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A novel cyclic titanasiloxane derived from $[Ph_2Si(OH)]_2O$: synthesis and crystal structure of $[Cp^*Ti(Cl)(OSiPh_2OSiPh_2OSiPh_2O)]$

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Dedicated to Professor B. Viswanathan on the occasion of his 60th birthday

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Abstract

Reaction of $Cp^*Ti(OAr)Cl_2$ ($Ar = 2,6\text{-}Me_2C_6H_3$) with dilithium salt of $[Ph_2Si(OH)]_2O$ in a 1:1 molar ratio in toluene at room temperature yields titanatrisiloxane ring compound $[Cp^*Ti(Cl)(OSiPh_2OSiPh_2OSiPh_2O)]$ (**1**). Siloxane chain-expansion effect has been observed in the product formation, which is presumed to be a consequence of the ring strain in the titanadisiloxane system. Compound **1** has been characterized by microanalysis, IR, and NMR spectroscopic techniques. The molecular structure of **1** determined by X-ray diffraction reveals that the central eight-membered $TiSi_3O_4$ siloxane-ring exists in an unusual *butterfly-like* conformation. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Titanasiloxanes; Cyclopentadienyl complexes; Silanols; Siloxides

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1. Introduction

Organosilicon compounds containing Si–O–M linkage have been around for the last hundred years [1–3]. However, only recently, metallasiloxanes derived from discrete molecular silanols such as silanediols $R_2Si(OH)_2$, silanetriols $RSi(OH)_3$, and incompletely condensed silasesquioxanes $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$ have been reported [4–6]. Their chemistry has evoked a lot of interest among chemists, material scientists and physicists in view of their potential applications. The presence of metal in the siloxane framework often results in high thermal stability, catalytic and conducting properties. Moreover, silicon polymers containing metal centers in the backbone have metallasiloxanes as their precursors. A variety of organic transformations, which are catalyzed by transition metal complexes anchored on silica surfaces, make the metallasiloxane chemistry more relevant because of the structural similarities of modified silica surfaces to molecular metallasiloxanes [6].

In view of the proven properties of titanasilicates as catalysts in several organic transformations, there has been an upsurge in the synthesis of molecular and organic-soluble titanasiloxanes with a variety of structures [7,8]. A few examples of recently reported ring-like and cage-like molecular titanasiloxanes are shown in Charts 1 and 2, respectively. As these examples indicate, it is possible to vary the titanium to silicon ratio by a proper choice of the starting materials. Thus, titanasiloxanes with a Ti:Si ratio of 1:1, 1:3, 1:4, 1:6, 1:7, and 1:8 have been so far realized [8–18]. Among these titanasiloxanes, compound E (Chart 2) [16] has been in focus in view of its diverse utility as (a) a homogeneous catalyst [19]; (b) a heterogeneous catalyst after anchoring inside MCM-41 [20]; and (c) a molecular precursor for mixed oxide materials [21].

Continuing our interest in the chemistry of titanasiloxanes [22], we wish to report in this paper on the synthesis and characterization of a novel titanasiloxane with a ring structure having a metal to silicon ratio of 1:3.

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2. Results and discussion

Apart from the above described interest in the chemistry of titanasilicates, the last few years have also witnessed a sudden upsurge in the chemistry of titanium aryloxides due to their use as Diels–Alder and cross-coupling/oligomerization catalysts [23]. There have been also reports on the use of [Cp*Ti(OAr)C1_2] [24,25] for the preparation of cationic alkyl derivatives of titanium which have been found to be useful homogeneous catalysts [23b]. In order to study the reactivity of these aryloxide compounds, we have now investigated the reactions of [Cp*Ti(OAr)C1_2] with [$Ph_2Si(OH)]_2O$.

*2.1. Synthesis and characterization of [Cp*Ti(Cl){O(SiPh$_2$O)$_2$SiPh$_2$O}} (**1**)*

A 1:1 molar ratio reaction of [Cp*Ti(OAr)C1_2] (Ar = 2,6-$Me_2C_6H_3$) with dilithium salt of [$Ph_2Si(OH)]_2O$ was carried out at the room temperature (r.t.) (Scheme 1). The work-up of the reaction mixture to remove LiCl followed by slow crystallization of the resulting brownish–yellow solid from light petroleum ether solution resulted in the deposition of golden-yellow crystals of **1** along with a dark-brown amorphous material which could not be fully characterized. Titanosiloxane **1** did not contain the aryloxide group, and it has probably formed via an aryloxide–siloxide exchange reaction. The examination of the dark-brown byproduct by ^{1}H-NMR showed the presence of aryloxy groups, indicating a possible redistribution reaction during the formation of **1**.

