

# Cobalt(II) and iron(II) tris(trimethylsilyl)siloxides: synthesis, structure and reactivity

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## Abstract

A series of cobalt(II) and iron(II) siloxide complexes,  $[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{M}(\text{L}_n)$  ( $\text{M} = \text{Co}$ ,  $\text{L}_n = \text{none}$  (**1**), (THF) (**3**), (THF)<sub>2</sub> (**4**), (DME) (**5**), (MeCN)<sub>2</sub> (**6**), (PhCN)<sub>2</sub> (**7**), (2,2'-dipyridyl) (**8**), 4,4'-dipyridyl (**9**), (Ph<sub>3</sub>P)<sub>2</sub> (**10**);  $\text{M} = \text{Fe}$ ,  $\text{L}_n = \text{none}$  (**2**), (2,2'-dipyridyl) (**11**)) were prepared by the reaction of metal silylamides  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{M}$  ( $\text{M} = \text{Co}$ , Fe) with tris(trimethylsilyl)silanol. The crystal structures of compounds **1** and **11** have been determined by the X-ray diffraction method. Complex **1** has a dimeric structure with two  $[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}$  units bonded via the two  $\mu_2\text{-O}$  atoms. The central  $[\text{Co}(\mu_2\text{-O})]_2$  cycle has a 'butterfly shape' being bent along the bridging oxygen atoms. The dihedral angle between the Co(1)O(4)Co(2) and Co(1)O(3)Co(2) planes is 143.1°. The  $\mu_2$ -bridging and terminal Co–O distances are 1.945(7)–1.963(7) and 1.781(8), 1.793(7) Å, respectively. The Co...Co distance in **1** is relatively short, 2.735(2) Å. However, the high value of magnetic moment (6.0  $\mu_B$ ) of compound **1** indicates the absence of a direct interaction between the Co atoms in **1**. The molecule of **11** is monomeric. The Fe atom is bonded to 2,2'-dipyridyl and two terminal OSi(SiMe<sub>3</sub>)<sub>3</sub> groups and has a distorted tetrahedral environment. The Fe–N(1), Fe–N(2) and Fe–O(1), Fe–O(2) distances in **11** are 2.148(1), 2.164(1) and 1.863(1), 1.900(1) Å, respectively. Addition of one equivalent of PhC≡CH to **7** results in the substitution of one tris(trimethylsilyl)siloxy-group with the formation of the diamagnetic dimer  $\{(\text{PhCN})(\text{PhC}_2)\text{CoOSi}(\text{SiMe}_3)_3\}_2$ . Subsequent addition of PhC<sub>2</sub>H causes its oligomerisation. Complexes **1**, **3** and **10** absorb carbon monoxide at ambient temperature and pressure while the others remain unreactive. Electronic spectra show fluxional behavior of complexes **1**, **3** and **4** in solution. © 2002 Published by Elsevier Science B.V.

**Keywords:** Transition metals; Siloxides; Polysilanes; X-ray diffraction

## 1. Introduction

The chemistry of low-valent transition metal complexes is of great interest in having to do with the catalytic transformations and activation of small molecules. Transition metal bulky siloxides occupy a specific place among other oxy-derivatives, because they are the models of catalytic centers in the widely used zeolites. Siloxides containing a system of Si–Si bonds and possessing strong donor properties are a

novel and intriguing class of organometallic compounds. Their stability, synthetic ways and reactivity depend on various factors such as the redox potential and oxidation state of the metal atom, reducing properties of the polysilyl substituent, polarity of the M–O bond, and the enthalpy of rearrangement  $\text{Si–Si–O–M} \rightarrow \text{Si–O–Si–M}$ .

As a part of our continuing study of low-coordinate transition metal siloxides this report describes the preparation and characterization of the homoleptic cobalt(II) and iron(II) tris(trimethylsilyl)siloxides, Lewis-base derivatives of these compounds as well as their thermal rearrangements and reactivity.

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## 2. Results and discussion

### 2.1. Synthesis

The homoleptic cobalt(II) and iron(II) tris(trimethylsilyl)siloxides were synthesized by silanolysis of the corresponding bis(trimethylsilyl)amides:

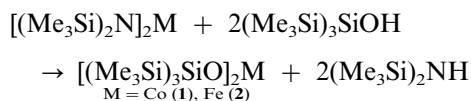
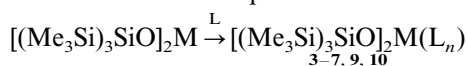


Table 1  
Crystal data and structure refinement parameters for compounds **1** and **11**

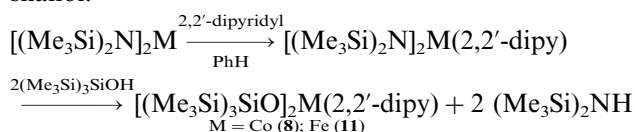
	<b>1</b>	<b>11</b>
Diffractometer	Siemens P3/PC	Smart
Empirical formula	C <sub>36</sub> H <sub>108</sub> Co <sub>2</sub> O <sub>4</sub> Si <sub>16</sub>	C <sub>28</sub> H <sub>62</sub> FeN <sub>2</sub> O <sub>2</sub> Si <sub>8</sub>
Formula weight	1172.52	739.37
Temperature (K)	213(2)	100(2)
Wavelength (Å)	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Monoclinic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	P2 <sub>1</sub> /n
Unit cell dimensions		
<i>a</i> (Å)	14.017(10)	13.2394(4)
<i>b</i> (Å)	22.73(2)	24.3198(7)
<i>c</i> (Å)	22.746(11)	13.7720(5)
$\alpha$ (°)	90	90
$\beta$ (°)	90	93.18(2)
$\gamma$ (°)	90	90
<i>V</i> (Å <sup>3</sup> )	7247(8)	4427.5(2)
<i>Z</i>	4	4
<i>D</i> <sub>calc</sub> (mg m <sup>-3</sup> )	1.075	1.109
Absorption coefficient (mm <sup>-1</sup> )	0.750	0.581
<i>F</i> (000)	2536	1592
Crystal size (mm)	0.7 × 0.5 × 0.3	0.5 × 0.5 × 0.4
Theta range for data collection (°)	1.27–23.05	1.67–30.99
Index ranges	–15 < <i>h</i> < 15, 0 < <i>k</i> < 2, 5–22 < <i>l</i> < 25	–14 < <i>h</i> < 18, –29 < <i>k</i> < 33, –16 < <i>l</i> < 18
Reflections collected	5867	35 499
Independent reflections	5602	12 691
Reflections observed [ <i>I</i> > 2σ( <i>I</i> )]	3492	9842
Data/restraints/parameters	5602/0/524	12691/0/618
Absolute structure parameter	0.38(4)	–
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.093	1.022
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0855, <i>wR</i> <sub>2</sub> = 0.1681	<i>R</i> <sub>1</sub> = 0.0366, <i>wR</i> <sub>2</sub> = 0.0927
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1539, <i>wR</i> <sub>2</sub> = 0.1995	<i>R</i> <sub>1</sub> = 0.0529, <i>wR</i> <sub>2</sub> = 0.1035
Largest difference peak and hole (e Å <sup>-3</sup> )	0.663 and –0.514	1.057 and –0.410

The reactions proceed in hexane for 10 h at ambient temperature affording crystalline products after solvent removal. Complexes **3–7**, **9**, **10** were prepared by the treatment of homoleptic **1** with Lewis bases:



M = Co, (L<sub>*n*</sub>) = THF (**3**), (THF)<sub>2</sub> (**4**), DME (**5**), MeCN (**6**), PhCN (**7**), 4,4'-dipy (**9**), (Ph<sub>3</sub>P)<sub>2</sub> (**10**).

2,2'-Dipyridyl complexes of cobalt (**8**) and iron (**11**) were synthesized by the workup of the corresponding dipyridyl silylamide complexes with tris(trimethylsilyl)silanol:

