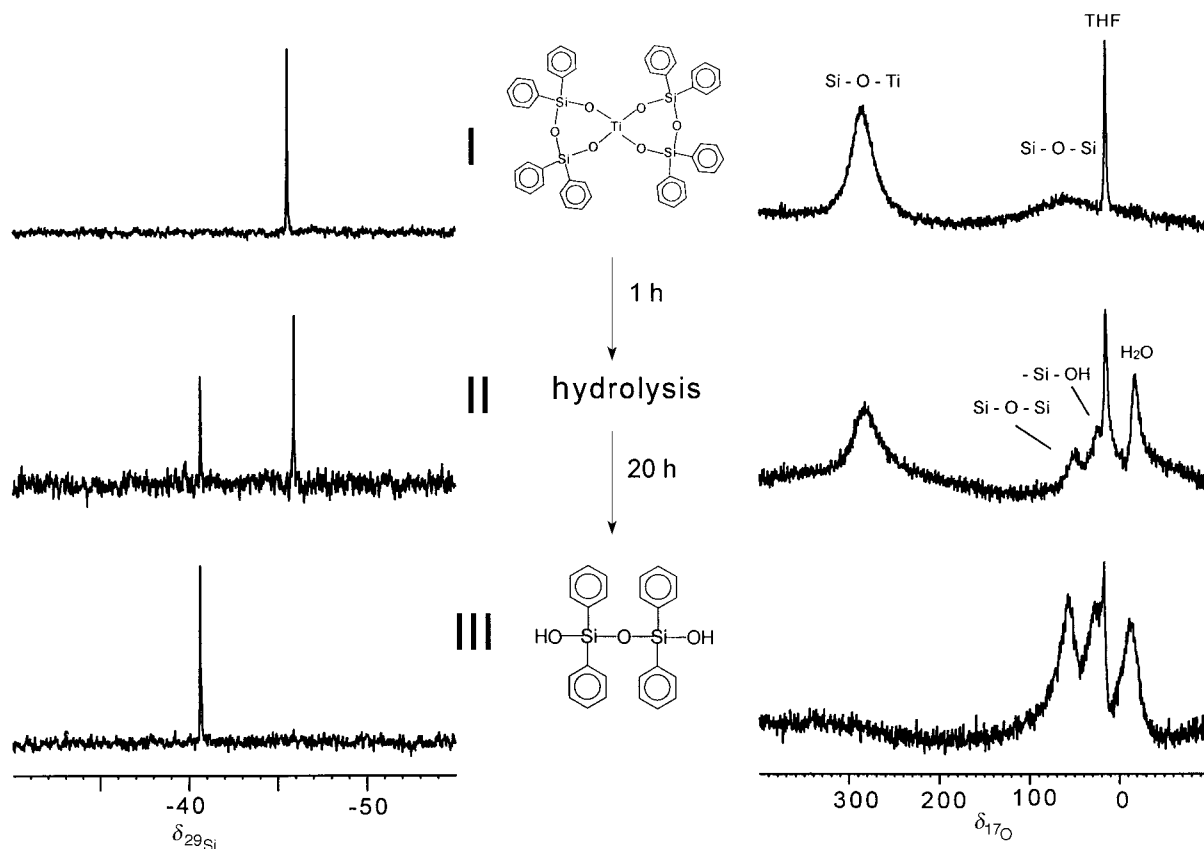
The titanodiphenylsiloxanes **A**, **B**, **C** and **D** show a high solubility in dioxane and tetrahydrofuran, whereas the cyclo-tetrameric titanodisiloxane **E** is only poorly soluble in these solvents. Nevertheless, for comparison all examinations of the hydrolytic stability of the Si–O–Ti bonds were performed in THF solutions of the samples. The conditions of hydrolysis are an important point for comparing the hydrolytic stability of different structures. Generally, the amount of water is related to the number of Si or Ti atoms in the samples. It is better for comparison of the hydrolytic stabilities to relate the amount of water to the number of Si–O–Ti bonds in the molecule. Therefore, two different series were used for the examination of the hydrolytic stability. The first series was performed with the defined molar ratio ( $H$ ) of water to titanium of 1:1 and 6:1 ( $H=1$  and 6) and a constant (0.5 and 0.048  $\text{mol l}^{-1}$ ) Si concentration and for comparison with previous results on indefinite heterometal structures.<sup>6,11,13</sup> In the second series a constant molar ratio ( $K$ ) water:(Si–O–Ti) bonds of 1:1 and Ti concentrations in the range 0.16–0.23  $\text{mol l}^{-1}$  for samples **A–D** and 0.048  $\text{mol l}^{-1}$  for **E** were used. The slightly different

