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Preparation of bistrimethylsilylmethylniobiumtetrafluoride and the application of KHF_2 and n-Bu_4NHF_2 as fluorinating reagents

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Dedicated to Professor Henri Brunner on the occasion of his 65th birthday

Abstract

$BisTiCl_3$ (**1**), $BisNbCl_4$ (**2**) and $BisNbBr_4$ (**3**) were prepared by alkylation of $NbCl_5$, $NbBr_5$ and $TiCl_4$ with Bis_2Zn (**4**) ($Bis = (SiMe_3)_2CH$). Compounds **2** and **3** were obtained as solids in moderate yields and are sensitive to moisture and air. In addition, the corresponding fluoride derivative of **2**, i.e. $BisNbF_4$ (**5**) was prepared in moderate yield via chlorine–fluorine metathesis employing Me_3SnF (**6**) as a fluorinating reagent. In another attempt $Ti(O$*i*$\text{-}Pr)_4$ was reacted with KHF_2 to give the fluorine-containing titanium cluster μ_3-fluoro-μ_3-oxo-tris(μ-*iso*propoxy)-hexakis(*iso*propoxy)-tri-titanium (**7**). The fluorine-free tantalum cluster bis(μ_3-oxo)-hexakis(μ-ethoxy)-octakis(μ-oxo)-tetradecakis(ethoxy)-octa-tantalum (**8**) was obtained from n-Bu_4NHF_2 and $Ta(OEt)_5$. The identity of all new compounds was documented by analytical/spectroscopic (IR, ^1H-, ^{29}Si-, ^{19}F-NMR, MS) data. The crystal structures of **2**, **7** and **8** were determined by single crystal X-ray diffraction. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Alkoxides; Fluorinating reagents; Group 4 and 5 metals; Organometallic fluorides

1. Introduction

Zinc organyls are widely used for alkylation of early transition metal halides [1]. It has been reported that the yields of niobium and tantalum alkyles are found to be higher when zinc organyls are employed as alkylating reagent compared to lithium or magnesium reagents [2]. Furthermore the niobium compounds are found to be thermally less stable and the yields are lower compared to the tantalum analogs.

Due to the differences in structure, solubility, volatility and thermal stability, the organometallic fluorides are of particular interest compared to the heavier congeners. These differences in properties are mainly due to the strong π donor property of fluoride [3]. Several examples are known in the literature, for instance $BisTaCl_4$, Cp^*TaCl_4 and Cp^*TiCl_3 ($Cp^* = C_5Me_5$) are monomers whereas the corresponding fluoride derivatives are either dimeric or polymeric systems [4]. The chlorine fluorine metathesis for Group 5 compounds was established for the preparation of π complexes like Cp^*NbF_4 and Cp^*TaF_4 using AsF_3 as fluorinating reagent [5]. Initially an adduct of two AsF_3 was formed which was converted to the adduct-free complex by heating in vacuo. Later on the synthesis of Cp^*TaF_4 was improved by exploiting Me_3SnF as fluorinating reagent [6], however this synthetic strategy has not been used for niobium compounds so far. Tantalum fluorides containing a carbon metal σ bond were first prepared by Schrock in 1978 by reacting a carbene complex with HBF_4 to give Np_3TaF_2 (Np = neopentyl) in moderate yield [7]. Recently a more efficient synthetic approach was established for the preparation of $BisTaF_4$, p-Tol_3TaF_2, Ns_3TaF_2 (Ns = neosilyl) and Ph_3TaF_2 using Me_3SnF as a fluorinating reagent [8]. However, the corresponding niobium fluorides containing a C–Nb σ bond are not known so far. We report herein $BisNbF_4$ (**5**) as the first example of chlorine fluorine metathesis using Me_3SnF for the preparation of a niobium fluoride.

