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# Reactions of (trimethylsilyl)tetramethylcyclopentadiene with (benzene)titanium(II) bis(tetrachloroaluminate). Crystal structures of $[C_5Me_4(SiMe_3)]Ti(AlCl_4)_2$ and $\{[C_5Me_4(SiMe_3)]Ti(AlCl_4)(\mu\text{-}Cl)\}_2$

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## Abstract

(Trimethylsilyl)tetramethylcyclopentadiene $C_5HMe_4(SiMe_3)$ reacts with one equivalent of $(C_6H_6)Ti(II)(AlCl_4)_2$ to give the paramagnetic trinuclear complex $[C_5Me_4(SiMe_3)]Ti(III)(AlCl_4)_2$ (**1**). At a five-fold molar excess of $C_5HMe_4(SiMe_3)$, the paramagnetic binuclear complex $[C_5Me_4(SiMe_3)]_2Ti(III)(AlCl_4)$ (**2**) and the diamagnetic centrosymmetric dimer $\{[C_5Me_4(SiMe_3)]Ti(III)(AlCl_4)(\mu\text{-}Cl)\}_2$ (**3**) are obtained as a major and a minor product, respectively. The molecular structures of **1** and **3** have been obtained by X-ray crystal analysis. The structure of **2** has been deduced from its ESR spectrum which shows the unpaired electron coupling to one Al nucleus. © 1998 Elsevier Science S.A.

*Keywords:* (Trimethylsilyl)tetramethylcyclopentadiene; (Benzene)titanium(II) bis(tetrachloroaluminate); ESR spectrum

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## 1. Introduction

Effects of the $SiMe_3$ substituent at cyclopentadienyl ligands on electron density at the metal atom in metallocene derivatives are not well understood [1]. Both electron attracting and electron donating effects have been experimentally observed in early transition metal metallocene derivatives, depending on evaluated parameters. For example, the reduction potential ($E_{1/2}^{red}$) of $Cp'_2ZrCl_2$ compounds increases in the series of substituents in the order $(SiMe_3)_2 < SiMe_3 < Me < Et$, thus qualifying the $SiMe_3$ group to be an electron acceptor with respect to hydrogen [2,3]. This is compatible with the ease of reduction of the $[C_5H_{5-n}(SiMe_3)_n]_2ZrCl_2$ compounds, increasing in the order of $n = 0 < 2$ [4]. In contrast, the binding energies of inner-shell electrons in the series of compounds $[C_5H_{5-n}(SiMe_3)_n]_2ZrCl_2$ ($n = 0$–$3$) and $[C_5H_{5-n}(SiMe_3)_n]_2HfCl_2$ ($n = 0$ and $3$) showed that the $SiMe_3$ group is a 1.25-times stronger electron donor than the Me group [5]. The measurement of free energies of ionization of ruthenocene complexes puts the $SiMe_3$ group to be a similar electron donor as the Me group [6]. Absorption maxima of the low energy transitions in UV–VIS spectra of ring-substituted titanocene dichlorides also indicated that the $SiMe_3$ group is stronger electron donor than the Me group [7]. The latter observation has been recently shown to be valid also for $[C_5Me_4(SiMe_3)]_2TiCl_2$ whereas the observable affinity of $[C_5Me_4(SiMe_3)]_2TiCl$ towards 2-methyltetrahydrofuran resembled the affinity of $(C_5HMe_4)_2TiCl$ [8]. The X-ray crystal structures of the above chlorides showed that their CE–Ti–CE (CE-centroid of the Cp ring) angles do not differ from those of the appropriate $(C_5Me_5)_2Ti$ derivatives since the bulky $SiMe_3$ groups are placed in opposite side positions with respect to the CE, Ti, CE plane [8]. Recently, the $SiMe_3$ group in the $C_5Me_4(SiMe_3)$ ligand has been shown to be highly reactive towards the reductive action of magnesium. The hydrogen abstraction from the $SiMe_3$ group occurs in the $[C_5Me_4(SiMe_3)]_2TiCl_2/Mg/THF$ system, resulting in the formation of $Ti–CH_2–Si$ and $Mg–CH_2–Si$ bonds [9].