Ti concentrations for samples **A–D** result from the chosen equal number of hydrolysable Si–O–Ti bonds per volume.

Fig. 3 shows the  $^{29}\text{Si}$  and  $^{17}\text{O}$  NMR spectra of the spirocyclic compound **A** in THF solution before and after hydrolysis at a molar ratio  $H=9$  as an example for the degradation of Si–O–Ti bonds by hydrolytic cleavage. The decrease in intensity of the signal at  $\delta$  284 in the  $^{17}\text{O}$  NMR spectra, attributed to oxygen in Si–O–Ti bonds, with increasing time of hydrolysis reveals the degradation of the Si–O–Ti bonds in the spirocyclic structure **A**. New signals in the region  $\delta$  0–80 are caused by oxygen atoms in Si–O–Si ( $\delta$  56) and SiOH(OR) ( $\delta$  27) groups.<sup>14</sup> With increasing time of hydrolysis the  $^{29}\text{Si}$  NMR spectrum shows a decrease in intensity of the signal of the spirocyclic compound and a new signal at  $\delta$  40.63 due to tetraphenyldisiloxanediol.<sup>13</sup> Complete degradation of the Si–O–Ti bonds in the spirocyclic compound **A** occurs (both  $^{17}\text{O}$  and  $^{29}\text{Si}$  NMR measurements) after 20 h of hydrolysis. The degradation product of the hydrolysis, tetraphenyldisiloxanediol containing the stable Si–O–Si bond, is a constituent of the spirocyclic structure **A**; the structure of the primary hydrolysis product appears to give information on the Si constituents of the titanodiphenylsiloxane structure. This assumption is supported by the identification of octaphenyl tetrasiloxanediol as a degradation product in the hydrolysate of the spirocyclic compound **B**.<sup>13</sup> Accordingly, the monomeric diphenylsilanediol was found as a degradation product in the hydrolysates of the compounds **C**, **D** and **E** by means of  $^{29}\text{Si}$  NMR spectroscopy.

In the following, the results of the  $^{29}\text{Si}$  NMR spectroscopic analyses of the hydrolysates and their dependence with time were used for the examination of the hydrolytic stability of the Si–O–Ti bonds in titanodiphenylsiloxanes.

**Hydrolysis at molar ratios  $H=1$  and 6.** The results of the  $^{29}\text{Si}$  NMR spectroscopic examination of the hydrolytic stability



**Fig. 3**  $^{29}\text{Si}$  and  $^{17}\text{O}$  NMR spectra of the spirocyclic titanodiphenylsiloxane **A** before (I), after 1 h (II) and 20 h (III) hydrolysis at  $H=9$ , (reproduced by permission of the Materials Research Society from ref. 14)

of the titanodiphenylsiloxanes **A** and **E** at  $H=1$  and 6 are summarised in Fig. 4 and 5. From Fig. 4, it can be seen that the cyclotetrameric titanodiphenylsiloxane **E** and the spirocyclic structures **A** and **B** show a high hydrolytic stability in the range of 90–100% of their Si–O–Ti bonds at  $H=1$  up to 1 d. The sample **E** also shows a high stability after 7 d, whereas 30–50% of the heterometal bonds were cleaved in the hydrolysates **A** and **B** after the same hydrolysis time. The much lower Si or Ti concentration in the hydrolysate of **E** in comparison to **A** and **B** influences its hydrolytic degradation but only to some extent. The bicyclic structures **C** and **D** are already decomposed at  $H=1$  by 50–60% after 0.5 h and to an extent of 90% after 7 d. As expected no significant difference in the stability of **C** and **D** is detected owing to the same basic structure of these molecules. A decreasing hydrolytic stability follows from the results in the order cyclotetramer (**E**) > spirocyclo (**A**, **B**) > bicyclo (**C**, **D**).