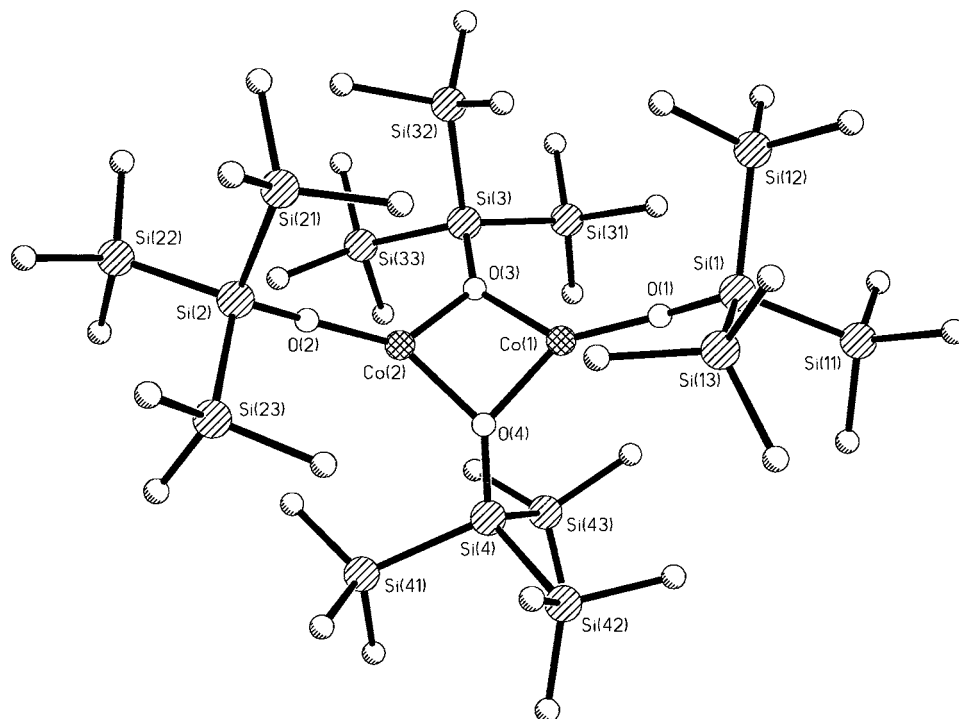


Homoleptic compounds **1** and **2** crystallize well from hexane solution. Oxygen-donor molecules (THF, DME) form complexes **3–5** that represent oil (**4**) or solids of poor crystallinity, apparently owing to the considerable lability of their coordination bond with the metal atom. Indeed, simple pumping of the THF solution of **4** in vacuo at 20 °C affords violet oil that corresponds to the complex, containing two THF ligands. Further prolonged pumping of **4** in vacuo for 5 h affords a green solid **3**. IR-spectra of **3** shows new absorption (Si–O–Co) at 935 cm<sup>-1</sup> instead of 955 cm<sup>-1</sup> (**4**) and still shows absorption at 1020 cm<sup>-1</sup>, but of less intensity. Note that the analogous cobalt(II) triphenylsiloxide, containing one THF molecule, [Co(OSiPh<sub>3</sub>)<sub>2</sub>(THF)]<sub>2</sub>, has a dimeric structure in the solid state [1]. Dipyridyl ligands are favorable toward the separation of complexes **8**, **9**, and **11** in the crystalline form. [(Me<sub>3</sub>Si)<sub>3</sub>SiO]<sub>2</sub>Co moieties form very stable fine crystalline coordination polymer (**9**) with 4,4'-dipyridyl. Its solubility is very poor in comparison with derivatives of 2,2'-dipyridyl.

### 2.2. Structures

The structure of complexes **1** and **11** has been determined by the X-ray diffraction method. (Although the full X-ray experiment for complex **2** has not been carried out, it was found that the unit cell parameters of **1** and **2** are close to each other, i.e. the crystals of **1** and **2** are isostructural). The crystal data and some details on data collection and refinement for **1** and **11** are given in Table 1.

As expected [2], complex **1** has a dimeric structure with the two [(Me<sub>3</sub>Si)<sub>3</sub>SiO]<sub>2</sub>Co units bonded via the two μ<sub>2</sub>-O atoms (Fig. 1). The central [Co(μ<sub>2</sub>-O)]<sub>2</sub> cycle has a 'butterfly shape' being bent along the bridging oxygen atoms. The dihedral angle between the Co(1)O(4)Co(2) and Co(1)O(3)Co(2) planes is 143.1°. A similar angle between the two average O<sub>3</sub>Co(1) and O<sub>3</sub>Co(2) planes is 144.2°. Each Co atom has a slightly distorted planar-

Fig. 1. X-ray structure of **1**.

trigonal environment. The sums of these angles (358.0 and 357.8° at the Co(1) and Co(2) atoms, respectively) are close to 360°. At the same time Co(1)–O(3)–Co(2) and Co(1)–O(4)–Co(2) angles are orthogonal, being 89.4(3) and 88.5(3)°, respectively (Table 2). The Co(1)–O(3) and Co(2)–O(3) distances (1.945(7) and 1.945(8) Å) in one  $\mu_2$ -bridge are slightly shorter than the Co(1)–O(4) and Co(2)–O(4) distances (1.963(7) and 1.957(7) Å) in the other. All bridging Co–O distances are significantly longer than the terminal Co–O distances (1.793(7) Å and 1.781(8) Å for Co(1)–O(1) and Co(2)–O(2) bonds, respectively).

There are very few X-ray structurally characterized low-coordinate Co(II) complexes. The bridging Co–O distances found in **1** are very close in the lengths of similar bonds in  $\{[\text{Co}(\text{OCPh}_3)_2]_2(n\text{-C}_6\text{H}_{14})\}$  with a planar-trigonal environment at the Co atom (1.964–1.982 Å); in  $\{\text{Co}[\text{OC}(\text{C}_6\text{H}_{11})_3]_2 \cdot \text{CH}_3\text{OH} \cdot 1/2\text{C}_6\text{H}_{12} \cdot \text{THF}\}$  (1.951–1.966 Å) and slightly more than those in the THF-adduct  $[\text{Co}(\text{OSiPh}_3)_2(\text{THF})_2]$  with a distorted tetrahedral coordination of the Co atom (1.977–1.991 Å) [1].

The Co–O–Si angles in the terminal  $(\text{Me}_3\text{Si})_3\text{SiO}$  groups in **1** (159.4(5) and 160.9(5)°) are large due to the non-bonded repulsion and close to those in  $[\text{Co}(\text{OSiPh}_3)_2(\text{THF})_2]$  (161.3 and 170.7°).

The Co(1)⋯Co(2) distance in **1**, 2.735(2) Å, is noticeably shorter than in the above-mentioned compounds  $[\text{Co}(\text{OCPh}_3)_2]_2 \cdot (n\text{-C}_6\text{H}_{14})$  2.910 Å,  $\text{Co}[\text{OC}(\text{C}_6\text{H}_{11})_3]_2 \cdot \text{CH}_3\text{OH} \cdot 1/2\text{C}_6\text{H}_{12} \cdot \text{THF}$  2.904 Å, and  $[\text{Co}(\text{OSiPh}_3)_2$

$(\text{THF})_2]$  2.916 Å. However, the high value of the magnetic moment (6.0  $\mu_B$ ) testifies against the existence of the Co–Co bond in **1**. Both cobalt atoms in **1** seem to be independent paramagnetic centers. Further, it may be assumed that d-electrons of both cobalt atoms have parallel spins. High possibility of ferromagnetic coupling of transition metal atoms in dimers  $\text{R}_3\text{SiO}-\text{M}(\mu\text{-OSiR}_3)_2\text{M}-\text{OSiR}_3$  was predicted by the density functional Hartree–Fock theory in Ref. [3].

In contrast to the homoleptic complexes **1** and **2**, complex **11** (Fig. 2) with an additional coordinated ligand has a monomeric structure with the pseudotetrahedral cobalt atom surrounded by a single 2,2'-dipyridyl molecule and two  $(\text{Me}_3\text{Si})_3\text{SiO}$  ligands. 2,2'-Dipyridyl molecule is planar within 0.055 Å. The O(1) and O(2) atoms are below and above the average plane of 2,2'-dipyridyl molecule. The O–Fe–O angle, 137.14(5)°, is significantly more than the ideal tetrahedral angle 109.47°. The Fe–O and Fe–N distances in **11** are 2.148(1), 2.164(1) and 1.863(1), 1.900(1) Å. Selected bond distances and angles for **11** are given in Table 3.

### 2.3. IR and electronic spectra

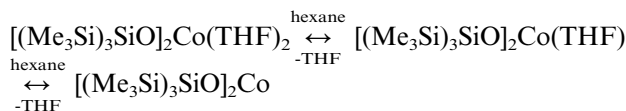
Selected IR spectral data of complexes **1–11** are given in Table 4. Generally,  $\nu(\text{M}-\text{O}-\text{Si})$  stretching frequencies are in the 900–1000  $\text{cm}^{-1}$  range. These bands disappear when the sample of the complex is maintained in open air for several minutes owing to hydrolysis. All compounds contain strong  $\nu(\text{Si}-\text{Me})$