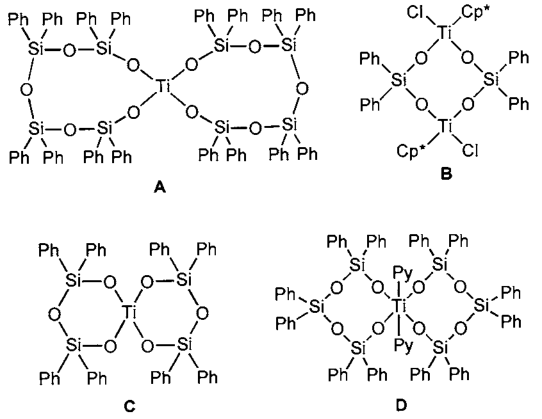


Chart 1. Cyclic titanosiloxanes derived from Ph_2SiO_2 unit.

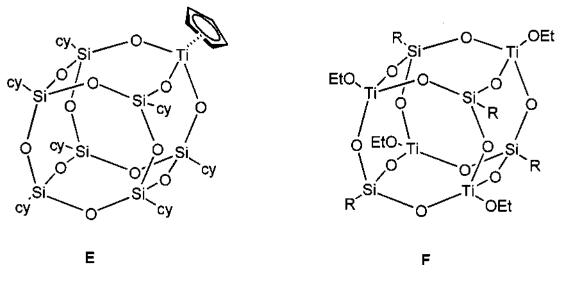
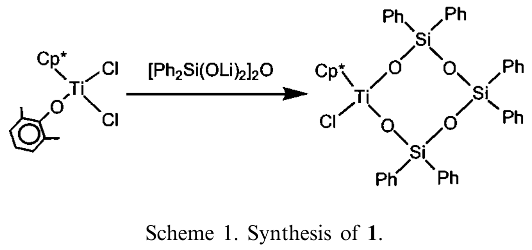


Chart 2. Cage-like titanosiloxanes.



Scheme 1. Synthesis of **1**.

The titanasiloxane **1** has been fully characterized with the aid of elemental analysis, and IR and NMR spectroscopic studies. The compound shows good thermal stability and melts only at 206°C. It can also be handled in air for extended periods, suggesting its good hydrolytic stability. The microanalysis of the product suggested a possible ring-expansion reaction to result in a trisiloxane unit compared to the disiloxane unit in the starting material.

The IR spectrum of the compound contains bands due to the ν(Ti–O) at ca. 910 cm^{-1} and ν(Si–O–Si) at ca. 1156 cm^{-1}. There is also strong absorption around 980 cm^{-1} which we attribute to the Ti–O–Si stretching vibration based on the earlier assignment made by Roesky and coworkers through ^{18}O labeling studies [10]. However, it should be mentioned that this vibration has been attributed to the Ti=O group by some authors [26] and Si–O [27] or Si–$O^{\delta-}$–$Ti^{\delta+}$ [28] by others. The ^{1}H-NMR spectrum of **1** shows a singlet for the protons of the methyl groups of C_5Me_5 ring (δ 1.94) and a very complex multiplet pattern for the protons of the phenyl rings present on the three different silicon atoms.

*2.2. Crystal structure of [Cp*Ti(Cl){(O(SiPh$_2$O)$_2$SiPh$_2$O}] (**1**)*

In order to clearly establish the structure of **1** in the solid-state, its molecular structure was determined by a single crystal X-ray diffraction study. A perspective view of the molecule in the asymmetric part of the unit cell is depicted in Fig. 1. The Ti atom in the compound has a distorted tetrahedral geometry. Further, the structure of **1** reveals that the eight-membered siloxane ring exists in a *butterfly-like* conformation, in contrast to the commonly observed crown structure in several metallasiloxanes [4]. This conformation of the Si_3TiO_4 ring is quite evident when the ring is viewed along the Ti···Si axis as shown in Fig. 2. Titanasilixoanes with an eight-membered ring structure serve as useful model for the S4R secondary building units of titanasilicates and zeolites [29]. Compound **1** is one of the rare examples of such a system, especially with titanium to silicon