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The study of the reactivity of new fluorinating reagents has been one of the primary objectives in our group. As part of this program we recently investigated the potential of tetra-*n*-butyl-ammoniumhydrogendifluoride, n-Bu_4NHF_2 (TBADF) as fluorinating agent for the preparation of gallophosphonates [9] and Group 13 difluorodiorganometalates [10]. In another investigation the application of TBADF was exploited for the preparation of the complex $[n\text{-}Bu_4N][(Oi\text{-}Pr)_3Ti(\mu\text{-}F)_2(\mu\text{-}Oi\text{-}Pr)Ti(Oi\text{-}Pr)_3]$ from $Ti(Oi\text{-}Pr)_4$ [11]. Here we report on the reactivity of KHF_2 and TBADF respectively with $Ti(Oi\text{-}Pr)_4$ and $Ta(OEt)_5$. The former case resulted in the formation of the trimer **7** while in the latter case an unexpected cluster **8** consisting of eight tantalum metal centers free of fluorine has been obtained in low yields.

Titanium fluorides have been used as catalysts for the olefin polymerization along with MAO (methylaluminoxan) as a cocatalyst, where the yields of polymer formation are higher in comparison to the corresponding chloride catalysts [12].

2. Experimental

All reactions were performed in a deoxygenated dinitrogen atmosphere using a glove box and high vacuum techniques. The starting materials were prepared according to literature methods (Bis_2Zn [13], Me_3SnF [14]) and were freshly sublimed or distilled prior to use. Commercially available $TiCl_4$, $NbCl_5$, $NbBr_5$ and $Ti(Oi\text{-}Pr)_4$ (Aldrich), TBADF, KHF_2 and $Ta(OEt)_5$ (Fluka) were used as such. Aromatic, hydrocarbon and etherated solvents were dried over Na/K alloy and vacuum transferred to the reaction flasks prior to use. Dichloromethane was dried over CaH_2 and vacuum transferred prior to use. NMR spectra were recorded on Bruker AM 200 and Bruker AM 250 instruments. Chemical shifts are reported in δ scale with reference to external $SiMe_4$ for ^1H and ^{29}Si and CCl_3F for ^{19}F nuclei. Mass spectra were obtained on Finnigan MAT system 8230 and a Varian MAT CH5 mass spectrometer. FT-IR spectra were measured on Bio-Rad FTS-7 as Nujol mulls between CsI plates. Melting points were obtained on a HWS-SG 3000 apparatus. Elemental analyses were performed by the Analytical Laboratory of the Institute of Inorganic Chemistry, University of Göttingen. X-ray data were collected on a STOE AED2 four circle diffractometer and all calculations were done with SHELXTL.

2.1. *BisTiCl₃* (**1**)

Compound **4** (4.0 g, 11 mmol) was added slowly at 0°C to a solution of $TiCl_4$ (5.0 g, 27 mmol) in hexane (60 ml). The reaction mixture turned red immediately. After stirring for 2 h at room temperature (r.t.) the solution was filtered using celite. The solvent was removed in vacuo and the resulting residue was fractionated (58°C, 0.02 mbar) to give **1** (5.4 g, 83%) as an orange liquid which solidifies at −30°C. After a second distillation the elemental analyses were still found to be unsatisfactory due to some impurities. ^1H-NMR ($CDCl_3$): δ 0.38 (s, 18 H, CH_3), 6.29 (s, 1 H, CH). ^{29}Si-NMR ($CDCl_3$): δ 3.36 (s, $SiMe_3$). Mass spectrum: *m/e* (%): 299 (20, $M^+ - Me$), 73 (100, $SiMe_3^+$). IR (Nujol, cm^{-1}): 1254 (s), 941 (m), 853 (s), 832 (s), 775 (m), 751 (m), 707 (m), 648 (m), 619 (m), 493 (s), 472 (s), 440 (m), 390 (m).

