Supporting Information

REACTIONS OF SF_6 WITH ORGANOTITANIUM AND ORGANOZIRCONIUM COMPLEXES: THE "INERT" SF_6 AS A REACTIVE FLUORINATING AGENT

Rehan Basta, Benjamin G. Harvey, Atta M. Arif, and Richard D. Ernst*

Department of Chemistry, University of Utah, 315 S. 1400 E., Salt Lake City, Utah 84112-0850

Experimental

All reactions were carried out with rigorous exclusion of air in Schlenk apparatus. Solvents were dried using activated alumina under nitrogen. Elemental analyses were obtained from Desert Analytics. Initial reactions used SF_6 (99.8%) obtained from Matheson Gas Products, while subsequently SF_6 (99.9%) was obtained from Praxair. The absence of significant amounts of SF_4 or other lower fluorides was established through aqueous acid/base titrations of the SF_6 with standardized base solutions, and also by F-19 NMR. The magnetic susceptibility measurement was carried out using a Quantum Design $MPMS_2$ magnetometer.

(Trimethylphosphine)(1,3-di-t-butylcyclopentadienyl)(6,6-dimethylcyclohexadienyl)titanium, $Ti[1,3\text{-}(t\text{-}Bu)_2C_5H_3](6,6\text{-}dmch)(PMe_3)$.

A reaction mixture consisting of $Ti[1,3\text{-}(\underline{t}\text{-}Bu)_2C_5H_3]Cl_3$ (2.30 g, 6.84 mmol) and Zn (0.90 g, 14 mmol) in 26 mL THF was allowed to stir overnight, resulting in a dark green solution. The following day, PMe_3 (0.85 mL, 8.2 mmol) was added and the mixture was stirred for 2 h. K(6,6-dmch) (3.00 g, 20.5 mmol) in 30 mL THF was added dropwise via a pressure equalizing addition funnel at -78º C. The reaction mixture turned dark brown and was slowly warmed to room temperature, and thereafter allowed to stir for 2 h. Next, the solvent was removed in vacuo to give a dark brown solid. Extraction of the solid with ca. 150 mL ether and filtration through a Celite pad on a medium frit gave a brown-orange filtrate. Concentration of the solution to ca. 10 mL and cooling to -60º C for 2 days gave 1.48 g (53%) of brown-orange solid. Single crystals suitable for a diffraction study were grown by slowly cooling concentrated solutions of the compound in hexane to -30º.

^{1}H NMR (benzene-d_6, ambient): δ -0.33 (s, 3H, exo CH_3), 0.36 (d, 9H, J = 4.2 Hz, PMe_3), 0.73 (s, 18H, $C(CH_3)_3$), 1.39 (s, 3H, endo CH_3), 1.86 (d, $2H_{1,5}$, J = 6 Hz), 5.82 (t, 2H, J = 7.2 Hz, Cp), 6.36 (d, $2H_{2,4}$, J = 2.1 Hz), 6.97 (t, $1H_3$, J = 7.1 Hz), 7.29 (t, 1H, J = 2.3 Hz, Cp).

^{13}C NMR (benzene-d_6, ambient): δ 4.35 (s, $1C_6$), 19.28 (q, 3C, J = 124.6 Hz, PMe_3), 26.05 (q, 1C, J = 125.5 Hz, exo CH_3), 26.89 (q, 1C, J = 125.0 Hz, endo CH_3), 32.34 (s, 2C, $(CH_3)_3C$), 32.60 (d of quintets, 6C, J = 125.1, 4.8 Hz, $C(CH_3)_3$), 92.16 (dd, $2C_{1,5}$, J = 163.0, 7.9 Hz), 96.10 (d, $2C_{2,4}$, J = 167.7 Hz), 106.27 (dt, 2C, J = 169.5, 6.6 Hz, Cp), 108.31 (dt, 1C, J = 162.4, 7.2 Hz, Cp), 114.96 (dt, $1C_3$, J = 158.1, 7.2 Hz), 131.21 (s, 2C, Cp).

Anal. Calc. for $C_{24}H_{41}PTi$: C, 70.58; H, 10.12. Found: C, 70.54; H, 10.28.