In this work, we examine the behaviour of (trimethylsilyl)tetramethylcyclopentadiene

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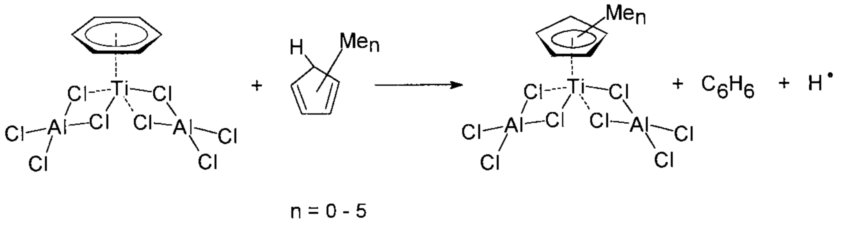
$C_5HMe_4(SiMe_3)$ in the redox reaction with the bis(tetrachloroaluminate) ($\eta^6$-benzene)titanium(II) complex $[(C_6H_6)Ti(AlCl_4)_2]$. This reaction proceeds in a stoichiometric way with cyclopentadiene and its methyl-substituted derivatives Cp′H ($Cp' = C_5H_{5-n}Me_n$; $n =$ 0–5) according to Eq. (1) [10–12].



(1)

The oxidation of Ti(II) to Ti(III) is accompanied by the release of the coordinated benzene molecule and by the liberation of hydrogen. The acidity of the cyclopentadienes decreases with the increasing number of Me groups [13], however, all the compounds react immeasurably fast under ambient conditions. In the case that $C_5HMe_4(SiMe_3)$ is yet a weaker acid than $C_5HMe_5$ a measurably slow reaction could be observed. Furthermore, the Ti(III) products of reaction (1) decrease in stability with the number of Me groups so that the complex $(C_5Me_5)Ti(AlCl_4)_2$ partly decomposes in the solid state to give a green-brown solid [12]. Hence, the stability of the expected $[C_5Me_4(SiMe_3)]Ti(AlCl_4)_2$ complex will be another criterion to estimate the $SiMe_3$ effect.

## 2. Experimental details

### 2.1. General data and methods

The synthesis, purification and crystallization procedures and the measurements of ESR and UV–VIS spectra in solutions were carried out in evacuated all-sealed glass devices equipped with magnetically breakable seals. A combined device equipped with a pair of quartz cuvettes (1 cm and 1 mm) and a quartz ESR tube was used for the UV–VIS and ESR measurements. ESR spectra were recorded on an ERS-220 spectrometer (Centre for Production of Scientific Instruments, Academy of Sciences of GDR, Berlin, Germany) in the X-band. $g$-Values were determined using a $Mn^{2+}$ ($M_1 = -1/2$ line) standard at $g = 1.9860$ and a proton magnetometer MJ-110 R (Radiopan, Poznan, Poland). Concentrations of the paramagnetic compounds were estimated from integrated first derivative records. A variable temperature STT-3 unit was used for the measurement in the range $-150$–$+20$°C. UV–VIS spectra were registered in the range 280–2000 nm on a Varian Cary 17D spectrometer using all-sealed quartz cuvettes (Hellma). Infrared spectra of solid complexes were recorded on a Mattson Galaxy 2020 spectrometer. KBr pellets were prepared in a Labmaster 130 glovebox (Braun) and were measured in a gas-proof cuvette under nitrogen atmosphere. Electron dispersive X-ray analyses (EDX) were carried out on a Zeiss DSM-962 scanning electron microscope equipped with an EDAX PV9800 analyser. Acceleration voltage of 25 kV was used for the generation of cathodic radiation. The samples were in contact with air shortly before the measurement.

### 2.2. Chemicals

The solvents hexane and toluene were purified by conventional methods, dried by refluxing over $LiAlH_4$ and stored as solutions of ‘dimeric titanocene’ $(C_{10}H_8)[(C_5H_5)Ti(\mu\text{-}H)]_2$ [14]. The reagent $C_5HMe_4(SiMe_3)$ was obtained from $Li(C_5HMe_4)$ and $Me_3SiCl$ as described recently [8]. It was further purified by standing with dimeric titanocene followed by vacuum distillation thereof.

$(C_6H_6)Ti(AlCl_4)_2$ was prepared as described earlier [15] and was purified by precipitation with hexane from benzene solution. The finely crystalline compound was dissolved in toluene to give a 0.04 M solution.

### 2.3. Preparation of bis(tetrachloroaluminate)[tetramethyl(trimethylsilyl)cyclopentadienyl]titanium(III), $[C_5Me_4(SiMe_3)Ti(AlCl_4)_2$ (**1**)

The solution of $C_5HMe_4(SiMe_3)$ in toluene (0.4 mmol in 4 ml) and the solution of $(C_6H_6)Ti(AlCl_4)_2$ in toluene (0.40 mmol in 10 ml) were mixed together in an evacuated ampoule. A dirty green solution formed immediately. All volatiles were evaporated under dynamic vacuum and the residue was extracted by hexane. The green solution was separated. This was evaporated to dryness and then washed by condensing hexane vapour. First several drops of a yellow-green solution were removed. The remainder was dissolved in a minimum amount of hexane for crystallization. The crop of green crystals was used for the X-ray diffraction, IR and EDX measurement, and for the ESR and UV–VIS measurements in solution.

