Oxo Fluorides of Titanium and Vanadium. Preparation and Crystal Structures of $[Cp^*TiF(\mu\text{-}O)]_4$ and $OVF_2N{=}PPh_3$

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The reaction of Cp^*TiF_3 ($Cp^* = C_5Me_5$) (**1**) with $O(SnBu_3)_2$ affords the eight-membered ring compound $[Cp^*TiF(\mu\text{-}O)]_4$ (**2**) with elimination of Bu_3SnF. This is the first example of an organometallic oxo fluoride of group 4 of the periodic table. The molecular structure of **2** has been determined by X-ray crystallography. It shows that the eight-membered ring is almost planar. The reaction of OVF_3 with $Ph_3P{=}NSiMe_3$ yields $OVF_2N{=}PPh_3$ (**3**), which can be treated again with $Ph_3P{=}NSiMe_3$ to give $OVF(N{=}PPh_3)_2$ (**4**). The crystal structure of **3** shows that this compound is a monomer in the solid state. The oxo fluorides have characteristic differences in their structures or reactions compared to the corresponding chlorides.

Introduction

The hydrolysis of $CpTiCl_3$,[1] Cp^*TiCl_3,[1,2] and Cp^*TiBr_3[3] ($Cp = C_5H_5$, $Cp^* = C_5Me_5$) resulted in the formation of aggregated titanoxanes. Crystal structural analyses of various monocyclopentadienyl derivatives showed that four-, six-, and eight-membered ring systems containing titanium and oxygen were formed.[4]

Recently we reported on the preparation of Cp^*TiF_3[5] by metathesis reaction of Cp^*TiCl_3 with AsF_3. The hydrolysis of Cp^*TiF_3 with a stoichiometric amount of water, however, gave only a mixture of compounds.

Herein the syntheses of the first organometallic oxo fluoride of titanium and complexes of vanadium(V) oxo fluorides containing $Ph_3P{=}N$ ligands are described.

Experimental Section

General Data. ^1H NMR spectra were recorded on a Bruker WP 80 SY, and ^{19}F, ^{31}P, and ^{51}V NMR spectra on a Bruker AM 250 instrument, using $CFCl_3$, 85% H_3PO_4, and $VOCl_3$ as external standards. In all cases $CDCl_3$ was used as the solvent. The infrared spectra were obtained using a Bio-Rad FTS-7 spectrophotometer. Mass spectra were recorded on a Varian MAT CH5 and Finnigan MAT 8230 system. Diffraction data were collected on a Siemens-Stoe AED instrument. Melting points (uncorrected) were obtained by using a Büchi 510 apparatus. Elemental analyses were performed by the analytical laboratory of the inorganic institute at Göttingen.

Preparation of $[Cp^*TiF(\mu\text{-}O)]_4$. Cp^*TiF_3 (0.9 g, 3.9 mmol) is dissolved in 20 mL of toluene. To this solution $O(SnBu_3)_2$ (2.4 g, 3.9 mmol) in toluene (10 mL) is added dropwise under stirring. After 12 h $FSnBu_3$ is removed by filtration. The solvent is removed from the filtrate in vacuo and the residue recrystallized from *n*-hexane; 0.8 g (91%) of $[Cp^*TiF(\mu\text{-}O)]_4$ is isolated as yellow crystals from the hexane solution, mp 325 °C. ^1H NMR: δ 2.09. ^{19}F NMR: δ 83.97. IR (Nujol): 1026 m, 922 m, 863 s, 813 s, 605 s, 472 m, 383 s cm^{-1}. MS (EI): *m/z* 872 (M^+). Anal. Calcd for $C_{40}H_{60}F_4O_4Ti_4$ (872.5): C, 55.1; H, 6.9. Found: C, 55.8; H, 6.8.

Preparation of Ph_3PNVOF_2. To a solution of VOF_3[6] (1.5 g, 12.1 mmol) in ether (20 mL) is added at –78 °C under stirring a solution of $Ph_3PNSiMe_3$[7] (4.3 g, 12.1 mmol) in ether (20 mL). The reaction is warmed to room temperature. After stirring of the mixture for an additional 12 h, a yellow powder is recovered by filtration. This powder is recrystallized from CH_3CN to yield 4.3 g (94%) of Ph_3PNVOF_2, mp 205 °C. Single crystals of **3** are obtained by recrystallization from hot acetonitrile. ^1H NMR: δ 7.18–8.14 m. ^{31}P NMR: δ 27.8 (br, $\Delta_{1/2}$ = 610 Hz). ^{19}F NMR: δ 35.5 (br, $\Delta_{1/2}$ = 280 Hz). ^{51}V NMR: δ –516.9 (br, $\Delta_{1/2}$ = 320 Hz). IR (Nujol): 1439 sst, 1231 st, 1161 sst, 1105 sst, 843 st, 698 st cm^{-1}. MS (EI): *m/z* 381 (M^+, 100%). Anal. Calcd for $C_{18}H_{15}F_2NOPV$ (381.2): C, 56.7; H, 3.9; N, 3.7; P, 8.1. Found: C, 56.6; H, 3.9; N, 3.7; P, 7.9.

