

Short communication

Synthesis of Organotitanium(IV) Fluoride Phosphates and the Crystal Structure of $[(C_5Me_4Et)TiF(\mu-F)\{\mu-O_2P(OSiMe_3)_2\}]_2$

Andrej Pevec,^{1,*} Alojz Demšar,¹ Jiri Pinkas² and Marek Necas²

¹ Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, SI-1000 Ljubljana, Slovenia

² Department of Chemistry and CEITEC MU, Masaryk University, Kotlarska 2, CZ-61137 Brno, Czech Republic

* Corresponding author: E-mail: andrej.pevec@fkt.uni-lj.si

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Abstract

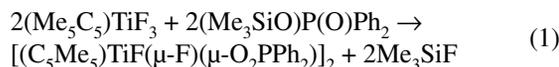
The complexes $[(C_5Me_4R)TiF(\mu-F)\{\mu-O_2P(OSiMe_3)_2\}]_2$ [R = Me (1), Et (2)] were prepared from $[(C_5Me_4R)TiF_3]_2$, (R = Me, Et) and $OP(OSiMe_3)_3$. The molecular structure of **2** has been determined by single-crystal X-ray diffraction analysis. An eight-membered $Ti_2O_4P_2$ metallacycle bridged by two fluorine ligands between two titanium centers is observed.

Keywords: Titanium, fluoride, phosphate, X-ray structure.

1. Introduction

In the recent years, a number of the Group 4 organometallic fluorides and organotitanium mixed-metal complexes have been prepared and structurally characterized.¹ This work was made possible by the discovery of Me_3SnF as a mild and very effective fluorinating agent in comparison with other fluorinating reagents.² This tool opened the chemistry of organotitanium fluoride complexes and number of them have been well characterized by X-ray crystallography.

In many of these cases, the driving force in the reactions is the formation of trimethylsilyl fluoride as a byproduct. Thus, the reaction of trimethylsilyl esters of sulfonic, phosphonic and carboxylic acids in combination with $(C_5Me_5)TiF_3$ can lead to the formation of organotitanium sulphonates, phosphinates and carboxylates.^{3,4} The phosphinate complex which is derived from the reaction (1) is covalent dinuclear complex with the titanium atoms bridged by two fluorine atoms as well as by two phosphinate groups.



Titanium fluoride complexes were found as very efficient and enantioselective bifunctional asymmetric ca-

talysts.⁵ The high electronegativity of fluorine makes the titanium atom a strongly Lewis acidic centre capable of binding a carbonyl oxygen atom while fluorine interacts with silicon or aluminium of the nucleophilic reagents.^{6–8} We are interested in the preparation of new organotitanium mixed fluoro-oxo complexes as new potential catalysts. For this purpose, we explored the reactions of organotitanium fluorides $[(Me_5C_4R)TiF_3]_2$, (R = Me, Et) with trimethylsilyl ester of phosphoric acid. We are not aware of any other report of organotitanium(IV) fluoride containing phosphate ligand.⁹ The present article discusses the synthesis, characterization and structural properties of the first organotitanium fluoride phosphates $[(C_5Me_4R)TiF(\mu-F)\{\mu-O_2P(OSiMe_3)_2\}]_2$ [R = Me (1), Et (2)].

2. Experimental

2.1. General

All manipulations were performed under a dry nitrogen atmosphere by Schlenk techniques or in a M. Braun Unilab dry box. Solvents were dried over and distilled from Na/benzophenone under nitrogen. Compounds $[(C_5Me_5)TiF_3]_2$, $[(C_5Me_4Et)TiF_3]_2$ were prepared according to the previously published procedures.² $OP(OSiMe_3)_3$ was purchased from Aldrich. NMR spectra (¹H, ¹⁹F and ³¹P) were acquired on Avance DRX 300 MHz spectro-

meter at 30 °C. Chemical shifts were referenced to the residual resonances of solvent (7.26 ppm for ^1H in CDCl_3). IR spectra (4000–400 cm^{-1}) were collected on an EQUINOX 55/S/NIR FTIR spectrometer. The samples were prepared as KBr pellets.