2.2. *BisNbCl₄* (**2**)

To a suspension of $NbCl_5$ (5.4 g, 20 mmol) in hexane (50 ml) was added **4** (3.1 g, 8.1 mmol) during 1 h at −70°C. Immediately the color changed from yellow to orange brown. The reaction mixture was warmed to r.t. and filtered using celite. The amount of solvent was reduced to ca. 20 ml and crystallization at −70°C afforded **2** (3.8 g, 60%). Melting point: 82°C. Anal. Calc. for $C_7H_{19}Cl_4NbSi_2$ (394.12): C, 21.33; H, 4.86; Cl, 35.98. Found: C, 21.5; H, 5.0; Cl, 35.7%. ^1H-NMR ($CDCl_3$): δ 0.49 (s, 18 H, CH_3), 6.20 (s, 1 H, CH). ^{13}C-NMR ($CDCl_3$): δ 3.8 (s, CH_3), 170.7 (s, CH). ^{29}Si-NMR ($CDCl_3$): δ 9.37 (s, $SiMe_3$). Mass spectrum *m/e* (%): 379 (5, $M^+ - Me$), 73 (100, $SiMe_3^+$). IR (Nujol, cm^{-1}): 1406 (m), 1255 (s), 906 (s), 879 (s), 853 (s), 832 (s), 791 (m), 777 (m), 751 (m), 698 (m), 669 (s), 637 (s), 601 (s), 445 (m), 395 (m) 369 (s), 322 (m).

2.3. *BisNbBr₄* (**3**)

Compound **3** was prepared by the above method from $NbBr_5$ (2.8 g, 5.6 mmol) and **4** (0.9 g, 2.3 mmol) to afford **3** (0.4 g, 15%). Melting point: 91°C. Due to the high sensitivity of **3** elemental analysis could not be done. ^1H-NMR ($CDCl_3$): δ 0.53 (s, 18 H, CH_3), 5.99 (s, 1 H, CH). ^{29}Si-NMR ($CDCl_3$): δ 5.54 (s, $SiMe_3$). Mass spectrum *m/e* (%): 493 (1, $M^+ - Br$), 73 (100, $SiMe_3^+$). IR (Nujol, cm^{-1}): 1405 (m), 1253 (s), 940 (m), 909 (m), 849 (s), 776 (s), 752 (s), 669 (s), 638 (s), 624 (s), 596 (s), 302 (s), 275 (s), 261 (s), 238 (s).

2.4. *BisNbF₄* (**5**)

A solution of **2** (0.8 g, 2.0 mmol) in CH_2Cl_2 (40 ml) was added to the solid **6** (1.5 g, 8.0 mmol) at −70°C. The reaction mixture was warmed to r.t. and insoluble **6** started to dissolve as the reaction proceeded leading to the liberation of Me_3SnCl. The solvent and the byproduct were removed in vacuo over a period of 6 h. Sublimation (50°C, 0.02 mbar, 5 h) afforded **5** (0.13 g, 20%) as a yellow solid. Decomposition point: 110°C. Anal. Calc. for $C_7H_{19}F_4NbSi_2$

(328.30): C, 25.61; H, 5.83; F, 23.15. Found: C, 25.6; H, 5.7; F, 22.9%. ^{1}H-NMR ($CDCl_3$): δ 0.31 (s, 18 H, CH_3), 4.65 (s, 1 H, CH). ^{19}F-NMR ($CDCl_3$): δ 126.03 (s, NbF). ^{29}Si-NMR ($CDCl_3$): δ 10.14 (s, SiMe$_3$). Mass spectrum m/e (%): 313 (25, $M^+ - Me$), 221 (100, $M^+ - SiMe_3 - Me - F$), 73 (50, $SiMe_3^+$). IR (Nujol, cm^{-1}): 1255 (s), 954 (m), 944 (m), 904 (s), 865 (s), 840 (s), 758 (m), 716 (m), 687 (m), 661 (s), 624 (s), 521 (m), 509 (m).

2.5. *μ_3-Fluoro-μ_3-oxo-tris(μ-isopropoxy)-hexakis(isopropoxy)-tri-titanium (7)*