Preparation of $(Ph_3PN)_2VOF$. A yellow suspension of Ph_3PNVOF_2 (1.9 g, 5.0 mmol) and $Ph_3PNSiMe_3$ (1.8 g, 5.0 mmol) in toluene (40 mL) is heated under reflux for 12 h. The volatiles are removed in vacuo, and the residue is recrystallized from hot DMF. A 2.8-g amount (88%) of yellow crystalline $(Ph_3PN)_2VOF$ is obtained, mp 183 °C. ^1H NMR: δ 7.03–7.88 m. ^{31}P NMR: δ 14.1 (br, $\Delta_{1/2}$ = 680 Hz). ^{19}F NMR: δ –31.5 (br, $\Delta_{1/2}$ = 1500 Hz). ^{51}V NMR: δ –219.2 (br, $\Delta_{1/2}$ = 230 Hz). IR (Nujol): 1439 st, 1403 sst, 1261 st, 1093 sst, 1018 st, 800 st, 722 st cm^{-1}. MS (EI): *m/z* 277 (Ph_3PNH, 100%), 638 (M^+, 15). Anal. Calcd for $C_{36}H_{30}FN_2OP_2V$ (638.6): C, 67.7; H, 4.7; N, 4.4. Found: C, 66.7; H, 4.7; N, 4.4.

Crystal Structure Solution and Refinement. Diffraction data were collected on a Siemens-Stoe AED2 four-circle instrument at room temperature with Mo Kα radiation, on-line profile fitting, and variable scan speeds. The structures were solved by Patterson methods (SHELX-86) and refined by full-matrix least squares on F^2 (SHELXL-92). Non-hydrogen atoms were refined anisotropically and hydrogen atoms inserted at calculated positions.

Atomic coordinates of compounds **2** and **3** are given in Tables I and II.

Crystal Data for $[Cp^*TiF(\mu\text{-}O)]_4$: $C_{40}H_{60}F_4O_4Ti_4$·solvent, M_r = 872.5, space group tetragonal $I\bar{4}2m$, a = 1686.5(2) pm, c = 864.4(2) pm, V = 2.4586(7) nm^3, Z = 2, ρ(calcd) = 1.243 mg/m^3, μ = 0.677 mm^{-1}, $F(000)$ = 960, crystal size (mm) 0.8 × 0.4 × 0.4, 1090 collected reflections, 554 independent reflections, goodness of fit 0.971, refinement converged with $R1$ = 0.0406 and R_w2 = 0.1116 [$I > 2\sigma(I)$], and for all data $R1$ = 0.0466 and R_w2 = 0.1306. The structure contains disordered solvent molecules and the pseudoatoms L(1) and L(2) had to be introduced in order to reduce the rest electron density below 236 e·nm^3 (minimum –216 e·nm^3).

Crystal Data for $OVF_2N{=}PPh_3$: $C_{18}H_{15}F_2NOPV$, M_r = 381.2, space group monoclinic $P2_1/n$, a = 1059.0(1) pm, b = 869.8(1) pm, c = 1882.7(4) pm, β = 91.15(2)°, V = 1.7338(4) nm^3, Z = 4, ρ(calcd) = 1.460 mg/m^3, μ = 0.688 mm^{-1}, $F(000)$ = 776, crystal size (mm) 0.7 × 0.6 × 0.2, 2274 collected reflections, 2273 independent reflections, goodness of fit 1.061, refinement converged with $R1$ = 0.0558 and R_w2 = 0.1271 [I

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Table I. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$) for **2**

	x	*y*	*z*	*U*(eq)[a]
Ti(1)	3934(1)	3934(1)	38(2)	46(1)
C(1)	3318(3)	2742(3)	−846(7)	68(3)
C(2)	3910(3)	2953(3)	−1929(7)	63(3)
C(3)	3683(3)	3683(3)	−2548(10)	61(3)
C(1*)	3313(5)	1996(3)	96(15)	115(6)
C(2*)	4633(4)	2483(4)	−2387(11)	92(4)
C(3*)	4152(4)	4152(4)	−3763(11)	94(5)
O(1)	3783(2)	5000	0	54(2)
F(2)	3646(2)	3646(2)	2018(6)	78(3)
L(1)	0	5000	0	359(30)
L(2)	5000	0	2500	423(23)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$) for **3**