The spirocyclic compounds **A** and **B** and the cyclotetrameric structure **E** show a significant degradation of their structure with increasing hydrolysis time at a higher molar ratio of water to Ti ( $H=6$ ). About 20% of compounds **A** and **B** are already hydrolysed after 0.5 h and about 45–60% after 8 h hydrolysis time (Fig. 5). The bicyclic structures **C** and **D** are degraded to an extent of 90% after 0.5 h hydrolysis time at  $H=6$ . A decreased hydrolytic stability for all examined structures is seen upon increasing the ratio of water to Ti. The difference in the stability of the titanodiphenylsiloxane structures toward hydrolysis at  $H=6$  is nearly in the same order as at  $H=1$ : viz., cyclotetramer (**E**) > spirocyclo (**B**) > spirocyclo (**A**) > bicyclo (**C**, **D**).

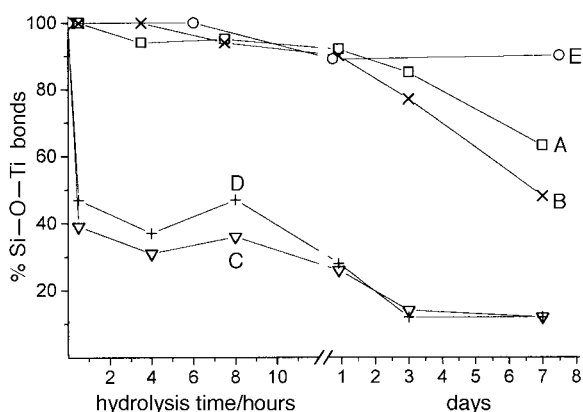


Fig. 4 Hydrolytic degradation of the Si–O–Ti bonds in the titanodiphenylsiloxanes **A**–**D** [ $c(\text{Si})=0.5 \text{ mol l}^{-1}$ ] and **E** [ $c(\text{Si})=0.048 \text{ mol l}^{-1}$ ] at  $H=1$  vs. time

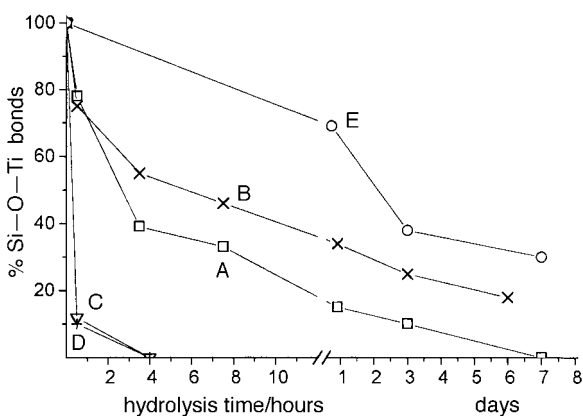


Fig. 5 Hydrolytic degradation of the Si–O–Ti bonds in the titanodiphenylsiloxanes **A**–**D** [ $c(\text{Si})=0.5 \text{ mol l}^{-1}$ ] and **E** [ $c(\text{Si})=0.048 \text{ mol l}^{-1}$ ] at  $H=6$  vs. time