2. 2. Typical Procedure for the Reactions

Neat $\text{OP}(\text{OSiMe}_3)_3$ (0.131 g, 0.417 mmol) was added dropwise by a syringe to the stirred solution of $[(\text{C}_5\text{Me}_5)\text{TiF}_3]_2$ (0.100 g, 0.417 mmol) in dry deoxygenated THF (20 mL). The reaction mixture was then stirred for 24 h, and all the volatiles were removed under vacuum.

2. 3. Spectral Data of New Compounds

$[(\text{C}_5\text{Me}_5)\text{TiF}(\mu\text{-F})\{\mu\text{-O}_2\text{P}(\text{OSiMe}_3)_2\}]_2$ (**1**). The residue was dissolved in hexane (6 mL) and cooled to -24 °C. Orange crystals of **1** were obtained in three days. ^1H NMR (300 MHz, CDCl_3): δ 2.19 and 2.16, 1.10 (three s, 30H, C_5Me_5), 0.38 (s, 36H, SiCH_3) ppm. ^{19}F NMR (282 MHz, CDCl_3): δ 6.50 and 6.20 (two d, $J_{\text{FF}} = 61$ Hz), -19.05 (two overlapping t, $J_{\text{FF}} = 96$ Hz), -35.17 and -35.53 (two t, $J_{\text{FF}} = 37$ Hz), -53.14 (t, $J_{\text{FF}} = 29$ Hz) ppm. ^{31}P NMR (122 MHz, CDCl_3): δ -17.80 (d), -20.60 (s), -24.54 (s) ppm. IR (KBr pellet, cm^{-1}): 3436 bs, 2960 s, 2912 s, 1256 s, 1110 vw, 1032 vw, 851 s, 758 s, 656 s, 588 bs, 494 bs.

$[(\text{C}_5\text{Me}_4\text{Et})\text{TiF}(\mu\text{-F})\{\mu\text{-O}_2\text{P}(\text{OSiMe}_3)_2\}]_2$ (**2**). The solid residue was dissolved in hexane (6 mL). The compound **2** crystallized overnight in the form of orange crystals by a slow evaporation of the solvent at a reduced pressure. ^1H NMR (300 MHz, CDCl_3): δ 2.69 and 2.57 (two q, 4H, CH_2CH_3), 2.18 and 2.07 (two m, 24H, C_5Me_4), 0.96 and 0.86 (two t, 6H, CH_2CH_3), 0.34 (m, 36H, SiCH_3) ppm. ^{19}F NMR (282 MHz, CDCl_3): δ 7.40 and 7.12 (two d, $J_{\text{FF}} = 63$ Hz), -12.53 (t, $J_{\text{FF}} = 94$ Hz), -35.18 and -35.55 (two t, $J_{\text{FF}} = 38$ Hz), -53.25 (t, $J_{\text{FF}} = 28$ Hz) ppm. ^{31}P NMR (122 MHz, CDCl_3): δ -16.29 (s), -19.44 (s), -24.55 (s) ppm. IR (KBr pellet, cm^{-1}): 3433 bs, 2963 s, 2912 s, 2872 s, 1254 s, 1133 vw, 1108 vw, 1031 vw, 851 s, 760 s, 655 s, 596 s, 500 s, 415 bs.

2. 4. X-ray Structure Determination

Diffraction data were collected on a KUMA KM-4 κ -axis diffractometer with graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073$ Å) and a CCD camera at 120 K. The intensity data were corrected for Lorentz and polarization effects. The structures were solved by direct methods using SIR-92¹⁰ and refined with a full-matrix least-squares procedure based on F^2 using SHELXL-97.¹¹ All of the non-hydrogen atoms were refined anisotropically while the hydrogen atoms were positioned geometrically and refined as riding.