	x	*y*	*z*	*U*(eq)[a]
V(1)	4727(1)	1987(1)	8274(1)	52(1)
F(1)	4996(3)	1509(5)	7381(2)	85(3)
F(2)	5450(4)	3743(5)	8496(3)	103(3)
O(1)	5305(4)	664(6)	8760(3)	85(3)
N(1)	3127(4)	2091(5)	8429(2)	48(3)
P(1)	2122(1)	1248(2)	8933(1)	41(1)
C(11)	595(5)	1383(6)	8509(3)	44(3)
C(12)	−328(6)	265(7)	8596(4)	62(4)
C(13)	−1495(6)	430(9)	8286(4)	73(4)
C(14)	−1764(6)	1703(9)	7882(4)	68(4)
C(15)	−871(6)	2807(8)	7795(3)	67(4)
C(16)	298(6)	2692(7)	8105(3)	56(4)
C(21)	2477(5)	−750(6)	9080(3)	42(3)
C(22)	2586(6)	−1680(7)	8482(4)	65(5)
C(23)	2909(7)	−3229(8)	8567(4)	81(6)
C(24)	3122(7)	−3817(7)	9231(5)	75(5)
C(25)	3015(7)	−2902(8)	9815(4)	73(5)
C(26)	2689(6)	−1351(7)	9739(3)	59(4)
C(31)	2069(5)	2219(6)	9779(3)	39(3)
C(32)	3184(6)	2396(7)	10165(3)	57(4)
C(33)	3188(7)	3212(8)	10789(3)	68(5)
C(34)	2088(8)	3849(8)	11031(4)	74(7)
C(35)	975(7)	3661(8)	10657(4)	68(5)
C(36)	954(6)	2851(7)	10025(3)	55(4)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

$> 2\sigma(I)$], and for all data $R1 = 0.0911$ and $R_w2 = 0.1590$ (maximum/minimum rest electron density +430/−342 e·nm^{-3}).

Further details of the crystal structure determination are available upon request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the deposition number CSD-57247, the authors, and the journal citation.

Results and Discussion

The reaction of Cp*TiF$_3$ (**1**) and O(SnBu$_3$)$_2$ in a molar ratio of 1:1 gives a viscous solution. After the solution was stirred for 12 h, the color changed from orange to yellow, a white solid separated, and a turbid solution resulted.

This solution was filtered through Celite and was evaporated to dryness in vacuo. Recrystallization of the residue from *n*-hexane gave [Cp*TiF(μ-O)]$_4$ (**2**) as yellow needles.

The EI mass spectrum indicates the tetrameric structure of **2** with the molecular ion at *m/z* = 872. In the ^{19}F NMR (δ = 65.0 ppm) as well as in the ^{1}H NMR spectra (δ = 2.03 ppm) a singlet is observed. A comparison of the proton chemical shifts of **1** and **2** indicates a shift of 0.1 ppm to higher field for **2**.

The single-crystal X-ray structural analyses reveal that [Cp*TiF(μ-O)]$_4$ consists of an eight-membered almost planar ring (Figure 1). Four Cp*TiF units are connected by four oxygen atoms forming the ring skeleton. The positions of the Cp* group are alternating above and below the plane of this ring.

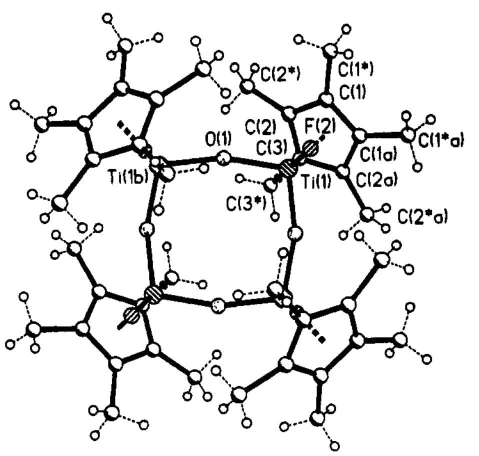

Figure 1. Molecular structure of [Cp*TiF(μ-O)]$_4$ (**2**). Selected bond lengths (pm) and angles (deg): Ti(1)–O(1) = 181.61(9), Ti(1)–F(2) = 184.5(5), O(1)–Ti(1b) = 181.61(9); O(1)–Ti(1)–O(1) = 106.1(3), O(1)–Ti(1)–F(2) = 103.91(2), Ti(1)–O(1)–Ti(1b) = 163.9(3).