To a stirred mixture of KHF_2 (0.5 g, 6.8 mmol) and toluene (50 ml) was injected Ti(Oi-Pr)$_4$ (4.0 ml, 3.8 g, 13.6 mmol) at r.t. After refluxing for 4 h the solution was filtered and the solvent was evaporated. The oily colorless material obtained was recrystallized from Et_2O (5 ml) at −30°C and was identified as **7** (2.1 g, 65%). Melting point: 89°C. Anal. Calc. for $C_{27}H_{63}FO_{10}Ti_3$ (710.47): C, 45.65; H, 8.94; F, 2.67. Found: C, 45.2; H, 8.8; F, 2.9%. ^{1}H-NMR ($CDCl_3$): δ 1.27–1.49 (m, 54 H, OCH(CH_3)$_2$), 4.51–4.89 (m, 9 H, OCH). ^{19}F-NMR ($CDCl_3$): δ −130.15 (s, Tiμ_3-F), −122.39 (s, Tiμ-F), 110.40 (s, Ti$F_{\text{(terminal)}}$). Mass spectrum m/e (%): 269 (100, Ti(Oi-Pr)$_4$ − Me), 229 (40, Ti(Oi-Pr)$_3^+$). IR (Nujol, cm^{-1}): 2620 (m), 1615 (m), 1327 (s), 1261 (m), 1164 (s), 1128 (s), 1007 (s), 960 (s), 855 (m), 804 (m), 643 (m), 592 (s).

$$2\,TiCl_4 + \underset{(4)}{Bis_2Zn} \rightarrow \underset{(1)}{2\,BisTiCl_3} + ZnCl_2$$

Scheme 1.

$$2\,NbX_5 + \underset{(4)}{Bis_2Zn} \rightarrow 2\,BisNbX_4 + ZnX_2$$

$$X = Cl\ (\mathbf{2}),\ X = Br\ (\mathbf{3})$$

Scheme 2.

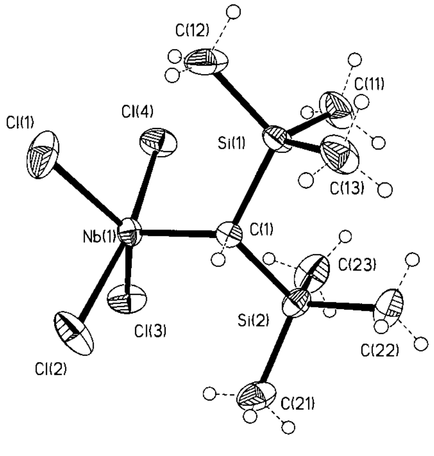


Fig. 1. X-ray single crystal structure of **2**.

2.6. *Bis(μ_3-oxo)-hexakis(μ-ethoxy)-octakis(μ-oxo)-tetradecacis(ethoxy)-octa-tantalum (8)*

To a stirred solution of Ta(OEt)$_5$ (1.0 ml, 1.6 g, 3.9 mmol) in CH_2Cl_2 (30 ml), a solution of n-Bu_4NHF_2 (1.0 ml, 1.9 mmol, 50% CH_2Cl_2) was added at r.t. The reaction mixture was stirred over night. The solvent was evaporated under vacuum and the oily residue was dissolved in toluene (10 ml). The resultant solution was kept at −30°C which afforded **8** as colorless crystals in low yield. Melting point: 223°C. Anal. Calc. for $C_{40}H_{100}O_{30}Ta_8$ (2508.80): C, 19.15; H, 4.02. Found: C, 19.3; H, 4.1%. ^{1}H-NMR ($CDCl_3$): δ 1.2–1.3 (m, 60 H, OCH_2CH_3), 4.3–4.8 (m, 40 H, OCH_2CH_3). Mass spectrum m/e (%): 2463 (100, $M^+ - OEt$). IR (Nujol, cm^{-1}): 1261 (m), 1154 (m), 1114 (s), 1070 (s), 876 (m), 803 (s), 739 (s), 511 (s).

3. Results and discussion

3.1. *Alkylation with Bis_2Zn*

We investigated the alkyl transferring properties of Bis_2Zn (**4**) towards various metal halides. In this connection compound **4** was reacted with several metal halides such as $ZrCl_4$, $HfCl_4$, TaF_5, WCl_6, $ReCl_5$, $SmCl_3$, $LaCl_3$ and $SiCl_4$ in n-hexane at elevated temperature. However, we observed that these metal halides remained unreacted in the solution. Interestingly compounds $BisTiCl_3$ (**1**), $BisNbCl_4$ (**2**) and $BisNbBr_4$ (**3**) have been isolated respectively from reacting $TiCl_4$, $NbCl_5$ and $NbBr_5$ with **4**. The reactions were carried out in hexane at −70°C under stirring for 1 h and subsequent removal of the precipitated salts by filtration.