The mother liquor gave the same ESR and UV–VIS spectra as the solution made from crystals. The structure of compound **1** was deduced from its ESR spectrum and was confirmed by the X-ray crystal analysis.

**1:** Yield 0.17 g (75%). ESR (toluene, 23°C): $g =$ 1.9698, $a_{Al} = 5.6$ G, $a_{Ti} = \sim 16$ G; (toluene, $-140$°C):

$g_\perp = 1.991$, $g_\parallel = 1.929$, $g_{av} = 1.970$, $A_\perp(\mathrm{Al}) = 5.9$ G. IR (KBr) (cm$^{-1}$): 1385(m), 1331(w), 1254(m), 1022(m), 845(s), 760(w), 694(w), 565(s), 503(vs), 424(s). UV–VIS (hexane): 325sh ~ 402 > 485sh ≫ 660 nm. EDX (K$\alpha$): approximate ratio Ti:Al:Si = 1:2:1.

Addition of a 10-fold excess of $Et_2AlCl$ to **1** in toluene induced the following spectral changes. ESR (toluene, 23°C): $g = 1.9713$, $a_{Ti} = 15.2$ G, $\Delta H = 10$ G; (toluene, −140°C): $g_\perp = 1.992$, $g_\parallel = 1.932$, $g_{av} = 1.972$; UV–VIS: 420 ≫ 700(broad) nm.

### *2.4. Reaction of $(C_6H_6)Ti(AlCl_4)_2$ with a 5-fold excess of $C_5HMe_4(SiMe_3)$*

A solution of $C_5HMe_4(SiMe_3)$ in toluene (10.0 mmol in 20 ml) was mixed with a solution of $(C_6H_6)Ti(AlCl_4)_2$ in toluene (2.0 mmol in 50 ml). A green solution was immediately formed. After standing overnight a crop of turquoise crystals of bis{($\mu$-chloro)(tetrachloroaluminate)[tetramethyl(trimethylsilyl)cyclopentadienyl]titanium(III)}, $\{[C_5Me_4(SiMe_3)]Ti(AlCl_4)(\mu\text{-}Cl)\}_2$, (**3**) was obtained. These were used for the X-ray crystal analysis and for ESR/UV–VIS measurements. The toluene solution prepared from these crystals did not exhibit any ESR signal at room temperature and in frozen glass at −140°C in addition to a trace signal of six-line pattern of apparently (tetrachloroaluminate) bis[tetramethyl(trimethylsilyl)cyclopentadienyl]titanium(III), $[C_5Me_4(SiMe_3)]_2Ti(AlCl_4)$ (**2**). The mother liquor was evaporated and the residue was dissolved in hexane. The crystallization afforded a mixture of several large turquoise crystals and overwhelming amount of fine pale green crystals. The turquoise crystals were hand-separated in a glovebox. The finely crystalline material was recrystallized from hexane to give 0.5 g of the pale green crystalline compound **2**. The crystals were unsuitable for X-ray diffraction analysis. Compound **2** was characterized by the ESR, IR, UV–VIS spectra and by EDX for its content of Ti, Al, and Si, and by the chemical analysis for Ti, Al and Cl. On the basis of these measurements a minor admixture of **3** in **2** cannot be excluded.

**2**: Yield 0.5 g (41%). ESR (toluene, 23°C): $g = 1.9755$, $a_{Al} = 7.7$ G, $a_{Ti} = 10.3$ G, $\Delta H = 3.7$ G; (−140°): $g_\perp = 1.990$, $g_\parallel = 1.944$, $g_{av} = 1.975$; $A_\perp = 8.3$ G, $A_\parallel = 8.3$ G. UV–VIS (toluene): 320sh > 410 > 480sh ≫ 660 nm. EDX (K$\alpha$): Ti:Al:Si = 1:1:2.

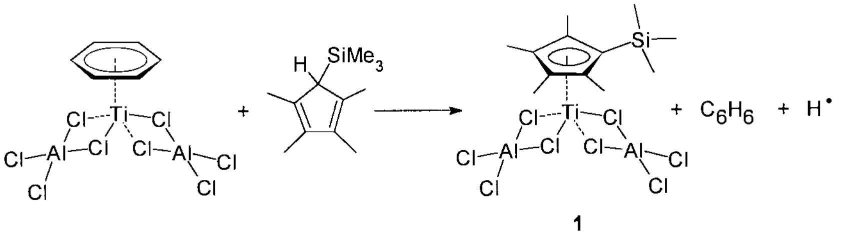
**3**: Yield 0.18 g (20%). IR (KBr) (cm$^{-1}$: 1384(w), 1333(m), 1252(s), 1022(m), 843(vs), 760(m), 735(m), 694(w), 633(w), 537(s), 511(vs), 434(m), 424(s), 415(m). UV–VIS (toluene): 320sh > 440sh > 600 (broad,extending to 800) nm. EDX (K$\alpha$): Ti:Al:Si = 1:1:1.