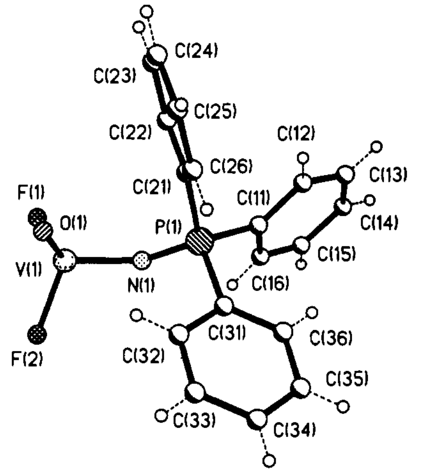

Figure 2. Molecular structure of OVF$_2$N=PPh$_3$ (**3**). Selected bond lengths (pm) and angles (deg): V(1)–O(1) = 158.6(4), V(1)–F(2) = 175.5(4), N(1)–P(1) = 161.6(5), V(1)–N(1) = 172.7(4), V(1)–F(1) = 176.0(4); O(1)–V(1)–N(1) = 108.0(2), N(1)–V(1)–F(2) = 109.8(2), N(1)–V(1)–F(1) = 110.6(2), P(1)–N(1)–V(1) = 137.4(3), O(1)–V(1)–F(2) = 109.4(2), O(1)–V(1)–F(1) = 108.1(2), F(2)–V(1)–F(1) = 110.8(2).

The structure of **2** is unique. The corresponding [Cp*TiBr(μ-O)]$_4$[3] compound has a nonplanar ring conformation. In this compound the four oxygen atoms lie in a plane but the four titanium atoms are alternately positioned above and below that plane by 19.1(2) pm. In general it is found that fluorine rather than oxygen occupies bridging positions. The terminal Ti–F distances in **2** [184.5(5) pm] are comparable to those in **1**. The Ti–O bond lengths fall in the range of those in [Cp*TiBr(μ-O)]$_4$[3] [179.7(7)–181.5(7) pm] and [Cp*TiCl(μ-O)]$_3$[1] [181.2(5)–183.3(5) pm]. A list of selected bond lengths and angles is given in the caption of Figure 1.

In previous contributions we have shown that ligands of the type Ph$_3$P=N–,[8] Me$_2$S(O)=N–,[9] and Ph$_2$S=N–[10] may be used for stabilizing metals in high oxidation states. Consequently we were interested in extending this chemistry to oxo fluorides of transition metals.[11]

The reaction of VOF$_3$[6] with Ph$_3$P=NSiMe$_3$[7] leads to the

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formation of Ph_3PNVOF_2 (**3**), which was obtained as a yellow crystalline solid.

The EI mass spectrum exhibits the molecular ion (*m/z* 381) with 100% relative intensity. The ^{19}F NMR (δ 35.5) as well as the ^{51}V NMR (δ –516.9) spectra give a broad singlet, while the ^{31}P NMR signal is extremely broad ($\Delta_{1/2}$ = 610 Hz).

The molecular structure of **3** is shown in Figure 2. Compound **3** is a monomer in the solid state. The structure is comparable to the $-Ph_2P{=}N{-}ReO_3$ parts of $(O_3ReN{=}PPh_2)_2C_2H_4$.[12] The vanadium atom in **3** has a tetrahedral coordination, a short V–N bond distance (172.7(4) pm), and a far from linear V–N–P angle of 137.4(3)°. The VO bond length (158.6(4) pm) is comparable with that in $Ph_2SNVOCl_2$[11] (155.2(6) pm). A selection of bond lengths and angles is given in the caption of Figure 2.

The reaction of $OVF_2N{=}PPh_3$ (**3**) with $Ph_3PNSiMe_3$ yields nearly quantitatively $OVF(N{=}PPh_3)_2$ (**4**).

$Ph_2PCl{=}NSiMe_3$ reacts with $VOCl_3$ to form a six-membered ring with elimination of $(Me_3Si)_2O$[13] in contrast to the elimination of Me_3SiF in the above mentioned reactions. The formation of Me_3SiF is favored due to the strong SiF bond energy. Compound **4** is a yellow crystalline solid exhibiting in the mass spectrum (EI) the molecular ion (*m/z* 638) with 15% relative intensity. The ^{51}V, ^{19}F, and ^{31}P NMR spectra give very broad signals. A similar broadening of the NMR lines was also observed in $(NPPh_2N)_2V_2Cl_2(OSiMe_3)_2$. Paramagnetic impurities could be excluded due to ESR investigations.[14]

Conclusion. The described reactions of titanium and vanadium fluorides demonstrate the differences using fluorides instead of the corresponding chlorides. Especially the elimination of Bu_3SnF and Me_3SiF is favored rather than the elimination of oxygen species. This is due to the exothermic reactions of the formation of the Sn–F and Si–F bonds.

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Supplementary Material Available: Listings of crystal data, hydrogen positional and thermal parameters, anisotropic displacement parameters, and bond distances and angles and ORTEP diagrams (9 pages). Ordering information is given on any current masthead page.

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