Table 2  
Selected bond lengths (Å) and bond angles (°) for **1**

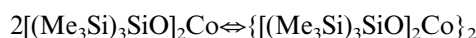
<i>Bond lengths</i>	
Co(1)–O(1)	1.793(7)
Co(1)–O(3)	1.945(7)
Co(1)–O(4)	1.963(7)
Co(1)···Co(2)	2.735(2)
Co(2)–O(2)	1.781(8)
Co(2)–O(3)	1.945(8)
Co(2)–O(4)	1.957(7)
O(1)–Si(1)	1.644(8)
O(2)–Si(2)	1.641(8)
O(3)–Si(3)	1.703(8)
O(4)–Si(4)	1.686(7)
Si(1)–Si(12)	2.363(6)
Si(1)–Si(11)	2.368(5)
Si(1)–Si(13)	2.375(5)
Si(2)–Si(23)	2.310(7)
Si(2)–Si(22)	2.326(6)
Si(2)–Si(21)	2.399(8)
Si(3)–Si(32)	2.339(7)
Si(3)–Si(31)	2.357(6)
Si(3)–Si(33)	2.404(6)
Si(4)–Si(42)	2.356(6)
Si(4)–Si(43)	2.361(6)
Si(4)–Si(41)	2.391(7)
<i>Bond angles</i>	
O(1)–Co(1)–O(3)	137.4(3)
O(1)–Co(1)–O(4)	135.5(3)
O(3)–Co(1)–O(4)	85.1(3)
O(2)–Co(2)–O(3)	134.6(4)
O(2)–Co(2)–O(4)	137.9(3)
O(3)–Co(2)–O(4)	85.3(3)
Si(1)–O(1)–Co(1)	159.4(5)
Si(2)–O(2)–Co(2)	160.9(5)
Si(3)–O(3)–Co(2)	133.3(4)
Si(3)–O(3)–Co(1)	137.3(5)
Co(2)–O(3)–Co(1)	89.4(3)
Si(4)–O(4)–Co(2)	132.5(4)
Si(4)–O(4)–Co(1)	127.7(4)
Co(2)–O(4)–Co(1)	88.5(3)
O(1)–Si(1)–Si(12)	112.6(3)
O(1)–Si(1)–Si(11)	110.2(3)
O(1)–Si(1)–Si(13)	110.6(3)
Si(12)–Si(1)–Si(11)	107.6(2)
Si(12)–Si(1)–Si(13)	105.3(2)
Si(11)–Si(1)–Si(13)	110.3(2)
O(2)–Si(2)–Si(23)	109.1(4)
O(2)–Si(2)–Si(22)	110.8(4)
O(2)–Si(2)–Si(21)	111.7(4)
Si(23)–Si(2)–Si(22)	111.6(4)
Si(23)–Si(2)–Si(21)	105.1(4)
Si(22)–Si(2)–Si(21)	108.2(4)
O(3)–Si(3)–Si(32)	106.4(4)
O(3)–Si(3)–Si(31)	111.6(3)
O(3)–Si(3)–Si(33)	113.6(4)
Si(32)–Si(3)–Si(31)	109.9(3)
Si(32)–Si(3)–Si(33)	109.1(2)
Si(31)–Si(3)–Si(33)	106.2(2)
O(4)–Si(4)–Si(42)	112.2(3)
O(4)–Si(4)–Si(43)	107.2(3)
O(4)–Si(4)–Si(41)	112.5(3)
Si(42)–Si(4)–Si(43)	110.1(2)
Si(42)–Si(4)–Si(41)	108.0(2)
Si(43)–Si(4)–Si(41)	106.7(3)

absorption (1240, 840 cm<sup>−1</sup>) that has a fixed position. Complexes **3–5**, containing THF or DME ligands show the  $\nu(\text{C–O})$  band at 1020 cm<sup>−1</sup> shifted by 60 cm<sup>−1</sup> relatively to those specific for the free ligand (1080 cm<sup>−1</sup>). Poor soluble 4,4'-dipyridyl complex **9** contains the band 1590 cm<sup>−1</sup> shifted by 15 cm<sup>−1</sup> relatively to those specific for the free 4,4'-dipyridyl ligand (1575 cm<sup>−1</sup>). It should be noted that the analogous changes in IR spectra were observed for coordinate polymers of transition metals bearing bridged 4,4'-dipyridyl ligands [**4**] in contrast to monomer complexes, R<sub>n</sub>M(4,4'-dipy)<sub>2</sub>, where dipyrindyl bands are not shifted and remain of the same intensity as those that are inherent to the free base.

The electronic spectral measurements of some cobalt complexes were made in order to understand their behavior in solution. Homoleptic complex **1** shows three d–d absorptions in hexane solution (Table 5). The lowest energy transition, 685 nm is of the highest intensity. Bis(THF)-adduct (**4**) has quite a different spectrum of low intensity in THF-solution, however, being dissolved in hexane, the color of the solution turned greenish-violet and the spectrum became more similar to homoleptic **1**. The solution of mono THF-adduct (**3**) in hexane has an electronic spectrum identical to **1**. Therefore, this indicates the loss of two THF molecules according to the following equation:



Moreover, we also observed a concentration-dependent shift of the two bands in the electronic spectrum of homoleptic complex **1**. This may be due to the existence of equilibrium between the monomeric and dimeric forms of **1** in solution.



In a week's time, the splitting in the spectra of compounds **1–3** disappears while the overall intensity is enhanced. This corresponds to the slow decomposition of compounds **1–3** in solution. The benzonitrilic complex **7** shows a more intensive highest energy transition than **1–3**. Its stability in hexane solution is approximately three times higher than those found for compounds **1–3**.

Triphenylphosphine ligands possess a more appreciable stabilization effect; the solutions of complex **10** are stable for an unlimited period and the crystals possess optical dichroism.

#### 2.4. Reactivity

All complexes are air and moisture sensitive. Hydrolysis of complexes prepared under an inert atmosphere yields metal(II) hydroxide and tris(trimethylsilyl)silanol. Homoleptic iron(II) compound is inflammable in open

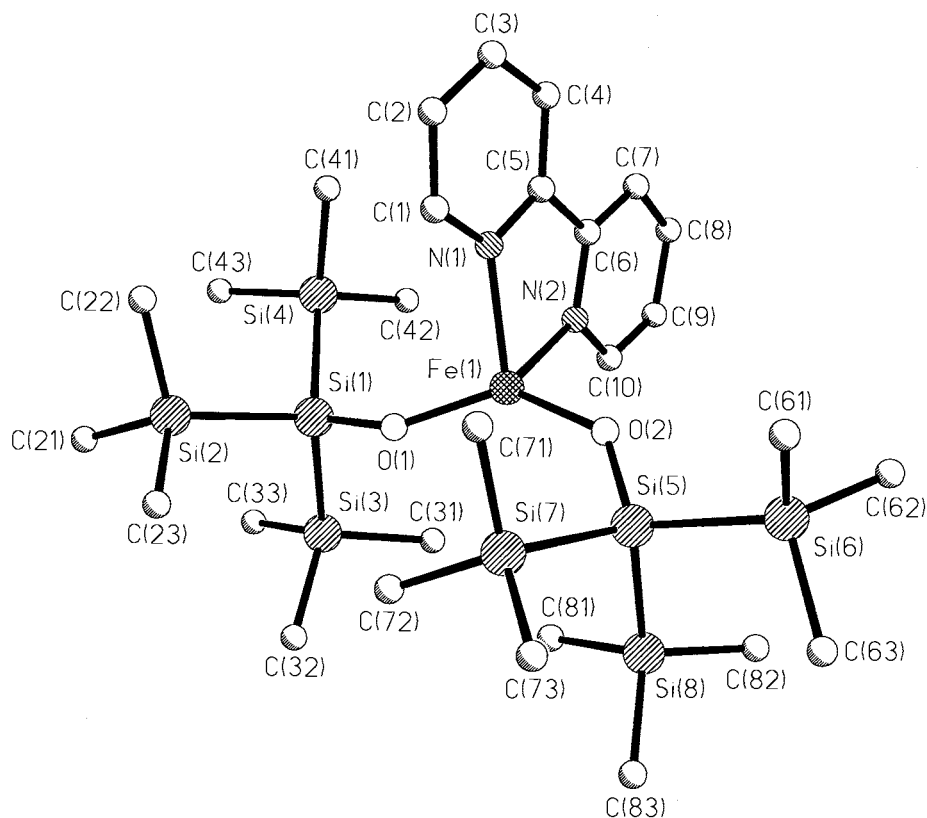


Fig. 2. X-ray structure of **11**.

air in the powder state while tris(trimethylsilyl)silanol is partially oxidized in a period of several weeks [5].

#### 2.4.1. Oxygen activation

We have studied the oxidation of **1** and **2** in various ( $O_2$ -complex) ratios. The addition of 0.9 mol  $O_2$  per 1 mol of **2** in benzene solution yields the mixture that gives a set of silanols after hydrolysis (Table 6). Nearly 50% of tris(trimethylsilyl)silanol was recovered. At the same time, the major product was the twice oxidized silanol,  $(Me_3SiO)_2(Me_3Si)SiOH$ , while it should have been  $(Me_3SiO)_2(Me_3Si)SiOH$  statistically. In our earlier investigations, we found that one  $Me_3SiO$ -substituent at the Si-Si bond increases the rate of its electrophilic oxidation in comparison with the unsubstituted disilane. However, the presence of two  $Me_3SiO$ -groups at the same silicon atom causes an opposite effect [6]. The molar ratio of the products observed coincides well with this rule. Moreover, it was noticed that the process of Si-Si bond oxidation is accompanied with the oxidation of iron. Therefore, 36% of iron was turned to the three-valent state. When 1.25 mol of oxygen was added, all Fe(II) turned to Fe(III), the process of catalytic oxidation stopped and the following reaction with oxygen proceeded very slowly, over weeks. The tentative scheme of oxidation may be depicted as a sequence of

parallel processes (Scheme 1). In the case of the cobalt complex (**1**), all the oxygen is consumed for the oxidation of Si-Si bonds. Compounds of three-valent cobalt were not detected during the process of oxidation. Therefore, cobalt shows a better oxygen activation effect than iron.