### *2.5. Crystal structure analyses of **1** and **3***

Selected crystal fragments of **1** and **3** were mounted into Lindemann glass capillaries under purified nitrogen in a Labmaster 130 glovebox (Braun) and sealed by wax. All X-ray measurements were performed at room temperature. Compound **1** was measured on an STOE IPDS Imaging Plate System (planar graphite monochromator, MoK$\alpha$ radiation, $\lambda = 0.71069$ Å). Diffraction data for **3** were collected on a Philips PW1100 single crystal diffractometer (graphite monochromator, MoK$\alpha$ radiation, $\lambda = 0.71069$ Å). The intensity data were collected by $\omega/2\theta$ scans. The absorption correction was applied using $\Psi$-scans. In both structures the titanium atoms were localized by the Patterson method and all other non-hydrogen atoms by the difference Fourier synthesis [16]. Anisotropic refinement was performed by full matrix least-squares methods based on $F^2$ applying variance-based weighting schemes (SHELXL93, Ref. [17]). The Cp hydrogens were included at their calculated positions and the methyl hydrogens were refined using a riding model. The unit cell of compound **1** contains 3 inequivalent molecules. Compound **3** crystallizes with one molecule of toluene of crystallization in the unit cell. The carbon atoms of this molecule were strongly disordered. The crystal, collection and refinement data for **1** and **3** are summarized in Table 1. Atomic coordinates, thermal parameters, bond lengths and angles and isotropic thermal parameters for **1** and **3** are available together with further details concerning the crystal structure analyses upon request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein–Leopoldshafen, by quoting the deposition numbers CSD-407484 (compound **1**) and CSD-407483 (compound **3**). The data are stored having the CIF and FCF standard of the International Union of Crystallography.

## 3. Results and discussion

(Trimethylsilyl)tetramethylcyclopentadiene reacts with one equivalent of a (benzene)titanium(II) complex in redox reaction (Eq. (2)).



(2)

Table 1
Crystal and structure refinement data for **1** and **3**

| | **1** | **3** |
|---|---|---|
| Chemical composition | $C_{12}H_{21}Al_2Cl_8SiTi$ | $C_{24}H_{42}Al_2Cl_{10}Si_2Ti_2$ |
| Formula weight | 579.5 | 892.3 |
| Crystal system | monoclinic | triclinic |
| Space group | $P2_1/a$ (No. 14) | $P\bar{1}$ (No. 2) |
| $a$, Å | 22.281(5) | 10.372(2) |
| $b$, Å | 10.605(1) | 10.654(1) |
| $c$, Å | 34.395(7) | 11.839(2) |
| $\alpha$, ° | 90 | 76.341(8) |
| $\beta$, ° | 108.70(2) | 73.569(8) |
| $\gamma$, ° | 90 | 68.091(10) |
| Volume, Å$^3$ | 7698(2) | 1151.6(3) |
| $Z$ | 12 | 1 |
| $d_{calc}$ [g cm$^{-1}$] | 1.498 | 1.285 |
| $\mu$ [mm$^{-1}$] | 1.279 | 1.032 |
| $F(000)$ | 3492 | 454 |
| Crystal size [mm$^3$] | 0.4 × 0.5 × 0.8 | 0.7 × 0.4 × 0.2 |
| $\theta$ range for data collection (°) | 1.83–24.26 | 3.11–25.01 |
| Reflections collected | 48453 | 4044 |
| Unique reflections, $R_{int}$ | 12213, 0.0713 | 4044, 0.000 |
| Data, restraints, parameters | 12213, 0, 649 | 4016, 0, 199 |
| Final $R_1$, $wR_2$ [$I > 2\sigma(I)$] | 0.0494, 0.1321 | 0.0560, 0.1233 |
| Final $R1$, $wR_2$ (all data) | 0.0694, 0.1409 | 0.0875, 0.1559 |
| Goodness-of-fit on $F^2$ | 1.09 | 1.194 |
| Largest peak, hole [e Å$^3$] | 1.360, −0.376 | 0.482, −0.489 |