Difluoro(1,3-di-t-butylcyclopentadienyl)titanium tetramer, $\{Ti[1,3\text{-}(t\text{-}Bu)_2C_5H_3]F_2\}_4$

An orange solution of $Ti[1,3\text{-}(t\text{-}Bu)_2C_5H_3](6,6\text{-dmch})(PMe_3)$ (0.68 g, 1.66 mmol) in 10 mL toluene was prepared under a nitrogen atmosphere in a 200 mL flask, which was subsequently filled with SF_6 gas. The reaction mixture was allowed to stand at room temperature for 2 days. Green crystals precipitated out of solution, often of suitable quality for a diffraction study, and were washed with pentane and ether, affording 0.23 g of product (53%). No attempt was made to optimize the yield of this reaction, although there appeared to be only traces of other organotitanium products (very small amount of red crystals). When the quality of the initially deposited crystals was insufficient, higher quality crystals could be grown by slowly cooling hot solutions of the compound in toluene.

Anal. Calc. for $C_{52}H_{84}F_8Ti_4$: C, 59.31; H, 8.04. Found: C, 59.39; H, 7.74.

Magnetic Susceptibility: $\mu = 1.74\ \mu_B$ (per titanium).

Structural Studies

Single crystals of the two compounds were mounted on a glass fiber with Paratone© oil, and transferred to a Nonius Kappa CCD autodiffractometer for unit cell determination and data collection. Initial structure solutions were obtained straightforwardly, and improved by subsequent difference Fourier and least-squares refinement methods. For the phosphine adduct two independent molecules were present in the asymmetric unit, which exhibited nearly identical structures. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms on metal-bound carbon atoms were refined isotropically, while all others were placed in idealized positions. For the fluoride complex, two tetrameric units were found in the unit cell, each located on a center of inversion. Their nonhydrogen atoms were readily refined anisotropically, while the hydrogen atoms were refined isotropically. All other hydrogen atoms were placed in idealized locations. Although the solution based on this model appeared quite acceptable, a faint second image of each tetramer was observed, accounting for about 8% of the overall electron density (i.e., a ratio of 92:8), and related to the major images by a rotation of ca. 20º around the z axis. Their titanium and fluorine atoms were refined isotropically, while the metal-bound carbon atoms were refined as rigid groups. Most but not all of the other carbon atoms were refined isotropically, and most hydrogen atoms were included in idealized locations. Notably, the quaternary carbon atoms of the t-butyl groups overlapped for the two images.

Table S1. Crystallographic Data for $Ti[1,3-(\underline{t}-Bu)_2C_5H_3](6,6\text{-dmch})(PMe_3)$ and $\{Ti[1,3-(\underline{t}-Bu)_2C_5H_3]F_2\}_4$.

formula	$C_{24}H_{41}PTi$	$C_{52}H_{84}F_8Ti_4$
formula wt.	408.44	1052.79
crystal system	monoclinic	triclinic
space group	$\underline{P}2_1/\underline{n}$	$\underline{P}\bar{1}$
color	orange	green
a (Å)	14.8106(3)	10.6523(2)
b (Å)	10.4950(3)	14.1425(2)
c (Å)	30.8449(10)	19.0644(3)
α (deg)	90	90.7670(11)
β (deg)	103.2967(16)	103.0287(8)
γ (deg)	90	92.0666(11)
temp. (K)	150(1)	150(1)
Z	8	2
R (2σ)	0.0502	0.0451
wR^2 (2σ)	0.0982	0.0989
GOF	1.018	1.055

Table S2. Pertinent Bonding Parameters for Ti[1,3-C_5H_3(t-Bu)$_2$](6,6-dmch)(PMe_3).

Bond Distances (Å)

Ti1-C1	2.191(2)	Ti1-C9	2.418(2)	Ti2-C1A	2.196(2)	Ti2-C9A	2.413(2)
Ti1-C2	2.291(2)	Ti1-C10	2.460(2)	Ti2-C2A	2.301(2)	Ti2-C10A	2.468(2)
Ti1-C3	2.351(2)	Ti1-C11	2.424(2)	Ti2-C3A	2.356(2)	Ti2-C11A	2.445(2)
Ti1-C4	2.287(2)	Ti1-C12	2.317(2)	Ti2-C4A	2.293(2)	Ti2-C12A	2.325(2)
Ti1-C5	2.195(2)	Ti1-C13	2.315(2)	Ti2-C5A	2.193(2)	Ti2-C13A	2.307(2)
Ti1-P1	2.6499(7)	C9-C10	1.412(3)	Ti2-P2	2.6481(7)	C9A-C10A	1.418(3)
C1-C2	1.419(3)	C9-C13	1.417(3)	C1A-C2A	1.417(3)	C9A-C13A	1.422(3)
C2-C3	1.408(3)	C10-C11	1.414(3)	C2A-C3A	1.416(3)	C10A-C11A	1.414(3)
C3-C4	1.412(3)	C11-C12	1.417(3)	C3A-C4A	1.401(3)	C11A-C12A	1.418(3)
C4-C5	1.421(3)	C12-C13	1.418(3)	C4A-C5A	1.428(3)	C12A-C13A	1.422(3)