#### 2.4.2. Reactions with carbonyl compounds

Iron tris(trimethylsilyl)siloxide reacts readily with acetone to give  $(Me_3Si)_3SiOH$ , mesityl oxide and iron(II) oxide. Formation of these products apparently proceeds via bis-ketolate complexes, according to Scheme 2 proposed earlier for zinc alkoxide complexes [7].

#### 2.4.3. Interaction with CO

We found that cobalt tris(trimethylsilyl)siloxides **1** and **3** in toluene solution absorb ca. 2 mol of carbon monoxide per cobalt atom at ambient conditions to form a dark brown solution. After concentrating the solution and cooling at 0 °C dark brown thermally unstable crystals were formed. The IR spectrum of the new complex contains strong absorptions at 840 and 1240  $cm^{-1}$  corresponding to Si-Me fragments and a number of carbonyl bands (2040, 2030, 2000 and 1870  $cm^{-1}$ ) that may be assigned to the cobalt carbonyl

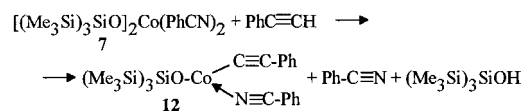
Table 3  
Selected bond lengths (Å) and bond angles (°) for **11**

<i>Bond lengths</i>	
Fe(1)–O(1)	1.8626(10)
Fe(1)–O(2)	1.8997(10)
Fe(1)–N(1)	2.1477(12)
Fe(1)–N(2)	2.1644(13)
O(1)–Si(1)	1.6316(11)
O(2)–Si(5)	1.6453(11)
Si(1)–Si(2)	2.3660(6)
Si(1)–Si(3)	2.3659(6)
Si(1)–Si(4)	2.3794(6)
Si(2)–C(23)	1.883(2)
Si(2)–C(21)	1.887(2)
Si(2)–C(22)	1.890(2)
Si(3)–C(31)	1.885(2)
Si(3)–C(32)	1.885(2)
Si(3)–C(33)	1.889(2)
Si(4)–C(42)	1.884(2)
Si(4)–C(41)	1.885(2)
Si(4)–C(43)	1.895(2)
Si(5)–Si(8)	2.3602(6)
Si(5)–Si(7)	2.3627(6)
Si(5)–Si(6)	2.3825(6)
Si(6)–C(62)	1.880(2)
Si(6)–C(63)	1.881(2)
Si(6)–C(61)	1.881(3)
Si(7)–C(73)	1.879(2)
Si(7)–C(72)	1.884(2)
Si(7)–C(71)	1.894(2)
Si(8)–C(83)	1.883(2)
Si(8)–C(81)	1.883(2)
Si(8)–C(82)	1.891(2)
N(1)–C(1)	1.345(2)
N(1)–C(5)	1.357(2)
N(2)–C(10)	1.345(2)
N(2)–C(6)	1.359(2)
C(1)–C(2)	1.392(2)
C(2)–C(3)	1.390(2)
C(3)–C(4)	1.392(2)
C(4)–C(5)	1.397(2)
C(5)–C(6)	1.489(2)
C(6)–C(7)	1.395(2)
C(7)–C(8)	1.396(2)
C(8)–C(9)	1.385(2)
C(9)–C(10)	1.388(2)
<i>Bond angles</i>	
O(1)–Fe(1)–O(2)	137.14(5)
O(1)–Fe(1)–N(1)	105.26(5)
O(2)–Fe(1)–N(1)	105.76(5)
O(1)–Fe(1)–N(2)	111.87(5)
O(2)–Fe(1)–N(2)	103.92(5)
N(1)–Fe(1)–N(2)	75.77(5)
Si(1)–O(1)–Fe(1)	149.24(7)
Si(5)–O(2)–Fe(1)	138.92(6)
O(1)–Si(1)–Si(2)	110.74(4)
O(1)–Si(1)–Si(3)	107.64(4)
O(1)–Si(1)–Si(4)	115.91(4)
Si(2)–Si(1)–Si(3)	109.81(2)
Si(2)–Si(1)–Si(4)	105.90(2)
Si(3)–Si(1)–Si(4)	106.70(2)
O(2)–Si(5)–Si(8)	109.60(5)
O(2)–Si(5)–Si(7)	107.75(4)
O(2)–Si(5)–Si(6)	115.35(4)
Si(8)–Si(5)–Si(7)	110.42(2)
Si(8)–Si(5)–Si(6)	106.67(2)
Si(7)–Si(5)–Si(6)	107.02(2)

fragments and bridged CO-group [8,9]. At the same time a strong siloxane band ( $1050\text{ cm}^{-1}$ ) arises while the Si–O–Co absorption ( $935\text{ cm}^{-1}$ ) disappears. Hydrolysis of this complex did not yield tris(trimethylsilyl)silanol. Tentatively we assigned the complex as the cobalt–carbonyl cluster compound,  $(\text{Me}_3\text{Si})_2(\text{Me}_3\text{SiO})\text{Si–Co}_x(\text{CO})_y$ . Unfortunately, full characterization of the complex is difficult because of its low stability. Interestingly, coordinatively saturated bis-THF-adduct, **4**, and the other compounds except phosphine complex **10** did not react with carbon monoxide. It is known, that the reaction of cobalt(I) tris(trimethylsilyl)silyltelluroate,  $\text{Co}[\text{TeSi}(\text{SiMe}_3)_3](\text{PMe}_3)_3$ , with carbon monoxide yields dicarbonyl cobalt(I) complex  $\text{Co}(\text{CO})_2[\text{TeSi}(\text{SiMe}_3)_3](\text{PMe}_3)_2$  [10]. Carbon monoxide stabilizes the low valent state of the metal that causes the rearrangement of the more electronegative tris(trimethylsilyl)siloxide substituent to form the cobalt–silyl complex. Note that the rearrangement products of **1** or **3** did not absorb carbon monoxide. Triphenylphosphine complex **10** slowly reacts with CO to form an insoluble yellow powder which shows a wide absorption in the IR spectrum at  $1900\text{--}2000\text{ cm}^{-1}$  corresponding to carbonyl ligands, and the presence of organosilicon fragments ( $840, 1240\text{ cm}^{-1}$ ) along with triphenylphosphine ligands ( $500, 530, 550\text{ cm}^{-1}$ ). The Si–O–Co absorption is absent and the hydrolysis of this complex did not yield tris(trimethylsilyl)silanol. Further characterization was also found to be difficult because of poor solubility and crystallinity of this compound.

#### 2.4.4. Interaction with phenylacetylene

Catalytic amounts of cobalt(II) and iron(II) tris(trimethylsilyl)siloxides cause exothermic oligomerisation of phenylacetylene in a solution of hydrocarbons. The gradual addition of  $\text{PhC}\equiv\text{CH}$  to a solution of complexes **1–7** (0.01 mol%) in toluene or hexane yields a dark-red gel for 10 min. Cobalt-containing complexes yield the mixture consisting of 1.3.5-triphenylbenzene (20%) and insoluble polymer. In the case of iron complex **2** as a catalyst, the amount of 1.3.5-triphenylbenzene rises up to 90%. We found that the first stage of oligomerisation is the exchange of one tris(trimethylsilyl)silanol group for  $-\text{C}\equiv\text{CPh}$ . Therefore, benzonitrile complex **7** reacts with 1 mol of phenylacetylene to afford cobalt(II) siloxyacetylenid **12**.



Compound **12** is stable in the solid state; however, it decomposes for 2 h in solution. Hydrolysis of **12** yields tris(trimethylsilyl)silanol, phenylacetylene, benzonitrile and cobalt(II) hydroxide in quantitative yield. Magnetic measurements show that **12** is diamagnetic. Since low

Table 4  
IR spectra of Co(II) and Fe(II) tris(trimethylsilyl)siloxides

No.	Compound	$\nu(\text{CoOSi})$ ( $\text{cm}^{-1}$ )	Other bands ( $\text{cm}^{-1}$ )	Colour
1	$[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}$	935	1240, 840 (Si–Me)	Green
2	$[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Fe}$	960	1240, 840 (Si–Me), 750, 680, 620	Pale yellow
3	$[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}(\text{THF})$	935	1020 (THF); 1240, 840 (Si–Me)	Green
4	$[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}(\text{THF})_2$	955	1020 (THF); 1240, 840 (Si–Me)	Violet
5	$[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}(\text{DME})$	950	1020 (DME); 1240, 840 (Si–Me)	Green
6	$[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}(\text{MeCN})_2$	940	2280, 2260 (CN); 1030; 1240, 840 (Si–Me)	Violet
7	$[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}(\text{PhCN})_2$	950	2240 (CN), 930, 550 (Ar); 1240, 840 (Si–Me)	Dark vinous
8	$[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}(2,2'\text{-dipy})$	920sh, 950	1585, 1430, 760 (2,2'-dipy); 1240, 840 (Si–Me)	Dark brown
9	$\{[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}(4,4'\text{-dipy})\}_n$	960, 980sh	1590(4,4'-dipy); 1240, 840 (Si–Me)	Red
10	$[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}(\text{Ph}_3\text{P})_2$	960, 980sh	1580, 1240, 850 (Si–Me), 550, 520, 500 (Ph <sub>3</sub> P)	Blue-violet
11	$[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Fe}(2,2'\text{-dipy})$	950	1580, 760 (2,2'-dipy); 1240, 840 (Si–Me)	Dark green