Crystal structure analysis for **2**: $\text{C}_{34}\text{H}_{70}\text{F}_4\text{O}_8\text{P}_2\text{Si}_4\text{Ti}_2$, $M = 953.00$ g mol $^{-1}$, triclinic system, space group $P-1$, $a = 10.046(2)$, $b = 11.109(2)$, $c = 12.111(2)$ Å, $\alpha = 66.49(2)$, $\beta = 72.18(2)$, $\gamma = 79.16(1)^\circ$, $V = 1176.5(3)$ Å 3 , $Z = 1$, $D_x = 1.345$ g cm $^{-3}$, $\mu = 0.568$ mm $^{-1}$, 16304 reflections measured, 5359 were independent of symmetry, of which 3474 were observed [$I > 2\sigma(I)$], $R_1 = 0.0378$, wR_2 (all data) = 0.0824, 255 parameters.

CCDC-844363 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3. Results and Discussion

The reaction of $[(\text{C}_5\text{Me}_5)\text{TiF}_3]_2$ and $[(\text{C}_5\text{Me}_4\text{Et})\text{TiF}_3]_2$ with $\text{OP}(\text{OSiMe}_3)_3$ in a 1:1 molar ratio in THF resulted in the formation of $[(\text{C}_5\text{Me}_5)\text{TiF}(\mu\text{-F})\{\mu\text{-O}_2\text{P}(\text{OSiMe}_3)_2\}]_2$ (**1**) and $[(\text{C}_5\text{Me}_4\text{Et})\text{TiF}(\mu\text{-F})\{\mu\text{-O}_2\text{P}(\text{OSiMe}_3)_2\}]_2$ (**2**), respectively. The structures of **1** and **2** have been determined by a single-crystal X-ray diffraction analysis at a low temperature. Compounds **1** and **2** crystallize in the monoclinic $P2_1/c$ and triclinic $P-1$ space group, respectively. The molecular structures of both compounds are similar with the exception of organic ligand but the quality of the crystals of **1** was not sufficient for a refinement of the structure.¹² The molecular structure of **2** is shown in Fig. 1 and the selected bond distances and angles are given in Table 1.

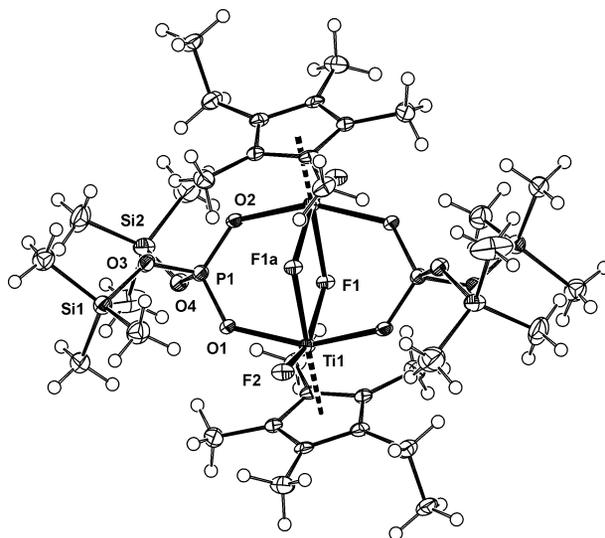


Figure 1. ORTEP plot of **2**. Ellipsoids are drawn at 50% probability level.

The asymmetric unit of **2** consists of a half of the complex $[(\text{C}_5\text{Me}_4\text{Et})\text{TiF}(\mu\text{-F})\{\mu\text{-O}_2\text{P}(\text{OSiMe}_3)_2\}]_2$ with the center of symmetry in the middle of the molecule. Two titanium atoms are connected by two bridging fluorine