Reaction (2) affords crystalline **1** in 75% yield. Compound **1** forms green, paramagnetic crystals from hexane solution. The ESR spectrum of the toluene solution shows a poorly resolved 11-line spectrum at $g = 1.9698$ indicating the interaction of the Ti(III) $d^1$ electron with two equivalent Al($I_N = 5/2$) nuclei ($a_{Al} = 5.6$ G). In frozen toluene glass, the anisotropic spectrum of cylindrical symmetry shows coupling to the Al nuclei on the perpendicular component of the $g$-tensor ($A(Al)_{\perp} = 5.9$ G). Addition of a ten-fold molar excess of $Et_2AlCl$ results in a coalescence of the solution ESR spectrum into a single line $\Delta H = 10.0$ G at $g = 1.9713$. Coupling to $^{49}Ti$ and $^{47}Ti$ isotopes $a_{Ti} = 15.2$ G, typical of the $Cp'Ti(AlCl_4)_2$ complexes [11,12], is well discernible in spectrum wings of low intensity. In toluene glass, sharp features of the cylindrical $g$-tensor well correspond to $g_{iso}$. These changes follow from the replacement of outer chlorine atoms in the $[AlCl_4]$ ligands by Et groups. The electron-donating effect of Et groups leading to a strong decrease of the unpaired electron density at the aluminium nuclei has been recognized already by Henrici-Olivé and Olivé [18] for the series of cyclopentadienyl derivatives. Similar shifts of $g$-factor to higher values and the disappearance of $a_{Al}$ coupling were generally observed for the methylated cyclopentadienyl [12], pentabenzylcyclopentadienyl [19] and isodicyclopentadienyl [20] complexes of this type upon replacement of $[AlCl_4]$ by $[AlCl_2Et_2]$ ligands. In the series of the $(C_5H_{5-n}Me_n)Ti(AlCl_{4-m}Et_m)_2$ ($n = 0$–5; $m = 0$–2) compounds $g$-factors are shifted by Me groups at the cyclopentadienyl ligand to lower values [12] and hence, $g$-values of **1** and of its ethylated derivative $[C_5Me_4(SiMe_3)]Ti(AlCl_2Et_2)_2$ (**1a**) may indicate whether the effect at the Ti atom of the $C_5Me_4(SiMe_3)$ ligand is closer to that of the $C_5Me_5$ or to that of the $C_5HMe_4$ ligand. Unfortunately, the $g$-factor of **1** is close to that of $(C_5Me_5)Ti(AlCl_4)_2$ ($g = 1.9696$) and the $g$-factor of **1a** is closer to that of $(C_5HMe_4)Ti(AlCl_2Et_2)_2$ ($g = 1.9715$) than to that of $(C_5Me_5)Ti(AlCl_2Et_2)_2$ ($g = 1.9708$) [12]. The electronic absorption spectrum of **1** shows two intense absorption bands at 402 (A) and 485 (B) nm and a weak band at 660 (C) nm. The intense bands were tentatively assigned to charge transfer transitions and the weak band to a d–d transition similarly as in the series of the methyl substituted complexes [12]. Of these bands, the band denoted (A), which is the most sensitive to the numbers of Me ($n$) and Et ($m$) substituents, is close to the position of analogous band (A) of the $(C_5H_2Me_3)Ti(AlCl_4)_2$ complex (405 nm); the bands (B) and (C) in **1** are close to the bands of the $Me_4$ or $Me_5$ complexes. In **1a**, the band (C) is shifted to longer wavelength (700 nm), the position found in $(C_5HMe_4)Ti(AlCl_2Et_2)_2$, however, the CT bands

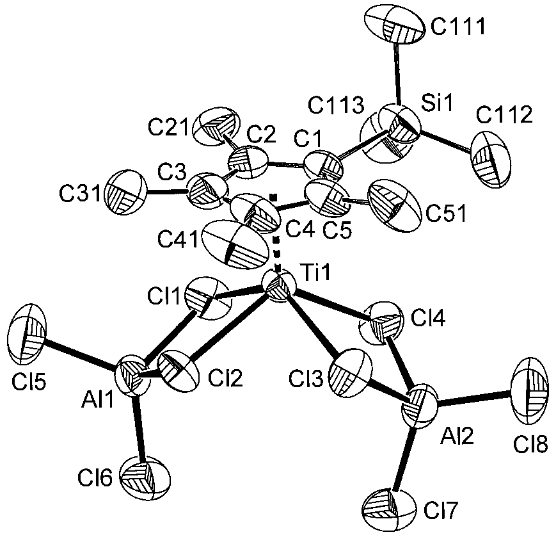
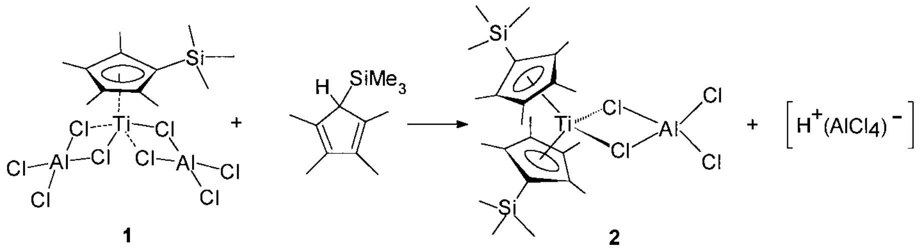


Fig. 1. ORTEP representation of **1** drawn at 30% probability level and atom numbering scheme for molecule (**1**).

merged into one band at 420 nm, the effect which has not been previously observed. These results mean that the $SiMe_3$ group has to be considered as a specific substituent and not as a ligand bearing a proportional equivalent of electron donating/attracting strength of Me or H substituents. The molecular structure of **1** is further confirmed by the X-ray crystal diffraction analysis (vide infra).