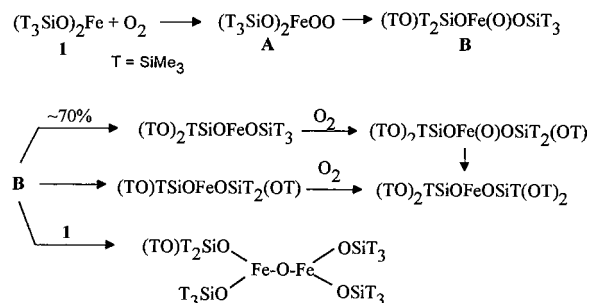
Table 5  
Electronic spectra of selected compounds

Compound	$\lambda$ (nm), ( $\epsilon$ ) colour of solution
$[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}$ ( <b>1</b> ), green crystals	Hexane, 10.0 $\text{mmol l}^{-1}$ , 575 (15), 640 (20), 685 (420), green
$[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}(\text{THF})$ ( <b>3</b> ), green crystals	Hexane, 2.5 $\text{mmol l}^{-1}$ 515 (15) 575 (70) 685 (400), green
$[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}(\text{THF})_2$ ( <b>4</b> ), violet oil	Hexane, 2.5 $\text{mmol l}^{-1}$ , green
$[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}(\text{PhCN})_2$ ( <b>7</b> ), dark vinous crystals	THF, 505 (20), 590 (30), 670 (55), 740 (15), violet
$[(\text{Me}_3\text{Si})_3\text{SiO}](\text{PhCN})\text{Co}-\text{C}\equiv\text{CPh}$ ( <b>12</b> ), blue crystals	Hexane, 505 (30), 580 (65), 695 (230), 740 (25), greenish-violet
$[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}(\text{Ph}_3\text{P})_2$ ( <b>12</b> ), blue-violet crystals( <b>10</b> )	Hexane, 515 (120), 610 (120), 700 (380), 735 (sh)
	Hexane, vinous
	$\text{CH}_2\text{Cl}_2$ , green
	Hexane, green

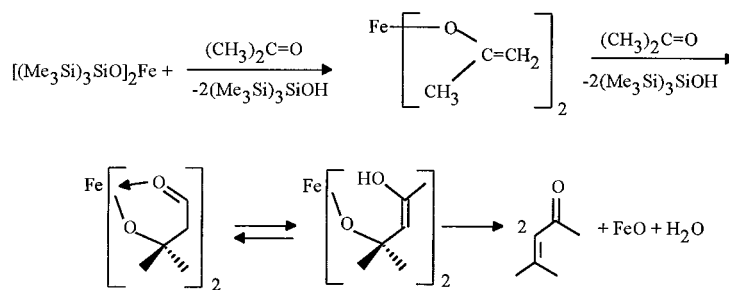
Table 6  
Hydrolysis of the oxidized complexes **1** and **2**

Compound	Absorbed $\text{O}_2$ , mol/mol <b>1</b> or <b>2</b>	Products, mol/mol <b>1</b> or <b>2</b> (T = $\text{Me}_3\text{Si}$ )			
		$\text{T}_2(\text{TO})\text{SiOH}$	$\text{T}(\text{TO})_2\text{SiOH}$	$\text{T}_3\text{SiOH}$	$\text{M}(\text{OH})_3$
$[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Fe}$ ( <b>2</b> )	0.90	0.26	0.68	1.06	0.36
	1.25	0.28	0.86	0.86	1.00
	1.79	0.08	1.50	0.40	1.00
$[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}$ ( <b>1</b> )	0.81	0.30	0.66	1.04	–
	1.74	0.52	1.48	0	–

spin two-valent cobalt has to possess one unpaired electron, compound **12** should be a dimer to compensate the spins. At ambient temperature, the  $^1\text{H-NMR}$  spectrum of **12** revealed a singlet assigned to the  $(\text{Me}_3\text{Si})_3\text{SiO}$ -group and a multiplet corresponding to the  $\text{C}_6\text{H}_5$ -ring of phenylacetylene and benzonitrile groups. The subsequent addition of  $\text{PhC}\equiv\text{CH}$  to complex **12** causes its decomposition and oligomerisation of the monomer. Diphenylacetylene does not form a complex with compounds **1–10** perhaps due to steric hindrances.



Scheme 1.



Scheme 2.

### 2.5. Thermal transformations

Although compounds **1** and **2** are isostructural, they differ in their thermal stability significantly. Iron siloxides are the most stable. Homoleptic complex **2** decomposes at a temperature over 180 °C. The products of its slow thermolysis in the temperature range of 180–250 °C are  $(\text{Me}_3\text{Si})_3\text{SiOH}$ ,  $(\text{Me}_3\text{Si})_3\text{SiOSiMe}_3$  and solid polyferrosiloxane, soluble in hexane or THF. The process is accompanied with hydrogen evolution. Metal iron was not found in the products of thermolysis. Hydrolysis of the solid residue in THF solution gave soluble oligosiloxane of unknown structure and iron(II) hydroxide;  $\text{Fe}^{+3}$  ions were absent. Earlier we had found that the thermolysis of the ate-complex  $\{(\text{Me}_3\text{Si})_3\text{SiOFe}[\mu\text{-OSi}(\text{SiMe}_3)_2\text{Na}(\text{DME})]\}$  gave somewhat different products: polyferrisiloxane and oligosilanes  $(\text{Me}_3\text{Si})_4\text{Si}$  and  $(\text{Me}_3\text{Si})_3\text{SiSi}(\text{SiMe}_3)_3$  [11]. The reason for thermolysis in a different way in the last case may be explained by the presence of sodium-silanolate fragments of the basic nature that is usually known to cause the disproportionation [12]. Interestingly lithium tris(trimethylsilyl)siloxide,  $(\text{Me}_3\text{Si})_3\text{SiOLi}$ , gave  $(\text{Me}_3\text{Si})_3\text{SiH}$  (!) as the main product in the course of thermolysis [13].

Cobalt(II) tris(trimethylsilyl)siloxides are significantly less stable. Homoleptic complex **1** remains unchangeable in the solid state at 0 °C for a long time. However, in hydrocarbon solutions at ambient temperature it undergoes a slow transformation which is accompanied with the formation of  $\text{Me}_3\text{SiOSi}(\text{SiMe}_3)_3$  and gas evolution. GLC analysis showed the presence of methane and hydrogen in the molar ratio of 1:0.13 per mole of **1**. The color of the solution turned dark brown. Acid hydrolysis of the liquid gave  $\text{Me}_3\text{SiH}$  and oligosilanes containing hydride function (absorption at 2100, 1050, 1240 and 840  $\text{cm}^{-1}$ ). Distillation of the residue in vacuo gave  $\text{Me}_3\text{SiOSi}(\text{SiMe}_3)_3$  (which remains unchangeable in the course of hydrolysis) and the product, been tentatively characterized as  $(\text{Me}_3\text{Si})_3\text{Si-O-SiH}(\text{SiMe}_3)(\text{OSiMe}_3)$  according to NMR and IR spectral data. The cobalt-silyl bonds formed in the course of the transformation of **1**, evidences the presence of the silicon hydrides as main products of hydrolysis.

Complexes **3–7**, containing THF, DME, MeCN, PhCN or 2,2'-dipyridyl ligands, also undergo transformations in solution. 4,4'-Dipyridyl adduct (**9**), in contrast to the other cobalt tris(trimethylsilyl) siloxides is stable at 20 °C for an indefinite period of time partly due to insolubility.

On comparing the tendency of the transition metal tris(trimethylsilyl)siloxides toward rearrangement ( $\text{Si-Si-O-M} \rightarrow \text{Si-O-Si-M}$ ), it should be noted that it depends on several factors: redox potential of the metal atom; polarity of the M–O bond; reducing properties of polysilyl substituents; and the enthalpy of oxygen migration into the Si–Si bond. On going from iron to cobalt and nickel, the rearrangement becomes more favorable (Table 7) that is confirmed experimentally. Analogous nickel and palladium derivatives are non-existent at room temperature. The attempt of synthesizing them from  $(\text{Me}_3\text{Si})_3\text{SiONa}$  and metal salt yields a mixture of unidentified products.

Recently Levitsky et al. [15] report a new way of introducing the metal oxide fragment into polysilane chains by the heterofunctional condensation of permethyl- $\alpha$ ,  $\omega$ -dichlorooligosilanes with cobalt(II) and copper(II) acetates. Apparently, linear polysilyl fragments such as  $-(\text{R}_2\text{Si-SiR}_2)\text{O}-$  in oligosilanes possess lesser reducing properties than the tris(trimethylsilyl)siloxy one; therefore, metal-oxide oligomers on their base seems to be more stable.