Compound $BisTiCl_3$ (**1**) could be isolated in 83% yield by reacting $TiCl_4$ and **4** and subsequent distillation (Bp. 58°C, 0.02 mbar) gave **1** as an orange liquid (Scheme 1).

Compounds **2** and **3** were obtained after crystallization from hexane at −70°C in moderate yields (**2** 60%, **3** 15%). **2** and especially **3** are air and moisture sensitive solids that can be stored at −30°C for some days (Scheme 2).

The molecular structure of **2** was obtained by single crystal X-ray diffraction studies (Fig. 1). The crystals were obtained from hexane at −30°C over a one week period. Compound **2** crystallizes in a monoclinic crystal system with four molecules per unit cell. The structure of **2** is similar to the analogous tantalum compound [8] which is found to be monomeric.

$$\underset{(\mathbf{2})}{\mathrm{BisNbCl_4}} + 4\,\underset{(\mathbf{6})}{\mathrm{Me_3SnF}} \rightarrow \underset{(\mathbf{5})}{\mathrm{BisNbF_4}} + 4\,\mathrm{Me_3SnCl}$$

Scheme 3.

3.2. Fluorinations using Me_3SnF

Our attempt to fluorinate Ns_3NbCl_2 (Ns = neosilyl) using Me_3SnF (**6**) ended up with indefinite products. The fluorination of compound **2** resulted in the formation of a new fluoride containing a C–Nb σ bond. A solution of **2** in CH_2Cl_2 was added to **6** at −70°C (Scheme 3). After 30 min the insoluble **6** completely dissolved in the solution and the subsequent formation of the byproduct Me_3SnCl was noticed. After evaporating all volatiles, the residue was sublimed at 50°C and 0.02 mbar to give analytically pure **5** as a yellow solid in 20% yield. Compound **5** was found to be significantly more stable towards temperature than **2** or **3** and can be stored at −30°C for several months without decomposition.

We also tried to fluorinate **1** following the procedure described above. The formation of Me_3SnCl was observed but the residue was insoluble in any organic solvent which prevented further characterization.

3.3. Fluorinations using $n\text{-}Bu_4NHF_2$ and KHF_2

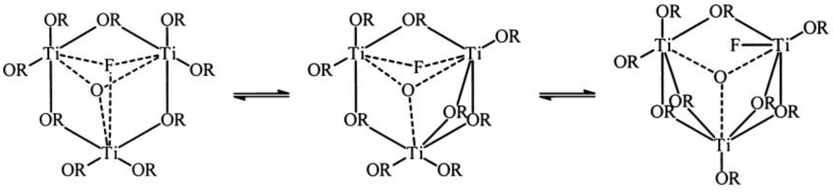
Compound **7** was prepared from $Ti(O\textit{i}\text{-}Pr)_4$ and KHF_2 in refluxing toluene. An insoluble residue formed was filtered off. The consumption of KHF_2 indicates that one KHF_2 reacted with three $Ti(O\textit{i}\text{-}Pr)_4$ with the formation of KF which is supported by the elemental analysis of the residue. In this reaction the fluorinating reagent KHF_2 showed a reaction pathway comparable to HF. One alkoxy ligand is replaced by one fluorine. However the reaction between $n\text{-}Bu_4NHF_2$ and $Ti(O\textit{i}\text{-}Pr)_4$ (Scheme 4) gave an ionic product which was obtained by substituting one alkoxy by two fluorine atoms [11].