Bond Angles (Deg.)

C1-C2-C3	118.8(2)	C1A-C2A-C3A	117.5(2)
C2-C3-C4	121.6(2)	C2A-C3A-C4A	122.1(2)
C3-C4-C5	118.1(2)	C3A-C4A-C5A	118.7(2)
C4-C5-C6	115.6(2)	C4A-C5A-C6A	114.0(2)
C6-C1-C2	114.6(2)	C6A-C1A-C2A	115.6(2)
C9-C10-C11	110.5(2)	C9A-C10A-C11A	110.9(2)
C10-C11-C12	106.1(2)	C10A-C11A-C12A	106.1(2)
C11-C12-C13	108.7(2)	C11A-C12A-C13A	108.7(2)
C12-C13-C9	108.5(2)	C12A-C13A-C9A	108.5(2)
C13-C9-C10	106.3(2)	C13A-C9A-C10A	105.8(2)
Ti1-P1-C22	117.34(8)	Ti2-P2-C22A	114.77(9)
Ti1-P1-C23	115.21(9)	Ti2-P2-C23A	117.18(9)
Ti1-P1-C24	124.00(8)	Ti2-P2-C24A	124.48(9)
C1-C6-C5	103.9(2)	C1A-C6A-C5A	103.9(2)

Table S3. Pertinent Bonding Parameters for $\{Ti[1,3\text{-}C_5H_3(\underline{t}\text{-}Bu)_2]F_2\}_4$.

Bond Distances (Å)

Ti1-C1	2.370(2)	Ti3-C27	2.359(2)	Ti12-C1'	2.38(2)	Ti34-C27'	2.37(3)
Ti1-C2	2.332(2)	Ti3-C28	2.330(2)	Ti12-C2'	2.37(3)	Ti34-C28'	2.38(3)
Ti1-C3	2.361(2)	Ti3-C29	2.370(2)	Ti12-C3'	2.36(3)	Ti34-C29'	2.36(3)
Ti1-C4	2.366(2)	Ti3-C30	2.374(2)	Ti12-C4'	2.36(2)	Ti34-C30'	2.34(2)
Ti1-C5	2.367(2)	Ti3-C31	2.369(2)	Ti12-C5'	2.37(2)	Ti34-C31'	2.35(2)
Ti2-C14	2.370(2)	Ti4-C40	2.371(2)	Ti21-C14'	2.34(3)	Ti43-C40'	2.37(2)
Ti2-C15	2.335(2)	Ti4-C41	2.335(2)	Ti21-C15'	2.37(3)	Ti43-C41'	2.35(2)
Ti2-C16	2.374(2)	Ti4-C42	2.370(2)	Ti21-C16'	2.37(3)	Ti43-C42'	2.33(3)
Ti2-C17	2.377(2)	Ti4-C43	2.369(2)	Ti21-C17'	2.36(3)	Ti43-C43'	2.35(2)
Ti2-C18	2.371(2)	Ti4-C44	2.369(2)	Ti21-C18'	2.34(3)	Ti43-C44'	2.38(2)
Ti1-F1	2.023(2)	Ti3-F5	2.010(2)	Ti12-F1'	2.06(2)	Ti34-F5'	2.01(2)
Ti1-F2	2.023(2)	Ti3-F6	2.019(2)	Ti12-F2'	2.09(2)	Ti34-F6'	1.96(2)
Ti1-F3	2.015(2)	Ti3-F7	2.022(2)	Ti12-F3'	1.99(3)	Ti34-F7'	2.00(2)
Ti1-F4	2.017(2)	Ti3-F8	2.012(2)	Ti12-F4'	2.00(3)	Ti34-F8'	2.03(3)
Ti2-F1	2.015(2)	Ti4-F5	2.022(2)	Ti21-F1'	2.01(2)	Ti43-F5'	2.03(2)
Ti2-F2	2.008(2)	Ti4-F6	2.020(2)	Ti21-F2'	1.96(2)	Ti43-F6'	2.06(2)
Ti2-F3	2.022(2)	Ti4-F7	2.016(2)	Ti21-F3'	2.02(3)	Ti43-F7'	2.02(2)
Ti2-F4	2.018(2)	Ti4-F8	2.013(2)	Ti21-F4'	2.05(3)	Ti43-F8'	1.99(3)
C1-C2	1.427(3)	C27-C28	1.424(3)	C1'-C2'	1.420	C27'-C28'	1.420
C1-C5	1.410(3)	C27-C31	1.412(4)	C1'-C5'	1.420	C27'-C31'	1.420