Interestingly, the tellurium analog of compound **1** does not exist. Attempt in synthesizing it from cobalt(II) bromide and lithium tris(trimethylsi-

Table 7

Redox potentials of selected metals and enthalpy of oxygen migration into Si–Si bond<sup>a</sup>

$\varphi^\circ$ (V), $\text{M}^{2+} \rightarrow \text{M}^0$	Rearrangement	$\Delta H$ (kcal mol <sup>-1</sup> )
Fe–0.44	Fe–O–Si–Si $\rightarrow$ Fe–Si–O–Si	–72
Co–0.28	Co–O–Si–Si $\rightarrow$ Co–Si–O–Si	–77
Ni–0.25	Ni–O–Si–Si $\rightarrow$ Ni–Si–O–Si	–88
Pd+0.91	Pd–O–Si–Si $\rightarrow$ Pd–Si–O–Si	–107

<sup>a</sup> Enthalpy of rearrangements were calculated from bond energies according to Ref. [14].



ly)tellurolate leads to the monovalent cobalt derivative,  $(\text{Me}_3\text{Si})_3\text{SiTeCo}(\text{Ph}_3\text{P})_3$  [10], while the analogous reaction with iron(II) chloride affords the divalent iron tellurolate,  $[(\text{Me}_3\text{Si})_3\text{SiTe}]_2\text{Co}(\text{dmpe})_2$ .

### 3. Experimental

#### 3.1. General considerations

The solvents were purified following standard methods [16]. THF and DME were thoroughly dried over Na/benzophenone; hexane, MeCN, benzene and toluene over  $\text{P}_2\text{O}_5$  and distilled prior to use. The compounds  $(\text{Me}_3\text{Si})_3\text{SiOH}$  [13,17],  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Co}$  [18,19],  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Fe}$  [18] were prepared according to known methods. The reagents 2,2'-dipyridyl and 4,4'-dipyridyl were obtained commercially (Aldrich) and purified by vacuum sublimation prior to use. All manipulations were performed with a rigorous exclusion of oxygen and moisture, in vacuum or under an Ar atmosphere using standard Schlenk techniques.

Simultaneous spectrophotometric determination of iron(II) and total iron with 1,10-phenantroline was provided by the method in Ref. [20]; spectrophotometric determination of cobalt(II) with 1-nitroso-2-naphthol was provided by the method in Ref. [21].

IR spectra (Table 4) were recorded on a Perkin–Elmer 577 spectrometer from 4000 to  $200\text{ cm}^{-1}$  in Nujol. Electronic spectra (Table 5) were measured on a Specord M-40 device from 200 to 800 nm.

Room-temperature magnetic moments were measured by the Faraday method.

NMR spectra were recorded in  $\text{CDCl}_3$  or  $\text{C}_6\text{D}_6$  solutions using the 'Bruker DPX-200' device, with  $\text{Me}_4\text{Si}$  as the internal standard.

Thermal decomposition of compound **1** was carried out in vacuo (or in an Ar atmosphere) with a heating rate of  $3\text{ }^\circ\text{C min}^{-1}$ . The temperature range studied extended from 20 to  $300\text{ }^\circ\text{C}$ .

Gas chromatography analysis of organosilicon products were carried out on a Tsvet-500 chromatograph, equipped with stainless steel columns  $0.4\text{ cm} \times 200\text{ cm}$ , packed with 5% SE-30 on Chromatone N-Super. Gaseous products ( $\text{H}_2$ ,  $\text{CH}_4$ ) were analyzed on a column  $0.4\text{ cm} \times 300\text{ cm}$ , packed with zeolite NaX with a thermoconductivity detector and with helium (Ar for  $\text{H}_2$  analysis) as carrier gas.

#### 3.2. X-ray diffraction studies

X-Ray data were collected on a Siemens P3/PC (**1**) and SMART CCD (**11**) diffractometers at 213 (**1**) and 100 K (**11**). The crystal data and some details on data collection and refinement for **1** and **11** are given in Table 1. Both structures were determined using a com-

bination of direct methods and calculations of Fourier maps. The positions of the H atoms were calculated using the general geometrical conditions and the H atoms were refined in a rigid group model. All calculations were performed using the SHELXTL-PLUS package [22]. Selected bond distances and angles in **1** and **11** are given in Tables 2 and 3, respectively.

#### 3.3. Synthesis

##### 3.3.1. $[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}$ (**1**)

Tris(trimethylsilyl)silanol (7.37 g, 28.0 mmol) in 15 ml of hexane was added to a solution of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Co}$  (5.28 g, 14.0 mmol) in 15 ml of the same solvent. The mixture was maintained for 5 h at  $20\text{ }^\circ\text{C}$ . The solvent and hexamethyldisilazane were removed in vacuo to give green crystals that were recrystallized from hexane. Yield: 7.40 g (90%). Anal. Calc. for  $\text{C}_{18}\text{H}_{54}\text{Si}_8\text{O}_2\text{Co}$ : C, 36.88; H, 9.28; Co, 10.05. Found: C, 36.13; H, 9.17; Co, 9.93%.  $\mu_{\text{eff}} = 6.0\text{ } \mu_{\text{B}}$ .

##### 3.3.2. $[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Fe}$ (**2**)

Tris(trimethylsilyl)silanol (3.27 g, 12.4 mmol) in 15 ml of hexane was added to a solution of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Fe}$  (2.13 g, 6.18 mmol) in 15 ml of the same solvent. The mixture was heated for 5 h at  $70\text{ }^\circ\text{C}$ . The green solution slowly turned light brown. The solvent and hexamethyldisilazane were removed in vacuo to give pale-yellow crystals that were recrystallized from hexane. Yield: 3.44 g (95%). Anal. Calc. for  $\text{C}_{18}\text{H}_{54}\text{Si}_8\text{O}_2\text{Fe}$ : C, 37.07; H, 9.33; Fe, 9.58. Found: C, 36.94; H, 9.39; Fe, 9.50%.  $\mu_{\text{eff}} = 4.0\text{ } \mu_{\text{B}}$ .

##### 3.3.3. $[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}(\text{THF})_n$ , $n = 1$ (**3**), $n = 2$ (**4**)

Hexane was removed in vacuo from a solution of homoleptic complex (**1**) and changed for THF. The starting green solution immediately turned violet. Further removal of THF in vacuo at  $20\text{ }^\circ\text{C}$  affords a violet oil showing intensive absorption at  $1020\text{ (C–O, THF)}$  and  $955\text{ cm}^{-1}$  ( $\text{Si–O–Co}$ ) in IR spectra and corresponds to **4** by elemental analysis. Anal. Calc. for  $\text{C}_{26}\text{H}_{70}\text{Si}_8\text{O}_4\text{Co}$ : C, 42.75; H, 9.66; Co, 8.07. Found: C, 43.05; H, 9.70; Co, 7.98%.

A sample of **4** was pumped in vacuo at  $50\text{ }^\circ\text{C}$  for 4 h to give green crystals of **3**. The IR spectra of **3** still show absorption at  $1020\text{ cm}^{-1}$ , but of less intensity and a new absorption ( $\text{Si–O–Co}$ ) at  $935\text{ cm}^{-1}$ . Anal. Calc. for  $\text{C}_{22}\text{H}_{62}\text{Si}_8\text{O}_3\text{Co}$ : C, 40.13; H, 9.49; Co, 8.95. Found: C, 40.08; H, 9.43; Co, 9.07%.

##### 3.3.4. $[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}(\text{DME})$ (**5**)

Hexane was removed in vacuo from a solution of homoleptic complex (**1**) and changed for DME. The green color of the solution gets dark. Further removal of DME in vacuo at  $20\text{ }^\circ\text{C}$  affords green crystalline solid showing absorption at  $1020\text{ (C–O, DME)}$  and  $950$

$\text{cm}^{-1}$  (Si–O–Co) in IR spectra and corresponds to **5** by elemental analysis. Anal. Calc. for  $\text{C}_{22}\text{H}_{64}\text{Si}_8\text{O}_4\text{Co}$ : C, 39.06; H, 9.54; Co, 8.71. Found: C, 39.11; H, 9.60; Co, 8.65%.

### 3.3.5. $[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}(\text{MeCN})_2$ (**6**)

$[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}(\text{MeCN})_2$  (**6**) was prepared similar to **5** using **1** and MeCN. Pink plate crystals were obtained. Anal. Calc. for  $\text{C}_{22}\text{H}_{60}\text{Si}_8\text{O}_2\text{N}_2\text{Co}$ : C, 39.53; H, 9.05; Co, 8.82. Found: C, 39.60; H, 9.11; Co, 8.91%.

### 3.3.6. $[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}(\text{PhCN})_2$ (**7**)

Benzonitrile (0.20 g, 2 mmol) was added to a solution of  $[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}$  (0.58 g, 1 mmol) in 10 ml of toluene. Green color of the solution turned vinous. The mixture was maintained for 3 h at 20 °C and the solvent was removed in vacuo. Further crystallization from cold toluene affords dark vinous crystals. Yield: 0.75 g (96%). Anal. Calc. for  $\text{C}_{32}\text{H}_{64}\text{Si}_8\text{O}_2\text{N}_2\text{Co}$ : C, 48.50; H, 8.14; Co, 7.44. Found: C, 48.12; H, 8.21; Co 7.30%.