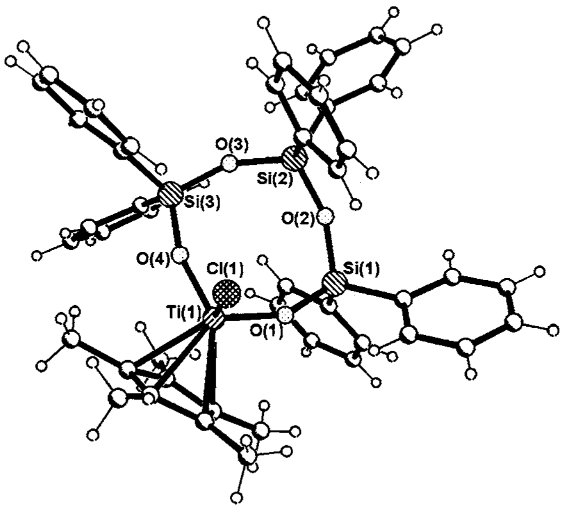


Fig. 1. A perspective view of titanasiloxane **1**.

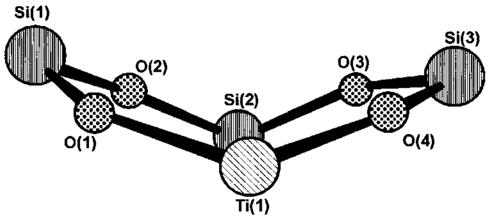


Fig. 2. A plot depicting the conformation of the central eight-membered ring in **1**.

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

Ti(1)–O(1)	1.804(2)	Ti(1)–O(4)	1.825(2)
Ti(l)–Cl(1)	2.271(1)	Si(1)–O(2)	1.625(2)
Si(1)–O(1)	1.629(2)	Si(2)–O(2)	1.614(2)
Si(2)–O(3)	1.630(2)	Si(3)–O(4)	1.627(2)
Si(3)–O(3)	1.631(2)		
O(1)–Ti(1)–O(4)	103.9(1)	O(1)–Ti(1)–Cl(1)	102.3(1)
O(4)–Ti(1)–Cl(1)	103.3(1)	O(1)–Ti(1)–C(61)	105.2(1)
O(4)–Ti(1)–C(61)	93.1(1)	Cl(1)–Ti(1)–C(61)	143.4(1)
O(1)–Ti(1)–C(65)	139.5(1)	O(4)–Ti(1)–C(65)	88.7(1)
Cl(1)–Ti(1)–C(65)	112.1(1)	O(1)–Ti(1)–C(62)	84.8(1)
O(4)–Ti(1)–C(62)	126.4(1)	Cl(1)–Ti(1)–C(62)	126.7(1)
O(1)–Ti(1)–C(64)	135.4(1)	O(4)–Ti(1)–C(64)	116.9(1)
CI(1)–Ti(1)–C(64)	85.7(1)	O(1)–Ti(1)–C(63)	100.9(1)
O(4)–Ti(1)–C(63)	146.1(1)	Cl(1)–Ti(1)–C(63)	93.5(1)
O(2)–Si(1)–O(1)	109.5(1)	O(2)–Si(1)–C(11)	108.8(1)
O(1)–Si(1)–C(11)	107.9(1)	O(2)–Si(1)–C(1)	107.6(1)
O(1)–Si(1)–C(1)	108.3(1)	C(11)–Si(1)–C(1)	114.8(1)
Si(1)–O(1)–Ti(1)	152.7(1)	Si(2)–O(2)–Si(1)	156.8(2)
Si(2)–O(3)–Si(3)	144.9(1)	Si(3)–O(4)–Ti(1)	163.0(1)

ratio of 1:3. Incidentally, only one other titanatrisiloxane, $[Ti(acac)_2\{O(SiPh_2O)_2SiPh_2O\}]$, with this Ti:Si stoichiometry has been reported earlier [30]. However, in this molecule, the titanium atom is in an octahedral coordination environment, compared to the pseudo-tetrahedral environment around Ti in **1**.

Selected bond distances and angles in molecule **1** are listed in Table 1. A structural comparison of **1** with related titanasiloxanes $Ti(O(SiPh_2O)_3\ SiPh_2O)_2$ (**A**) [18] and *cis*-$[Ti\{O(SiPh_2O)_2SiPh_2O\}(py)_2]$ (**D**) [14] is presented in Table 2. The formation of all the products listed in Table 2 has involved a chain-expansion reaction in order to relieve the ring strain in the titanadisiloxane system. The bond parameters for all the three compounds are almost similar. The Si atom adopt nearly ideal tetrahedral geometry; the average O–Si–O angle around it being 109.62°.

3. Conclusion

Thus, it has been shown here that the reaction between the aryloxy derivative of Cp^*TiCl_3 and a disiloxanesilanediol can be used to synthesize an eight-membered ring titanatrisiloxane which structurally resembles the S4R secondary building unit of zeolites [29]. The presence of a reactive Ti–Cl bond in complex **1** offers additional opportunities for further derivatization reactions (e.g. substitution of Cl by an alkyl, –OH or $-NR_2$ groups).