**Hydrolysis at molar ratio  $K=1$ .** At  $K=1$  ( $\text{H}_2\text{O}:\text{Si}-\text{O}-\text{Ti}$  bond = 1)  $H$  values in the examined hydrolyses are as follows: **A** and **B**:  $H=4$ , **C** and **D**:  $H=3$ , **E**:  $H=2$ . Thus, an identical amount of water per Si–O–Ti bond in the molecules ( $K=1$ ) corresponds to different amounts of water per titanium atom. The results of the  $^{29}\text{Si}$  NMR spectroscopic examination of the hydrolytic stability at  $K=1$  are summarised in Fig. 6. The high hydrolytic stability of the cyclotetrameric structure **E** is again remarkable. The spirocyclic compounds **A** and **B** show a degradation of their structure of ca. 40% after 0.5 h. A larger discrepancy in their hydrolytic stabilities is observed with increasing hydrolysis time. The spirocyclic structure **A** containing six membered rings is more stable than **B** containing ten membered rings (4 h hydrolysis time). A similar degradation of ca. 90% is, however, found after longer hydrolysis times (3 d). The bicyclic structures **C** and **D** again show the highest degradation (60–70%) in the hydrolysates after 0.5 h. The degradation rates of the bicyclic structures are closer to that of the spirocyclic compound **B** after 4 h hydrolysis time. It can be seen from Fig. 6 that the titanodiphenylsiloxane structures **A**–**D** degrade to an extent of 85–90% after 3 d. Comparing the results of hydrolysis at  $H=1$  and 6 with those at  $K=1$  it follows that the order in the hydrolytic stability of the various structures is the same but more moderate at  $K=1$  when the amount of water is related to the number of Si–O–Ti bonds. Nevertheless, in all cases, significant differences in the hydrolytic stability can be detected which depends on the titanodiphenylsiloxane structure.

Besides the examination of the hydrolytic stabilities of the titanodiphenylsiloxanes at  $H=1$  and 6 the hydrolysates of bicyclic compounds **C** and **D** were also studied at the high molar ratio  $\text{H}_2\text{O}:\text{Ti}=20$ . Crystals appeared in low yield in the hydrolysates after a reaction time of 24 h. The crystals were identified by X ray structural analysis as the cyclotetrameric titanodiphenylsiloxane **F** with only one Ti atom in the ring which is complexed by two acac ligands (Table 1). The result reveals that in the hydrolysates a partial reorganisation of the bicyclic structures **C** or **D** occurs via monomeric diphenylsilanediol units to more stable cyclotetrameric structures. The establishment of structure **F** is only possible by a partial hydrolysis of the acac ligands at the Ti atoms<sup>27</sup> in structures **C** or **D** and the reaction of the released acac molecules with existing mono complexed Ti atoms in the hydrolysate. These results allow a first insight into the complicated reaction mechanism in hydrolysates of titanodiphenylsiloxanes.

Finally, the influence of the Si concentration in the hydrolysates on the degradation rate was examined comparing a dilute hydrolysate of sample **E** with the other samples. Fig. 7 shows the hydrolytic stability of the spirocyclic sample **B** measured

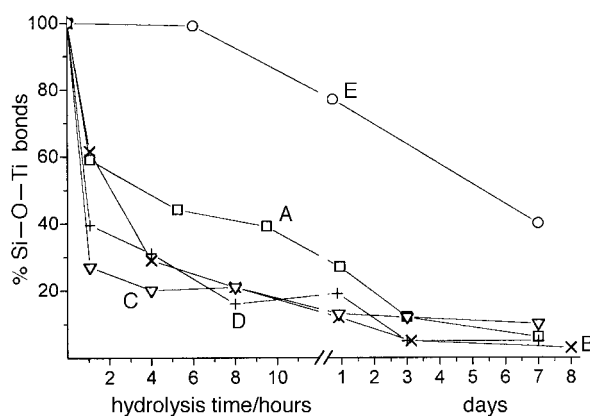


Fig. 6 Hydrolytic degradation of the Si–O–Ti bonds in the titanodiphenylsiloxanes **A** and **B** [ $c(\text{Ti})=0.16 \text{ mol l}^{-1}$ ], **C** and **D** ( $0.23 \text{ mol l}^{-1}$ ) and **E** ( $0.048 \text{ mol l}^{-1}$ ) at  $K=1$  vs. time