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

Ti1-F1	1.971(1)	P1-O2	1.501(2)
Ti1-F2	1.828(1)	P1-O3	1.564(2)
Ti1-F1a	2.155(1)	P1-O4	1.559(2)
Ti1-O1	2.038(2)	Si1-O3	1.675(2)
Ti1a-O2	2.047(2)	Si2-O4	1.678(2)
P1-O1	1.504(2)		
F1-Ti1-F2	150.20(6)	O1-P1-O2	116.95(9)
F1-Ti1-F1a	70.41(6)	O1-P1-O3	109.2(1)
Ti1-O1-P1	132.48(9)	O1-P1-O4a	107.73(9)
Ti1-F1-Ti1a	109.59(6)	P1-O3-Si1	134.6(1)

atoms and by two phosphate groups. The coordination geometry around Ti atoms is best described as a distorted octahedron, a geometry which is commonly observed for other Ti^{IV} complexes.¹ The Ti–F distances for the two bridging F atoms are different (difference 0.18 Å). This is also the case in organotitanium fluoro-phosphinate [(C₅Me₅)TiF(μ-F)(μ-O₂PPh₂)]₂³ and fluoro-carboxylate complexes [(C₅Me₅)TiF(μ-F)(μ-O₂CR)]₂ (R = CF₃, C₆F₅)⁴ but not in the fluoro-sulphonate [(C₅Me₅)TiF(μ-F)(μ-O₂S(O)-*p*-C₆H₄CH₃)]₂³ complex with more symmetrical central Ti₂F₂ rhomboid. The Ti–F distance for the terminal F atoms in **2** (1.828 Å) is also typical for other organotitanium fluoride complexes with pentamethylcyclopentadienyl ligands.¹³ These cyclopentadienyl ligands in complexes **1** and **2** adopt a *trans* mutual arrangement. This is also the arrangement found in dimeric [(C₅Me₅)TiF₃]₂ but not in tetrameric [(C₅Me₅)TiF₃]₄ complexes.¹⁴ The same *trans* arrangement was also found in the previously reported organotitanium fluoro-phosphinate and -carboxylate structures but not in the sulfonate complex in which a *cis* mutual arrangement of pentamethylcyclopentadienyl ligands is more favourable in the crystal structure.^{3,4} There are no significant intermolecular contacts in the crystal lattice of compound **2**.

The ¹H, ¹⁹F and ³¹P NMR spectra of **1** and **2** suggest the presence of isomers in the solution. The spectra of **1** have three ¹H NMR Cp* resonances, three ³¹P NMR resonances and four ¹⁹F NMR resonances of bridging fluorine atoms.¹⁵ Two of the bridging-fluorine resonances (approx. –19 and –35 ppm) could be simulated with the same coupling constants and belong presumably to the same isomer with two nonequivalent bridging fluorines. The other two bridging-fluorine resonances (approx. 6.5 and –53 ppm) originate from additional two isomers, each with two equivalent bridging fluorines, resembling the structure found in the solid state of **2**. The presence of three isomers in the solution of **1** is also in accordance with the ¹H and ³¹P NMR spectra. The ¹H, ¹⁹F and ³¹P NMR spectra of **2** are similar to the spectra of **1**. The isomers were previously observed in solution of sulfonates, phosphinates and carboxylates of organotitanium fluorides^{3,4} and in solutions of organotitanium fluorides.¹⁴

4. Conclusions

Molecular and macromolecular titanium phosphates have found variety of applications, including as catalysts (see ref. 16 and citations therein). Since the fluoride ligand bonded to titanium increases its Lewis acidity,⁵ the reported compounds could be seen as a model for Lewis-acid titanium fluoride phosphates catalysts with increased activity.

5. Acknowledgement

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6. References

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Povzetek

Izolirali smo dve spojini s formulo $[(C_5Me_4R)TiF(\mu-F)\{\mu-O_2P(OSiMe_3)_2\}]_2$ [R = Me (**1**), Et (**2**)] pri reakciji med $[(C_5Me_4R)TiF_3]_2$, (R = Me, Et) in $OP(OSiMe_3)_3$. Kristalna struktura spojine **2** je bila določena s pomočjo rentgenske strukturne analize. V strukturi je opažen osemčlenski obroč $Ti_2O_4P_2$, povezan z dvema mostovnima fluorovima ligandoma med obema titanovima atomoma.