### 3.3.7. $[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}(2,2'\text{-dipy})$ (**8**)

A mixture of 2,2'-dipyridyl (0.58 g, 3.7 mmol) and of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Co}$  (1.40 g, 3.7 mmol) in 10 ml of benzene was stirred at room temperature (r.t.) for 3 h. The solvent was removed in vacuo to give brown crystals that were recrystallized from *n*-hexane. Yield: 1.80 g (91%) of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Co}(2,2'\text{-dipy})$ . Anal. Calc. For  $\text{C}_{22}\text{H}_{44}\text{Si}_4\text{N}_4\text{Co}$ : C, 49.31; H, 8.28; Co, 11.00. Found: C, 49.44; H, 8.23; Co, 10.95%. IR ( $\text{cm}^{-1}$ ): 1240 (s), 840 (vs), 750 (m), 675 (m), (SiMe); 975 (m) (NSi<sub>2</sub>), 1580 (m), 760 (m) (2,2'-dipy).

Tris(trimethylsilyl)silanol (2.50 g, 9.5 mmol) in 10 ml of benzene was added to a solution of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Fe}(2,2'\text{-bipy})$  (3.53 g, 4.75 mmol) in 15 ml of the same solvent. The mixture was maintained for 24 h at 20 °C. Solvent was removed in vacuo. Dark brown crystals of the product were obtained from cold toluene. Yield of 2.75 g (92%) of **8**. Anal. Calc. for  $\text{C}_{28}\text{H}_{62}\text{Si}_8\text{O}_2\text{N}_2\text{Co}$ : C, 45.29; H, 8.42; Co, 7.94. Found: C, 45.38; H, 8.50; Co 7.88%.  $\mu_{\text{eff}} = 3.5 \mu_{\text{B}}$ .

### 3.3.8. $\{[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}(4,4'\text{-dipy})\}_n$ (**9**)

4,4'-Dipyridyl (0.18g, 1.14 mmol) in 5 ml of THF was added to a solution of  $[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}$  (0.83 g, 1.14 mmol) in 15 ml of the same solvent. Red fine crystalline precipitate was formed immediately. It was washed with THF and dried in vacuo. Yield: 0.68 g (97%). Anal. Calc. for  $\text{C}_{28}\text{H}_{62}\text{Si}_4\text{O}_2\text{N}_2\text{Co}$ : C, 45.30; H, 8.42. Found: C, 44.99; H, 8.39%.  $\mu_{\text{eff}} = 5.4 \mu_{\text{B}}$ .

### 3.3.9. $[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Co}(\text{Ph}_3\text{P})_2$ (**10**)

Triphenylphosphine (1.10 g, 4.0 mmol) was added to a solution of homoleptic **1** (1.22 g, 2.0 mmol) in 20 ml of toluene. The green solution turned dark green–vio-

let. The mixture was maintained for 2 h. Toluene was removed in vacuo and replaced with hexane. Slow cooling to 0 °C overnight gave dark blue–violet crystals. Yield: 1.88 g (81%). Anal. Calc. for  $\text{C}_{54}\text{H}_{84}\text{Si}_8\text{O}_2\text{P}_2\text{Co}$ : C, 58.38; H, 7.62; Co, 5.31. Found: C, 58.48; H, 7.81; Co, 5.28%.  $\mu_{\text{eff}} = 5.1 \mu_{\text{B}}$ .

### 3.3.10. $[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Fe}(2,2'\text{-dipy})$ (**11**)

A mixture of 2,2'-dipyridyl (0.95 g, 6.1 mmol) and  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Fe}$  (2.30 g, 6.10 mmol) in 15 ml of benzene was maintained at r.t. for 3 h. The solvent was removed in vacuo to give green crystals that were recrystallized from *n*-hexane. Yield of 3.2 g (93%) of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Fe}(2,2'\text{-dipy})$ . Anal. Calc. for  $\text{C}_{22}\text{H}_{44}\text{Si}_4\text{N}_4\text{Fe}$ : C, 49.56; H, 8.32; Fe, 10.48. Found: C, 49.94; H, 8.26; Fe, 9.90%. IR ( $\text{cm}^{-1}$ ): 1250 (s), 1240 (sh), 840 (vs), 750 (m), 680 (m), 620 (w) (SiMe); 1175 (w), 1020 (w), 990 (m), 970 (m) (NSi<sub>2</sub>), 1580 (m), 760 (m) (2,2'-dipy).

Tris(trimethylsilyl)silanol (2.23 g, 8.46 mmol) in 10 ml of benzene was added to a solution of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Fe}\cdot 2,2'\text{-bipy}$  (2.25 g, 4.23 mmol) in 15 ml of the same solvent. The mixture was maintained for 24 h at 20 °C. The green solution slowly turned dark green–brown. Benzene was removed in vacuo and the solid residue recrystallized from toluene affords greenish-brown crystals. Yield: 2.99 g (96%). Anal. Calc. for  $\text{C}_{28}\text{H}_{62}\text{Si}_8\text{O}_2\text{N}_2\text{Fe}$ : C, 45.49; H, 8.45; Fe, 7.55. Found: C, 43.94; H, 9.56; Fe, 8.11%.

## 3.4. Reactivity

### 3.4.1. Reaction of **2** with oxygen and subsequent hydrolysis

The calculated volume of dry oxygen was slowly bubbled through a benzene solution of **1** or **2** at 17 °C. The solvent was removed in vacuo and changed for THF. Twofold excess of water was added. The mixture was stirred for 20 min, filtered and then concentrated. Quantitative GLC analysis of the resulting solution showed the presence of three silanols,  $(\text{Me}_3\text{Si})_3\text{SiOH}$ ,  $\text{Me}_3\text{SiO}(\text{Me}_3\text{Si})_2\text{SiOH}$ ,  $(\text{Me}_3\text{SiO})_2(\text{Me}_3\text{Si})\text{SiOH}$  which were characterized as described earlier [11]. The precipitate was washed with THF and water, and then dissolved in dilute HCl for subsequent simultaneous spectrophotometric determination of iron(II) and total iron (Table 6). The precipitate of iron hydroxides did not contain the organic impurities according to the IR spectrum and elemental analysis.

### 3.4.2. Interaction of **2** with acetone

An excess of dry acetone was added to a solid compound **2**. After initial dissolution, the slow precipitation of FeO began. The mixture was maintained for 24 h and then filtered. The filtrate contained mesityl oxide and tris(trimethylsilyl)silanol in quantitative yield

according to GLC analysis. The FeO precipitate did not contain HO-groups according to the IR spectrum. Iron content was found to be 76.03% (Calc. 77.73%).

### 3.4.3. Interaction of **1** with CO

The ampoule containing 0.59 g (1 mmol) of **1** in 5 ml of toluene was attached to a mercury burette with carbon monoxide and maintained for 24 h at 20 °C. The green color of the solution slowly turned dark brown. The overall volume of the consumed gas was 40 ml. Nearly all the solvent part was removed under reduced pressure; the liquid residue was maintained at 0 °C for 1 h affording a small amount of unstable dark brown crystals. IR (cm<sup>-1</sup>): (2040 (s), 2030 (s), 2000 (s), 1870 (m), 1240 (s), 1050 (s), 840 (vs)).

### 3.4.4. Interaction of **7** with PhC≡CH. Synthesis of (Me<sub>3</sub>Si)<sub>3</sub>SiOC<sub>o</sub>-C≡CPh(PhCN) (**12**)

Phenylacetylene (0.10 g, 1 mmol) in 5 ml of hexane was added to a solution of [(Me<sub>3</sub>Si)<sub>3</sub>SiO]<sub>2</sub>Co(PhCN)<sub>2</sub> (**7**) (0.54 g, 1 mmol) in 8 ml of hexane. The resulting solution was maintained for 3 h at 20 °C. For this period of time a blue fine crystalline precipitate was formed. The supernatant was decanted, and the remaining blue crystals were washed with cold toluene and dried in vacuo. Yield: 0.51 g (95%). Anal. Calc. for Si<sub>4</sub>C<sub>24</sub>H<sub>37</sub>ONCo: C, 54.71; H, 7.08; Co, 11.19. Found: C, 54.55; H, 7.12; Co 11.23%. IR (cm<sup>-1</sup>): ν(SiMe) 1235 (vs), 840 (vs); ν(C≡N) 2222 (m); ν(C<sub>6</sub>H<sub>5</sub>) 1580 (m), 1560 (sh); ν(SiC<sub>3</sub>) 780 (m), 755 (m), 745 (m) 680 (s), 620 (w); 550 (m), 500 (s), 435 (m). <sup>1</sup>H-NMR (δ ppm): 7.2–7.5 (m, 10 H), 0.15 (27 H). Hydrolysis of **12** yields tris(trimethylsilyl)silanol, phenylacetylene, benzonitrile in the molar ratio (1:1:1) according to the quantitative GLC analysis and cobalt(II) hydroxide that did not contain the organic impurities according to the IR spectrum and elemental analysis. Cobalt content was found to be 62.14% (Calc. 63.40%).