A five-fold excess of $C_5HMe_4(SiMe_3)$ with respect to $(C_6H_6)Ti(AlCl_4)_2$ affords a mixture of two products which have been separated by fractional crystallization. The paramagnetic complex $[C_5Me_4(SiMe_3)]_2Ti(III)(AlCl_4)$ (**2**) is a major product and the diamagnetic dimer $\{[C_5Me_4(SiMe_3)]Ti(AlCl_4)(\mu\text{-}Cl)\}_2$ (**3**) is a minor product. The identification of pale green **2** is based on its ESR spectrum ($g = 1.9755$, $a_{Al} = 7.7$ G, $a_{Ti} = 10.2$ G) showing the interaction of the unpaired electron with one Al nucleus and the coupling to $^{47}Ti$ and $^{49}Ti$ isotopes typical of the series of $(C_5H_{5-n}Me_n)_2Ti(AlCl_4)$ compounds. The ESR parameters of **2** fit closely to the parameters of the $(C_5HMe_4)_2Ti(AlCl_4)$ complex [21]. The presence of one $SiMe_3$ group at the cyclopentadienyl ligand follows from the EDX measurement showing the ratio Ti:Al:Si ~ 1:1:2 and from IR spectrum showing bands at 1250 $cm^{-1}$ and 845 $cm^{-1}$ which are characteristic of the $SiMe_3$ group. The composition is further corroborated by chemical analysis yielding the Ti:Al:Cl ratio 1:1:4.

The molecular structure of turquoise compound **3** has been determined by the X-ray crystal analysis (vide



(3)

In the case of monomeric cyclopentadiene, the proton induced a rapid and effective polymerisation of cyclopentadiene, and the polymer formed precluded the isolation of $(C_5H_5)_2Ti(AlCl_4)$ [10]. This is observed neither in the present case, nor in the case of highly methylated cyclopentadienes [12,21]. The protonisation

Table 2
Selected bond distances (Å) and angles (°) for compound **1** (minimum and maximum values found in **3** inequivalent molecules)

| Atoms | Distances | Atoms | Angles |
|---|---|---|---|
| Ti–CE | 1.983(4)–1.992(4) | CE–Ti–Cl | 110.7(1)–122.3(1) |
| Ti–C | 2.251(4)–2.393(4) | $Cl–Ti–Cl_{bridge}$ | 77.73(4)–79.05(4) |
| Ti–Cl | 2.515(2)–2.570(2) | Cl–Ti–Cl | 79.04(5)–81.26(5) |
| $Al–Cl_{bridge}$ | 2.169(2)–2.186(2) | Al–Cl–Ti | 91.70(6)–94.19(6) |
| $Al–Cl_{outer}$ | 2.066(2)–2.088(2) | $Cl–Al–Cl_{bridge}$ | 94.55(7)–95.70(7) |
| $C_{Cp}–Si$ | 1.890(4)–1.905(4) | $Cl–Al–Cl_{outer}$ | 114.64(9)–117.19(9) |
| $Si–C_{Me}$ | 1.843(6)–1.874(6) | $\phi$[a] | 91.6–94.4 |
| $(C–C)_{Cp}$ | 1.381(6)–1.461(6) | $\Omega$[b] | 85.0–96.2 |
| $C–C_{Me}$ | 1.489(7)–1.532(7) | $\epsilon$[c] | 1.0–6.7 |

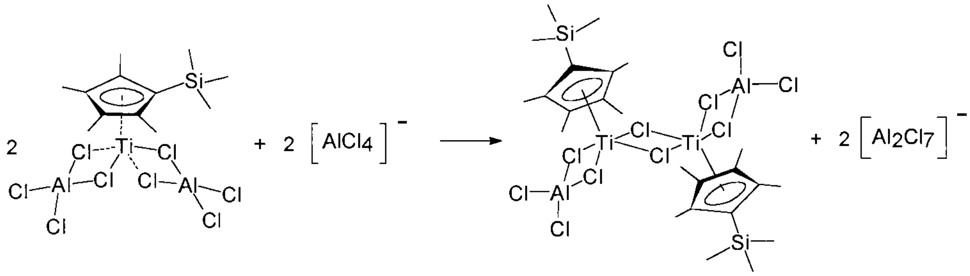
[a] Dihedral angle between the Al–Ti–Al plane and the least squares plane of the $C_5Me_4(SiMe_3)$ ring.