at  $c(\text{Ti})=0.024 \text{ mol l}^{-1}$  and those of the cyclotetrameric compound **E** [ $c(\text{Ti})=0.048 \text{ mol l}^{-1}$ ] at  $K=1$ . The different Ti concentrations result from the chosen equal number of Si—O—Ti bonds per volume. For comparison, the curve of compound **B** at  $c(\text{Ti})=0.16 \text{ mol l}^{-1}$  [ $c(\text{Si})=1.28 \text{ mol l}^{-1}$ ] is added in Fig. 7. The result shows that a decreased concentration of **B** in the hydrolysate leads to a slightly increased hydrolytic stability of the Si—O—Ti bonds. Nevertheless, the stability of **B** in both dilute and concentrated solutions is significantly lower than the stability of the cyclotetrameric compound **E**.

The examination of the effect of  $\text{H}^+$  concentration in the hydrolysate ( $1.1 \times 10^{-3} \text{ M HCl}$ ) on the hydrolytic stability of the Si—O—Ti bonds at  $K=1$  showed no experimentally significant differences compared with the hydrolysates obtained from water ( $\text{pH}=6.7$ ).

The reason for the high hydrolytic stability of the cyclotetrameric titanodiphenylsiloxane **E** could be the presence of the low strained eight membered ring *cf.* siloxanes.<sup>28</sup> Further reasons for the stability of **E** are the shielding of the Si and Ti atoms by the large phenyl and acac ligands which can reduce the contact of the water with the metal atoms as well as the stable six coordination of Ti atom by oxygen. The Ti atoms in the bicyclic structures **C** and **D** likewise show six coordination but this includes weak bonds to dioxane or tetrahydrofuran molecules. The weakness of these bonds in **C** and **D** is supported by the results of the time of flight experiments (no mass spectrum for **D**, basic mass spectrum of **C** without coordinating solvent) and the rapid degradation of structures **C** and **D** in  $\text{CHCl}_3$  solution owing to the easy removal of the stabilising dioxane or THF molecules. Exchange of the solvent molecules in **C** and **D** by water should be rapid followed by a

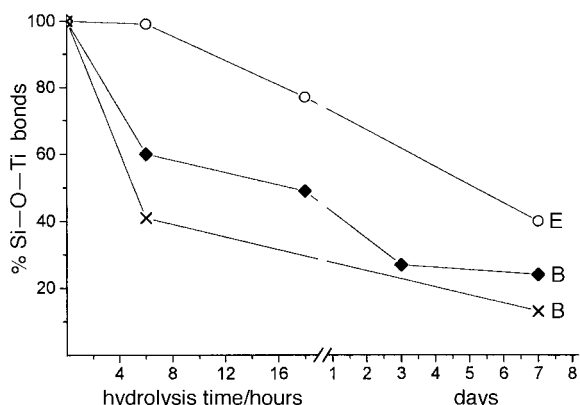


Fig. 7 Hydrolytic degradation of the Si—O—Ti bonds in the titanodiphenylsiloxanes **B** [ $c(\text{Ti})=0.024$  (◆) and  $0.16 \text{ mol l}^{-1}$  (×)] and **E** ( $0.048 \text{ mol l}^{-1}$ ; ○) at  $K=1$  vs. time