Compound **7** was characterized by ^{1}H-, ^{19}F-NMR, IR, mass spectroscopy and elemental analysis. The ^{19}F-NMR spectrum at room temperature exhibits three resonances (δ −130.15, −122.39 and 110.40 ppm). These resonances can be explained by assuming an equilibrium in solution as shown in Scheme 5. The broad resonance at δ 110.40 ppm corresponds to the terminal fluorine shown in structure **7b**. The resonances at δ −130.15 and −122.39 ppm are assignable to the bridging fluorine atom in **7** and **7a**, respectively. The variable temperature ^{19}F-NMR data of the compounds **7**, **7a** and **7b** are listed in Table 1. In agreement with the structure in the solid state the solution spectrum gives an enlarged resonance at δ −130.15 while the intensity

$$3\,\mathrm{Ti(O\textit{i}Pr)_4} + \mathrm{KHF_2} \rightarrow \underset{(\mathbf{7})}{[(\mathrm{O\textit{i}Pr})_2\mathrm{Ti}(\mu\text{-}\mathrm{O\textit{i}Pr})]_3(\mu_3\text{-F})(\mu_3\text{-O})} + \mathrm{KF} + \textit{i}\mathrm{Pr_2O} + \textit{i}\mathrm{PrOH}$$

$$2\,\mathrm{Ti(O\textit{i}Pr)_4} + \textit{n}\text{-}\mathrm{Bu_4NHF_2} \rightarrow [\textit{n}\text{-}\mathrm{Bu_4N}][(\mathrm{O\textit{i}Pr})_3\mathrm{Ti}(\mu\text{-F})_2(\mu\text{-O\textit{i}Pr})\mathrm{Ti}(\mathrm{O\textit{i}Pr})_3] + \textit{i}\mathrm{PrOH}$$

Scheme 4.



7 **7a** **7b**

Scheme 5.

Table 1
^{19}F-NMR spectral data of the compounds **7**, **7a** and **7b** at variable temperatures and $1/T$ ($1/\mathrm{K} \times 10^{-3}$) and ln *K*

T (°C)	δ −130.15 ppm	δ −122.39 ppm	δ 110.40 ppm	$1/T$ (1/K)	ln *K*
30	56 [a]	23 [a]	21 [a]	(3.3003)	(−0.8916)
25	75	13	12	3.3557	−1.7719
0	88	6	6	3.6630	−2.6882
−25	94	3	3	4.0323	−3.4420
−50	98	1	1	4.4843	−4.6052

[a] Percentage given.

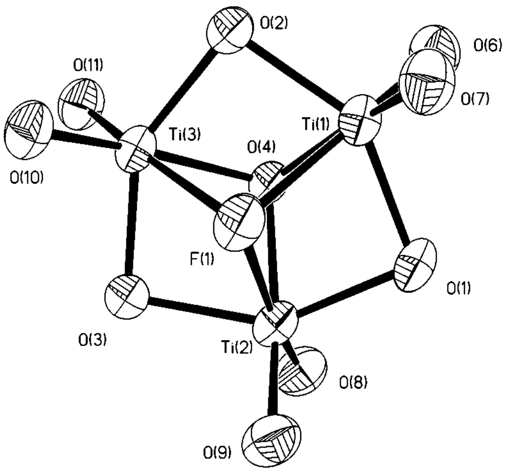


Fig. 2. X-ray single-crystal structure of **7**. Carbon and hydrogen atoms have been omitted for clarity.

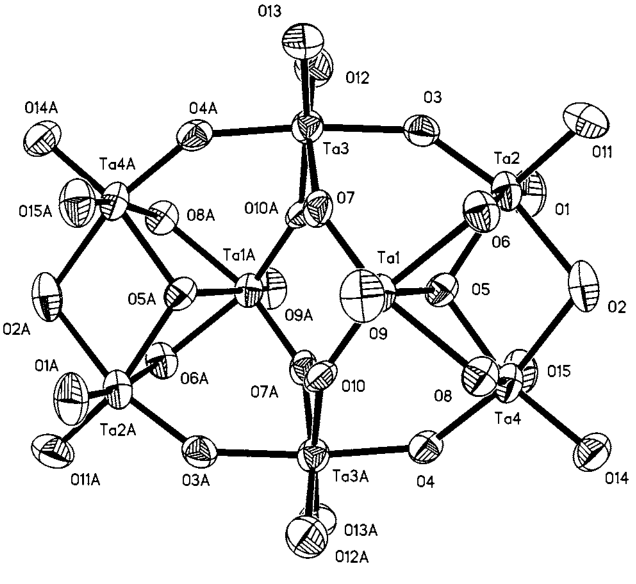


Fig. 3. X-ray single-crystal structure of **8**. Carbon and hydrogen atoms have been omitted for clarity.