[b] Dihedral angle between the Al–Ti–Al and $Cl_{bridge}–Ti–Cl_{bridge}$ planes.

[c] Dihedral angle between the Al–Ti–Al and $Cl_{outer}–Al–Cl_{outer}$ planes.

of these cyclopentadienes apparently leads to a low-molecular products.

The minor product **3** probably arises from elimination of one molecule of $AlCl_3$ from **1** under the action of a base. The latter can be either the $[AlCl_4]^-$ anion yielding a more stable anion $[Al_2Cl_7]^-$ (Eq. (4))



**1** **3** (4)

or an organic product arising from above suggested conversions of excess $C_5HMe_4(SiMe_3)$.

### *3.1. X-ray structures of **1** and **3***

The X-ray analysis of **1** found 3 inequivalent molecules in a monoclinic unit cell, differing mostly by the orientation of the $C_5Me_4(SiMe_3)$ ligand with respect to the Al–Ti–Al molecular plane and by bending of the bridging Ti($\mu$-Cl)$_2$Al skeletons. A PLUTO drawing of molecule (1) with the atom numbering scheme is shown in Fig. 1. The pyramidal structure of the (CE)Ti$(AlCl_4)_2$ (CE-centroid of the $C_5$-ring) skeleton with CE at the apex and four bridging chlorine atoms in the basis is very similar to previously established structures of Cp′Ti$(AlCl_4)_2$ compounds [19,20]. The minimum and maximum values of selected bond lengths and angles for the 3 molecules of **1** are listed in Table 2. The previously found parameters of $(C_5H_5)Ti(AlCl_4)_2$, $(C_5Bz_5)Ti(AlCl_4)_2$ [19], and (isodicp)Ti$(AlCl_4)_2$ (isodicp-tricyclo[5.2.1.0$^{2,6}$]deca-2,5-dien-4-yl, $C_{10}H_{11}$) [20] fall within the values found for the three molecules of **1**. The $SiMe_3$ group of the $C_5Me_4(SiMe_3)$ ligand is orientated into the sector determined by two neighbouring chlorine atoms of two $[AlCl_4]$ ligands, and the three molecules slightly differ in the position of the $SiMe_3$ group. All carbon atoms of Me groups deviate from the least-squares plane of the $C_5Me_4(SiMe_3)$ ligand farther away from the Ti atom (max. by 0.17 Å); deviations of silicon atoms in the same sense are yet larger (max. by 0.32 Å). The CE point lies by 0.1 Å from the Al–Ti–Al plane on the opposite side than the $SiMe_3$ group. The distance of Ti from the least-squares plane is only about one esd's shorter than the CE–Ti distance. The inorganic skeleton is essentially regular. The least-squares plane of the $C_5Me_4(SiMe_3)$ ring and the planes of Ti and bridging Cl atoms and Al and bridging Cl atoms are perpendicular to the Al–Ti–Al molecular plane within 5°. The planes formed by bridging Cl atoms and Al and by outer Cl atoms and Al are mutually perpendicular within 1°. Discernible deviations of some parameters in one of the three inequivalent molecules are apparently caused by the crystal packing effects.

The minor product **3** has been identified by X-ray crystal analysis as a centrosymmetric dimer (see Fig. 2). The Ti atoms are linked by two bridging chlorine atoms in a planar bridging skeleton with slightly unequal Ti–Cl bond lengths (2.440(2) Å and 2.500(2) Å). The Ti–Ti distance of 3.818 Å does not imply any direct bonding interaction. The $SiMe_3$ group of the $C_5Me_4(SiMe_3)$ ligand is orientated in a side position with respect to the CE–Ti–Ti′ plane. The angle between the least-squares plane of the $C_5Me_4(SiMe_3)$ ring and the reference Ti–Cl–Cl′ plane is 32.6°. The angle between the latter plane and the Ti, Cl(2), Cl(3) plane is 113.2°. The bridging four-membered ring between the Ti and Al atoms is planar within 3.9°. The planes of bridging and outer chlorine atoms involving the central aluminium atom are mutually perpendicular. The molecule is slightly distorted as the planes defined by CE, Ti and Ti′ atoms and by CE, Ti, and Al atoms form a dihedral angle of 5.3°. The selected bond distances