C2-C3	1.418(3)	C28-C29	1.427(3)	C2’-C3’	1.420	C28’-C29’	1.420
C3-C4	1.413(3)	C29-C30	1.417(3)	C3’-C4’	1.420	C29’-C30’	1.420
C4-C5	1.409(4)	C30-C31	1.404(4)	C4’-C5’	1.420	C30’-C31’	1.420
C14-C15	1.429(3)	C40-C41	1.425(3)	C14’-C15’	1.420	C40’-C41’	1.420
C14-C18	1.416(3)	C40-C44	1.409(3)	C14’-C18’	1.420	C40’-C44’	1.420
C15-C16	1.429(3)	C41-C42	1.425(3)	C15’-C16’	1.420	C41’-C42’	1.420
C16-C17	1.413(3)	C42-C43	1.415(3)	C16’-C17’	1.420	C42’-C43’	1.420
C17-C18	1.412(4)	C43-C44	1.416(4)	C17’-C18’	1.420	C43’-C44’	1.420

Bond Angles (Deg.)

F1-Ti1-F2	71.19(7)	F5-Ti3-F6	71.60(7)	F1’-Ti12-F2’	70.8(9)	F5’-Ti34-F6’	73.3(9)
F1-Ti1-F3	83.04(8)	F5-Ti3-F7	82.49(8)	F1’-Ti12-F3’	80.5(10)	F5’-Ti34-F7’	124.8(9)
F1-Ti1-F4	124.10(8)	F5-Ti3-F8	123.02(8)	F1’-Ti12-F4’	123.7(10)	F5’-Ti34-F8’	82.0(10)
F2-Ti1-F3	123.85(8)	F6-Ti3-F7	124.10(8)	F2’-Ti12-F3’	121.2(10)	F6’-Ti34-F7’	83.8(9)
F2-Ti1-F4	82.96(8)	F6-Ti3-F8	82.69(8)	F2’-Ti12-F4’	82.1(10)	F6’-Ti34-F8’	125.0(10)
F3-Ti1-F4	71.57(7)	F7-Ti3-F8	71.28(7)	F3’-Ti12-F4’	72.9(11)	F7’-Ti34-F8’	71.3(10)
F1-Ti2-F2	71.65(7)	F5-Ti4-F6	71.34(7)	F1’-Ti21-F2’	74.4(10)	F5’-Ti43-F6’	70.8(9)
F1-Ti2-F3	123.77(8)	F5-Ti4-F7	123.80(8)	F1’-Ti21-F3’	121.9(10)	F5’-Ti43-F7’	82.8(9)
F1-Ti2-F4	82.68(8)	F5-Ti4-F8	82.46(8)	F1’-Ti21-F4’	81.4(10)	F5’-Ti43-F8’	123.7(10)
F2-Ti2-F3	82.50(8)	F6-Ti4-F7	83.35(8)	F2’-Ti21-F3’	80.0(10)	F6’-Ti43-F7’	124.4(9)
F2-Ti2-F4	123.53(8)	F6-Ti4-F8	123.86(7)	F2’-Ti21-F4’	123.8(10)	F6’-Ti43-F8’	83.6(10)
F3-Ti2-F4	71.40(7)	F7-Ti4-F8	71.37(7)	F3’-Ti21-F4’	71.2(11)	F7’-Ti43-F8’	71.8(10)