of the resonances at lower temperatures (δ -122.39 and 110.40) is reduced to zero. The equilibrium constants ($K_{(T)}$) of **7** and **7a** have been calculated from the ^{19}F-NMR integral ratio. Fig. 2 shows the plot of ln K versus $1/T$ yielding ΔH and ΔS values {(20.4(0.9) kJ mol^{-1} and (53.2(3.3) J mol^{-1} K^{-1} ($R^2 = 0.996$)}. Bradley et al. reported that the energy for the Zr–OR → Zr bond is 37 kJ mol^{-1} and moreover postulated that the energy for a comparable titanium system has similar values [15]. The results of our experiment show a lower energy due to the change from a μ_3-F to a μ-F linkage. In agreement with the above result, this transformation can be estimated having an energy of -17 kJ mol^{-1}.

Compound **7** crystallizes from Et$_2$O at -30°C as colorless crystals over night. **7** crystallizes in the monoclinic space group $P2_1/n$ with four molecules per unit

Table 2
Selected bond lengths and angles for **2**, **7** and **8**

Complex	Bond length (Å)		Bond angle (°)	
2	Nb(1)–C(1)	2.019(4)		
	Nb(1)–Cl(1)	2.2910(13)	C(1)–Nb(1)–Cl(1)	112.70(10)
	Nb(1)–Cl(2)	2.3265(13)	C(1)–Nb(1)–Cl(2)	97.58(10)
	Nb(1)–Cl(3)	2.3354(12)	C(1)–Nb(1)–Cl(3)	113.64(10)
	Nb(1)–Cl(4)	2.3304(13)	C(1)–Nb(1)–Cl(4)	96.00(10)
7	Ti(1)–F(1)	2.163(3)	F(1)–Ti(1)–O(4)	70.26(13)
	Ti(2)–F(1)	2.133(3)	F(1)–Ti(2)–O(4)	70.94(13)
	Ti(3)–F(1)	2.135(3)	F(1)–Ti(3)–O(4)	70.69(12)
	Ti(1)–O(4)	2.052(3)		
	Ti(2)–O(4)	2.049(3)		
	Ti(3)–O(4)	2.060(3)		
8	Ta(1)–O(5)	2.087(9)		
	Ta(2)–O(5)	2.059(10)		
	Ta(4)–O(5)	2.023(9)		
	Ta(2)–O(3)	1.846(10)		
	Ta(3)–O(3)	2.018(10)		
	Ta(2)–O(2)	2.128(12)		
	Ta(4)–O(2)	2.150(11)		
	Ta(1)–O(9)	1.865(9)		

Table 3
Crystallographic data for the complexes **2**, **7**, and **8**

	2	**7**	**8**
Formula	$C_7H_{19}Cl_4Si_2Nb$	$C_{27}H_{63}FO_{10}Ti_3$	$C_{40}H_{100}O_{30}Ta_8$
FW	394.12	710.47	2508.80
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
Unit cell parameters			
a (Å)	15.362(3)	12.775(2)	14.668(3)
b (Å)	9.159(2)	17.592(3)	13.974(2)
c (Å)	12.116(2)	17.103(2)	16.917(3)
β (°)	106.42(3)	92.58(2)	91.48(3)
V (nm^3)	1.6351(6)	3.8399	3.4662(10)
Z	4	4	2
μ(Mo–K$_\alpha$) (mm^{-1})	1.506	0.657	12.642
D_{calc} (g cm^{-3})	1.601	1.229	2.404
Color	Orange	Colorless	Colorless
Crystal dimensions (mm^3)	0.9 × 0.4 × 0.4	1.0 × 0.6 × 0.6	0.8 × 0.6 × 0.4
T (K)	200(2)	200(2)	200(2)
θ scan limits (°)	3.51–24.94	3.55–25.05	3.63–25.01
No. of reflections collected	3028	10063	7740
No. of independent reflections	2842	6766	6096
Goodness-of-fit	1.052	1.048	1.059
R (all data)	0.0562	0.0979	0.0688
wR_2 (all data)	0.1427	0.1831	0.1824
Residual density (e nm^3)	−715 to 4719	−639 to 745	−2864 to 3411