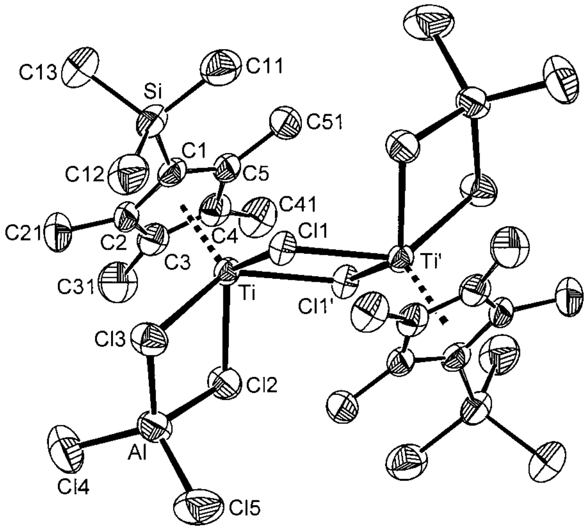


Fig. 2. ORTEP representation of **3** drawn at 30% probability level and atom numbering scheme.

Table 3
Selected bond distances[a] (Å) and angles (°) for **3**

| Atoms | Distance | Atoms | Distance |
|---|---|---|---|
| Ti–C(1) | 2.317(5) | Ti–C(2) | 2.399(5) |
| Ti–C(3) | 2.413(5) | Ti–C(4) | 2.340(5) |
| Ti–C(5) | 2.280(5) | Ti–Cl(1) | 2.440(2) |
| Ti–Cl(1)′ | 2.4995(14) | Ti–Cl(2) | 2.542(2) |
| Ti–Cl(3) | 2.620(2) | Ti–CE | 2.014(6) |
| Al–Cl(2) | 2.186(2) | Al–Cl(3) | 2.176(2) |
| Al–Cl(4) | 2.082(2) | Al–Cl(5) | 2.092(3) |
| $(C-C)_{Cp}$(av.) | 1.424(7) | C(1)–Si(1) | 1.896(5) |
| $(C_{Cp}-C_{Me})$(av.) | 1.503(8) | $(Si-C_{Me})$(av.) | 1.861(6) |

| Atoms | Angle | Atoms | Angle |
|---|---|---|---|
| Cl(1)–Ti–Cl(1)′ | 78.78(5) | Ti–Cl(1)–Ti′ | 101.22(5) |
| Cl(1)–Ti–Cl(2) | 125.01(5) | Cl(1)′–Ti–Cl(2) | 79.98(5) |
| Cl(1)–Ti–Cl(3) | 82.68(5) | Cl(1)′–Ti–Cl(3) | 134.01(5) |
| Cl(2)–Ti–Cl(3) | 77.04(5) | Cl(1)–Ti–CE | 121.1(2) |
| Cl(2)–Ti–CE | 113.9(2) | Cl(3)–Ti–CE | 112.3(2) |
| Cl(1)′–Ti–CE | 113.4(2) | Al–Cl(2)–Ti | 94.89(7) |
| Al–Cl(3)–Ti | 92.94(7) | Cl(3)–Al–Cl(2) | 94.99(8) |
| Cl(4)–Al–Cl(5) | 114.54(11) | Cl(4)–Al–Cl(3) | 113.45(10) |
| Cl(5)–Al–Cl(3) | 111.22(11) | Cl(4)–Al–Cl(2) | 111.22(10) |
| Cl(5)–Al–Cl(2) | 109.75(10) | C(2)–C(1)–Si | 123.8(4) |
| C(5)–C(1)–Si | 130.1(4) | | |

[a] Non bonding distance: Ti–Ti′ 3.818(2) Å.

and angles for **3** are listed in Table 3. Those which concern the $[AlCl_4]$ and $C_5Me_4(SiMe_3)$ ligands fall into the limits found for **1**.

## 4. Conclusions

The redox reaction of (trimethylsilyl)tetramethylcyclopentadiene with $(C_6H_6)Ti(AlCl_4)_2$ affords an effective entry into the chemistry of $[C_5Me_4(SiMe_3)]Ti(III)$ derivatives via compound $[C_5Me_4(SiMe_3)]Ti(AlCl_4)_2$ (**1**). The replacement of one Me group in $C_5Me_5$ by $SiMe_3$ does not observably slow down the redox reaction of the cyclopentadiene with the (benzene)Ti(II) complex, and compound **1** exerts a good thermal stability as exemplified by its X-ray structure determination. Since the steric hindrance is absent in this type of complexes stability of **1** can be attributed to an electron releasing effect of the $SiMe_3$ group. Analogous preparation of titanocene complex $[C_5Me_4(SiMe_3)]_2Ti(AlCl_4)$ (**2**) is less suitable since a large excess of $C_5HMe_4(SiMe_3)$ is required, and the dimeric byproduct $\{[C_5Me_4(SiMe_3)]Ti(AlCl_4)(\mu\text{-}Cl)\}_2$ (**3**) is formed. The isolation of **3** gives a good prospect for obtaining of the so far unexplored class of dimeric complexes analogous to **3**.

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