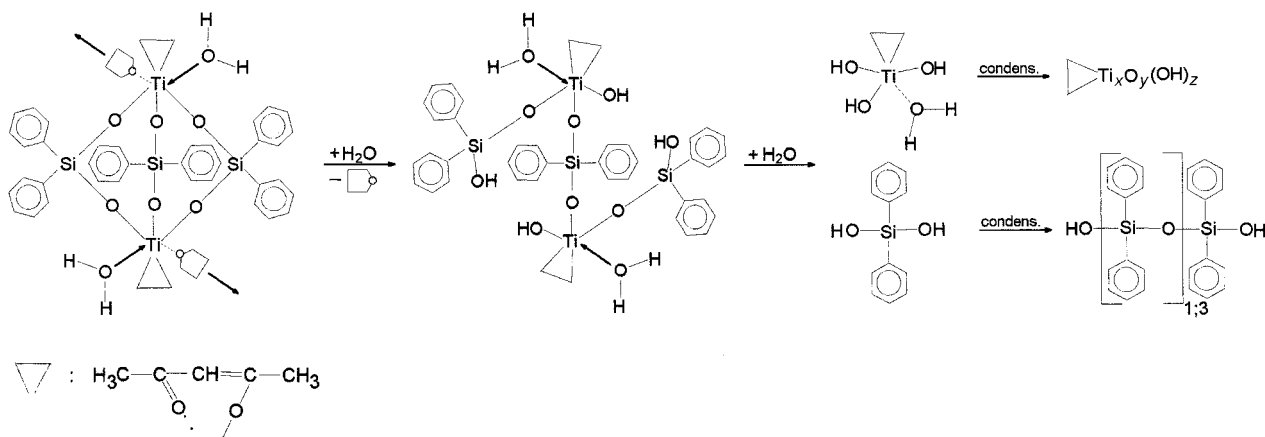


Fig. 8 Scheme of the hydrolysis reaction of the bicyclic titanodiphenylsiloxane **C**

quick hydrolytic attack on Si—O—Ti bonds according to the mechanism in Fig. 8. The released hydroxylated titanium species condense to higher molecular complexed titanium oxide hydroxides whereas the primarily formed diphenylsilanediol partially condenses under the catalytic influence of Ti species to tetraphenyldisiloxanediol and octaphenyltetrasiloxanediol.<sup>18</sup> Probably, the medium hydrolytic stability of the Si—O—Ti bonds in the spirocyclic structures **A** and **B** is primarily caused by the shielding effect of the directly neighbouring eight phenyl groups to the Ti atom and the induction effect of the phenyl groups on the Si atom which lowers the charge difference between the Si and Ti atoms and increases the hydrolytic stability of the oxygen bridged heterometal bond.

## Conclusions

The investigation of titanodiphenylsiloxanes with different structures by X ray structural analysis, NMR and IR spectroscopies and time of flight mass spectrometry results in a good correlation of the different experimental data. Furthermore, the results show that all examined titanodiphenylsiloxanes of different structures undergo hydrolytic degradation of their Si—O—Ti bonds. Relatively stable monomeric, dimeric or tetrameric siloxane structures are primary products of the hydrolysis which appear as building blocks in the original titanodiphenylsiloxane structures. The cyclotetrameric titanodiphenylsiloxane structure **E** shows the highest hydrolytic stability followed by the spirocyclic structures **A** and **B** and finally by the bicyclic structures **C** and **D**. The different shielding of the metal atoms, induction effects of the ligands and differences in the stability of the six fold Ti coordination by non complexing solvent molecules are assumed as reasons for the differences in the hydrolytic stability of the titanodiphenylsiloxanes. The results show that, generally, it cannot be said that all Si—O—Ti bonds are equally unstable towards hydrolysis, rather it depends on the structure of the titanodiphenylsiloxanes, the ligands and the hydrolytic conditions (*e.g.* amount of water, concentration of the sample). The results reveal that an integration of hydrolytically stable heterometal bonds in materials *via* the sol gel process with the aim of highly homogeneous structures requires detailed knowledge of the chemical compositions, the structure of the building units and the hydrolytic stability of the species. Thus, the results of this work can contribute to a better understanding of the problems concerning the homogeneity of sol gel derived materials on a molecular scale.

The authors gratefully acknowledge Ms S. Carstensen and Ms S. Korte for experimental and organisational work, Dr P. Toledano (Chimie de la Matière Condensée, Université P. et M. Curie, Paris) for support in X ray crystallographic analysis, Dr R. P. Krüger (Institut für Angewandte Chemie,

Berlin) for time of flight measurements and Dipl. Chem. T. Reinert for his help in NMR measurements.

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