### 3.4.5. Oligomerisation of phenylacetylene with [(Me<sub>3</sub>Si)<sub>3</sub>SiO]<sub>2</sub>Fe (**2**)

Phenylacetylene (5 g, 0.049 mol) was gradually added for 5 min to a 15 ml of 0.01 M solution of **2** in toluene with vigorous stirring. A dark red gel was centrifuged, the centrifugate was pumped in vacuo, and the residue was recrystallized from glacial AcOH and sublimated in vacuo to form pure 1,3,5-triphenylbenzene. Yield: 4.5 g (90%). M.p. 170 °C (lit. data 170 °C [23]). Anal. Calc. for C<sub>24</sub>H<sub>18</sub>: C, 93.84; H, 6.16%. Found: C, 93.80; H, 6.13%.

## 3.5. Thermal decomposition

### 3.5.1. Thermal decomposition of cobalt(II) tris(trimethylsilyl)siloxide (**1**)

A solution of 1.77g (3 mmol) of homoleptic (**1**) in 10

ml of toluene was maintained at 40 °C for 8 h. Green color of the solution slowly turned dark brown. The volume of gaseous products (0 °C) was found to be 75 ml. GLC analysis showed the presence of methane and hydrogen in the molar ratio of 1:0.13 per mole of **1**. Toluene was removed in vacuo. IR spectra of the residue showed the absence of (Co–O–Si) bond. Hydrolysis of the residue in THF solution with 10% HCl (5 ml) gave hydrogen and Me<sub>3</sub>SiH according GLC analysis and IR spectrum (ν(SiH) = 2135 cm<sup>-1</sup> (gas phase) or 2118 cm<sup>-1</sup> in solution [24]; 840, 1250 cm<sup>-1</sup> (SiMe)).

Organic layer after THF removal contained oil which was distilled in vacuo to give 0.3 g of crystalline (Me<sub>3</sub>Si)<sub>3</sub>SiOSiMe<sub>3</sub> (subl. at ~80 °C/0.01 mmHg [13]), <sup>1</sup>H-NMR (300 K, C<sub>6</sub>D<sub>6</sub>, δ ppm): 0.14 (s, 27H, (Me<sub>3</sub>Si)<sub>3</sub>Si), 0.02 (s, 9H, OSiMe<sub>3</sub>) and 0.6 g of viscous oil (b.p. 105 °C/0.01 mmHg), which was tentatively characterized as (Me<sub>3</sub>Si)<sub>3</sub>Si–O–SiH(SiMe<sub>3</sub>)(OSiMe<sub>3</sub>). <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz, 300 K, δ ppm): 0.32 (s, 27H, (Me<sub>3</sub>Si)<sub>3</sub>), 0.35 (s, 9H, Si(SiMe<sub>3</sub>)), 0.18 (s, 9H, OSiMe<sub>3</sub>), 5.00 (s, 1H, SiH). <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>, 50 MHz, 300 K, δ ppm): -0.36 (s, OSiMe<sub>3</sub>), -0.08 (s, (Me<sub>3</sub>Si)<sub>3</sub>), 0.21 (s, Si(SiMe<sub>3</sub>)). <sup>29</sup>Si-NMR (C<sub>6</sub>D<sub>6</sub>, 40 MHz, 300 K, δ ppm): 7.5 (OSiMe<sub>3</sub>), -9.5 (Si(SiMe<sub>3</sub>), -10.0 ((Me<sub>3</sub>Si)<sub>3</sub>), -16.3 (SiH), -16.6 ((Me<sub>3</sub>Si)<sub>3</sub>SiO). IR (cm<sup>-1</sup>): ν(SiH) 2110 m, ν(SiMe) 1240s, 840vs, 675s, 620m, ν(SiOSi) 1050 m.

### 3.5.2. Thermal decomposition of iron(II) tris(trimethylsilyl)siloxide (**2**)

Thermal decomposition was carried out in vacuo (0.01 mmHg) with a heating rate of 3 °C min<sup>-1</sup>. The temperature range studied extended to 250 °C. Volatile products of thermolysis were collected at 180–250 °C to be (Me<sub>3</sub>Si)<sub>3</sub>SiOH and (Me<sub>3</sub>Si)<sub>3</sub>SiOSiMe<sub>3</sub> in the molar ratio 0.15:0.10 per mole of **2** according GLC. The hydrogen evolution being slow at 200 °C rises significantly above 220 °C. The solid residue with IR absorption at ν(SiMe) 1240 (m), 840 (s), ν(Si–O–Si) 1050 (vs), ν(SiOFe) 950 (w) was dissolved in THF and hydrolyzed to form a green precipitate of Fe(OH)<sub>2</sub> (Fe<sup>2+</sup> content 58.66%, Calc. 62.15%) and soluble oligosiloxane. Filtration followed by the solvent removal gave viscous oil showing broad <sup>1</sup>H-NMR signals at 0.2–0.3 ppm and IR absorption at ν(SiMe) 3400 (w), 1240 (m), 840 (s), ν(Si–O–Si) 1050 (vs). Hydrochloric solution of the precipitate also gave also negative test with K<sub>4</sub>[Fe(CN)<sub>6</sub>] showing the absence of Fe<sup>+3</sup> ions in the products of thermolysis.

## 4. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic

Data Centre, CCDC no. 159595 for compound **11** and the refcode FOVLAD for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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### References

- [1] G.A. Sigel, R.A. Bartlett, D. Decker, M.M. Olmstead, P.P. Power, *Inorg. Chem.* 26 (1987) 1773.
- [2] While tris(trimethylsilyl)silyl group seems quite bulky, its steric parameter  $E_s$  (effective size) is approximately equal or slightly more than those found for *tert*-butyl group. See: J. Frey, E. Schottland, Z. Rappoport, D. Bravo-Zhivotovskii, M. Nakash, M. Botoshansky, M. Kaftory, Y. Apeloig, *J. Chem. Soc. Perkin Trans. 2* 12 (1994) 2555.
- [3] E. Ruiz, S. Alvarez, P. Alemany, *J. Chem. Soc. Chem. Commun.* (1998) 2767.
- [4] M. Hanack, S. Deder, A. Lange, *Coord. Chem. Rev.* 83 (1988) 115.
- [5] Conversion of tris(trimethylsilyl)silanol was found to be ~30% after staying in open air for a month. At least five products was observed according GLC analysis, while oxidation with peroxibenzoic acid gives only two intermediates and one final product,  $(\text{Me}_3\text{SiO})_3\text{SiOH}$  [11]. Apparently, oxidation with oxygen involves free radical processes.
- [6] V.V. Semenov, E.Yu. Ladilina, T.A. Chesnokova, A.N. Kornev, M.A. Lopatin, A.N. Egorochkin, *Organomet. Chem. USSR* 5 (1992) 368.
- [7] A. Vioux, *Chem. Mater.* 9 (1997) 2292.
- [8] O. Vohler, *Chem. Ber.* 91 (1958) 1161.
- [9] K.M. Abraham, G. Urry, *Inorg. Chem.* 12 (1973) 2850.
- [10] D.E. Gindelberger, J. Arnold, *Inorg. Chem.* 32 (1993) 5813.
- [11] A.N. Kornev, T.A. Chesnokova, V.V. Semenov, E.V. Zhezlova, L.N. Zakharov, L.G. Klapshina, G.A. Domrachev, V.S. Rusakov, *J. Organometal. Chem.* 547 (1997) 113.
- [12] S.K. Mehrotra, H. Kawa, J.R. Baran Jr., M.M. Ludvig, R.J. Lagow, *J. Am. Chem. Soc.* 112 (1990) 9003.
- [13] A.N. Kornev, T.A. Chesnokova, V.V. Semenov, Yu.A. Kurskii, *Russ. Chem. Bull.* 44 (1995) 1107.
- [14] V.I. Vedeneev, L.V. Gurvich, V.N. Kondrat'yev, V.A. Medvedev, Ye.L. Frankevich, *Bond Energies, Ionization Potentials and Electron Affinities*, St. Martin's Press, New York, 1966.
- [15] M.M. Levitsky, B.G. Zavin, A.I. Chernyavsky, V.V. Erokhin, *Russ. Chem. Bull.* 9 (1999) 1811.
- [16] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 1980.
- [17] B.H. Boo, H.K. Kang, S.K. Kang, S.S. Lee, *J. Organomet. Chem.* 436 (1992) 1.
- [18] R.A. Andersen, K. Faegri, J.C. Green, A. Haaland, M.F. Lappert, W.-P. Leung, K. Rypdal, *Inorg. Chem.* 27 (1988) 1782.
- [19] H. Burger, U. Wannagat, *Monatsh. Chem.* 94 (1963) 1007.
- [20] A.E. Harvey, J.A. Smart, E.S. Amis, *Anal. Chem.* 127 (1955) 26.
- [21] G. Graue, S. Eckhard, W. Gradtke, *Angew. Chem.* 71 (1959) 28.
- [22] G.M. Sheldrick, *Structure Determination Software Program Package (PC version)*, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1989.
- [23] R.D. Rose, F.S. Statham, *J. Chem. Soc.* (1950) 69.
- [24] G. Kessler, H. Kriegsmann, *Z. Anorg. Allg. Chem.* 342 (1966) 53.