4. Experimental

All the experimental manipulations were carried out in a dry pre-purified nitrogen atmosphere using Schlenk techniques excluding moisture and air. Solvents were purified by conventional procedures and were freshly distilled prior to use. Unless otherwise stated, reagents were obtained from commercial sources and used as received. $[Cp^*Ti(OAr)C1_2]$ ($Ar = 2,6\text{-}Me_2C_6H_3$) was prepared according to a reported method [25].

IR spectra was recorded in Nujol mulls between CsI pellets over the range 4000–400 cm^{-1} on a Nicolet Impact-400 FTIR spectrophotometer. The ^1H-NMR spectra were recorded on a Varian VXR 300S spectrometer. Chemical shifts (δ ppm) were measured relative to residual ^1H-resonances for chloroform-d_1 used as

Table 2
Comparison of structural parameters of **1** with related ring titanosiloxanes derived from disilanediols

Parameter	1	A	D
Av. Ti–O(*endo*) (Å)	1.815	1.782	1.855
Av. Si–O(*endo*) (Å)	1.626	1.623	1.618
Si–O–Si (°)	144.85, 156.8	143.8–172.5	146.4, 156.0
Si–O–Ti (°)	157.865	156.4–173.3	154.85
Av. O–Si–O (°)	109.62	109.2	111.53
Av. O–Ti–O (°)	103.92	109.467	99.05

solvent. C, H and N analyses were carried out on a Carlo Eraba 1106 microanalyser. The X-ray intensity data for **1** were obtained on a Nonius MACH-3 X-ray diffractometer at r.t.

4.1. Synthesis of [CP*Ti(Cl){O(SiPh$_2$O)$_2$SiPh$_2$O}] (1)

A solution of Cp*Ti(OAr)Cl$_2$ (Ar = 2,6-Me$_2$C$_6$H$_3$) [25] (0.648 g, 1.72 mmol) in toluene (50 ml) was added to a solution of dilithium salt of [Ph$_2$Si(OH)]$_2$O [31] (0.737 g, 1.7 mmol) in THF and the mixture was stirred overnight at 25°C. It was then refluxed for 5 h and the solvent was removed in vacuo. The residue was redissolved in petroleum ether (b.p. 60–80°C) and the solution was filtered off. The solution is concentrated by removing half of the solvent in vacuo and left for crystallization. Golden yellow crystals were obtained at 0°C after 2 days. Yield: 40% (based on Cp*Ti(OAr)Cl$_2$). M.p. 206°C. Anal. Calcd. for $C_{46}H_{45}ClO_4Si_3Ti$: C, 66.6; H, 5.47. Found: C, 67.03; H, 5.03%. IR (Nujol, CsI): 1383, 1274, 1056, 980, 910, 807, 737, 519 cm^{-1}. ^{1}H-NMR (300 MHz, CDCl$_3$): δ 1.94 (s, 15H, C$_5$Me$_5$), 7.0–7.6 (complex multiplets, 30H, Ph).

4.2. X-ray structure determination of 1

Golden yellow single crystals of **1** were grown from a dilute petroleum ether solution at 0°C. Smaller crystals suitable for X-ray diffraction studies were chosen from the bulk and mounted on a Nonius MACH3 four circle diffractometer for the cell determination and intensity data collection. The unit cell parameters were derived and refined by using randomly selected 25 reflections in the 2θ range 20–25°. The structure was solved by direct-methods using SHELXS-86 [32] and refined by SHELXL-97 [33]. The hydrogen atoms attached to carbon atoms were geometrically fixed and refined using a riding model. Crystal data: $C_{46}H_{45}ClO_4Si_3Ti$, $M = 829.44$, monoclinic, $P2_1/a$, $a = 20.520(2)$, $b = 10.570(2)$, $c = 21.059(2)$ Å, $\beta = 105.093(8)°$, $U = 4410(1)$ Å^3, $D_{calc} = 1.249$ Mg m^{-3}, $Z = 4$, $F(000) = 1736$, $\lambda = 0.71073$ Å, $\mu = 0.377$ mm^{-1}, unique reflections = 7737, $T = 293(2)$ K. θ range = 2.0–25.0°. Final R [$I > 2\sigma(I)$]: $R_1 = 0.0472$, $wR_2 = 0.1091$, R (all data): $R_1 = 0.0985$, $wR_2 = 0.1191$.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 151485. 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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