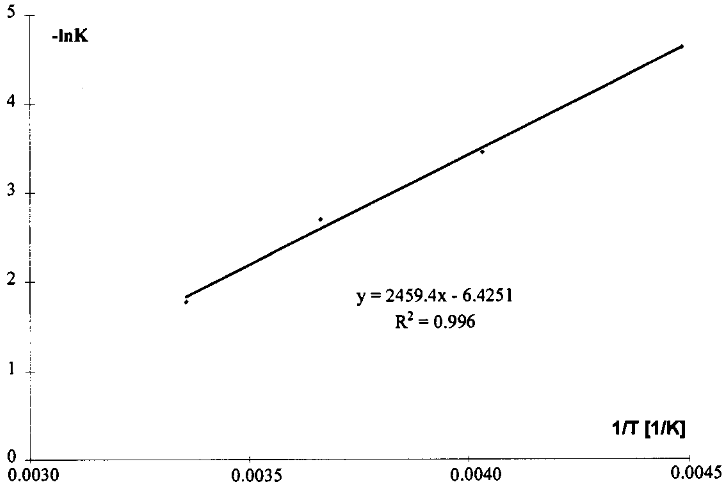


Fig. 4. A plot of $-\ln K$ versus $1/T$ for the equilibrium of **7** and **7a**.

cell (Fig. 3). A six-membered ring system has been built up by alternating titanium and alkoxy ligands. In the core of this system an oxygen and fluorine is placed. The same basic unit can be found in μ_3-chloro-μ_3-oxo-tris(μ-neopentoxy)-hexakis(neopentoxy)-tris-titanium [16], where a chlorine atom is found in the product. Though many titanium complexes containing a μ_3-O are known in the literature [16,17], no titanium complex is known showing a μ_3-F linkage. The average μ_3-O bond length in **7** is found to be 2.054 Å which is consistent with the literature value. The average μ_3-F bond length is 2.144 Å which is significantly larger compared to μ_3-O. The complex $(Cp^*TiF_3)_4CaF_2$ [18] exhibits a μ_4-F that shows one calcium and three titanium linkages. In this case the average Ti–F bond length (μ_4-F) is 2.175 Å which is consistent with that in **7**. Selected bond angles and lengths are listed in Table 2, and crystallographic data for **7** are given in Table 3.

To investigate the fluorinating properties of TBADF towards other metal alkoxides we selected $Ta(OEt)_5$. After the reaction was carried out as described in Section 2, we collected an oily crude product. The ^{19}F-NMR spectrum of the oil exhibits resonances at δ -42.8 and -33.7 ppm which are assignable to some unidentified products. Crystallization of the crude product from toluene afforded colorless crystals of **8** in low yield. X-ray crystal diffraction studies of **8** document the formation of a large tantalum oxygen ethanolat cluster (Fig. 4) employing 20 alkoxide, 10 oxygen and 8 metal centers. This centrosymmetric cluster is built up by two six-membered ring systems capturing a μ_3-O, four six-membered ring systems and one central eight-membered ring. A comparable structure of niobium is known [19]. It is prepared from $NbO(OEt)_3$ by the liberation of Et_2O under prolonged storage at room temperature [20].

4. Conclusions

This paper describes the first successful use of Me_3SnF (**6**) as a fluorinating reagent for the replacement of chlorine in the metalorganic niobium compound $BisNbCl_4$ (**2**). $BisNbF_4$ (**5**) represents the first niobium fluoride without Cp ligands containing a σ bonded alkyl ligand. Furthermore **5** shows a higher thermal stability compared to the corresponding chloride **2** and bromide **3**.

The fluorinating properties of KHF_2 and n-Bu_4NHF_2 have been investigated using $Ti(O\textit{i}\text{-}Pr)_4$ and $Ta(OEt)_5$. A six-membered ring system **7** showing a μ_3-F and a fluorine-free tantalum cluster **8** have been obtained.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos CCDC 147049-51. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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